



Formation of highly oxygenated organic molecules from α -pinene photochemistry

Sungah Kang

Energie & Umwelt / Energy & Environment

Band / Volume 557

ISBN 978-3-95806-596-3

Forschungszentrum Jülich GmbH
Institut für Energie- und Klimaforschung
Troposphäre (IEK-8)

Formation of highly oxygenated organic molecules from α -pinene photochemistry

Sungah Kang

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment

Band / Volume 557

ISSN 1866-1793

ISBN 978-3-95806-596-3

Contents

Declaration of Authorship	iii
Acknowledgements	v
Abstract	vii
1 Introduction	1
1.1 Highly oxygenated organic molecules	1
1.1.1 Volatile Organic Compounds in the atmosphere	1
1.1.2 Secondary Organic Aerosol (SOA)	1
1.1.3 Highly Oxygenated organic Molecules (HOM)	2
1.2 HOM formation: atmospheric VOC oxidation by OH and O ₃	3
1.2.1 Atmospheric oxidants	3
1.2.2 Classical photochemistry and peroxy radicals	5
1.2.3 Autoxidation and HOM formation	7
1.2.4 Importance of alkoxy radicals	9
1.3 Goals of the thesis	10
2 Experiments and Methods	13
2.1 Experimental setup	13
2.1.1 Jülich Plant Atmosphere Chamber (JPAC)	13
2.1.2 Experiment descriptions	15
2.2 Chemical Ionisation Mass Spectrometer (CIMS)	23
2.2.1 Introduction of the CIMS	23
2.2.2 Calibration of detected HOM	26
2.3 Data Evaluation	28
2.3.1 High resolution peak analysis	28
2.3.2 CIMS analyzer	32
2.3.3 Families and markers	32
2.3.4 Kendrick mass defect plot	35
2.4 Corrections and assumptions	37
2.4.1 Corrections for turnover and particle surface in NO _x experiments	37
2.4.2 Assumptions	39

3	Photochemical oxidation of α-pinene: Dependency on OH concentration and effect of CO and small peroxy radicals	41
3.1	Ozonolysis of α -pinene	41
3.1.1	Mass spectrum of α -pinene ozonolysis	42
3.1.2	Comparison of mass spectra of α -pinene ozonolysis in different experiments	43
3.2	Photochemical oxidation of α -pinene: Dependency on OH concentration	43
3.2.1	Effect of increasing turnover on the concentration of sum of HOM, monomers and accretion products	46
3.2.2	Changes of families with increasing turnover	48
3.2.3	Closer look into families: Marker analysis	58
	C ₁₀ peroxy radical marker analysis	58
	C ₂₀ marker analysis	60
	C ₁₀ marker analysis	64
3.3	Photochemical oxidation of α -pinene: Effect of CO	68
3.3.1	Mass spectrum comparison	71
3.3.2	Monomer and accretion product comparison	71
3.3.3	The effect of CO on C ₁₀ and C ₂₀ families	72
3.3.4	The effect of CO on C ₁₀ and C ₂₀ marker compounds	74
	C ₁₀ peroxy radicals	74
	C ₂₀ marker compounds	76
	C ₁₀ marker compounds	79
3.4	Photochemical oxidation of α -pinene: Effect of isoprene	82
4	Photochemical oxidation of α-pinene: Impact of NO_x	89
4.1	Monomer HOM pattern change	89
4.2	Fragmentation	93
4.3	Accretion product suppression	97
4.4	Alkoxy-peroxy pathway	101
4.5	Family analysis	105
4.6	Concluding the effect of NO _x on α -pinene photooxidation	110
5	Summary, conclusion and outlook	113
	Bibliography	119
A	Peaklists	127
A.1	α -pinene OH oxidation	127
A.2	α -pinene OH oxidation in the presence of CO	127
A.3	α -pinene OH oxidation in the presence of isoprene	127
A.4	α -pinene OH oxidation in the presence of NO _x	127

B	CIMS analyzer	151
B.1	CIMS analyzer	151
C	Abbreviation	155

Energie & Umwelt / Energy & Environment
Band / Volume 557
ISBN 978-3-95806-596-3