



Formation of Secondary Organic Aerosol from Photo-Oxidation of Benzene: a Chamber Study

Sebastian Harald Schmitt

Energie & Umwelt / Energy & Environment

Band / Volume 412

ISBN 978-3-95806-305-1

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

Formation of Secondary Organic Aerosol from Photo-Oxidation of Benzene: a Chamber Study

Sebastian Harald Schmitt

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

Band / Volume 412

ISSN 1866-1793

ISBN 978-3-95806-305-1

Contents

1	Introduction, motivation and objectives	1
1.1	The role of atmospheric aerosol in the Earth system	1
1.2	Motivation for studying secondary organic aerosol from benzene	9
1.3	Objectives of this thesis	11
2	Analytical techniques	13
2.1	Particle phase	13
2.1.1	Chemical composition measurements by the Aerosol Mass Spectrometer	15
2.1.1.1	General description of the AMS	15
2.1.1.2	Quantification using the AMS	19
2.1.1.3	Size resolved measurements using particle time of flight	25
2.1.1.4	Parameters describing organic aerosol	26
2.1.1.5	Evaluation of deuterated aerosol	28
2.1.1.6	Quantification of organic nitrates with the AMS	31
2.1.2	Particle number concentration measurements by CPC	32
2.1.3	Particle size distribution measurements by SMPS	33
2.1.4	Data evaluation of SMPS and CPC datasets	33
2.1.5	Methods for estimating particle density	34
2.2	Gas phase	36
2.2.1	VOC measurements by GC-MS	36
2.2.2	VOC measurements by PTR-MS	38
2.2.3	SOA precursor measurements by CIMS	39
2.3	Additional instrumentation	41
2.4	Data analysis tools	41
3	Experimental setup	43
3.1	Jülich Plant Atmosphere Chamber	43
3.1.1	Description of the JPAC experimental setup	43
3.1.2	Rate equations for the JPAC chamber	46
3.1.3	Corrections	48
3.1.3.1	General losses due to dilution	48
3.1.3.2	Particle losses to chamber walls	49
3.1.3.3	Gas-phase losses to chamber walls	50

3.2	Simulation of Atmospheric PHotochemistry In a large Reaction chamber	53
3.2.1	Description of the SAPHIR experimental setup	53
3.2.2	Corrections	55
3.2.2.1	General losses due to dilution	55
3.2.2.2	Particle losses to chamber walls	56
3.2.2.3	Gas-phase losses to chamber walls	57
4	Determination of SOA mass yields	61
4.1	General introduction to SOA mass yield concepts	61
4.2	Applied yield concepts and necessary corrections for JPAC and SAPHIR	66
5	Overview on conducted experiments	69
5.1	JPAC chamber experiments	69
5.1.1	Unseeded experiments	69
5.1.2	Seeded experiments	72
5.2	SAPHIR chamber experiments	74
6	Results	77
6.1	JPAC experiments	77
6.1.1	Wall loss rates for aerosol particles	77
6.1.2	Additional experiments for validating AMS assumptions	79
6.1.2.1	Determination of the fragmentation table entry for H ₂ O as an organic fragment for benzene SOA	79
6.1.2.2	Determination of relative ionization efficiency for benzene SOA	81
6.1.3	Determination of gaseous precursor loss to the chamber walls	87
6.1.4	Estimation of uncertainties related to measurements and corrections	96
6.1.5	SOA mass yield from photo-oxidation of benzene and benzene-d6 under varying oxidising conditions in JPAC	99
6.1.5.1	SOA mass yield from photo-oxidation of benzene-d6 without NO _x addition	99
6.1.5.2	SOA mass yield from photo-oxidation of benzene without NO _x addition .	100
6.1.5.3	SOA mass yield from photo-oxidation of benzene in the presence of NO _x	103
6.1.6	Elemental analysis of SOA from photo-oxidation of benzene	107
6.1.7	Suppression of nucleation by NO _x	109
6.2	SAPHIR experiments	112
6.2.1	Determination of particle loss rates in SAPHIR	112
6.2.2	Evaluation of mixed experiments using benzene-d6 as a model substance . . .	117
6.2.3	SOA mass yield of benzene-d6 in pure and mixed experiments without addition of NO _x	121
6.2.4	Influence of NO _x on SOA mass yields of benzene-d6	123
6.2.5	SOA mass yield of monoterpenes in pure and mixed experiments	126

6.2.6	SOA mass yield curves as function of particle mass and particle surface	128
7	Discussion	133
7.1	Overall uncertainties in quantification of organics using the AMS	133
7.2	JPAC experiments	135
7.2.1	The influence of nucleation on SOA mass yields	135
7.2.2	Missing dependence of SOA mass yields from benzene on OH levels	137
7.2.3	Missing dependence of SOA mass yields from benzene on NO _x levels	141
7.2.4	The influence of SVOCs on SOA mass production	143
7.2.5	SOA yields of benzene-d6 and benzene	144
7.3	SAPHIR experiments	149
7.3.1	The influence of possible vapour wall losses on the determined SOA yield . . .	149
7.3.2	Missing NO _x dependence of SOA mass yields	151
7.3.3	Anthropogenic enhancement	155
7.4	Overall SOA yield of benzene	157
7.5	Aerosol surface vs. aerosol mass	163
7.6	Outlook and suggestions for future experiments	164
8	Conclusions	167
	List of abbreviations	175
	List of figures	179
	List of tables	183
	Literature	185
	Appendix A: Additional information	207
A.1	List of CPCs used	208
A.2	Instrumentation at JPAC and SAPHIR	209
A.3	Determination of humidity dependent sensitivity for PTR-ToF-MS	211
A.4	NO _x calibration at JPAC	213
A.5	Data analysis tools developed for Igor Pro	214
A.6	Overview on JPAC experiments	215
A.7	Overview on SAPHIR experiments	221
A.8	Overview on AMS calibration results	222
A.9	HR ions used for AMS analysis of SOA from benzene-d6	223
A.10	HR ions for comparing SOA from benzene and benzene-d6	229
A.11	Adjustments in fragmentation table for H ₂ O	231
A.12	Magnitude of correction applied to unseeded JPAC experiments	234
	Appendix B: additional figures	235
	Acknowledgements	249
	(Eidesstattliche)Versicherungen und Erklärungen	251

Energie & Umwelt / Energy & Environment
Band / Volume 412
ISBN 978-3-95806-305-1