



# THESE

Pour obtenir le grade de

# DOCTEUR

## En Chimie-Physique

Présentée à

# L'UNIVERSITE DE REIMS CHAMPAGNE-ARDENNE

Groupe de Spectrométrie Moléculaire et Atmosphérique

# Par Mariam EL RACHIDI

ETUDE CINETIQUE ET MECANISTIQUE DES REACTIONS HETEROGENES DU FOLPEL ET DU DIMETHOMORPHE AVEC L'OZONE ET LES RADICAUX OH. PHOTOOXYDATION HOMOGENE DES COMPOSES MORPHOLINIQUES PAR LES RADICAUX OH.

Thèse soutenue publiquement le 9 mai 2012 devant le jury:

MELLOUKI, A. TOMAS, A. WORTHAM, H. EL DIB, G. PICQUET-VARRAULT, B. CHAKIR, A. ROTH, E.

Directeur de recherche (ICARE-CNRS) MCF-HDR Ecole des Mines de Douai Professeur (LCP-IRA, Marseille) MCF Université de Rennes 1 MCF Université Paris Est Créteil MCF-HDR Université de Reims MCF-HDR Université de Reims Rapporteur Rapporteur Rapporteur Examinatrice Examinatrice Directeur de thèse Co-directrice de thèse

## Table des Matières

Liste des	Figures	X
Liste des	Tableaux	xvi
ACKNO	OWLEDGEMENTS	xix
INTRO	DUCTION	1
Bibliogı	raphic Synthesis	7
<b>I.</b> 7	The atmosphere	8
I.1	Atmospheric oxidants and photolysis	
I.1.1	Photolysis	9
I.1.2	Hydroxyl radical (OH)	
I.1.3	Ozone (O <sub>3</sub> )	
I.1.4	Nitrate radical (NO <sub>3</sub> )	14
I.1.5	Chlorine atom (Cl)	15
I.2	Atmospheric pollutants	16
I.2.1	Volatile organic compounds (VOC)	17
I.2.2	Semi-Volatile Organic Compounds (SVOC)	17
I.3	Atmospheric reactivity of organic compounds	
I.3.1	Degradation by photolysis, OH, Cl and NO <sub>3</sub> radicals	
I.3.2	Degradation by ozone	
II. I	Pesticides	
II.1	What is a pesticide?	
II.2	Types of pesticides	

II.3	History of pesticide use	25
II.4	Pesticide use today	27
II.4.1	International level	27
II.4.2	National level	
II.5	Health and environmental hazards	29
II.6	Regulations and legislation	31
II.7	Transfer of pesticides	33
II.7.1	Transfer to soil	33
II.7.2	Transfer to water	34
II.7.3	Transfer to the atmosphere	34
III. Pes	sticides in the atmosphere	35
III.1	Atmospheric phases of airborne pesticides	35
III.1.1	Gas/particle partitioning	36
III.1.2	Incorporation into the liquid phase	38
III.2	Concentrations of pesticides in the atmosphere	39
III.3	Fate of pesticides in the atmosphere	41
III.3.1	Transport of airborne pesticides	41
III.3.2	Elimination of pesticides from the atmosphere	42
III.3.2.	1 Dry deposition	42
III.3.2.	2 Wet deposition	43
IV. Rea	activity of pesticides in the atmosphere	45
IV.1	Photolysis	46
IV.2	Homogeneous reactivity with ozone and OH-radicals	46
IV.2.1	Methodology	47

IV.	2.2	Results	
IV.3		Heterogeneous reactivity with ozone and OH-radicals	
IV.	3.1	Methodology	
Ι	V.3.1.1	Sample preparation	
Ι	V.3.1.2	Experimental setup	
Ι	V.3.1.3	Extraction and analysis	
IV.	3.2	Results	
IV.4		Conclusion	61
V.	Life	times of pesticides in the atmosphere	61
VI.	Pest	icides investigated in this study	63
VI.1	]	Folpet	
VI.2		Dimethomorph	66
VII.	Con	clusion	67
VIII.	Rést	ımé du Chapitre	70
Tech	nique	es Expérimentales et Méthodes	
I.	Etuc	le des cinétiques hétérogènes	74
I.1		Préparation, extraction et analyse des échantillons	74
I.1.	1	Préparation des échantillons	74
I.1.	2	Extraction du dépôt	
I.1. I.1.	2 : 3 :	Extraction du dépôt	
I.1. I.1. I.2	2	Extraction du dépôt Analyze en GC/MS Montage expérimental	
I.1. I.1. I.2 I.2.	2 : 3 : 1 :	Extraction du dépôt Analyze en GC/MS Montage expérimental Ozonolyse	

I.3	Exploitation des expériences	
I.3.1	Ozonolyse	81
I.3.1.1	Le modèle de Langmuir-Hinshelwood (LH)	81
I.3.1.2	Le modèle de Langmuir-Rideal (LR)	
I.3.2	Réaction avec les radicaux OH	84
I.4	Identification des produits de dégradation	86
II. Etu	des en phase gazeuse	87
II.1	Etudes spectroscopiques	87
II.1.1	Dispositif expérimental	88
II.1.2	Protocole expérimental	
П.2	Oxydation par les radicaux OH	91
II.2.1	Chambre de simulation atmosphérique	91
II.2.1.1	Le réacteur photochimique	91
П.2.1.2	Le système d'introduction des réactifs et de contrôle	
II.2.1.3	Le système de photolyse	
II.2.2	Technique analytique IRTF	
II.2.2.1	Rappel du principe de la spectroscopie Infrarouge	95
II.2.2.2	La spectroscopie infrarouge à transformée de Fourier (IRTF)	95
П.2.2.3	Dispositif IRTF utilisé	97
П.2.2.4	Couplage IRTF chambre de simulation atmosphérique	
II.2.2.5	Conditions expérimentales	
II.2.2.6	Procédure expérimentale	
Heterogen	eous Reactivity	102
I. Het	erogeneous oxidation by ozone	103

П.3.4	Comparison of reactivity with other compounds	
П.3.3	Influence of photolysis	131
П.3.2	Validation of kinetic measurements	
II.3.1	Sources of error	
Ш.З	Discussion	
П.2	Determination of rate constants	
II.1	Experimental conditions	
II. Het	terogeneous oxidation by OH-radicals	124
I.5.3	LH and LR model comparison	
I.5.2.3	Comparison of second order rate constants $(k_{O3})$	
I.5.2.2	Comparison of $k_{max}$ values	
I.5.2.1	Comparison of equilibrium partitioning constants $(K_{O3})$	121
I.5.2	Comparison of reactivity with other compounds	
I.5.1	Influence of initial analyte concentration	117
I.5	Discussion	117
I.4.2	Langmuir-Hinshelwood (LH) Model	115
I.4.1	Langmuir-Rideal (LR) Model	114
I.4	Analysis and exploitation of the kinetic results	
I.3	Determination of degradation kinetics	
I.2	Experimental conditions	
I.1.2	Photolysis	
I.1.1	Volatilization	
I.1	Preliminary studies	103

III.1		Description of SPME	
III.2		Optimization of SPME parameters	
III.3		Identified products	
III.4		Proposed mechanisms	
III.	.4.1	Oxidation by Ozone	
III.	.4.2	Oxidation by OH-radicals	
IV.	Atr	nospheric implications	148
IV.1		Life-times	
IV.2		Degradation products	
V.	Co	nclusion	153
VI.	Rés	sumé du Chapitre	154
Abso	rptio	n Spectra and Homogeneous Reactivity	159
Abso I.	rptio Int	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds	
<b>Abson</b> <b>I.</b> I.1	rptio Int	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds	<b>159</b> <b>160</b> 
<b>Abson</b> <b>I.</b> I.1 I.2	rptio Int	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity	<b>159</b> <b>160</b> 
Abson I. I.1 I.2 I.2	rptio Int	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine	
Abson I. I.1 I.2 I.2 I.2	<b>Int</b>	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM)	
Abson I. I.1 I.2 I.2 I.2 I.2 I.2	<b>rptio</b> <b>Int</b> 2.1 2.2 2.3	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM) N-acetylmorpholine (NAM)	
Abson I. I.1 I.2 I.2 I.2 I.2 I.2 I.2	<b>rptio</b> <b>Int</b> 2.1 2.2 2.3 2.4	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM) N-acetylmorpholine (NAM)	<b>159 160</b> 161161163163163165
Abson I. I.1 I.2 I.2 I.2 I.2 I.2 I.2	<b>rptio</b> <b>Int</b> 2.1 2.2 2.3 2.4 <b>UV</b>	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM) N-acetylmorpholine (NAM) Conclusion	
Abson I. I.1 I.2 I.2 I.2 I.2 I.2 I.2 I.1	<b>rptio</b> <b>Int</b> 2.1 2.2 2.3 2.4 <b>UV</b>	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM) N-acetylmorpholine (NAM) Conclusion Absorption Spectra Experimental conditions	
Abson I. I.1 I.2 I.2 I.2 I.2 I.2 I.2 I.2 I.2 I.2 I.2	rptio Int 2.1 2.2 2.3 2.4 UV	n Spectra and Homogeneous Reactivity roduction to the analyzed compounds Physical properties Reactivity Morpholine N-formylmorpholine (NFM) N-acetylmorpholine (NAM) Conclusion Absorption Spectra Experimental conditions Determination of the absorption cross-section values	

II.4		Discussion	175
II.4	4.1	Sources of error	
II.4	4.2	Comparison with similar compounds	
II.5		Atmospheric implications	
III.	Ho	mogeneous oxidation by OH-radicals	
III.1		Experimental conditions	
III.2		Selection of a Reference Compound	
III.3		Determination of Rate Constants	
III.4		Discussion	
III.	4.1	Sources of error	
III.	4.2	Comparison of reactivity with other compounds	
III.5		Mechanism of Oxidation by OH-radicals:	
III.	5.1	Morpholine	
III.	.5.2	NFM and NAM	
III.6		Atmospheric Implications	197
III.	6.1	Life-times	197
III.	.6.2	Products of degradation	
IV.	Co	onclusion	
V.	Ré	sumé du Chapitre	
CON	CLU	USIONS ET PERSPECTIVES	
ANNI	EX I	Surface coverage	
ANNI	EX I	I Derivatization of relation (22) (chapter II)	
ANNI	EX I	<b>II Fluorescent Blacklight Spectrum</b> viii	212

ANNEX IV Michelson Interferometer	
ANNEX V Solid Phase Micro-Extraction (SPME)	217
Abbreviation List	219
REFERENCES	220
ABSTRACT	235

## Liste des Figures

## Chapter I

Figure I.1	Mechanistic scheme of the ozonolysis reaction of alkenes in the gas and condensed
	phases (taken from Finlayson-Pitts and Pitts, 2000)21
Figure I.2	EPA classification of pesticides by chemical structure23
Figure I.3	B Distribution of net pesticide consumption by country for the year 2000
	(FAOSTAT)27
Figure I.4	Yearly consumption quantities of insecticides, herbicides and fungicides in France
	and in the world for the year 2009, as reported by the FAO (the values are
	reported in units of tons of active ingredients)28
Figure I.5	Market value of phytosanitary in Europe for the year 2010 (units of millions of
	euros) (UIPP)29
Figure I.6	Processes of transfer of pesticides to soil water and atmosphere (source: Ministry
	of Agriculture of British Columbia)33
Figure I.7	Environmental processes influencing the fate of pesticides after application (taken
	from Pflieger, 2009)62
Figure I.8	Scheme of the chemical structures of folpet and dimethomorph, the pesticides
	investigated in this study 64

## Chapitre II

Figure II.1 Dispositif expérimental utilisé dans l'étude de l'ozonolyse des pesticides\_\_\_\_\_78

Figure II.2 Dispositif expérimental utilisé dans l'étude de l'oxydation des pesticides p	ar les
radicaux OH	80
Figure II.3 Dispositif expérimental pour l'étude des spectres d'absorption UV-Vis morpholine, du N-formylmorpholine et du N-acetylmorpholine	de la <u>8</u> 9
Figure II.4 Chambre de simulation atmosphérique	94

Figure II.5 Schéma du système optique de l'IRTF	99
---	----

## Chapter III

Figure III.1 Influence of volatilization on the degradation of the analyzed compounds	104
Figure III.2 Degradation of the analyzed compounds by photolysis	105
Figure III.3 The variation of $A/A_0$ ratio as a function of time at specified concentrations for Z-dimethomorph	ozone 108
Figure III.4 The variation of $A/A_0$ ratio as a function of time at specified concentrations for E-dimethomorph	ozone 108
Figure III.5 The variation of $A/A_0$ ratio as a function of time at specified concentrations for Folpet	ozone 109
Figure III.6 The variation of $A/A_0$ ratio as a function of time at specified concentrations for CPMPM	ozone 109
<b>Figure III.7</b> Plot of $k_{obs}$ as a function of $[O_3]_g$ for Z-dimethomorph	112
<b>Figure III.8</b> Plot of $k_{obs}$ as a function of $[O_3]_g$ for E-dimethomorph	112
<b>Figure III.9</b> Plot of $k_{obs}$ as a function of $[O_3]_g$ for Folpet	113
<b>Figure III.10</b> Plot of $k_{obs}$ as a function of $[O_3]_g$ for CPMPM	113

**Figure III.11** Plots of  $1/k_{obs}$  against  $1/[O_3]_g$  for dimethomorph, folpet and CPMPM \_\_\_\_\_116

<b>Figure III.12</b> The variation of A/A <sub>0</sub> ratio as a function of time at an initial dimethomorph mass equivalent to 0.2 µg per sample ( $[O_3] = 8.5 \times 10^{14}$ molecules.cm <sup>3</sup> )119
<b>Figure III.13</b> Plot of $ln([D]_{t0}/[D]_t)/t$ as a function of $ln([T]_{t0}/[T]_t)/t$ for Z-dimethomorph126
<b>Figure III.14</b> Plot of $ln([D]_{t0}/[D]_t)/t$ as a function of $ln([T]_{t0}/[T]_t)/t$ for E-dimethomorph127
<b>Figure III.15</b> Plot of $ln([F]_{t0}/[F]_t)/t$ as a function of $ln([T]_{t0}/[T]_t)/t$ for Folpet127
<b>Figure III.16</b> Plot of $ln([M]_{t0}/[M]_t)/t$ as a function of $ln([T]_{t0}/[T]_t)/t$ for CPMPM128
<b>Figure III.17</b> Plot of $ln([F]_{t0}/[F]_t)/t$ as a function of $ln([D]_{t0}/[D]_t)/t$ 131
Figure III.18 Optimization of extraction time at 40°C extraction temperature, 230°C desorption temperature and 0% NaCl136
Figure III.19 Optimization of extraction temperature at 70 min extraction time, 230°C desorption temperature and 0% NaCl137
Figure III.20 Optimization of desorption temperature at 70 min extraction time, 40°C extraction temperature and 0% NaCl137
<b>Figure III.21</b> Optimization of ionic strength of the sample solution at 70 min extraction time, 40°C extraction temperature and 230°C desorption temperature138
<b>Figure III.22</b> Chromatogram of a dimethomorph sample oxidized by OH-radicals at $2 < [HONO] < 4 \times 10^{16}$ molecules.cm <sup>-3</sup> for five hours139
<b>Figure III.23</b> Scheme of the proposed mechanism of ozonolysis of dimethomorph141
Figure III.24 Decomposition pathways for the Criegee intermediates that are generated upon the ozonolysis of dimethomorph142
Figure III.25 Scheme of formation of secondary ozonide144

re III.26 Proposed mechanism of oxidation of dimethomorph by OH-radicals (pathway	dation of dimethomorph by C	<b>II.26</b> Proposed mechanism of	Figure
A)146		A)	
re III.27 Proposed mechanism of oxidation of dimethomorph by OH-radicals (pathway	dation of dimethomorph by C	II.27 Proposed mechanism of	Figure

0	1	1	<b>,</b>	
В	3)			147

# Chapter IV

Figure IV.1 Scheme of the chemical structures of morpholine, NFM and NAM	160
Figure IV.2 Absorption cross-section of morpholine as a function of wavelength	_167
Figure IV.3 Absorption cross-section of NFM as a function of wavelength	_168
Figure IV.4 Absorption cross-section of NAM as a function of wavelength	_168
Figure IV.5 The variation of the absorbance of morpholine as a function of concentration	n at 4
different wavelengths	_170
Figure IV.6 The variation of the absorbance of NFM as a function of concentration	at 4
different wavelengths	_170
Figure IV.7 The variation of the absorbance of NAM as a function of concentration	at 4
different wavelengths	171
Figure IV.8 Average absorption spectra of the three analytes	<u>174</u>
Figure IV.9 The room temperature UV-absorption spectrum of morpholine in the gas p	phase
as reported by (Oliver et al., 2010)	_176
Figure IV.10 UV-spectra of morpholine (determined in this study) and N,N-dimethyla	mine
(determined by Meller, 1999) at 298 K	177

Figure IV.11	UV-spectra of NFM (determined in this study at $T = 337$ K) and	DMF
	(determined by Chakir et al., 2005, at #13-333 K in GSMA and 298-31	3 K in
	LCSR)	178
Figure IV.12	UV-spectra of morpholine (determined in this study) and N,N-dimethy	lamine
	(determined by Meller, 1999) at 298 K	179
Figure IV.13	Overlapped FTIR spectra of morpholine and isoprene	183
Figure IV.14	Overlapped FTIR spectra of N-formylmorpholine and benzaldehyde	
Figure IV.15	Overlapped FTIR spectra of N-acetylmorpholine and benzaldehyde	184
Figure IV.16	Plot of $ln([MORP]_{t0}/[MORPH]_t)/t$ as a function of $ln([ISO]_{t0}/[ISO]_t)/t$	for the
	homogeneous oxidation of morpholine by OH-radicals	185
Figure IV.17	Plot of $ln([NFM]_{t0}/[NFM]_t)/t$ as a function of $ln([BENZ]_{t0}/[BEZ]_t)/t$	for the
	homogeneous oxidation of NFM by OH-radicals	186
Figure IV.18	Plot of $ln([NAM]_{t0}/[NAM]_t)/t$ as a function of $ln([BENZ]_{t0}/[BENZ]_t)/t$	for the
	homogeneous oxidation of NAM by OH-radicals	186
Figure IV.19	Scheme of the mechanism of OH-oxidation of morpholine	193
Figure IV.20	Scheme of the possible sites for H-abstraction from NFM and NAM	194
Figure IV.21	Scheme of the mechanism of OH-oxidation of NFM and NAM ( $R_1$ d	lenotes
	either H or CH <sub>3</sub> )	195
Figure IV.22	Products of OH-oxidation of NFM and NAM (R1 denotes either H or	CH <sub>3</sub> )
		196
Figure IV.23	Scheme of the addition of O <sub>2</sub> to an alkoxy radical	<u>   197                                 </u>

### Annexes

<b>Figure AI.1</b> topographic image of 6 x 6 $\mu$ m <sup>2</sup> surface sample	207
Figure AI.2 scheme of the plaque surface and the corresponding dimensions	208
Figure AIII.1 Emission spectrum of Fluorescent blacklight lamps	212
Figure AIV.1 Schematic diagram of a Michelson interferometer	213
Figure AIV.2 Interference pattern of a disperse beam	215
Figure AIV.3 Interferogram of white light ( <u>http://www.willeyoptical.com/FTIR.html</u> )	216
Figure AV.1 Configuration of an SPME device ( <u>http://accessscience.com/search.aspx?</u>	topic=
CHEM:ANAL&term=Forensic+chemistry)	217
Figure AV.2 Direct injection and head space modes of extraction (Hinshaw)	218

## Liste des Tableaux

## Chapter I

Table I.1 Kinetic rate constants of ozonolysis and OH-oxidation of pesticic	les in the gas phase
(literature review)	
Table I.2 Kinetic rate constants of heterogeneous oxidation of pesticides	by ozone and OH-
radicals (literature review)	58
<b>Table I.3</b> Physical and chemical properties of dimethomorph and folpet	64

## Chapitre II

Tableau	II.1 Paramètres optimisés des méthodes GC-MS mises au point pour	les quatre
	composés étudiés	76
Tableau	II.2 Paramètres expérimentaux utilisés dans l'étude de l'oxydation par le	es radicaux
	OH en phase gazeuse de la morpholine, du N-formylmorpholine (N	JFM) et du
	N-acetylmorpholine (NAM)	101

## Chapter III

Table III.1 Experimental conditions of heterogeneous ozonolysis of dimeth	omorph, folpet
and CPMPM	106
Table III.2 k <sub>obs</sub> values at different ozone concentrations	110
<b>Table III.3</b> 2 <sup>nd</sup> order ozonolysis rate constant values of the analyzed species	114

**Table III.4**  $k_{max}$  and  $K_{O3}$  values determined for all investigated species117

 Table III.5 Summary of the ozonolysis rate constants obtained for the compounds investigated in this study as well as other similar compounds \_\_\_\_\_\_120

 Table III.6 Experimental conditions of heterogeneous OH-oxidation of dimethomorph, folpet

 and CPMPM
 125

- Table III.7 2<sup>nd</sup> order rate constant values of the oxidation of the analyzed species by OH-radicals
   128
- Table III.8 Summary of the OH-oxidation rate constants obtained for the compounds investigated in this study as well as some other pesticides and PAHs\_\_\_\_\_133
- Table III.9 Kinetic rate constants and life-times of the analyzed compounds with respect to both ozonolysis and oxidation by OH-radicals
   152

### Chapter IV

Table IV.1 Physical and chemical properties of morpholine, NFM and NAM in Mater	rial
Safety Datasheet (MSDS)1	60
Table IV.2 Experimental conditions for the absorption cross-section measurements       1	66
Table IV.3 Average absorption cross-section values of morpholine, NFM and NAM obtain	ıed
in this study1	71
Table IV.4 Experimental conditions of OH-oxidation experiments of morpholine, NFM a         NAM1	ınd 81
Table IV.5 2 <sup>nd</sup> order rate constant values of the homogeneous oxidation of the analyz	zed
species by OH-radicals1	87
Table IV.6 Kinetic rate constants of the homogeneous oxidation of morpholine, NFM a	ınd
NAM compared to those reported for similar compounds1	89

 Table IV.7 Kinetic rate constants of the homogeneous oxidation of morpholine, NFM and NAM and the corresponding life-times compared to those reported for similar compounds

 198

### ACKNOWLEDGEMENTS

Many people helped me to achieve this work on many different levels and in many different ways. To all these people I say "Thank You". I would not be where I am today if it weren't for you.

First of all I would like to thank all jury members for honoring me with their acceptance to examine my work. I would also like to thank the members of the GSMA laboratory, headed by *Dr. George Durry*, for their warm welcome these last three years. I especially thank my office-mates *Mélanie Ghysele* and *Iréne Mappe* for the jovial ambience they helped create at work. I equally acknowledge all my lab-mates: *Mohammad Errami*, *Lyamine Lessadiya* and *Ahmad El Masri* who were tolerant of my erratic mood swings and with whom I was able to discuss my problems on the professional as well as the personal level.

A great "thank you" goes to my directors *Dr. A. Chakir* and *Dr. E. Roth* who were always available and ready to give their advice and support whenever needed. I really appreciate everything you have done for me and I am honestly thankful to have had such compassionate people as my directors.

Thank you to all my friends here in France, and I have made many over the years, for making this a wonderful and enriching experience. Thank you for being attentive and for being good listeners. Living alone away from your family can be very hard to bear at times, but your presence and your friendship has made it tolerable.

My most sincere and profound gratitude is addressed to the SAAD family, particulary my friend *Jélane Saad* and her mother *Sawsan Saad*. I can not find the words to express the depth of my love and gratitude for you and everything you have done for me. You are my family and I will always carry you in my heart.

Finally, I would like to dedicate this thesis to my parents *Raja'a* and *Jihad*. I love you more than anything and anyone and I hope that I made you proud!

### INTRODUCTION

La problématique de la pollution atmosphérique est un phénomène très ancien bien ancré dans l'histoire de l'humanité. En effet, il y a 2000 ans, le philosophe Sénèque se plaignait des odeurs dans Rome en écrivant: « Dès que j'aurai laissé derrière moi l'oppressant air de la ville et la puanteur des fumantes cheminées qui, une fois leurs feux allumés, vomissent toutes les pestilentes fumées et suies qu'elles contiennent, je me sentirai tout à fait un autre homme ». Au moyen âge le physicien médecin Moses Maïmonides (vers 1200) élabore une description documentée de la qualité de l'air de l'époque (Rosner, 2002). Dès l'ère préindustrielle, avec une utilisation massive de la biomasse comme source d'énergie ce phénomène prend de plus en plus d'ampleur et ses impacts sur notre environnement se sont faits de plus en plus marquants. Les conséquences de la pollution atmosphérique sont très variées. Elles affectent aussi bien l'être humain, que l'écosystème dans lequel il vit.

Les différents phénomènes engendrés par la pollution, à savoir, la pollution photochimique, les pluies acides, l'effet de serre et la destruction de la couche d'ozone sont des problèmes complexes et difficiles à résoudre. Ils focalisent un intérêt grandissant de la part de la communauté scientifique. Plusieurs programmes de recherche internationaux ont été développés dans ce sens (Altshuller and Bufalini, 1965; Likens et al., 1972; Seinfeld and Pandis, 2006). L'objectif de ces projets est d'élaborer des stratégies efficaces permettant de contrôler les problématiques de la pollution atmosphérique pour améliorer la qualité de l'air. Cela exige une meilleure compréhension du devenir des différents polluants atmosphériques d'origine anthropogénique.

Depuis quelques décennies, la pollution atmosphérique se retrouve au centre des préoccupations que rencontrent tous les états du monde dans le sens où l'atmosphère n'a pas

de frontières et que les effets connexes de la pollution atmosphérique sont planétaires. Cette prise de conscience collective de la pollution atmosphérique et des conséquences environnementales des différents rejets d'origine anthropique a incité les législateurs des différents pays à se concerter et éventuellement à imposer de nouvelles normes sur les émissions.

Parmi les polluants d'origine anthropique qui altèrent les différentes sphères de l'environnement se trouvent les pesticides. Ce sont des produits chimiques ou biologiques élaborés pour réduire et éliminer les activités des organismes nuisibles. Afin d'améliorer la productivité agricole et pour nourrir une population qui est en augmentation permanente, l'utilisation des produits phytosanitaires ou pesticides n'a cessé de croître partout dans le monde. Cet usage excessif de pesticides a entraîné de nombreux effets néfastes sur l'environnement (pollution des eaux, de l'air et appauvrissement des sols) et aussi sur la santé des populations. De ce fait, l'utilisation des pesticides nécessite d'approfondir, nos connaissances sur leur comportement, dans toutes les sphères de l'environnement.

Les études faites sur le devenir et le comportement des pesticides sont généralement perçues au travers de leur présence dans les eaux, les sols et dans les denrées alimentaires. Ces dernières années, la compréhension de la problématique de la pollution de l'air par les produits phytosanitaires a connu un intérêt grandissant. En effet, selon le mode d'application ainsi que les conditions météorologiques, environ 90 % des pesticides appliqués n'atteignent pas les ravageurs ciblés (Gil and Sinfort, 2005; van der Werf and Zimmer, 1998). Entre 30 et 50 % de ces produits sont perdus dans l'atmosphère (Van Den Berg et al., 1999) via la dérive, la volatilisation et l'érosion éolienne. La contamination de l'atmosphère par les produits phytosanitaires constitue dès alors, une composante importante de la pollution. Des mesures sur le terrain ont montré que la concentration de ces produits dans l'air est de l'ordre de

quelques dizaines de nanogramme par mètre cube aussi bien en milieu rural qu'en milieu urbain. Dans l'atmosphère, un pesticide se trouve partagé entre la phase gazeuse et la phase particulaire (particules, aérosols). Pendant son séjour atmosphérique il peut subir un ensemble de processus réactionnels impliquant sa dégradation photochimique. Comme pour les autres catégories de composés organiques, les pesticides peuvent être photooxydés en phase gazeuse ou à l'interface air/particule par réaction avec les principaux oxydants atmosphériques. Ces processus d'oxydation conduisent à la formation de produits qui peuvent présenter un caractère environnemental plus ou moins nocif comparé aux molécules parentes. Il apparaît donc nécessaire de connaître les cinétiques et les mécanismes de ces réactions pour pouvoir évaluer la persistance et l'impact atmosphérique des composés phytosanitaires et leurs produits de dégradation, que ces derniers se trouvent en phase gazeuse ou particulaire.

La grande variété de structure chimique des produits phytosanitaires (plusieurs centaines de composés) et des facteurs influençant leur activité atmosphérique (propriétés physico-chimiques, nature de la phase particulaire support....) font de ces composés un objet d'étude particulièrement complexe. Or l'oxydation hétérogène des composés semi-volatils auxquels appartiennent la plupart des pesticides est en mesure de modifier la capacité oxydante de l'atmosphère en conduisant à la formation de produits de dégradation qui restent en phase solide ou qui sont susceptibles d'être transféré en phase gazeuse en fonction de leur volatilité.

C'est dans ce contexte que se situe le présent travail qui consiste à déterminer les paramètres cinétiques et mécanistiques du diméthomorphe et du folpel sous l'action de deux des principaux photo-oxydants atmosphériques, à savoir l'ozone et les radicaux hydroxyles. Notre choix s'est porté sur deux fongicides, le diméthomorphe et le folpel, qui sont utilisés conjointement dans le traitement du mildiou notamment dans la Région Champagne Ardenne dont les formules développées sont :



Ces pesticides ont d'ailleurs été détectés à des concentrations jusqu'à quelques centaines de ng.m<sup>-3</sup> (folpel) dans l'atmosphère rémoise (ATMO-CHAMPAGNE ARDENNE, 2010) justifiant l'intérêt d'études de ces composés dans l'atmosphère.

Ce mémoire de thèse s'articule en quatre chapitres. Dans le premier chapitre, une présentation générale de l'atmosphère et des phénomènes qui s'y déroulent sont abordés. Le cas particulier des pesticides est détaillé avec une description des différents processus de transfert de ces produits à partir du sol vers l'atmosphère. Une étude bibliographique sur les récentes études concernant la réactivité atmosphérique des pesticides clôt ce chapitre.

Dans le second chapitre « Techniques Expérimentales et Méthodes », nous préciserons les techniques expérimentales développées pour les études de réactivité cinétique des pesticides et de leurs métabolites attendus. Les protocoles analytiques utilisés pour suivre la réactivité des différents systèmes réactifs étudiés sont détaillés. Ce chapitre inclut également le développement des méthodes de traitement des résultats utilisées pour extraire les paramètres cinétiques.

Le chapitre III intitulé «Réactivité Hétérogène » concerne la caractérisation des paramètres cinétiques de l'oxydation hétérogène du diméthomorphe (isomères Z et E) et du folpel par deux des plus importants photo-oxydants atmosphériques (radicaux OH et ozone). La première partie est consacrée à la détermination expérimentale des paramètres cinétiques des réactions d'oxydation. Ces données sont utilisées ensuite pour estimer les durées de vie troposphérique de ces composés par rapport à chaque photo-oxydant. Ainsi ces résultats permettent d'évaluer la persistance de ces espèces dans l'atmosphère sous forme particulaire. La seconde partie de ce chapitre concerne l'identification des produits formés et l'élucidation des schémas réactionnels d'oxydation. Les produits sont identifiés en phase condensée au moyen de la technique de micro-extraction en phase solide (SPME) couplée à une chromatographie en phase gazeuse / spectrométrie de masse (GC/MS). Les mécanismes d'oxydation proposés nous permettent l'évaluation de l'impact de ces composés sur l'environnement.

Le chapitre IV intitulé « Spéctroscopie UV-Visible et Réactivité Homogène » concerne l'étude cinétique de la réaction, en phase gazeuse, entre les radicaux OH et les composés morpholiniques suivants : morpholine, le N- formylmorpholine et le N-acétylmorpholine.



Morpholine

N-formylmorpholine

N-acetylmorpholine

Ces composés sont attendus dans l'oxydation atmosphérique du diméthomorphe et d'autres pesticides. Par ailleurs ces produits étant susceptibles d'être transférés en phase gazeuse, leurs études cinétiques sont effectuées au moyen de chambre de simulation rigide couplée avec un spectromètre Infra Rouge à Transformé de Fourier. En outre, les spectres d'absorption UV de ces composés sont enregistrés dans le but de déterminer la contribution des processus de photolyse dans leur dégradation atmosphérique d'une part et d'autre part d'enrichir les bases des données spectroscopiques.

Enfin, ce manuscrit se termine avec une conclusion synthétique des principaux résultats obtenus et propose des pistes de recherche futures.

Chapter I

# **Bibliographic Synthesis**

### I. The atmosphere

The atmosphere is the layer of gases that surrounds the earth, and that is held near to earth's surface under the influence of the latter's gravitational attraction. This layer of gases is vital for the maintenance of human life, since it provides protection by absorbing harmful UV radiation, warming the earth, as well as reducing diurnal temperature variations. In general, the atmosphere is divided into different sub-layers based on altitude, temperature and composition. The sub-layer closest to the earth's surface is the troposphere, which is composed mainly of  $N_2$  (78 %) and  $O_2$  (21 %), as well as other gases, including argon and carbon dioxide.

### I.1 Atmospheric oxidants and photolysis

Although the present atmosphere is strongly oxidizing, the early atmosphere of the earth was of a mildly reducing nature with a composition consisting of carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), water vapor (H<sub>2</sub>O) and trace amounts of hydrogen (H<sub>2</sub>), a gaseous mixture similar to that emitted by volcanoes. Over the years, water vapor condensed to form oceans,  $CO_2$  dissolved in water and consequently formed carbonate sediments, whereas N<sub>2</sub> accumulated in the atmosphere due to its inert, non-water-soluble and non-condensable chemical nature (Seinfeld and Pandis, 2006). 2300 million years ago the amounts of atmospheric oxygen increased dramatically for ambiguous reasons. The amount of oxygen present in the earth's atmosphere today is responsible for its oxidizing nature, and is maintained by a balance between production from photosynthesis and removal through respiration and decay of organic carbon.

Other gases of much greater oxidizing capacity, such as OH-radicals (OH), nitrate radicals (NO<sub>3</sub>), ozone and chlorine, exist in the atmosphere, albeit in smaller trace amounts. These gases contribute greatly to the elimination of a wide variety of chemical compounds emitted to the atmosphere including volatile and semi-volatile organic compounds, nitrogen oxides, and sulfur oxides. In addition to direct photolysis reactions, oxidation reactions play an important role in controlling the life-times of the degraded species and ultimately in influencing their atmospheric concentrations. Following is a brief description of photolysis and the main oxidizing agents of the atmosphere.

#### I.1.1 Photolysis

Photolysis is the chemical process of dissociation of a molecule under the influence of photons. Photolysis of a particular compound in the atmosphere depends on the capacity of this compound to absorb solar radiation. Since stratospheric ozone absorbs solar radiation of wavelength < 290 nm, only radiation of wavelength > 290 nm reaches the troposphere.

When a particular molecule is struck by a photon of energy exactly equal to the energy gap between two of the molecule's electronic, vibrational or rotational energy levels, the molecule absorbs the energy of the photon and is transported to a higher (excited) energy level. A molecule in an excited energy state may either re-emit the excess energy and fall back to its ground (most stable) state, or dissociate. When molecules dissociate upon absorption of solar radiation, they are said to have been photolysed.

The rate of a photo-dissociation reaction (1) of an analyte A is governed by first order kinetics as shown in relation (2) (Finlayson-Pitts and Pitts, 2000).

$$A + h\nu \xrightarrow{J_p} Products \tag{1}$$

$$-\frac{d[A]}{dt} = J_p[A] \tag{2}$$

 $J_p$ , the rate constant of reaction (1), depends on three main factors (Finlayson-Pitts and Pitts, 2000):

- i) The spherically integrated actinic flux,  $F(\lambda)$ , which describes the intensity of available light that a molecule can absorb. This parameter depends on geographical location (latitude), season, and time of day.
- ii) The absorption cross-section of the analyte,  $\sigma(\lambda)$ , which describes the intrinsic ability of the analyte molecule to absorb light of wavelength  $\lambda$ .
- iii) The quantum yield,  $\Phi(\lambda)$ , which measures the efficiency of the photo-dissociation process.

All three parameters vary as a function of wavelength, and the photolysis rate constant is given by (Finlayson-Pitts and Pitts, 2000):

$$J_{p} = \int \sigma(\lambda) . \phi(\lambda) . F(\lambda) . d\lambda$$
(3)

Photolysis reactions play an important role in defining the chemical composition and oxidative capacity of the Earth's atmosphere.

### I.1.2 Hydroxyl radical (OH)

Although they are present in minimal amounts, OH-radicals are considered the primary oxidizing agents of the troposphere due to the fact that they are highly reactive (much more so than either  $O_2$  or  $O_3$ ). Photolysis of ozone, at wavelengths ranging between 290 and

336 nm, constitutes the main route of formation of OH-radicals in the atmosphere, based on the following mechanism (Finlayson-Pitts and Pitts, 2000):

$$O_3 + h\nu(\lambda < 336nm) \rightarrow O_2 + O(^1D) \tag{4}$$

$$O(^{1}D) + H_{2}O \to 2OH \tag{5}$$

In polluted areas, nitrous acid as well as hydrogen peroxide may also be considered as sources of OH-radicals (Finlayson-Pitts and Pitts, 2000):

$$HONO + h\nu(\lambda < 400nm) \to OH + NO \tag{6}$$

$$H_2O_2 + h\nu(\lambda < 370nm) \to OH + OH \tag{7}$$

In addition, HO<sub>2</sub> radicals, produced upon the photo-oxidation of carbon monoxide (CO) and volatile organic compounds (VOC), may also lead to the formation of OH-radicals via the following reactions (Finlayson-Pitts and Pitts, 2000):

$$HO_2 + NO \rightarrow OH + NO_2$$
 (8)

$$HO_2 + O_3 \to OH + 2O_2 \tag{9}$$

Formaldehyde (HCHO) is an example of a VOC that produces HO<sub>2</sub> radicals upon photolysis which ultimately leads to the formation of OH-radicals as shown below:

$$HCHO+h\nu(\lambda<330nm)\rightarrow H+HCO$$
(10)

$$H + O_2 + M \to HO_2 \tag{11}$$

$$HCO + O_2 \to CO + HO_2 \tag{12}$$

 $HO_2 + NO \rightarrow OH + NO_2$ 

Finally, OH-radicals may be formed upon the atmospheric ozonolysis of alkenes (Finlayson-Pitts and Pitts, 2000). Under certain conditions, these reactions are considered significant sources of HO<sub>x</sub> radicals (Paulson and Orlando, 1996).

Due to its high oxidative capacity, the hydroxyl radical reacts rapidly and efficiently with a wide variety of organic species in the atmosphere (Finlayson-Pitts and Pitts, 2000). Since it is highly reactive, the atmospheric lifetime of OH-radicals is very short, less than one second. However, the presence of this oxidant in the atmosphere is maintained by its regeneration in catalytic cycles when it reacts with organic species (Seinfeld and Pandis, 2006). Knowing that photolysis represents an important pathway for the formation of OH-radicals, the concentration of the latter exhibits diurnal variations and ranges between 5 x  $10^5$  molecules.cm<sup>-3</sup> at night and 1 x  $10^7$  molecules.cm<sup>-3</sup> at noon (Finlayson-Pitts and Pitts, 2000). Peak OH concentration of OH-radicals used in this study is 1 x  $10^6$  molecules.cm<sup>-3</sup>, the same as that used by several authors (Feigenbrugel et al., 2006; Palm et al., 1999; Palm et al., 1997).

#### **I.1.3** Ozone (O<sub>3</sub>)

Ozone is one of the most abundant, naturally occurring, oxidants of the atmosphere. It is mostly concentrated (90 %) in the stratosphere (10-50 km altitude) where it plays an important role in screening and absorbing harmful UV radiation ( $\lambda < 290$  nm). The remaining atmospheric ozone (10 %) is found in the troposphere (Seinfeld and Pandis, 2006).

10 % of tropospheric ozone comes from the stratosphere, whereas the rest (90 %) is formed mostly upon the the photolysis of NO<sub>2</sub> at  $\lambda < 420$  nm (Finlayson-Pitts and Pitts, 2000).

Photochemical reactions of volatile organic compounds (VOC) with nitrogen oxides (NO and NO<sub>2</sub>) constitute an additional source of ozone in the troposphere (Vingarzan, 2004).

A non-polluted troposphere exhibits a naturally occurring photochemical cycle between  $NO_2$ , NO and  $O_3$ . This cycle is described by the following three reactions:

$$NO_2 + h\nu(\lambda < 420nm) \rightarrow NO + O({}^3P) \tag{13}$$

$$O(^{3}P) + O_{2}(+M) \rightarrow O_{3}(+M) \tag{14}$$

$$NO + O_3 \to NO_2 + O_2 \tag{15}$$

where M is a third body, mostly an  $N_2$  or  $O_2$  molecule.

Via reactions (13), (14) and (15) a steady state equilibrium is established between ozone and nitrogen oxides resulting in stable concentrations of ozone and rapid interconversion between NO and NO<sub>2</sub> molecules.

Lately tropospheric ozone concentrations have been increasing as a result of rising anthropogenic VOC and  $NO_x$  emissions. The photo-oxidation of these compounds results in the formation of peroxyl (RO<sub>2</sub>) and hydroperoxyl (HO<sub>2</sub>) radicals. In turn, these radicals interfere with the cycle described above by evoking ozone-free NO/NO<sub>2</sub> interconversions. Moreover, (RO<sub>2</sub>) and (HO<sub>2</sub>) radicals react with NO to form RO and OH radicals (reaction (16) and (8), respectively).

$$RO_2 + NO \rightarrow RO + NO_2$$
 (16)

These reactions result in the regeneration of  $NO_2$  without passing through reaction (15). Such processes perturb the stability in the concentration of ozone and result in its

#### **BIBLIOGRAPHIC SYNTHESIS**

accumulation in the troposphere. Consequently, atmospheric ozone concentrations have increased significantly since the beginning of the industrial revolution. Unfortunately, whereas stratospheric ozone serves to protect the earth's surface and mankind from harmful UV radiations, tropospheric ozone, also known as "bad" ozone is known to incite respiratory problems when present in high concentrations (Seinfeld and Pandis, 2006). Today, tropospheric ozone concentrations range between 30 and 40 ppb, and may reach up to 500 ppb in polluted urban areas (Finlayson-Pitts and Pitts, 2000). Although ozone is mostly produced via photolysis processes, it is sufficiently long-lived that it survives into the night-time hours. Therefore, ozone concentrations do not exhibit diurnal variations, and this oxidant plays an equally important role in both day-time and night-time chemistry (Finlayson-Pitts and Pitts, 2000). However, since ozone decomposes thermally, its atmospheric concentration exhibits geographical (latitude-based) and altitudinal dependence (Finlayson-Pitts and Pitts, 2000). Meanwhile, as expected, ozone concentrations in rural areas (30-40 ppb), where VOC and NO<sub>x</sub> emissions are minimal, are less than those measured in urban regions (80-150 ppb) (Finlayson-Pitts and Pitts, 2000). The value of atmospheric ozone concentration used in our study is 40 ppb, a value frequently used in kinetic studies for the assessment of the life-times of various organic species relative to ozone (Al Rashidi et al., 2011; Pflieger et al., 2011; Pflieger et al., 2009b).

### I.1.4 Nitrate radical (NO<sub>3</sub>)

Although the tropospheric concentration of nitrate radicals is relatively low (in the order of ppt), this radical is believed to play a major role in night-time chemistry (Finlayson-Pitts and Pitts, 2000). It is mostly formed upon the oxidation of NO and NO<sub>2</sub> by ozone, as follows:

$$NO + O_3 \to NO_2 + O_2 \tag{17}$$

$$NO_2 + O_3 \to NO_3 + O_2 \tag{18}$$

Since this radical undergoes rapid photolysis to give NO and NO<sub>2</sub> at  $\lambda$  < 670 nm, it is relatively short lived during day hours, and its day-time chemistry is of little importance. However, at night, in the absence of solar radiation, NO<sub>3</sub> concentrations may reach values as high as 350 ppt (Finlayson-Pitts and Pitts, 2000).

#### I.1.5 Chlorine atom (Cl)

The evaporation of water from airborne seawater droplets generated via wave action in marine areas results in the formation of suspended NaCl particles (Finlayson-Pitts and Pitts, 2000). The reactions of NaCl with atmospheric  $N_2O_5$ , formed upon the association of  $NO_2$  and  $NO_3$ , and  $ClONO_2$ , formed upon the reaction of ClO with  $NO_2$ , in the presence of solar radiation, lead to the formation of chlorine as shown below:

$$N_2O_5(g) + NaCl(s) \rightarrow ClNO_2(g) + NaNO_3(s)$$
<sup>(19)</sup>

$$ClNO_2(g) + h\nu \to Cl + NO_2 \tag{20}$$

$$ClONO_2(g) + NaCl(s) \rightarrow Cl_2(g) + NaNO_3(s)$$
 (21)

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (22)

Peak concentrations of chlorine range from  $10^3$  to  $10^6$  radicals.cm<sup>-3</sup> in the marine boundary layer. However, the global annual average of Cl concentration is estimated at less than  $10^3$  radicals.cm<sup>-3</sup> (Finlayson-Pitts and Pitts, 2000). This concentration is significantly inferior to those of hydroxyl and nitrate radicals. However, the reactivity of chlorine is very high, and therefore, oxidation of VOC by Cl cannot be neglected, particularly in coastal regions and industrial sites where  $Cl_2$  emissions are strong.

### I.2 Atmospheric pollutants

The chemical composition of the atmosphere is delicately balanced to the extent that even the slightest variation in this composition may result in grievous and disastrous consequences. Unfortunately, the industrial revolution, which started in the 1800s, has set in motion an interminable cycle leading to an exponential increase in the emission of atmospheric pollutants. The environmental consequences of this vast movement towards mechanization, such as global warming, acid rain, photochemical pollution and ozone depletion, are only today becoming evident.

Atmospheric pollution arises from the emission, mostly anthropogenic, of harmful and toxic chemicals to the atmosphere. Although the amounts of polluting chemicals emitted to the atmosphere are minimal relative to its total composition, their atmospheric impact is massive. Primary pollutants, such as  $SO_x$ ,  $NO_x$ , CO, particulate matter (PM) and volatile organic compounds (VOCs) are directly emitted to the atmosphere. Industry, transportation and agriculture are the most important anthropogenic sources of such pollutants. Once in the atmosphere, primary pollutants may react with other chemical species to form secondary pollutants.

In this thesis we will be discussing the reactivity and fate of some volatile and semivolatile organic compounds in the troposphere. Further details concerning these two groups of atmospheric pollutants may be found in the following sections.

#### I.2.1 Volatile organic compounds (VOC)

The characterization of volatile organic compounds differs from one organization or country to the next. As defined by the United States Environmental Protection Agency (US EPA), "Volatile Organic Compounds (VOCs) are a large group of organic chemicals that include any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) and that participate in atmospheric photochemical reactions" (U.S.EPA, 2003). Based on the European Union's Directive 1999/13/EC for solvent emissions, VOCs are "organic compounds having at 293.15 K (i.e. 20°C) a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under particular conditions of use" (EU, 1999).

Plants, particularly forests, are the major natural source of VOCs (Geron et al., 1994), with tropical forests producing about half the global natural VOC emissions (Kesselmeier et al., 2000). Meanwhile, solvents (mostly paints), aerosol sprays, cleansers, air fresheners, combustion processes and fuel emissions constitute the most important anthropogenic sources of VOCs (Colls, 2002).

### I.2.2 Semi-Volatile Organic Compounds (SVOC)

According to the US EPA, "a semi-volatile organic compound is an organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature". These compounds generally have vapor pressures ranging between  $1.013 \times 10^{-6}$  and 1.013 Pa (Goldstein and Galbally, 2007). Unlike VOCs which are mostly associated with the gas phase, SVOCs are partitioned between the gas and particle phases of the atmosphere. Examples of SVOCs emitted to the atmosphere include
some phenols, polycyclic aromatic hydrocarbons (PAH) as well as pesticides, alternatively referred to as phytosanitary products.

The atmospheric degradation of organic compounds, including pesticides, under the influence of UV-Vis radiation and atmospheric photo-oxidants is discussed below.

# I.3 Atmospheric reactivity of organic compounds

Organic compounds in the atmosphere are eliminated either by physical processes, such as dry and wet deposition, or photo-chemical processes mainly involving the degradation of these compounds via reaction with the atmospheric photo-oxidants (OH, Cl, NO<sub>3</sub>, O<sub>3</sub>) or via photolysis.

## I.3.1 Degradation by photolysis, OH, Cl and NO<sub>3</sub> radicals

OH, Cl and NO<sub>3</sub> radicals, symbolized by *X*, may react with an organic compound via two different mechanisms:

Hydrogen Abstraction 
$$RH + X \rightarrow R + XH$$
 (23)

Addition 
$$R_1 R_2 C = C R_3 R_4 + X \rightarrow R_1 R_2 C - C X R_3 R_4$$
(24)

In the presence of double or triple bonds (alkenes and alkynes), addition is the dominant mechanistic pathway. The favored addition is the one that leads to the most substituted, i.e. most stable, radical (Atkinson and Arey, 2003). In addition to these reactions, organic compounds in the atmosphere may undergo photolysis under the effect of UV-Vis solar radiation. In fact a large group of organic compounds, particularly carbonyl compounds, exhibit strong absorptions of radiation in the spectral range 280-800 nm, which renders them susceptible to photolysis reactions. In most cases, photolysis of a particular organic compound

proceeds via a mechanism that leads to the formation of an alkyl radical (R), the same as those produced upon oxidation by OH, Cl and NO<sub>3</sub> radicals. The alkyl radical reacts rapidly with  $O_2$ to form peroxy (RO<sub>2</sub>) radicals which in turn react with nitrogen oxides and other peroxy radicals to form other products that influence tropospheric chemistry (Finlayson-Pitts and Pitts, 2000).

#### Fate of peroxy radicals (RO<sub>2</sub>)

In an atmosphere relatively rich in  $NO_x$  (urban zones),  $RO_2$  radicals mainly react with NO to produce alkoxy radicals (RO) as shown below (Atkinson, 1997b; Finlayson-Pitts and Pitts, 2000):

$$RO_2 + NO \rightarrow RO + NO_2$$
 (25)

For large RO<sub>2</sub> radicals, another reactional pathway is possible, involving the addition of NO followed by isomerization to form alkyl nitrates (Atkinson, 1997b; Finlayson-Pitts and Pitts, 2000):

$$RO_2 + NO \rightarrow RONO_2$$
 (26)

In the case of  $RO_2$  radicals where R represents a carbonylic group (R'C=O), the reaction of  $RO_2$  with NO<sub>2</sub> leads to the formation of peroxyalkylnitrates (ex. PAN).

Meanwhile, in non-polluted atmospheres where the concentrations of  $NO_x$  are relatively low,  $RO_2$  radicals may react with the hydroperoxy radical (HO<sub>2</sub>) via the following pathways (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006):

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$
 (27)

$$RO_2 + HO_2 \rightarrow R'CHO + H_2O + O_2 \tag{28}$$

$$RO_2 + HO_2 \to ROH + O_3 \tag{29}$$

Although reaction (27) is the primary reaction pathway of RO<sub>2</sub> and HO<sub>2</sub> radicals, evidence of the contribution of the other two pathway has been documented for complex RO<sub>2</sub> radicals (Finlayson-Pitts and Pitts, 2000). Finally, an RO<sub>2</sub> radical may react with other peroxy radicals as shown below (Atkinson, 1997b; Finlayson-Pitts and Pitts, 2000):

$$RO_2 + RO_2 \to RO + RO + O_2 \tag{30}$$

$$RO_2 + RO_2 \rightarrow ROH + R'CHO + O_2$$
 (31)

$$RO_2 + RO_2 \to ROOR + O_2 \tag{32}$$

#### Fate of alkoxy radicals (RO)

The fate of the alkoxy radicals (RO) formed upon the reaction of the peroxy radicals (RO<sub>2</sub>) with NO and other RO<sub>2</sub> radicals depends on the following three reactional pathways. The relative importance of each one of these pathways is governed by the nature of the R-branch of the alkoxy radical (Atkinson, 1997a; Finlayson-Pitts and Pitts, 2000).

i) Addition of O<sub>2</sub> followed by rearrangement and elimination of HO<sub>2</sub>:

$$RR'HCO + O_2 \to RR'C = O + HO_2 \tag{33}$$

ii) Unimolecular decomposition leading to the formation of an alkyl radical and a carbonyl compound:

$$RR'R''CO \xrightarrow{M} R + R'R''C = O \tag{34}$$

iii) Isomerization: if the alkoxy radical possesses a long carbon chain (at least 4 carbons) it may isomerize to give a hydroxyalkyl radical. The transition state involves the formation of a 6-membered ring.

### I.3.2 Degradation by ozone

Ozonolysis reactions are important in the case of unsaturated organic compounds. These reactions proceed via addition of ozone to the unsaturated double or triple bond to form a primary ozonide as shown in Figure I.1 (Finlayson-Pitts and Pitts, 2000). The ozonide decomposes rapidly to give a carbonyl compound and a biradical intermediate referred to as the Criegee intermediate. The latter may stabilize or decompose via the reactional routes depicted in Figure I.1 (Finlayson-Pitts and Pitts, 2000).



Figure I.1 Mechanistic scheme of the ozonolysis reaction of alkenes in the gas and condensed phases (Finlayson-Pitts and Pitts, 2000)

# **II.** Pesticides

Before we go into further details concerning the reactivity of pesticides in the atmosphere, a brief review of pesticides (definitions, types, history of use, distribution, health hazards and legislation) is given in this section.

### **II.1** What is a pesticide?

In the International Code of Conduct on the distribution and Use of pesticides, the Food and Agriculture Organization of the United Nations defines a pesticide as "any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies" (FAO, 2002). They go further so as to explain that "the term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport" (FAO, 2002).

# **II.2** Types of pesticides

Pesticides may be organized in different groups based on several parameters such as their chemical structure, the pests they control, how/when they work, and their mode of action (site of action). The Environmental Protection Agency's (EPA) classification of pesticides based on chemical structure is given below (Figure I.2).



Figure I.2 EPA classification of pesticides by chemical structure

This is in addition to some inorganic pesticides that are usually derived from mineral ores extracted from the earth such as copper sulphate and ferrous sulphate.

Meanwhile, based on the criterion of the nature of the targeted pest, pesticides are grouped into the following categories: **algicides** (algae), **antifouling agents** (organisms that attach to under-water surfaces), **avicide** (birds), **bactericide** (bacteria), **disinfectants and sanitizers** (disease-causing micro-organisms), **fungicides** (fungi, mildews, mold, and rusts), **herbicide** (weeds and control plant growth), **insecticide** (insects), **miticides** (mites that feed on plants and animals), **molluscicide** (snails and slugs), **nematicides** (nematodes , i.e. microscopic organisms that feed on plant roots), **ovicides** (eggs of insects and plants), **piscicide** (fish), and **rodenticide** (rodents).

Finally, the different groups of pesticides sorted based on the mode of action are given below:

- Contact pesticides: control pests upon direct contact. These generally need to cover large surfaces.
- Systemic pesticides: these are absorbed by plants or animals and move to untreated tissue. Only partial coverage is required.
- Foliar vs. Soil-applied pesticides: the former are applied to plant leaves, stems and branches, while the latter are applied to the soil.
- Broad-spectrum vs. Narrow-spectrum pesticides: the former are used to control a wide range of pests while the latter will only control certain pests.
- Residual vs. Non-residual pesticides: the former have a long life-time (several weeks) as they don't degrade quickly while the latter are quickly made inactive.
- Protectant vs. Eradicant pesticides: the former are used prior to infection (like fungicides) while the latter destroy fungi that have already invaded plants.
- Pre-plant vs. Pre-emergence vs. Post-emergence pesticides: the first are applied to the soil before seeding, the second are applied after planting but before emergence of the crop, while the last are used after the crop has emerged from the soil.

Folpet and Dimethomorph, the pesticides investigated in this study are both fungicides. Dimethomorph is a systemic fungicide whereas folpet is only efficient upon direct contact, i.e. non-systemic.

Now that we have defined pesticides and their types, we may move on to a discussion concerning their history of use. How and when were pesticides first discovered, and how did their use evolve over time?

# **II.3** History of pesticide use

Agriculture is an ancient practice that dates back as far as 8000 b.c. when people gathered edible seeds in the fertile crescent of Mesopotamia (Unsworth, 2010). The evolution of this practice was inevitable considering that it provides human beings with one of their most essential needs, nourishment. Consequently, man quickly learned to cultivate various crops such as wheat, barley, peas, lentils and rice. Unfortunately, agriculture was not an easy practice to undertake in early human history. Crops were often damaged and rendered inedible for unknown reasons, resulting in famine and strife. At the time, people attributed these occurrences to divine punishment, and attempted to alleviate the gods' wrath by prayer or magic. Little did they know that the solution to their problems rests in the use of pesticides.

However, as the years progressed, man came to realize that the destruction of the grown crops is due to certain diseases that may be cured if the proper treatment is applied. 4500 years ago, the Sumerians succeeded in controlling insects and mites through the use of sulfur. 1300 years later, the Chinese are reported to have used mercury and arsenical compounds to eliminate lice. It should be kept in mind though that, at the time, chemical synthesis was unknown to man. Therefore, all treatments were readily available in nature, and derived from plant, animal or mineral origins. Subsequent decades brought the discovery of new natural pesticides including rotenone and pyrethrum, until the 1930s when synthetic pesticides emerged in the commercial markets. Chemically synthesized nitrophenols, chlorophenols, creosote, naphthalene and petroleum oils were used to control and eliminate fungal and insect pests, whilst ammonium sulphate and sodium arsenate were used as herbicides. Although the synthesis of organic pesticides was considered a breakthrough in the field of agricultural development, several drawbacks were associated with the use of the chemical, such as the need for high rates of application, lack of selectivity and phytotoxicity.

However, the scientific community did not give up on the concept of synthetic pesticides, and so, the year 1943 marked the commercialization of a new, effective, inexpensive and broadspectrum pesticide, the DDT (dichlorodiphenyltrichloroethane). DDT was used to control and reduce insect-borne diseases such as malaria, yellow fever and typhus. It was widely used and very popular until the discovery of its potentiality to cause cancer, resulting in its interdiction for agricultural use worldwide in the 1970s. The production and use of pesticides proliferated throughout the 1950s, which led to an increase in agricultural yields, and consequently a decrease in food prices. However, little attention was paid to the potential health and environmental hazards of these products before the publication of Rachel Carson's Silent Springs in1962 (Unsworth, 2010). This book shed light on the dangers of indiscriminate pesticide use, and emphasized the need for safer and more environmentally friendly products. Afterwards, this issue became the subject of numerous research studies, and the period stretching between the 1970s and 1980s witnessed the introduction of a vast array of chemically synthesized herbicides (glyphosate, imidazolinone...), insecticides (avermectins, benzoylureas...) and fungicides (triazole, morpholine, imidazole, pyrimidine and dicarboxamide families). In the 1990s, research focused on the amelioration of the selectivity of the synthesized products (Unsworth, 2010).

Ever since their introduction into the commercial market, pesticides have revolutionized the fields of agriculture and food industry to the extent that they have become indispensible. The past 50 years have witnessed a monumental increase in the global consumption of these products due to the fact that they provide an effective means of enhancing agricultural yields.

So, what about today? What pesticides are being used in the 21<sup>st</sup> century, and in what quantities? And what are the factors that govern pesticide use nowadays?

# **II.4** Pesticide use today

## **II.4.1 International level**

The Statistics Division of the Food and Agriculture Organization (FAO) of the United Nations collects data on the consumption of major pesticide products in different countries on a global level. Figure I.3 shows that India and South America are the regions where pesticide use is most concentrated, followed by Europe and some parts of Africa and Asia. However, it should be noted that, due to the unavailability of the requested information, for some countries the reported figures are adopted from those describing sales, distribution or import of these products. The global sales of pesticides for the year 2010 have attained a value of 40 billion dollars.



Net pesticides consumption

Figure I.3 Distribution of net pesticide consumption by country for the year 2000

(FAOSTAT) 27 More than 600,000 tons of pesticides were consumed worldwide during 2009 as reported by the FAO, with herbicides and fungicides being more frequently used than insecticides. France's share in this global consumption reaches up to 1, 10 and 15 % of the quantities of insecticides, herbicides and fungicides used worldwide, respectively (Figure I.4).



**Figure I.4** Yearly consumption quantities of insecticides, herbicides and fungicides in France and in the world for the year 2009, as reported by the FAO (the values are reported in units of tons of active ingredients)

## **II.4.2** National level

France is considered among the first producers in Europe, agriculture wise, with a production accounting for 20 % of the total agricultural yield of the European Union. In France, data concerning pesticide market and consumption are provided by the Union des Industries pour la Protection des Plantes (UIPP), a professional organization created in 1918. In 2010, the sales of pesticides reached 1.8 billion euros for 61,900 tons of active ingredients,

rendering France the 1<sup>st</sup> European consumer of such products, as reported by the European Crop Protection Association. As can be seen in Figure I.5 herbicide and fungicide consumption is favored to that of insecticides in France as well as in other European countries. A comparison between the values reported in 2010 and those reported in previous years shows that although there is a 10 % decrease in total pesticide consumption (market values) relative to the year 2009, this consumption has been relatively stable over the last 10 years.



Figure I.5 Market value of phytosanitary in Europe for the year 2010 (units of millions of euros) (UIPP)

# II.5 Health and environmental hazards

So far, we have described pesticides and the evolution of their use throughout human history. However, the reasons that have compelled the scientific community to conduct research concerning the reactivity of these compounds remain unclear. Why is it important to evaluate the fate of pesticides in the environment (soil, water and atmosphere)? The answer to this question lies in that fact that over the years the association between pesticide use and health and environmental hazards has become more and more evident.

All pesticides must be toxic or poisonous to kill the pests they are intended to control; but because pesticides are toxic, they are potentially hazardous to humans and animals as well as to pests. In fact, according to the Stockholm Convention on Persistent Organic Pollutants, 9 of the 12 most dangerous and persistent organic chemicals are pesticides (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene and DDT). Considering that the use of pesticides results in the contamination of respired air as well as ingested water and food, exposure to these toxic compounds is inevitable. The toxicity of pesticides varies from acute to chronic based on their chemical and physical properties as well as the duration of exposure.

The rising agricultural demand for phytosanitary products has created a need for the establishment of rules and regulations that govern pesticide use. In turn these regulations had to be based on certifiable data concerning the health and environmental risks associated with different kinds of pesticides. Therefore, toxicity of pesticides and their health hazards have been the subject of numerous research studies all over the world since the 1940s (Ahmed Azmi et al., 2006; Amr, 1997; Atreya, 2008; Koh and Jeyaratnam, 1998; Maroni et al., 1999; Maumbe and Swinton, 2003; Piazza Recena et al., 2006; Salameh et al., 2004; van der Hoek et al., 1998). In brief, these studies show that in some cases, pesticide exposure may cause a variety of adverse health effects ranging from simple skin and eye irritation to more severe problems such as asthma and bronchial diseases (Canal-Raffin et al., 2008; Canal-Raffin et al., 2007), reduction in fertility (Al-Thani et al., 2003; Clementi et al., 2008; Petrelli and Figa-Talamanca, 2001; Petrelli and Mantovani, 2002), birth defects and fetal death (Clementi et al., 2007; Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007; Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007; Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), reduction et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007; Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), reduction et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), Regidor et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), Recent et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), Recent et al., 2004), Parkinson's disease (Hatcher et al., 2008; Le Couteur et al., 2007), Parkinso

1999), neurotoxicity (Axelrad et al., 2002; Raffaele et al., 2010), as well as lung, prostate and breast cancer (de Brito Sa Stoppelli and Crestana, 2005; Lee et al., 2006; O'Leary et al., 2004; Van Maele-Fabry and Willems, 2003).

Considering that over 98 % of sprayed insecticides and 95 % of herbicides reach a destination other than their target species, mainly air, soil and water, it is important to assess the impact of these species on the environment. The presence of pesticides in the environment is known to reduce biodiversity in various ecosystems (McLaughlin and Mineau, 1995), reduce nitrogen fixation, contribute to pollinator decline (Richards, 2001), and threaten endangered species (Miller, 2004). Still, the main environmental concern lies in the fact that most pesticides are persistent and may be transported to regions far from their points of application. This means that pesticide contamination is not limited to the areas where these compounds are used, but may spread regionally and in some cases even globally. On the other hand, although there is no danger of transport of non-persistent pesticides, their products of degradation are more often than not more hazardous than the mother compound.

# **II.6** Regulations and legislation

Considering that pesticides are being used in large quantities all over the world, and knowing that these compounds may pose serious health and environmental risks, world governments and health organizations have been obliged to interfere so as to control and regulate the sales and use of these chemical species. Attempts to govern pesticide use date as far back as 1972 when the U.S. government banned the use of DDT.

Though pesticide regulations differ from country to country, pesticides are traded across international borders. To deal with inconsistencies in regulations among countries, delegates to a conference of the United Nations Food and Agriculture Organization adopted an International Code of Conduct on the Distribution and Use of Pesticides in 1985 to create voluntary standards of pesticide regulation for different countries (Wilson, 1996). The Code was updated in 1998 and 2002. The FAO claims that the code has raised awareness about pesticide hazards and decreased the number of countries without restrictions on pesticide use. Two other efforts to improve regulation of international pesticide trade are the United Nations London Guidelines for the Exchange of Information on Chemicals in International Trade and the United Nations Codex Alimentarius Commission. The former seeks to implement procedures that ensure prior informed consent between countries buying and selling pesticides, while the latter seeks to create uniform standards for maximum levels of pesticide residues among participating countries (Reynolds, 1997). Both initiatives operate on a voluntary basis (Reynolds, 1997). In 2004, the global treaty signed at the Stockholm Convention for Persistent organic Pollutants (POPs) was implemented. This treaty interdicts the use of 12 POPs, 9 of which are pesticides (aldrine, chlordane, DDT, dieldrine, endrine, heptachlore, hexachlorobenzene, mirex and toxaphene). Recently, in 2010, nine additional POPs were appended to the convention including lindane, a well known insecticide.

Regulations governing the use of pesticides in France are adopted from European and international directives, particularly the directive  $n^{\circ}$  91/414/CEE of the European Union established in 1991, which bans the use of 115 pesticides. In an additional attempt to further protect the population and the environment from pesticide hazards, France implemented the Ecophyto 2018 program, which has been established at le Grenelle de l'Environment in 2008, and which aims at reducing by 50 % the amounts used, within a delay of 10 years.

Now that we have cultivated a general background regarding pesticides we may move on to a discussion of the environmental fate of these chemical species during and after application.

# **II.7** Transfer of pesticides

Depending on the mode of application as well as the meteorological conditions, up to 90 % of the applied pesticides do not reach the targeted pests (Gil and Sinfort, 2005; van der Werf and Zimmer, 1998). During and after application pesticides may be lost to the soil, water and atmosphere via a multitude of processes illustrated in Figure I.6.



Figure I.6 Processes of transfer of pesticides to soil, water and atmosphere

(source: Ministry of Agriculture of British Columbia)

## **II.7.1** Transfer to soil

The contamination of soil by pesticides is a phenomenon that has been extensively studied throughout the world (Andreu and Pico, 2004; Bermudez-Couso et al., 2007; Dagnac et al., 2005; Hilber et al., 2008; Schreck et al., 2008). Pesticides are normally transferred to soils through adsorption. Adsorption is the binding of pesticides to soil particles. The amount of pesticide adsorbed to the soil varies depending on the type of pesticide, soil moisture, soil pH, and soil texture.

#### **II.7.2** Transfer to water

Numerous studies over the past four decades have established that pesticides contaminate underground and surface waters at detectable concentrations (Beltran et al., 1998; Berijania et al., 2006; Johnson et al., 1991; Ritter, 1990). The routes for the transfer of pesticides to ground water are:

- Leaching, which is the process of transfer of pesticides to water through the soil. Leaching occurs downward, upward, or sideways. It is influenced by the pesticide water-solubility, the texture of the soil as well as the strength of adsorption of the pesticide to the soil.
- Runoff, which is the movement of pesticides in water over a sloping surface. The pesticides are either mixed in the water or bound to eroding soil. Pesticides may move with runoff as compounds dissolved in the water or attached to soil particles. Losses from runoff are greatest when it rains heavily right after application.

Once in ground water, pesticides and their degradation products can persist for years, depending on the chemical structure of the compounds and the environmental conditions.

### **II.7.3** Transfer to the atmosphere

Pesticide loss to the atmosphere during application is estimated at 30-50 % of the applied amount (Van Den Berg et al., 1999). This loss is governed by a multitude of factors including the chemical and physical properties of the pesticide, the amount used, the mode of application, the weather conditions (temperature, wind speed, and humidity), as well as the nature of the crop and soil characteristics (van Dijk and Guichert, 1999). During application pesticide transfer to the atmosphere occurs through spray drift (wind effect) and evaporation (Gil and Sinfort, 2005). Meanwhile volatilization from soil and crops and wind erosion of soil

#### **BIBLIOGRAPHIC SYNTHESIS**

particles containing adsorbed pesticides constitute the major pathways for transfer of phytosanitary products to the atmosphere after application (Glotfelty et al., 1984). Volatilization is the conversion of solids or liquids into a gas, which can move away from the initial application site. This movement is called vapor drift, and pesticides volatize most readily from sandy and wet soils. Hot, dry, or windy weather and small spray drops increase volatilization. The dynamics (rate and extent) of volatilization of pesticides have been the subject of numerous research studies (Bedos and Cellier, 2002; Glotfelty et al., 1984; Rudel, 1997; Van Den Berg et al., 1999). Once airborne, pesticides may be transported and dispersed by wind resulting in the pollution of the atmosphere on a large scale (van Pul et al., 1999). Airborne pesticides may exist in one of three forms: solid, gas and liquid (Bedos and Cellier, 2002). The partitioning of pesticides between the solid, gaseous and liquid phases is discussed in the following section.

# **III.** Pesticides in the atmosphere

This section discusses the contamination of the atmosphere by pesticides. In what atmospheric phases do these compounds exist? What are their tropospheric concentrations? And what is their fate?

## III.1 Atmospheric phases of airborne pesticides

Atmospheric transport and removal of phytosanitary products via deposition or degradation are affected to a large extent by the distribution of these compounds between the different atmospheric phases (Kaupp and Umlauf, 1992). Depending on their physico-chemical properties (vapor pressure, boiling point, Henry's constant...), as well as the meteorological conditions (temperature and humidity), pesticides are partitioned between the

three atmospheric phases: gas (Sanusi et al., 1999; Sanusi et al., 2000; Scheyer et al., 2005b), particle (Sanusi et al., 1999; Sanusi et al., 2000; Sauret et al., 2000; Scheyer et al., 2007b; Yao et al., 2008) and liquid (Bester et al., 1995; Bossi et al., 2002; Kumari et al., 2007; Scheyer et al., 2007b; Vogel et al., 2008).

#### **III.1.1 Gas/particle partitioning**

As mentioned before, pesticides normally enter the atmosphere via volatilization in the gaseous state. Generally speaking, once airborne, compounds with vapor pressures higher than 2 x 10<sup>-4</sup> Pa are predominantly observed in the gas phase (Junge, 1977). Meanwhile, compounds with vapor pressures less than 10<sup>-5</sup> Pa at 20°C (Unsworth et al., 1999) may adsorb to the surface of airborne particles and thus become a part of the particulate phase of the atmosphere (Bidleman, 1988). Numeric-wise, the partitioning equilibrium between the gas and particle phases for a particular compound is usually described by the partitioning coefficient,  $K_p$  (m<sup>3</sup>.µg<sup>-1</sup>) which is given by the following relation:

$$K_p = \frac{[P]}{[G].[TSP]} \tag{35}$$

where [P] ( $\mu$ g.m<sup>-3</sup>) and [G] ( $\mu$ g.m<sup>-3</sup>) are the concentrations of the investigated compound in the particulate and gaseous phases, respectively, and [TSP] ( $\mu$ g.m<sup>-3</sup>) is the concentration of Total Suspended Particulate matter (Finlayson-Pitts and Pitts, 2000).

The fractional coverage of the surface,  $\theta$ , is a function of  $K_p$  and P, the partial pressure of the gas or its concentration. It is given by:

$$\theta = \frac{K_p \cdot P}{1 + K_p \cdot P} \tag{36}$$

Relation (36) is derived from the Junge-Pankow model for the distribution of semivolatile organic compounds between the gas and particle phases. This model is simplistic in that it is based on the assumption that equilibrium between the phases is rapidly attained in the atmosphere (Junge, 1977). However, knowing that equilibrium does not always hold in the atmosphere, another model, the Langmuir isotherm, is used to describe the partitioning of SOCs between the atmospheric gas and particle phases (Pankow, 1987; Yamasaki et al., 1982).

Various research studies have been carried out concerning the partitioning of SOCs between the gas and particle phases of the atmosphere as well as the correlation between this phenomenon on one hand and the transport and elimination of these chemicals on the other hand (Gotz et al., 2008; Junge, 1977; Pankow, 1987; Sanusi et al., 1999; Sauret et al., 2008; Scheyer et al., 2008; Unsworth et al., 1999; Yamasaki et al., 1982). These studies show that SOCs that are more favored by the particulate phase of the atmosphere are primarily removed by dry deposition and washout (Bidleman et al., 1986) (further details may be found in sections III.3.2.1 and III.3.2.2). Thus, their atmospheric life-times are generally in the order of days or less, depending on the size of the particle as well as the reactivity of the compound (Junge, 1977; Muller, 1984). On the other hand, the atmospheric life-times of gaseous SVOCs are governed by Henry's constant (H) of each particular species. Compounds with low H values tend to be removed from the atmosphere via wet deposition (washed out by rain) and their life-times are thusly influenced by the meteorological conditions. Meanwhile, gaseous compounds with high H values are usually persistent, depending on their reactivity (Bidleman, 1988; Eisenreich et al., 1981).

Furthermore, the research study conducted by Sauret et al. (2008) has established several trends, such as:

- The partitioning of highly soluble SVOCs is primarily governed by atmospheric temperatures;
- The partitioning of slightly soluble or non-soluble SVOCs is mostly influenced by relative humidity;
- The partitioning of polar compounds is affected by the fraction of organic matter (i.e. polarity) in the atmospheric aerosol.

### **III.1.2 Incorporation into the liquid phase**

Pesticides typically enter the liquid phase of the atmosphere via one of three possible pathways (Sauret, 2002):

- i) During application as a suspension of droplets that are later carried away by wind;
- ii) After application by exchange between the gas phase and suspended water (clouds, mist...);
- By the condensation of water vapor around particles with adsorbed pesticides on their surface.

The equilibrium between the liquid and gaseous phases is mostly dictated by Henry's constant of the investigated pesticide. However, other factors, such as the presence of the suspended particles, may interfere (Pflieger, 2009).

In conclusion to this section, pesticides may exist in the three atmospheric phases: gas, particle and aqueous. The distribution of a particular pesticide between these phases depends on many factors including the physicochemical properties of the compound as well as the environmental conditions.

## III.2 Concentrations of pesticides in the atmosphere

Due to the diverse health and environmental risks related to pesticide use, and knowing that a great portion of the applied pesticides do not reach the targeted pests, pesticide contamination of soil (Andreu and Pico, 2004; Bermudez-Couso et al., 2007; Dagnac et al., 2005; Schreck et al., 2008), water (Benitez et al., 2006; Oubina et al., 1998), food residues (Akiyama et al., 1998; Rosenblum et al., 2001; Zang et al., 2008) and atmosphere (Alegria et al., 2006; Aulagnier et al., 2008; Bailey and Belzer, 2007; Baraud et al., 2003; Bedos et al., 2002; Ferrari et al., 2004; Gioia et al., 2005; Millet et al., 1997; Moreau-Guigon et al., 2007; Raina et al., 2009; Sanusi et al., 2000; Scheyer et al., 2005a; Scheyer et al., 2005b; Scheyer et al., 2007b; Schummer et al., 2010; Yao et al., 2008; Yusa et al., 2009) has been the focus of numerous recent studies. Considering that this thesis is concerned with the degradation of pesticides in the atmosphere, only atmospheric concentrations of pesticides will be discussed in this section.

In their review Yusa et al. (2009) report that the concentrations of over 100 pesticides identified in both the gas and particulate phases of the ambient rural and urban atmospheres of different countries range from a few pg.m<sup>-3</sup> to many ng.m<sup>-3</sup>. An overview of the investigated pesticides shows that almost 50 % of the detected chemicals are herbicides, more than half of which are banned from use today according to the EU regulations (Yusa et al., 2009). As expected, pesticide concentrations in the troposphere exhibit regional as well as seasonal variations. Generally speaking, higher concentrations are detected in areas where the pesticides are applied (mostly rural areas) (Baraud et al., 2003; Scheyer et al., 2007b; Yusa et al., 2009). For a particular region, concentrations are usually highest during spring and summer seasons when pesticides are applied and temperatures are warm (Tuduri et al., 2006). In addition, other factors such as the physical and chemical properties of the pesticides, the

meteorological conditions and the soil conditions also influence pesticide concentrations in the atmosphere (Scheyer et al., 2007b).

In France, pesticides have been observed in all atmospheric phases. Herbicides constitute the majority of the detected species, with mecoprop being the most abundant in the gas and particle phases (38.7 ng.m<sup>-3</sup>) (Bedos et al., 2002). Generally, concentration values in the gas and particle phases were in the order of several tenths to several tents of  $ng.m^{-3}$ . In 2006 a campaign (AIRPARIF) has been launched for the assessment of pesticide concentrations in the Ile de France. Out of the 80 compounds sought out, only 30 were detected in ambient air. 80 % of the identified species were either herbicides or fungicides. Trifularine, pendimethaline and chlorothalonil were among the most abundant pesticides with concentrations as high as 215 ng.m<sup>-3</sup> (AIRPARIF, 2007). Other campaigns in other French regions have also been effectuated for the purpose of evaluating the concentrations of different pesticides in the troposphere. ATMO Champagne-Ardenne is another organization that is dedicated to the monitoring of air quality in the French vine-growing region of Champagne-Ardenne. Since 2001 this organization has been launching annual campaigns for the measurement of pesticide concentrations in both urban and agricultural zones. In 2010, among the pesticides identified in ambient air, only six (folpet, chlorothalonil, cymoxanil, spiroxamine, methylkresoxim, and oxadiazon) exhibited daily concentrations (gas + particle) greater than 1 ng.m<sup>-3</sup>. Among these pesticides, folpet, a pesticide investigated in this study, was the most abundant with daily concentrations ranging between 129 and 623 ng.m<sup>-3</sup> depending on the site of measurement. Such concentrations account for 78 to 96 % of the total pesticide concentrations in the region of Champagne-Ardenne. Being the most abundant pesticide in the atmosphere of the Champenoise region, the study of the reactivity of atmospheric folpet is of utmost importance.

# III.3 Fate of pesticides in the atmosphere

Once airborne, pesticides may either be transported to regions far from their areas of application or eliminated from the atmosphere via a multitude of processes such as deposition and photochemical reactivity.

#### **III.3.1** Transport of airborne pesticides

The transfer of pesticides in the atmosphere from one region to another is directly related to the life-times of these species, and is governed by two main factors: the meteorological conditions and the elimination processes (both physical and chemical) (Aubertot et al., 2005; van Pul et al., 1999). Knowing that the partitioning of a particular compound between the gas and particle phases of the atmosphere plays an important role in dictating the fate of this compound, this factor should also be taken into consideration when attempting to foresee the fate of pesticides in the atmosphere and evaluate the extent of their transfer. In some cases, if the pesticide is highly persistent and the meteorological conditions are conducive, transfer on a global level is possible. In fact some pesticides such as HCH (hexachlorohexane), HCB (hexachlorobenzene) and DDT (dichlorodiphenyltrichloroethane) have been identified in the Arctic and Antarctic polar regions, thousands of kilometers far from their emission areas (Dickhut et al., 2005; Hung et al., 2005; Kallenborn et al., 1998; Su et al., 2008).

Information concerning the transport of pesticides in the atmosphere is essential for the evaluation of the environmental impact and hazards of pesticide use. Considering that the lifetime of a particular pesticide, and consequently its transport potential, is influenced by several factors including its partitioning between the atmospheric phases and degradation potential, the need for research studies regarding these subjects has become imperative.

#### **III.3.2** Elimination of pesticides from the atmosphere

Phyto-sanitary products are eliminated from the atmosphere via several physical and chemical processes. The contribution of each process towards the total elimination of a particular pesticide depends on the chemical nature of the pesticide as well as the meteorological conditions. The elimination processes that will be discussed here are dry and wet deposition, both of which are physical processes, and chemical degradation under the effect of light (photolysis), ozone and OH-radicals.

#### III.3.2.1 Dry deposition

Dry deposition denotes the direct transfer, excluding precipitation, of gaseous and particulate species to the earth's surface (Seinfeld and Pandis, 2006). This process basically involves the uptake, diffusion or adsorption of chemical species on soil, vegetation or water surfaces (van Pul et al., 1999). It is influenced to a great extent by the nature of the surface upon which adsorption occurs, the physical and chemical properties of the pesticide, as well as the meteorological conditions. The dependence of pesticide deposition on the surface temperature results in the migration of these compounds towards colder regions, a phenomenon referred to as the grasshopper-effect, and ultimately leads to their global fractionation, particularly in polar regions and mountainous areas (Blais et al., 1999; McConnell et al., 1998; Wania and Mackay, 1993).

The speed of deposition is governed by atmospheric turbulence, particularly close to the surface, and depends on whether the concerned compound is in the gas or particle phase (van Pul et al., 1999). Generally speaking, the uptake of gaseous species by the surface is governed by the solubility and the chemical reactivity of the species. Meanwhile, particle size density and shape are the factors that influence the deposition of particulate species (Seinfeld and Pandis, 2006). The process of dry deposition occurs in three consecutive steps (Seinfeld and Pandis, 2006):

- Aerodynamic transport of the species (gaseous or particulate) downwards through the atmosphere till it reaches a very thin layer of stagnant air, the quasi-laminar sub-layer, just above the surface.
- Molecular and Brownian transport of gases and particles, respectively, across the quasi-laminar sub-layer to the surface.
- Uptake at the surface via absorption or adsorption.

Knowing that deposited pesticides may re-volatilize, deposition/reemission fluxes are assessed using specialized models (Bidleman, 1988; Teske et al., 2011). The modeled fluxes may be compared to the few field measurements reported in the literature (Bester et al., 1995; Teil et al., 2004; Thurman and Cromwell, 2000). Annual deposition rates are known to exhibit substantial seasonal variations. However, despite the scarcity in the number of published studies concerning dry deposition of pesticides, typical values of deposition rates are in the order of several  $\mu$ g.m<sup>-2</sup> (Bester et al., 1995; Park et al., 2001; Teil et al., 2004).

#### III.3.2.2 Wet deposition

The scavenging of material from the atmosphere by natural atmospheric hydrometeors, such as clouds and fog drops, rain, and snow, and the consequent transport of these materials to the Earth's surface is referred to as wet deposition (Seinfeld and Pandis, 2006). Several processes fall under the label of wet deposition. These processes include rain-out (in-cloud scavenging), wash-out (below-cloud scavenging), and precipitation scavenging. Wet deposition takes place in three consecutive steps (Seinfeld and Pandis, 2006):

- 1- The species is brought into the presence of condensed water.
- 2- The species is scavenged by the hydrometeors.
- 3- The species is carried by the hydrometeor to the Earth's surface.

Similar to dry deposition, wet deposition rates for pesticides are governed by numerous factors including cloud and raindrop size distribution, the type of hydrometeor, molecular diffusion and Henry's law constant (H) of the pesticide (van Pul et al., 1999). For gaseous species, ambient air concentration plays an important role in deciding the rate of deposition. In fact, depending on its concentration, a gaseous species may accumulate in clouds and raindrops resulting in the reduction of the scavenging rate and in some cases, in revolatilization of the species. Moreover, wet deposition is favored for gaseous species with low H values (Bidleman, 1988). Particulate species on the other hand have deposition rates that are independent of the species' concentration, and that are influenced instead by the physical properties of the particles themselves, particularly the particle diameter (van Pul et al., 1999). The washout ratio of particular species is given by the following relation:

$$W_{p} = \frac{concentration in aqueous phase}{concentration in gas phase}$$
(37)

Typical washout ratios  $(W_p)$  range between  $10^5$  and  $10^6$  (Bidleman, 1988). These values are used in modeling studies.

Besides physical processes (dry and wet deposition), pesticides may be chemically eliminated from the atmosphere and degraded under the effect of light (photolysis), ozone and OH-radicals (the most important oxidizing species of the atmosphere). The major chemical pathways for elimination of pesticides from the atmosphere are discussed in the following section.

# IV. Reactivity of pesticides in the atmosphere

As already mentioned in section I.1.2, OH radicals are the main chemical species controlling the oxidizing capacity of the troposphere. They play an important role in regulating the concentration and distribution of greenhouse gases and pollutants in the atmosphere. In fact, reaction with OH-radicals is considered the major pathway for elimination of volatile and semi-volatile organic pollutants, including pesticides, from the atmosphere (Atkinson, 1989; Atkinson, 1994). Although reactions with OH-radicals are generally a lot faster than those with ozone, in some cases, pesticide elimination by ozone is more important than by OH-radicals due to the fact that tropospheric ozone concentrations. Therefore, generally speaking, ozonolysis reactions of pesticides in the atmosphere are just as important as OH-oxidation reactions. In some cases, photolysis may also be an important atmospheric degradation pathway. The relative importance of each process with respect to the other depends on the chemical nature of the pesticide.

Although several studies have been performed for the purpose of assessing the reactivity of pesticides in soils and water, little is known concerning the atmospheric fate of these species (Le Person et al., 2007). In this section we review the kinetic studies published in the literature concerning the homogeneous and heterogeneous degradation of pesticides in the atmosphere.

# **IV.1** Photolysis

Unfortunately, the assessment of the photolysis rates for pesticides is not evident due to the lack of the required cross-section values. The latter are very difficult to measure by spectroscopic means due to the fact that the vapor pressures of pesticides are generally low ( $< 10^{-7}$  Pa) (Feigenbrugel, 2005). Moreover, quantum yield values for pesticides are also unavailable. As a consequence of these constraints, data available in the literature concerning the photolysis rates of pesticides are basically limited to the aqueous phase (Burrows et al., 2002). Still a small number of studies regarding the photolysis of gaseous (Carter et al., 1996; Hebert et al., 2000b; Le Person et al., 2007) and particulate pesticides (Bossan et al., 1995; Samsonov and Pokrovskii, 2001; Segal-Rosenheimer and Dubowski, 2008) may be found in the literature. These studies show a great variability in the rates of photolysis of pesticides ( $10^{-6}$  to  $10^{-3}$  s<sup>-1</sup>), depending on their chemical structure, the nature of the aerosol in the case of particulate pesticides and the intensity of solar radiation (Bossan et al., 1995).

# IV.2 Homogeneous reactivity with ozone and OH-radicals

As mentioned in section III.1, depending on their physico-chemical properties, pesticides, a group of semi-volatile organic compounds, are distributed between the three phases of the atmosphere: gas, particle and aqueous. Therefore, in order to provide a comprehensive assessment of the reactivity of these species in the atmosphere, information regarding their heterogeneous as well as homogeneous reaction potential is needed.

Studies concerning the kinetics of homogeneous reactivity of pesticides are scarce due to the difficulties associated with manipulating compounds of relatively low vapor pressures in the gas phase. Atkinson et al. (1999) provide a review of such studies published before 1999. This review reports the homogeneous OH-reactivity of 10 pesticides (methylbromide, 1,2-dibromo-3-chloropropane, cis and trans-1,3-dichloropropane, EPTC, cycloate,  $\alpha$  and  $\gamma$ -hexachlorohexan, hexachlorobenzene and phosphine) (Atkinson et al., 1997; Atkinson et al., 1999; Brubaker and Hites, 1998; Kwok et al., 1992; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1984). The homogeneous O<sub>3</sub>-reactivity constants of 5 of these 10 compounds (1,2-dibromo-3-chloropropane, cis and trans-1,3-dichloropropane, EPTC, cycloate) are also reported (Atkinson et al., 1999; Kwok et al., 1992; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1999; Kwok et al., 1992; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1999; Kwok et al., 1992; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1999; Kwok et al., 1992; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1984). More recent studies are limited to OH-reactivity and they include those performed on dichlorvos, trifluralin and diazinon using the European PhotoReactor (EUPHORE) in Valencia, Spain (Feigenbrugel et al., 2006; Le Person et al., 2007; Munoz et al., 2011), as well as the study published by Hebert et al. (2000a) regarding the homogeneous OH-reactivity of diazinon and chlorpyrifos. The employed methodologies and obtained results are discussed in detail in the following sections.

### **IV.2.1 Methodology**

Basically, studies concerning the kinetics of homogeneous oxidation of pesticides have been carried out using the technique of a simulation chamber coupled to an analytical system such as FTIR or GC (Atkinson et al., 1997; Kwok et al., 1992; Le Person et al., 2007; Munoz et al., 2011; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1984).

The kinetics of OH-oxidation of gaseous dichlorvos, trifluralin and diazinon were investigated using EUPHORE, a photoreactor composed of two large semi-spherical simulation chambers installed outdoors at the Centro de Estudios Ambientales del Mediterraneo in Valencia, Spain (Feigenbrugel et al., 2006). The semi-spherical simulation chamber employed in these studies is made of fluorinated ethylene propylene (FEP) foil, material that is highly transparent to sunlight. Its volume is approximately 204 m<sup>3</sup>. The rate constant of homogeneous OH-oxidation for each of the three compounds was determined

relative to a reference a compound whose rate constant is known, a technique that we have adopted in our study as well (Feigenbrugel et al., 2006; Le Person et al., 2007; Munoz et al., 2011). The irradiation of an HCHO/NO gaseous mixture was used to generate OH-radicals. All experiments were performed at ambient temperature. Identification and quantification of the reactive species was achieved using the technique of Fourier Transform Infrared spectroscopy (FTIR) as well as a Gas Chromatograph (GC) coupled to either a Mass Spectrometer (MS), a Flame-Ionization Detector (FID) or a photo-ionization detector (Feigenbrugel et al., 2006; Le Person et al., 2007; Munoz et al., 2011).

Similarly, the experimental technique employed by Hebert et al. (2000a, 2000b) for the assessment of the kinetics of degradation of diazinon and chlorpyrifos pesticides by OHradicals in the gas phase involves the use of a simulation chamber whose volume is 57 L (Hebert et al., 2000a; Hebert et al., 2000b). However, unlike the experiments performed using EUPHORE, the OH-oxidation of diazinon and chlorpyrifos was carried out at temperatures ranging between 60 and 80°C (Hebert et al., 2000a). Rate constant values were determined relative to reference compounds (triethylphosphate and 2-methylnaphthalene). A flow of highpurity-grade air, previously heated to the desired temperature was used to introduce analyte and reference samples into the chamber. The irradiation of gaseous methyl nitrite by light issued from a xenon arc served as a source of OH-radicals inside the chamber. Analyses were performed using Solid Phase Micro-extraction (SPME) in order to avoid the loss of sensitivity associated with the use of other analytical techniques that require repetitive gas-volume sampling which leads to the dilution of the reaction mixture (Hebert et al., 2000a). A polysiloxane SPME fiber exposed to the reaction mixture for 60 s was directly desorbed in the heated injection port of a GC/MS analytical system. The afore-mentioned OH-oxidation experiments were all performed in the relative mode, meaning that the rate constant of degradation of each analyte by OH-radicals was determined relative to the known rate constant of OH-oxidation of a reference compound. Rate constant values obtained for pesticides are discussed in the following section.

## **IV.2.2 Results**

The kinetic rate constants available in the literature concerning the homogeneous oxidation of pesticides by ozone and OH-radicals are reported in Table I.1. All rate constant values correspond to ambient temperature except for those reported by (Hebert et al., 2000a) for which the temperature was varied between 60 and  $80^{\circ}$ C.

Table I.1 Kinetic rate constants of ozonolysis and OH-oxidation of pesticides in the gas phase

Compound	Ozonolysis	OH-oxidation	Reference
	$\mathbf{k}_{\mathbf{O3}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	$\mathbf{k}_{\mathbf{OH}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	
Trifluarine	_	$(1.7 \pm 0.4) \ 10^{-11}$	(Le Person et al., 2007)
Dichlorvos	_	$(2.6 \pm 0.3) \ 10^{-11}$	(Feigenbrugel et al., 2006)
Diazinon	-	$(3.5 \pm 1.2) \ 10^{-11}$	(Munoz et al., 2011)
		$(2.6 \pm 1.0) \ 10^{-11}$	(Hebert et al., 2000a)
Chlorpyrifos		$(7.2 \pm 1.7) \ 10^{-11}$	(Hebert et al., 2000a)
cis-1,3-dichloropropene	1.5 x 10 <sup>-19</sup>	8.4 x 10 <sup>-12</sup>	(Tuazon et al., 1988; Tuazon et al., 1984)
trans-1,3-dichloropropene	6.7 x 10 <sup>-19</sup>	1.4 x 10 <sup>-11</sup>	(Tuazon et al., 1988; Tuazon et al., 1984)
EPTC	< 1.3 x 10 <sup>-19</sup>	3.2 x 10 <sup>-11</sup>	(Kwok et al., 1992)
Cycloate	< 3.0 x 10 <sup>-19</sup>	3.5 x 10 <sup>-11</sup>	(Kwok et al., 1992)

(literature review)

#### **BIBLIOGRAPHIC SYNTHESIS**

a-hexachlorocyclohexane		1.4 x 10 <sup>-13</sup>	(Brubaker and Hites, 1998)
B-hexachlorocyclohexane		1.9 x 10 <sup>-13</sup>	(Brubaker and Hites, 1998)
Hexachlorobenzene		2.7 x 10 <sup>-14</sup>	(Brubaker and Hites, 1998)
Methylbromide		2.9 x 10 <sup>-14</sup>	(Atkinson et al., 1997)
1,2-dibromo-3- chloropropane	< 3.0 x 10 <sup>-20</sup>	4.3 x 10 <sup>-13</sup>	(Tuazon et al., 1986)
Phosphine		1.6 x 10 <sup>-11</sup>	(Fritz et al., 1981)

As shown in Table I.1, OH-reactivity is  $10^5$  to  $10^9$  times greater than O<sub>3</sub>-reactivity. Generally speaking, ozonolysis rate constants are in the order of  $10^{-19}$  to  $10^{-20}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>, whereas OH-oxidation rate constants are in the order of  $10^{-11}$  to  $10^{-14}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>. This shows that the reactivity of pesticides depends on their chemical structure.

Based on the kinetic data obtained from these studies as well as data concerning the identification of degradation products of pesticides (Munoz et al., 2011), it is possible to establish tentative degradation mechanisms.

So far, kinetic assessments of the homogeneous reactivity of pesticides relative to ozone and OH-radicals include those performed on thiocarbamates (Kwok et al., 1992), chloropropanes/propenes (Brubaker and Hites, 1998; Tuazon et al., 1986; Tuazon et al., 1988; Tuazon et al., 1984) and other pesticides such as chlorpyrifos (Hebert et al., 2000a) trifluarin (Le Person et al., 2007), phosphine (Fritz et al., 1981), methylbromide (Atkinson et al., 1997), diazinon (Hebert et al., 2000a; Munoz et al., 2011) and dichlorvos (Feigenbrugel et al., 2006). Gaseous model compounds for pesticides containing amine (Koch et al., 1996) and amide (Koch et al., 1997) groups have also been investigated. Knowing that pesticides generally

have low vapor pressures, they are probably found in the condensed phase of the atmosphere. The heterogeneous reactivity of pesticides in the atmosphere is discussed in section IV.3

#### IV.3 Heterogeneous reactivity with ozone and OH-radicals

Although studies concerning the atmospheric reactivity of pesticides are limited, they are very important for the assessment of these species' atmospheric impact particularly since they are readily transferred to the atmosphere. Knowing that pesticides are semi-volatile organic compounds with relatively low vapor pressures ( $< 10^{-7}$  Pa), a significant portion of these products may exist in the particulate phase of the atmosphere. Therefore, the study of the homogeneous degradation of these compounds does not suffice if we aim to provide a comprehensive view of their atmospheric fate. This section provides a summary of the published research studies concerning the degradation of condensed pesticides under the influence of ozone and OH-radicals.

#### IV.3.1 Methodology

Experimental studies with the objective of characterizing the kinetic parameters of oxidation of a particular organic compound in the condensed phase usually proceed via three main steps. These steps are discussed in detail, as it pertains to pesticides, in sections IV.3.1.1, IV.3.1.2, and IV.3.1.3

# IV.3.1.1 Sample preparation

This step basically involves the adsorption or deposition of the analyte on a solid surface. Due to the fact that silica  $(SiO_2)$  is an important constituent of atmospheric mineral dust (Usher et al., 2003) silica particles are frequently chosen as support material for the preparation of samples of condensed pesticides (Palm et al., 1999; Palm et al., 1997; Palm et

al., 1998; Pflieger et al., 2011; Pflieger et al., 2009b). The procedure involved in preparing these samples usually consists of mixing known quantities of silica and pesticide in a defined volume of organic solvent such as acetonitrile (Palm et al., 1998) and dichloromethane (Palm et al., 1997; Pflieger et al., 2011) with the aid of an ultrasonic bath. After mixing, the solvent is evaporated and the pesticide-coated particles are dried. Sample preparation may be concluded at this stage and the prepared particles may be exposed directly to a controlled oxidizing atmosphere as is the case in the study published by Pflieger et al. (2011). However, authors usually take the sample preparation procedure one step further by mixing known amounts of the pesticide-coated aerosol material with a definite volume of distilled water and then injecting this mixture into a chamber of specific volume through a nozzle where it is combined with a flow of purified air (Palm et al., 1999; Palm et al., 1997; Palm et al., 1998). This results in the atomization of the mixture and the suspension of the aerosol material in a volume of air. The generated suspension is either directly introduced into the photo-reactor where oxidation takes place (after which pesticides-coated aerosol samples are collected on Teflon filters at predetermined time intervals) (Palm et al., 1997) or collected on a Teflon filter prior to installation in the photo-reactor (Palm et al., 1998).

In addition to the liquid/solid equilibrium frequently employed in the adsorption of organic compounds on aerosol material, it is also possible to make use of gas/solid equilibrium, particularly if the analyte of interest is sufficiently volatile. This method of adsorption (gas/solid equilibrium) is of marked interest since it emulates adsorption and gas/particle partitioning processes in the atmosphere (Pflieger et al., 2009b). To the best of our knowledge only one study has been effectuated in such a manner as it pertains to pesticides (Pflieger et al., 2009b). In this study, samples were prepared by coating the internal walls of a 375 mL flow reactor with silica particles and then gently introducing a gaseous

stream of pesticide into this reactor (Pflieger et al., 2009b). After exposing the silica particles to the gaseous stream of pesticide for an optimal duration of time, the sample is ready to be oxidized.

For studies making use of liquid/solid or gas/solid equilibrium in sample preparation the efficiency of adsorption of the analyte on the aerosol material was optimized by varying either the temperature or the carrier flow rate when applicable.

Although adsorption on silica particles is a popular method for the preparation of pesticide samples in the condensed phase, other methods may also be found in the literature. One such method involves the generation of organic aerosols through homogeneous nucleation (Gan et al., 2010; Yang et al., 2010). The aerosol generator consists of two heated quartz tubes placed in tandem. The first tube contains the organic material which is to be the nucleus of the generated aerosol, whereas the second tube contains the pesticide. Gan et al. (2010) and Yang et al. (2010) chose alezaic acid as nucleus material due to its low reactivity potential with the oxidant (in this case,  $O_3$ ). Under the combined influence of heating the quartz tubes and passing a flow of  $N_2$  through the first then second tube, aerosols of alezaic acid coated with the pesticide are generated (Gan et al., 2010; Yang et al., 2010). The generated aerosols are directly introduced into the reaction chamber where they are exposed to an oxidizing atmosphere.

Another method for pesticide sample preparation relies on the deposition of small volumes of analyte dissolved in an organic solvent on a non-reactive solid surface (Al Rashidi et al., 2011; Segal-Rosenheimer and Dubowski, 2007; Segal-Rosenheimer et al., 2011). The solvent is left to evaporate resulting in the formation of thin films of pesticides that are directly exposed to the oxidant of choice. This method was employed by Segal-Rosenheimer
and Dubowski (2007), Segal-Rosenheimer et al. (2011) and Al Rashidi et al. (2011) in their studies of the heterogeneous ozonolysis and/or OH-oxidation of cypermethrin and difenoconazole.

Once the pesticide sample is prepared oxidation experiments may be carried out. The different experimental setups used to perform these experiments are discussed in the following section.

#### IV.3.1.2 Experimental setup

The experimental setup employed in the study of the heterogeneous oxidation of pesticides usually consists of a reaction chamber made of non-reactive material such as Teflon, equipped with a few ports used for the introduction of reactive species or for sampling (Al Rashidi et al., 2011; Gan et al., 2010; Palm et al., 1999; Palm et al., 1997; Palm et al., 1998; Pflieger et al., 2009b; Yang et al., 2010). This chamber is frequently coupled to a photolysing system consisting of low-pressure mercury lamps or sunlamps used to generate the oxidant when necessary. Pesticide-coated aerosol samples may be introduced into the reaction chamber in different forms:

- Suspension of aerosols in gas. This is done with the aid of a gaseous flow (ex. purified air) (Gan et al., 2010; Palm et al., 1997; Yang et al., 2010).
- ii) Filter samples of pesticide-coated particles. These filters are placed in filter holders installed inside the reaction chamber (Palm et al., 1999; Palm et al., 1998).
- iii) Introduction of a gaseous pesticide into a reaction chamber which has been previously coated with aerosol material (Pflieger et al., 2009b).

In an innovative attempt to simplify the experimental setup, Pflieger et al. (2011) placed pesticide-coated aerosol samples in a de-activated round-bottom flask of a rotary evaporator. The flask was partially immersed in a thermostatic water bath in order to maintain a constant temperature (25°C) inside the reaction medium (Pflieger et al., 2011). Upon generation, the oxidant was introduced into the pesticide-containing flask via a Teflon tube. Homogeneous contact between the pesticide-coated aerosols and the oxidant was ensured by the rotation of the flask (Pflieger et al., 2011).

In the case of ozonolysis experiments, ozone was generated either by the irradiation of  $O_2$  at 185 nm (Pflieger et al., 2011; Segal-Rosenheimer and Dubowski, 2007; Segal-Rosenheimer et al., 2011) or via an ozone generator (submitting an oxygen flow to an electric discharge) (Al Rashidi et al., 2011; Gan et al., 2010; Pflieger et al., 2009b; Yang et al., 2010). Meanwhile, OH-radicals were produced upon photolysis of hydrogen peroxide, ozone, nitrogen dioxide, nitrous acid or methyl nitrite (Al Rashidi et al., 2011; Palm et al., 1999; Palm et al., 1997; Palm et al., 1998). OH-oxidation experiments were mostly conducted relative to a reference compound of known OH-reactivity constant just like the homogeneous OH-oxidation experiments described in section IV.2. Pflieger (2009) generated OH-radicals via ozonolysis of 2,3-dimethyl-2-butene (DMB). The concentration of these radicals was determined by measuring the concentration of DMB using the technique of Proton Transfer Reaction – Mass Spectrometry (PTR-MS). It should be kept in mind that the reference compound does not necessarily have to be in the particulate phase. In fact, Palm et al. (1997; 1998; 1999) made use of gaseous reference compounds such as butane and toluene in their studies of the heterogeneous oxidation of pesticides by OH-radicals.

Once all the reactive species are introduced into the reaction chamber the oxidation commences. At predetermined time intervals pesticide samples are removed from the reaction

chamber, extracted and analyzed in order to measure the quantity of residual pesticide in each sample and ultimately determine its rate of degradation. In some cases analyses are performed for the identification of degradation products of the pesticide.

## IV.3.1.3 Extraction and analysis

After oxidation, pesticide samples are normally extracted from the solid support on which they have been adsorbed or deposited into a liquid solvent. This extraction is effectuated by immersing the filter or aerosol pesticide sample in the liquid solvent (dichloromethane or acetonitrile) and shaking manually or with the aid of an ultrasonic bath (Al Rashidi et al., 2011; Palm et al., 1999; Palm et al., 1997; Palm et al., 1998; Pflieger et al., 2011; Pflieger et al., 2009b). The extracts are then filtered or centrifuged to remove solid impurities before analysis.

The most common analytical techniques employed in the quantification of pesticides are Gas Chromatography (GC) (Al Rashidi et al., 2011; Palm et al., 1999; Palm et al., 1997; Pflieger et al., 2009b) and High Performance Liquid Chromatography (HPLC) (Palm et al., 1998; Pflieger et al., 2011). These two analytical systems may be coupled to a wide variety of detectors including and not limited to Flame Ionization Detector (FID) and Mass Spectrometry for GC and UV detection for HPLC. Fourier Transform Infrared Spectroscopy (FTIR) is another analytical technique that has been employed by Segal-Rosenheimer and Dubowski (2007) and Segal-Rosenheimer et al. (2010) for the analysis of thin films of pesticide deposited on ZnSe Attenuated Total Reflection (ATR) crystals. The advantage of using such a technique is that it is possible to skip the extraction step. However, GC and HPLC systems are more selective. All the afore-mentioned analytical techniques allow for the quantification of pesticides in each sample. The degradation rate of a particular pesticide may be obtained by following the evolution of this pesticide's concentration as a function of time. Details regarding the obtained results are given in the following section.

#### **IV.3.2 Results**

Experimental data pertaining to the heterogeneous ozonolysis of an organic compound may be treated and analyzed using two different kinetic models:

- *i)* The model of Langmuir-Hinshelwood
- ii) The model of Langmuir-Rideal

Further details concerning these two kinetic models are given in sections I.3.1.1 and I.3.1.2 of chapter II.

Meanwhile, as mentioned before, kinetic investigations regarding the heterogeneous oxidation of pesticides by OH-radicals are usually performed in the relative mode whereby the reactivity constant of an analyte is determined relative to the known OH-reactivity constant of a reference compound (Al Rashidi et al., 2011; Palm et al., 1999; Palm et al., 1997; Palm et al., 1998). This kinetic treatment has been adopted in this thesis and is explained in detail in section I.3.2.

The reactivity constants of heterogeneous oxidation of pesticides by ozone and OHradicals available in the literature are summarized in Table I.2. In the case of ozonolysis experiments, values of  $k_{max}$  and  $K_{O3}$  determined using the *LH* model are also included if available.

Compound	Support	Ozonolysis		<b>OH-oxidation</b>	Reference	
		LH Mechanism		LR Mechanism		
		$\mathbf{k}_{\max}(s^{-1})$	$\mathbf{K}_{\mathbf{O3}}$ (cm <sup>3</sup> )	$\mathbf{k_{O3}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	<b>k</b> <sub>OH</sub> (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	
Difenoconazole	quartz plaques	$(4.9 \pm 0.5) \ 10^{-5}$	$(9.1 \pm 1.0) \ 10^{-16}$	$(2.6 \pm 0.4) \ 10^{-20}$	$(7.1 \pm 0.8) \ 10^{-14}$	(Al Rashidi et al., 2011)
Bromoxynil	SiO <sub>2</sub> aerosol			-	$(2.5 \pm 0.4) \ 10^{-11}$	(Palm et al., 1998)
Alachlore	silica	_	-	$< 0.5 \text{ x } 10^{-19}$	_	(Pflieger, 2009)
Isoproturon	SiO <sub>2</sub> aerosol			_	$(5.6 \pm 1.1) \ 10^{-12}$	(Palm et al., 1998)
Simazine	SiO <sub>2</sub> aerosol	-	-	-	$(9.7 \pm 1.4) \ 10^{-12}$	(Palm et al., 1998)
Cypermethrin	ZnSe crystals	$(7.0 \pm 1.0) \ 10^{-4}$	$(4.7 \pm 1.7) \ 10^{-16}$	-	-	(Segal-Rosenheimer and Dubowski, 2007)
	ZnSe crystals	$(1.0 \pm 0.4) \ 10^{-3}$	$(5\pm2)\ 10^{-16}$	-	-	(Segal-Rosenheimer et al., 2011)
Z-Pyrifenox	SiO <sub>2</sub>			-	$(2.8 \pm 0.1) \ 10^{-11}$	( <b>Dalm</b> at al. 1000)
E-Pyrifenox	aerosol	_	_	-	$(3.4 \pm 0.1) \ 10^{-11}$	(raini et al., 1999)

**Table I.2** Kinetic rate constants of heterogeneous oxidation of pesticides by ozone and OH-radicals (literature review)

## BIBLIOGRAPHIC SYNTHESIS

Terbythylazine	silica	-	-	$< 0.5 \text{ x } 10^{-19}$	$(1.5 \pm 0.1) \ 10^{-13}$	(Pflieger, 2009)
	silica	-	-	$< 5 \text{ x } 10^{-19}$	$(1.1 \pm 0.2) \ 10^{-11}$	(Palm et al., 1997)
Trifluarine	silica	$(1.1 \pm 0.9) \ 10^{-3}$	$(3.4 \pm 3.6) \ 10^{-16}$	$(2.9 \pm 0.1) \ 10^{-19}$	_	(Pflieger et al., 2009b)
	silica	$(4.6 \pm 7.4) \ 10^{-4}$	$(2.4 \pm 4.2) \ 10^{-16}$	$(1.1 \pm 0.1) 10^{-19}$	_	(Pflieger et al., 2011)
Pirimiphos- methyl	azelaic acid	_	_	$(2.0 \pm 0.3) \ 10^{-17}$	_	(Yang et al., 2010)
Vinclozolin	azelaic acid	-	-	$(2.4 \pm 0.4) \ 10^{-17}$	_	(Gan et al., 2010)

Table I.2 shows that the pesticides investigated so far exhibit weak reactivity towards ozone with  $k_{O3}$  values in the order of  $10^{-20}$ - $10^{-17}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>. When treated by the LH model, studies of ozonolysis of pesticides give an array of  $k_{max}$  values that range between 4.9 x  $10^{-5}$  and 1.1 x  $10^{-3}$  s<sup>-1</sup>. A non-negligible difference (up to 2 times) is evident even for two separate determinations of  $k_{max}$  values of the same pesticide adsorbed or deposited on the same surface as is the case for cypermethrin (Segal-Rosenheimer and Dubowski, 2007; Segal-Rosenheimer et al., 2011) and trifluralin (Pflieger et al., 2011; Pflieger et al., 2009b). This shows that  $k_{max}$  values are to a certain extent influenced by the experimental technique employed. Therefore it is very hard to establish correlations between these values and other parameters such as the chemical nature of the analyte or the supporting material. Meanwhile,  $K_{O3}$  values obtained for different analytes adsorbed on different support material (silica, alezaic acid or quartz) are of the same order. Although the scarcity of the available literature does not allow for the establishment of conclusive theories and correlations, it is still possible to tentatively postulate that the gas-particle partitioning constant of ozone is independent of the chemical nature of the ozonised species.

A quick review of the values reported in Table I.1 also shows that the OH-reactivity of pesticides is much greater than their O<sub>3</sub>-reactivity. In the case of oxidation by OH-radicals, the kinetic rate constants are in the order of  $10^{-14}$ - $10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>. For an average tropospheric OH-radical concentration of 1 x  $10^6$  molecules.cm<sup>-3</sup>, pesticides with reactivity constants in the order to  $10^{-14}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> are relatively persistent and may be transported to regions far from their points of application. However, pesticides with reactivity constants in the order of  $10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> are non-persistent and consequently are short-lived in the troposphere.

As shown above, data concerning the reactivity of pesticides in simulated atmospheres allow for the evaluation of the atmospheric impact and fate of these species. Knowing that pesticides are relatively non-volatile species, special attention should be given to the characterization of their heterogeneous reactivity.

## **IV.4** Conclusion

The limitedness and scarcity of information concerning the reactivity of pesticides in the atmosphere, particularly in the condensed phase, has created a need for performing numerous studies concerning this issue, especially considering the health and environmental hazards that are incurred by the use of these compounds. Knowledge concerning the atmospheric fate of pesticides is indispensible for the assessment of their impact on the atmosphere and consequently on human life. Knowing that the degradation of pesticides via direct (photolysis) and indirect (oxidation with ozone, OH, NO<sub>3</sub> and Cl radicals) photochemical pathways may lead to the formation of chemical products that differ from the parent molecule in stability, toxicity and mobility, the assessment of the different atmospheric interactions of these pesticides is crucial (Segal-Rosenheimer and Dubowski, 2007).

It should be kept in mind that other atmospheric photochemical reactions, such as reaction with  $NO_3$  and Cl radicals may also occur. However, these reactions tend to be less important except when evaluating night-time ( $NO_3$ ) or marine (Cl) chemistry.

# V. Lifetimes of pesticides in the atmosphere

Upon application, pesticides are susceptible to a variety of physical and chemical processes that determine their fate. The most important phenomena are summarized in Figure I.7.



**Figure I.7** Environmental processes influencing the fate of pesticides after application (taken from Pflieger, 2009)

The total atmospheric lifetime ( $\tau_{tot}$ ) of a particular pesticide in the atmosphere, defined as the time it takes for the concentration of a compound to reach 1/e of its initial value, depends on the speed of elimination of this compound via both physical (dry and wet deposition) and chemical (photolysis and oxidation) pathways. It is given by the following relation (Finlayson-Pitts and Pitts, 2000):

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{phot}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O3}} + \frac{1}{\tau_{dry}} + \frac{1}{\tau_{wet}}$$

where  $\tau_{phot}$ , the lifetime relative to photolysis, is equivalent to the inverse of the photolysis rate. Meanwhile, assuming second order kinetics, the lifetime of a compound relative to an oxidant X (O<sub>3</sub>, OH...) may be calculated using the following formula:

$$\tau_x = \frac{1}{k_x[X]}$$

When experimental kinetic data are not available, lifetime estimates are calculated using the Structure-Activity Relationship (SAR) method. Based on this method the rate constants of oxidation of complex pesticide molecules are determined as a function of molecular structure. However, SAR is a method that has several limitations, the most important of which is that it can only be applied for gaseous molecules. Knowing that a significant portion of pesticides exist in the particulate phase of the atmosphere, the simulated rate constant values may not always be in accord with the actual values. In fact, such a discrepancy has already been observed (Scheringer et al., 2004). Typically, SAR calculations provide values that are overestimated, and that do not take into account certain parameters such as temperature and the variability in oxidant concentration (Scheyer, 2004).

# VI. Pesticides investigated in this study

The pesticides investigated in this study are folpet and dimethomorph (Figure I.8). They were chosen due to the fact that they are frequently used together in vine-growing regions, including the region of Champagne-Ardenne, and also because they have been previously identified in the Champenoise atmosphere.



Figure I.8 Scheme of the chemical structures of folpet and dimethomorph, the pesticides investigated in this study

The physiochemical properties of these two compounds are summarized in Table I.3. A brief description of each compound, its mode of action, health hazards and concentration in the atmosphere, is given below.

	Dimethomorph	Folpet
Physical state	colorless crystalline solid	colorless crystalline solid
Molecular Weight (g.mol <sup>-1</sup> )	387.9	296.6
<i>Melting point</i> ( $^{o}C$ )	125-149	177
Density $(g.cm^{-3})$	1.318 at 20°C	0.65-0.75
Solubility in water (mg. $L^{-1}$ )	18 (pH=7)	1 (pH=7)
Solubility in dichloromethane $(mg.L^{-1})$	461	not available
Vapor pressure (Pa)	E-isomer: 9.7 x 10 <sup>-7</sup> at 25°C Z-isomer: 1.0 x 10 <sup>-6</sup> at 25°C	$< 1.3 \text{ x } 10^{-7} \text{ at } 20^{\circ} \text{C}$

Table I.3 Physical and chemical properties of dimethomorph and folpet

## VI.1 Folpet

It is a trihalomethylthio fungicide belonging to the dicarboximide family. It is a protective, contact, non-systemic fungicide used on vines and several vegetable crops as a preventative or curative treatment against diverse fungi such as mildew. This compound is a multi-site inhibitor. Upon application, it inhibits the cell division of a broad spectrum of micro-organisms that damage the crops (Corbett et al., 1984; Gisi and Sierotzki, 2008).

Exposure to folpet has been shown to cause skin lesions including hand eczema or dermatitis (Peluso et al., 1991). Canal-Raffin et al. have also been able to show that some respirable forms of commercial folpet are cytotoxic upon deposition in the human tracheobronchial region (Canal-Raffin et al., 2008; Canal-Raffin et al., 2007). Moreover, studies concerning the carcinogenicity of folpet show that this compound does indeed exhibit carcinogenic activity (Quest et al., 1993).

Folpet is a widely used pesticide, particularly in the vine-growing region of Champagne-Ardenne in France, where it was found to be the main air-polluting pesticide in both urban and rural areas (Chretien, 2004a; Chretien, 2004b). Since 2001, ATMO Champagne-Ardenne has launched a series of annual campaigns concerning the measurement of phyto-sanitary product concentrations during and after application in this region (ATMO Champagne-Ardenne, 2007). The campaign of 2010 shows that daily folpet concentrations vary between 129 and 623 ng.m<sup>-3</sup> as a function of sampling site. These concentrations account for 78 to 96 % of the total pesticide concentrations, which indicates that folpet, by far, is the major polluting pesticide in the region of Champagne-Ardenne (ATMO Champagne-Ardenne, 2010).

This product has also been identified in other regions. Total concentrations of folpet (gas + particle) in air samples collected weekly from May 2004 to December 2005 in Abbotsford, British Columbia, Canada ranged between 2.2 x  $10^{-2}$  and 4.9 ng.m<sup>-3</sup>. The major portion of this pesticide was detected in the gas phase of the air samples collected (Bailey and Belzer, 2007; Raina et al., 2009). Meanwhile, in the agricultural region of Fraser Valley in Canada, a maximum concentration of 1.7 ng.m<sup>-3</sup> was detected for folpet (gas + particle) over the period ranging between 2004 and 2006 (Raina et al., 2009). Folpet was also detected in the atmosphere of Strasbourg, France during April-May 2007 at an average concentration of 5.86 ± 3.75 ng.m<sup>-3</sup> (Schummer et al., 2010). Approximately 70 % of the detected concentration was associated with the gas phase.

The distribution of folpet between the gas and particle phases of the atmosphere depends to a great extent on the concentration of this compound. The vapor pressure of folpet at  $20^{\circ}$ C (< 1.3 x  $10^{-7}$  Pa) corresponds to a maximum gaseous concentration of 15 ng.m<sup>-3</sup>. This means that when the atmospheric concentration of folpet is less than 15 ng.m<sup>-3</sup>, this compound is mostly found in the gas phase, which is the case for Schummer et al. (2010), Raina et al. (2009) and Bailey and Balzer (2007). However, in the region of Champagne-Ardenne, the atmospheric concentration of folpet is 9 to 42 times greater than the concentration corresponding to its vapor pressure. Under such conditions folpet is expected to be found mostly in the particle phase.

## VI.2 Dimethomorph

Dimethomorph is a systemic morpholine fungicide with both curative and preventative properties. It is used on grapes, potatoes and other vegetables as a protector against downy mildew and late blight. Its mode of action is the inhibition of sterol (ergosterol) synthesis, which ultimately affects cell wall production in fungi. Dimethomorph exists in 2 isomers, but only the Z-isomer exhibits fungicidal activity (Kidd and James, 1991; Meister, 1994).

Although it has been shown that exposure to dimethomorph does not increase the susceptibility for developmental and reproductive toxicity in rats and rabbits (U.S.EPA, 1998), other studies have demonstrated that dimethomorph exposure may affect the blood and liver of rats resulting in mild cases of anemia. The increased incidence of pulmonary tumors in rats upon dimethomorph exposure was not taken as an indication of human carcinogenicity (APVMA, 1997). In general, dimethomorph is considered to be only slightly toxic.

In their review concerning the occurrence of pesticides in ambient air, Yusa et al. report that when detected, dimethomorph concentrations are less than or equal to 0.1 ng.m<sup>-3</sup> (Yusa et al., 2009). Meanwhile, the concentration of dimethomorph in the atmosphere of Yamaska Basin in Quebec was found to be less than the limit of detection (Aulagnier et al., 2008). Average daily concentrations of dimethomorph in the ambient air of the vine-growing region of Champagne-Ardenne in France were found to vary between 0.1 and 0.2 ng.m<sup>-3</sup>, depending on the site of sampling (ATMO Champagne-Ardenne, 2007).

# VII. Conclusion

Due to the extensive proliferation and advancement in the agricultural field on a global level, the last few decades have witnessed a monumental increase in the use of pesticides. These products are used on a large scale to protect grown crops from ailments and diseases caused by insects, fungi, rodents, etc. Unfortunately, depending on the mode of application as well as the meteorological conditions, up to 90 % of the applied pesticides do not reach the targeted pests (Gil and Sinfort, 2005; van der Werf and Zimmer, 1998). Depending on their physico-chemical properties (vapor pressure, Henry's constant, etc.), significant portions (30-

50 %) of the applied chemicals are lost to the atmosphere (Van Den Berg et al., 1999) via drift, volatilisation and wind erosion. Partitioning of pesticides between the gaseous and particulate phases of the atmosphere depends on their vapor pressure, temperature and humidity (Sauret et al., 2008).

Once in the atmosphere, pesticides may be eliminated via physical (dry and wet deposition) and/or chemical (photolysis and oxidation by  $O_3$ , OH, NO<sub>3</sub> and Cl radicals) processes. Photo-chemical oxidation of pesticides results in the generation of metabolites that could be more hazardous than the parent molecule. Such processes contribute to the formation of aerosols as well as secondary pollutants such as ozone and HO<sub>x</sub>. On the other hand, chemically stable pesticides are normally persistent, and may be transported over large distances, thus polluting areas as remote as the Antarctic region (Bidleman et al., 1993). Generally speaking, the presence of pesticides in the atmosphere may influence, to a certain extent, its physico-chemical properties, such as acidity, oxidation capacity and particle formation.

Although the photo-oxidation of pesticides in water is abundantly studied and well characterized (Burrows et al., 2002; Niang-Gaye and Karpel Vel Leitner, 2005), the photo-oxidation of their gaseous and particulate counterparts (Palm et al., 1997; Palm et al., 1998) remains relatively vague. Knowing that most pesticides are rather non-volatile, it is particularly interesting to investigate the heterogeneous reactivity of particulate pesticides relative to gaseous oxidants, such as OH radicals and ozone. Unfortunately, the degradation of particulate or condensed pesticides in the atmosphere continues to be an ambiguous subject, due to lack of research in this field. Lately, the heterogeneous kinetics of atmospheric reactivity of some pesticides has been investigated (Palm et al., 1997; Palm et al., 1998; Pflieger, 2009; Pflieger et al., 2009a; Pflieger et al., 2009b). Such research allows for the

estimation of the life-times of these contaminants, which in turn aids in the assessment of their persistence in the ambient atmosphere.

In their review, Atkinson et al. (1999) have made a compilation of the major research studies that have been undertaken concerning the photo-oxidation of pesticides in the gas and particulate phases (Atkinson et al., 1999). Their work highlights the gaps existing in this domain, especially those related to kinetic and mechanistic evaluations. Recently, several studies were carried out to assess the atmospheric fate of pesticides from a kinetic and a mechanistic point of view (Feigenbrugel et al., 2006; Le Person, 2006; Le Person et al., 2007; Vera et al., 2010). Such studies are very important since they allow for the validation of correlations between pesticide structure and reactivity.

This study is concerned with the determination of the kinetic parameters (rate constants and lifetimes) of the heterogeneous oxidation of two pesticides (folpet and dimethomoroph) frequently used in the vine-growing region of Champagne-Ardenne in France, by ozone as well as by OH radicals. The study also investigates the products of degradation in both the gaseous and particulate phases. Finally, the homogeneous and heterogeneous kinetics of degradation of gaseous and particulate products, respectively, are examined.

# VIII. Résumé du Chapitre

Les pesticides appartiennent à la famille des composés organiques semi volatils. Ils sont utilisés pour protéger et augmenter le rendement des cultures agricoles en éliminant les différents prédateurs des cultures. Au cours des dernières décennies l'utilisation de ces composés phytosanitaires est devenue de plus en plus répandue dans le monde. A l'échelle mondiale la quantité consommée est de l'ordre de centaines de milliers de tonnes. Au niveau national, la France est considérée comme un pays grand consommateur de pesticides, il contribue pour environ 10 % de la valeur de la consommation mondiale. Sur la quantité totale de pesticides appliqués, 90 % est perdue dans les différents compartiments de l'environnement pendant et après l'application. Cela engendre un certain nombre d'impacts négatifs sur l'environnement, sur la qualité des produits agricoles et sur la santé des populations. De ce fait l'utilisation des pesticides nécessite certaines connaissances pour garantir une production de qualité, compétitive au niveau des marchés de consommation.

Les principaux processus de transfert des pesticides dans le compartiment atmosphérique sont la volatilisation, l'érosion éolienne et la dérive. Le transfert atmosphérique des molécules dépend de leurs propriétés physiques et chimiques (pression de vapeur, constante de Henry ...) ainsi que des conditions météorologiques (température, humidité relative, vitesse du vent ...). Une fois dans l'atmosphère, le pesticide se répartit entre les phases aqueuse, gazeuse et particulaire et atteint un état d'équilibre entre ces différentes phases.

Pour caractériser le devenir atmosphérique des pesticides, il est essentiel de comprendre les différentes voies qui gouvernent l'élimination de ces composés durant leur séjour atmosphérique. Ces processus regroupent les dépôts secs et humides ainsi que les réactions photochimiques. Ces dernières sont principalement activées, en plus de la lumière, par les radicaux OH et l'ozone troposphérique, deux oxydants atmosphériques hautement réactifs. Les concentrations moyennes d'ozone troposphérique et de radicaux OH sont de 40 ppb et 10<sup>6</sup> molecules.cm<sup>-3</sup>, respectivement. De ce fait l'oxydation des pesticides par ces espèces devrait être une voie importante de leur élimination atmosphérique. Cependant, les études concernant la réactivité homogène ou hétérogène des pesticides relativement à ces photooxydants atmosphériques sont rares.

Dans ce chapitre nous avons fait une synthèse des principales études effectuées dans ce domaine. Ces travaux ont pour objectif la détermination des constantes cinétiques des différentes réactions éliminant les pesticides, en phase homogène et en phase hétérogène, nous permettant de déterminer leur durée de vie relativement à chaque oxydant atmosphérique. L'intérêt de ce paramètre est de pouvoir évaluer la persistance de ces produits et leur devenir dans l'atmosphère. Ces études ont montré que d'une manière générale la réactivité des pesticides vis-à-vis des radicaux OH est plus grande comparée à celle de l'ozone. Le rapport des constantes de vitesse des deux processus k<sub>OH+pesticide</sub>/k<sub>O3+ pesticide</sub> varie de 10<sup>9</sup> à 10<sup>3</sup>. En outre, la bibliographie montre qu'il y a une différence de réactivité entre la phase homogène et l'hétérogène. Cette différence dépend de plusieurs facteurs à savoir la structure moléculaire du produit phytosanitaire et la nature de surface sur laquelle le pesticide est adsorbé. De ce fait, il important d'effectuer des études de réactivité atmosphérique pour d'autres pesticides pour être en mesure d'établir des comparaisons de réactivité.

L'objectif de cette thèse est de déterminer les constantes cinétiques de l'oxydation du diméthomorphe et le folpel, deux pesticides fréquemment utilisés dans les régions viticoles, y compris la région de Champagne-Ardenne, par l'ozone et les radicaux OH. Etant donné que la pression de vapeur de ces deux composés (1  $10^{-6}$  et 1.3  $10^{-7}$  Pa à température ambiante pour le

diméthomorphe et le folpel respectivement) est faible et que leurs concentrations atmosphériques dans la région Champagne-Ardenne sont élevées (valeurs dépassant parfois 623 ng.m<sup>-3</sup>pour le folpel), une partie importante de ces deux pesticides est susceptible de se trouver dans la phase particulaire atmosphérique. Par conséquent, nos études cinétiques et mécanistiques sont effectuées en phase hétérogène. Les produits d'oxydation seront étudiés dans les deux phases condensée et gazeuse selon leurs propriétés physico-chimiques. Chapitre II

# **Techniques Expérimentales et Méthodes**

# I. Etude des cinétiques hétérogènes

Un protocole expérimental permettant la détermination des constantes de vitesse recherchées a été mis au point. Une plaque de quartz, sur laquelle est déposé un film de pesticide, est introduite dans un réacteur photo-chimique cylindrique. Le dépôt de pesticide est soumis à un balayage gazeux lent contenant le photo-oxydant (O<sub>3</sub> ou OH). Les concentrations d'ozone ou d'acide nitreux (dans le cas d'OH) sont suivies par spectroscopie UV-VIS. A intervalles de temps croissants, la concentration résiduelle du pesticide dans le dépôt est suivie par GC/MS en mode SIM.

## I.1 Préparation, extraction et analyse des échantillons

## I.1.1 Préparation des échantillons

Un aliquot d'un mL d'une solution de 1 ppm de pesticide dissous dans du dichlorométhane est transféré dans chaque nacelle de quartz de dimension  $6x_3x_1$  (*Lxlxh*) cm<sup>3</sup>. Après évaporation du solvant, il reste un fin film de pesticide solide, invisible à l'œil, qui recouvre le fond de la nacelle de quartz. Une analyse AFM (Atomic Force Microscopy) de la surface des nacelles de quartz montre que la rugosité correspond à une ellipse de 10 nm de large et 16 nm de profondeur en moyenne. En utilisant ces valeurs, la surface réelle est estimée à 56 cm<sup>2</sup>. L'Annexe I détaille ce calcul de surface. En considérant que les molécules sont sphériques, les surfaces d'une molécule de folpet, de dimethomorphe, de terbuthylazine et de (4-chlorophenyl)(3,4-dimethoxyphenyl)methanone (CPMPM), un produit de dégradation du dimethomorphe, sont respectivement de 3.8, 3.0, 2.0 et de 2.5 x  $10^{-18}$  m<sup>2</sup>. Les structures chimiques du CPMPM et du terbuthylazine sont représentées ci-dessous :





-dimethoxyphenyl)methanone 2-chloro-4-ethylamino-6-tert-butylam CPMPM Terbuthylazine

Si on considère que dans le dépôt, les molécules ne sont au maximum en contact avec la surface de quartz qu'avec la moitié de leur surface (demi-sphère), le taux de recouvrement de la plaque en quartz pour 1  $\mu$ g de composé est d'environ de 42, 69, 49 et 47 % pour le dimethomorphe, le folpet, le CPMPM et le terbuthylazine, respectivement (Annexe I). Le film de pesticide déposé dans la nacelle peut donc être considéré comme monocouche.

## I.1.2 Extraction du dépôt

Les résidus de pesticides sont extraits trois fois de suite dans 3 mL de dichloromethane. Le volume final est complété à 10 mL. Le rendement d'extraction de la méthode est respectivement de  $(92 \pm 3 \%)$ ,  $(102 \pm 4 \%)$ ,  $(95 \pm 3 \%)$ , et  $(96 \pm 3 \%)$  pour le dimethomorphe, le folpet, le terbuthylazine et la CPMPM. Des échantillons non exposés et extraits sont utilisés comme témoin dans nos analyses. Les résultats sont exprimés en concentrations relatives A / A<sub>0</sub> où A est la réponse analytique du résidu de pesticide extrait ayant été exposé à une atmosphère oxydante et A<sub>0</sub> la réponse analytique du pesticide déposé dans une nacelle puis ré-extrait sans avoir subi d'oxydation.

#### I.1.3 Analyze en GC/MS

La quantification des résidus de pesticide est réalisée par chromatographie en phase gazeuse couplée à un spectromètre de masse Thermofisher (Trace Ultra – DSQII). La colonne utilisée est une Thermo TR-5ms ou Agilent DB-5ms de dimensions 15 m x 0.25 mm x 0.25  $\mu$ m. 2  $\mu$ L de l'extrait de résidu de pesticide sont injectés en mode splitless (pendant 1 minute) dans un injecteur à 230°C. De l'helium Alpha gas 2 (Air Liquide) est utilisé comme gaz de balayage à un débit constant de 1 mL min<sup>-1</sup>. Le spectromètre de masse fonctionne en impact électronique avec une source maintenue à 220°C. Les concentrations de nos extraits de pesticides étant au maximum de 0.1 ppm, les analyses sont réalisées en mode SIM (Selective Ion Monitoring) pour une meilleure sensibilité. Les paramètres optimisés des méthodes analytiques utilisées pour chaque composé étudié sont résumés dans le Tableau II.1. La reproductibilité de la méthode analytique est de 14, 10 et 7 % pour respectivement le folpet, le dimethomorphe et le CPMPM.

		Dimethomorphe	Folpet	Terbuthylazine	СРМРМ
ramètres Trace GC Ultra	Température Initial (°C)	35	35	35	40
	Temps Initial (min)	0.5	0.5	0.5	1
	Rampe (°C/min)	40	40	40	25
	Température Finale (°C)	250	250	250	260
Pa	Temps Final (min)	7.5	2	0.5	0.5

composés étudiés

	<i>Température</i> d'Injecteur ( <sup>°</sup> C)	230	230	230	230
	Débit Gazeux (mL/min)	1	1	1	1
	Température de la Ligne de Transfert ( <sup>°</sup> C)	260	260	260	280
Paramètres DSQII	Température de la Source (°C)	220	220	220	220
	Gain du détecteur (V)	1668	1668	1633	1426
	SIM Mass	301	260/262	214	165
	SIM Width	0.5	0.5 (les 2)	0.5	1
	Dwell Time (ms)	100	50 (les 2)	50	100
	Vitesse de Balayage (scans/s)	7.7	7.1	14.3	7.7

## I.2 Montage expérimental

Le montage expérimental est composé d'un réacteur photo-chimique de 1 m de long et 5 cm de diamètre. A ses extrémités sont placées des fenêtres de quartz permettant le passage du faisceau d'analyse UV émanant de la lampe à deutérium. Des lentilles sont utilisées pour focaliser ce faisceau UV sur une caméra CCD d'Andor Technology. La pression dans le réacteur est mesurée grâce à un capteur 0-1000 mbar MKS Baratron. Les flux des différents gaz introduits dans le réacteur sont régulés par des débitmètres massiques (type Tylan) et la température mesurée à l'aide d'une sonde (Pt100-DIN 43760). Dix lampes à lumière noire émettant dans le domaine spectral 280-400 nm sont disposées régulièrement autour du réacteur à une distance d'environ 40 cm et utilisées au besoin (expérience de photolyse et oxydation par les radicaux OH). Ce dispositif constitue la configuration de base. Toutefois, certaines modifications y sont ajoutées en fonction du photo-oxydant à générer.

#### I.2.1 Ozonolyse

L'ozone est généré selon une méthode décrite par Griggs (1968). Une décharge électrique produite entre les deux électrodes en cuivre d'un ozoniseur (400 Hz/1500 V) permet la dissociation des molécules de dioxygène en oxygène atomique excité, ce dernier formant rapidement de l'ozone par réaction avec le dioxygène présent. Le mélange gazeux constitué d'ozone et de dioxygène est introduit dans le réacteur à des débits compris entre 58 et 508 mL.min<sup>-1</sup> accompagné d'un courant d'azote de dilution à 96-580 mL.min<sup>-1</sup> à des pressions comprises entre 29 et 130 Torr (Figure II.1). Dans ces conditions le temps de séjour du mélange oxydant dans le réacteur est de quelques dizaines de secondes. L'ozone qui n'a pas réagi en sortie de réacteur est converti catalytiquement en dioxygène grâce à un fil d'argent chauffé à environ 70°C. Par sécurité, le flux gazeux passe par un piège à azote liquide avant son évacuation dans l'atmosphère.



Figure II.1 Dispositif expérimental utilisé dans l'étude de l'ozonolyse des pesticides

L'absorbance de l'ozone dans le réacteur est suivie à 254 nm par spectrométrie UV-VIS et sa concentration est obtenue grâce à la loi de Lambert Beer sachant que la section efficace est  $\sigma_{254} = 1.128 \text{ x } 10^{-17} \text{ cm}^2$ molecule<sup>-1</sup> (Brion et al., 1998). La concentration d'ozone est modifiée en changeant le débit d'oxygène, le débit d'azote diluant et/ou la tension de décharge de l'ozoniseur. Les expériences d'ozonolyse sont réalisées dans l'obscurité pour éviter tout risque de photolyse. Enfin, à intervalles de temps croissants les nacelles sont retirées du réacteur, extraites et les extraits sont analysés comme indiqué précédemment.

## I.2.2 Oxydation par les radicaux OH

Un système de génération de radicaux OH est ajouté au dispositif de base décrit précédemment. Le système chimique utilisé pour produire ces radicaux est basé sur la photolyse de l'acide nitreux à des longueurs d'onde inférieures à 400 nm (Finlayson-Pitts and Pitts, 2000):

$$HONO(g) + h\nu(\lambda < 400 \text{ nm}) \rightarrow OH + NO$$
(1)

L'acide nitreux est produit en ajoutant de l'acide sulfurique à 10 % goutte à goutte à une solution 0.2 M de nitrite de sodium maintenue à quelques degrés Celsius afin de minimiser l'entraînement de la vapeur d'eau dans le milieu réactionnel (Figure II.2):

$$2NaNO_{2}(aq) + H_{2}SO_{4}(aq) \rightarrow 2HONO(g) + Na_{2}SO_{4}(aq)$$
<sup>(2)</sup>

L'acide nitreux est entraîné dans le réacteur par un courant d'azote à un débit de 78.5 mL.min<sup>-1</sup>. La pression est comprise, selon les expériences, entre 33 et 110 Torr. L'allumage de six lampes à lumière noire permet la formation des radicaux OH par photodissociation de l'acide nitreux. (Figure II.2).



Figure II.2 Dispositif expérimental utilisé dans l'étude de l'oxydation des pesticides par les radicaux OH

Dans ces conditions le temps de séjour du flux gazeux dans le réacteur est environ de quelques dizaines de minutes. Ne possédant pas les techniques analytiques permettant la détermination des concentrations en radicaux OH, sa concentration dans le réacteur n'est pas mesurée. Néanmoins, la concentration en HONO(g), précurseur de OH, est suivie par spectrométrie UV-VIS à  $\lambda_{HONO} = 354$  nm (Finlayson-Pitts and Pitts, 2000) où la section efficace de HONO est forte ( $\sigma_{HONO} = 4.87 \times 10^{-19}$  cm<sup>2</sup>.molecule<sup>-1</sup> (Sander et al., 2006)). Les concentrations d'HONO sont calculées avec la loi de Lambert-Beer. Elles s'étendent entre 1 et 33 x 10<sup>15</sup> molecules.cm<sup>-3</sup>. Un ventilateur est incorporé au montage pour éviter le surchauffage lié à l'utilisation des lampes UV et maintenir ainsi la température autour de 29 ± 1°C.

Etant dans l'incapacité technique de mesurer la concentration en radicaux OH, la cinétique d'oxydation du pesticide est étudiée relativement à un composé référence dont la constante de réaction vis à vis des radicaux OH en phase hétérogène sur un support similaire est connue. Ainsi, des nacelles contenant 1 µg de la référence sont introduites dans le réacteur

aux côtés de celles contenant le pesticide à étudier. A intervalles de temps croissants, une nacelle de référence et une autre du pesticide à étudier sont retirées du réacteur puis extraites dans 10 mL du dichlorométhane. Les solutions sont analysées par GC-MS et permettent d'établir l'évolution du pesticide et de la référence résiduels contenus dans les nacelles exposées à l'atmosphère oxydante en fonction du temps.

## I.3 Exploitation des expériences

#### I.3.1 Ozonolyse

Les expériences d'ozonolyse impliquent la réaction entre deux espèces. L'une est sous forme gazeuse (l'ozone) l'autre est solide (le pesticide). Il est possible de modéliser la cinétique de cette réaction selon deux approches, le modèle de *Langmuir-Hinshelwood (LH)* et celui de *Langmuir-Rideal (LR)*.

#### I.3.1.1 Le modèle de Langmuir-Hinshelwood (LH)

Ce modèle est fréquemment utilisé pour caractériser la cinétique en phase hétérogène (Kahan et al., 2006; Kwamena et al., 2006; Kwamena et al., 2007; Kwamena et al., 2004; Pflieger, 2009; Pöschl et al., 2001; Rosen et al., 2008; Segal-Rosenheimer and Dubowski, 2007). Il est basé sur un certain nombre d'hypothèses fondamentales, dont la plus importante est que la réaction entre deux espèces gazeuses n'intervient qu'une fois les deux espèces adsorbées sur des sites adjacents.

Dans notre cas, l'une des deux espèces, le pesticide *P* en l'occurrence, est déjà déposée sur la surface de quartz. C'est pourquoi, dans le cadre du modèle de LH, seules les molécules d'ozone vont devoir s'adsorber sur les sites disponibles avant de réagir avec le pesticide. La vitesse de la réaction va alors dépendre de la concentration d'ozone gazeux et du nombre de sites disponibles. Le mécanisme réactionnel se déroule selon les deux étapes suivantes:

#### Etape 1: Adsorption de l'ozone

$$O_3(g) \leftrightarrow O_3(ads)$$
 (3)

où  $K_{O3}$  est la constante d'adsorption en cm<sup>3</sup>.

#### Etape 2: Réaction entre les deux espèces adsorbées

$$O_3(ads) + P(s) \rightarrow Produits$$
  $k_{O3}{}^s$  (4)

où  $k_{O3}$ <sup>s</sup> est la constante de vitesse de la réaction (4) (cm<sup>2</sup>.molécule<sup>-1</sup>. s<sup>-1</sup>)

Considérant que la concentration en ozone gazeux est constante, la dégradation du pesticide suit une cinétique de pseudo premier ordre. La vitesse de la réaction (4) s'écrit de la manière suivante:

$$-\frac{d[P]_{s}}{dt} = k_{O3}^{s} \cdot [P]_{s} \cdot [O_{3}]_{ads} = k_{obs} [P]_{s}$$
(5)

avec 
$$k_{obs} = k_{O3}^s \cdot [O_3]_{ads}$$
 (6)

où  $k_{obs}$  est la constante "observée" de pseudo premier ordre entre l'ozone adsorbé et le pesticide (s<sup>-1</sup>).  $[O_3]_{ads}$  et  $[P]_s$  sont respectivement les concentrations surfaciques de O<sub>3</sub> et du pesticide (molécule.cm<sup>-2</sup>) avec:

$$[O_3]_{ads} = [SS].\theta_{O3} \tag{7}$$

 $\theta_{O3}$  est le taux de recouvrement de la surface par l'ozone et [SS] représente la quantité totale des sites d'adsorption en terme de concentration surfacique. En supposant que tous les sites d'adsorption ont une surface et une énergie d'adsorption équivalentes et qu'aucune interaction horizontale n'existe entre les molécules adsorbées,  $\theta_{O3}$  est donné par une relation relative à la théorie des isothermes d'adsorption de Langmuir (Seinfeld and Pandis, 1998):

$$\theta_{O3} = \frac{K_{O3} \cdot [O_3]_g}{1 + K_{O3} \cdot [O_3]_g}$$
(8)

 $K_{O3}$  et  $[O_3]_g$  sont respectivement la constante d'équilibre de l'ozone entre la phase gazeuse et la surface et la concentration de l'ozone en phase gazeuse.

En substituant  $\theta_{O3}$  par son expression (8) dans (6), on obtient:

$$k_{obs} = \frac{k_{O3}^{s}[SS].K_{O3}[O_{3}]_{g}}{1 + K_{O3}[O_{3}]_{g}} = \frac{k_{max}K_{O3}[O_{3}]_{g}}{1 + K_{O3}[O_{3}]_{g}}$$
(9)

Avec 
$$k_{\max} = k_{O3}^s [SS]$$
 (10)

L'équation (9) peut aussi être réarrangée comme suit:

$$\frac{1}{k_{obs}} = \frac{1}{k_{max} \cdot K_{O3}} \cdot \frac{1}{[O_3]_g} + \frac{1}{k_{max}}$$
(11)

La représentation de  $1/k_{obs}$  en fonction de  $1/[O_3]_g$  est une droite dont la pente et l'ordonnée à l'origine permettent la détermination de  $k_{max}$ , la constante de vitesse maximale qui puisse être atteinte et de la constante d'adsorption de l'ozone sur la surface ( $K_{O3}$ ).

#### I.3.1.2 Le modèle de Langmuir-Rideal (LR)

Ce modèle est utilisé par un certain nombre d'auteurs (Palm et al., 1999; Palm et al., 1997; Pflieger et al., 2009b) dans leurs études cinétiques entre l'ozone gazeux et un pesticide en phase solide. Il suppose que la réaction a lieu directement et exclusivement suite à une collision entre l'ozone gazeux et le pesticide déjà en phase solide selon le processus:

$$O_3(g) + P(s) \rightarrow Products$$
  $k_{O3}$  (12)

avec  $k_{O3}$  en cm<sup>3</sup>.molécule<sup>-1</sup>.s<sup>-1</sup>.

O<sub>3</sub> peut être adsorbé sur la surface mais selon ce modèle, l'ozone adsorbé ne réagit pas avec le composé adsorbé. L'expression de la cinétique de réaction du pesticide est:

$$-\frac{d[P]_{s}}{dt} = k_{03} \cdot [O_{3}]_{g} \cdot [P]_{s} = k_{obs} \cdot [P]_{s} = k_{obs} \cdot [SS] \cdot \theta_{p}$$
(13)

avec 
$$[P]_s = [SS].\theta_p$$
 (14)

et 
$$k_{obs} = k_{O3} \cdot [O_3]_g$$
 (15)

Dans ce cas, le tracé de  $k_{obs}$  en fonction de la concentration du réactif gazeux, l'ozone, est une droite dont la pente n'est autre que la constante de vitesse  $k_{O3}$ .

#### I.3.2 Réaction avec les radicaux OH

La méthodologie utilisée pour l'étude de la réactivité vis à vis des radicaux OH implique l'oxydation de l'analyte (P) et de la référence (Ref) par les radicaux OH. D'autres réactions secondaires comme la photolyse, la réaction avec HONO, le précurseur de radicaux

OH, et la réaction avec NO (etc.) sont susceptibles de se dérouler. Les réactions impliquées sont donc les suivantes:

$$P(s) + OH(g) \rightarrow Produits \qquad \qquad (16)$$

$$P(s) \to Produits \qquad \qquad K_p \tag{17}$$

avec 
$$\frac{-d[P]_s}{dt} = k_{OH} \cdot [P]_s \cdot [OH]_g + K_p \cdot [P]_s$$
 (18)

 $\operatorname{Ref}(s) + \operatorname{OH}(g) \to \operatorname{Produits} \qquad k_{ref}$  (19)

$$\operatorname{Ref}(s) \to \operatorname{Produits} \qquad K_p$$
' (20)

avec 
$$\frac{-d[Ref]_s}{dt} = k_{OH} . [Ref]_s . [OH]_g + K_p' . [Ref]_s$$
(21)

où  $[P]_s$  et  $[Ref]_s$  sont respectivement les concentrations de l'analyte et de la référence (terbuthylazine) et  $[OH]_g$  la concentration des radicaux OH en phase gazeuse. Les réactions (17) et (20) représentent toutes les réactions secondaires du pesticide et de la référence de premier ou pseudo premier ordre (photolyse, réactions avec HONO, NO etc.).  $K_p$  et  $K_p$ ' sont donc les sommes des constantes de pseudo premier ordre des réactions secondaires et de la constante de photolyse de respectivement l'analyte et la référence.

En supposant que la concentration des espèces parasites est constante, les équations (18) et (21) conduisent à la relation suivante:

$$\frac{1}{t-t_0} \cdot \ln\left(\frac{[P]_t}{[P]_{t_0}}\right) = \frac{R}{t-t_0} \cdot \ln\left(\frac{[Ref]_t}{[Ref]_{t_0}}\right) + \left(K_p - R \cdot K_p'\right)$$
(22)

où  $[P]_{t0}$  et  $[Ref]_{t0}$  sont respectivement les concentrations initiales, à  $t_0$ , de l'analyte et de la référence dans le dépôt,  $[P]_t$  et  $[Ref]_t$  les concentrations résiduelles de chaque pesticide au

temps *t*.  $k_{OH}$  et  $k_{ref}$  sont les constantes de vitesse hétérogènes entre les radicaux OH et respectivement l'analyte et la référence. *R* réprésente le rapport des constantes cinétiques de second ordre du compsé et de la référence ( $R = k_{OH}/k_{ref}$ ). Le tracé de  $ln([P]_{t0}/[P]_t)/(t-t_0)$  en fonction de  $ln([Ref]_{t0}/[Ref]_t)/(t-t_0)$  est une droite dont la pente est égale à  $k_{OH}/k_{ref}$ . Connaissant  $k_{ref}$ , il est donc possible de déterminer la constante de vitesse recherchée  $k_{OH}$ , caractérisant la réactivité du pesticide avec les radicaux OH en phase hétérogène (pour plus des détails consulter l'Annexe II).

## I.4 Identification des produits de dégradation

Dans l'optique de déterminer le mécanisme de dégradation des pesticides, des expériences ont été menées pour identifier les produits de dégradation en phase condensée. Les expériences ont été menées en utilisant le montage expérimental décrit au paragraphe I.2. Toutefois, le fait de travailler à de faibles concentrations initiales de pesticide pour disposer d'un dépôt monocouche rend la recherche de traces difficile. Pour améliorer la sensibilité, nous avons utilisé la technique d'échantillonnage par micro extraction en phase solide, Solid Phase Micro-Extraction (SPME), couplée au GC/MS.

Les expériences d'ozonolyse dédiées à l'identification des métabolites ont été conduites à 100 Torr et à un débit de 3 L.min<sup>-1</sup> avec une concentration d'ozone de  $2.1 \times 10^{15}$  molécules.cm<sup>-3</sup>. Par contre, les expériences d'oxydation par les radicaux OH ont été réalisées à 120 T et à un débit de 85 mL.min<sup>-1</sup>. La concentration de HONO était entre 2 et 4 x  $10^{16}$  molécules.cm<sup>-3</sup>. Les résidus de pesticide des 5 nacelles sont extraits du réacteur en même temps. Chaque nacelle est extraite trois fois par 2 mL de dichlorométhane. Les solutions d'extraction sont disposées dans un bécher propre et laissées à température et pression ambiantes jusqu'à évaporation complète du dichlorométhane. Le résidu sec est repris par 10

mL d'une solution saturée de chlorure de sodium. Une fibre préconditionnée de PDMS (polydimethylsiloxane) est utilisée pour extraire les composés organiques présents dans l'extrait pendant 70 min à 40°C avant désorption dans l'injecteur du GC-MS à 230°C pendant 10 min. Les paramètres tels que le temps et la température d'extraction, le temps et la température de désorption, la force ionique de la solution de chlorure de sodium ont été optimisés (voir paragraphe III.2 du chapitre III).

Les paramètres GC sont les mêmes que ceux utilisés lors des études cinétiques (paragraphe I.1.3) à la différence que le spectromètre de masse est utilisé en mode de courant ionique total (TIC) (30 < m/z < 500) pour permettre l'identification des composés élués dans la colonne grâce aux bibliothèques de spectres de masse.

# II. Etudes en phase gazeuse

En phase gazeuse nos travaux consistent à réaliser des études pour déterminer les spectres d'absorption UV des composés étudiés et déterminer la cinétique de leur réaction avec les radicaux OH. Ainsi nous avons utilisé les dispositifs suivants:

- Sur le plan spectroscopique, nous avons utilisé un monochromateur couplé à un photomultiplicateur.
- Sur le plan cinétique, nous avons utilisé une chambre de simulation atmosphérique rigide couplée avec un FTIR qui nous permet de réaliser des mesures de la constante de vitesse en relatif par rapport à un composé référence.

## **II.1** Etudes spectroscopiques

Ces études consistent à déterminer les spectres d'absorption UV–Visible des composés étudiés. L'intérêt de ces déterminations est d'enrichir les bases de données spectroscopiques, utilisées pour mesurer la concentration de ces composés in-situ. Ces données, couplées aux mesures de rendement quantique, permettent également de calculer leur constante de photodissociation atmosphérique.

#### **II.1.1 Dispositif expérimental**

Le montage utilisé est composé par les éléments suivants:

- Une cellule en pyrex à simple passage de 2 cm de diamètre et de 1.6 m de longueur. Sur toute sa longueur la cellule est entourée par des résistances chauffantes pour réguler la température entre 25 et 100°C. Aux extrémités de cette cellule sont collées des fenêtres optiques en quartz transparentes aux rayonnements UV qui proviennent d'une lampe à deutérium.
- Une source de fond continu. C'est une lampe classique à deutérium (30W). Cette source fournit un spectre continu entre 180 et 400 nm. Le faisceau lumineux fourni par cette source est focalisé à l'entrée du monochromateur au moyen d'un système de lentilles.
- Un monchromateur de type Czerny-Turner Jobin-Yvon HR 640. Celui-ci est équipé de deux réseaux holographiques 1200 et 2400 traits/mm avec une dispersion 0.26 nm mm<sup>-1</sup>. La calibration du monochromateur en longueur d'onde est effectuée à l'aide d'une lampe de mercure à basse pression. La précision du spectrophotomètre est estimée à ± 0.02 nm. La fente du monochromateur peut varier de 80 à 180 µm ce qui donne une résolution spectrale variant de 0.05 à 0.2 nm. A la sortie du monochromateur, le faisceau passe longitudinalement dans la cellule en pyrex qui contient le composé à étudier.

- Un photomultiplicateur (Hamamatsu R955). Placé à l'autre extrémité de la cellule, il nous permet de mesurer le signal lumineux. L'ensemble est relié à un système de saisie de données informatisées.
- Une ampoule contenant l'échantillon préalablement purifié est connectée à la cellule.
   La température de cette ampoule est régulée par des éléments chauffants. A noter que la purification de l'échantillon est réalisée par plusieurs cycles successifs incluant refroidissement, pompage et retour à la température ambiante.

La pression est mesurée par un capteur de pression, type MKS Baratron, opérant dans le domaine (0-10) Torr. La température est mesurée par deux sondes collées à chaque extrémité de la cellule. Ce dispositif présente l'avantage de n'envoyer dans la cellule qu'un faisceau monochromatique, minimisant ainsi les réactions de photolyse des composés étudiés (Figure II.3).



**Figure II.3** Dispositif expérimental pour l'étude des spectres d'absorption UV-Vis de la morpholine, du N-formylmorpholine et du N-acetylmorpholine
## **II.1.2 Protocole expérimental**

Avant chaque manipulation, le bruit de fond du spectromètre est mesuré. Après avoir nettoyé la cellule par un flux de diazote et par pompage, l'intensité émise par la lampe à deutérium à vide,  $I_0(\lambda)$ , à laquelle on soustrait le bruit de fond,  $I_b(\lambda)$ , est enregistrée. On introduit ensuite le composé dans la cellule sous forme gazeuse à une pression inférieure à sa pression de vapeur. La concentration introduite est reliée à la pression suivant la relation des gaz parfaits:

$$C = 3.24.10^{16} (298/T).P \tag{23}$$

où *C* est la concentration du composé (molécule.cm<sup>-3</sup>), *P* la pression mesurée en Torr et *T* la température en K. La détermination des sections efficaces d'absorption est réalisée à l'aide de la relation de Beer Lambert:

$$\sigma_{\lambda} = \ln\left(\frac{I_0(\lambda) - I_b(\lambda)}{I(\lambda) - I_b(\lambda)}\right) \frac{R.T}{P.I.N_A}$$
(24)

où  $\sigma_{\lambda}$  est la section efficace absolue d'absorption (cm<sup>2</sup>.molécule<sup>-1</sup>), *l*: le trajet optique (cm),  $I_0(\lambda)$  l'intensité du faisceau incident,  $I(\lambda)$  l'intensité du faisceau après absorption par l'échantillon gazeux, *R* la constante des gaz parfaits (cm<sup>3</sup>.atm.mol<sup>-1</sup>.K<sup>-1</sup>), *T* la température (K), *P* la pression (atm) et  $N_A$  nombre d'Avogadro (mol<sup>-1</sup>).

Un certain nombre de précautions s'imposent pour minimiser les sources d'erreur sur la détermination des sections efficaces à savoir:

 la calibration en longueur d'onde λ du monochromateur à l'aide des raies atomiques de référence (Hg, Cd, Cs, Zn) proches du domaine spectral étudié.

- l'élimination des impuretés (pour les COV en particulier) par distillation des produits sous vide.
- l'optimisation des conditions expérimentales (pression et longueur optique) pour obtenir une densité optique comprise entre 0.1 et 2.5, domaine où l'erreur sur la section efficace est minimale.
- l'enregistrement, pour un même domaine spectral, de 8 à 10 expériences. La valeur moyenne de ces différentes déterminations fournit alors la valeur de la section efficace pour la longueur d'onde considérée.

# II.2 Oxydation par les radicaux OH

Les études de la réactivité des composés morpholiniques vis-à-vis des radicaux OH ont été réalisées dans une chambre de simulation atmosphérique rigide nous permettant de réaliser des expériences dans des conditions simplifiées proches des conditions atmosphériques. L'évolution du milieu réactionnel est suivie par analyse optique dans le moyen Infra Rouge. Ce montage est composé par un réacteur photochimique et un spectromètre IRTF (Figure II.4).

## **II.2.1** Chambre de simulation atmosphérique

## II.2.1.1 Le réacteur photochimique

C'est un réacteur à triple paroi, réalisé en pyrex pour minimiser d'une part l'effet des réactions hétérogènes au niveau des parois et d'autre part pour être transparent aux rayonnements lumineux photolytiques supérieurs à 300 nm. Ce réacteur est composé d'une cellule à réflexions multiples de 20 cm de diamètre et de 2m longueur. Son volume total est de 63 L et présente un rapport surface/volume de 21 m<sup>-1</sup>. Les réflexions multiples sont assurées par des miroirs dont le

rayon de courbure est de 2 m. Ils sont conçus pour travailler dans le domaine spectral Infra Rouge. Protégés par une couche d'or, leur pouvoir réflecteur est supérieur à 90 % dans le moyen IR. L'ensemble est contenu dans une enceinte en pyrex dans laquelle le vide est fait, pour éviter les phénomènes de condensation sur les fenêtres optiques et les parois. Le réacteur est thermalisable (-60°C à 100°C) à l'aide de la circulation d'un fluide entre la première et la deuxième paroi. Le réacteur est enfermé dans un caisson en bois recouvert intérieurement d'aluminium pour uniformiser le rayonnement. Les extrémités du réacteur sont fermées par deux flasques en inox qui supportent:

- Les différentes lignes d'introduction des composés dans le milieu réactionnel.
- Les supports des miroirs et les vis micrométriques permettant les réglages de trajet optique dans la cellule.
- Deux fenêtres optiques type ZnSe dont les caractéristiques physiques et optiques permettent l'acquisition de spectres dans la région comprise entre (750-4000 cm<sup>-1</sup>).

#### II.2.1.2 Le système d'introduction des réactifs et de contrôle

Il est composé par des contrôleurs de débit gazeux (débitmètres massiques). Un capteur de pression (MKS Baratron) préalablement calibré permet de mesurer la pression dans le réacteur.

Le composé à étudier, contenu dans flacon en verre sous sa pression de vapeur, est purifié. Il est introduit dans la cellule, préalablement vidée, par détente isotherme. La quantité introduite est traduite par la pression affichée sur le capteur. Cette pression est inférieure à sa pression de vapeur. Dans le cas où plusieurs composés sont introduits, l'ordre d'introduction se fait dans le sens croissant de leur pression de vapeur. La température est régulée par une circulation de fluide entre les deux parois de la cellule. La circulation du fluide est commandée par un thermostat Julabo FPW 90 qui nous permet d'atteindre de basses ou de hautes températures (éthanol, eau). Le domaine de travail du thermostat se situe entre -60 et +100°C. Le suivi de la température du milieu réactionnel est réalisé au moyen de deux sondes platine (Pt 100-DIN 43760), placées aux extrémités du réacteur.

#### II.2.1.3 Le système de photolyse

Afin de générer les radicaux OH à partir de l'acide nitreux, une série de 24 lampes fluorescentes entourent le réacteur de manière symétrique pour produire une photolyse homogène du milieu réactionnel. Ces lampes de 120 cm de longueur émettant entre 300 et 460 nm (maximum vers 365nm, voir spectres en Annexe III) (Philips, TL 40W/05). Chaque lampe est commandée individuellement par un interrupteur ce qui permet de fixer la quantité de lumière nécessaire.

#### **II.2.2 Technique analytique IRTF**

Nous avons choisi de coupler notre chambre de simulation atmosphérique à la technique analytique Infra Rouge à Transformée de Fourier (IRTF). En effet tous les composés organiques présentent une structure d'absorption caractéristique en infrarouge. Cela nous permet de suivre l'évolution de la réactivité in situ du milieu réactionnel en temps réel. En outre le diagnostic par IRTF est une analyse non destructrice, rapide, multi-composant et qui peut être réalisée en mode transmission ou réflexion.



Réacteur photochimique

Figure II.4 Chambre de simulation atmosphérique

#### II.2.2.1 Rappel du principe de la spectroscopie Infrarouge

La spectroscopie infrarouge est basée sur l'interaction de la lumière avec le nuage électronique des liaisons chimiques qui composent une molécule. En effet, l'absorption du rayonnement infrarouge par une molécule peut provoquer la transition des électrons entre les niveaux de rotation et de vibration des liaisons atomiques (4-40 kJ mol<sup>-1</sup>). Plusieurs modes de vibrations sont possibles. Seuls les modes vibrationnels qui entraînent une variation du moment dipolaire de la molécule peuvent absorber les radiations infrarouges et donner lieu à des bandes d'absorption infrarouge. Le coefficient d'extinction sera proportionnel à l'intensité de la variation du moment dipolaire. Le spectre infrarouge est la représentation graphique de cette absorbance en fonction de la longueur d'onde  $\lambda$  exprimée sous forme de nombre d'onde  $\upsilon$ .

#### II.2.2.2 La spectroscopie infrarouge à transformée de Fourier (IRTF)

Deux facteurs fondamentaux ont fait que, ces dernières 20 années, la spectrométrie IRTF a connu un développement considérable avec:

L'utilisation de l'interférométrie, basée sur la génération d'interférences constructives et destructives, dans le rayonnement IR polychromatique, au moyen d'un d'interféromètre de Michelson. La lumière infrarouge émise par la source est dirigée vers l'interféromètre. Ce dernier va moduler chaque longueur d'onde du faisceau à une fréquence différente. Dans l'interféromètre, le faisceau lumineux arrive sur la séparatrice qui divise le faisceau en deux parties de même énergie. La première partie est alors dirigée sur le miroir fixe, le reste passe à travers la séparatrice et est dirigé sur le miroir mobile. Quand les deux faisceaux se recombinent, des interférences destructives ou constructives apparaissent en fonction de la position du miroir mobile. Le faisceau passe alors à travers l'échantillon avant d'atteindre le détecteur. Le signal

transmis par le détecteur apparaît comme un interférogramme. Ce dernier représente l'intensité globale du faisceau en fonction de la différence de marche optique. Le spectre est calculé à partir de l'interférogramme grâce à l'algorithme de transformation de Fourier. L'Annexe IV détaille le principe de l'interféromètre de Michelson.

- L'application de la transformée de Fourier (TF). Cet outil permet de convertir, en quelques secondes, l'interférogramme collecté en spectre (émission, absorption, transmission, etc.). Le processus de conversion se fait par l'algorithme de transformation Fourier rapide. Un certain nombre de traitements sont nécessaires avant l'application de la transformée de Fourier à savoir:
  - i) l'apodisation qui permet de réduire la taille des pics secondaires crées artificiellement grâce à la troncature du balayage à ses limites (présence des pics secondaires de part et d'autre de l'interférogramme).
  - ii) la correction de la phase. Cette correction supplémentaire doit être apportée pour tenir compte des déphasages introduits par les imperfections instrumentales. Elle est liée au déplacement rapide du miroir mobile entraînant une imprécision dans la mesure de la position  $\delta=0$ .
  - iii) le zéro filling qui consiste à ajouter des zéro aux deux extrémités de l'interférogramme pour produire un prolongement artificiel de ses branches et simuler un accroissement de la différence de marche optique  $\delta$ . Cela permet d'améliorer le spectre en augmentant artificiellement la résolution spectrale.

#### II.2.2.3 Dispositif IRTF utilisé

L'appareil que nous avons utilisé pour nos études est un spectrophotomètre infrarouge à transformée de Fourier de type Equinox 55 (Bruker, Wissembourg, France). Les principales caractéristiques de cet appareil sont les suivantes:

- Domaine spectral: 4000 cm<sup>-1</sup> 400 cm<sup>-1</sup>
- Résolution maximale: 0.5 cm<sup>-1</sup>
- Source: de type « Globar ». Elle est constituée d'un filament de carbure de silicium (SiC) et fonctionne à des températures de l'ordre de 1500°C. Elle rayonne dans un domaine spectral compris entre 10000 et 250 cm<sup>-1</sup>. Il peut être ajusté par l'utilisation d'un diaphragme dont l'ouverture permet de modifier l'intensité de la lumière entrant dans l'interféromètre
- Séparatrice: lame multicouche de KBr
- Laser d'asservissement: Helium-Néon émettant à  $\lambda = 632.8$  nm. Celui-ci sert à mesurer la position du miroir mobile afin de calibrer les fréquences du spectromètre avec une précision supérieure à 0,0005 cm<sup>-1</sup> pour une résolution de 2 cm<sup>-1</sup>
- Détecteurs: L'appareil est équipé de deux détecteurs; un détecteur du type pyroélectrique (générant un courant proportionnel au différentiel de température entre les 2 faces du détecteur) au sulfate de triglycine deutéré DTGS (Deuterated Tri-glycine Sulfate) et un détecteur, photovoltaïque, (générant une différence de potentiel par l'absorption de photons) au tellure de mercure et de cadmium MCT (Mercure Cadmium Tellure), qui nécessite un refroidissement à l'azote liquide.

- 6 ports d'entrée-sortie permettant différents couplages avec différents systèmes réactifs (échantillons) ou avec d'autres moyens analytiques.
- Un ordinateur, en interface avec le spectromètre IRTF: il permet la commande des mesures. L'acquisition des spectres et leurs traitements sont réalisés au moyen du logiciel OPUS (Bruker Optics, version3.1).

#### II.2.2.4 Couplage IRTF chambre de simulation atmosphérique

Le spectromètre IRTF, Brucker Equinox 55 est posé sur une table conçue pour atténuer les vibrations et solidaire au support de la chambre de simulation atmosphérique. Dans le compartiment échantillon du spectromètre un système optique composé par deux miroirs sphériques, de quatre miroirs plans et des vis micrométriques est placé afin d'extraire le faisceau infrarouge en provenance du spectromètre et de l'orienter à l'entrée de la cellule à réflexion multiple (Figure II.5). A la sortie de la cellule le faisceau d'analyse est focalisé, par un jeu de miroirs vers le détecteur (MCT ou DTGS). Le réglage et l'alignement du spectromètre IR et de la chambre de simulation atmosphérique sont réalisés au moyen d'un laser d'alignement He-Ne.



Spectromètre IRTF

# Figure II.5 Schéma du système optique de l'IRTF

# II.2.2.5 Conditions expérimentales

L'ensemble de ce dispositif, nous permet de travailler dans des conditions expérimentales très variées:

- Température: -60 à 100°C
- Pression: quelques Torr à 760 Torr
- Trajet optique: peut atteindre 80 m et permet ainsi la mesure des absorptions très faibles et la détection des espèces à l'état de trace

Grâce à cette technique, nous pouvons suivre l'évolution, en temps réel et in situ, des composés chimiques au cours d'une réaction et d'étudier des systèmes réactifs en régime statique.

## II.2.2.6 Procédure expérimentale

Les expériences sont réalisées selon le protocole suivant:

- Conditionnement de la chambre atmosphérique à la température de l'expérience.
- Les ampoules contenant l'échantillon et la référence purifiés sont connectées au réacteur dans lequel le vide a préalablement été réalisé (Figure II.4). C'est le composé qui possède la plus faible pression de vapeur qui est introduit le premier.
- Introduction de l'air à quelques centaines de Torrs. Ce mélange est laissé dans le noir pendant 1 heure afin de contrôler s'il y a perte de réactifs par des réactions secondaires.
- Entraînement de HONO par un faible débit d'air jusqu'à élévation de pression de quelques dizaines de Torrs (10-15 Torrs). Pour la synthèse de HONO, la même procédure que celle décrite dans le paragraphe I.2.2 est utilisée.
- Introduction de l'air jusqu'à atteindre la pression atmosphérique puis enregistrement de plusieurs spectres pour vérifier que les concentrations initiales du composé et de la référence sont constantes.
- Allumage des lampes photolytiques et suivi de l'évolution du milieu réactionnel en fonction de temps.

Dans l'étude de la réactivité de composés présentant de faibles pressions de vapeur, la température de la cellule est maintenue autour de 40°C pour minimiser les risques de condensation de ces produits. Ce chauffage n'est pas nécessaire dans le cas de la morpholine, dont la pression de vapeur est plus élevée. Les paramètres analytiques utilisés sont résumés dans Tableau II.2.

Tableau II.2 Paramètres expérimentaux utilisés dans l'étude de l'oxydation par les radicaux

OH en phase gazeuse de la morpholine, du N-formylmorpholine (NFM) et du N-

	Morpholine	NFM	NAM
Source	MIR (graphite)	MIR (graphite)	MIR(graphite)
Detecteur	DTGS/MCT	МСТ	МСТ
Vitesse de Balayage (KHz)	6 à 10	7 à 20	8 à 20
Résolution $(cm^{-1})$	2	2	2
Gain de Détecteur	128/16	16	16

acetylmorpholine (NAM)

La cinétique de dégradation de chaque composé est obtenue en suivant l'évolution de l'aire d'une bande d'absorption du produit dans le temps. Il est important de s'assurer que la bande considérée est spécifique au produit étudié et ne subit aucune interférence avec celles de la référence et des produits de réaction formés. La constante de vitesse vis à vis des radicaux OH est déterminée en utilisant l'équation (22). Chapter III

# **Heterogeneous Reactivity**

This chapter reports in detail the results obtained regarding the heterogeneous oxidation of Dimethomorph (Z and E isomers) and Folpet by ozone and OH-radicals, in terms of kinetic rate constants as well as degradation products. Based on the identification of CPMPM ((3,4-dimethoxypheny)(4-chlorophenyl)methanone) as a product of ozonolysis and OH-oxidation of dimethomorph in the condensed phase, a mechanistic scheme of degradation has been proposed. Moreover, this chapter contains data concerning the kinetic rate constants of heterogeneous degradation of CPMPM by both oxidants (ozone and OH-radicals).

Also included, is a discussion of the atmospheric implications of the obtained results, particularly the fate of the analyzed species adsorbed or deposited on atmospheric aerosols, as well as their atmospheric lifetimes. The chapter is concluded with a brief synthesis and a comparison of our results to those reported for the heterogeneous oxidation of other nonvolatile pesticides and species.

# I. Heterogeneous oxidation by ozone

# I.1 Preliminary studies

Before starting with the oxidation experiments, a couple of preliminary studies were performed in order to ensure that the experimental setup and conditions employed are suitable.

### I.1.1 Volatilization

Considering that all experiments were conducted at relatively low pressures (30-150 Torr) under continuous gaseous flows, it was necessary to verify if some of the deposited sample can be lost by volatilization during an oxidation experiment. Therefore, preliminary experiments were conducted at 25 Torr and at  $N_2$  flow rates similar or superior to those

employed in oxidation experiments (approximately 700 mL.min<sup>-1</sup> at ambient temperature and 25 Torr), in the absence of oxidant gases, in order to assess whether or not any of the analyzed compounds is lost by volatilization within 8 to 9 hours, which is the maximum duration of an oxidation experiment.



Figure III.1 Influence of volatilization on the degradation of the analyzed compounds

The results show that none of the analyzed compounds volatilizes under the experimental conditions used in this study (Figure III.1). This means that volatilization does not contribute to the loss in the initial concentration of the deposited sample during an oxidation experiment.

## I.1.2 Photolysis

The contribution of photolysis to the total degradation of the analyzed compounds has been evaluated. As shown in Figure III.2, folpet, dimethomorph, and terbuthylazine do not degrade under the effect of the UV lamps used in OH-oxidation experiments within 8 to 9 hours of exposure. However, CPMPM is degraded by the UV source employed in our study at a rate equivalent to  $6.5 \times 10^{-5} \text{ s}^{-1}$ .



Figure III.2 Degradation of the analyzed compounds by photolysis

In conclusion, the results show that folpet, dimethomorph and terbuthylazine are not susceptible to photolysis under the experimental conditions employed in our study. The photolysis of CPMPM under these conditions is accounted for in relation (22) of chapter II. The obtained results can not be extrapolated to the atmosphere since the actininc flux of solar radiation is different than that of the black UV lamps employed.

# I.2 Experimental conditions

Ozonolysis experiments were carried out in the dynamic mode at constant ozone concentrations as explained in section I.2.1 of chapter II. The experiments were performed at ambient temperatures (T = 298 K) with ozone concentrations ranging between 3 and 23 x  $10^{14}$ 

molecules.cm<sup>-3</sup>. Meanwhile, the initial quantity of analyte in each sample was set at 1  $\mu$ g. The mean residence time of gases inside the reaction medium is in the order of several seconds (15 to 20 s). Table III.1 summarizes the experimental conditions employed in the study of the heterogeneous ozonolysis of dimethomorph, folpet and CPMPM. Uncertainties in pressure, absorbance and ozone concentration correspond to the standardad devaiation of the different values recorded at regular time intervals throughout an experiment.

Table III.1 Experimental conditions of heterogeneous ozonolysis of dimethomorph, folpet

	Exp.	Pressure (Torr)	Absorbance at 254 nm	<b>O<sub>3</sub> Concentration</b> * (x $10^{14}$ molecules.cm <sup>-3</sup> )
	1	$29 \pm 1$	$0.35\pm0.02$	$3.1 \pm 0.2$
Чd	2	$30 \pm 2$	$0.34\pm0.04$	$3.0\pm0.4$
iouc	3	$53 \pm 2$	$0.72\pm0.13$	$6.4\pm1.2$
netha	4	$53 \pm 3$	$0.69\pm0.05$	$6.1\pm0.4$
Din	5	$100 \pm 7$	$1.05\pm0.08$	$9.3\pm0.7$
	6	$99\pm4$	$1.09\pm0.03$	$9.7\pm0.3$
Folpet	1	$130\pm10$	$1.50\pm0.24$	$13.3 \pm 2.1$
	2	$118\pm15$	$1.10\pm0.19$	$9.8 \pm 1.7$
	3	$116 \pm 5$	$2.05\pm0.23$	$18.2\pm2.0$
	4	$114 \pm 7$	$0.96 \pm 0.26$	$8.5\pm2.3$
	5	124 ±31	$2.35\pm0.39$	$20.8\pm3.5$
	6	$114\pm18$	$2.56\pm0.30$	$22.8\pm2.6$
ν	1	$110\pm7$	$1.99\pm0.10$	$17.6 \pm 0.9$
VdWd	2	$110 \pm 2$	$1.59\pm0.06$	$14.1\pm0.5$
C	3	$106 \pm 3$	$1.14\pm0.15$	$10.1 \pm 1.3$

and CPMPM

\*values calculated using  $\sigma_{O3}(254 \text{ nm}) = 1.128 \text{ x } 10^{-17} \text{ cm}^2$ .molecule<sup>-1</sup> (Brion et al., 1998) and a

path-length of 1 m

# I.3 Determination of degradation kinetics

Kinetic rate constants of the heterogeneous ozonolysis of folpet, dimethomorph and CPMPM were determined by following the evolution of the ratio of chromatographic peak areas  $A/A_0$  (peak area of the analyte sample divided by the area of the same peak corresponding to the analyte blank) with time. The blank was analyzed before and after each sample analysis so as to minimize any uncertainties originating from the deviation of the MS signal and GC response. Therefore, the value of  $A_0$  is actually the average of the peak areas of the same blank solution injected into the GC before and after each sample analysis. Figures III.3 to III.6 depict the variation of  $A/A_0$  ratio as a function of time for three different experiments corresponding to three different ozone concentrations for each of the analyzed compounds. It should be noted that the dimethomorph standard used in this study is a mixture of Z- and E-dimethomorph isomers which were analyzed separately.

As ozonolysis experiments were carried out at constant ozone concentrations the obtained data-points depicted in Figures III.3 to III.6 were treated by pseudo 1<sup>st</sup> order kinetics based on the following equation:

$$[A]_t / [A]_0 = exp(-k_{obs}t) \tag{1}$$

where  $k_{obs}$ , the pseudo 1<sup>st</sup> order rate constant is equivalent to the product of the 2<sup>nd</sup> order rate constant ( $k_{O3}$ ) and the concentration of gaseous ozone ( $[O_3]_g$ ).  $[A]_0$  and  $[A]_t$  are the concentrations of the chromatographic analyte peaks (directly proportional to the concentrations of the analyzed compounds) at t<sub>0</sub> and t, respectively.



**Figure III.3** The variation of A/A<sub>0</sub> ratio as a function of time at specified ozone concentrations for Z-dimethomorph





concentrations for E-dimethomorph



Figure III.5 The variation of  $A/A_0$  ratio as a function of time at specified ozone

#### concentrations for Folpet





concentrations for CPMPM

As shown in Figures III.3 to III.6, the rate of degradation of Z- and E-dimethomorph by ozone is greater than those found for folpet and CPMPM, even though ozonolysis experiments of dimethomorph were carried out at concentrations lower than those employed for the other analytes. Within 2 to 3.5 hours of exposure to an ozone rich atmosphere ( $3.0 < [O_3] < 9.7 \times 10^{14}$  molecules.cm<sup>-3</sup>) 70-80 % of the initial concentration of Z-dimethomorph was lost via degradation, as compared to 75-85 % degradation for E-dimethomorph. This shows that among the two isomers, E-dimethomorph is slightly more reactive towards ozone than Zdimethomorph. Meanwhile, only 40-65 % degradation was obtained for either folpet or CPMPM within 6 to 7 hours of exposure to ozone at concentrations ranging between 8.5 and 22.8 x 10<sup>14</sup> molecules.cm<sup>-3</sup> for folpet, and 10.1 and 17.6 x 10<sup>14</sup> molecules.cm<sup>-3</sup> for CPMPM.

Using relation (1) we were able to determine the values of  $k_{obs}$  which increase with increasing ozone concentrations. The values of  $k_{obs}$  obtained at different ozone concentrations for the three analytes are reported in Table III.2. Uncertainties in the values of  $k_{obs}$  are determined using the least squares method.

	Exp.	<b>O<sub>3</sub> Concentration</b> $(10^{14} \text{ molecules.cm}^{-3})$	$k_{obs}$ (x 10 <sup>-5</sup> s <sup>-1</sup> )
	1	$3.1 \pm 0.2$	$8.9\pm0.6$
hqrc	2	$3.0 \pm 0.4$	$6.3 \pm 0.4$
юто	3	$6.4 \pm 1.2$	$14.5\pm0.1$
neth	4	$6.1 \pm 0.4$	$9.3\pm0.1$
Ţ-Di	5	$9.3\pm0.7$	$16.5\pm0.2$
	6	$9.7\pm0.3$	$13.9\pm0.1$
Чd	1	$3.1 \pm 0.2$	$11.7\pm0.7$
mor	2	$3.0 \pm 0.4$	$8.3\pm0.2$
etho	3	$6.4 \pm 1.2$	$17.0 \pm 0.1$
Dime	4	$6.1 \pm 0.4$	$13.6\pm0.1$
E-L	5	$9.3 \pm 0.7$	$14.3 \pm 0.1$

Table III.2 kobs values at different ozone concentrations

	6	$9.7\pm0.3$	$18.0\pm0.1$
	1	$13.3 \pm 2.1$	$3.6\pm0.3$
	2	$9.8\pm1.7$	$2.5\pm0.4$
pet	3	$18.2\pm2.0$	$4.5\pm0.4$
1 9 5 6	$8.5\pm2.3$	$2.6\pm0.6$	
	5	$20.8\pm3.5$	$5.3 \pm 0.3$
	6	$22.8\pm2.6$	$5.2\pm0.3$
М	1	$17.6\pm0.9$	$4.7\pm0.3$
2 2 3	$14.1\pm0.5$	$3.6\pm0.2$	
	3	$10.1 \pm 1.3$	$3.0\pm0.2$

# I.4 Analysis and exploitation of the kinetic results

In order to determine the kinetic rate constants of the heterogeneous reactions of dimethomorph, folpet and CPMPM with ozone, the obtained  $k_{obs}$  values were plotted against  $[O_3]_g$  for each compound as shown in Figures III.7- III.10. The experimental data-points were then analyzed using the LH and the LR heterogeneous models described in detail in sections I.3.1.1 and I.3.1.2, so as to determine the mechanism of heterogeneous ozonolysis for each analyte.



**Figure III.7** Plot of  $k_{obs}$  as a function of  $[O_3]_g$  for Z-dimethomorph







**Figure III.9** Plot of  $k_{obs}$  as a function of  $[O_3]_g$  for Folpet





#### I.4.1 Langmuir-Rideal (LR) Model

This model is described in detail in section I.3.1.2. It supposes that gaseous ozone reacts directly with the deposited analyte as follows:

Analyte (s) + O<sub>3</sub> (g) 
$$\rightarrow$$
 Products (2)

Based on the LR model, the kinetics of reaction (2) is described by relation (1) when ozone concentration is constant. The real second order kinetic rate constants,  $k_{O3}$ , of ozonolysis of the investigated compounds are equivalent to the slopes of the linear curves fitted to the plots of  $k_{obs}$  as a function of  $[O_3]_g$  as shown in Figures III.7 to III.10. The obtained values of the kinetic rate constants,  $k_{O3}$ , for each analyte are reported in Table III.3. The uncertainties in  $k_{O3}$  values are equivalent to the standard deviation of the non-averaged  $k_{O3}$  values, calculated for each individual pair of  $k_{obs}$  and ozone concentration values reported in Table III.2.

Compound	Ozonolysis		
	LR Mechanism		
	$\frac{\mathbf{k_{O3}}}{(\mathrm{cm}^{3}.\mathrm{molecule}^{-1}.\mathrm{s}^{-1})}$		
Z-Dimethomorphe	$(1.7 \pm 0.5) \ 10^{-19}$		
E-Dimethomorphe	$(2.1 \pm 0.8) \ 10^{-19}$		
Folpet	$(2.6 \pm 0.2) \ 10^{-20}$		
СРМРМ	$(2.7 \pm 0.2) \ 10^{-20}$		

**Table III.3** 2<sup>nd</sup> order ozonolysis rate constant values of the analyzed species

A comparison between these values shows that, based on the LR model, dimethomorph is approximately 10 times more reactive than either folpet or CPMPM towards ozone, with the reactivity of the E-isomer being slightly greater than that of the Z-isomer. Meanwhile, the reactivities of folpet and CPMPM are similar.

## I.4.2 Langmuir-Hinshelwood (LH) Model

According to the Langmuir-Hinshelwood mechanism, the reaction between the pesticide and ozone takes place in two steps. First, ozone must adsorb on the surface, and then the adsorbed ozone reacts with the pesticides as follows:

Analyte (s) + O<sub>3</sub> (ads) 
$$\rightarrow$$
 Products (3)

When treating the experimental results with the LH model, it is no longer possible to determine the  $2^{nd}$  order kinetic rate constant  $k_{O3}$  since this value becomes dependant on the concentration of ozone. As explained in section I.3.1.1, the LH model yields the following relation between  $k_{obs}$  and the concentration of gaseous ozone (see chapter II section I.3.1.1):

$$\frac{1}{k_{obs}} = \frac{1}{k_{max}.K_{O3}} \cdot \frac{1}{[O_3]_g} + \frac{1}{k_{max}}$$
(4)

The plots of  $1/k_{obs}$  against  $1/[O_3]_g$  yield the values of  $k_{max}$  (the maximum rate constant that may be attained) and  $K_{O3}$  (the equilibrium constant of adsorption of ozone) for the different analytes, as shown in Figure III.11.



Figure III.11 Plots of 1/k<sub>obs</sub> against 1/[O<sub>3</sub>]g for dimethomorph, folpet and CPMPM

The plotted curves of  $1/k_{obs}$  vs  $1/[O_3]_g$  are linear with R<sup>2</sup> values of 0.95 and 0.96 for folpet and CPMPM, respectively. However, correlation values are much less for dimethomorph (0.78 and 0.72, for the Z- and E-isomers, respectively). Such an observation may be attributed to the fact that ozonolysis experiments of dimethomorph were carried out at ozone concentrations 2-3 times lower than those used for folpet and CPMPM, as well as to the uncertainty in the values of  $k_{obs}$  (up to 7 %).

Table III.4 summarizes the values of  $k_{max}$  and  $K_{O3}$  obtained for all species investigated in this study. Uncertainties in these values were calculated using the method of least squares and were found to range between 40 and 60 %. As shown in this table, among the analyzed species, dimethomorph has the highest  $k_{max}$  value. This means that based on the LH model, dimethomorph is the most reactive of the species towards ozone. Meanwhile, the values obtained for  $K_{03}$  vary between 0.2 and 1.9 x 10<sup>-15</sup> cm<sup>3</sup>.

Compound	Ozonolysis			
	LH Me	LH Mechanism		
	$k_{max}$ (s <sup>-1</sup> )	$K_{O3}$ (cm <sup>3</sup> )		
Z-Dimethomorph	$(2.8 \pm 1.4) \ 10^{-4}$	$(1.1\pm0.6)\ 10^{-15}$		
E-Dimethomorph	$(2.7 \pm 1.0) \ 10^{-4}$	$(1.9 \pm 0.9) \ 10^{-15}$		
Folpet	$(1.9 \pm 0.9) \ 10^{-4}$	$(1.8 \pm 0.9) \ 10^{-16}$		
СРМРМ	$(1.7 \pm 1.0) \ 10^{-4}$	$(2.1 \pm 1.2) \ 10^{-16}$		

**Table III.4**  $k_{max}$  and  $K_{O3}$  values determined for all investigated species

# I.5 Discussion

# I.5.1 Influence of initial analyte concentration

Although surface coverage of the quartz plaques employed in this study does not exceed 70 % for any of the analyzed compounds, it may be possible to attain multi-layer coverage at certain sites on the surface, due to its rugosity. Such multi-layer coverage may influence the rate of oxidation since some of the analyte molecules deposited on the quartz surface would be hidden under other similar molecules, thus rendering them unavailable for oxidation. Therefore, ozonolysis experiments have been carried out using initial analyte quantities (0.2  $\mu$ g per sample) five times less than those otherwise employed in this study (1  $\mu$ g per sample). This experiment is used to show whether or not the surface coverage for 1  $\mu$ g of deposited analyte exceeds a certain limit beyond which the analyte molecules are no longer

totally exposed to the oxidizing atmosphere. The measured rate constants are valid only if the surface coverage is less than the afore-mentioned limit.

Preliminary assessments show that, when extracted by 10 ml of dichloromethane, the 0.2  $\mu$ g samples of dimethomorph yield solutions whose concentractions (0.02 ppm) are too low to be well detected by the GC/MS analytical system, even in the SIM mode. Therefore, a technique of higher sensitivity was employed for the extraction and analysis of the oxidized samples of dimethomorph (0.2  $\mu$ g). This technique is Solid Phase MicroExtraction (SPME) for which the parameters have been optimized (further details in section III.2 of chapter III). After oxidation, each sample was extracted 3 times by 2 ml of dichloromethane. The extracts were collected in a beaker and the solvent was left to evaporate at ambient conditions. Upon the evaporation of the solvent, the residue was dissolved in 10 ml of a saturated NaCl solution. Afterwards, the residue was extracted by a polydimethylsiloxane fiber for 70 min at 40°C and then analyzed by a GC/MS system in the SIM mode. The final extraction and injection processes were automated.

Figure III.12 depicts the rate of degradation of dimethomorph using 0.2  $\mu$ g samples, and an ozone concentration equal to 8.5 x 10<sup>14</sup> molecules.cm<sup>3</sup>.



Figure III.12 The variation of A/A<sub>0</sub> ratio as a function of time at an initial dimethomorph mass equivalent to 0.2  $\mu$ g per sample ([O<sub>3</sub>] = 8.5 x 10<sup>14</sup> molecules.cm<sup>3</sup>)

The kinetic rate constants calculated using pseudo first order kinetics, for an initial concentration of 0.2 µg per sample are 1.2 and 1.7 x  $10^{-19}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for Z and E-dimethomorph, respectively. These values are similar to the values reported in the previous sections ((1.7 ± 0.5) and (2.1 ± 0.8) x  $10^{-19}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for Z and E-dimethomorph, respectively) for a higher initial mass of dimethomorph (1 µg), especially considering that the extraction and injection techniques used for the two concentrations were different: aqueous-SPME extraction and dichloromethane extraction for 0.2 µg and 1 µg samples, respectively. This proves our hypothesis that, when working with an initial mass of 1 µg, surface coverage is less than 100 %; and so, we may conclude that the values of kinetic rate constants of ozonolysis and of oxidation by OH-radicals determined using 1 µg analyte samples are representative of the actual rate constant values.

## I.5.2 Comparison of reactivity with other compounds

The results summarized in Table III.5 show that the heterogeneous reactivity of folpet and CPMPM relative to ozone is weak. This is to be expected since it is known that aromatic cycles are not greatly disposed to degradation under the influence of ozone (Atkinson and Carter, 1984; Pate et al., 1976). Dimethomorph, on the other hand is approximately 10 times more reactive than either folpet or CPMPM with respect to ozone. This may be explained by the presence of an unsaturated, non-aromatic, double bond in dimethomorph; a bond known to be susceptible to ozone addition. Nevertheless, with a kinetic rate constant in the order of  $10^{-19}$ cm<sup>-3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>, the reactivity of dimethomorph with respect to ozone is considered weak. Such weakness may be attributed to the hindering stereochemical effect of aromatic groups of dimethomorph which mask the active site of reaction (the double bond) and ultimately slow it down.

Compound	Support	LH Mechanism		LR Mechanism	Reference
		$\mathbf{k}_{\max}$ (s <sup>-1</sup> )	<b>K</b> <sub>03</sub> (cm <sup>3</sup> )	<b>k</b> <sub>03</sub> (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	
Z-Dimethomorph	quartz plaques	$(2.8 \pm 1.4) \ 10^{-4}$	(1.1±0.6) 10 <sup>-15</sup>	$(1.7 \pm 0.5) \ 10^{-19}$	present study
E-Dimethomorph	quartz plaques	$(2.7 \pm 1.0) \ 10^{-4}$	$(1.9 \pm 0.9) \ 10^{-15}$	$(2.1 \pm 0.8) \ 10^{-19}$	present study
Folpet	quartz plaques	$(1.9 \pm 0.9) \ 10^{-4}$	$(1.8 \pm 0.9) \ 10^{-16}$	$(2.6 \pm 0.2) \ 10^{-20}$	present study
СРМРМ	quartz plaques	$(1.7 \pm 1.0) \ 10^{-4}$	$(2.1 \pm 1.2) \ 10^{-16}$	$(2.7 \pm 0.2) \ 10^{-20}$	present study
Difenoconazole	quartz plaques	$(4.9 \pm 0.5) \ 10^{-5}$	$(9.1 \pm 1.0) \ 10^{-16}$	$(2.6 \pm 0.4) \ 10^{-20}$	(Al Rashidi et al., 2011)
Alachlore	silica		_	< 0.5 x 10 <sup>-19</sup>	(Pflieger et al., 2009b)
Cypermethrin	ZnSe crystals	$(7.0 \pm 1.0) \ 10^{-4}$	$(4.7 \pm 1.7) \ 10^{-16}$	_	(Segal-Rosenheimer and Dubowski, 2007)

 Table III.5 Summary of the ozonolysis rate constants obtained for the compounds

 investigated in this study as well as other similar compounds

Terbuthylazine	silica	_	-	< 0.5 x 10 <sup>-19</sup>	(Pflieger et al., 2009b)
Terbunyuzine	silica	-	-	$< 5 \times 10^{-19}$	(Palm et al., 1997)
Trifluarine	silica	$(1.1 \pm 0.9) \ 10^{-3}$	$(3.4 \pm 3.6) \ 10^{-16}$	$(2.9 \pm 0.1) \ 10^{-19}$	(Pflieger et al., 2009b)
Anthracene	organic films	$(2.5 \pm 0.2) \ 10^{-3}$	$(5.6 \pm 1.2) \ 10^{-16}$	_	(Kahan et al., 2006)
Benzo[a]pyrene a	soot	$(1.5 \pm 0.1) \ 10^{-2}$	$(2.8 \pm 0.2) \ 10^{-13}$	_	(Pöschl et al., 2001)
	azelaic acid aerosols	$(4.8 \pm 0.8) \ 10^{-2}$	$(1.2 \pm 0.4) \ 10^{-15}$	-	(Kwamena et al., 2004)
	organic films	$(5.5 \pm 0.2) \ 10^{-3}$	$(3.6 \pm 0.5) \ 10^{-16}$	-	(Kahan et al., 2006)
	organic films	$(0.9 \pm 0.1) \ 10^{-3}$	$(10.0 \pm 0.6) \ 10^{-16}$	_	(Kahan et al., 2006)
Naphthalene	silica	$(7.8 \pm 1.7) \ 10^{-5}$	$(4.6 \pm 1.3) \ 10^{-15}$	$(2.3 \pm 0.1) \ 10^{-17}$	(Pflieger et al., 2009a)
	XAD-4	$(1.0 \pm 0.9) \ 10^{-5}$	$(9.6 \pm 14) \ 10^{-15}$	$(4.3 \pm 1.1) \ 10^{-19}$	(Pflieger et al., 2009a)
	gas phase	-	-	< 3.0 x 10 <sup>-19</sup>	(Atkinson et al., 1986)

# I.5.2.1 Comparison of equilibrium partitioning constants (K<sub>03</sub>)

The discrepancy between the different values of the equilibrium partitioning coefficient of ozone ( $K_{O3}$ ) reported in this study is non-negligible, with the highest value (obtained for dimethomorph) being approximately 11 times greater than the lowest value (obtained for folpet). Normally, the partitioning of ozone to the surface is governed by the nature of the adsorbing surface, and is independent of the adsorbed analyte (Kahan et al., 2006; Kwamena et al., 2007). This is evident in the case of our analyte dimethomorph and difenoconazole, an analyte investigated by Al Rashidi et al. (2011) using the same technique as that employed in this thesis (both were deposited on a quartz surface).  $K_{O3}$  values of these two compounds are very similar (( $1.1 \pm 0.6$ )  $10^{-15}$  and ( $9.1 \pm 1.0$ )  $10^{-16}$ , for Z-dimethomorph and difenoconazole, respectively). However, in the case of the other investigated compounds (all deposited on quartz plaques) values show discrepancies. We can hypothesize that, since in

our study the deposited analyte has an infinite residence time on the surface, it may be considered as part of this surface. Therefore, upon deposition of the analyte, the nature of the surface might be slightly modified, yielding different  $K_{O3}$  values for different analytes.

Alternatively, a comparison between the values obtained in this study for quartz surface and those reported by Pflieger et al. (2009a; 2009b) for silica surface shows that the two sets of values are of the same order of magnitude. This is to be expected, since both surfaces are of the same chemical nature (SiO<sub>2</sub>). Meanwhile,  $K_{O3}$  values obtained for analytes adsorbed on soot are 10 and 100 times greater than those reported for XAD-4 and silica surfaces, respectively (Pöschl et al., 2001). All these comparisons prove that the equilibrium partitioning coefficient ( $K_{O3}$ ) depends mostly on the nature of the support.

## I.5.2.2 <u>Comparison of *k<sub>max</sub>* values</u>

The values of  $k_{max}$  are of the same order for the different investigated compounds (varying between 1.7 and 2.8 x 10<sup>-4</sup> s<sup>-1</sup>). This implies that once ozone is adsorbed on the surface, there is an inherent barrier, independent of the identity of the adsorbed chemical species, that governs the rate of the reaction (Kwamena et al., 2007). Kawamena et al. (2007) suggest that this barrier is one of two phenomena:

- the mobility of the two reactants adsorbed on the surface, which influences their proximity (if the two adsorbed reactants are not sufficiently close to each other the reaction may not occur)
- (ii) a rate-determining step of transformation of ozone (if ozone must transform to a more reactive form prior to reacting with the other reactant).

Based on these hypotheses, the calculated  $k_{max}$  values should be similar, whatever the investigated analyte. However, the interaction between ozone and the surface, represented by

122

 $K_{O3}$ , also influences the value of  $k_{max}$ , since it affects the availability of ozone for reaction with the analyte. Generally, the greater the value of  $K_{O3}$ , the less the value of  $k_{max}$  (Kwamena et al., 2007). Our results do not exhibit such a trend, most probably due to the fact that the interactions between ozone and the quartz surface employed in this study are very weak.

## I.5.2.3 Comparison of second order rate constants $(k_{O3})$

As shown in Table III.5, the second order kinetic rate constant ( $k_{O3}$ ) of heterogeneous ozonolysis of dimethomorph, calculated based on the *LR* model, is of the same order of magnitude as that reported by Pflieger et al. (2009b) for trifluarine (1.7, 2.1 and 2.9 x 10<sup>-19</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for Z-dimethomorph, E-dimethomorph and trifluarine, respectively). Similarly,  $k_{O3}$  values of folpet, CPMPM and terbuthylazine are of the same order of magnitude (10<sup>-20</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>).

Meanwhile, the kinetic rate constant ( $k_{O3}$ ) values reported for pesticides, ranging between 2 and 21 x 10<sup>-20</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>, are 20 to 200 times less than that reported by Pflieger et al. (2009a) for the heterogeneous oxidation of naphthalene (2.3 x 10<sup>-17</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>), a polycyclic aromatic hydrocarbon, on a surface whose chemical nature is the same as that used in our study. This goes to show that pesticides are relatively nonreactive towards ozone. It is hard to explain this result except to say that the heterogeneous reactivity of a particular chemical species is of great complexity, and is influenced by several factors including the chemical nature of the pesticide, and the type of adsorbing surface employed.

## I.5.3 LH and LR model comparison

As shown in Figures III.7 to III.10, the experimental datapoints are fitted equally well by both models with  $R^2$  values being similar (for example,  $R^2 = 0.93$  and 0.91 for the *LR* and LH fitting of the CPMPM datapoints, respectively). In other words, both treatments (LH and LR) yield similar results in terms of the deviation between the experimental and the simulated results. Therefore, it is not possible to determine the mechanistic model that is most suited to the ozonolysis reactions of the analytes.

# **II.** Heterogeneous oxidation by OH-radicals

As mentioned before, the kinetic rate constants of the heterogeneous oxidation of dimethomorph, folpet and CPMPM by OH-radicals have been determined relative to the rate constant of a reference compound, due to the unavailability of the analytical techniques that allow for the detection and quantification of OH-radicals directly. In this study, terbuthylazine was chosen as a reference compound for several reasons, one of which is that the value of the kinetic rate constant of heterogeneous oxidation of terbuthylazine by OH-radicals has already been determined. Another reason is that the reactivity of this compound is similar to that expected for the analyzed compounds. Two  $k_{ref}$  values were found in the literature concerning the heterogeneous reactivity of terbuthylazine with OH radicals (Palm et al., 1997; Pflieger, 2009). The first value  $(1.1 \times 10^{-11} \text{ cm}^3 \text{ .molecule}^{-1} \text{ s}^{-1})$  was reported by Palm et al. (1997) for the heterogeneous OH-oxidation of terbuthylazine deposited on silica at 50 % relative humidity. Meanwhile, Pflieger et al. (2009) report a value of  $(1.5 \pm 0.1) 10^{-13}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for the same reaction under dry conditions (0.7 % relative humidity). Considering that our study was conducted under conditions similar to those employed by Pflieger et al. (2009), their reported value was used to calculate the rate constants of heterogeneous OH-oxidation of the analyzed compounds.

# **II.1** Experimental conditions

As in the case of ozonolysis experiments, the OH oxidation experiments were carried out in the quasi static mode in order to maintain constant concentrations of HONO between 3 and 23 x  $10^{14}$  molecules.cm<sup>-3</sup> at an average residence time of 18 min. 1 µg samples of each analyte and reference were oxidized at ambient temperature and pressures ranging between 33 and 110 Torr. The influence of the sample position inside the reactor on reactivity was assessed and was found to be negligible. The experimental set-up is described in detail in chapter II, section I.2.2. The experimental conditions employed for each experiment are summarized in Table III.6. The reported uncertainties in pressure correspond to the standardad devaiation of the different values recorded at regular time intervals throughout an experiment.

Table III.6 Experimental conditions of heterogeneous OH-oxidation of dimethomorph, folpet

	Exp.	Pressure (Torr)	HONO Absorbance at 365 nm	<b>HONO Concentration</b> * $(x \ 10^{15} \text{ molecules.cm}^{-3})$
orph	1	$33\pm8$	0.06 - 0.13	1.2 - 2.7
thom	2	$33\pm 6$	0.07 - 0.19	1.4 – 3.9
Dime	3	$38\pm8$	0.07 - 0.19	1.4 – 3.9
t	1	$52\pm5$	0.27 - 0.45	5.5 - 9.2
olpe	2	$57 \pm 4$	0.16 - 0.32	3.3 - 6.6
H	3	$58\pm7$	0.22 - 0.40	4.5 - 8.2
Ŵ	1	$105 \pm 3$	$0.75 \pm 1.53$	15.4 - 31.4
dWc	2	$107\pm5$	$0.82 \pm 1.60$	16.8 – 32.9
C	3	$110 \pm 4$	$0.63 \pm 1.24$	12.9 - 25.5

and CPMPM

\*Values calculated using  $\sigma_{\text{HONO}}$  (254 nm) = 4.87 x 10<sup>-19</sup> cm<sup>2</sup>.molecule<sup>-1</sup> (Sander et al., 2006)

and a pathlength of 1 m
## **II.2** Determination of rate constants

A mathematical treatment of the kinetic equations of both analyte and reference yields relation (22) (see section I.3.2 in chapter II) which takes into account all secondary reactions that may take place, such as photolysis and oxidation by HONO. Figures III.13 to III.16 depict the plots of  $ln([P]_{t0}/[P]_t)/t$  as a function of  $ln([T]_{t0}/[T]_t)/t$ , where *P* represents the analyte for Z-dimethomorph (D), E-dimethomorph (D), folpet (F) and CPMPM (M) respectively and *T* represents terbuthylazine. These plots are fitted by linear curves the slopes of which are equivalent to the ratios (*R*) of the kinetic rate constants of each analyte to that of the reference compound, relative to OH-radicals. All experiments were carried out in triplicates, and the error for each data point corresponds to that of the analytical system, which is equivalent to 7, 10 and 14 % for CPMPM, dimethomorph and folpet, respectively.



**Figure III.13** Plot of  $ln([D]_{t0}/[D]_t)/t$  as a function of  $ln([T]_{t0}/[T]_t)/t$  for Z-dimethomorph



**Figure III.14** Plot of  $ln([D]_{t0}/[D]_t)/t$  as a function of  $ln([T]_{t0}/[T]_t)/t$  for E-dimethomorph



**Figure III.15** Plot of  $ln([F]_{t0}/[F]_t)/t$  as a function of  $ln([T]_{t0}/[T]_t)/t$  for Folpet



**Figure III.16** Plot of  $ln([M]_{t0}/[M]_t)/t$  as a function of  $ln([T]_{t0}/[T]_t)/t$  for CPMPM

Knowing the ratio *R* of the kinetic rate constants for each analyte, and knowing the kinetic rate constant of the heterogeneous oxidation of the reference compound, terbuthylazine, by OH-radicals ( $k_{OH}$  (terbuthylazine) = (1.5 ± 0.1) 10<sup>-13</sup> cm<sup>3</sup>.molecule<sup>-1</sup> (Pflieger, 2009)), we were able to calculate the kinetic rate constants of the analyzed compounds, the values of which are reported in Table III.7. Uncertainties in  $k_{OH}$  values are calculated by propagation of error.

Table III.7 2<sup>nd</sup> order rate constant values of the oxidation of the analyzed species by OH-

Compound	Exp.	R	$\mathbf{k}_{\mathbf{OH}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> )	
Z-Dimethomorph	1	$(1.4 \pm 0.7)10^{-1}$	$(2.1 \pm 0.2)10^{-14}$	
	2	$(1.3 \pm 0.2)10^{-1}$	$(2.0\pm0.3)10^{-14}$	
	3	$(1.2 \pm 0.2)10^{-1}$	$(1.8 \pm 0.3)10^{-14}$	
	Average	$(1.3 \pm 0.3)10^{-1}$	$(2.0 \pm 0.5)10^{-14}$	
E-Dimethomorph	1	$(1.2 \pm 0.2)10^{-1}$	$(1.8 \pm 0.3)10^{-14}$	

radicals

	2	$(0.9\pm0.1)10^{\text{-}1}$	$(1.4 \pm 0.2)10^{-14}$
	3	$(1.2 \pm 0.2)10^{-1}$	$(1.8 \pm 0.3)10^{-14}$
	Average	$(1.1 \pm 0.3)10^{-1}$	$(1.7 \pm 0.4)10^{-14}$
	1	$(10.7\pm0.8)10^{\text{-1}}$	$(1.6 \pm 0.2)10^{-13}$
Folpet	2	$(10.9\pm1.5)10^{\text{-1}}$	$(1.6 \pm 0.3)10^{-13}$
	3	$(11.0\pm0.8)10^{\text{-1}}$	$(1.7 \pm 0.2)10^{-13}$
	Average	$(10.9 \pm 1.9)10^{-1}$	$(1.6 \pm 0.3)10^{-13}$
СРМРМ	1	$12.7\pm2.0$	$(1.9 \pm 0.3)10^{-12}$
	2	$13.4\pm1.7$	$(2.0 \pm 0.3)10^{-12}$
	3	$11.8 \pm 2.4$	$(1.8 \pm 0.4)10^{-12}$
	Average	12.6 ± 3.6	$(1.9 \pm 0.5)10^{-12}$

\*values calculated using  $k_{ref} = (1.5 \pm 0.1) \ 10^{-13} \text{ cm}^3$ .molecule<sup>-1</sup> (Pflieger, 2009)

As shown in Table III.7, among the analyzed compounds, CPMPM is almost 10 times more reactive than folpet, and 100 times more reactive than dimethomorph, relative to OH-radicals.

# **II.3** Discussion

### **II.3.1** Sources of error

The uncertainties in the reported average rate constants are calculated using the method of propagation of error. These uncertainties range between 7 and 18 % of the mean values (Table III.7), and may be attributed to various sources of error, including:

Error in concentration measurements. This error is estimated by the assessment of the reproducibility of the GC/MS analytical system which was found to vary between 7 and 14 % depending on the analyzed compound.

- Error in the reported value of the kinetic rate constant of the reference, terbuthylazine. This error is equivalent to approximately 7 % as reported by Pflieger et al. (2009).
- Error due to secondary reactions that do not follow first order, or pseudo first order kinetics. These reactions may occur between one of the formed products and the analyte itself and are not accounted for in the relation used for the determination of the rate constants (relation (22) section I.3.2 chapter II).

#### **II.3.2** Validation of kinetic measurements

In order to validate the kinetic measurements effectuated using terbuthylazine as a reference we have carried out an additional experiment that was used to determine the relative reactivity of folpet and Z-dimethomorph. This relative reactivity is compared to that obtained for the experiments of OH-oxidation of folpet and Z-dimethomorph relative to terbuthylazine. Figure III.17 shows the results obtained for this experiment.

As shown in Figure III.17, the value of the ratio R which is equivalent to  $k_{OH}(folpet)/k_{OH}(dimethomorph)$  is 6.5. Meanwhile, the values of  $k_{OH}(folpet)$ and  $k_{OH}(dimethomorph)$  determined using terbuthylazine as reference are (1.6 ± 0.3) 10<sup>-13</sup> and (2.0  $10^{-14}$  $cm^3$ .molecule<sup>-1</sup>.s<sup>-1</sup>, respectively. 0.5) which leads R  $\pm$ to = $k_{OH}(folpet)/k_{OH}(dimethomorph)$  being equal to 8.0 ± 2.5. The value of relative reactivity R of folpet and dimethomorph determined using this experiment (R = 6.5) falls within the range of relative reactivity assessed using terbuthylazine as a reference (5.5 < R < 10.5).



**Figure III.17** Plot of  $ln([F]_{t0}/[F]_t)/t$  as a function of  $ln([D]_{t0}/[D]_t)/t$ 

This experiment confirms the validity of the relative reactivity values (R) determined in this study. This means that if a rate constant value ( $k_{OH}$ ) for one of the compounds, dimethomorph, folpet, CPMPM or terbuthylazine, is later provided in the literature with higher precision, it may be used along with the values of R reported in this study to recalculate the values of  $k_{OH}$  constants of the other compounds.

#### **II.3.3 Influence of photolysis**

As shown in section I.1.2, among the analyzed compounds, only CPMPM undergoes photolysis under the experimental conditions of OH-oxidation employed in this study. A comparison between the rates of photolysis and OH-oxidation shows that within the same time of exposure to the oxidizing/photolysing medium the amount of CPMPM degraded by OH-radicals is approximately 70 % greater than that degraded under the effect of UV irradiation. This means that, within the conditions and parameters of our experiment, OH- oxidation constitutes the primary route of degradation of CPMPM. Moreover, considering that the rate constant of degradation by OH-radicals is determined relative to a reference compound, using a mathematical formula (relation (22)) that eliminates the contributions of any secondary reactions, including photolysis, the obtained results are not influenced by the fact that CPMPM undergoes photolysis during OH-oxidation experiments.

### **II.3.4** Comparison of reactivity with other compounds

Table III.8 compares the kinetic rate constants reported in this study and those determined for other pesticides. As in the case of ozonolysis, it is fairly difficult to establish definite trends and conclusions concerning heterogeneous reactivity, especially considering the difference in chemical structure of the compared compounds.

In the heterogeneous phase, the kinetics of oxidation of the analyzed compounds by OH-radicals is greater than that by ozone. Moreover, it seems that, contrary to polycyclic aromatic hydrocarbons (Esteve et al., 2004; Esteve et al., 2006), the heterogeneous reactivity of the investigated pesticides depends to a great extent on the molecular structure (kinetic rate constants vary over 3 orders of magnitude) (Table III.8).

Knowing that pesticides are slightly volatile, and that they may exist in both the gas and particulate phases, information concerning the homogeneous as well as the heterogeneous reactivities of these species are needed in order to provide a valid depiction of their atmospheric fates. Since experimental values are not available in the literature, the Estimation Programs Interface (EPI. AOPWIN v.1.92a, 2000) was used to provide theoretical estimates of the kinetic rate constant values of the homogeneous oxidation reactions of the analyzed compounds with OH-radicals. As shown in Table III.8, calculated homogeneous reactivity is 10 to 10000 times greater than heterogeneous reactivity. Such discrepancy is to be expected since it has already been shown that homogeneous and heterogeneous reactivities vary significantly for both, ozonolysis and OH-oxidation experiments (Perraudin et al., 2007b; Pflieger, 2009).

Table III.8 Summary of the OH-oxidation rate constants obtained for the compounds

Compound Support		$\frac{\mathbf{k_{OH}}}{(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1})}$	Reference	
	quartz plaques	$(2.0\pm0.2)10^{\text{-14}}$	present study	
Z-Dimethomorph	gas phase	1.1 x 10 <sup>-10</sup>	(EPI. AOPWIN v.1.92a, 2000)	
	quartz plaques	$(1.7\pm0.3)10^{\text{-14}}$	present study	
E-Dimethomorph	gas phase	1.1 x 10 <sup>-10</sup>	(EPI. AOPWIN v.1.92a, 2000)	
	quartz plaques	$(1.6\pm0.1)10^{\text{-13}}$	present study	
Folpet	gas phase	1.1 x 10 <sup>-11</sup>	(EPI. AOPWIN v.1.92a, 2000)	
	quartz plaques	$(1.9\pm0.2)10^{\text{-12}}$	present study	
СРМРМ	gas phase	2.0 x 10 <sup>-11</sup>	(EPI. AOPWIN v.1.92a, 2000)	
Difenoconazole	quartz plaques	$(7.1 \pm 0.8) \ 10^{-14}$	(Al Rashidi et al., 2011)	
Bromoxynil	<i>comoxynil</i> SiO <sub>2</sub> aerosol		(Palm et al., 1998)	
Isoproturon	SiO <sub>2</sub> aerosol	$(5.6 \pm 1.1) \ 10^{-12}$	(Palm et al., 1998)	
Simazin	SiO <sub>2</sub> aerosol	$(9.7 \pm 1.4) \ 10^{-12}$	(Palm et al., 1998)	
Z-Pyrifenox	SiO aarosol	$(2.8 \pm 0.1) \ 10^{-11}$	$(\mathbf{Palm ot al} \ 1000)$	
E-Pyrifenox	310 <sub>2</sub> actosor	$(3.4 \pm 0.1) \ 10^{-11}$	(Faim et al., 1999)	
Terbythylazine	silica	$(1.5 \pm 0.1) \ 10^{-13}$	(Pflieger, 2009)	
	silica	$(1.1 \pm 0.2) \ 10^{-11}$	(Palm et al., 1997)	
Trifluarine	gas phase	$(1.7 \pm 0.4) \ 10^{-11}$	(Le Person et al., 2007)	

investigated in this study as well as some other pesticides and PAHs

Dichlorvos	gas phase	$(2.6 \pm 0.3) \ 10^{-11}$	(Feigenbrugel et al., 2006)
Diazinon	gas phase	$(3.5 \pm 1.2) \ 10^{-11}$	(Munoz et al., 2011)

# **III.** Degradation products

To the best of our knowledge, the products of the heterogeneous oxidation of the investigated pesticides have never been identified. In this work, we have attempted to identify the chemical species produced upon the ozonolysis, and the oxidation by OH-radicals of dimethomorph. One of the major constraints that we have faced in this study concerns the limited sensitivity of the analytical technique employed, especially since we were obliged to work in the total ion chromatogram (TIC) mode. The use of the Solid Phase Micro-Extraction (SPME) technique (theory explained in Annex V.) allowed us to overcome this obstacle.

## **III.1 Description of SPME**

SPME is a relatively new technique, developed in 1989 by Belardi and Pawliszyn, and commercialized in 1993 by Supelco (Belardi and Pawliszyn, 1989; Beltran et al., 2000). Since its introduction into the field of analytical chemistry, it has been used by many authors for the analysis of organic compounds, including pesticides, in complex matrices, particularily water (Beltran et al., 2000; Berrada et al., 2000; Boussahel et al., 2002; Choudhury et al., 1996; Eisert and Levsen, 1995; Ferrari et al., 2004; Filho et al., 2010; Lambropoulou et al., 2000; Scheyer et al., 2007a; Scheyer et al., 2006; Tomkins and Ilgner, 2002; Urruty and Montury, 1996; Wang et al., 2009). It is based on the concept of partitioning of organic compounds between two phases:

i) the aqueous phase in which the analyte originally exists

ii) the solid phase, represented by a polymeric coating of a silica microfiber probe

Several coatings of different polarity are commercially available nowadays so as to cover as wide a range of organic species as possible. The most frequently used coatings are polydimethylsiloxane (PDMS), suitable for the extraction of non-polar compounds, and polyacrylate (PA), commonly used for the extraction of polar compounds. The SPME technique is innovative in that it is a solvent-free extraction technique. When coupled to a GC, this system automatically performs the processes of extraction, pre-concentration and injection, thus effectively economizing time and effort.

## **III.2** Optimization of SPME parameters

Before performing the experiments regarding the identification of products, the analytical parameters associated with the SPME technique, such as the nature of the fiber, the extraction mode, the extraction/desorption temperature and the extraction time were optimized. Knowing that the addition of salt (sodium chloride or sodium sulfate) usually modifies the efficiency of extraction (Beltran et al., 2000), the percentage of saturated NaCl in the sample solution was also optimized. This salting out effect is due to the fact that the solubility, as well as the activity coefficient, of many organic compounds in an aqueous solution decreases as the ionic strength of the latter increases (Pawliszyn, 1997). Figures II.18 to II.21 illustrate the results of the optimization trials that have been carried out for dimethomorph.

Two types of SPME fibers were used for the extraction of dimethomorph, the polydimethylsiloxane (PDMS) and the polyacrylate (PA) fibers. As expected for a molecule of a non-polar nature such as dimethomorph, higher sensitivity was achieved using the PDMS fiber. Therefore, the use of the PA fiber was discontinued. Moreover, direct injection (DI)

(fiber immersed directly in the sample solution) and head space (HS) (fiber just above the heated sample solution) extractions were performed in order to select the optimal extraction mode. The obtained results showed that the DI mode always exhibited higher sensitivity, irrespective of the other analytical conditions, and so, all analyses were performed using the DI extraction mode.



**Figure III.18** Optimization of extraction time at 40°C extraction temperature, 230°C desorption temperature and 0 % NaCl ( \_\_\_\_\_ chosen parameter)



Figure III.19 Optimization of extraction temperature at 70 min extraction time, 230°C

desorption temperature and 0 % NaCl ( \_\_\_\_\_ chosen parameter)





extraction temperature and 0 % NaCl ( \_\_\_\_\_ chosen parameter)



**Figure III.21** Optimization of ionic strength of the sample solution at 70 min extraction time, 40°C extraction temperature and 230°C desorption temperature ( \_\_\_\_\_\_ chosen parameter)

As shown in Figures II.18 to III.21, optimal extraction time and temperature are 70 min and 40°C, respectively. Moreover, maximum sensitivity is obtained for samples prepared in 100 % saturated NaCl solutions. These optimal parameters were used for the preparation and analysis of the samples intended for the identification of products in the pesticide residue. Meanwhile, although the optimal desorption temperature was found to be 270°C, we chose to work with a temperature of 230°C so as to minimize the risk of thermal decomposition of any of the species contained in the sample inside the injector (desorption port).

# **III.3 Identified products**

The only product that we have been able to identify and correlate with the dimethomorph molecule is the (4-chlorophenyl)(3,4-dimethoxyphenyl)methanone (CPMPM). Figure III.22 shows a chromatogram of a dimethomorph sample (combination of the extracts

of 5 1  $\mu$ g samples) exposed to an OH-containing atmosphere at 2 < [HONO] < 4 x 10<sup>16</sup> molecules.cm<sup>-3</sup> for five hours.



Figure III.22 Chromatogram of a dimethomorph sample oxidized by OH-radicals at  $2 < [HONO] < 4 \times 10^{16}$  molecules.cm<sup>-3</sup> for five hours

CPMPM has been identified as a product of both ozonolysis and OH-oxidation of dimethomorph. The degradation mechanisms by which this product is formed are discussed in section III.4.

# III.4 Proposed mechanisms

The identification of CPMPM in the residue of dimethomorph samples has enabled us to propose mechanisms of ozonolysis and OH-oxidation of the latter.

#### **III.4.1 Oxidation by Ozone**

The proposed mechanism of ozonolysis of dimethomorph is illustrated in Figure III.23. The chemical bond most susceptible to ozone addition is the double bond highlighted in red. The addition of ozone to this double bond leads to the formation of a primary ozonide. Due to the chemical instability of this species, it quickly dissociates via two mechanistic pathways, of similar yields, to give either CPMPM and morpholinic Criegee intermediate or 2-morpholino-2-oxoacetaldehyde and the corresponding Criegee intermediate (Seinfeld and Pandis, 2006). This mechanism is frequently used to describe the process, as well as predict the products, of ozonolysis of organic species containing unsaturated chemical bonds, such as PAHs (Perraudin et al., 2007a; Perraudin et al., 2007b), cypermethrin (Segal-Rosenheimer and Dubowski, 2007), and simple alkenes (Grosjean et al., 1996). In the subsequent mechanistic scheme, the dimethomorph molecule will be represented as follows:



with





Figure III.23 Scheme of the proposed mechanism of ozonolysis of dimethomorph

The fate of the generated Criegee intermediate is described by one of the following processes (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006):

- i) Stabilization: the energy-rich intermediate may stabilize upon collision with another body
- ii) Decomposition via ester channel (a): the intermediate rearranges to form an ester which decomposes to give  $CO_2$  and the complementary product (Figure III.24)
- iii) Decomposition via O-atom elimination (b): the intermediate loses an oxygen atom to form a ketone (Figure III.24)
- iv) Decomposition via hydroperoxide channel: this process involves an H-shift, and is structurally prohibited for our compound



2-morpholino-2-oxoacetaldehyde



Figure III.24 Decomposition pathways for the Criegee intermediates that are generated upon the ozonolysis of dimethomorph

It should be noted that in some cases, usually for liquid and condensed phase reactions, the carbonyl compound and the Criegee intermediate produced upon ozonolysis of an alkene may recombine to form a secondary ozonide as shown below in Figure III.25 (Finlayson-Pitts and Pitts, 2000).



Figure III.25 Scheme of formation of secondary ozonide

As shown above, the proposed mechanism of ozonolysis of dimethomorph leads to the formation of CPMPM and 2-morpholino-2-oxacetaldehyde as major products. CPMPM has been identified in the residue of dimethomorph samples exposed to ozone. However, 2-morpholino-2-oxacetaldehyde was undetected in the residue, probably because it was transferred to the gas phase. As shown, other products produced upon the decomposition of the generated Criegee intermediates include N-formyl morpholine and 4'-chloro-3,4-dimethoxybiphenyl.

#### **III.4.2 Oxidation by OH-radicals**

The reaction of dimethomorph with OH-radicals is similar to that of an alkene molecule (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006). It starts with an

addition of the OH-radical on the double bond of dimethomorph resulting in the formation of an alkyl radical. Considering that the OH-radical may add to the ( $R_1R_2C_=$ ) carbon or the (=CH(CO)) carbon, two reaction pathways (A and B) are possible as shown in Figures III.26 and III.27. Since the carbon attacked by the OH-radical via pathway A is less crowded than that attacked via pathway B, the yield of the former is expected to be greater than that of the latter. The mechanism of oxidation of dimethomorph by OH-radicals is given below (Figures III.26 and III.27 for pathways A and B, respectively). In this mechanism, the dimethomorph molecule is represented as follows:



## HETEROGENEOUS REACTIVITY

Pathway A:



4-formylmorpholine

Figure III.26 Proposed mechanism of oxidation of dimethomorph by OH-radicals (pathway A)

## HETEROGENEOUS REACTIVITY

Pathway B:



Figure III.27 Proposed mechanism of oxidation of dimethomorph by OH-radicals (pathway B)

The formation of the alkyl radical is followed by the addition of an oxygen molecule resulting in the generation of a peroxy radical. In the presence of NO the peroxy radical quickly loses an oxygen atom to form the alkoxy radical. Afterwards, the alkoxy radical decomposes to give a carbonyl compound and an alkyl radical (Seinfeld and Pandis, 2006). Similarily, the alkyl radical reacts quickly with oxygen to form a carbonyl compound and HO<sub>2</sub>. Knowing that HO<sub>2</sub> radicals react with NO to form NO<sub>2</sub> and OH radicals, we may conclude that oxidation of dimethomorph by OH radicals results in the regeneration of the latter (Seinfeld and Pandis, 2006). Experimental evidence of this mechanism has been reported by several authors for the reactions of OH-radicals with unsaturated dicarbonyls (Bethel et al., 2001; Liu et al., 1999), dichlorvos (Feigenbrugel et al., 2006), and PAHs (Bunce et al., 1997; Nishino et al., 2009; Saski et al., 1997; Wang et al., 2007).

As can be seen in the figures above, both pathways, A and B lead to the formation of the same products, CPMPM and a morpholinic glyoxal. The formed glyoxal may lose a CO entity to give N-formylmorpholine.

# **IV.** Atmospheric implications

The atmospheric impact of pesticide use is assessed based on two main parameters: i) the life-time of a particular species in the troposphere, and ii) its products of degradation. The life-times are used to evaluate the persistence of an organic pollutant in the atmosphere, and to ultimately predict its transport. Meanwhile, the identification of the products of degradation of a pesticide is used to determine whether or not the products are more hazardous than the mother compound.

## IV.1 Life-times

The determination of the kinetic rate constants of photo-oxidation of pesticides in the atmosphere, in both the gaseous and particulate phases, is of great importance since it constitutes the only route through which we may assess the fate of these contaminants once they are emitted to the troposphere. This fate is expressed in terms of their persistence and tropospheric life-times with respect to each atmospheric photo-oxidant.

Table III.9 summarizes the entirety of the results obtained in this study regarding rate constants and life-times. The value of OH-radical concentration adopted in the calculation of the life-times of the analyzed compounds is  $1 \times 10^6$  molecules.cm<sup>-3</sup>. This value corresponds to the mean concentration, measured over 24 hours, and is frequently used when evaluating the life-times of relatively persistent organic compounds in the atmosphere (Finlayson-Pitts and Pitts, 2000). Meanwhile, the life-times of the investigated analytes relative to ozone were determined using an average value of ozone concentration in the northern hemisphere equivalent to 40 ppb (Vingarzan, 2004). The life-time of each analyte with respect to either ozone (Langmuir-Rideal model) or OH-radicals is given by the following relation:

$$\mathcal{T}_{ox} = \frac{1}{k_{ox} \cdot [Ox]_g}$$

where  $k_{ox}$  is the 2<sup>nd</sup> order rate constant of oxidation of the analyte by either ozone or OH-radicals, and  $[Ox]_g$  is the atmospheric concentration of the oxidant (10<sup>6</sup> molecules.cm<sup>-3</sup> and 40 ppb for OH-radicals and ozone, respectively).

In the case of ozonolysis, the life-times of the analyzed species were estimated using the Langmuir-Hinshelwood model as well. The following relation was employed in the calculation of the life-times of the analytes within the frame of the Langmuir-Hinshelwood model ( $[O_3]_g$  represents the gaseous concentration of ozone in the atmosphere):

$$\mathcal{T}_{O3} = \frac{1 + K_{O3}[O_3]_g}{k_{\max} K_{O3}[O_3]_g}$$

The obtained results show that although OH-reactivity of the analyzed compounds is  $10^{5}$ - $10^{8}$  times greater than O<sub>3</sub>-reactivity, the life-time of dimethomorph depends on its reaction with O<sub>3</sub> and not with OH-radicals (Table III.9). This is basically due to the fact that ozone is a million times more abundant in the atmosphere than OH-radicals. Meanwhile, folpet is primarily removed by OH-radicals. Generally speaking, the atmospheric life-times of dimethomorph and folpet with respect to either ozone or OH-radicals are relatively long, ranging from one month to two years. Therefore, we may conclude that these pesticides are persistent, and once emitted to the atmosphere, may be transported to regions far from their application area. This hypothesis is only valid under the assumption that dimethomorph and folpet exist in the atmosphere in the particulate form, and that they primarily react with ozone and OH-radicals.

Meanwhile, the results obtained for CPMPM are distinctive in that the OH-reactivity of this compound, which has been identified as a product of degradation of dimethomorph, is 100 times greater than the OH-reactivity of the mother molecule. This trend in reactivity is contrary to that expected and the reason behind it is not evident. Consequently, the atmospheric life-time of CPMPM is relatively short, in the order of several days. This means that CPMPM is a fairly reactive species.

The total atmospheric life-time of each analyzed compound depends on its reactivity with each and every photo-oxidant. It should be noted that despite the fact that OH-radicals and ozone are the most important oxidizing agents of the atmosphere, there are other oxidizing agents, such as NO<sub>3</sub> and Cl, which may also contribute to the elimination of a particular chemical species from the atmosphere. The relative importance of each atmospheric oxidant in the total scheme of reactivity of a particular organic compound depends on the former's concentration, which may exhibit diurnal and geographical variations (Finlayson-Pitts and Pitts, 2000). Moreover, the fate of organic pollutants in the atmosphere is also influenced by various physical phenomena such as dry and wet deposition (McConnell et al., 1998; Park et al., 2001).

Compound	Support	Ozonolysis				OH-oxid	ation	
		LH Mechanism		LR Mechanism				
		k <sub>max</sub> <sup>1</sup>	$K_{03}^{2}$	τ <sub>03</sub> *	k <sub>03</sub> <sup>3</sup>	τ <sub>03</sub> *	k <sub>OH</sub> <sup>3</sup>	$ au_{OH}^{**}$
Z-Dimethomorph	quartz plaques	$(2.8 \pm 1.4) \ 10^{-4}$	$(1.1 \pm 0.6) \ 10^{-15}$	38 days	$(1.7 \pm 0.5) \ 10^{-19}$	70 days	$(2.0 \pm 0.2)10^{-14}$	19 months
E-Dimethomorph	quartz plaques	$(2.7 \pm 1.0) \ 10^{-4}$	$(1.9 \pm 0.9) \ 10^{-15}$	23 days	$(2.1 \pm 0.8) \ 10^{-19}$	56 days	$(1.7\pm0.4)10^{-14}$	23 months
Folpet	quartz plaques	$(1.9 \pm 0.9) \ 10^{-4}$	$(1.8 \pm 0.9) \ 10^{-16}$	12 months	$(2.6 \pm 0.2) \ 10^{-20}$	15 months	$(1.6 \pm 0.3)10^{-13}$	71 days
СРМРМ	quartz plaques	$(1.7 \pm 1.0) \ 10^{-4}$	$(2.1 \pm 1.2) \ 10^{-16}$	11 months	$(2.7 \pm 0.2) \ 10^{-20}$	15 months	$(1.9 \pm 0.5)10^{-12}$	6 days

Table III.9 Kinetic rate constants and life-times of the analyzed compounds with respect to both ozonolysis and oxidation by OH-radicals

 $^{-1}$  s<sup>-1</sup>;  $^{2}$  cm<sup>3</sup>;  $^{3}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>; \*calculated for [O<sub>3</sub>] = 40ppb; \*\*calculated for [OH] = 10<sup>6</sup> molecules.cm<sup>-1</sup>

## **IV.2** Degradation products

The products of ozonolysis and OH-oxidation of dimethomorph are CPMPM and morpholinic compounds in the condensed and gaseous phases, respectively. CPMPM is more reactive than the parent molecule and its degradation may lead to the formation of chemical species that may promote photochemical pollution at the local scale once formed. In the case of folpet, it is hard to discuss its atmospheric impact in terms of degradation products since we have not been able to identify any of these products due to the limited sensitivity of the analytical system employed (GC/MS).

# V. Conclusion

The results reported and discussed in this chapter show that the compounds investigated in this study, namely dimethomorph, folpet and CPMPM, exhibit comparative reactivity constants (of the same order of magnitude) with respect to ozone, but different reactivity constants (varying over 2 orders of magnitude) with respect to OH-radicals. In general, the analytes are  $10^5$  to  $10^8$  times more reactive towards OH-radicals than towards ozone. However, it turns out that since the atmospheric ozone concentration is  $10^6$  times greater than that of OH-radicals, dimethomorph is removed by ozone. Meanwhile, the reactivities of folpet and CPMPM are such that they are chemically removed from the atmosphere by OH-radicals. An overview of the calculated lifetimes shows that folpet and dimethomorph are relatively persistent with lifetimes in the order of several months; and thus, they may be transported to regions far from their application sites. Meanwhile, CPMPM, a product of oxidation of dimethomorph, is more reactive than the mother molecule towards OH and has a lifetime of the order of several days. This means that it is relatively non-persistent.

# VI. Résumé du Chapitre

Ce chapitre rassemble les études de réactivité hétérogène vis à vis de l'ozone et des radicaux OH du folpel, du diméthomorphe ainsi que du (3,4-dimethoxyphenyl)(4-chlorophenyl)méthanone (CPMPM), qui sera identifié comme produit de dégradation du diméthomorphe dans son oxydation hétérogène par l'ozone comme par les radicaux OH. Les études cinétiques sont précédées par des expériences préliminaires permettant de vérifier l'impact des conditions expérimentales sur la perte du composé étudié par volatilisation et par photolyse dans le réacteur photo-chimique. Ces essais préliminaires montrent qu'aucun des composés étudiés ne subit de perte par volatilisation dans les conditions de débit et de pression utilisées. De même, il a été établi que le folpel, le diméthomorphe et le terbuthylazyne (utilisé comme référence dans certaines expériences) ne sont pas sensibles à la photolyse contrairement au CPMPM qui est photolysé par les lampes UV utilisées dans l'oxydation par les radicaux OH à une vitesse de 6.5 x 10<sup>-5</sup> s<sup>-1</sup>.

#### Ozonolyse

La constante de vitesse d'ozonolyse est déterminée par le suivi du rapport entre l'aire du pic chromatographique du composé extrait du dépôt solide à un temps t sur l'aire du pic chromatographique correspondant au composé non exposé à l'ozone. Les expériences sont réalisées pour plusieurs concentrations d'ozone.

Les résultats obtenus sont traités par une cinétique de pseudo premier ordre donnant accès à une constante observée,  $k_{obs}$ . Le tracé de  $k_{obs}$  en fonction de la concentration en ozone est modélisé selon les modèles de cinétique hétérogène de Langmuir-Hinshelwood (LH) et de Langmuir-Rideal (LR). Le modèle de LH, qui suppose que l'ozone gazeux est d'abord adsorbé sur la surface avant de réagir avec le composé étudié, permet de déterminer la constante de vitesse de premier ordre maximale qui puisse être atteinte,  $k_{max}$ , et la constante d'équilibre d'adsorption de l'ozone sur le support solide  $K_{O3}$ . Quant au modèle de LR, il permet de déterminer la constante de vitesse de second ordre,  $k_{O3}$ , entre le composé étudié en phase solide et l'ozone gazeux.

Les résultats, présentés dans le Tableau III.5, montrent que la réactivité hétérogène du diméthomorphe est dix fois plus grande que celle du folpel et du CPMPM. Cette différence de réactivité s'explique par la présence d'une insaturation non aromatique dans le diméthomorphe sensible à une addition d'ozone.

La comparaison des valeurs du coefficient de partition de l'ozone entre le support et la phase gazeuse montre qu'il dépend en grande partie de la nature du support et dans une moindre mesure de la nature chimique du composé déposé sur la plaque de quartz (pesticide ou CPMPM). Les valeurs de  $k_{max}$ , variant entre 1.7 et 2.8 x 10<sup>-4</sup> s<sup>-1</sup>, sont du même ordre de grandeur quelque soit le composé étudié. Cela implique qu'une fois l'ozone adsorbé sur le support solide, il existe une barrière inhérente indépendante de l'espèce chimique déjà présente sur le support qui gouverne la vitesse de réaction (Kwamena et al., 2007).

Enfin, la comparaison des constantes de vitesse  $(k_{O3})$  des pesticides avec des Hydrocarbures Aromatiques Polycycliques montre que les pesticides sont peu réactifs vis à vis de l'ozone.

#### **Oxydation par les radicaux OH**

Ne disposant pas au laboratoire des technologies nécessaires à la mesure de la concentration des radicaux OH, les constantes de vitesse de la réaction hétérogène entre les radicaux OH et le folpel, le diméthomorphe et le CPMPM sont déterminées par rapport au terbuthylazyne. En utilisant la relation (22) (paragraphe I.3.2 in chapitre II), le rapport *R* entre les constantes de vitesse des composés étudiés et de la référence est déterminé par le trace de  $(ln[P]_{t0}/[P]_t)/t$  en fonction de  $(ln[Ref]_{t0}/[Ref]_t)/t$ , où *P* et *Ref* sont respectivement le composé à

étudier et la référence. Ayant déterminé R et connaissant la constante de vitesse hétérogène du terbuthylazyne sur un support de nature similaire, les constantes de vitesse des espèces étudiées en sont déduites (Tableau III.7).

Les constantes de réaction hétérogènes ainsi déterminées varient entre 2.0 x  $10^{-14}$  (CPMPM) et 1.9 x  $10^{-12}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> (diméthomorphe). Il semblerait que, contrairement aux Hydrocarbures Aromatiques Polycycliques, la réactivité hétérogène des pesticides ou du CPMPM étudiés dépend largement de leur structure chimique (Esteve et al., 2004; Esteve et al., 2006).

#### **Produits de dégradation**

Les produits de dégradation de l'ozonolyse et de l'oxydation par les radicaux OH ont été identifiés par microextraction en phase solide (SPME) couplée à une chromatographie en phase gazeuse et un spectromètre de masse utilisé en mode de courant ionique total.

Dans un premier temps les paramètres d'utilisation de la SPME (nature de la fibre, mode d'extraction, température et temps d'extraction, force ionique de la solution) ont été optimisés. Une sensibilité analytique maximale est obtenue pour une extraction en mode direct de 70 min à 40°C dans une solution à saturation de chlorure de sodium par une fibre en polydiméthylsiloxane (PDMS). Malgré une meilleure sensibilité pour une désorption à 270°C, l'injecteur est maintenu à 230°C pour minimiser les risques de décomposition thermique des produits à identifier.

Le seul produit identifié dans le résidu d'oxydation du diméthomorphe est le (4chlorophenyl)(3,4-dimethoxyphenyl)méthanone (CPMPM). Le mécanisme de dégradation du diméthomorphe sous l'effet de l'ozone comme des radicaux OH conduit à la formation du CPMPM et du N-formylmorpholine, un composé qui, d'après ses propriétés physiques est probablement transféré en phase gazeuse.

#### **Implications atmosphériques**

Les constantes de vitesse obtenues dans cette étude sont utilisées pour calculer le temps de vie des composés analysés relativement à leur réaction avec l'ozone atmosphérique et les radicaux OH (Tableau III.9).

Composé	Ozonolyse				Oxydation par les radicaux OH		
	Mécanisme LH			Mécanisme	Mécanisme LR		
	k <sub>max</sub> (s <sup>-1</sup> )	K <sub>03</sub> (cm <sup>3</sup> )	$\tau_{03}^{*}$	<b>k</b> <sub>03</sub> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\tau_{03}^{*}$	$\mathbf{k}_{OH}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$ au_{OH}^*$
Z-Dimethomorph	$(2.8 \pm 1.4) \ 10^{-4}$	$(1.1 \pm 0.6) \ 10^{-15}$	38 jours	$(1.7 \pm 0.5) \ 10^{-19}$	70 jours	$(2.0 \pm 0.2)10^{-14}$	19 mois
E-Dimethomorph	$(2.7 \pm 1.0) \ 10^{-4}$	$(1.9 \pm 0.9) \ 10^{-15}$	23 jours	$(2.1 \pm 0.8) \ 10^{-19}$	56 jours	$(1.7\pm0.4)10^{-14}$	23 mois
Folpet	$(1.9 \pm 0.9) \ 10^{-4}$	$(1.8 \pm 0.9) \ 10^{-16}$	12 mois	$(2.6 \pm 0.2) \ 10^{-20}$	15 mois	$(1.6 \pm 0.3)10^{-13}$	71 jours
СРМРМ	$(1.7 \pm 1.0) \ 10^{-4}$	$(2.1 \pm 1.2) \ 10^{-16}$	11 mois	$(2.7 \pm 0.2) \ 10^{-20}$	15 mois	$(1.9 \pm 0.5)10^{-12}$	6 jours

Tableau III.9 Constantes de vitesse hétérogènes et temps de vie des composés analysés

\*calculé pour  $[O_3] = 40$  ppb; \*\*calculé pour  $[OH] = 10^6$  molecules.cm<sup>-3</sup>

D'après le Tableau III.9, le folpel et le CPMPM montrent des réactivités comparables vis à vis de l'ozone. Quant au diméthomorphe, il est dix fois plus réactif que les deux autres composés par rapport à l'ozone. Les réactivités relatives aux radicaux OH s'étalent sur deux ordres de grandeur, le CPMPM étant le plus réactif, suivi du folpel puis du diméthomorphe. De manière générale, les composés étudiés sont 10<sup>5</sup> à 10<sup>8</sup> fois plus réactifs par rapport aux radicaux OH que par rapport à l'ozone. Cependant, les concentrations atmosphériques de l'ozone étant 10<sup>6</sup> fois supérieures à celles des radicaux OH, le diméthomorphe est principalement éliminé par l'ozone dans l'atmosphère. Le folpel et le CPMPM sont quant à eux principalement éliminés de l'atmosphère par les radicaux OH.

Les durées de vie montrent que le folpel et le diméthomorphe sont relativement persistants vis à vis des processus étudiés avec des durées de vie supérieures au mois. Ils sont donc susceptibles d'être transportés loin de leur point d'application. Par contre le CPMPM, avec une durée de vie relative aux radicaux OH de l'ordre de quelques jours, est plus réactif que sa molécule parent et donc moins persistant. Chapter IV

# Absorption Spectra and Homogeneous Reactivity

As mentioned in chapter III section III.4.1, the mechanism of ozonolysis of dimethomorph leads to the formation of N-formylmorpholine, a compound that is volatile enough to be transferred to the gas phase. This chapter presents the UV-spectra and kinetic rate constants of homogeneous oxidation by OH-radicals of N-formylmorpholine (NFM), and two other compounds of the same family: morpholine and N-acetylmorpholine (NAM) in order to determine the effect of molecular structure on reactivity.

# I. Introduction to the analyzed compounds

# I.1 Physical properties

The chemical structures of the analyzed compounds are given below (Figure IV.1).



Figure IV.1 Scheme of the chemical structures of morpholine, NFM and NAM

Their physical and chemical properties are summarized in Table IV.1.

Table IV.1 Physical and chemical properties of morpholine, NFM and NAM in Material

Safety Datasheet (MSDS)

	Morpholine	NFM	NAM
Physical state	Colorless hygroscopic liquid	Clear yellowish liquid	Clear yellowish liquid
Molecular Weight (g.mol <sup>-1</sup> )	87.1	115.1	129.2

Boiling point $(^{\circ}C)$	129	236-237	245.5
Density $(g.cm^{-3})$	1.0	1.1 at 25°C	1.1
Solubility in water	miscible	Soluble	Miscible
Vapor pressure (Torr)	7 at 20°C	0.047 at 25°C	0.016 at 25°C

#### ABSORPTION SPECTRA AND HOMOGENEOUS REACTIVITY

## I.2 Reactivity

#### I.2.1 Morpholine

Based on a report published by the World Health Organization (WHO) in 1995, at least 25 thousand tons of morpholine are produced yearly, worldwide. It is used as a chemical intermediate in the rubber industry, an additive for pH adjustment in fossil fuel and nuclear power plant steam systems; as a corrosion inhibitor in steam boiler systems; as a catalyst in condensation reactions of aldehydes and ketones containing active methyl or methylene groups; as emulsifier for wax and polish production; and as an anti-oxidant for lubricating oils. Moreover, it is used in the synthesis of optical brighteners, pharmaceutical products, crop protection agents, and dyes (WHO, 1995). The applications that make use of morpholine are numerous, and so, it is not surprising that this compound has been detected in a wide variety of foods and tobacco.

Data concerning the concentration levels of morpholine in ambient and indoor air are currently unavailable. The main routes of exposure of the general population to this product are oral (food ingestion), dermal (application of cosmetics) and respiratory (inhalation of tobacco smoke). There is ample evidence that this substance can be nitrosated to the carcinogenic *N*-nitrosomorpholine (NMOR) by reactions outside, or within, the human body. Lung hemorrhage, damage to the kidneys and liver, weight loss and eye irritation are some of the health hazards that may be instigated by morpholine exposure. However, at the usual
levels of exposure, it seems that morpholine does not present a toxic risk for humans (WHO, 1995).

Being an amine, morpholine is expected to react rapidly with OH-radicals, as well as NO<sub>x</sub> (Grosjean, 1991). However, it has been shown that this compound is not likely to undergo photolysis in the atmosphere since its UV spectrum does not exhibit absorption bands at  $\lambda > 260$  nm (BUA, 1991). Based on the available experimental data for alkyl amines, Grosjean (1991) proposed a value in the order of 2-10 x 10<sup>-11</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for the rate constant of oxidation of morpholine by OH-radicals, as well as a tentative reaction scheme. For many years, the work of Grosjean (1991) has been the only base of information regarding the OH-reactivity of morpholine. The first experimental study concerning the kinetics of homogeneous oxidation of morpholine by OH-radicals has only recently been carried out by Sengupta et al. (2010) who make use of the technique of Laser-Photolysis (LP) coupled to Laser Induced-Fluorescence (LIF) (Sengupta et al., 2010). In their study, OH-radicals were generated by photolysis of H<sub>2</sub>O<sub>2</sub>, and their concentration in the reaction medium was directly determined using pulsed laser-induced fluorescence. At ambient temperature, Sengupta et al. (2010) report a kinetic rate constant value of morpholine equivalent to  $(8.0 \pm 0.1) \times 10^{-11}$ cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>. By varying the temperature between 298 and 363 K they were able to estimate the activation energy of the oxidation reaction at  $Ea/R = -590 \pm 20$  K. According to the authors, the fact that the activation energy of the reaction is negative indicates that the rate-determining step involves the formation of a prereactive complex that is more stable than morpholine. Based on this hypothesis, Sengupta et al. (2010) propose a mechanism of degradation of morpholine by OH-radicals. Up until now, this study has been the only source of experimental kinetic and mechanistic data concerning the degradation of morpholine by OH-radicals in the gas phase. However, considering the similarity in structure (secondary amine), it is also possible to compare the homogeneous OH-reactivity of morpholine to that of diethylamine. The kinetic rate constant of homogeneous oxidation of diethylamine by OHradicals was determined relative to a reference compound (1,3,5-trimethybenzene) using the technique of simulation chamber coupled to an FTIR spectrometer (Tuazon et al., 2011). This technique is very similar to that employed in our study. OH-radicals were generated via ozonolysis of 2,3-dimethy-2-butene in the absence of light. The rate constant value of diethylamine reported by Tuazon et al. (2011) is  $(1.2 \pm 0.3) \times 10^{-10}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>.

#### I.2.2 N-formylmorpholine (NFM)

It is a virtually non-toxic synthesized organic compound that is mainly used as an extraction solvent for aromatics and butene. It is also used for the treatment of natural gases containing high concentrations of  $CO_2$  and/or  $H_2S$ .

To the best of our knowledge, no information has been previously published concerning the homogeneous reactivity of NFM relative to OH-radicals. However, similar heterocyclic molecules such as N,N-dimethylformamide exhibit homogeneous reactivity constants in the order of  $10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> (Solignac et al., 2005). Solignac et al. (2005) and Hayon et al. (1971) suggest reaction mechanisms that proceed via H-abstraction. Moreover, by analogy with formates and acetates Solignac et al. (2005) argue that abstraction from the H-C(O) and CH<sub>3</sub>-C(O) entities constitutes a minor reaction pathway due to the limited reactivity of these moeties. Similarly, in their study concerning the OH reactivity of some amides in aqueous solution, Hayon et al. (1971) suggest that H-abstraction reactivity at position  $\alpha$  to the carbonyl group is reduced due to increased dipole-dipole repulsion in the transition state.

#### I.2.3 N-acetylmorpholine (NAM)

It is mostly used in the synthesis of pesticides such as dimethomorph and flumorph. Like NFM, it is also used for the removal of acidic  $CO_2$  and  $H_2S$  gases from natural and synthetic gas. Information concerning toxicology and health hazards of this compound is not yet available in the literature.

Although studies regarding the degradation of NAM by OH-radicals have not yet been published, it is still possible to discuss the OH-reactivity of similar compounds such as N,Ndimethylformamide, N,N-dimethylacetamide and 1-methyl-2-pyrrolidinone. In one study, Koch et al. (1996) investigated the kinetics of homogeneous oxidation of 4 amides, including N,N-dimethylacetamide (DMA), by OH-radicals using flash photolysis/resonance fluorescence. Their employed method for the generation of OH-radicals was based on N<sub>2</sub>O photolysis, followed by a rapid reaction with H<sub>2</sub>O molecules. The concentration of the generated OH-radicals was measured directly using resonance fluorescence at 308 nm. The kinetic rate constant of degradation of DMA was found to be 1.4 x 10<sup>-11</sup> cm<sup>3</sup>.molecule.s<sup>-1</sup> at 300 K. By varying the temperature of the reaction medium Koch et al. (1996) were able to show that the activation energy of the oxidation reaction is negative, which, according to the authors, signifies that the mechanism proceeds via addition at the amide group followed by Habstraction. A similar study was conducted by Solignac et al. (2005). In this study, N,Ndimethylacetamide (DMA) was one of three amides whose homogeneous reactivity relative to OH-radicals has been investigated. The reported rate constants were determined relative to reference compounds (cyclohexane, propene and ethane) using the technique of a simulation chamber coupled to an FTIR spectrometer, and OH-radicals were generated by photolysis of CH<sub>3</sub>NO. The reported value of the rate constant of degradation of DMA is  $(1.9 \pm 0.3) \times 10^{-11}$ cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> at 298 K (Solignac et al., 2005). Meanwhile, the kinetics of homogeneous OH-oxidation of 1-methyl-2 pyrrolidinone, a cyclic amide, has been studied by Aschmann and Atkinson (1999) using the technique of relative rates. The reported rate constant is (2.2  $\pm$ 0.4)×10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 K. *N*-methylsuccinimide and 1-formyl-2-pyrrolidinone

were identified as OH-oxidation products at  $44 \pm 12$  and  $41 \pm 12$  % yields, respectively (Aschmann and Atkinson 1999).

#### I.2.4 Conclusion

The review of the available literature regarding the homogeneous OH-reactivity of the investigated compounds has shown that the degradation rate constants of NFM and NAM have never been experimentally determined, whereas only one study reports this value for morpholine. Knowing that these compounds, of non-negligible hazard potential, may be formed upon the degradation of morpholinic pesticides, it is important to assess their atmospheric fates, particularly in view of the absence or limitedness of the required data. The investigation of the photolysis potential and homogeneous OH-reactivity of these compounds takes us one step further towards achieving that goal.

# II. UV Absorption Spectra

The atmospheric fate of organic species depends on several phenomena, including deposition, oxidation by ozone,  $NO_3$  and OH radicals, as well as photolysis. Therefore, in order to provide a comprehensive assessment of the atmospheric fate of a particular atmospheric species, it is important to evaluate the contribution of each of the aforementioned processes to the removal of this species from the atmosphere. UV-absorption spectra allow for the determination of the photo-dissociation constant of a particular species. Moreover, the absorption spectra may be used to identify and quantify the analyzed species in the atmosphere as well as in reactive systems employed in photo-chemical studies.

## **II.1** Experimental conditions

Since absorption cross-section values for a particular species, at different wavelengths, are acquired through the measurement of its UV-Vis absorption spectrum, the UV absorption spectra of gaseous morpholine, N-formylmorpholine and N-acetylmorpholine were recorded in the spectral ranges 200-300 nm, 200-300 and 200-350, respectively. Table IV.2 summarizes the experimental conditions, in terms of pressure and temperature, employed for each compound.

Table IV.2 Experimental conditions for the absorption cross-section measurements

	Pressure (mTorr)	<b>Temperature</b> (K)	Pathlength (m)
Morpholine	46-85	$296\pm3$	1.6
N-Formylmorpholine	30-169	$337 \pm 4$	1.6
N-Acetylmorpholine	140-306	$336 \pm 4$	1.6

## **II.2** Determination of the absorption cross-section values

The absorption cross-section values at each wavelength were calculated using Lambert-Beer's law (equation (24) of chapter II). Figures IV.2 to IV.4 show the profiles of the absorption cross-sections at different wavelengths for each of the analyzed compounds. Several measurements (8 to 10) were recorded for each analyte so as to minimize the uncertainty in the cross-section values. Although the pressure of the introduced analyte was varied from one measurement to the next, the operating temperature was kept constant.

As can be seen in Table IV.2, absorption cross-section measurements for morpholine, whose vapor pressure is 7 Torr at 20°C, were conducted at ambient temperature. Meanwhile, absorption cross-section measurements for NFM and NAM were conducted at slightly elevated temperatures (332-341 K). The temperature was increased when working with these compounds, whose vapor pressures are very low (47 and 16 mTorr at 25°C for NFM and

NAM, respectively) so as to facilitate their introduction in the gaseous form, and to minimize their condensation on the walls of the cell.



Figure IV.2 Absorption cross-section of morpholine as a function of wavelength



Figure IV.3 Absorption cross-section of NFM as a function of wavelength



Figure IV.4 Absorption cross-section of NAM as a function of wavelength

It should be noted that the absorption cross-section values were not obtained directly using the spectrophotometer. Instead, the UV spectrophotometer was used to measure the intensity of the light transmitted through the sample, which was in turn used to calculate the absorbance of a specific concentration of the chemical species inside the cell. Knowing the absorbance and the concentration (determined from the pressure using the equation of ideal gases) of the analyte inside the cell, its absorption cross-section was determined using Lambert-Beer's law (relation (24) section II.1.2 of chapter II). However, Lambert-Beer's law applies over a limited range of analyte concentration, beyond which the absorbance of the analyte becomes independent of its concentration, and the calculated absorption cross-section values are no longer valid. Therefore, in order to ensure the validity of the absorption crosssection values determined in this study for morpholine, NFM and NAM, we plotted the absorbance of each analyte as a function of concentration, at different wavelengths. As shown in Figures IV.5 to IV.7, the plots of absorbance as a function of concentration are linear for all three of the analyzed compounds, with  $R^2$  values ranging between 0.86 and 0.98. This means that Lambert-Beer's law is applicable within the range of analyte concentration employed in this study, and that the calculated absorption cross-section values are all valid.



Figure IV.5 The variation of the absorbance of morpholine as a function of concentration at 5

different wavelengths



Figure IV.6 The variation of the absorbance of NFM as a function of concentration at 5

different wavelengths



Figure IV.7 The variation of the absorbance of NAM as a function of concentration at 5 different wavelengths

The obtained cross-section values are listed in Table IV.3 for 1 nm intervals of wavelength. Each cross-section value reported in Table IV.3 is the average of 8-10 independent measurements at several different vapor pressures, so that uncertainties due to different sources would be minimized. The quoted error is the standard deviation  $1\sigma$ .

 Table IV.3 Average absorption cross-section values of morpholine, NFM and NAM obtained

in this study

$\lambda$ (nm)	Abso	<b>Absorption Cross-sections</b> (10 <sup>-19</sup> cm <sup>2</sup> .molecule <sup>-1</sup> )			
-	Morpholine	N-Formylmorpholine	N-Acetylmorpholine		
200	$105.9\pm9.2$	$56.1\pm5.8$	$13.0 \pm 1.0$		
201	$99.7{\pm}~8.4$	$57.6\pm5.7$	$12.3\pm1.1$		
202	$91.9\pm6.0$	$59.1\pm6.2$	$11.6\pm1.0$		
203	$84.2\pm5.1$	$60.5\pm6.2$	$11.1\pm0.9$		
204	$76.0\pm3.9$	$60.8\pm6.0$	$10.8\pm0.9$		

205	$68.5 \pm 3.2$	$60.9\pm6.2$	$10.2 \pm 0.9$
206	$61.2 \pm 3.1$	$60.6 \pm 6.2$	$10.3 \pm 0.8$
207	$54.2\pm2.5$	$59.6\pm5.9$	$9.8\pm0.8$
208	$47.6\pm2.4$	$58.4\pm5.6$	$9.7\pm0.7$
209	$42.4\pm1.9$	$56.6\pm5.4$	$9.6\pm0.7$
210	$38.2\pm1.9$	$53.2 \pm 5.2$	$9.2\pm0.7$
211	$32.7 \pm 1.7$	$49.1\pm4.6$	$8.9\pm0.7$
212	$28.8 \pm 1.3$	$44.6\pm4.0$	$8.5\pm0.7$
213	$26.4\pm1.3$	$39.5\pm3.7$	$8.1\pm0.6$
214	$23.6\pm0.9$	$34.5 \pm 3.1$	$7.5\pm0.6$
215	$19.7\pm0.9$	$29.8\pm2.7$	$6.9\pm0.5$
216	$17.8\pm0.9$	$25.3 \pm 2.2$	$6.2\pm0.5$
217	$16.5\pm0.8$	$21.4\pm1.9$	$5.6\pm0.4$
218	$16.1\pm0.8$	$18.0\pm1.6$	$4.8\pm0.3$
219	$14.1\pm0.6$	$15.0\pm1.3$	$4.2\pm0.3$
220	$11.9\pm0.8$	$12.5 \pm 1.3$	$3.5\pm0.3$
221	$15.8\pm0.5$	$10.4\pm0.9$	$3.0\pm0.3$
222	$11.3\pm0.6$	$8.6\pm0.9$	$2.5\pm0.2$
223	$11.6\pm0.5$	$7.4 \pm 0.8$	$2.1\pm0.2$
224	$11.2\pm0.6$	$6.3\pm0.6$	$1.8\pm0.2$
225	$11.6\pm0.5$	$5.5\pm0.6$	$1.6\pm0.1$
226	$11.3\pm0.6$	$4.8\pm0.4$	$1.4 \pm 0.1$
227	$11.3\pm0.6$	$4.3\pm0.4$	$1.3\pm0.1$
228	$11.3\pm0.5$	$3.9\pm0.4$	$1.2\pm0.1$
229	$11.0\pm0.6$	$3.7\pm0.5$	$1.0\pm0.1$
230	$10.9\pm0.5$	$3.4 \pm 0.4$	$1.0\pm0.1$
231	$10.7\pm0.6$	$3.1 \pm 0.4$	$0.92\pm0.13$
232	$10.3\pm0.6$	$3.1 \pm 0.4$	$0.86\pm0.12$
233	$10.0\pm0.7$	$2.8\pm0.5$	$0.80\pm0.12$
234	$9.7\pm0.5$	$2.6\pm0.4$	$0.76\pm0.15$
235	$9.3 \pm 0.4$	$2.5 \pm 0.4$	$0.71\pm0.16$
236	$8.6\pm0.3$	$2.5\pm0.3$	$0.67\pm0.13$
237	$8.1 \pm 0.4$	$2.3\pm0.3$	$0.68\pm0.10$
238	$7.6 \pm 0.3$	$2.3\pm0.6$	$0.58\pm0.12$
239	$7.1 \pm 0.3$	$2.1 \pm 0.4$	$0.56\pm0.13$
240	$6.4 \pm 0.3$	$1.9 \pm 0.3$	$0.53\pm0.14$
241	$5.7\pm0.2$	$1.8\pm0.3$	$0.50\pm0.14$
242	$5.0\pm0.3$	$1.8\pm0.3$	$0.50\pm0.13$
243	$4.7\pm0.2$	$1.6 \pm 0.3$	$0.51\pm0.12$
244	$4.2\pm0.2$	$1.6 \pm 0.4$	$0.44\pm0.16$
245	$3.3 \pm 0.2$	$1.4 \pm 0.2$	$0.42 \pm 0.12$

246	$2.8 \pm 0.3$	$1.4 \pm 0.3$	$0.36\pm0.10$
247	$2.6 \pm 0.3$	$1.3 \pm 0.4$	$0.34\pm0.06$
248	$2.0 \pm 0.2$	$1.2 \pm 0.3$	$0.36\pm0.10$
249	$1.4 \pm 0.2$	$1.2 \pm 0.3$	$0.31\pm0.13$
250	$1.3 \pm 0.3$	$1.1 \pm 0.3$	$0.25\pm0.03$
251		$0.94\pm0.20$	$0.29\pm0.05$
252		$0.86\pm0.26$	$0.24\pm0.05$
253		$0.78\pm0.14$	$0.24\pm0.08$
254		$0.80\pm0.18$	$0.25\pm0.09$
255		$0.74\pm0.21$	$0.23\pm0.06$
256		$0.66\pm0.12$	$0.21\pm0.09$
257		$0.61\pm0.14$	$0.18\pm0.03$
258		$0.63\pm0.15$	$0.20\pm0.06$
259		$0.47\pm0.12$	$0.17\pm0.03$
260		$0.61\pm0.10$	$0.17\pm0.06$
261		$0.59\pm0.15$	$0.15\pm0.06$
262		$0.67\pm0.14$	$0.15\pm0.07$
263		$0.60\pm0.17$	$0.15\pm0.08$
264		$0.49\pm0.10$	$0.15\pm0.08$
265		$0.55\pm0.13$	$0.12\pm0.01$
266		$0.52\pm0.21$	
267		$0.49\pm0.11$	
268		$0.40\pm0.12$	
269		$0.48\pm0.13$	
270		$0.44\pm0.13$	
271		$0.47\pm0.11$	
272		$0.47\pm0.14$	
273		$0.47\pm0.06$	
274		$0.49\pm0.15$	
275		$0.46\pm0.21$	
276		$0.43\pm0.05$	
277		$0.43\pm0.15$	
278		$0.44 \pm 0.11$	
279		$0.42\pm0.09$	
280		$0.37\pm0.02$	

## **II.3** General Characteristics of the obtained spectra

As shown in Figure IV.8, the spectra obtained for the three analyzed compounds are similar in shape and consist of a broad continuum. However, morpholine's spectrum exhibits 2 absorption bands: i) a sharp and intense band, whose maximum is located below the scanned range, and ii) a broad band with maximum cross-section at  $\lambda \approx 235$  nm ( $\sigma \approx 9.3 \times 10^{-19}$  cm<sup>2</sup>.molecule<sup>-1</sup>). A very similar shape is observed by Oliver et al. (2010) for the UV spectrum of gaseous morpholine. The broad band is attributed to the *n* to  $\sigma^*$  transition of one of the lone pair electrons of nitrogen; whereas the more intense band at shorter wavelengths is assigned to the transition of one of the lone pair electrons from the non-bonding level *n* to a non-occupied Rydberg orbital higher in energy than  $\sigma^*$  (Oliver et al., 2010).



Figure IV.8 Average absorption spectra of the three analytes

Moreover, Figure IV.8 shows that both morpholine and NAM exhibit strong absorption ( $\sigma > 10.6$  and 1.3 x  $10^{-18}$  cm<sup>2</sup>.molecule<sup>-1</sup>) at wavelengths lower than 200 nm.

Meanwhile, maximum absorption ( $\sigma \approx 6.1 \times 10^{-18} \text{ cm}^2$ .molecule<sup>-1</sup>) for NFM is attained at 205 nm. The same shifting tendency is observed for N,N-dimethylacetamide when compared to dimethylformamide (Chakir et al., 2005). Apparently, this difference is attributed to the varying structures of the analytes, mainly the presence of an electron donating group, –CH<sub>3</sub>, in NAM. The absorption bands observed in the amide spectra (spectra of NFM and NAM) may be assigned to the *n*- $\pi$ \* electronic transition involving the carbonyl group (Calvert and Pitts, 1966). Although the afore-mentioned transition normally occurs at around 270 to 280 nm in aldehydes and ketones, it is shifted towards shorter wavelengths in the studied amides. The same tendency is observed for esters and carboxylic acids compared to ketones and aldehydes. Calvert and Pitts (1966) attribute this shift to the presence of an electron donating group (RR'N-).

## **II.4** Discussion

#### **II.4.1 Sources of error**

Although the UV spectra were recorded at wavelengths as high as 360 nm, acceptable reproducibility (< 30 %) in the absorption cross-section values was attained for  $\lambda$  < 250,  $\lambda$  < 280 and  $\lambda$  < 265 in the cases of morpholine, NFM and NAM, respectively. The great uncertainty (> 30 %) which was found at higher wavelengths may be attributed to the following reasons:

- (i) the difficulties in handling and measuring the concentrations of the studied compounds with good accuracy due to their low vapor pressure,
- (ii) the weak optical density of the studied compounds in this spectral region (absorbance  $\leq$  0.05),
- (iii) the purity degree of the studied compounds.

Other parameters that may also contribute to the uncertainty include the errors in pressure and absorbance measurements.

#### **II.4.2** Comparison with similar compounds

To the best of our knowledge, this work presents the first gas-phase UV-absorption spectra and absorption cross-section values of NFM and NAM to have ever been recorded. Meanwhile, the UV spectrum of morpholine in the wavelength range 190-280 nm has already been reported by Oliver et al. (2010). The spectrum presented by these authors is very similar in shape to that determined in our own study, with a sharp and intense absorption band at around 200 nm and a secondary rise at approximately 230 nm as shown in Figure IV.9. However, the authors do not specify the analytical method employed in recording this spectrum nor do they provide absorption cross-section values (Oliver et al., 2010). So far, the absorption cross-section values available for morpholine are only those reported in our study.





The UV-spectrum and absorption cross-section values of morpholine obtained in this study may also be compared to those of a secondary amine such as N,N-dimethylamine. As shown in Figure IV.10, the two spectra have very similar profiles and the absorption cross-section values are of the same order as well (Meller, 1999). Since the spectrum of N,N-dimethyl amine was recorded at very high resolution (0.08 nm), it exhibits fine structuring that is not evident in the spectrum of morpholine. Unfortunately, it is not possible to provide further details concerning the methodology employed in acquiring the UV-spectrum of N,N-dimethyl amine since this study has not been published. The spectral datapoints were taken from the MPI-Mainz-UV-VIS Spectral Atlas of gaseous molecules.



Figure IV.10 UV-spectra of morpholine (determined in this study) and N,N-dimethylamine (determined by Meller, 1999) at 298 K

In the case of NFM and NAM, the spectra were compared to those of N,Ndimethylformamide (DMF) and N,N-dimethyl acetamide (DMA), respectively. The UV spectrum of N,N-dimethylformamide in the gas phase was recorded using  $D_2$  lampmonochromator-photomultiplier and  $D_2$  lamp-diode array detector systems in GSMA (Reims) and LCSR (Orléans) laboratories, respectively (Chakir et al., 2005). As shown in Figure IV. 11, within the common wavelength range of acquired data, the UV-spectra of NFM and DMF have the same profile. Moreover, the absorption cross-section values of both compounds are of the same order of magnitude.



**Figure IV.11** UV-spectra of NFM (determined in this study at T = 337 K) and DMF (determined by Chakir et al., 2005, at T = 13-333 K in GSMA and 298-313 K in LCSR)

Since both compounds are amides of the form  $(R_1R_2-N-C(O)-R_3)$ , where  $R_1$ ,  $R_2$  and  $R_3$  represent mono or poly carbon chains, the UV absorption spectrum of NAM was compared to

that of DMA. The latter was measured by Chakir et al. (2005) at 333-363 and 298-313 K in the laboratories of GSMA and LCSR, respectively, using the same systems employed in the study of DMF. As shown in Figure IV.12, the UV spectra of NAM and DMA exhibit profiles that are relatively dissimilar. It seems that the spectral peak of NAM is shifted towards lower wavelengths. Moreover, the absorption cross-section values of DMA reported by Chakir et al. (2005) are approximately 10 times greater than those determined in this study of NAM. Although we cannot assuredly provide an explanation for these observations, they could be, in some way, related to cyclization and/or the presence of the ether group in NAM. Further measurements at higher pressures are needed to verify these results.



**Figure IV.12** UV-spectra of NAM (determined in this study at T = 336 K) and DMA (determined by Chakir et al., 2005, at T = 13-333 K in GSMA and 298-313 K in LCSR)

## **II.5** Atmospheric implications

Since none of the analyzed compounds exhibits strong absorption at wavelengths greater than 280 nm ( $\sigma_{\lambda>280nm}$  in the order of  $10^{-20}$  cm<sup>2</sup>.molecule<sup>-1</sup>), it may be concluded that the contribution of photolysis to the removal of the investigated analytes from the troposphere is negligible. However, the cross-section values reported in this study are still important in that they constitute additional resources to be used for the completion of spectral databases. In addition, they are employed in the quantification of the corresponding analytical species in both the laboratory and the atmosphere.

# III. Homogeneous oxidation by OH-radicals

The kinetic rate constants of the oxidation reaction of the three analytes by OHradicals were measured using the technique of an Atmospheric Simulation Chamber coupled to an FTIR spectrometer. The experimental setup employed is described in detail in chapter II. The reactions whose kinetic rate constants have been measured are the following:

- i) Morpholine(g) +  $OH(g) \xrightarrow{k_{OH}} Products$
- ii)  $NFM(g) + OH(g) \xrightarrow{k_{OH}} Products$
- iii)  $NAM(g) + OH(g) \xrightarrow{k_{OH}} Products$

#### **III.1** Experimental conditions

The study of the homogeneous oxidation of morpholinic compounds was conducted relative to a reference compound, similarly to the study of heterogeneous reactivity. Experiments were carried out in doublets, and Table IV.4 summarizes the experimental conditions. Experiments were performed using a Mercury Cadmium Telluride (MCT) detector. In the case of morpholine a Deuterated Triglycine Sulfate (DTGS) detector was also used. By manipulating the number of reflections, the path-length was varied between 16 and 24 m. The initial amounts of the analyte and reference compounds were in the order of a few tens to a few hundreds of mTorrs. After introducing the analyte and the reference compounds into the reaction medium, the gaseous mixture was monitored for 30 min before oxidation in order to ensure that the relevant concentrations are stable and that condensation is negligible.

Table IV.4 Experimental conditions of OH-oxidation experiments of morpholine, NFM and

	Exp.	Reference	Temperature (°C)	<b>Total</b> <b>Pressure</b> (Torr)	<b>Integrated</b> <b>Band</b> (cm <sup>-1</sup> )
holine	1	Isoprene	$22 \pm 2$	630 ± 5	1292-1350
Morp	2	Isoprene	22 ± 2	612 ± 5	1292-1350
$M_{z}$	1	Benzaldehyde	43 ± 2	697 ± 5	1100-1150
NI	2	Benzaldehyde	43 ± 2	680 ± 5	1100-1150
MI	1	Benzaldehyde	38 ± 2	670 ± 5	1100-1150
$N_{F}$	2	Benzaldehyde	$38 \pm 2$	708 ± 5	1100-1150

NI	Λ.	NЛ
IN.	H.	IVI

## **III.2** Selection of a Reference Compound

In the case of homogeneous reactivity, the choice of reference was relatively hard to make since the analytical technique employed in this study is FTIR. This means that in addition to the original constraints (having a well documented kinetic rate constant, and the same order of reactivity as the analyte) we had to choose a reference whose FTIR spectrum is sufficiently different from that of the analyzed compound. More specifically, the reference compound was chosen in such a way that its FTIR spectrum does not interfere with all the absorption bands of the analyte spectrum and vice versa. After consulting the kinetic databases, as well as a few trial and error examinations, we were able to assign isoprene, whose kinetic rate constant is  $k_{OH} = (1.00 \pm 0.05) \times 10^{-10} \text{ cm}^3$ .molecule<sup>-1</sup>.s<sup>-1</sup> at 299 K (Atkinson, 1986), as a reference compound for morpholine, and benzaldehyde, whose kinetic rate constant is  $k_{OH} = (1.3 \pm 0.1) \times 10^{-11} \text{ cm}^3$ .molecule<sup>-1</sup>.s<sup>-1</sup> at room temperature (Atkinson, 1986; Baulch et al., 1994; Semadeni et al., 1995), as a reference compound for NFM and NAM. Only Semadeni et al. (1995) examine the temperature dependence of  $k_{OH}$  of benzaldehyde. Considering that the oxidation experiments of NFM and NAM were carried out at 43 and 38°C, respectively, the values of the kinetic rate constant of benzaldehyde at these temperatures were calculated using the following Arrhenius equation provided by (1995):

$$k = 5.33 \times 10^{-12} \exp(243/T)$$

where k (cm<sup>3</sup>.molecule<sup>-1</sup>s<sup>-1</sup>) is the kinetic rate constant and T (K) is th temperature.

At 43 and 38°C, the kinetic rate constants of benzaldehyde are  $(1.15 \pm 0.31)$  and  $(1.16 \pm 0.32) \times 10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>, respectively. These values are used to calculate the 2<sup>nd</sup> order kinetic rate constants of NFM and NAM relative to benzaldehyde.

The overlapped spectra for each analyte/reference system are given below.



Figure IV.13 Overlapped FTIR spectra of morpholine and isoprene



Figure IV.14 Overlapped FTIR spectra of N-formylmorpholine and benzaldehyde



Figure IV.15 Overlapped FTIR spectra of N-acetylmorpholine and benzaldehyde

## **III.3** Determination of Rate Constants

The kinetics of degradation of both the reference and the analyte inside the reaction medium was followed by monitoring the evolution of the areas of the absorption bands of both compounds. The absorption bands whose areas were monitored are indicated in Figures IV.13 to IV.15 which depict the overlapped FTIR spectra of each reference/analyte pair in the range of 900 to  $3200 \text{ cm}^{-1}$ .

Based on relation (22) of section I.3.2 of chapter II, when fitted by linear trendlines the plots of  $ln([A]_{t0}/[A]_t)/t$  as a function of  $ln([Ref]_{t0}/[Ref]_t)/t$  (where A represents the analyte; A=MORPH for morpholine, A=NFM for N-formylmorpholine and A=NAM for N-acetylmoprpholine; and *Ref* the reference; *Ref*=ISO for isoprene and *Ref*=BENZ for benzaldehyde) for each analyte/reference system allow for the determination of *R*, the slope of

each fitted curve, as well as the ratio of the kinetic rate constants of each analyte to that of the reference compound, relative to OH-radicals (Figures IV.16 to IV.18). All experiments were carried out in duplicates.



**Figure IV.16** Plot of  $ln([MORPH]_{t0}/[MORPH]_t)/t$  as a function of  $ln([ISO]_{t0}/[ISO]_t)/t$  for the

homogeneous oxidation of morpholine by OH-radicals



**Figure IV.17** Plot of  $ln([NFM]_t)/t$  as a function of  $ln([BENZ]_t)/t$  for the



homogeneous oxidation of NFM by OH-radicals

**Figure IV.18** Plot of  $ln([NAM]_{t0}/[NAM]_t)/t$  as a function of  $ln([BENZ]_{t0}/[BENZ]_t)/t$  for the

homogeneous oxidation of NAM by OH-radicals

Knowing the ratio R of the kinetic rate constants for each analyte, and knowing the kinetic rate constant of the homogeneous oxidation of the reference compound by OH-radicals, we were able to calculate the kinetic rate constants of the analyzed compounds, the values of which are reported in Table IV.5. Uncertainty values are determined using propagation of error.

 Table IV.5 2<sup>nd</sup> order rate constant values of the homogeneous oxidation of the analyzed

 species by OH-radicals

Compound	Exp.	R	$\mathbf{k}_{\mathbf{OH}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> )
Morpholine	1	$1.3 \pm 0.1$	$(1.3 \pm 0.1)10^{-10}$
	2	$1.4\pm0.1$	$(1.4 \pm 0.1)10^{-10}$
	Average	$1.4 \pm 0.1$	$(1.4 \pm 0.1)10^{-10}$
N-formylmorpholine	1	$3.0 \pm 0.1$	$(3.5 \pm 1.0)10^{-11}$
	2	$3.6 \pm 0.1$	$(4.1 \pm 1.1)10^{-11}$
	Average	$3.3 \pm 0.4$	$(3.8 \pm 1.1)10^{-11}$
N-acetylmorpholine	1	$3.2 \pm 0.2$	$(3.7 \pm 1.0)10^{-11}$
	2	$3.1 \pm 0.2$	$(3.6 \pm 1.0)10^{-11}$
	Average	$3.2 \pm 0.1$	$(3.7 \pm 1.0)10^{-11}$

 $k_{OH-isoprene} = (1.00 \pm 0.05) \times 10^{-10}$ ,  $k_{OH-benzaldehyde} = (1.15 \pm 0.31)$  and  $(1.16 \pm 0.32) \times 10^{-10}$ 

10<sup>-11</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> for NFM and NAM, respectively

The values of the kinetic rate constants of the analyzed compounds are relatively high, in the order of  $10^{-11}$  to  $10^{-10}$ , which means that they react with OH-radicals relatively quickly. As shown in Table IV.5, among the analyzed compounds, morpholine is the most reactive towards OH-radicals; whereas NFM and NAM exhibit similar reactivities. The implications of the obtained results are discussed below.

## **III.4** Discussion

#### **III.4.1 Sources of error**

The uncertainty in the rate constant values reported in this chapter is due to two different types of error: i) random error, whose influence is minimized by repeating the experiments, and ii) systematic error, which may be calculated based on the following relation:

$$\Delta k = k \, \left[ \left( \Delta k_{ref} \, / \, k_{ref} \right)^2 + \left( \Delta R \, / \, R \right)^2 \right]^{1/2}$$

The main sources of systematic error include:

- > Error in the reported values of  $k_{Ref}$ . This error is estimated at 5 % for isoprene and 8 % for benzaldehyde (Atkinson, 1986; Baulch et al., 1994).
- Error in the determination of the slope  $k_{OH}/k_{Ref}$ . The slope  $R = k_{OH}/k_{Ref}$  is determined directly from the experimental datapoints. The latter represent the areas of spectroscopic peaks corresponding to both the analyte and the reference. This uncertainty is high when:
  - The integrated peaks are of low intensity, resulting in weak area values. In order to minimize the uncertainty we have introduced sufficient amounts of the analyte and reference compounds, which led to relatively intense peaks.
  - Interference between the peaks of the reacting species and those of the products formed during the experiment. The peaks used for the determination of the rate constants were chosen in such a way so as to minimize this interference.

A great number of spectra (30 to 65) were collected at different time intervals for each experiment in order to minimize the uncertainty in the determination of the slope. This

uncertainty is about 7-12 % which incurs an uncertainty of the order of 7-14 % in the rate constant values (values calculated by propagation of error).

## III.4.2 Comparison of reactivity with other compounds

Table IV.6 provides a list of the kinetic rate constant values obtained in this study concerning the homogeneous oxidation of morpholine, NFM and NAM by OH-radicals, as well as those reported in the literature for some amines and amides. The experimental values determined in this study are also compared to the ones obtained by the Estimation Programs Interface (EPI. AOPWIN v.1.92a, 2000) for the homogeneous oxidation of the analytes. The estimated and experimental values of homogeneous reactivity constants of morpholine relative to OH-radicals were found to be exactly the same  $(1.4 \pm 0.1) 10^{-10}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>. Meanwhile, the estimated rate constant values of NFM and NAM were found to be 25 and 54 % greater than the experimental values, respectively.

 Table IV.6 Kinetic rate constants of the homogeneous oxidation of morpholine, NFM and

 NAM compared to those reported for similar compounds

Compound	State	k <sub>OH</sub> (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	Reference
	gas phase	$(1.4 \pm 0.1) \ 10^{-10}$	present study
Morpholine	gas phase	1.4 x 10 <sup>-10</sup>	(EPI. AOPWIN v.1.92a, 2000)
	gas phase	$(8.0 \pm 0.1) \ 10^{-11}$	(SenGupta et al., 2010)
Diethylamine	gas phase	$(1.2 \pm 0.3) \ 10^{-10}$	(Tuazon et al., 2011)
N-Formylmorpholine	gas phase	$(3.8 \pm 1.1) \ 10^{-11}$	present study
	gas phase	5.6 x 10 <sup>-11</sup>	(EPI. AOPWIN v.1.92a, 2000)
N,N-dimethylformamide	gas phase	$(1.4 \pm 0.3) \ 10^{-11}$	(Solignac et al., 2005)
N A actulmorpholine	gas phase	$(3.7 \pm 1.0) \ 10^{-11}$	present study
w-Aceryinior photine	gas phase	8.9 x 10 <sup>-11</sup>	(EPI. AOPWIN v.1.92a, 2000)

	gas phase	1.4 x 10 <sup>-11</sup>	(Koch et al., 1997)
N,N-dimethylacetamide	gas phase	$(1.9 \pm 0.3) \ 10^{-11}$	(Solignac et al., 2005)
1-methyl-2-pyrrolidinone	gas phase	$(2.2 \pm 0.4) \ 10^{-11}$	(Aschmann and Atkinson, 1999)

#### ABSORPTION SPECTRA AND HOMOGENEOUS REACTIVITY

Based on their chemical structure, the analyzed compounds may be divided into two groups: amines (morpholine) and amides (NFM and NAM). As shown in Table IV.6, only one study has been found in the literature regarding the kinetics of OH-oxidation of morpholine in the gas-phase. In this study, SenGupta et al. (2010) report a value of  $k_{OH}$  for morpholine that is only 46 % less than that obtained in our study. This variation is probably due to the difference in the employed experimental techniques: the values reported by Sengupta et al. (2010) are determined in the absolute mode using Laser Photolysis-Laser Induced Fluorescence technique, whereas our values were determined relative to a reference compound using FTIR spectroscopy. It can be noted that the AOWPIN estimation is closer to our value to that reported by SenGupta et al. (2010). It is also possible to compare the reactivity of morpholine to that of diethyl amine, another secondary amine. The value of the kinetic reactivity constant of the oxidation of gaseous diethylamine by OH-radicals is (1.2  $\pm$  0.3) x 10<sup>-10</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> (Tuazon et al., 2011), very close to that determined in our study for the oxidation of morpholine, (1.4  $\pm$  0.1) x 10<sup>-10</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>.

Meanwhile, to the best of our knowledge, this work constitutes the first and only study concerning the homogeneous oxidation of NFM and NAM by OH-radicals. However, it is still possible to compare our results to those obtained for some of the amides that have been investigated in the literature. The kinetic rate constant of oxidation of NFM is compared to that reported by Solignac et al. (2005) for the homogeneous oxidation of N,N-dimethylformamide. Although NFM is slightly more reactive (2-3 times), the values are of the

same order of magnitude, indicating that, as expected for two compounds of similar structure, the mechanism of oxidation might be the same. As for reactivity of NAM, it was compared to those of N,N-dimethylacetamide and 1-methyl-2-pyrrolidinone (Aschmann and Atkinson, 1999; Koch et al., 1997; Solignac et al., 2005). Similarly, the rate constants are of the same order, with NAM being 2-3 times more reactive towards OH-radicals.

Generally speaking, the gaseous OH-reactivity of the compounds investigated in this study is greater than that of compounds with similar structure (morpholine and NFM more reactive than diethyamine and N,N-dimethylformamide, respectively, and NAM more reactive than either N,N-dimethylacetamide or 1-methyl-2-pyrrolidinone). This may be attributed to the presence of the ether group in morpholine, NFM and NAM, which favors degradation by OH-radicals. In addition, the fact that the investigated compounds as well as 1-methyl-2-pyrrolidinone are somewhat more reactive than the non-cyclic amines and amides listed in Table IV.6, indicates that cyclization may also favor reactivity.

Furthermore, although the kinetic rate constants of NFM and NAM are similar, morpholine is approximately 4 times more reactive than either compound. Such a trend is to be expected since it is has been observed that the OH reactivity of amides is lower than that of the corresponding amines (Aschmann and Atkinson, 1999; Barnes et al., 2010; Koch et al., 1997; Solignac et al., 2005). The similarity in the rate constants for NFM and NAM intimates that the reaction proceeds via attack on a (-N-CH<sub>2</sub>-) or a (-O-CH<sub>2</sub>-) entity and not on a (-C(O)-H) or a (-C(O)-CH<sub>3</sub>) entity.

## **III.5** Mechanism of Oxidation by OH-radicals:

#### **III.5.1** Morpholine

Although we have not attempted to identify the products of oxidation of the analyzed compounds, it is still possible to propose a mechanism of degradation based on the literature. As already mentioned, the analyzed compounds belong to two different chemical groups: amines and amides, and the mechanism of degradation differs for each group. In the case of morpholine, the reaction is expected to proceed via H-abstraction from either the (N-H) or the (-NH-CH<sub>2</sub>-) or the (-O-CH<sub>2</sub>-) entities. This abstraction is favored by the presence of heteroatoms (N and O), which weakens the C-H bond. However, the activation energy of the reaction was found to be negative, which suggests that the reaction proceeds via OH-addition instead (SenGupta et al., 2010). The experimental and theoretical study conducted by SenGupta et al. (2010) verifies that although the oxidation of morpholine by OH-radicals proceeds via H-abstraction, this step is preceded by a rate-determining step involving the formation of pre-reactive complex, whose energy is lower than that of morpholine. This prereactive complex results from the H-bond interaction between either N and H or O and H, with the N-adduct being more stable, as shown in Figure IV.19 (SenGupta et al., 2010). The formation of the pre-reactive complex is followed by H-abstraction from three possible sites (Figure IV.19). Knowing that the (N-H) bond is usually stronger than the (C-H) bond, the reaction is expected to continue predominantly through pathways A and C, resulting in the formation of an amide and an ester. The complete mechanism of OH-oxidation of morpholine is depicted in Figure IV.19. This mechanism is proposed based on that reported for N,Ndimethyl amine (Finlayson-Pitts and Pitts, 2000), as well as the findings of SenGupta et al. (2010).



Figure IV.19 Scheme of the mechanism of OH-oxidation of morpholine

#### **III.5.2NFM and NAM**

The mechanistic studies found in the literature concerning the oxidation of amides by OH-radicals are scarce. However, it is still possible to elucidate the mechanism of degradation of NFM and NAM from the few studies that have been published so far (Aschmann and Atkinson, 1999; Barnes et al., 2010; Hayon et al., 1971; Koch et al., 1997; Solignac et al., 2005). In their study concerning the kinetics of oxidation of several amides by OH-radicals, Koch et al. (1997) show that the activation energy of the reaction is negative, which indicates that the reaction probably proceeds via addition, followed by subsequent H-abstraction. The same conclusions have been drawn by other authors who stress that although a negative activation energy indicates an addition mechanism, it does not totally exclude the possibility of direct abstraction (Barnes et al., 2010; Solignac et al., 2005). In any case, whether or not the reaction starts by an addition step, it involves the abstraction of a hydrogen atom. For NFM and NAM, there are several sites at which H-abstraction may take place, as shown in Figure IV.20.



Figure IV.20 Scheme of the possible sites for H-abstraction from NFM and NAM

By analogy with formates and acetates, the (H-C(O)-) and (CH<sub>3</sub>-C(O)-) moieties in NFM and NAM are expected to have low reactivity (Mellouki et al., 2003; Solignac et al., 2005). However, in their study to investigate the sites of attack of OH radicals on amides in an aqueous solution, Hayon et al. (1971) have found that for formamide, abstraction may occur from either the (CH<sub>3</sub>-C(O)-) or the (NH<sub>2</sub>-) moieties. Meanwhile, for other amides such as N-methylformamide, N,N-dimethylformamide (etc.), the abstraction was found to occur mostly the N-methyl groups (Hayon et al., 1971; Solignac et al., 2005). Assuming that for NFM and NAM H-abstraction occurs either at the (-N-CH<sub>2</sub>-) or (-O-CH<sub>2</sub>-), the expected products of oxidation of these compounds by OH-radicals are illustrated in Figures IV.21 and IV.22



Figure IV.21 Scheme of the mechanism of OH-oxidation of NFM and NAM (R1 denotes

either H or CH<sub>3</sub>)



Figure IV.22 Products of OH-oxidation of NFM and NAM (R<sub>1</sub> denotes either H or CH<sub>3</sub>)

The abstraction of an H-atom from a  $-CH_2$  moiety results in the formation of an alkyl radical which rapidly adds  $O_2$  to form the corresponding peroxy radical as shown in Figures IV.21 and IV.22 (Atkinson, 1994). The peroxy radical generated may then react with i) NO to form an alkoxy radical and NO<sub>2</sub> or the corresponding nitrate; ii) HO<sub>2</sub> to form a product of the type (-HC-OOH), or iii) RO<sub>2</sub> to form products of the type (-C(O)-N-C(O)-), (-C(O)-N-C(OH)-), (-C-C(O)-O-C) and (-C-C(OH)-O-C) (Aschmann and Atkinson, 1999). The alkoxy radicals that are formed subsequently react with O<sub>2</sub> to form the corresponding carbonyl groups as shown in Figure IV.23.



Figure IV.23 Scheme of the addition of O<sub>2</sub> to an alkoxy radical

## **III.6** Atmospheric Implications

## III.6.1 Life-times

Similar to the case of heterogeneous oxidation, the atmospheric lifetimes of gaseous morpholine, NFM and NAM, based on their reactions with OH radicals, were calculated using the following relation, assuming a second order reaction kinetics between each analyte and OH.

$$\mathcal{T}_{OH} = \frac{1}{k_{OH} \cdot [OH]_g}$$

where  $k_{OH}$  is the 2<sup>nd</sup> order rate constant of oxidation of the analyte by OH-radicals, and  $[OH]_g$  is the gaseous concentration of OH-radicals in the atmosphere, the mean value of which is 1 x 10<sup>6</sup> molecules.cm<sup>-3</sup> (Finlayson-Pitts and Pitts, 2000).

The calculated life-times of the analyzed compounds are listed in Table IV.7. As can be seen from this table, the life-times of morpholine, NFM and NAM relative to OH-radicals
are in the order of a few hours. This means that these compounds are non-persistent in the atmosphere, and thus their environmental impact is local.

**Table IV.7** Kinetic rate constants of the homogeneous oxidation of morpholine, NFM and

 NAM and the corresponding life-times compared to those reported for similar compounds

Compound	State	$\mathbf{k}_{\mathbf{OH}}$ (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	$ au_{\mathrm{OH}}^{*}$
Morpholine	gas phase	$(1.4 \pm 0.1) \ 10^{-10}$	2 hours
N-Formylmorpholine**	gas phase	$(3.8 \pm 1.1) \ 10^{-11}$	7 hours
N-Acetylmorpholine**	gas phase	$(3.7 \pm 1.0) \ 10^{-11}$	7 hours

\*values calculated for  $[OH] = 1 \times 10^6$  molecule.cm<sup>-3</sup>

\*\* values determined at 43 and 38°C for NFM and NAM, respectively

#### **III.6.2 Products of degradation**

The homogeneous oxidation of morpholine by OH-radicals leads to the formation of heterocyclic esters and amides. Meanwhile, the degradation of NFM and NAM leads to the formation of numerous heterocyclic products such as (R-C(O)-N-C(O)-R'), (R-C(OOH)-N-C(O)-R'), (R-C(ONO2)-N-C(O)-R') and (R-O-C(O)-CH2-N-C(O)-R').

## IV. Conclusion

With rate constants in the order of 10<sup>-10</sup> to 10<sup>-11</sup> cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup>, morpholine, NFM and NAM are highly susceptible to oxidation by OH-radicals. Such high reactivities incur atmospheric life-times that do not exceed 7 hours. Therefore, the atmospheric impact of these species is limited to the local scale. On the other hand, upon oxidation, morpholine, NFM and NAM produce a variety of chemical species that may be more hazardous than their parent molecules.

### V. Résumé du Chapitre

Comme il a été montré au chapitre III, l'ozonolyse du diméthomorphe conduit à la formation du N-formylmorpholine (NFM), un composé relativement volatil, donc susceptible d'être transféré dans la phase gazeuse de l'atmosphère.

Le chapitre IV porte sur l'étude cinétique de la réaction entre le NFM et les radicaux OH ainsi que la détermination de son spectre d'absorption UV. Deux autres composés de la famille des morpholines ont été aussi étudiés dans ce chapitre à savoir le morpholine et le Nacétylmorpholine (NAM). Ces travaux consistent à étudier la cinétique de leurs réactions avec les radicaux OH et à déterminer leurs spectres absorption UV.

#### **Spectres d'absorption UV**

Les spectres d'absorption des trois composés cités ci-dessus ont été déterminés au moyen d'un spectromètre UV-Vis dans la gamme spectrale 200-300 nm. Les déterminations spectroscopiques de la morpholine ont été effectuées à température ambiante alors que celles du NFM et du NAM ont été réalisées à des températures supérieures à 313 K. Les autres conditions expérimentales, pression et trajet optiques, ont été choisies de telle sorte que la loi de Beer Lambert soit applicable. La section efficace d'absorption pour une longueur d'onde est extraite au moyen de la relation de Beer Lambert (équation (24) chapitre II). Les données rapportées constituent la moyenne d'un grand nombre de spectres enregistrés.

Les spectres UV obtenus pour les trois composés sont similaires en forme. En outre ces spectres sont des continuums non structurés pour une résolution de 0,1 nm. Le spectre de la morpholine présente 2 bandes d'absorption: une bande forte et intense, dont le maximum se situe en dessous de la gamme spectrale enregistrée, et une large bande avec un maximum ( $\sigma \approx 9.3 \times 10^{-19} \text{ cm}^2$ .molecule<sup>-1</sup>) au voisinage de  $\lambda \approx 235$  nm.

Le NFM absorbe fortement ( $\sigma > 1.3 \times 10^{-18} \text{ cm}^2$ .molecule<sup>-1</sup>) à faibles longueurs d'onde, le maximum d'absorption de ce composé est localisé en dessous de 200 nm. Quant au NAM, il présente aussi une forte absorption avec un maximum d'absorption au voisinage de la longueur d'onde  $\lambda \approx 205$  nm. Pour ces deux composés cette bande d'absorption est attribuée la transition électronique interdite n- $\pi$ \* du groupement carbonyle.

La comparaison des spectres d'absorption UV de la morpholine et du NFM obtenus dans cette étude par rapport aux spectres des amines et des amides, trouvés dans la littérature, dont les structures sont similaires montre que d'une manière générale ces spectres présentent une allure similaire avec une absorption du même ordre de grandeur. Cependant dans le cas du NAM, le spectre UV est relativement différent de celui de son homologue amide, la diméthylacétamide (DMA). En effet, dans le domaine spectral étudié l'absorption du DMA est 10 fois plus élevée à celle du NAM. D'autres mesures à des pressions plus élevées sont nécessaires pour vérifier ces résultats.

Il est important de noter que ces mesures montrent que les processus de photolyse atmosphérique de ces composés sont peu probables étant donnée leur faible absorption à des longueurs d'onde supérieures à 280 nm. En outre, ces études sont importantes puisqu'elles complètent les bases de données spectroscopiques utilisées pour quantifier ces composés dans divers systèmes réactifs.

#### Réaction avec les radicaux OH

Les constantes cinétiques de la réaction d'oxydation des trois composés (morpholine NFM, NAM) par les radicaux OH ont été déterminées en mode relatif dans une chambre de simulation atmosphérique rigide couplée à un spectromètre FTIR. Le composé de référence a été choisi de telle sorte que son spectre IR ne perturbe pas les analyses cinétiques. Dans ce travail nous avons utilisé l'isoprène ( $k_{OH} = (1.00 \pm 0.05) \times 10^{-10} \text{ cm}^3$ .molecule<sup>-1</sup>.s<sup>-1</sup> à 299 K)

comme composé de référence lors de l'étude cinétique de la réaction de morpholine. Les études cinétiques du NFM et du NAM sont réalisées par rapport au benzaldehyde.

Les cinétiques de dégradation de l'analyte et de la référence sont suivies en relevant l'évolution des aires de leurs bandes d'absorption IR spécifiques. En se basant sur la relation (22) du chapitre II, la pente du tracé de  $(\ln[P]_{t0}/[P]_t)/t$  en fonction de  $(\ln[Ref]_{t0}/[Ref]_t)/$ , pour chaque composé, permet d'extraire le rapport des deux constantes de vitesse. Connaissant la constante de vitesse k<sub>Réf</sub> on peut extraire les constantes de vitesse des réactions recherchées. Les résultats obtenus sont résumés dans le Tableau IV.8 ci-dessous

Une seule étude cinétique, SenGupta et al. (2010) concernant la réaction entre le morpholine et les radicaux OH existe dans la littérature. La constante cinétique déterminée dans ce travail présente une différence de l'ordre de 43% par rapport à la nôtre. L'origine de cette différence est probablement d'ordre expérimentale. Par ailleurs il est intéressant de noter que d'après le modèle AOPwin, basé sur les relations structure/réactivité, la constante de vitesse calculée correspond au chiffre significatif près à notre détermination expérimentale.

Les constantes de vitesse du NFM et du NAM relativement aux radicaux OH sont similaires. En outre, elles sont du même ordre de grandeur que celles obtenues pour les réactions entre les radicaux OH et les amides dont les structures sont similaires au NFM et au NAM. La comparaison de la réactivité de la morpholine avec celles du NFM et du NAM, montre que ces derniers composés sont 4 fois moins réactifs que la morpholine. Une telle tendance est attendue, car il a été montré que les amines sont plus réactives que leurs homologues amides relativement aux radicaux OH (Aschmann and Atkinson, 1999; Barnes et al., 2010; Koch et al., 1997; Solignac et al., 2005).

Les temps de vie des composés par rapport aux radicaux OH sont calculés à partir des constantes de vitesse déterminées expérimentalement (Tableau IV.7).

Tableau IV.7 Constantes de vitesse d'oxydation homogène de la morpholine, du NFM et du

Compound	<b>k</b> <sub>OH</sub> (cm <sup>3</sup> .molecule <sup>-1</sup> .s <sup>-1</sup> )	$\tau_{OH}^{*}$ (heures)
Morpholine	$(1.4 \pm 0.1) \ 10^{-10}$	2
N-Formylmorpholine	$(3.8 \pm 1.1) \ 10^{-11}$	7
N-Acetylmorpholine	$(3.7 \pm 1.0) \ 10^{-11}$	7

NAM par les radicaux OH et temps de vie correspondants.

\*calculé pour  $[OH] = 1 \times 10^6$  molecule.cm<sup>-3</sup>

Les temps de vie de la morpholine, du NFM et du NAM par rapport aux radicaux OH sont de quelques heures (Tableau IV.7). Ces composés ne sont donc pas persistants dans l'atmosphère et leur impact environnemental est plutôt local.

Une étude bibliographique du mécanisme de dégradation des amines et des amides permet de proposer un mécanisme de dégradation des produits étudiés par les radicaux OH. Ces mécanismes montrent que la dégradation de la morpholine conduirait à la formation d'esters et d'amides hétérocycliques alors que celle du NFM et du NAM conduit à la formation de composés type (R-C(O)-N-C(O)-R'), (R-C(OOH)-N-C(O)-R'), (R-C(ONO<sub>2</sub>)-N-C(O)-R') et (R-O-C(O)-CH<sub>2</sub>-N-C(O)-R').

### CONCLUSIONS ET PERSPECTIVES

Le travail présenté dans cette thèse sur l'étude cinétique et mécanistique de la dégradation de pesticides et de composés organiques volatils se compose de deux parties.

La première concerne l'étude de la cinétique d'oxydation hétérogène de pesticides en phase condensée par deux oxydants atmosphériques, à savoir l'ozone et les radicaux OH. Les pesticides ciblés sont le folpel et le diméthomorphe, deux fongicides très utilisés dans la viticulture en Champagne Ardenne. Ces fongicides ont d'ailleurs été identifiés et quantifiés dans des prélèvements atmosphériques dans cette région.

Les cinétiques d'ozonolyse et de réaction avec les radicaux OH ont été étudiées dans un réacteur photo-chimique couplé à un spectromètre UV utilisé pour déterminer la concentration des oxydants gazeux ou de leur précurseur. La concentration résiduelle de pesticide obtenue après son exposition à une atmosphère oxydante est déterminée par chromatographie en phase gazeuse couplée à un spectromètre de masse en mode SIM pour plus de sensibilité. La cinétique d'ozonolyse a été déterminée en mode absolu et les résultats obtenus ont été exploités par les modèles de cinétique hétérogène de Langmuir-Rideal et Langmuir-Hinshelwood. Par contre, la cinétique de dégradation des pesticides par les radicaux OH a été déterminée relativement à un composé de référence dont la constante de vitesse hétérogène relative au même type de support est connue. Les constantes de vitesse déterminées sont utilisées pour calculer les durées de vie relativement à l'ozone et aux radicaux OH. Pour des concentrations atmosphériques d'ozone et de radicaux OH de 40 ppb et 10<sup>6</sup> molecules.cm<sup>-3</sup> respectivement, les temps de vie du folpel et du diméthomorphe varient d'un à quelques mois. Ces deux fongicides sont donc relativement persistants et susceptibles d'être transportés sous forme de particules atmosphériques, sur de longues distances. La première partie de cette thèse cherche également à identifier les produits de dégradation du diméthomorphe en phase solide tout comme ceux qui sont susceptibles d'être transférés en phase gazeuse. Grâce à la technique de micro-extraction en phase solide, le (4-chlorophényl)(3,4-dimethoxyphenyl)méthanone (CPMPM) a été identifié dans le résidu solide comme produit de dégradation de l'ozonolyse et de l'oxydation par les radicaux OH du diméthomorphe. Le mécanisme de dégradation conduisant à la formation du CPMPM conduit également à la formation de N-formylmorpholine (NFM), un produit qui, au vu de ses propriétés physico-chimiques, est probablement transféré en phase gazeuse. La dégradation hétérogène du CPMPM relativement à l'ozone et aux radicaux OH a été étudiée de la même manière que la molécule parent. Les résultats montrent que le CPMPM est plus réactif que le diméthomorphe relativement aux radicaux OH et moins réactif relativement à l'ozone.

La détermination des spectres d'absorption UV et l'étude cinétique de la réactivité en phase homogène du NFM, et de deux composés similaires, à savoir la morpholine et le N-acétylmorpholine (NAM), relativement aux radicaux OH fait l'objet de la deuxième partie de la thèse. Les spectres UV de ces espèces ont été étudiés dans le domaine 200-300 nm. Ces déterminations spectroscopiques sont importantes puisqu'elles complètent les bases de données spectroscopiques utilisées pour mesurer la concentration de ces composés dans différents systèmes réactifs in-situ. Les spectres obtenus montrent que ces espèces absorbent fortement vers 200 - 210 nm. Les absorbances à des longueurs d'onde supérieures à 280 nm sont négligeables. Ces espèces ne sont donc pas susceptibles d'être photolysées dans la troposphère.

Les études de réactivité homogène relativement aux radicaux OH ont été menées dans une chambre de simulation atmosphérique. Cette chambre est composée d'un réacteur à triple parois équipé d'un système de réflexion multiple et couplée à un spectromètre Infra Rouge. Le milieu réactionnel est chauffé pour éviter la condensation sur les parois grâce à un fluide régulateur de la température. Tout comme en phase hétérogène la réactivité vis à vis des radicaux OH est réalisée relativement à une référence dont la cinétique est connue. Les constantes de vitesse déterminées sont de l'ordre de 10<sup>-11</sup> à 10<sup>-10</sup> cm<sup>3</sup>.molecules<sup>-1</sup>.s<sup>-1</sup> et sont similaires à celles estimées par les méthodes de corrélation SAR. En estimant la concentration des radicaux OH à 10<sup>6</sup> molecules.cm<sup>-3</sup>, les temps de vie de la morpholine, du NFM et du NAM ne dépassent guère quelques heures. Ces composés morpholiniques sont très réactifs et donc non persistants dans la troposphère. Ils se dégradent rapidement dans des zones non loin de leur source.

Les recherches menées dans cette thèse sont de grand intérêt, et ce pour deux raisons :

- Les pesticides sont des composés dangereux pour l'homme et pour l'environnement. Ils sont utilisés en grande quantité partout dans le monde et gagnent en partie le compartiment atmosphérique démuni de frontières.
- Peu d'informations relatives au comportement des pesticides dans l'atmosphère sont disponibles.

Le manque de connaissances relatives au comportement des espèces dangereuses dans l'atmosphère rend difficile la prise de mesures pour minimiser leur impact sur l'homme et l'environnement. Cette thèse contribue à fournir des indicateurs de persistance et d'évolution de deux fongicides et de certains de leurs produits de dégradation vis à vis de deux des principaux oxydants atmosphériques. Toutefois, il faut garder en mémoire que le devenir atmosphérique des espèces étudiées ne dépend pas seulement de leur réactivité avec l'ozone et les radicaux OH. En effet, d'autres processus, comme les dépositions sèches et humides, les réactions avec les autres oxydants tels que les radicaux chlore et nitrate, peuvent avoir leur importance. L'importance relative de chaque processus dépend d'un certain nombre de facteurs incluant les conditions météorologiques (température, humidité relative, précipitations...), la localisation géographique (proche de la mer et donc de sources de radicaux chlore...), et les propriétés physico-chimiques des composés (pression de vapeur, constante de Henry, coefficient de partition gaz/particule...). C'est pourquoi, pour une compréhension globale du comportement de ces espèces dans l'atmosphère, des études sur la contribution individuelle de chacun des processus évoqués précédemment sont nécessaires. De plus, sachant que la nature du support du pesticide a une grande importance sur sa réactivité hétérogène, d'autres modèles de supports représentatifs des particules atmosphériques, comme le carbone élémentaire par exemple, doivent être testés.

### ANNEX I Surface coverage

Estimation of surface area of the rugose surface of the quartz plaque

AFM (Atmomic Force Microscopy) measurements were carried out in order to determine the real area of the plaque surface. Random  $6 \ge 6 \ \mu m^2$  surface samples have been analyzed by AFM. Figure AI.1 presents the topographic image of one of these samples.



**Figure AI.1** topographic image of  $6 \times 6 \mu m^2$  surface sample

The obtained results show that the mean roughness of the surface ranges between 10 and 16 nm. Assuming that the entire surface of each quartz plaque ( $18 \text{ cm}^2$ ) is composed of semi-elliptic holes as shown in Figure AI.2, the effective surface (*S*) may be calculated as follows:

*S* = (*Number of holes*).(*Surface area of each hole*)



Figure AI.2 scheme of the plaque surface and the corresponding dimensions

The number of holes (*N*) is given by the following relation:

$$N = \frac{\text{Observed area of the plaque}}{\text{Area of the top surface of each hole}} = \frac{18cm^2}{\pi \left(\frac{d_1}{2}\right)^2} = \frac{18cm^2}{(7.9)10^{-13}cm^2} = (2.25)10^{13} \text{ holes}$$

Therefore,

$$S = (Number of holes).(Surface area of each hole = (2.2)10^{13} holes x (2.5)10^{-12} cm2.hole-1$$
$$= 56 cm2$$

So, the real surface is estimated at  $56 \text{ cm}^2$ .

#### Estimation of the area of an analyte molecule (ex. dimethomorph)

Assuming that dimethomorph molecules are spherical in shape, their surface has been estimated as follows:

 $Density = \frac{mass}{volume} = 1.318 g.mol^{-1} (U.S.EPA, 1998)$ 

Therefore, 
$$V_m = \frac{M}{density} = \frac{387.9 \, g.mol^{-1}}{1.318 \, g.ml^{-1}} = 294.3 \, ml.mol^{-1}$$
; where  $V_m$  and  $M$  are the molar

volume and molar mass of dimethomorph, respectively.

Also,  $V_m = \frac{4}{3} \cdot \pi \cdot r^3 \cdot N_A$ ; where  $N_A$  is Avogadro's number and r is the molecular radius.

Consequently, 
$$r = \left(\frac{3.V_m}{4.\pi.N_A}\right)^{\frac{1}{3}} = \left(\frac{882.9}{7.6x10^{24}}\right)^{\frac{1}{3}} = 4.9x10^{-8} \, cm$$

Therefore, the surface of a dimethomorph molecule is:

$$A = 4.\pi r^2 = 3.0 \times 10^{-14} cm^2.molecule^{-1}$$

The surface of 1  $\mu$ g of difenoconazole is equivalent to:

$$\frac{A.m.N_A}{M} = \frac{3.0E - 14 \text{ cm}^2.\text{molecule}^{-1} \text{ x } 1E - 6 \text{ g } \text{ x } 6.023E23 \text{ molecules.mol}^{-1}}{387.9 \text{ g.mol}^{-1}} = 46.5 \text{ cm}^2$$

#### Estimation of surface coverage

Considering that upon deposition, the area occupied by a molecule is approximately half its total surface, the % surface coverage of a quartz plaque by 1 µg of dimethomorph is:

% surface coverage = 
$$\frac{\text{area of } 1 \,\mu\text{g of dimethomorph}}{2 \,x \,\text{area of quartz plaque}} = \frac{46.5 \,\text{cm}^2}{2 \,x \,56 \,\text{cm}^2} \approx 42 \,\%$$

Similarly, the % surface coverage for folpet, CPMPM and terbuthy lazine are 69, 49 and 47 %

### ANNEX II Derivatization of relation (22) (chapter II)

$A(s) + OH(g) \rightarrow Produits$	k <sub>OH</sub>
$A(s) + Para \rightarrow Produits$	$k_p$
$\operatorname{Ref}(s) + \operatorname{OH}(g) \rightarrow Produits$	k <sub>ref</sub>
$\operatorname{Ref}(s) + \operatorname{Para} \rightarrow Produits$	$k_p$ '

The kinetic rate laws of consumption of the analyte (A) and the reference (Ref) are as follows:

$$\frac{-d[A]_s}{dt} = k_{OH} \cdot [A]_s \cdot [OH]_g + k_p \cdot [A]_s \cdot [Para]$$
$$\frac{-d[\operatorname{Ref}]_s}{dt} = k_{\operatorname{ref}} \cdot [\operatorname{Ref}]_s \cdot [OH]_g + k_p' \cdot [\operatorname{Ref}]_s \cdot [Para]$$

When rearranged, the above equations become as follows:

$$\frac{-d[A]_{s}}{[A]_{s}} = k_{OH} \cdot [OH]_{g} \cdot dt + k_{p} \cdot [Para] \cdot dt \qquad -k_{OH} \cdot [OH]_{g} \cdot dt = \frac{d[A]_{s}}{[A]_{s}} + k_{p} \cdot [Para] \cdot dt$$

$$\frac{-d[\operatorname{Ref}]_{s}}{[\operatorname{Ref}]_{s}} = k_{\operatorname{ref}} \cdot [OH]_{g} \cdot dt + k_{p} \cdot [Para] \cdot dt \qquad -k_{\operatorname{ref}} \cdot [OH]_{g} \cdot dt = \frac{d[\operatorname{Ref}]_{s}}{[\operatorname{Ref}]_{s}} + k_{p} \cdot [Para] \cdot dt$$

By dividing the above equations by each other, and assuming that [Para] is constant  $(K_p = k_p . [Para] \text{ and } K_p' = k_p' . [Para])$  we get the following relation:

The integral of the above relation gives the following:

$$\ln \frac{[A]_{t}}{[A]_{t0}} = R.\ln \frac{[\text{Ref}]_{t}}{[\text{Ref}]_{t0}} + (RK_{p}' - K_{p})(t - t_{0})$$

Dividing by  $(t-t_0)$ , and knowing that  $t_0$  is zero, we get:

$$\frac{1}{t} \ln \frac{[A]_{t}}{[A]_{t0}} = \frac{1}{t} R \cdot \ln \frac{[\text{Ref}]_{t}}{[\text{Ref}]_{t0}} + (RK_{p} - K_{p})$$



ANNEX III Fluorescent Blacklight Spectrum

Figure AIII.1 Emission spectrum of Fluorescent blacklight lamps

### **ANNEX IV** Michelson Interferometer

The Michelson interferometer, invented by Albert Abraham Michelson in the 1800s, produces interference fringes by splitting of monochromatic light into two beams of nearly equal amplitude, so that one beam strikes a fixed mirror and the other a movable mirror. The incident beam is split by a half silvered mirror, called the beam-splitter, inclined at 45° angle with respect to the incoming beam. Half the radiation is reflected perpendicularly and directed towards the fixed mirror, while the other half passes through to fall first onto the compensation plate, then onto a movable mirror as shown in Figure AIV.1. The compensation plate is made of the same material as the beam-splitter, and has the same thickness. It is used to compensate for the fact that the beam directed towards the movable mirror traverses the thickness of the beam-splitter three times, whereas the other beams traverses it only once. When the reflected beams are brought back together, an interference pattern is produced.



Figure AIV.1 Schematic diagram of a Michelson interferometer

The mirrors (M1 and M2) are aligned in such a way that the beam is reflected straight back along the incoming path. When the beams recombine at the beam splitter, they will interfere with each other. Whether the interference will be constructive or destructive depends on the relative phase of each of the combining light beams. This is determined by the path length difference, 2d, where d represents the difference  $L_m$ - $L_f$ . With constructive interference, the wave amplitudes add in such a way so as to produce a maximum intensity beam striking the screen. The condition for maximum constructive interference is:

$$2d = m.\lambda \tag{1}$$

where m is an integer and  $\lambda$  is the wavelength of the incoming light. When the path length difference is an integer multiple of the wavelength, the recombining light beams will be in phase since both light beams originated from the same source. The resulting amplitude of the combined beam is then the sum of the amplitudes of each beam. With destructive interference, the recombined beams are out phase, meaning that the cancel each other out. The condition for maximum destructive interference is:

$$2d = \left(m + \frac{1}{2}\right) \lambda \tag{2}$$

When the path length is an odd half integer multiple of the wavelength, the recombining light beams will be exactly out of phase. The resulting amplitude of the combined beam will be the difference of the amplitudes of each beam. Moreover, since the amplitudes of the split beams are equal, the combined light beam will have zero amplitude.

By moving one of the mirrors, we can change the path length difference and the relative phase of the light beams. As the path length difference changes, we would see both constructive and destructive interference.

A more complex scenario occurs when the light source employed provides a dispersed beam instead of a linear one. With a dispersed beam, the interferometer produces an interference pattern of concentric circles instead of a single point. The interference pattern produced appears as the combined reflections of mirror M1 and the virtual reflection of the movable mirror (M2') as shown in Figure AIV.2. For convenience, the primary elements of the interferometer are shown in a linear arrangement.



Figure AIV.2 Interference pattern of a disperse beam

Similarly, the reflected parallel beams interact with each other in a constructive or destructive manner, depending on the path length difference. However, for a disperse beam, in addition to *d*, the path length difference depends on the beam angle,  $\theta$ , and equivalent to 2dcos $\theta$ . The condition for constructive interference is now:

$$2d\cos\theta = m\lambda \tag{3}$$

Note that equation (1) still holds as a special case where  $\theta=0$ , corresponding to the center of the interference pattern.

The interferogram is the plot of the intensity of the recombined light beam (y axis) versus the mirror position (x axis). Considering that the mirror is in motion at a constant velocity, the interferogram may be plotted as a function of time. The interferogram of white light is given below.



Figure AIV.3 Interferogram of white light (<u>http://www.willeyoptical.com/FTIR.html</u>)

The raw interferogram, as it is sometimes termed, is converted to a spectrum using the Fourier transform, and a spectrum is determined by ratioing a spectrum determined with a sample in the beam (as the sample spectrum) to a spectrum determined with no sample in the beam (as the background spectrum).

### ANNEX V Solid Phase Micro-Extraction (SPME)

Solid phase micro-extraction, or SPME, is a sample preparation technique that has been developed in the early 1990s at the University of Waterloo by Dr. Pawliszyn's group. It involves the use of a fiber coated with a solid extracting phase which extracts different kinds of analytes from different kinds of media (liquid or gas phase). The quantity of analyte extracted by the fiber is proportional to its concentration in the sample as long as equilibrium is reached. Success relies upon choosing a fiber whose chemical nature favors the absorption of the analyte (Hinshaw). For example, polydimethylsiloxane (PDMS) fibers are suitable for the extraction of non-polar compounds, whereas polar analytes are extracted by polyacrylate (PA) fibers. Figure AV.1 depicts the components of an SPME device.



Figure AV.1 Configuration of an SPME device

(http://accessscience.com/search.aspx?topic=CHEM:ANAL&term=Forensic+chemistry)

For samples in the aqueous phase, extraction may be effectuated upon directly immersing the fiber into the solution for a time duration that is sufficiently long to attain equilibrium. If the analyte is volatile extraction may be carried out in the Head Space (HS) mode. This means that the fiber is immersed into the gaseous space directly above the heated sample solution as shown in Figure AV.2.



Figure AV.2 Direct injection and head space modes of extraction (Hinshaw)

After extraction, the SPME fiber is transferred to the injection port of an analytical system such as a Gas Chromatograph, where desorption of the analyte takes place and analysis is carried out.

The attraction of SPME is that the extraction is fast and simple and can be done usually without the use solvents. By eliminating the solvent the analyte is concentrated and the detection limits are lowered resulting in increased sensitivity (Hinshaw). For certain compounds, detection limits can reach parts per trillion (ppt) levels. SPME also has great potential for field applications; on-site sampling can be done even by nonscientists without the need to have gas chromatography-mass spectrometry equipment at each location. When properly stored, samples can be analyzed days later in the laboratory without significant loss of volatiles.

# **Abbreviation List**

AFM	Atomic Force Microscopy	
СРМРМ	(4-chlorophenyl)(3,4-dimethoxyphenyl)methanone	
DI	Direct Injection	
DMA	dimethylacetamide	
DMF	dimethylformamide	
DTGS	Deuterated Triglycine Sulfate	
EU	European Union	
FAO	Food and Agriculture Organization	
FTIR	Fourier Transform InfraRed	
GC	Gas Chromatography	
HS	Head Space	
LH	Langmuir-Hinshelwood	
LIF	Laser Induced Fluorescence	
LP	Laser Photolysis	
LR	Langmuir-Rideal	
МСТ	Mercury Cadmium Telluride	
MS	Mass Spectrometry	
NAM	N-acetylmopholine	
NFM	N-formylmorpholine	
РАН	Polycyclic Aromatic Hydrocarbons	
PM	Particulate Matter	
SPME	Solid Phase Micro-Extraction	
SVOC	Semi-Volatile Organic Compounds	
UIPP	Union des Industries pour la Protection des Plantes	
US EPA	United States Environmental Protection Agency	
VOC	Volatile Organic Compounds	

### REFERENCES

- Ahmed Azmi, M., Naqvi, S.N.H., Arshad Azmi, M. and Aslam, M., 2006. Effect of pesticide residues on health and different enzyme levels in the blood of farm workers from Gadap (rural area) Karachi—Pakistan. Chemosphere, 64, 1739–1744.
- AIRPARIF, 2007. Evaluations des concentrations en pesticides dans l'air Francilien: Campagne exploratoire.
- Akiyama, Y., Yoshioka, N. and Tsuji, M., 1998. Studies on pesticide degradation products in pesticide residue analysis. Journal of Food Hygeine Society Japan, 39, 303-309.
- Al-Thani, R.K., Al-Thani, A.S., Elbetieha, A. and Darmani, H., 2003. Assessment of reproductive and fertility effects of amitraz pesticide in male mice. Toxicology Letters, 138, 253-260.
- Al Rashidi, M., El Mouden, O., Chakir, A., Roth, E. and Salghi, R., 2011. The heterogeneous photo-oxidation of difénoconazole in the atmosphere. Atmospheric Environment, 45, 5997-6003.
- Alegria, H., Bidleman, T.F. and Figueroa, M.S., 2006. Organochlorine pesticides in the ambient air of Chiapas, Mexico. Environmental Pollution, 140, 483-491.
- Altshuller, A.P. and Bufalini, J.J., 1965. Photochemical aspects of air pollution: A review. Photochemistry and Photobiology, 4, 97-146.
- Amr, M.M., 1997. Pesticide monitoring and its health problems in Egypt, a Third World country. Toxicology Letters, 107, 1-13.
- Andreu, V. and Pico, Y., 2004. Determination of pesticides and their degradation products in soil: critical review and comparison of methods. Trends in Analytical Chemistry, 23, 772-789.
- APVMA, 1997. Dimethomorph in the product Acrobat MZ 690 Fungicide. Australian Pesticides and Veterinary Medicines Authority, Canberra
- Aschmann, S.M. and Atkinson, R., 1999. Atmospheric chemistry of 1-methyl-2pyrrolidinone. Atmospheric Environment, 33, 591-599.
- Atkinson, R., 1986. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chemical Reviews, 86.
- Atkinson, R., 1989. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. Journal of Physical and Chemical Reference Data Monograph 1.
- Atkinson, R., 1994. Gas-phase tropospheric chemistry of organic compounds. Journal of Physical and Chemical Reference Data Monograph 2, 1-216.
- Atkinson, R., 1997a. Atmospheric reactions of alkoxy and /3-hydroxyalkoxy radicals. International Journal of Chemical Kinetics, 29, 99-111.
- Atkinson, R., 1997b. Gas-phase tropospheric chemistry of volatile organic compounds: 1. alkanes and alkenes. Journal of Physical and Chemical Reference Data, 26, 215-290.
- Atkinson, R. and Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. Atmospheric Environment, 37, 197-219.

- Atkinson, R., Aschmann, S.M. and Pitts, J., 1986. Kinetics of the reaction of naphthalene and biphenyl with hydroxyl radicals and with ozone at 295 K. International Journal of Chemical Kinetics, 18, 569-573.
- Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J. and Troe, J., 1997. Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: Supplement V. □ IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Journal of Physical and Chemical Reference Data, 26, 521-1011.
- Atkinson, R. and Carter, W.P.L., 1984. Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chemical Reviews, 84, 437-470.
- Atkinson, R., Guicherit, R., Hites, R.A., Palm, W.-U., Seiber, J.N. and De Voogt, P., 1999. Transformations of pesticides in the atmosphere: A state of the art Water, Air, and Soil Pollution, 115, 219-243.
- ATMO Champagne-Ardenne, 2007. Evaluation de la repartition des pesticides dans l'air ambiant de la ville de Reims. Reims
- ATMO Champagne-Ardenne, 2010. Evaluation des teneurs en pesticides sur un transect de 10 Km dans la Marne.
- Atreya, K., 2008. Health costs from short-term exposure to pesticides in Nepal. Social Science & Medicine, 67, 511-519.
- Aubertot, J.N., Barbier, J.M., Carpentier, A., Gril, J.J., Guichard, L., Lucas, P., Savary, S., Savini, I. and Voltz, M., 2005. Pesticides, agriculture et environnement. Reduire l'utilisation des pesticides et limiter leurs impactes environnementaux. Rapport d'expertise scientifique collective, INRA et Cemagref.
- Aulagnier, F., Poissant, L., Brunet, D., Beauvais, C., Pilote, M., Deblois, C. and Dassylva, N., 2008. Pesticides measured in air and precipitation in the Yamaska Basin (Quebec):
   Occurance and concentration in 2004. Science of the Total Environment, 394, 338-348.
- Axelrad, J.C., Howard, C.V. and McLean, W.G., 2002. Interactions between pesticides and component of pesticide formulations in an in vitro neurotoxicity test. Toxicology, 173, 259-268.
- Bailey, R. and Belzer, W., 2007. Large volume cold on-column injection for gas chromatography-negative chemical ionization-mass spectrometry analysis of selected pesticides in air samples. Journal of Agricultural and Food Chemistry, 55, 11150-1155.
- Baraud, L., Tissier, D., Aaron, J.J., Quisefit, J.P. and Pinart, J., 2003. A multi-residue method for the characterization and determination of atmospheric pesticides measured at two French urban and rural sampling sites. Analytical and Bioanalytical Chemistry, 377, 1148-1152.
- Barnes, I., Solignac, G., Mellouki, A. and Becker, K.H., 2010. Aspects of the atmospheric chemistry of amides. ChemPhysChem, 11, 3844-3857.
- Baulch, D.L., Cobos, C.J., Cox, R.A., Frank, P., Hayman, G., Just, Th., Kerr, J.A., Murrells, T., Pilling, M.J., Troe, J., Walker, R.W. and Warnatz, J., 1994. Evaluated kinetic data for combustion modelling supplement I. Journal of Physical and Chemical Reference Data, 23, 847.

- Bedos, C. and Cellier, P., 2002. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. Agronomie, 22, 21-33.
- Bedos, C., Cellier, P., Calvet, R. and Barriuso, E., 2002. Occurance of pesticides in the atmosphere in France. Agronomie, 22, 35-49.
- Belardi, R.P. and Pawliszyn, J.B., 1989. Application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. Water Pollution Research Journal of Canada, 24, 179-191.
- Beltran, J., Lopez, F.J., Cepria, O. and Hernandez, F., 1998. Solid-phase microextraction for quantitative analysis of organophosphorus pesticides in environmental water samples. Journal of Chromatography A, 808, 257-263.
- Beltran, J., Lopez, F.J. and Hernandez, F., 2000. Solid-phase microextraction in pesticide residue analysis. Journal of Chromatography A, 885, 389-404.
- Benitez, F.J., Real, F.J., Acero, J.L. and Garcia, C., 2006. Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters. Journal of Hazardous Materials, B138, 278-287.
- Berijania, S., Assadia, Y., Anbiaa, M., Hosseinia, M. and Aghaee, E., 2006. Dispersive liquid–liquid microextraction combined with gas chromatography-flame photometric detection: Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. Journal of Chromatography A, 1123, 1-9.
- Bermudez-Couso, A., Arias-Estevez, M., Novoa-Munoz, J.C., Lopez-Periago, E., Soto-Gonzalez, B. and Simal-Gandara, J., 2007. Seasonal distributions of fungicides in soils and sediments of a small river basin partially devoted to vineyards. Water Research, 41, 4515-4525.
- Berrada, H., Font, G. and Molto, J.C., 2000. Indirect analysis of urea herbicides from environmental water using solid-phase microextraction. Journal of Chromatography A., 890, 303-312.
- Bester, K., Hühnerfuss, H., Neudorf, B. and Thiemann, W., 1995. Atmospheric deposition of triazine herbicides in Northern Germany and the German Bight (North Sea). Chemosphere, 30, 1639-1653.
- Bethel, H.L., Arey, J. and Atkinson, R., 2001. Products of the OH-initiated reaction of 3hexene-2,5-dione. Environmental Science and Technology, 35, 4477-4480.
- Bidleman, T.F., 1988. Atmospheric Processes. Environmental Science and Technology, 22, 361-367.
- Bidleman, T.F., Billings, W.N. and Foreman, W.T., 1986. Vapour-particle partitioning of semi-volatile organic compounds: Estimates from field collections. Environmental Science and Technology, 20, 1038-1043.
- Blais, J.M., Schindler, D.W., Muir, D.C.G., Donald, D.B. and Rosenberg, B., 1999. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature, 395, 585-588.
- Bossan, D., Wortham, H. and Masclet, P., 1995. Atmospheric transport of pesticides adsorbed on aerosols. I. Photodegradation in simulated atmospheres. Chemosphere, 30, 21-29.
- Bossi, R., Vejrup, K.V., Mogensen, B.B. and Asman, W.A.H., 2002. Analysis of polar pesticides in rainwater in Denmark by liquid chromatography–tandem mass spectrometry. Journal of Chromatography A, 967, 27-36.

- Boussahel, R., Bouland, S., Moussaoui, K.M., Baudu, M. and Montiel, A., 2002. Determination of chlorinated pesticides in water by SPME/GC. Water Research, 36, 1909-1911.
- Brion, J., Chakir, A., Charbonnier, J., Daumont, D., Parisse, C. and Malicet, J., 1998. Absorption spectra measurements for the ozone molecule in the 350-830 nm region. Journal of Atmospheric Chemistry, 30, 291-299.
- Brubaker, W.W. and Hites, R.A., 1998. OH reaction kinetics of gas-phase  $\alpha$  and  $\gamma$ -hexachlorocyclohexane and hexachlorobenzene. Environmental Science and Technology, 32, 766-769.
- BUA, 1991. Morpholine. BUA Report No. 56. Society of German Chemists, Advisory Committee on Existing Chemicals of Environmental Relevance, Weinheim, VCH Verlagsgesellschaft
- Bunce, N.J., Liu, L. and Zhu, J., 1997. Reaction of naphthalene and its derivatives with hydroxyl radicals in the gas phase. Environmental Science and Technology(31).
- Burrows, H.D., Canle L, M., Santaballa, J.A. and Steenken, S., 2002. Reaction pathways and mechanisms of photodegradation of pesticides. Journal of Photochemistry and Photobiology B: Biology, 67, 71-108.
- Calvert, J.G. and Pitts, J.N., 1966. Photochemistry. Wiley, New York.
- Canal-Raffin, M., l'Azou, B., Jorly, J., Hurtier, A., Cambar, J. and Brochard, P., 2008. Cytotoxicity of folpet fungicide on human bronchial epithelial cells. Toxicology, 249, 160-166.
- Canal-Raffin, M., l'Azou, B., Martinez, B., Sellier, E., Fawaz, F., Robinson, P., Ohayon-Courtes, C., Baldi, I., Cambar, J., Molimard, M., Moore, N. and Brochard, P., 2007.
  Psycochemical characteristics and bronchial epithelial cell cytotoxicity of Folpan 80WG and Myco 500, two commercial forms of folpet. Part. Fibre Toxicol., 4, 8.
- Carter, W.P.L., Luo, D. and Malkina, I.L., 1996. Investigation of the atmospheric reactions of chloropicrin. Atmospheric Environment, 31, 1425-1439.
- Chakir, A., Solignac, G., Mellouki, A. and Daumont, D., 2005. Gas phase UV absorption cross-sections for a series of amides. Chemical Physics Letters, 404, 74-78.
- Choudhury, T.K., Gerhardt, K.O. and Mawhinney, T.P., 1996. Solid-phase microextraction of nitrogen- and phosphorus-containing pesticides from water and gas chromatographic analysis. Environmental Science and Technology, 30, 3259-3265.
- Chretien, E., 2004a. Evaluation de la teneur en produits phytosanitaires de l'air dans la zone viticole champenoise. Rapport d'etude ATMO Champagne-Ardenne. http://www.atmo-ca.asso.fr/pdf/phyto-urbains-CA-2004.pdf
- Chretien, E., 2004b. Mesure des produits phytosanitaires en zone urbaine en Champagne-Ardenne en 2004. Rapport d'etude ATMO Champagne-Ardenne. <u>http://www.atmo.asso.fr/pdf/phyto-urbains-CA-2004.pdf</u>
- Clementi, M., Causin, R., Marzocchi, C., Mantovani, A. and Tenconi, R., 2007. A study of the impact of agricultural pesticide use on the prevalence of birth defects in northeast Italy. Reproductive Toxicology, 24, 1-8.
- Clementi, M., Tiboni, G.M., Causin, R., La Rocca, C., Maranghi, F., Raffagnato, F. and Tenconi, R., 2008. Pesticides and fertility: an epidemiological study in Northeast Italy and review of the literature. Reproductive Toxicology, 26, 13-18.

- Colls, J., 2002. Air Pollution. Spon Press, New York.
- Corbett, J.R., Wright, K. and Baillie, A.C., 1984. The Biochemical Mode of Action of Pesticides. Academic Press, pp. 291-309.
- Dagnac, T., Bristeau, S., Jeannot, R., Mouvet, C. and Baran, N., 2005. Determination of chloroacetanilides, triazines and phenylureas and some of their metabolites in soil by pressurised liquid extraction, GC-MS/MS, LC-MS and LC-MS/MS. Journal of Chromatography A, 1067, 225-233.
- de Brito Sa Stoppelli, I.M. and Crestana, S., 2005. Pesticide exposure and cancer among rural workers from Bariri, Sao Paulo State, Brazil. Environment International, 31, 731-738.
- Dickhut, R.M., Cincinelli, A., Cochran, M. and Ducklow, H.W., 2005. Atmospheric concentrations and air-water flux of organochlorine pesticides along the Western Antarctic Peninsula. Environmental Science and Technology, 39, 465-470.
- Eisenreich, S.J., Looney, B.B. and Thornton, J.D., 1981. Airborne organic contaminants in the Great Lakes ecosystem. Environmental Science and Technology, 23, 1389-1395.
- Eisert, R. and Levsen, K., 1995. Determination of pesticides in aqueous samples by solidphase microextraction in-line coupled to gas chromatography-mass spectrometry Journal of American Society for Mass Spectrometry, 6, 1119-1130.
- EPI. AOPWIN v.1.92a, 2000. Atmospheric Oxidation Program for Microsoft Windows, U.S. Environmental Protection Agency.
- Esteve, W., Budzinski, H. and Villenave, E., 2004. Relative rate constants for the heterogeneous reaction of OH, NO<sub>2</sub> and NO radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 1: PAHs adsorbed on 1-2 um calibrated graphite particles. Atmospheric Environment, 38, 6063-6072.
- Esteve, W., Budzinski, H. and Villenave, E., 2006. Relative rate constants for the heterogeneous reactions of NO2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a. Atmospheric Environment, 40, 201-211.
- EU, 1999. Council directive 1999/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. The Council of the European Union,
- FAO, 2002. International Code of Conduct on the Distribution and Use of Pesticides. Food and Agriculture Organization of the United Nations, Rome
- Feigenbrugel, V., 2005. Devenir atmosphérique des pesticides : distribution entre les différentes phases de l'atmosphère et oxydation photochimique. Thèse de l'Université Louis Pasteur, Strasbourg.
- Feigenbrugel, V., Le Person, A., Le Calvé, S., Mellouki, A., Muñoz, A. and Wirtz, K., 2006. Atmospheric fate of dichlorvos: Photolysis and OH-initiated oxidation studies Environmental Science and Technology, 40, 850-857.
- Ferrari, F., Sanusi, A., Millet, M. and Montury, M., 2004. Multiresidue method using SPME for the determination of various pesticides with different volatility in confined atmospheres. Analytical and Bioanalytical Chemistry, 379, 476-483.
- Filho, A.M., dos Santos, F.N. and de P. Pereira, P.A., 2010. Development, validation and application of a method based on DI-SPME and GC-MS for determination of

pesticides of different chemical groups in surface and groundwater samples. Microchemical Journal, 96, 139-145.

Finlayson-Pitts, B. and Pitts, J., 2000. Chemistry of the Upper and Lower Atmosphere.

- Fritz, B., Lorenz, K., Steinert, W. and Zellner, R., 1981. Proceedings of the 2<sup>nd</sup> European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants. D. Riedel Publishing Co., Dordrecht.
- Gan, J., Yang, B., Zhang, Y., Shu, X., Liu, C. and Shu, J., 2010. Products and kinetics of heterogeneous reaction of suspended vinclozolin particles with ozone. Journal of Physical Chemistry, 114, 12231-12236.
- Geron, C. D., Guenther, A. B. and Pierce, T. E., 1994. An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. Journal of Geophysical Research, 99, 12773-12791.
- Gil, Y. and Sinfort, C., 2005. Emission of pesticides to the air during sprayer application: A bibliographic review. Atmospheric Environment 39, 5183-5193.
- Gioia, R., Offenberg, J.H., Gigliotti, C.L., Totten, L.A., Du, S. and Eisenreich, S.J., 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. Atmospheric Environment, 39, 2309-2322.
- Gisi, U. and Sierotzki, H., 2008. Fungicide modes of action and resistance in downy mildews. European Journal of Plant Pathology, 122, 157-167.
- Glotfelty, D.E., Taylor, A.W., Turner, B.C. and Zoller, W.H., 1984. Volatilization of surfaceapplied pesticides from fallow soil. Journal of Agriculture and Food Chemistry, 32, 638-643.
- Goldstein, A.H. and Galbally, I.E., 2007. Known and unexplored organic constituents in the Earth's atmosphere. Environmental Science and Technology, 41, 1514-1521.
- Gotz, C.W., Scheringer, M., MacLeod, M., Wegmann, F. and Hungerbuhler, K., 2008. Regional differences in gas-particle partitioning and desorption of semivolatile organic compounds on a global scale. Atmospheric Environment, 42, 554-567.
- Grosjean, D., 1991. Atmospheric chemistry of toxic contaminants. 6. Nitrosamines: Dialkyl nitrosamines and nitrosomorpholine. Journal of Air and Waste Management Association, 41, 306-311.
- Grosjean, E., de Andrade, J.B. and Grosjean, D., 1996. Carbonyl products of the gas-phase reaction of ozone with simple alkenes. Environmental Science and Technology, 30(975-983).
- Hatcher, J.M., Pennell, K.D. and Miller, G.W., 2008. Parkinson's disease and pesticides: a toxicological perspective. Trends in Pharmacological Sciences, 29, 322-329.
- Hayon, E., Ibata, T., Lichtin, N.N. and Simic, M., 1971. Sites of attack of hydroxyl radicals on amides in aqueous solution. II. The effects of branching  $\alpha$  to carbonyl and to nitrogen Journal of the American Chemical Society, 93, 5388-5394.
- Hebert, V.R., Hoonhout, C. and Miller, G.C., 2000a. Reactivity of certain organophosphorus insecticides toward hydroxyl radicals at elevated air temperatures. Journal of Agriculture and Food Chemistry, 48, 1922-1928.

- Hebert, V.R., Hoonhout, C. and Miller, G.C., 2000b. Use of stable tracer studies to evaluate pesticide photolysis at elevated temperatures. Journal of Agriculture and Food Chemistry, 48, 1916-1921.
- Hilber, I., Mader, P., Schulin, R. and Wyss, G.S., 2008. Survey of organochlorine pesticides in horticultural soils and there grown Cucurbitaceae. Chemosphere, 73, 954-961.
- Hinshaw, J.V., Solid-Phase Microextraction. Serveron Corp., Hillsboro, Oregon, USA,
- Hung, H., Blanchard, T.P., Halsall, C.J., Bidleman, T.F., Stern, G.A., Fellin, P., Muir, D.C.G., Barrie, L.A., Jantunen, L.M., Helm, P.A., Ma, J. and Konoplev, A., 2005. Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring. Science of the Total Environment, 342, 119-144.
- Johnson, W.E., Fendinger, N.J. and Plimmer, J.R., 1991. Solid-phase extraction of pesticides from water: possible interferences from dissolved organic material. Analytical Chemistry, 63, 1510–1513.
- Junge, C.E., 1977. Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. Fate of pollutants in air and water environments. Wiley, New York.
- Kahan, T.F., Kwamena, N.-O.A. and Donaldson, D.J., 2006. Heterogeneous ozonation kinetics of polycyclic aromatic hydrocarbons on organic films. Atmospheric Environment, 40, 3448-3459.
- Kallenborn, R., Oehme, M., Wynn-Williams, D.D., Schlabach, M. and Harris, J., 1998. Ambient air levels and atmospheric long-range transport of persistent organochlorines to Signy Island, Antarctica. Science of the Total Environment, 220, 167-180.
- Kaupp, H. and Umlauf, G., 1992. Atmospheric gas-particle partitioning of organic compounds: Comparison of sampling methods. Atmospheric Environment, 26A, 2259-2267.
- Kesselmeier, J., Kuhn, U., Wolf, A., Andreae, M.O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Guenther, A., Greenberg, J., De Castro Vasconcellos, P., Telles de Oliva, Tavares, T. and Artaxo, P., 2000. Atmospheric volatile organic compounds (VOC) at a remote tropical forest site in central Amazonia. Atmospheric Environment, 34, 4063-4072.
- Kidd, H. and James, D. R., 1991. The Agrochemicals Handbook, Third Edition. Royal Society of Chemistry Information Services, Cambridge.
- Koch, R., Krüger, H.-U., Elend, M., Palm, W.-U. and Zetzsch, C., 1996. Rate constants for the gas-phase reaction of OH with amines: Tert-butylamine, 2,2,2-trifluoroethylamine, and 1,4-diazabicyclo[2.2.2.]octane. International Journal of Chemical Kinetics, 28, 807-815.
- Koch, R., Palm, W.-U. and Zetzsch, C., 1997. First rate constants for reactions of OH radicals with amides. International Journal of Chemical Kinetics, 29, 81-87.
- Koh, D. and Jeyaratnam, J., 1998. Pesticides hazards in developing countries. The Science of the Total Environment, 188Suppl., \$78-\$85.
- Kumari, B., Madan, V.K. and Kathpal, T.S., 2007. Pesticide residues in rain water from Hisar, India. Environmental Monitoring Assessment, 133, 467–471.

- Kwamena, N.-O.A., Earp, M.E., Young, C.J. and Abbatt, J.P.D., 2006. Kinetic and product yield study of heterogeneous gas-surface reaction of anthracene and ozone. Journal of Physical Chemistry, 110, 3638-3646.
- Kwamena, N.-O.A., Staikova, M.G., Donaldson, D.J., George, I.J. and Abbatt, J.P.D., 2007. Role of the aerosol substrate in the heterogeneous ozonation reactions of surfacebound PAHs. Journal of Physical Chemistry, 111, 11050-11058.
- Kwamena, N.-O.A., Thornton, J.A. and Abbatt, J.P.D., 2004. Kinetics of surface-bound benzo[a]pyrene and ozone on solid organic and salt aerosols. Journal of Physical Chemistry A 108, 11626-11634.
- Kwok, E.S.C., Atkinson, R. and Arey, J., 1992. Gas-phase atmospheric chemistry of selected thiocarbamates. Environmental Science and Technology, 26, 1798-1807.
- Lambropoulou, D.A., Konstantinou, I.K. and Albanis, T.A., 2000. Determination of fungicides in natural waters using solid-phase microextraction and gas chromatography coupled to electron-capture mass spectrometric detection. Journal of Chromatography A., 893, 143-156.
- Le Couteur, D.G., McLean, A.J., Taylor, M.C., Woodham, B.L. and Board, P.G., 1999. Pesticides and Parkinson's disease. Biomed and Pharmacother, 53, 122-130.
- Le Person, A., 2006. Pesticides et composés aromatiques : études des cinétiques et mécanismes de leur dégradation en atmosphère simulée, Université d'Orléans.
- Le Person, A., Mellouki, A., Muñoz, A., Borras, E., Martin-Reviejo, M. and Wirtz, K., 2007. Trifluralin: Photolysis under sunlight conditions and reaction with HO{radical dot} radicals. Chemosphere, 67, 376-383.
- Lee, W.J., Baccarelli, A., Tretiakova, M., Gorbanev, S., Lomtev, A., Klimkina, I., Tchibissov, V., Averkina, O. and Dosemeci, M., 2006. Pesticide exposure and lung cancer mortality in Leningrad province in Russia. Environment International, 32, 412-416.
- Likens, G.E., Bormann, F.H. and Johnson, N.M., 1972. Acid Rain. Environment: Science and Policy for Sustainable Development, 14, 33-40.
- Liu, X., Jeffries, H.E. and Sexton, K.G., 1999. Atmospheric photochemical degradation of 1,4-unsaturated dicarbonyls. Environmental Science and Technology, 33, 4212-4220.
- Maroni, M., Fait, A. and Colosio, C., 1999. Risk assessment and management of occupational exposure to pesticides. Toxicology Letters, 107, 145-153.
- Maumbe, B.M. and Swinton, S.M., 2003. Hidden health costs of pesticide use in Zimbabwe's smallholder cotton growers. Social Science & Medicine, 57, 1559-1571.
- McConnell, L. L., LeNoir, J. S., Datta, S. and Seiber, J. N., 1998. Wet deposition of currentuse pesticides in the Sierra Nevada Mountain Range California, USA. Environmental Toxicology and Chemistry, 17, 1908-1916.
- McLaughlin, A. and Mineau, P., 1995. The impact of agricultural practicies on biodiversity. Agriculture, Ecosystems and Environment, 55, 201-212.
- Meister, R.T., 1994. Farm Chemicals Handbook 1994. Meister Publishing Company, Willoughby.
- Meller, R., 1999. unpublished results. Max-Planck-Institut für Chemie, Mainz, Germany.

- Mellouki, A., Le Bras, G. and Sidebottom, H., 2003. Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas Phase. Chemical Reviews, 103, 5077-5096.
- Miller, G.T., 2004. Sustaining the Earth, 6th edition. Thompson Learning, Inc., Pacific Grove, California.
- Millet, M., Wortham, H., Sanusi, A. and Mirabel, P., 1997. Atmospheric contamination by pesticides: Determination in the liquid, gaseous and particulate phases. Environmental Science and Pollution Research, 4, 172-180.
- Moreau-Guigon, E., Motelay-Massei, A., Harner, T., Pozo, K., Diamond, M., Chevreuil, M. and Blanchoud, H., 2007. Vertical and temporal distribution of persistent organic pollutants in Toronto. 1. Organochlorine pesticides. Environmental Science and Technology, 41, 2172-2177.
- Muller, J., 1984. Atmospheric residence time of carbonaceous particles and particulate PAH compounds. Science of the Total Environment, 36, 339-346.
- Munoz, A., Le Person, A., Le Calve, S., Mellouki, A., Borras, E., Daele, V. and Vera, T., 2011. Studies on atmospheric degradation of diazinon in the EUPHORE simulation chamber. Chemosphere, 85, 724-730.
- Niang-Gaye, P. and Karpel Vel Leitner, N., 2005. Contribution of carbonate radicals to atrazine oxidation during ozonation of aqueous solutions containing bicarbonate ions | [Participation des radicaux carbonate à l'oxydation de l'atrazine lors de l'ozonation de solutions aqueuses contenant des ions hydrogénocarbonate] Revue des Sciences de l'Eau 18, 65-86.
- Nishino, N., Arey, J. and Atkinson, R., 2009. Yields of glyoxal and ring cleavage co-products from the OH radical-initiated reactions of naphthalene and alkylnaphthalenes. Environmental Science and Technology, 43, 8554-8560.
- O'Leary, E.S., Vena, J.E., Freudenheim, J.L. and Brasure, J., 2004. Pesticide exposure and risk of breast cancer: a nested case-control study of residentially stable women living in Long Island. Environmental Research, 94, 134-144.
- Oliver, T.A.A., King, G.A. and Ashfold, M.N.R., 2010. Electronic supplementary information for: "The conformer resolved ultraviolet photodissociation of morpholine". The Royal Society of Chemistry, Supplemet.
- Oubina, A., Martinez, E., Gascon, J., Barcelo, D. and De Alleluia, I.B., 1998. Monitoring of insecticides and fungicides in water and sediment samples in the Brazilian environment. Journal of Environmental Analytical Chemistry, 70, 75-91.
- Palm, W.-U., Elend, M., Krüger, H.-U. and Zetzsch, C., 1999. Atmospheric degradation of a semivolatile aerosol-borne pesticide: Reaction of OH with pyrifenox (an oxime-ether), adsorbed on SiO<sub>2</sub>. Chemosphere, 38, 1241-1252.
- Palm, W.-U., Elend, M., Krueger, H.-U. and Zetzsch, C., 1997. OH radical reactivity of airborne terbuthylazine adsorbed on inert aerosol. Environmental Science and Technology, 31, 3389-3396.
- Palm, W.-U., Millet, M. and Zetzsch, C., 1998. OH radical reactivity of pesticides adsorbed on aerosol materials: First results of experiments with filter samples Ecotoxicology and Environmental Safety 41, 36-43.

- Pankow, J. F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmospheric Environment, 21, 2275-2283.
- Park, J.S., Wade, T.L. and Sweet, S., 2001. Atmospheric deposition of organochlorine contaminants to Galveston Bay, Texas. Atmospheric Environment, 35, 3315-3324.
- Pate, C.T., Atkinson, R. and Pitts, J. , 1976. The gas phase reaction of  $O_3$  with a series of aromatic hydrocarbons. Journal of Environmental Science and Health . Part A: Environmental Science and Engineering, 11, 1-10.
- Paulson, S.E. and Orlando, J.J., 1996. The Reactions of Ozone with Alkenes: An Important Source of HOx in the Boundary Layer. Geophysical Research Letters, 23, 3727-3730.
- Pawliszyn, J.B., 1997. Solid Phase Microextraction: Theory and Practice. Wiley-VHC, New York.
- Peluso, A.M., Tardio, M., Adamo, F. and Venturo, N., 1991. Multiple sensitization due to bisdithiocarbamate and thiophthalimide pesticides. Contact Dermatology, 25, 327.
- Perraudin, E., Budzinski, H. and Villenave, E., 2007a. Identification and quantification of ozonation products of anthracene and phenanthrene adsorbed on silica particles. Atmospheric Environment, 41, 6005-6017.
- Perraudin, E., Budzinski, H. and Villenave, E., 2007b. Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles. Journal of Atmospheric Chemistry, 56, 57-82.
- Petrelli, G. and Figa-Talamanca, I., 2001. Reduction in fertility in male greenhouse workers exposed to pesticides. European Journal of Epidemiology, 17, 675-677.
- Petrelli, G. and Mantovani, A., 2002. Environmental risk factors and male fertility and reproduction. Contraception, 65, 297–300.
- Pflieger, M., 2009. Etude de la dégradation photochimique des produits phytosanitaires sorbés à la surface des aérosols atmosphériques, Université de Provence.
- Pflieger, M., Goriaux, M., Temime-Roussel, B., Gligorovski, S., Monod, A. and Wortham, H., 2009a. Validation of an experimental setup to study atmospheric heterogeneous ozonolysis of semi-volatile organic compounds. Atmospheric Chemistry and Physics, 9, 2215-2225.
- Pflieger, M., Grgic, I., Kitanovski, Z., Nieto, L. and Wortham, H., 2011. The heterogeneous ozonation of pesticides adsorbed on mineral pesticides: Validation of the experimental setup with trifluarin. Atmospheric Environment, 45, 7127-7134.
- Pflieger, M., Monod, A. and Wortham, H., 2009b. Kinetic study of heterogeneous ozonolysis of alachlor, trifluralin and terbuthylazine adsorbed on silica particles under atmospheric conditions. Atmospheric Environment, 43, 5597-5603.
- Piazza Recena, M.C., Pires, D.X. and Caldas, E.D., 2006. Acute poisoning with pesticides in the state of Mato Grosso do Sul, Brazil. Science of the Total Environment, 357, 88-95.
- Pöschl, U., Letzel, T., Schauer, C. and Niessner, R., 2001. Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[a]pyrene: O<sub>3</sub> and H<sub>2</sub>O adsorption, benzo[a]pyrene degradation, and atmospheric implications. Journal of Physical Chemistry, 105, 4029-4041.

- Quest, J.A., Fenner-Crisp, P.A., Burnam, W., Copley, M., Dearfield, K.L., Hamernik, K.L., Saunders, D.S., Whiting, R.J. and Engler, R., 1993. Evaluation of the carcinogenic potential of pesticides. 4. Chloroalkylthiodicarboximide compounds with fungicidal activity. Regul. Toxicol. Pharmacology, 17, 19-34.
- Raffaele, K.C., Rowland, J., May, B., Makris, S.L., Schumacher, K. and Scarano, L.J., 2010. The use of developmental neurotoxicity data in pesticide risk assessments. Neurotoxicology and Teratology.
- Raina, R., Belzer, W. and Jones, K., 2009. Atmospheric concentrations of captan and folpet in the lower Fraser Valley agricultural region in Canada. Air, Soil and Water Research, 2, 41-49.
- Regidor, E., Ronda, E., Garcia, A.M. and Dominguez, V., 2004. Paternal exposure to agricultural pesticides and cause specific fetal death. Occupational and Environmental Medicine, 61, 334-339.
- Reynolds, J.D., 1997. International pesticide trade: Is there any hope for the effective regulation of controlled substances? . Journal of Land Use & Environmental Law, 131.
- Richards, A.J., 2001. Does low biodeversity resulting from moden agricultural practice affect crop pollination and yield? Annals of Botany, 88, 165-172.
- Ritter, W.F., 1990. Pesticide contamination of ground water in the United States A review. Journal of Environmental Science and Health, Part B, 25, 1-29.
- Rosen, E.P., Garland, E.R. and Baer, T., 2008. Ozonolysis of oleic acid adsorbed to polar and nonpolar aerosol particles. Journal of Physical Chemistry, 112, 10315-10324.
- Rosenblum, L., Heiber, T. and Morgan, J., 2001. Determination of pesticides in composite dietary samples by gas chromatography/mass spectrometry in the selected ion monitoring mode by using a temperature-programmable large volume ion injector with preseparation column. Journal of AOAC International, 84, 891-900.
- Rosner, F., 2002. The life of Moses Maimonides, a prominent medieval physician. Einstein Quarterly Journal of Biology and Medicine, 19, 125-128.
- Rudel, H., 1997. Volatilization of pesticides from soil and plant surfaces. Chemosphere, 35, 143-152.
- Salameh, P.R., Baldi, I., Brochard, P. and Abi Saleh, B., 2004. Pesticides in Lebanon: a knowledge, attitude, and practice study. Environmental Research, 94, 1-6.
- Samsonov, Y.N. and Pokrovskii, L.M., 2001. Sensitized photodecomposition of high disperse pesticide chemicals exposed to sunlight and irradiation from halogen or mercury lamp. Atmospheric Environment, 35, 2133-2141.
- Sander, S.P., Friedl, R.R., D.M., Golden, Kurylo, M.G., Moortgat, G.K., Keller-Rudek, H., Wine, P.H., Ravishankara, A.R., Kolb, C.E., Molina, M.J., Finlayson-Pitts, B.J., Huie, R.E. and Orkin, V.L., 2006. Chemical kinetics and photochemical data for use in atmospheric studies. Evaluation number 15. JPL Publication. Jet Propulsion Laboratory, Pasedena
- Sanusi, A., Millet, M., Mirabel, P. and Wortham, H., 1999. Gas-particle partitioning of pesticides in atmospheric samples. Atmospheric Environment, 33, 4941-4951.
- Sanusi, A., Millet, M., Mirabel, P. and Wortham, H., 2000. Comparison of atmospheric pesticide concentrations measured at three sampling sites: local, regional and long-range transport. The Science of the Total Environment, 263, 263-277.

- Saski, J., Aschmann, S.M., Kwok, E.S.C., Atkinson, R. and Arey, J., 1997. Products of the gas-phase OH and NO<sub>3</sub> radical-initialted reactions of naphthalene. Environmental Science and Technology, 31, 3173-3179.
- Sauret, N., 2002. Etude de la distribution des produits de protection des plantes entre les trois phases atmosphériques: Incidences sur la contamination des écosystèmes, Thèse de l'Université Louis Pasteur, Strasbourg.
- Sauret, N., Millet, M., Herckes, P., Mirabel, P. and Wortham, H., 2000. Analytical method using gas chromatography and ion trap tandem mass spectrometry for the determination of Striazines and their metabolites in the atmosphere. Environmental Pollution, 110, 243-252.
- Sauret, N., Wortham, H., Putaud, J-P. and Mirabel, P., 2008. Study of the effects of environmental parameters on the gas/particle partitioning of current-use pesticides in urban air. Atmospheric Environment, 42, 544-553.
- Scheringer, M., Salzmann, M., Stroebe, M., Wegmann, F., Fenner, K. and Hungerbühler, K., 2004. Long-range transport and global fractionation of POPs: insights from multimedia modeling studies. Environmental Pollution, 128, 177-188.
- Scheyer, A., 2004. Développement d'une méthode d'analyse par CPG/MS/MS de 27 pesticides identifiés dans les phases gazeuse, particulaire et liquide de l'atmosphère. Application à l'étude des variations spatio-temporelles des concentrations dans l'air et dans les eaux de pluie, Université Louis Pasteur, Strasbourg.
- Scheyer, A., Briand, O., Morville, S., Mirabel, P. and Millet, M., 2007a. Analysis of trace levels of pesticides in rainwater by SPME and GC-tandem mass spectrometry after derivatisation with PFFBr. Analytical and Bioanalytical Chemistry, 387, 359-368.
- Scheyer, A., Graeff, C., Morville, S., Mirabel, P. and Millet, M., 2005a. Analysis of some organochlorine pesticides in an urban atmosphere (Strasbourg, east of France). Chemosphere, 58, 1517-1524.
- Scheyer, A., Morville, S., Mirabel, P. and Millet, M., 2005b. A multiresidue method using ion-trap gas chromatography-tandem mass spectrometry with or without derivatisation with pentafluorobenzylbromide for the analysis of pesticides in the atmosphere. Analytical and Bioanalytical Chemistry, 381, 1226-1233.
- Scheyer, A., Morville, S., Mirabel, P. and Millet, M., 2006. Analysis of trace levels of pesticides in rainwater using SPME and GC-tandem mass spectrometry. Analytical and Bioanalytical Chemistry, 384, 475-487.
- Scheyer, A., Morville, S., Mirabel, P. and Millet, M., 2007b. Variability of atmospheric pesticide concentrations between urban and rural areas during intensive pesticide application. Atmospheric Environment, 41, 3604-3618.
- Scheyer, A., Morville, S., Mirabel, P. and Millet, M., 2008. Gas/particle partitioning of lindane and current-used pesticides and their relationship with temperature in urban and rural air in Alsace region (east of France). Atmospheric Environment, 42, 7695-7705.
- Schreck, E., Geret, F., Gontier, L. and Treilhou, M., 2008. Development and validation of a rapid multiresidue method for pesticide determination using gas chromatography-mass spectrometry: A realistic case in vineyard soils. Talanta, 77, 298-303.

- Schummer, C., Mothiron, E., Appenzeller, B.M.R., Rizet, A-L., Wennig, R. and Millet, M., 2010. Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France. Evironmantal Pollution, 158, 576-584.
- Segal-Rosenheimer, M. and Dubowski, Y., 2007. Heterogeneous ozonolysis of cypermethrin using real-time monitoring FTIR techniques. Journal of Physical Chemistry, 111, 11682-11691.
- Segal-Rosenheimer, M. and Dubowski, Y., 2008. Photolysis of thin films of cypermethrin using in situ FTIR monitoring: Products, rates and quantum yields. Journal of Photochemistry and Photobiology A: Chemistry, 200, 262-269.
- Segal-Rosenheimer, M., Linker, R. and Dubowski, Y., 2011. Heterogeneous oxidation of the insecticide cypermethrin as thin film and airborne particles by hydroxyl radicals and ozone. Physical Chemistry and Chemical Physics, 13, 506-517.
- Seinfeld, J.H. and Pandis, S.N., 2006. Atmospheric Chemistry and Physics From Air Pollution to Climate Change. John Wiley and Sons Inc., New Jersey.
- Semadeni, M.; Stocker, D.W. and Kerr, J.A., 1995. The temperature dependence of the OH radical reactions with some aromatic compounds under simulated tropospheric conditions. International Journal of Chemical Kinetics, 27, 287-304.
- SenGupta, S., Indulkar, Y., Kumar, A., Dhanya, S., Naik, P.D. and Bajaj, P.N., 2010. Kinetics of the gas-phase reaction of Oh with morpholine: An experimental and theoretical study. Journal of Physical Chemistry A, 114, 7709-7715.
- Solignac, G., Mellouki, A., Le Bras, G., Barnes, I. and Benter, Th., 2005. Kinetics of the OH and Cl reactions with N-methylformamide, N,N-dimethformamide and N,N-dimethylacetamide. Journal of Photochemistry and Photobiology A: Chemistry, 176, 136-142.
- Su, Y., Hung, H., Blanchard, P., Patton, G.W., Kallenborn, R., Konoplev, A., Fellin, P., Li, H., Geen, C., Stern, G., Rosenberg, B. and Barri, L.A., 2008. A circumpolar perspective of atmospheric organochlorine pesticides (OCPs): Results from six Arctic monitoring stations in 2000–2003. Atmospheric Environment, 42, 4682-4698.
- Teil, M.-J., Blanchard, M. and Chevreuil, M., 2004. Atmospheric deposition of organochlorines (PCBs and pesticies)in northern France. Chemosphere, 55, 501-514.
- Teske, M.E., Thistle, H.W., Schou, W.C., Miller, P.C.H., Strager, J.M., Richardson, B., Butler Ellis, M.C., Barry, J.W., Twardus, D.B. and Thompson, D.G., 2011. A review of computer models for pesticide deposition prediction. American Society of Agricultural and Biological Engineers, 54, 789-801.
- Thurman, E.M. and Cromwell, A.E., 2000. Atmospheric transport, deposition and fate of triazine herbicides and their metabolites in pristine areas at Isle Royal National Park. Environmental Science and Technology, 34, 3079-3085.
- Tomkins, B.A. and Ilgner, R.H., 2002. Determination of atrazine and four organophosphorus pesticides in ground water using solid phase microextraction (SPME) followed by gas chromatography with selected-ion monitoring. Journal of Chromatography A., 972, 183-194.
- Tuazon, E.C., Atkinson, R., Aschmann, S.M., Arey, J., Winer, A.M. and Pitts, J., 1986. Atmospheric loss processes of 1,2-dibromo-3-chloropropane and trimethyl phosphate. Environmental Science and Technology, 20, 1043-1046.

- Tuazon, E.C., Atkinson, R., Aschmann, S.M., Goodman, M.A. and Winer, A.M., 1988. Atmospheric reactions of chloroethenes with the OH radical. International Journal of Chemical Kinetics, 20, 241-265.
- Tuazon, E.C., Atkinson, R., Winer, A.M. and Pitts, J., 1984. A study of the atmospheric reactions of 1,3-dichloropropene and other selected organochlorine compounds. Archives of Environmental Contamination and Toxicology, 13, 691-700.
- Tuazon, E.C., Martin, P., Aschmann, S.M., Arey, J. and Atkinson, R., 2011. Kinetics of the reactions of OH Radicals with 2-methoxy-6-(trifluoromethyl)pyridine, diethylamine, and 1,1,3,3,3-pentamethyldisiloxan-1-ol at 298 ± 2 K. International Journal of Chemical Kinetics, 43, 631-638.
- Tuduri, L., Harner, T., Blanchard, P., Waite, D., Belzer, W., Froude, F., Murphy, C. and Poissant, L., 2006. A review of Currently Used Pesticides (CUPs) in Canadian air and precipitation. Part 2: Regional information and perspectives. Atmospheric Environment, 40, 1579-1589.
- U.S.EPA, 1998. Pesticide fact sheet. Dimethomorph. United States Environmental Protection Agency,
- U.S.EPA, 2003. Requirements for preparation, adoption, and submittal of implementation plans: Definitions. Code of FederalRegulations 40CFR51.100(s).
- Unsworth, J., 2010. History of Pesticide Use. IUPAC,
- Unsworth, J., Wauchope, R.D., Klein, A.W., Dorn, E., Zeeh, E., Yeh, S.M., Akerblom, M., Racke, K.D. and Ruben, B., 1999. Significance of the long range transport of pesticides in the atmosphere. Pure and Applied Chemistry, 71, 1359-1383.
- Urruty, L. and Montury, M., 1996. Influence of ethanol on pesticide extraction in aqueous solutions by solid-phase microextraction. Journal of Agriculture and Food Chemistry, 44, 3871-3877.
- Usher, C.R., Michel, A.E. and Grassian, V.H., 2003. Reaction on mineral dust. Chemical Reviews, 103, 4883-4939.
- Van Den Berg, F., Kubiak, R., Benjey, W.G., Majewski, M.S., Yates, S.R., Reeves, G.L., Smelt, J.H. and Van Der Linden, A.M.A., 1999. Emission of pesticides into the air. Water, Air, and Soil Pollution 115, 195-218.
- van der Hoek, W., Konradsen, F., Athukorala, K. and Wanigadewa, T., 1998. Pesticide poisoning: a major health problem in Sri Lanka. Social Science & Medicine, 46, 495-504.
- van der Werf, H.M.G. and Zimmer, C., 1998. Un indicateur d'impact environnemental de pesticides basé sur un système expert à logique floue. INRA, Le Courier de l'Environnement, 34.
- van Dijk, H.F.G. and Guichert, R., 1999. Atmospheric dispersion of current-use pesticides: A review of the evidence from monitoring studies. Water, Air, and Soil Pollution, 115, 21-70.
- Van Maele-Fabry, G. and Willems, J.L., 2003. Occupation related pesticide exposure and cancer of the prostate: a meta-analysis. Occupational and Environmental Medicine, 60, 634-642.
- van Pul, W.A.J., Bidleman, T.F. and Brorstrom-Lunden, E., 1999. Atmospheric transport and deposition of pesticides: an assessment of current knowledge. Water, Air, and Soil Pollution, 115, 245-256.
- Vera, T., Muñoz, A., Ródenas, M., Vázquez, M., Mellouki, A., Treacy, J., Mulla, I.A. and Sidebottom, H., 2010. Photolysis of trichloronitromethane (Chloropicrin) under atmospheric conditions. Zeitschrift fur Physikalische Chemie, 224, 1039-1057.
- Vingarzan, R., 2004. A review of surface ozone background levels and trends. Atmospheric Environment, 38, 3431-3442.
- Vogel, J.R., Majewski, M.S. and Capel, P.D., 2008. Pesticides in rain in four agricultural watersheds in the United States. Journal of Environmental Quality, 37, 1101-1115.
- Wang, J., Tuduri, L., Mercury, M., Millet, M., Briand, O. and Montury, M., 2009. Sampling atmospheric pesticides with SPME: Laboratory developments and field study. Environmental Pollution, 157, 365-370.
- Wang, L., Atkinson, R. and Arey, J., 2007. Dicarbonyl products of the OH-radical initiated reactions of naphthalene and the C1 and C2-alkylnaphthalenes. Environmental Science and Technology, 41, 2803-2810.
- Wania, F. and Mackay, D., 1993. Global fractionation and cold condensation of low volatility organo-chlorine compounds in polar regions. Ambio, 22(10-18).
- WHO, 1995. Morpholine Health and Safety Guide. IPCS International Program on Chemical Safety. Health an Safety Guide No. 92. Geneva
- Wilson, H.R., 1996. Pesticide Regulations. University of Minnesota,
- Yamasaki, H., Kuwata, K. and Miyamoto, H., 1982. Effects of ambient temperature on aspects of airborne Polycyclic Aromatic Hydrocarbons. Environmental Science and Technology, 16, 189-194.
- Yang, B., Zhang, Y., Meng, J., Gan, J. and Shu, J., 2010. Heterogeneous reactivity of suspended pirimiphos-methyl particles with ozone. Environmental Science and Technology, 44, 3311-3316.
- Yao, Y., Harner, T., Blanchard, P., Tuduri, L., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F. and Sverko, E., 2008. Pesticides in the Atmosphere Across Canadian
- Agricultural Regions. Environmental Science and Technology, 42, 5931-5937.
- Yusa, V., Coscolla, C., Mellouki, W., Pastor, A. and de la Guardia, M., 2009. Sampling and analysis of pesticides in ambient air. Journal of Chromatography A, 1216, 2972-2983.
- Zang, X., Wang, J., Wang, O., Wang, M., Ma, J., Xi, G. and Wang, Z., 2008. Analysis of captan, folpet and captafol in apples by dispersive liquid-liquid microextraction combined with gas chromatography. Analytical and Bioanalytical Chemistry, 392, 749-754.

## ABSTRACT

The research study discussed in this thesis concerns the determination of the kinetic rate constants of the heterogeneous degradation of pesticides folpet and dimethomorph by ozone and OH-radicals using the technique of a simulation chamber coupled to a GC/MS analytical system. The study also involves the identification of the degradation products of the analyzed compound in the condensed phase using SPME/GC/MS. The heterogeneous OH and O<sub>3</sub>-reactivities of the identified degradation product of dimethomorph, (4-chlorophenyl)(3,4-dimethoxyphenyl)methanone (CPMPM), are also evaluated experimentally. The obtained results show that the rate constant values of the analytes are in the order of  $10^{-20}$ - $10^{-19}$  and  $10^{-14}$ - $10^{-12}$  cm<sup>3</sup>.molecule<sup>-1</sup>.s<sup>-1</sup> relative to heterogeneous O<sub>3</sub> and OH-oxidation, respectively. Such values implicate tropospheric life-times that vary from a few days to several months, meaning that these compounds are relatively persistent and may be transported to regions far from their point of application.

The UV-absorption spectra and homogeneous OH-reactivities of the expected degradation product of dimethomorph in the gas phase, N-formylmorpholine (NFM), and two other gaseous compounds, morpholine and N-acetylmorpholne (NAM) are also studied. The results show that these compounds are not susceptible to photolysis in the atmosphere and that they exhibit strong reactivity towards OH-radicals. Generally speaking, their atmospheric life-times are in the order of a few hours and thus they are non-persistent.

Keywords: pesticides, heterogeneous kinetics, homogeneous kinetics, ozone, OH-radicals, atmospheric lifetimes, UV-spectrum

Cette thèse porte sur la détermination des constantes cinétiques de la dégradation hétérogène de pesticide (folpel et diméthomorphe) par l'ozone et les radicaux OH en utilisant un réacteur photo-chimique couplé à un système GC/MS. Le (4-chlorophenyl)(3,4-dimethoxyphenyl)methanone (CPMPM), est identifié par SPME/GC/MS comme produit de dégradation hétérogène du diméthomorphe par les radicaux OH comme par l'ozone. La réactivité hétérogène du CPMPM vis-à-vis de l'ozone et les radicaux OH est également étudiée. Les résultats obtenus montrent que les valeurs des constantes cinétiques varient entre 10<sup>-20</sup> et 10<sup>-19</sup> cm<sup>3</sup>.molécules<sup>-1</sup>.s<sup>-1</sup> vis-à-vis de l'ozone, et entre 10<sup>-14</sup> et 10<sup>-12</sup> cm<sup>3</sup>.molécules<sup>-1</sup>.s<sup>-1</sup> vis-à-vis des radicaux OH. Ces valeurs impliquent des durées de vie atmosphériques de l'ordre de quelques jours à quelques mois. Par conséquent les composés étudiés sont relativement persistants et peuvent être transportés vers des régions éloignées de leur point d'application.

Les spectres UV et la réactivité homogène vis-à-vis des radicaux OH du N-formylmorpholine (NFM), produit gazeux attendu de la dégradation du diméthomorphe, et de deux autres composés gazeux, la morpholine et le N-acétylmorpholine (NAM), ont été déterminés. Les études cinétiques ont été réalisées dans une chambre atmosphérique couplée à un spectromètre IR. Les résultats obtenus montrent que les composés étudiés ne sont pas sensibles à la photolyse dans l'atmosphère et que leur réactivité vis-à-vis des radicaux OH est élevée. En général, les durées de vie atmosphériques de ces composés sont de l'ordre de quelques heures ; ils sont donc non-persistants dans l'atmosphère.

Mots Clés: pesticides, cinétique hétérogène, cinétique homogène, ozone, radicaux OH, durée de vie atmosphérique, spectre UV