



Atmospheric Chemistry – Aqueous Phase Chemistry

Final report

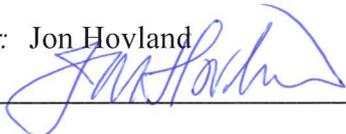
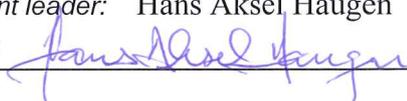
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<i>Abstract</i> <p>Aqueous phase reactivity experiments with the amines DMA, DEA, PYL and their corresponding nitrosamines have been performed. Furthermore, nitrosamine formation has been investigated. Gas- and aqueous phase oxidation schemes of amines, nitrosamines and amides have been built into an atmospheric chemistry box-model using published as well as experimental data from this work. Photolysis parameters for nitrosamines have been obtained from experiments. Solution phase photolysis can be an effective sink for nitrosamines, also in winter. Ozone is unreactive towards amines and nitrosamines and is not considered an important sink pathway. The importance of the turnover processes, NO₃, OH, Cl radical reaction and photolysis as well as the main turnover per compartment (gas- or aqueous phase) for the total turnover varies and has to be considered for each target substance separately differentiating summer and winter cases. No significant aqueous formation of nitrosamines was simulated with the box model.</p>		
We have reviewed this report and find it in accordance with Tel-Tek's quality system		
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About the Atmospheric Chemistry project

Gassnova has awarded Tel-Tek a contract (no. 257430177) for the project “Atmospheric chemistry”. The project has four sub-projects:

- Aqueous phase chemistry
- Nitrosamine photolysis
- Dark chemistry
- Chlorine chemistry

Tel-Tek has entered a consortium agreement with universities and research institutions to carry out the project:

- University of Oslo. Norway
- Leibniz-Institut für Troposphärenforschung. Germany
- Universität Innsbruck. Austria
- IRCELYON. France
- Universidad de Castilla-La Mancha. Spain
- Georgia Tech. USA
- Norwegian University of Life Sciences. Norway

Quality Assurance

The data and results in this report has been quality controlled and verified according to generally accepted principles for publication in internationally recognised scientific journals. This statement also includes the reports within the project that is used as a basis for the conclusions and recommendations in this report.

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CONTENTS

1	Aqueous Phase experiments.....	5
1.1	Scope of work	5
1.2	HSE	5
1.3	Aqueous nitrosamine photolysis	5
1.4	Aqueous phase reactivity of amines and nitrosamines	8
1.4.1	Amine and nitrosamine reactions with NO ₃ radical	8
1.4.1.1	Amine + NO ₃	8
1.4.1.2	Nitrosamine + NO ₃	9
1.4.2	Amine and nitrosamine reactions with ozone.....	11
1.4.2.1	Amine + O ₃	11
1.4.2.2	Nitrosamine + O ₃	12
1.5	Nitrosamine formation in the aqueous phase	13
1.5.1	Question of mechanism and reaction order	13
1.5.2	Experimental approaches.....	13
1.5.2.1	Direct UV-spectroscopic method	13
1.5.2.2	Differential UV-spectroscopic method.....	14
1.5.3	Nitrosamine formation experiments with amine and nitrite	14
1.5.3.1	Results from direct UV-spectroscopic method.....	14
1.5.3.2	Results from differential UV-spectroscopic method.....	16
1.5.4	Remarks and conclusion to nitrosamine formation experiments.....	16
1.5.5	Remarks to the question of nitrosating agents.....	17
2	Modelling of the multiphase chemical processing of amines	18
2.1	Scope of work	18
2.2	Development of a multiphase chemistry mechanism for amines.....	18
2.3	SPACCIM model description and performed model simulations.....	19
2.4	SPACCIM model results and discussion	20
3	Evaluation of the overall status of amine atmospheric chemistry.....	25
4	Remaining questions of atmospheric Multiphase amine chemistry.....	26
5	List of abbreviations.....	29
6	References	30

1 AQUEOUS PHASE EXPERIMENTS

1.1 Scope of work

The intention of this experimental laboratory work was to investigate nitrosamine photolysis, the reactions of amines and nitrosamines with ozone and NO_3 radical and nitrosamine formation in aqueous solution. The aim was to close gaps in the knowledge concerning aforementioned reactions and to provide reliable data for atmospheric chemical box modelling of clouds and wet particles.

1.2 HSE

The experiments involved handling of carcinogenic compounds (nitrosamines) and mixtures of their precursors. All experiments have been conducted in a dedicated laboratory using standard safety precautions for the handling of toxic substances (fume-hood, gloves, lab-coat, protective eye-wear). The laboratory was equipped with extra fumehoods over all sensitive experimental set-up areas. A safe-job analysis has been documented within the project. Toxic liquid waste has been disposed according to official regulations at a waste collecting site.

No accidents occurred during the duration of the project.

1.3 Aqueous nitrosamine photolysis

Photolysis of the selected nitrosamines nitrosodimethylamine (NDMA), nitrosodiethanolamine (NDEA) and nitrosopyrrolidine (NPYL) has been investigated in synthetic aqueous solutions at wavelengths 313 and 366 nm and pH values 1, 3 and 4.5. The experiments were carried out with a 1 cm sealed quartz cuvette containing $1 \cdot 10^{-4}$ M of the nitrosamine placed in front of the output of a prism-monochromator to select light of the desired wavelength from a 200 W Hg(Xe)-lamp. The decay of the nitrosamines was analysed by the disappearance of their characteristic absorption peak in the near UV using UV-spectroscopy. The outputs from the experiments used for box-modelling were the measured quantum yields and molar extinction coefficients (Figure 1 - Figure 3, Table 1). Further details on experimental techniques and calculation of the quantum yields as well as full experimental data can be found in the detailed final data report on aqueous phase experiments (Tel-Tek report 2211030-AQ06, eRoom FM07-APZ00-P-RA-0024). The measured quantum yields are similar to those previously reported in the literature¹ (Table 1).

Table 1 Summary of measured quantum yields of NDMA, NDEA and NPYL at photolysis wavelengths 313 and 366 nm and pH = 1; 3; 4.5 in aqueous solution

Compound	$\Phi_{313 \text{ nm}}$	$\Phi_{366 \text{ nm}}$	$\Phi_{290-800 \text{ nm}}$
NDMA			
pH = 6 (Plumlee and Reinhard 2007)			0.41 ± 0.02
pH = 1 (this work)	0.39 ± 0.03	0.39 ± 0.02	
pH = 3 (this work)	0.41 ± 0.06	0.39 ± 0.05	
pH = 4.5 (this work)	0.35 ± 0.05	0.41 ± 0.06	
NDEA			
pH = 6 (Plumlee and Reinhard 2007)			0.43 ± 0.04
pH = 1 (this work)	0.37 ± 0.06	0.38 ± 0.05	
pH = 3 (this work)	0.33 ± 0.04	0.38 ± 0.06	
pH = 4.5 (this work)	0.32 ± 0.05	0.36 ± 0.05	
NPYL			
pH = 6 (Plumlee and Reinhard 2007)			0.55 ± 0.06
pH = 1 (this work)	0.40 ± 0.06	0.43 ± 0.06	
pH = 3 (this work)	0.41 ± 0.06	0.39 ± 0.09	
pH = 4.5 (this work)	0.42 ± 0.06	0.41 ± 0.03	

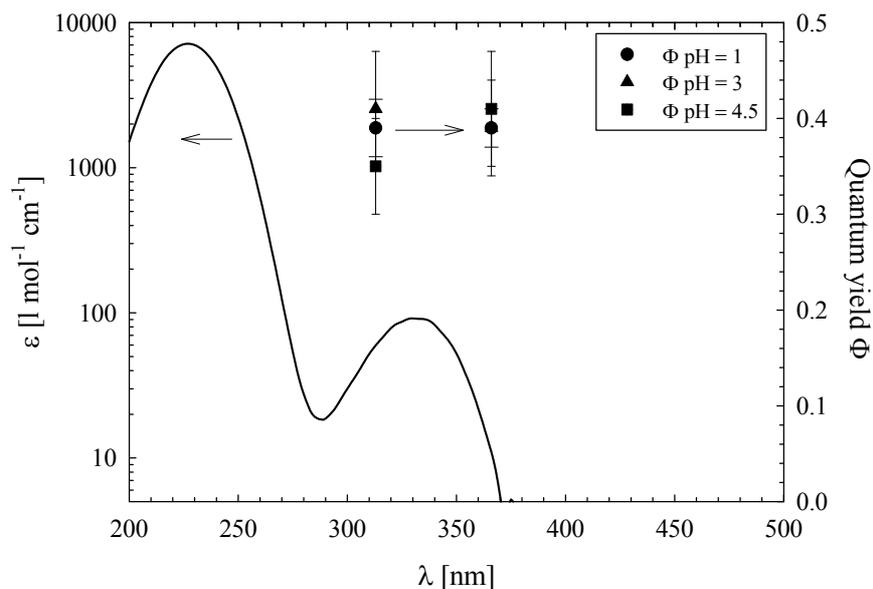


Figure 1 Molar extinction spectrum, measured quantum yields of NDMA at pH 1, 3 and 4.5 and wavelengths 313 and 366 nm

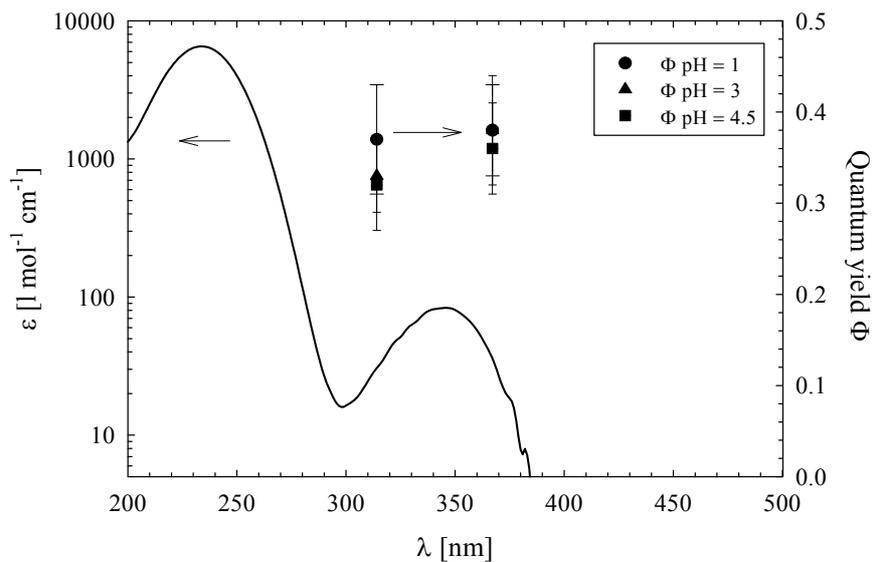


Figure 2 Molar extinction spectrum, measured quantum yields of NDEA at pH 1, 3 and 4.5 and wavelengths 313 and 366 nm

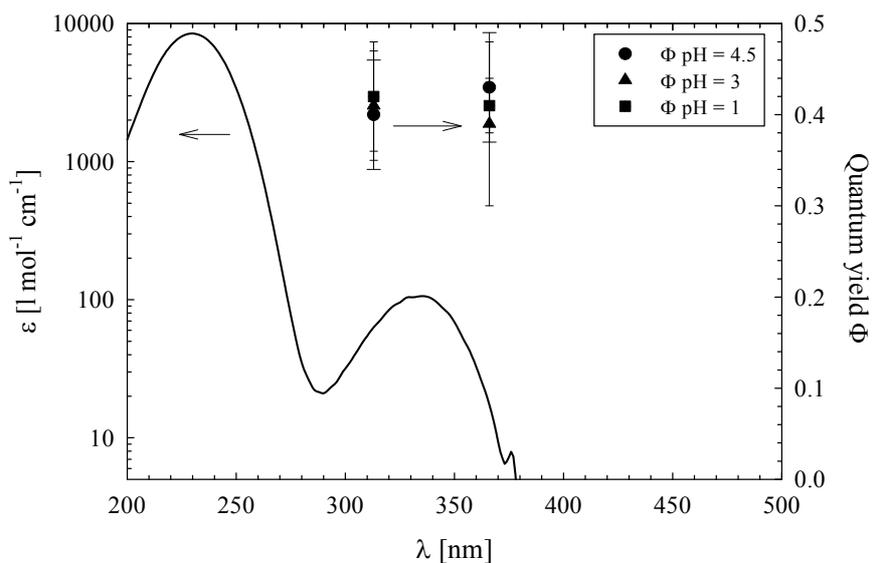


Figure 3 Molar extinction spectrum, measured quantum yields of NPYL at pH 1, 3 and 4.5 and wavelengths 313 and 366 nm

Conclusion

The measured quantum yields of NDMA, NDEA and NPYL have similar values between 0.32 and 0.43. There is no significant difference of quantum yields comparing both photolysis wavelengths 313 and 366 nm. Neither has the pH a significant influence on the quantum yield in the acidic range studied here which is characteristic for atmospheric waters, therefore there is no need to consider a pH dependence of aqueous nitrosamine photolysis in box- or dispersion modelling. Measured quantum yields and absorption spectra have been used to calculate photolysis rate constants for different irradiation scenarios which have been implemented in the box-model.

Recommendation

Measured quantum yields can be used for dispersion modelling.

1.4 Aqueous phase reactivity of amines and nitrosamines

1.4.1 Amine and nitrosamine reactions with NO₃ radical

Reactions of amines and nitrosamines with NO₃ radical have been measured using a laser flash photolysis long path absorption setup (see also final data report). Pseudo first order rate constants (k_{1st}) have been measured at a series of different reactant concentrations in excess over NO₃ radical to obtain the second order rate constants (k_{2nd}) from a plot of k_{1st} vs. reactant concentration. The pH of the solutions was kept at pH = 4 for nitrosamines and amines.

1.4.1.1 Amine + NO₃

All investigated amines namely dimethylamine (DMA), diethanolamine (DEA) and pyrrolidine (PYL) were fully protonated at the applied pH = 4. Therefore, the reaction mechanism taking place is an H-atom abstraction at the side chain. An H-abstraction at the protonated amino group is not possible at acidic pH values, which will be also found in the atmosphere. Temperature dependent measurements of the selected amines led to ambiguous results even after repetition of several experiments (see final experimental data report for further details). Therefore only the rate constants at 298 K are reported in this study and have been used for box-modelling. The reactions of NO₃ radical with amines are relatively slow with k_{2nd} of $\sim 10^5 \text{ M}^{-1}\text{s}^{-1}$ (Table 2) when compared with other NO₃ radical reactions with, e.g., nitrosamines (see next section), which are three orders of magnitude faster.

Table 2 Second order rate constants (k_{2nd}) for the reactions of DMA, DEA and PYL with NO₃ radical

Compound	DMA	DEA	PYL
k_{2nd} (298 K) [$\text{M}^{-1}\text{s}^{-1}$]	$(3.7 \pm 0.8) 10^5$	$(8.2 \pm 6.8) 10^5$	$(8.7 \pm 6.5) 10^5$

Conclusion

The rate constants of $\text{NO}_3 + \text{DMA}$, DEA and PYL have been determined for the first time and have been implemented in the box-model. The reactions are slow for the NO_3 radical in aqueous solution. Nitrosamine or nitramine-production is excluded when protonated amines react with NO_3 , which is the case due to their high pK_a values relative to the below neutral pH values in the atmospheric aqueous phase.

Recommendation

Measured rate constants can be used for dispersion modelling.

1.4.1.2 Nitrosamine + NO_3

The investigated nitrosamines react through an H-atom abstraction at the side chain. Measured rate constants at 298 K are on the order of $\sim 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Table 3). Furthermore, the temperature dependence of the rate constants has been determined (Figure 4 - Figure 6) from which the activation energy has been calculated (Table 3). Temperature has only a small effect on the rate constants.

Table 3 Second order rate constants (k_{2nd}) for the reactions of DMA, DEA and PYL with NO_3 radical

Compound	NDMA	NDEA	NPYL
k_{2nd} (298 K) [$\text{M}^{-1}\text{s}^{-1}$]	$(1.2 \pm 0.2) 10^8$	$(2.3 \pm 0.6) 10^8$	$(2.4 \pm 0.3) 10^8$
E_A [kJ mol^{-1}]	13.3 ± 5.7	8.5 ± 6.8	7.3 ± 5.3

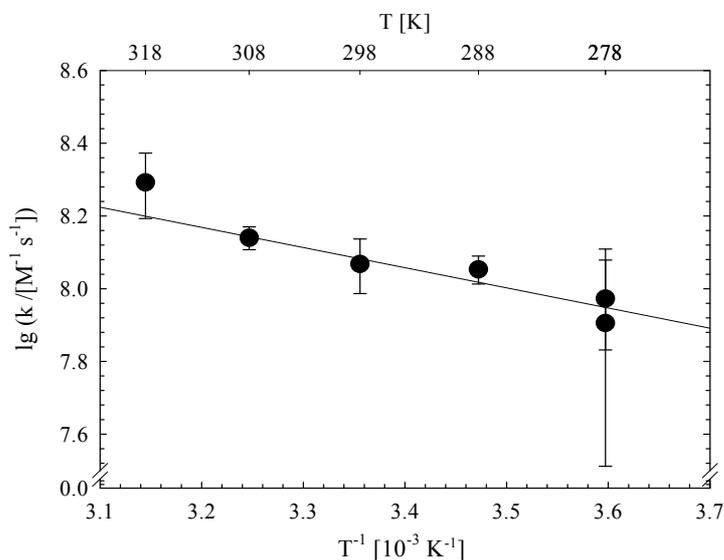


Figure 4 Plot of temperature dependent rate constants of NDMA with NO_3 radical (Arrhenius plot)

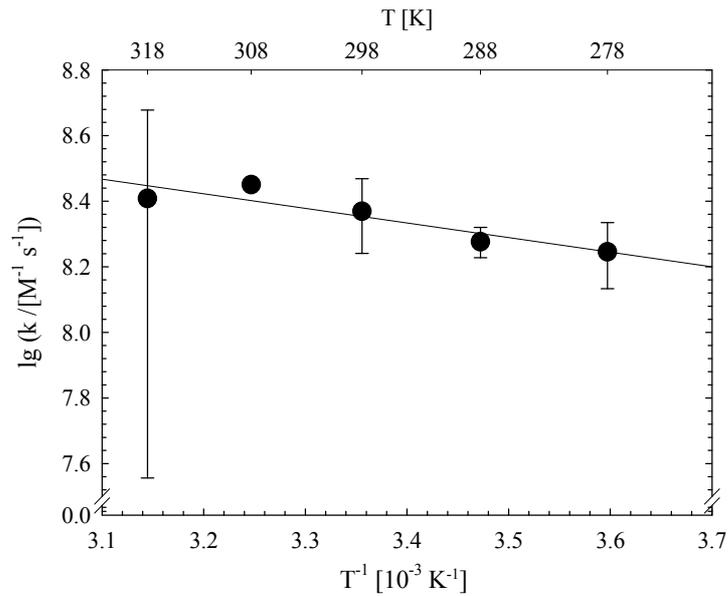


Figure 5 Plot of temperature dependent rate constants of NDEA with NO_3 radical (Arrhenius plot)

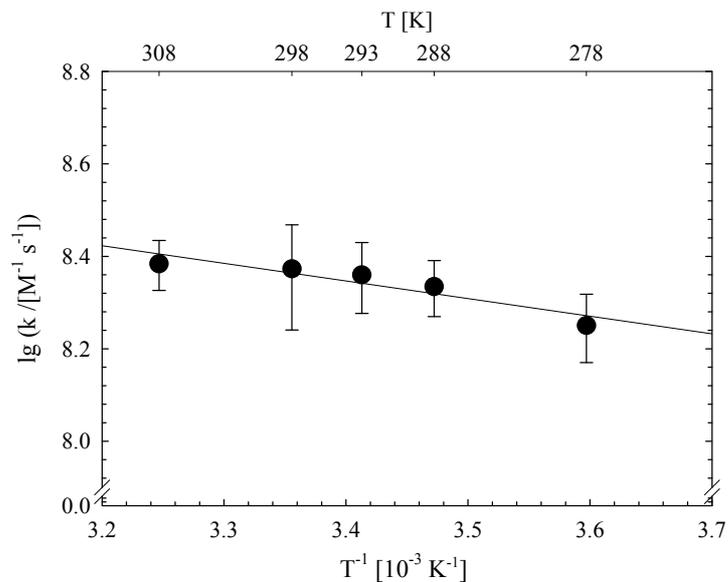


Figure 6 Plot of temperature dependent rate constants of NPYL reactions with NO_3 radical (Arrhenius plot)

Conclusion

The temperature dependent rate constants of $NO_3 + NDMA$, NDEA and NPYL have been determined for the first time and have been implemented in the box-model. The reactions are considerably faster than the corresponding NO_3 -amine reactions.

Recommendation

Measured rate constants can be used for dispersion modelling.

1.4.2 Amine and nitrosamine reactions with ozone

In aqueous solution, ozone undergoes a series of decomposition reactions initiated by hydroxide ion, OH⁻. This can be counteracted by using a low pH for the experiments, but the decomposition reactions are only suppressed, not completely shut down. Therefore, phosphate buffer has been used to adjust pH = 2 in the experimental solutions for both amine and nitrosamine reactions. Kinetic experiments always involved measurements of a blank solution with ozone besides the actual measurement of O₃ + reactant.

1.4.2.1 Amine + O₃

Ozone reactions with amines have been measured by a UV-differential absorption technique (double beam spectrometer) to account for the side reactions with a reference containing only O₃ and buffer and a probe containing O₃, buffer and the desired reactant. The time dependent decay of O₃ has been monitored directly via its local absorption maximum at 260 nm. Experimental details can be found in final data report.

The reactions of O₃ with the amines DMA, DEA and PYL have been investigated at pH = 2. At this pH = 2 and also in the atmospheric aqueous phase these amines are fully protonated and thus there is no location at the amine, where O₃ could possibly attack and react. Therefore, it is presumed that O₃ is unreactive towards amines. In the presence of DMA and PYL, O₃ did not decay faster as the reactant concentration was stepwise increased up to a thousand-fold excess. That means at least no measureable reaction with O₃ has been taking place. From the time dependent first order decay of O₃ in the absence of any reactant an upper limit for the second order rate constant k_{2nd} of amine + O₃ can be calculated as $k_{2nd} = k_{1st} / [\text{amine}]_{max}$. The concentration of ozone was $[O_3] = 1 \cdot 10^{-5}$ M and the maximum amine concentration was $[\text{amine}]_{max} = 0.01$ M whereas the decay of O₃ was $6 \cdot 10^{-5} \text{ s}^{-1}$. Consequently, the upper limit for a rate constant of O₃ + DMA or PYL was calculated to be $3 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. This is a very low value which leads to the conclusion, that these reactions are not important in the atmosphere. In case of DEA, one measured O₃ differential absorption time profile at $[DEA] = 5 \cdot 10^{-4}$ M showed faster O₃ decay compared to the reference which might suggest a reaction of O₃ with DEA. However, other O₃ differential absorption time profiles under systematic variation of $[DEA]$ showed no clear trend of increasing O₃ decay with increasing DEA concentration which suggests that O₃ is also not reactive towards DEA. From the O₃ differential absorption time profile at $[DEA] = 5 \cdot 10^{-4}$ M, a maximum value of k_{2nd} for DEA + O₃ is calculated as $0.6 \text{ M}^{-1} \text{ s}^{-1}$. This value is still low enough to conclude that this reaction is not important in the atmospheric aqueous phase.

Conclusion

The experiments confirmed the presumption that O₃ is unreactive towards protonated amines. An upper limit for the second order rate constant for the reaction DMA or PYL + O₃ is given as $3 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. The corresponding upper limit for DEA + O₃ is $0.6 \text{ M}^{-1} \text{ s}^{-1}$. The calculated upper limits for O₃ + amine rate constants suggest that these reactions are not important in the atmospheric aqueous phase. Therefore these reactions have not been considered in box-modelling.

Recommendation

No need to implement O₃ + amines for dispersion models.

1.4.2.2 Nitrosamine + O₃

In the case of nitrosamine + O₃ reactions the O₃ decay could not be monitored via direct UV-absorption of O₃ because of an overlapping absorption from the present nitrosamines. Therefore, the ozone scavenger indigotrisulfonate (shortly referred to as indigo) which reacts instantly and quantitatively with ozone has been used. Indigo has an intense absorption at 600 nm which is free of interfering absorptions under the applied conditions. The change in indigo absorption was used to determine the ozone concentration simultaneously in a reference sample to account for O₃ side reactions and in a probe containing also the nitrosamine reactant.

The decay of O₃ in the presence of NDMA, NDEA and NPYL was measured under variation of nitrosamine concentration in excess over O₃. In the case of NDMA and NPYL no significant increasing effect of the presence of nitrosamine on the O₃ decay was observed. This finding suggests that no reaction between O₃ and NDMA or NPYL takes place or is too slow to be detected. Similar to the case of DMA and PYL, an upper limit for the rate constant of a potential reaction of NDMA or NPYL with O₃ has been calculated from the maximum nitrosamine concentration used and the observed reference O₃ decay. The determined upper limits are 0.2 and 0.4 M⁻¹s⁻¹ for NDMA and NPYL, respectively. Hoigné and Bader (1983)² reported a value of $k_{2nd} \approx 10 \text{ M}^{-1}\text{s}^{-1}$ and Lee *et al.* (2007)³ found a rate constant for NDMA + ozone in aqueous solution, $k_{2nd} = 0.052 \pm 0.0016 \text{ M}^{-1}\text{s}^{-1}$. From the fastest measured O₃ decay in the presence of NDEA, an upper limit for a potential O₃ + NDEA reaction rate constant has been determined to be 27 M⁻¹s⁻¹. This could imply that a reaction of NDEA and ozone actually takes place, but the experimental data for O₃ + NDEA did not show a systematic increase of O₃ decay with increasing NDEA concentration. NDEA as purchased contained 0.2% isopropanol. It can be excluded that isopropanol is responsible for the O₃ decay. However, the purity of NDEA was not stated so that there remains the possibility, the observed decay was caused by an impurity. There is no information published what could be possible products of an O₃ + nitrosamine reaction. Therefore and knowing that the upper limits of the rate constants are low, it was concluded that aqueous O₃ + nitrosamine reactions do not play an important role for atmospheric nitrosamine removal and were not implemented in the box model. Another study concludes as well that nitrosamines are not degraded by ozone on the basis of gas chromatography analysis for the nitrosamine and possible products - after ozonisation, the nitrosamine was fully recovered and no other products were found⁴.

Conclusion

The experiments confirmed that O₃ reactions with nitrosamines are slow or do not take place. An upper limit for the second order rate constant for the reaction NDMA + O₃ is 0.2 M⁻¹s⁻¹ and NPYL + O₃ is 0.4 M⁻¹s⁻¹. The corresponding upper limit for NDEA + O₃ is 27 M⁻¹s⁻¹. The calculated upper limits for O₃ + nitrosamine rate constants suggest that these reactions are too slow to play a role in the atmospheric aqueous phase. Therefore these reactions have not been considered in box-modelling.

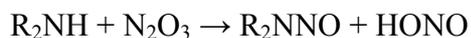
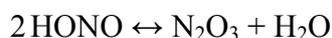
Recommendation

No need to implement O₃ + nitrosamines for dispersion models.

1.5 Nitrosamine formation in the aqueous phase

1.5.1 Question of mechanism and reaction order

Mirvish (1975)⁵ (and references therein) postulated that N_2O_3 is the active nitrosating agent and that the reaction is third order:



with the overall rate expression:

$$d[\text{R}_2\text{NH}]/dt = k_{3rd} [\text{R}_2\text{NH}][\text{HONO}]^2$$

On the contrary, Friedmann (1972)⁶ concluded that the reaction is second order with the overall reaction:



$$d[\text{R}_2\text{NH}]/dt = k_{2nd} [\text{R}_2\text{NH}][\text{HONO}]$$

A fact that opposes the action of N_2O_3 as nitrosation carrier is that the dinitrogen species will predominately act as the anhydride of the nitrogen oxy acid HONO and will tend to form this acid fast when in contact with a large excess of water. With the experiments conducted, it was intended to clarify the question of reaction order with respect to nitrite and measure rate constants to implement in the box-model.

1.5.2 Experimental approaches

DMA, DEA and PYL were each mixed with sodium nitrite (NaNO_2) at different pH values to observe the formation of the corresponding nitrosamines NDMA, NDEA and NPYL as a function of time. The possible effect of formaldehyde (HCHO) on the nitrosation at acidic pH values was also investigated. Two different UV-Vis spectroscopic methods were applied to obtain the kinetic data: a direct method and a differential method. Experiments were done at pH = 1 and 3 which determines the ratio of NO_2^- towards HONO (nitrous acid). At pH = 1, 99% of added nitrite is in the form of HONO, 1% is NO_2^- and at pH = 3, 57% of added nitrite is present as HONO and 43% as NO_2^- .

1.5.2.1 Direct UV-spectroscopic method

Both HONO and NO_2^- have a strong absorption in the UV which is overlapping with those of the nitrosamines. Consequently, a formation of nitrosamines was obscured by the decay of present HONO and NO_2^- when looking at the spectra directly. However, HONO has a marked absorption peak at 388 nm where an overlap with nitrosamines is not disturbing. Therefore, the absorbance at 388 nm could be used at any time step of the reaction to calculate the concentration of HONO and NO_2^- , since both are in equilibrium determined by the pH. The total absorbance could thus be corrected via a subtraction of the contribution from HONO and NO_2^- . After the correction, the sum of absorbance caused by the parent amine and that of the formed nitrosamine is left over. The parent amine absorption is much weaker and shifted to shorter wavelengths compared to that of nitrosamines, so that there is a wavelength range, where nitrosamine absorbance is theoretically freed of interference and its increase over time

could be evaluated for nitrosamine formation. This gives the advantage to have simultaneous kinetic information about product formation (nitrosamine) and educt decay (HONO). However, the concentration calculation of [HONO] and [NO₂⁻] via the 388 nm absorbance had an error of ±10% of the true HONO and NO₂⁻ concentration (in rare cases up to ±20%). This introduced an error into the determination of product formation and educt decay and subsequently the determination of the rate constants via this method. Series of experiments under variation of the nitrite concentration with amine in excess over nitrite and under variation of amine in excess over constant nitrite were conducted in this way, accepting the unavoidable source of error.

1.5.2.2 Differential UV-spectroscopic method

To overcome the problem that one cannot accurately correct for HONO/NO₂⁻ absorption which obscures the evolution of increasing absorption due to nitrosamine formation, a differential UV-spectroscopic technique was applied. Furthermore, a variation of the nitrite concentration in excess over the amine was needed to clarify the reaction order with respect to nitrite. A reference containing only added nitrite at fixed pH was put into the reference beam of the spectrometer while another probe containing the same amount of nitrite at the same pH plus amine was inserted into the sample beam. The monitoring wavelength was set to 330 nm, a point at which HONO and NO₂⁻ have the same molar extinction and are therefore more easily analysed. At low pH, HONO undergoes slow self-decomposition via:



in both the reference and the sample solution. Employing a nitrite solution as a reference accounts for the HONO self-decomposition and the disturbing absorption of HONO and NO₂⁻ so that an increase of absorption at 330 nm should belong to the formation of nitrosamine⁷. A series of experiments under variation of the nitrite concentration in excess over amine was conducted in this way.

1.5.3 Nitrosamine formation experiments with amine and nitrite

1.5.3.1 Results from direct UV-spectroscopic method

Rates of nitrosamine formation have been measured with the direct UV-spectroscopic method under variation of the amine or the nitrite concentration. Nitrite could not be varied in excess over the amine with the present method because this would have made the solution intransparent for product detection due to the large extinction coefficients of HONO and NO₂⁻. Consequently, pseudo first conditions are not applicable and only the slope of the measured rate vs. concentration is given. In the case of amine variation pseudo first conditions are met and the slope of the measured rate vs. concentration corresponds to $k_{2\text{nd}}$. The measured rates from product formation and HONO decay are shown in Table 4.

Table 4 Rates of nitrosamine formation and corresponding rates of HONO decay measured by the direct UV-spectroscopic method involving correction for residual HONO/ NO₂⁻

[Amin]	[NO ₂]	pH = 1		pH = 3	
		slope of $\frac{d[R_2NNO]}{dt}$ vs. C	slope of $-\frac{d[HONO]}{dt}$ vs. C	slope of $\frac{d[R_2NNO]}{dt}$ vs. C	slope of $-\frac{d[HONO]}{dt}$ vs. C
DMA					
const. 0.01M	var. 5·10 ⁻⁴ -1·10 ⁻³ M	(6.1 ± 2.9)·10 ⁻²	* (2.4 ± 1.7)·10 ⁻² # (2.4 ± 1.7)·10 ⁻²	-	-
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	(2.3 ± 3.6)·10 ⁻³ M ⁻¹ s ⁻¹	* (2.6 ± 4.0)·10 ⁻³ M ⁻¹ s ⁻¹ # (2.6 ± 4.0)·10 ⁻³ M ⁻¹ s ⁻¹	(4.0 ± 12)·10 ⁻³ M ⁻¹ s ⁻¹	*no increase with C # (1.3 ± 4.4)·10 ⁻³ M ⁻¹ s ⁻¹
DEA					
const. 0.01M	var. 5·10 ⁻⁴ -1·10 ⁻³ M	decrease with C	no increase with C	(1.5 ± 3.6)·10 ⁻²	no increase with C
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	(2.1 ± 2.2)·10 ⁻³ M ⁻¹ s ⁻¹	* (4.6 ± 19)·10 ⁻⁴ M ⁻¹ s ⁻¹ # (4.6 ± 19)·10 ⁻⁴ M ⁻¹ s ⁻¹	(1.8 ± 17)·10 ⁻⁴ M ⁻¹ s ⁻¹	* (1.1 ± 1.9)·10 ⁻³ M ⁻¹ s ⁻¹ # (1.1 ± 1.9)·10 ⁻³ M ⁻¹ s ⁻¹
PYL					
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	decrease with C	no increase with C	no increase with C	no increase with C

* corrected for HONO self-decomposition; # from uncorrected HONO decay

The rate of reaction showed no quadratic dependence on the nitrite concentration, which is an argument against a third order reaction. Measured k_{2nd} under variation of amine concentration were in the range of 10⁻⁴-10⁻³ M⁻¹s⁻¹, with an upper limit of 10⁻² M⁻¹s⁻¹. Because not in all cases the measured rate increased with increasing concentration of the varied reactant as normally expected which is attributed to the shortcomings of the applied method, k_{2nd} have been additionally calculated as $k_{2nd} = k_{1st} / \text{concentration}$ (Table 5). Rate constants obtained in this way range from 1 to 8·10⁻² M⁻¹s⁻¹, which leads to the conclusion that nitrosamine formation is a very slow process.

Table 5 Rate constants for nitrosamine formation and corresponding HONO decay measured by the direct UV-spectroscopic method involving correction for residual HONO/ NO₂⁻, k_{2nd} calculated as $k_{2nd} = k_{1st} / C$

[Amin]	[NO ₂]	pH = 1		pH = 3	
		$k_{2nd} = k_{1st} / C$ from product formation [M ⁻¹ s ⁻¹]	$k_{2nd} = k_{1st} / C$ from HONO decay [M ⁻¹ s ⁻¹]	$k_{2nd} = k_{1st} / C$ from product formation [M ⁻¹ s ⁻¹]	$k_{2nd} = k_{1st} / C$ from HONO decay [M ⁻¹ s ⁻¹]
DMA					
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	(7.7 ± 0.7)·10 ⁻²	* (2.6 ± 0.8)·10 ⁻²	(6.7 ± 1.9)·10 ⁻²	* (1.2 ± 0.7)·10 ⁻²
DEA					
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	(5.7 ± 0.5)·10 ⁻²	* (1.9 ± 0.3)·10 ⁻²	(7.0 ± 0.2)·10 ⁻²	* (1.8 ± 0.4)·10 ⁻²
PYL					
var. 8·10 ⁻³ -1.2·10 ⁻² M	const. 8·10 ⁻⁴ M	(6.3 ± 0.6)·10 ⁻²	* (4.1 ± 0.6)·10 ⁻²	(6.1 ± 4.2)·10 ⁻²	* (1.9 ± 0.4)·10 ⁻²

* corrected for HONO self-decomposition

Nitrosamine formation and HONO decay were not significantly faster in the presence of a large amount of HCHO (0.001 M) at pH = 3 for [DMA/ DEA /PYL] = 0.01 M and [NO₂⁻] =

0.001 M. Therefore, formaldehyde is considered not important for nitrosamine formation in acidic aqueous solution.

1.5.3.2 Results from differential UV-spectroscopic method

Rates of nitrosamine formation were measured under pseudo first order condition with respect to nitrite at pH = 1 and 3. The amine concentration was kept constant at 0.005 M and nitrite was varied between 0.05 and 0.09 M. The absorption measurements were adversely influenced by the formation of bubbles in the cuvettes. The tendency to form bubbles was higher in solutions with higher nitrite concentration and higher at lower pH. This points to the outgassing of HONO which is poorly soluble and to the outgassing of NO formed during self-decomposition of HONO. Most likely due to bubble disturbance, not all recorded differential absorbance-time profiles could be adequately interpreted. Moreover, not in all cases the measured pseudo first order rate constants showed a clear increase with increasing nitrite concentration. Therefore, k_{2nd} were calculated as $k_{2nd} = k_{1st} / \text{concentration}$ and are reported in Table 6. However, the observed range of k_{1st} within the varied concentration range suggests a linear dependence on nitrite concentration, rather than a linear dependence on the nitrite concentration squared. Therefore, a second order reaction is more likely.

Table 6 Rate constants for nitrosamine formation and corresponding HONO decay measured by the direct UV-spectroscopic method involving correction for residual HONO/ NO_2^- , k_{2nd} calculated as $k_{2nd} = k_{1st} / C$

[Amin]	[NO_2^-]	pH = 1 $k_{2nd} = k_{1st} / C$ from product formation [$\text{M}^{-1}\text{s}^{-1}$]	pH = 3 $k_{2nd} = k_{1st} / C$ from product formation [$\text{M}^{-1}\text{s}^{-1}$]
DMA const. 0.005 M	var. 0.05-0.09 M	$3.0 \cdot 10^{-3}$	$(7.3 \pm 3.0) \cdot 10^{-3}$
DEA const. 0.005 M	var. 0.05-0.09 M	$(1.4 \pm 1.5) \cdot 10^{-2}$	$(1.1 \pm 1.0) \cdot 10^{-1}$
PYL const. 0.005 M	var. 0.05-0.09 M	$(8.8 \pm 27) \cdot 10^{-2}$	$(8.3 \pm 6.7) \cdot 10^{-3}$

1.5.4 Remarks and conclusion to nitrosamine formation experiments

From the pure physico-chemical and experimental point of view, more time would be needed to generate a more comprehensive dataset for nitrosamine formation. The applied direct time-resolved measurement of the decay of reactants (HONO / nitrite) or formation of the nitrosamines by means of UV-spectroscopy has its limitations because of the overlap of the absorption spectra leading restricting the possibility to vary concentrations in excess kinetics. Other methods should be tested like destroying disturbing excess nitrite with urea⁶ as a stopping agent. Then, in addition, to study a wide regime of concentrations, it appears necessary to employ analytical offline methods such as HPLC and HPLC-MS for either or both educt and product analysis. Then, comprehensive method development and optimization experiments would be needed to follow the turnover of amines into nitrosamines in a batch reactor from which, at defined times, samples are taken, stopping reagent is added and then analytical analysis is performed. Due to the very strict timing of the present project such approach was beyond the scope in this study as already pointed out in the Tender 257430176.

However, we are confident that a reliable data set has been derived from an exhaustive effort to characterize nitrosamine formation by time-resolved spectrometric measurement allowing judging the effectiveness of these processes in atmospheric multiphase chemistry,

Conclusion

The experimental data suggest a second order reaction between $\text{NO}_2^-/\text{HONO}$ and amines. Implementation of N_2O_3 (third order reaction) is not recommended. Measured nitrosation rate constants range from 10^{-3} to $10^{-1} \text{ M}^{-1}\text{s}^{-1}$ with mean values in the order of $10^{-2} \text{ M}^{-1}\text{s}^{-1}$. Therefore, an upper limit of $0.1 \text{ M}^{-1}\text{s}^{-1}$ has been implemented in the box-model as nitrosation rate constant for aqueous phase nitrosation of all investigated amines. This approach is very likely the most realistic “worst case scenario”. This rate constant is small and consequently no significant aqueous phase nitrosation is expected.

Recommendation

At present, an upper limit of $k_{2\text{nd}} = 0.1 \text{ M}^{-1}\text{s}^{-1}$ was applied for the aqueous phase nitrosation reactions. As outlined before, refined measurements could be performed to even better characterize the kinetics of the nitrosation reactions but this would correspond to bigger effort for future work, cf. also the following remark. It is not necessary to take aqueous nitramine formation into account because of the very likely scavenging of the short-lived nitrating agents before a nitration of an amine can occur.

1.5.5 Remarks to the question of nitrosating agents

During our regular project meetings the option was discussed that it might be possible to implement single pathways of nitrosation into the box-model, each with individual rate constants, to observe which the most effective nitrosating agents are. As potential nitrosating agents were discussed: HONO, N_2O_3 , N_2O_4 , NO^+ and H_2ONO^+ . After thorough literature and kinetic constants database search it was realized, that the only explicit rate constants are given for the reaction $2 \text{HONO} \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} + \text{amine} \rightarrow \text{nitrosamine}$, a mechanism that is controversial in our opinion. At the present level of knowledge, it is therefore not possible to distinguish between all different proposed nitrosating agents and one has to use the overall expression $\text{NO}_2^-/\text{HONO} + \text{amine} \rightarrow \text{nitrosamine}$, for which overall rate constants are available. After running our model with a conservative assumption for $k_{2\text{nd}} \text{HONO/nitrite} + \text{amine} = 0.1 \text{ M}^{-1}\text{s}^{-1}$ as the upper limit from our measurements, we conclude that this approach satisfies the purpose of environmental risk assessment because no significant nitrosamine formation in the atmospheric aqueous phase has been simulated with the box-model. For the purpose of risk assessment, we regard it as of secondary importance what the exact nitrosating agents are. To be able to distinguish between different nitrosation pathways, additional and intensive fundamental research would be required.

2 MODELLING OF THE MULTIPHASE CHEMICAL PROCESSING OF AMINES

2.1 Scope of work

In order to investigate the chemical fate of amines (used in CO₂ capturing processes) and their oxidation products in the tropospheric multiphase, the development of a complex multiphase chemical mechanism and subsequent simulations with the complex Lagrangian parcel model SPACCIM (SPectral Aerosol Cloud Chemistry Interaction Model⁸) are proposed within this project. The chemical mechanism is aimed to reflect the chemistry of different amines and their main oxidation products in both the gas and aqueous phase including phase transfer description. The model application is further aimed to characterise the tropospheric fate of amines during the air mass transport away from the emission region of Mongstad. The modelling is proposed to simulate the chemical fate of amines by using typical environmental model scenarios for different characteristic trajectories, which have been prepared in a former subproject. Overall, diverse model runs with different initial amine concentrations in different seasons are intended with the complex Lagrangian parcel model SPACCIM.

Target: A more precise knowledge of the chemical fate of amines and their oxidation products in the tropospheric multiphase system including the potential to form environmental harmful compounds such as nitrosamines and amides. Finally, the parcel model results should provide the basis for planned regional scale dispersion modelling in the future.

2.2 Development of a multiphase chemistry mechanism for amines

In order to model the chemical processing of amines and their oxidation products in the tropospheric multiphase system, a detailed reaction mechanism was a key precondition. Hence, a chemical mechanism describing the gas and aqueous chemistry of selected amines was developed. The mechanism was aimed to consider (i) the primary amines, methylamine and ethanolamine, (ii) the secondary amines, dimethylamine and diethanolamine, the tertiary amine methyl diethanolamine and (iii) the cyclic secondary amine, pyrrolidine, and their main oxidation products. For the mechanism development, the following main tasks have been performed:

- Implementation of the gas phase chemistry based on available kinetic data and suitable estimations
- Implementation of the aqueous phase chemistry based on available kinetic data and suitable estimation methods
- Implementation of a phase transfer description for the selected amines and their oxidation products based on obtainable data and suitable estimation methods
- Implementation of the acid-base equilibria of amines and their oxidation products based on available kinetic data and suitable estimation methods
- Coupling of the amine module to the existing multiphase chemistry mechanism and introduction of the newly developed mechanism into the SPACCIM model framework
- Implementation of the developed environmental scenarios into the model framework

The reaction mechanism in the gas phase is based on Nielson et al.^{9, 10}, which covers the oxidation of methylamine (MA) and dimethyl amine (DMA), and Braten et al.¹¹ describing the oxidation of monoethanolamine (MEA) and methyl diethanolamine (MDEA). The implementation for diethanolamine (DEA) is very similar to MEA and MDEA. In the reaction

mechanism, currently just the initial step with the OH radical implemented and gaseous degradations of MEA, DEA and MDEA are up to now just implemented to the first stable compound. In contrast to the other amines, gaseous reactions for pyrrolidine (PYL) are not considered in the amine mechanism module. In case of missing measured reaction rate constants, kinetic data of similar organic compounds without the amino group was used based on the Master Chemical Mechanism¹².

Phase transfer is described in SPACCIM using the resistance model of Schwartz¹³, which needs the mass accommodation coefficients, gas phase diffusion coefficients and Henry's Law constants as input parameters. For the mechanism construction, a brief literature search on existing measured Henry's Law constants has been made and available data have been implemented in the mechanism. However, measured Henry's Law constants are not obtainable for most of the oxidised organics containing an amino-group and had to be estimated with the software EPI suite version 4.1. Gas phase diffusion coefficients of amines and their oxidation products were calculated after the Fuller-Schettler-Giddings method¹⁴. Mass accommodation coefficients of the soluble amines and oxidation products have been implemented with a value of 0.1, which is similar to the value of ammonia.

In the aqueous phase amine reaction mechanism, initial oxidation reactions by the OH, NO₃ and Cl radicals have been considered. A considerable pool of kinetic data is available for aqueous OH radical reactions with amines and their oxidation products. In case of missing kinetic constants, measured data of similar compounds have been applied to fill those gaps. No kinetic data were available for NO₃ and Cl reactions. Based on available kinetic data of OH and Cl radical reactions with organic compounds without an amino group, Cl radical reactions could be estimated with the same reaction rate constants as OH. For the NO₃ radical, reactions were considered based on results from kinetic measurements within the project and suitable estimates from correlation methods¹⁵. Five photolysis reactions of the nitrosamines nitrosomonoethanolamine, nitrosomonomethylamine, nitrosodimethylamine, nitrosodiethanolamine and nitrosopyrrolidine were implemented in the aqueous phase amine chemistry module, which were calculated with an extended TUV model^{16, 17} using measured extinction coefficients and quantum yields from the project. Finally, dissociations of amines have been implemented using the commercial software ACD/Labs PhysChem Suite to estimate most of the data as experimentally determined data were sparse.

Overall, the full amine mechanism module contains in total 71 gas phase reactions and 220 aqueous phase reactions, 39 equilibrium reactions as well as 42 phase transfers.

2.3 SPACCIM model description and performed model simulations

The Spectral Aerosol Cloud Chemistry Interaction Model (SPACCIM⁸) was used to investigate the tropospheric fate of selected amines. This 0-dimensional model comprises both a detailed microphysical and complex multiphase chemistry model. In SPACCIM, the description of both separate processes is performed for a highly size-resolved deliquescent particle and droplet spectrum.

The adiabatic air parcel model simulations were performed similarly to former applications (see Tilgner and Herrmann, 2010 and Nielsen et al., 2011 for details^{18, 19}). Model runs (see Table 7) were performed for summer and winter conditions, simulating high and lower photochemical activity. Additionally, model runs were performed for different initial amine concentrations (100 ppt and 1 ppb) and different environmental scenarios (marine-marine, marine-remote). In the scenarios, an air parcel moves along a predefined trajectory passing 4

cloud events (two times at noon and two times at midnight) for about 2 h each within 60 hours modelling time so that the air mass is subjected to a typical tropospheric in-cloud residence time²⁰ and to a characteristic aerosol residence time under the Mongstad meteorological conditions. For non-cloud time periods, an intermediate aqueous aerosol state is considered at 80% relative humidity representing typical conditions at the Mongstad area.

Additionally, simulations have been performed (i) with the RACM-MIM2ext/CAPRAM 3.0i coupled to the full chemical multiphase amine mechanism and (ii) with the RACM-MIM2ext/CAPRAM 3.0i coupled to the gas phase part of the amine mechanism only. The latter was done in order to characterise the importance of the aqueous phase degradation processes and the partitioning into the aqueous phase. Further details about the implemented model setup were reported in the former report and an overview on the performed simulations including the scenario acronyms used in the following is given in Table 7.

Table 7 Detailed overview on the performed simulations within this project.

#No.	Scenario Acronym	Environmental conditions (arriving air mass/ advection regime)	Season	Initial amine concentration	Amine mechanism
1	MMS100	Marine-Marine	Summer	100 ppt	Full mechanism
2	MMS100woAQ	Marine-Marine	Summer	100 ppt	Gas phase only
3	MMW100	Marine-Marine	Winter	100 ppt	Full mechanism
4	MMW100woAQ	Marine-Marine	Winter	100 ppt	Gas phase only
5	MMS1	Marine-Marine	Summer	1 ppb	Full mechanism
6	MMS1woAQ	Marine-Marine	Summer	1 ppb	Gas phase only
7	MMW1	Marine-Marine	Winter	1 ppb	Full mechanism
8	MMW1woAQ	Marine-Marine	Winter	1 ppb	Gas phase only
9	MRS100	Marine-Remote	Summer	100 ppt	Full mechanism
10	MRS100woAQ	Marine-Remote	Summer	100 ppt	Gas phase only
11	MRW100	Marine-Remote	Winter	100 ppt	Full mechanism
12	MRW100woAQ	Marine-Remote	Winter	100 ppt	Gas phase only

2.4 SPACCIM model results and discussion

Table 8 summarizes the main results from the Model runs. Due to the time restrictions the main focus lays on the scenarios MMS100 and MMW100.

Table 8 Model results overview, recommendation and implication from the SPACCIM parcel model simulations.

No.	Compound	Main sink/source pathways (MMS100/MMW100) ¹	Important model results (MMS100/MMW100 case)	Recommendations and implications from modelling
1	DMA (Dimethylamine)	<ul style="list-style-type: none"> ➤ Gaseous OH most important sink under summer conditions [-83% / -48%] ➤ Aqueous OH reaction particularly important under in-cloud daytime conditions [-17% / -16%] ➤ Cl radicals contributes substantially to the quite small DMA degradation under winter conditions in the deliquescent particles [-1% / -32%] ➤ Aq. NO₃ radical turnovers not important for DMA 	<ul style="list-style-type: none"> ➤ Rapidly oxidised in the gas phase under daytime summer conditions (DMA reduced by 80% within 13h of simulation, MMS100) ➤ Consideration of aq. phase processes increases the lifetime (due to the less effective aqueous phase degradation) ➤ Quite restricted photochemical degradation of DMA under winter conditions (long lifetime of DMA) due to restricted daytime OH chemistry (gaseous night-time chemistry probably needed to be considered) ➤ Just 12% of DMA oxidised after 60h of the winter simulation ➤ Aqueous phase reaction of DMA with HONO/NO₂⁻ unimportant for the multiphase formation N-nitroso-DMA (formation dominated by the gas phase) 	<ul style="list-style-type: none"> ➤ Consideration of gaseous NO₃ radical pathways in future mechanisms needed ➤ Deposition and the resulting input into other environmental compartments might be a relevant process under winter conditions because of the long lifetime ➤ Consideration of measured kinetic Cl data in future mechanisms might be suitable ➤ No need to consider aqueous phase DMA nitrosation
2	MA (Methylamine)	<ul style="list-style-type: none"> ➤ Gaseous OH less important [-3% / -16%] ➤ Aq. OH most important sink under summer conditions [-94% / -25% OH_(aq)] ➤ Cl radicals most important sink under winter conditions in the deliquescent particles [-3% / -53% Cl_(aq)] ➤ Aq. NO₃ radical only of minor importance for MA [0% / -6% NO₃] ➤ Formed from CN=C 	<ul style="list-style-type: none"> ➤ Quite similar pattern compared to DMA ➤ Effectively formed by the aqueous phase decay of N-methyl methanimine ➤ MA concentration reduced to about 12% after 60 h of simulation (MMS100) ➤ Just 10% of MA oxidised after 60h of the winter simulation (MMW100 case) ➤ Quite restricted photochemical degradation of MA under winter conditions (long lifetime of DMA) due to restricted daytime OH chemistry (gaseous nighttime chemistry probably needed to be considered) ➤ Degradation in deliquescent particles not as effective as in-cloud daytime degradations (MMS100) 	<ul style="list-style-type: none"> ➤ Consideration of gaseous NO₃ radical pathways in future mechanisms needed ➤ Deposition and the resulting input into other environmental compartments might be a relevant process under winter conditions because of the long modelled lifetime ➤ Consideration of measured kinetic data Cl and Cl₂⁻ radical reaction data in future mechanisms might be suitable

No.	Compound	Main sink/source pathways (MMS100/MMW100) ¹	Important model results (MMS100/MMW100 case)	Recommendations and implications from modelling
3	MEA (Mono-ethanolamine)	<ul style="list-style-type: none"> ➤ Aq. OH most important sink under summer conditions, particularly important under in-cloud daytime conditions [-97% / -33% OH_(aq)] ➤ Cl radicals most important sink under winter conditions particularly in the deliquescent particles [-3% / -66%] ➤ Aq. NO₃ radical turnovers not important for MEA [0% / -1%] ➤ Formed from OCCNCCO 	<ul style="list-style-type: none"> ➤ Mainly partitioned into the aqueous phase under the used model conditions ➤ Aqueous phase represents the main oxidising compartment for MEA ➤ Effective in-cloud oxidations under daytime summer conditions ➤ MEA concentration reduced to about 10% of the initial concentration after 60 h of simulation under summer conditions ➤ Just 2% lower MEA concentration after 60h under winter conditions ➤ Oxidation of MEA by NO₃ radicals not important under summer conditions ➤ In-cloud degradation fluxes during winter about 2 orders of magnitude smaller compared to summer conditions ➤ Both deliquescent particles and cloud droplets important for the quite restricted degradation of MEA under winter conditions 	<ul style="list-style-type: none"> ➤ Deposition and the resulting input into other environmental compartments might be a relevant process under winter conditions because of the long modelled lifetime ➤ Consideration of measured kinetic data Cl and Cl₂⁻ radical reaction data in future mechanisms might be suitable
4	DEA (Diethanolamine)	<ul style="list-style-type: none"> ➤ Aq. OH most important sink under summer conditions, particularly important under in-cloud daytime conditions [-96% / -33%] ➤ Aq. Cl radicals most important sink under winter conditions particularly in the deliquescent particles [-4% / -65%] ➤ Aq. NO₃ radical turnovers not important for DEA [0% / -3%] 	<ul style="list-style-type: none"> ➤ Substantial oxidation under daytime cloud conditions during summer ➤ DEA concentration reduced to about 3% of the initial concentration after 60 h of simulation under summer conditions ➤ Just 22% lower of DEA concentration after 60h under winter conditions ➤ Degradation fluxes about 2 orders of magnitude lower in the winter case ➤ Considerable contributions of the Cl radical pathway under deliquescent particle conditions in winter ➤ Aqueous reaction of DEA with HONO/NO₂⁻ leading to the formation of N-nitroso DEA not important 	<ul style="list-style-type: none"> ➤ Deposition and the resulting input into other environmental compartments might be a relevant process under winter conditions because of the long modelled lifetime ➤ Consideration of measured kinetic data Cl and Cl₂⁻ radical reaction data in future mechanisms might be suitable ➤ No need to consider aqueous phase DEA nitrosation reactions
5	PYL (Pyrrolidin)	<ul style="list-style-type: none"> ➤ Aq. OH only important sink under summer and winter conditions [-100% / -100%] 	<ul style="list-style-type: none"> ➤ Quite rapid oxidation of PYL under summer conditions ➤ Significant decay of PYL under daytime cloud conditions in summer ➤ After 36 hours of the simulation, PYL nearly fully converted to its oxidation products ➤ Deliquescent particle phase with considerable turnovers ➤ NO₃ radicals only of minor importance under summer conditions 	<ul style="list-style-type: none"> ➤ No need to consider aqueous phase PYL nitrosation reactions

No.	Compound	Main sink/source pathways (MMS100/MMW100) ¹	Important model results (MMS100/MMW100 case)	Recommendations and implications from modelling
6	N-nitroso-DMA	<ul style="list-style-type: none"> ➤ Photolysis is only sink under summer and winter conditions [-100% / -100% hv_(g)] ➤ Formed from CNC 	<ul style="list-style-type: none"> ➤ Formed exclusively in the gas phase on a relatively short timescale ➤ Modelled maximum concentrations with about 1·10⁷ molec cm⁻³ (MMS1woAQ) still rather small ➤ Aqueous phase reaction of DMA with HONO/NO₂⁻ unimportant for the multiphase formation N-nitroso-DMA ➤ Gaseous photolysis dominant sink for N-nitroso-DMA under both summer and winter conditions 	<ul style="list-style-type: none"> ➤ No need to consider aqueous phase DEA nitrosation reactions
7	N-nitroso-PYL	<ul style="list-style-type: none"> ➤ Aq. OH most important sink under summer conditions, particularly important under in-cloud daytime conditions [-63% / -29%] ➤ Photolysis substantial sink under summer and winter conditions [-37% / -37% hv_(aq)] ➤ Aq. NO₃ radical turnovers important for N-PYL under winter conditions [0% / -34% NO_{3(aq)}] ➤ Formed from PYL 	<ul style="list-style-type: none"> ➤ Just very small production fluxes of N-PYL modelled ➤ Aqueous phase reaction of PYL with HONO/NO₂⁻ unimportant 	<ul style="list-style-type: none"> ➤ No need to consider aqueous phase PYL nitrosation reactions
8	CNC=O (Methyl-formamide)	<ul style="list-style-type: none"> ➤ Aq. OH only important sink under summer and winter conditions [-100% / -98% OH_(aq)] ➤ Cl radical turnovers less important for DMA [0% / -2% Cl_(aq)] ➤ Formed from CNC 	<ul style="list-style-type: none"> ➤ Rapidly formed in the gas phase under daytime summer conditions ➤ Rapidly oxidised under daytime cloud conditions ➤ Production of CNC=O leading to gaseous concentration up to about 0.05 ppb in summer ➤ Clouds represent a compartment for aqueous formation of CNC=O from DMA ➤ NO₃ radical and Cl radical reaction pathways not important 	<ul style="list-style-type: none"> ➤ Aqueous phase chemistry important process to be considered for amides such as CNC=O
9	CN=C (N-methyl methanimine)	<ul style="list-style-type: none"> ➤ Hydrolysis important sink under cloud conditions ➤ Gaseous OH important sink under summer conditions [-46% / 0%]³³ 	<ul style="list-style-type: none"> ➤ Significant production modelled under daytime conditions ➤ Significant decay under cloud conditions ➤ Hydrolysis leads to the formation of MA 	<ul style="list-style-type: none"> ➤ Cloud may acts an important sink for imines in the troposphere

No.	Compound	Main sink/source pathways (MMS100/MMW100) ¹	Important model results (MMS100/MMW100 case)	Recommendations and implications from modelling
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Remarks:

¹ given numbers in brackets represents the percentage contribution (calculated for the whole simulation time) of the mentioned reaction pathway to the formation (form.; +) or degradation (-) of the corresponding compound in the MMS100 and MMW100 case, respectively.

3 EVALUATION OF THE OVERALL STATUS OF AMINE ATMOSPHERIC CHEMISTRY

An evaluation of the overall status of amine atmospheric chemistry has been prepared as part of this project in Tel-Tek report 2211030-AQ01 (eRoom FM07-APZ00-P-RA-0007). Comparing gas and aqueous phase atmospheric chemistry, the gas phase chemistry is the best understood part respective amine degradation and nitrosamine and nitramine formation.

There are currently not many studies available concerning aqueous phase nitrosamines with atmospheric background but no studies of nitramines with aqueous phase atmospheric background. Publications on the environmental fate of nitramines are often related to their use as explosives and therefore contamination of soil and groundwater during manufacturing and use and often lack applicability to atmospheric conditions. Studies available from physiology-, medical-, waste water- or drinking water treatment- and groundwater-background concerned with nitrosamine and nitramine formation, consider nitrosamine and nitramine via N_2O_3 , NO_2^- , NO_3^- , N_2O_4 , NO^+ , HONO or peroxyxynitrite. Additionally, aqueous N_2O_5 (dinitrogen-pentoxide) was discussed as a potential intermediate for the generation of nitrating agents. With regards to the chemistry of the N_2O_y species, these could in fact act as nitrosating agents in laboratory systems as frequently discussed in the literature leading to the formation of nitrosamines or nitramines, respectively. Different from technical systems or preparative chemistry, the expected concentration level of amines in tropospheric aqueous particles will most likely not lead to significant turnovers of the N_2O_y species by a direct reaction. Direct reactions of amines with transition metal ions are theoretically possible, but are expected to play a very subordinate role for the region of Mongstad. Further details can be found in Tel-Tek report 2211030-AQ01.

4 REMAINING QUESTIONS OF ATMOSPHERIC MULTIPHASE AMINE CHEMISTRY

Overview - missing information

When implementing the degradation schemes for the compounds (amines: DMA, DEA, PYL; nitrosamines: NDMA, NDEA, NPYL) currently under investigation for the box-model, it became obvious that (i) clarifications of the kinetics of nitrosamine formation are needed and (b) that it is necessary to include not only the first oxidation products in the reaction schemes. For example, the alkyl branches of DMA are first oxidised and to form an aldehyde group, secondly an alcohol and thirdly an acid. For most of these first-, second- and third-generation oxidation product of amines or nitrosamines there are no rate constants available for the reactions with the most important radicals in the Mongstad area, which are OH, NO₃ and Cl. SO₄⁻ is thought to play only a smaller role, but this will depend on the concentration regime of SO₂ in the atmosphere. At present, rate constants for reactions of amines or nitrosamines with Cl are completely missing and are estimated as to be equal as those for OH. Cl radical reactions are thought to play an important role in the degradation amines or nitrosamines in the Mongstad area where large amount of chloride is available due to the presence of marine particles. Rate constants for nitramine reactions with ozone are also not available in the literature, but are potentially important. Therefore, it could be useful to perform kinetic measurements of the degradation of key compounds by the radicals and ozone. It would be good to perform a sensitivity study on the influence of phase transfer parameters. Finally, as the goal is a state-of-art dispersion model application, such study should be prepared by a full atmospheric site characterisation and respective box modelling to avoid loss of information from the present work to the dispersion model implementation.

Nitrosamine formation studies deploying educt and product analytical measurements

As outlined in this report before, the applied time-resolved UV-measurements had their limitations. Therefore, it is suggested to kinetically fully describe the formation of nitrosamines from the target amines in their reactions with nitrite and HONO under reaction conditions applicable for the atmospheric aqueous phase. Measurements of NO₂⁻ by IC and of the formed nitrosamines by derivatisation and HPLC and HPLC-MS are desirable when the kinetics of each reaction are studied under controlled conditions in a stirred batch reactor. pH and T should be systematically varied.

Kinetic studies of OH, NO₃ and Cl reactions - reactivity correlations for substance classes

Given an input of 3-5 relevant amines and their corresponding nitrosamines, including important second and third oxidation products such as amides, one reaches very quickly a degradation scheme which includes more than 200 reactions. It is clear, that not every single reaction can and has to be measured. We would rather aim at a construction of a database for kinetic constants of differently substituted nitrogen containing compounds. From this database, we can perform reactivity correlations for the reaction of each radical OH, NO₃ and Cl with a certain class of compounds, or example amines, nitrosamines and amides. These reactivity correlations can then be used to estimate similar rate constants for modelling purposes. The reactions to be included in the kinetic studies are listed in Table 9. A prerequisite for the performance of the kinetic studies is the commercial availability of the

desired substances with a maximum level of purity. For some compounds the availability has already been verified, for other some time is needed to check with major chemical suppliers.

Table 9 Compounds to be included in the kinetic studies and commercial availability, planned measurements are marked with x, for those not-marked, data are available, are being currently measured in the ongoing project or estimated

Compounds	OH	NO ₃	Cl	Available
Dimethylamine			x	yes
Methylamine			x	yes
CH ₂ OHNH ₂	x	x	x	to be checked
(Formamide) CHONH ₂			x	yes
N-methyl-formamide		x	x	yes
Dimethanolamine	x	x	x	to be checked
N-methanolformamide	x	x	x	to be checked
Diformamide	x	x	x	to be checked
Monoethanolamine		x	x	yes
CHOCH ₂ NH ₂	x	x	x	to be checked
CHOCH(OH)NH ₂	x	x	x	to be checked
CH ₂ (OH)CH(OH)NH ₂	x	x	x	to be checked
(Glycolamide) CH ₂ (OH)C(O)NH ₂	x	x	x	yes
Methyldiethanolamine	x	x	x	yes
Diethanolamine	x		x	yes
Nitrosodiethanolamine	x		x	yes
Pyrrolidine	x		x	yes
Piperazine	x	x	x	yes
Nitrosopiperazine	x	x	x	yes

Kinetic studies of ozone reactions with nitramines

Reactions of nitramines with O₃ are planned to be investigated via UV-vis spectroscopy. The decay of O₃ can be monitored directly or indirectly in case of overlapping reactant-absorption via the addition of indigo-sulfonate which consumes O₃ instantly and is a quantitative measure for the ozone concentration. A prerequisite for the performance of the kinetic studies is the availability of the desired substances with a maximum level of purity. They are not commercially available. According to previous informal email contact, it was concluded that nitramines could be provided by Yngve Stenström at the Norwegian University of Life Sciences in Aas for a reasonable price in the required purity.

Sensitivity analysis for variation of mass accommodation coefficient

As only estimated mass accommodation coefficients were used, it could be very useful to study the sensitivity of the box model results on a variation of the α parameters. If the model result would show to be sensitive, it might become necessary to undertake laboratory measurements of the mass accommodation coefficients for the amines, Nitrosamines, amides and second generation oxidation products.

Reliable initiation parameters for a dispersion model by an atmospheric characterisation experiment at the CCM site

As the results of the foreseen future dispersion model runs might have severe consequences, it would be useful to initiate these model runs with the best available initialisation parameters. To this end, it would be useful to undertake an atmospheric conditions characterisation campaign at the Mongstad site with measuring all important atmospheric chemical and physical parameters of interest including full particle characterisation and HO_x budgets

The dispersion model application

The results of the present project should be used as input for a follow-up study of amines with means of dispersion modelling. 3D-modelling could be used to investigate the dispersion of key pollutants such as amines, nitrosamines, or amides in the Mongstad area. Therefore the chemistry transport model (CTM) COSMO-MUSCAT²¹ could be applied as one possible choice. Since 3-dimensional CTMs demand simple chemical mechanisms, the amine mechanism of the current project would have to be reduced to allow for those calculations. Further reductions concern the pre-existing mechanism CAPRAM 3.0 and the coupled halogen module 2.0. However, not only reduction is an important issue for future studies, but also the further development of the amine mechanism, such as the inclusion of NO₃ radical chemistry in the gas phase to consider dark chemistry, which is especially important during winter month. Besides the 3-dimensional dispersion modelling studies, further trajectory studies with the 0-dimensional box model SPACCIM⁸ are needed in preparation for the 3D runs. Those box model runs will help to evaluate the importance of reactions pathways in the environmental regime of the Mongstad area and, thus, are needed for the mechanism reduction. Furthermore, they can be used to derive parameterisations for the deposition of amines as an explicit description of the deposition process is unlikely to be treated in the COSMO-MUSCAT model.

5 LIST OF ABBREVIATIONS

C	concentration
CAPRAM	Chemical Aqueous Phase Radical Mechanism
DEA	diethanolamine
DMA	dimethylamine
DMA	dimethylamine
HO _x	Species: OH, HO ₂ , H ₂ O ₂
k _{1st}	(pseudo) first order rate constant
k _{2nd}	second order rate constant
k _{3rd}	third order rate constant
MA	methylamine
MDEA	methyl diethanolamine
MEA	monoethanolamine
NDEA	nitrosodiethanolamine
NDMA	nitrosodimethylamine
NPYL	nitrosopyrrolidine
PYL	pyrrolidine
RACM-MIM2ext	Regional Atmospheric Chemistry Model - Mainz Isoprene Mechanism 2 extended
SPACCIM	Spectral Aerosol Cloud Chemistry Interaction Model
UV	ultra violet

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