Theoretical evaluation of the fate of harmful compounds post emission

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Executive summary

The present report presents a systematic survey of the atmospheric chemistry of amines and amine degradation products reported in the literature before August 1, 2010. The report encompasses the current knowledge on gas phase processes, phase transfer processes and aqueous phase processes, and includes best estimates of the atmospheric partitioning, fate and lifetimes of amines and amine degradation products in the Mongstad area. Assuming model estimates of Henry´s Law coefficients to describe equilibrium conditions it is predicted that unsubstituted alkylamines will primarily be oxidized in the gas phase, and that alkanolamines will primarily be oxidized in the atmospheric aqueous phase.

Existing theoretical gas phase degradation schemes have been updated for methylamine, dimethylamine and trimethylamine, and the theoretical atmospheric aqueous phase chemistry of dimethylamine (DMA), monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA) and piperazine (PZ) has been developed.

The study has uncovered serious gaps in the current knowledge concerning the fate of harmful compounds post emission from amine based CO_2 capture plants. In particular the phase transfer processes are associated with large uncertainties. The report includes research recommendations to fill these gaps. The report, however, does not present any ranking of the studied amines/solvents – there are not enough data in the literature to justify such a ranking.

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Content

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1 Potential compounds in the effluent of a CO_2 capture plant.

The work carried out in WP1 (Theoretical evaluation of the probability to form and emit harmful components from aqueous amine solution for selected amines) has resulted in the following list of potential compounds in the effluent of CO_2 capture plant.

Amine in solvent	Compounds in effluent	Bp /ºC	Volatility	Reported
MEA	MEA ($NH_2CH_2CH_2OH$)	170	medium	yes
	NH_3		high	yes
	CH_2O	-21	high	no
	CH_3CHO	20.2	high	no
	MAE ($CH_3NHCH_2CH_2OH$)	155-156	medium	yes
	HEEDA ($H_2NCH_2CH_2NHCH_2CH_2OH$)	-	low	yes
	H_2NCHO	210	low	no
MDEA	MDEA	247	medium	yes
	NH_3		high	yes
	CH_2O	-21	high	no
	CH_3CHO	20.2	high	no
	DMAE ($(CH_3)_2NCH_2CH_2OH$)	133-134	medium	yes
	MAE ($CH_3NHCH_2CH_2OH$)	155-156	medium	yes
	DEA ($HN(CH_2CH_2OH)_2$)	217	medium	yes
	$(CH_3)_3N$	3	high	yes
	$(CH_3)_2NH$	7	high	no
AMP	AMP ($NH_2C(CH_3)_2CH_2OH$)	165	medium	yes
	NH_3		high	yes
	CH_2O	-21	high	no
	CH_3CHO	20.2	high	no
	CH_3COCH_3	56.5	high	no
	MAMP ($CH_3NHC(CH_3)_2CH_2OH$)		medium	yes
PZ	PZ ($HN(CH_2CH_2)_2NH$)	146	medium	yes
	CH_2O	-21	high	no
	CH_3CHO	20.2	high	no
	$H_2NCH_2CH_2NH_2$	116	low	yes
	H_2NCHO	210	low	no

The above information has been used as input to the present theoretical evaluation of the fate of harmful compounds post emission.

2 Literature review of amine gas phase chemistry and aerosol formation.

Compounds emitted into the atmosphere are, in turn, removed again from the atmosphere by wet and dry deposition, photolysis, and chemical reaction. Wet and dry depositions of organic compounds are controlled by their vapour-particle partitioning,[1] which in turn depends on their vapour pressure and Henry´s Law constants, and on the particle and droplet size and number density. Organics with vapour pressure $\approx 10^{-4}$ Pa will partition roughly 50:50 between the particulate and gas phases in areas with 100 μg m^{-3} background aerosol.[1] The dissolution of organics into rain and cloud droplets is determined by the Henry´s Law constant – this will be discussed elsewhere.

Reaction with OH radicals is the dominant loss process for the majority of the tropospheric trace gases.[2] Compounds such as aldehydes and ketones undergo direct photolysis, and reactions with O_3 and NO_3 radicals are important for many unsaturated hydrocarbons. In marine areas reactions with Cl atoms may also constitute important sinks.

Aliphatic amines have almost been left out of atmospheric and environmental sciences due to their low ppbV-range mixing ratios and their short lifetimes.[3] Consequently, the frequently used mechanistic database for modelling atmospheric photo-oxidation of organics, the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/MCM/home.htt),[4] does currently not include degradation schemes for amines.

There has only appeared one research publication and two publicly available reports with new experimental data on atmospheric amine chemistry since the previous Bråthen *et al.*[5] review of amine gas phase chemistry. Gai *et al.* reported the kinetics of the O_3 reactions with diethylamine and triethylamine.[6] The CLIMIT-project "193438 Atmospheric Degradation of Amines (ADA-2009)" reported the results from studies of the atmospheric photo-oxidation of 2-aminoethanol (MEA) (report available from: http://ada.nilu.no/).[7] The other new report, a M.Sc.-thesis by Derek Price,[8] primarily focuses on aerosol formation resulting from dimethylamine, diethylamine, dipropylamine, dibutylamine, diphenylamine and dibenzylamine reactions with NO_3 radicals. However, the thesis includes information of gas phase products in the NO_3-initiated oxidation reactions (http://digitalcommons.usu.edu/cgi/viewcontent.cgi?article=1588&context=etd). Further, some results in William Carter´s report *Reactivity estimates for selected consumer product compounds,*[9] and in the Erupe *et al.*[10] publication *Secondary organic aerosol formation from reaction of tertiary amines with nitrate radical* were not included in the Bråthen *et al*. review.

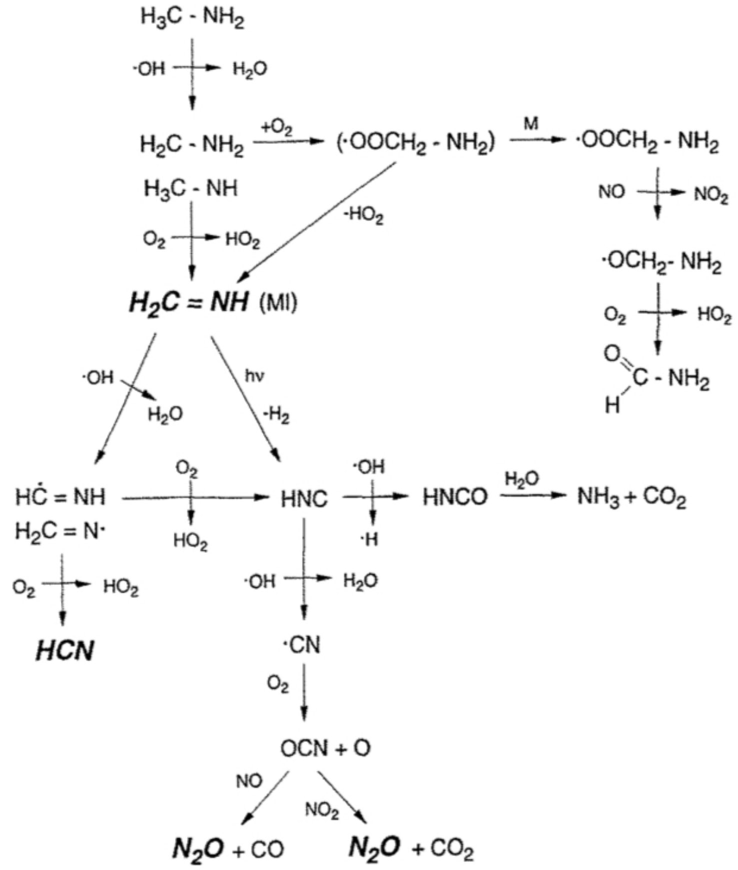
2.1 CH_3NH_2

Atkinson et al.[11] studied the kinetics of the OH radical reaction with CH_3NH_2 over the temperature range 299 – 426 K and reported a negative Arrhenius activation energy, $k_{OH}(T) = 1.02\times10^{-11} \times \exp\{(230 \pm 150)K/T\}$ and $k_{OH} = (2.20 \pm 0.22) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K. 20 years later, Carl and Crowley[12] reported a room temperature value for $k_{OH} = (1.73 \pm 0.11) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is ca. 30% below that of Atkinson *et al.*[11] The absolute value of Atkinson *et al.*[11] depends on a calibrated gas whereas Carl and Crowley[12] used the UV cross section of the amine for calibration, and they suggest that the earlier results suffer from a calibration error. Tuazon et al.[13] have determined the rate constant for reaction of methylamine with O_3 to be $k_{O3} = (7.4 \pm 2.4) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Rudic *et al.*[14] studied the product branching and dynamics of the reaction between methylamine and Cl atoms employing REMPI spectrocopy with TOF-MS detection. They found branching ratios for the C-H : N-H and the C-D : N-D abstractions of 0.48 : 0.52 and 0.58 : 0.42 in CH_3NH_2 and CD_3ND_2, respectively. Since OH radicals and Cl atoms often show similar selectivity in their reactions, one may expect that also hydrogen abstraction in primary amines by OH radicals will occur from both C and N.

Galano and Alvarez-Idaboy have calculated the rate constant for the methylamine reaction with OH radicals using Canonical Variational Therory employing results from CCSD(T) / 6-311++G(2d,2p)//BHandHLYP/6-311++G(2d,2p) calculations. Their result are $k_{OH}(T) = 5.89 \times 10^{-11} \times \exp(-757/RT)$ cm^3 $molecule^{-1}$ s^{-1} and $k_{OH} = 5.20 \times 10^{-12}$ at 298 K;[15] they predict a *positive* Arrhenius activation energy. They also predict a branching ratio for the C-H : N-H abstractions of 0.80 : 0.20 at 298 K. Tian *et al.*[16] have presented results from similar theoretical calculations at the CCSD(T)/6-311++G(2d,2p)// CCSD/6-31G(d) level of theory followed by improved canonical variational transition state theory incorporating small-curvature tunneling. Tian *et al.*[16] predict a *negative* Arrhenius activation energy at atmospheric temperatures, a positive Arrhenius activation energy at higher temperatures, and $k_{OH} = 2.98 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. They further report the teoretical branching ratio for the C-H : N-H abstractions to be 0.74 : 0.26 at 298 K.

There are no literature data on the products formed in the atmospheric photo-oxidation of methylamine. Schade and Crutzen speculated on the atmospheric degradation mechanism for the OH initiated photo-oxidation of CH_3NH_2 in a study of the emission of aliphatic amines from animal husbandry,[17] Scheme 2.1.



Scheme 2.1. Possible methylamine gas phase chemistry, leading to N_2O or HCN. (From Schade and Crutzen, Ref. 17).

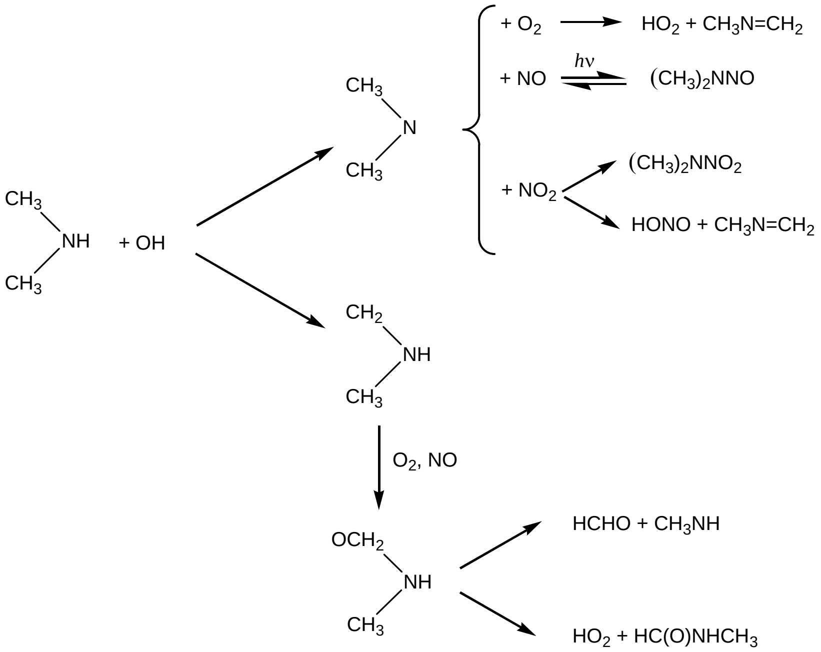
Murphy *et al.*[18] carried out 3 experiments in which the oxidant precursor(s) were *i)* NO_2, *ii)* H_2O_2/NO and *iii)* O_3. They found that nearly 100% of the aerosol formed during a photo-oxidation experiment with CH_3NH_2 consisted of methylammonmium nitrate (salt) and that less than 1% was non-salt organics. Though the formation of non-salt aerosol was small, the relative importance of non-salt organic aerosol increased through the course of the experiments.

2.2 $(CH_3)_2NH$

Atkinson *et al.*[19] studied the kinetics of the OH radical reaction with $(CH_3)_2NH$ over the temperature range 299 – 426 K and reported a *negative* Arrhenius activation energy, $k_{OH}(T) = 2.89\times10^{-11} \times \exp\{(245 \pm 150)K/T\}$ and $k_{OH} = (6.54 \pm 0.66) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Carl and Crowley[12] reported a room temperature value in perfect agreement with the results of Atkinson *et al.*, $k_{OH} = (6.49 \pm 0.64) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Pitts *et al.*[20] carried out an exploratory study of the products formed when a mixture of 500 ppb $(CH_3)_2NH$ + 80 ppb NO + 160 ppb NO_2 was subjected to natural sunlight conditions. They found $(CH_3)_2NNO_2$ (dimethylnitramine) and $CHON(H)CH_3$ (*N*-methyl formamide) as gas phase products, but did not quantify the amounts. About 1% yield of $(CH_3)_2NNO$ (dimethylnitrosmine) was formed in the dark and subsequently destroyed in sunlight. Aerosol was formed during the photo-oxidation but was not analyzed. There is no report on the mass balance in the photo-oxidation experiment of. $(CH_3)_2NH$.

Hanst *et al.*[21] were the first to report formation of $(CH_3)_2NNO$ under dark, humid conditions when dimethylamine was mixed HONO, NO and NO_2 in air. As mentioned above, Pitts *et al.*[20] found a similar, but smaller nitrosation reaction of dimethylamine in the dark. However, a later control experiment by Glasson,[22] however, suggests that the apparent gas phase nitrosation in reality may be a surface reaction. A theoretical study of the gas phase reaction between HONO and dimethylamine[23] suggests a barrier to the direct reaction of more than 90 kJ mol^{-1}, i.e. the reaction will not take place at atmospheric conditions. HONO is not a gas phase nitrosation agent under any atmospheric conditions. Grosjean has outlined the reaction of OH with $(CH_3)_2NH$,[24] Scheme 2.2.



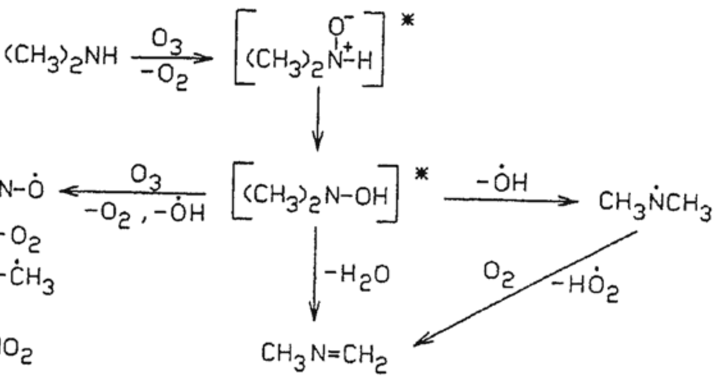
Scheme 2.2. Reaction of OH with dimethylamine. (From Grosjean, Ref. 24).

The branching ratio in the initial hydrogen abstraction by OH radicals was determined by Lindley *et al.*[25] who reported $k(1)/(k(1)+k(2)) = 0.37 \pm 0.05$

$$(CH_3)_2NH + OH \rightarrow (CH_3)_2N + H_2O \quad (1)$$
$$\rightarrow CH_3NHCH_2 + H_2O \quad (2)$$

Galano and Alvarez-Idaboy have calculated the rate constant for the dimethylamine reaction with OH radicals using Canonical Variational Therory employing results from CCSD(T) / 6-311++G(2d,2p)//BHandHLYP/6-311++G(2d,2p) calculations. Their result is $k_{OH}(T) = 2.72 \times 10^{-11} \times \exp(200/RT)$ cm^3 molecule^{-1} s^{-1} and $k_{OH} = 5.20 \times 10^{-12}$ at 298 K;[15] they predict a *negative* Arrhenius activation energy. They also predict a branching ratio for the C-H : N-H abstractions of 0.48 : 0.52 at 298 K.

Tuazon *et al.*[13] have determined the rate constant for reaction of dimethylamine with O_3 to be $k_{O3} = (1.67 \pm 0.20) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K. They reported $CH_3N{=}CH_2$, CH_3NO_2, CH_2O, HCOOH, $(CH_3)_2NCHO$ and CH_3NHCHO as products in the reaction; methyl-methanimine was formed with the largest yield. Tuazon *et al.* proposed a reaction mechanism for the amine – ozone reaction, Scheme 2.3.



Scheme 2.3. Proposed mechanism for the reaction of ozone with dimethylamine (From Tuazon *et al.*, Ref. 13).

In the exploratory study by Pitts *et al.*[20] aerosol was formed during the photo-oxidation of $(CH_3)_2NH$, but it was not analyzed. Derek Price[8] analyzed the aerosol formed in the $(CH_3)_2NH/O_3/NOx$ oxidation experiments by HR-TOF-AMS. The major ion peaks observed of the aerosol included *m/z* 30.034 (CH_4N^+), *m/z* 44.050 ($C_2H_6N^+$), *m/z* 58.066 ($C_3H_8N^+$), *m/z* 86.099 ($C_5H_{12}N^+$), and *m/z* 101.114 ($C_6H_{15}N^+$), which represent the backbone amine fragments. Fragments of large hydrocarbons including *m/z* 72.094 ($C_5H_{12}^+$), *m/z* 86.11 ($C_6H_{14}^+$), and *m/z* 94.078 ($C_7H_{10}^+$) were detected, with evidence of oxidation in *m/z* 72.058 ($C_4H_8O^+$) and *m/z* 97.065 ($C_6H_9O^+$). The thesis offers no further interpretation of the results, but it is clear that extensive processing has taken place in the aerosol phase.

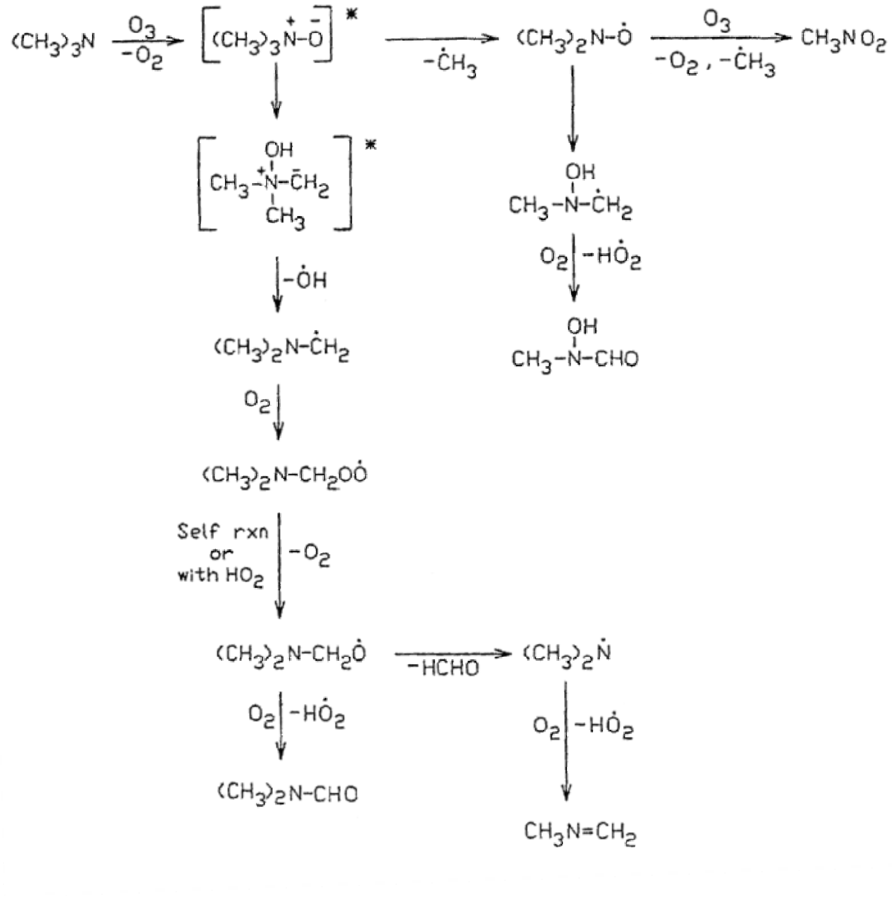
In a recent investigation of the NO_3 radical initiated atmospheric oxidation of $(CH_3)_2NH$ Derek Price[8] suggests the following interpretation of the major PTR-MS ion signals $[MH]^+$: *m/z* 44, CH_3NCH_2 (methyl-methyleneimine); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 46, $(CH_3)_2NH$ (dimethylamine); *m/z* 58, CH_3NCHCH_3 (methyl-ethyleneimine); *m/z* 59, $(CH_3)_2CO$ (acetone) and/or CH_3CH_2CHO (propanal); *m/z* 60, $(CH_3)_3N$ (trimethylamine) and or CH_3CH_2NO (nitrosoethane), *m/z* 62, CH_3NO_2 (nitromethane); *m/z* 91, $(CH_3)_2NNO_2$ (dimethyl-nitramine). There was no attempt to relate the compounds mentioned to any specific degradation mechanism in the thesis.

2.3 $(CH_3)_3N$

Atkinson *et al.*[19] studied the kinetics of the OH radical reaction with $(CH_3)_3N$ over the temperature range 299 – 426 K and reported a *negative* Arrhenius activation energy, $k_{OH}(T) = 2.62\times10^{-11} \times \exp\{(250 \pm 150)K/T\}$ and $k_{OH} = (6.09 \pm 0.61) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Carl and Crowley[12] presented a room temperature value for $k_{OH} = (3.58 \pm 0.22) \times 10^{-11}$ which differ by a factor of 2. The absolute value of Atkinson *et al.*[19] depends on a calibrated gas whereas Carl and Crowley[12] used the UV cross section of the amine for calibration, and the latter authors suggest that the earlier results suffer from a calibration error.

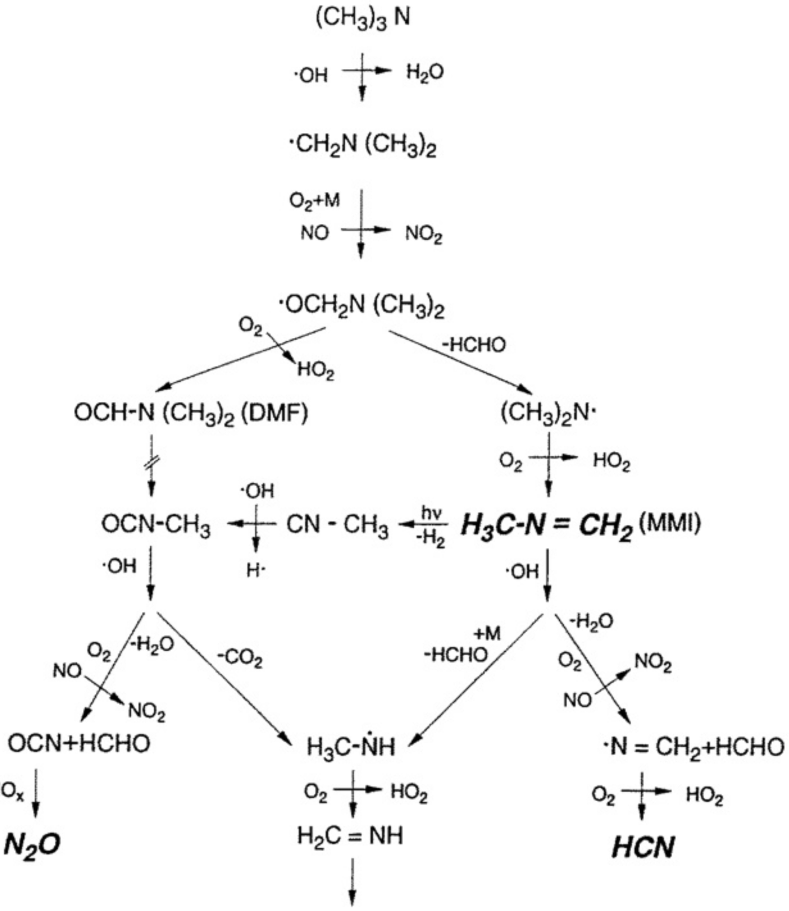
Pitts *et al.*[20] carried out an exploratory study of the products formed when a mixture of 500 ppb $(CH_3)_3N$ + 80 ppb NO + 160 ppb NO_2 was subjected to natural sunlight conditions. They found $(CH_3)_2NNO_2$ (dimethylnitramine) and $(CH_3)_2NCHO$ (*N,N*-dimethylformamide) as gas phase products, but they did not quantify the amounts formed. Large amounts (370 ppb) of HCHO (formaldehyde) was detected in the gas phase. Only trace amounts of $(CH_3)_2NNO$ (dimethylnitrosmine) was reported. There was no report on the mass balance in the $(CH_3)_3N$ photo-oxidation experiment.

Tuazon *et al.*[13] have determined the rate constant for reaction of trimethylamine with O_3 to be $k_{O3} = (7.84 \pm 0.87) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. They observed $(CH_3)_2NCHO$, $CH_3N=CH_2$, CH_3NO_2, CH_2O and HCOOH as products in the reaction. Formaldehyde was formed with the largest yield, followed by methylmethanimine. A reaction mechanism for the amine – ozone reaction was proposed, Scheme 2.4.



Scheme 2.4. Proposed mechanism for the reaction of ozone with trimethylamine (From Tuazon *et al.*, Ref. 13).

Grosjean outlined the mechanism for atmospheric photo-oxidation of $(CH_3)_3N$, in 1991.[24] In 1995 Schade and Crutzen speculated on the atmospheric degradation mechanism in a study of the emission of aliphatic amines from animal husbandry and their reactions,[17] Scheme 2.5.



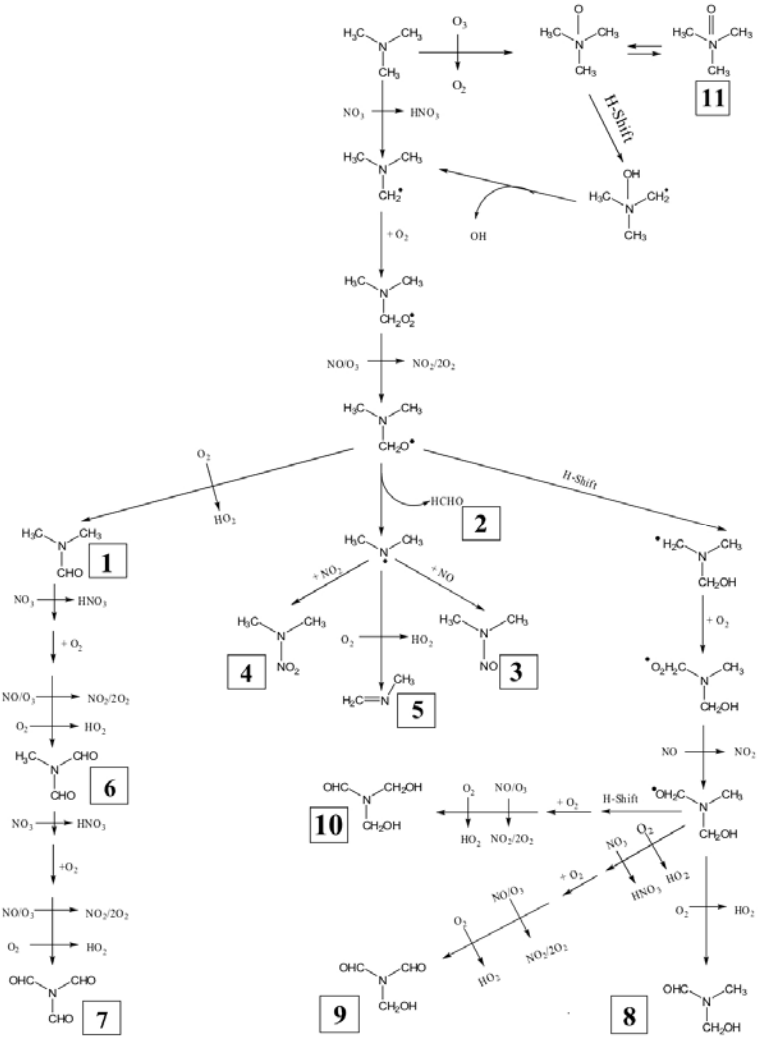
Scheme 2.5. Possible trimethylamine gas phase chemistry, leading to N_2O or HCN. (From Schade and Crutzen, Ref. 17).

In the exploratory $(CH_3)_3N$ photo-oxidation study by Pitts *et al.*[20] the aerosol formed contained ca. 3 µg m^{-3} (1.6 ppb) $CHONH_2$ (formamide) and another amide-like compound with M=87 was detected but not identified and quantified. Schade and Crutzen[17] suggested that this mass could correspond to CHO-N(CH_3)-CHO (*N*-formyl, *N*-methylformamide). Murphy *et al.*[18] reported that the aerosol which formed in high-NOx photo-oxidation experiments with $(CH_3)_3N$ mainly consisted of trimethylammonium nitrate salt. The nitrate particles were generated in a acid-base equilibrium reaction between nitric acid and $(CH_3)_3N$. Non-salt organic particles were formed with a mass yield of 23%.

Erupe *et al.*[10] investigated the secondary organic aerosol formation from reaction of trimethylamine with nitrate radicals, produced *in situ* by adding NO to a mixture of trimethylamine with excess O_3 under dark conditions, and followed the gas phase VOCs by PTR-MS. Their interpretation of the major ion masses $[MH]^+$ were as follows: *m/z* 31, HCHO (formaldehyde); *m/z* 33, CH_3OH (methanol); *m/z* 44, $CH_3N{=}CH_2$ (methylmethyleneimine); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 47, HCOOH (formic acid) and/or CH_3OH (methanol); *m/z* 59, $(CH_3)_2CO$ (acetone) and/or CH_3CH_2CHO (propanal); *m/z* 60, $(CH_3)_3N$ (trimethylamine); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol); *m/z* 62, CH_3NO_2 (nitromethane); *m/z* 74, $(CH_3)_2NCHO$ (dimethylformamide); *m/z* 75, $(CH_3)_2NNO$

(dimethylnitrosamine); m/z 88, $CH_3N(CHO)_2$ (methyldiformamide) m/z 90, $CH_2OH(CH_3)NCHO$ (hydroxymethyl-methylformamide); m/z 91, $(CH_3)_2NNO_2$ (dimethylnitramine); m/z 102, $(CHO)_3N$ (triformamide). Scheme 2.6 shows their proposed mechanism for the reaction of trimethylamine with the nitrate radical and includes the trimethylamine oxidation by O_3 previously proposed by Tuazon *et al.*[13]

Erupe *et al.*[10] reported ion peaks from the aerosol at m/z 44.052 ($C_2H_6N^+$) and m/z 58.066 ($C_3H_8N^+$) represent amine backbone fragments while m/z 58.030 ($C_2H_4NO^+$), 76.040 ($C_2H_6NO_2^+$), m/z 88.037 ($C_3H_6NO_2^+$) and m/z 104.040 ($C_3H_6NO_3^+$) represent fragments of amines that have been oxidized.



Scheme 2.6. Proposed mechanism for the reaction of trimethylamine with the nitrate radical and the trimethylamine oxidation by O_3 (From Erupe *et al.*, Ref. 10)

2.4 $CH_3CH_2NH_2$

Atkinson *et al.*[11] determined the rate constant for the reaction of OH radicals with $CH_3CH_2NH_2$ over the temperature range 299 – 426 K and reported a negative Arrhenius activation energy, $k_{OH}(T) = 1.47\times10^{-11} \times \exp\{(190 \pm 150)K/T\}$ and $k_{OH} = (2.77 \pm 0.28) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Carl and Crowley[12] reported a room temperature value that agree within 10%, $k_{OH} = (2.38+0.5/-0.15) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

The only data on products formed in the atmospheric photo-oxidation of ethylamine is from the ADA-2009 project identified $CH_3CH_2NHNO_2$ (*N*-nitro ethylamine, ethylnitramine) as one of the products in the photo-oxidation of $CH_3CH_2NH_2$ under high-NOx conditions.[7]

Galano and Alvarez-Idaboy have calculated the rate constant for the dimethylamine reaction with OH radicals at the CCSD(T)/6-311++G(2d,2p)//BHandHLYP/6-311++G(2d,2p) level of theory. Their result is $k_{OH}(T) = 1.39 \times 10^{-11} \times \exp(-49/RT)$ cm^3 $molecule^{-1}$ s^{-1} and $k_{OH} = 5.20 \times 10^{-12}$ at 298 K;[15] they predict a *positive* Arrhenius activation energy. They also predict a branching ratio for the C-H_3 : CH_2 : N-H_2 abstractions of 0.004 : 0.977 : 0.019 at 298 K.

Murphy *et al.*[18] conducted one photo-oxidation experiment with $CH_3CH_2NH_2$ employing NO_2 as oxidant precursor to study organic aerosol formation. Particles formed in this experiment exclusively consisted of ethylammonium nitrate - the contribution from non-salt organics was negligible.

2.5 $(CH_3CH_2)_2NH$

Pitts *et al.*[20] carried out a study of the products formed when a mixture of 500 ppb $(CH_3CH_2)_2NH$ + 80 ppb NO + 160 ppb NO_2 was subjected to natural sunlight conditions. They found the following molar conversion yields (taking into account the number of ethyl groups): 30% CH_3CHO (acetaldehyde), 4% $CH_3CO(OO)NO_2$ (PAN), 32% $(CH_3CH_2)_2NNO_2$ (diethyl nitramine), 2.4% $CH_3CH_2NC(O)CH_3$ (*N*-ethyl acetamide), 1.4% $(CH_3CH_2)_2NCHO$ (*N,N*-diethyl formamide), and 0.2% $(CH_3CH_2)_2NC(O)CH_3$ (*N,N*-diethyl acetamide) in the gas phase. In the course of the experiment up to 290 ppbV O_3 and 60 μg m^{-3} aerosol was registered; small amounts of CH_3CONH_2 (acetamide) was found in the aerosol phase, which otherwise mainly consisted of nitrate. The mass balance reported was 46% for nitrogen and 69% for carbon. Pitts *et al.* also reported the formation of $(CH_3CH_2)_2NNO$ under dark, humid conditions when diethylamine was mixed with NO and NO_2 in air.

The rate constant for O_3 reaction with diethylamine has been reported to be $k_{O3} = (1.33 \pm 0.15) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[6]

In a recent investigation of the NO_3 radical initiated atmospheric oxidation of $(CH_3CH_2)_2NH$ Derek Price[8] suggests the following interpretation of the major PTR-MS ion signals $[MH]^+$: *m/z* 31, CH_2O (formaldehyde); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 47, HCOOH (formic acid and/or CH_3OH (ethanol); *m/z* 58, $CH_3CH_2NCH_2$ (ethyl-methyleneimine); *m/z* 60, $(CH_3)_3N$ (trimethylamine) and/or CH_3CH_2NO (nitrosoethane); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol); *m/z* 72, $CH_3CH_2NCHCH_3$ (ethyl-ethyleneimine); *m/z* 74, CH_3CH_2NHCHO (ethyl-formamide); *m/z* 88, $CH_3CH_2NHCH_2CHO$ (ethyl-acetamide); *m/z* 119, $(CH_3CH_2)_2NNO_2$ (diethyl-nitramine). There are some inconsistencies between the chemical formulae and the names given in the thesis, and there is no attempt to relate the compounds mentioned to any specific degradation mechanism. In the above the chemical formulas have been corrected to reflect the chemical names stated in the thesis.

Murphy *et al.*[18] reported rapid particle formation during photo-oxidation experiments with $(CH_3CH_2)_2NH$ and, similar to the oxidation of CH_3NH_2, that the aerosol formed mainly is nitrate salt. Yields of non-salt organic aerosol were negligible. Derek Price[8] analyzed the aerosol formed in the $(CH_3CH_2)_2NH/O_3/NOx$ oxidation experiments by HR-TOF-AMS. The major ion peaks observed of the aerosol included the amine backbone m/z 30.034 (CH_4N^+), m/z 44.050 ($C_2H_6N^+$), m/z 58.066 ($C_3H_8N^+$), m/z 86.099 ($C_5H_{12}N$+), and m/z 100.113 ($C_6H_{14}N$+). Higher mass oxidized fragments included m/z 191.084 ($C_6H_{11}N_2O_5^+$). The thesis offers no further interpretation of the results, but it is clear that extensive processing has taken place in the aerosol phase.

2.6 $(CH_3CH_2)_3N$

Pitts *et al.*[20] carried out a study of the products formed when a mixture of 500 ppb $(CH_3CH_2)_2NH$ + 80 ppb NO + 160 ppb NO_2 was subjected to natural sunlight conditions. They found the following molar conversion yields (taking into account the number of ethyl groups): 47% CH_3CHO (acetaldehyde), 5% $CH_3CO(OO)NO_2$ (PAN), 1.8% $(CH_3CH_2)_2NNO$ (diethylnitrosamine), 7.4% $(CH_3CH_2)_2NNO_2$ (diethylnitramine), 8.6% $(CH_3CH_2)_2NCHO$ (diethylformamide), 0.6% $(CH_3CH_2)_2NC(O)CH_3$ (diethylacetamide), 2.6% $CH_3CH_2NC(O)CH_3$ (*N*-ethyl acetamide), 2.4% "unknown amide-like compound with M=87", and trace amounts of $(CH_3CO)_2NH$ (diacetamide) in the gas phase. In the course of the experiment up to 260 ppbV O_3 and 370 $\mu g\ m^{-3}$ aerosol was registered The aerosol formed contained ca. 8.7 $\mu g\ m^{-3}$ CH_3CONH_2 (acetamide), 7.6 $\mu g\ m^{-3}$ $(CH_3CH_2)_2NOH$ (diethylhydroxylamine) and otherwise essentially only nitrate. The mass balance reported was 59% for nitrogen and 69% for carbon. Pitts *et al.*[7] reported a minor formation of $(CH_3CH_2)_2NNO$ under dark, humid conditions when triethylamine was mixed HONO, NO and NO_2 in air. The rate constant for O_3 reaction with diethylamine has been reported to be $k_{O3} = (8.20 \pm 1.01) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[6]

Murphy *et al.*[18] reported a 5% mass yield of non-salt aerosol during ozonolysis experiments and a 8% mass yield of non-salt aerosol during photo-oxidation experiments with $(CH_3CH_3)_3N$. A particulate phase compound with molecular weight of triethylamine-N-oxide was identified that previously had been detected by Angelino *et al.* [26] Murphy *et al.*[18] also studied the stability of the nitrate aerosol forming from $(CH_3CH_3)_3N$ relative to the stability of ammonium nitrate aerosol. They concluded that the stability of triethylammonium nitrate is close to that of ammonium nitrate. Erupe *et al.*[10] investigated the secondary organic aerosol formation from reaction of triethylamine with nitrate radicals, produced *in situ* by adding NO to a mixture of triethylamine with excess O_3 under dark condition, and followed the gas phase VOCs by PTR-MS. Their interpretation of the major ion masses $[MH]^+$ were as follows: *m/z* 31, HCHO (formaldehyde); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 47, HCOOH (formic acid) and/or CH_3OH (methanol); *m/z* 59, $(CH_3)_2CO$ (acetone) and/or CH_3CH_2CHO (propanal); *m/z* 60, CH_3CH_2NO (nitrosoethane); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol) ; *m/z* 72, $CH_3CH_2N{=}CHCH_3$ (ethylidine-ethanamine); *m/z* 74, CH_3CH_2NHCHO (ethyl formamide); *m/z* 76, $CH_3CH_2NO_2$ (nitroethane); *m/z* 102, $(CH_3CH_2)_3N$ (triethylamine); *m/z* 103, $(CH_3CH_2)NNO$ (diethylnitrosamine); *m/z* 116, $(CH_3CH_2)_2NC(O)CH_3$ (diethyl-acetamide); *m/z* 119, $(CH_3CH_2)_2NNO_2$, (diethylnitramine).

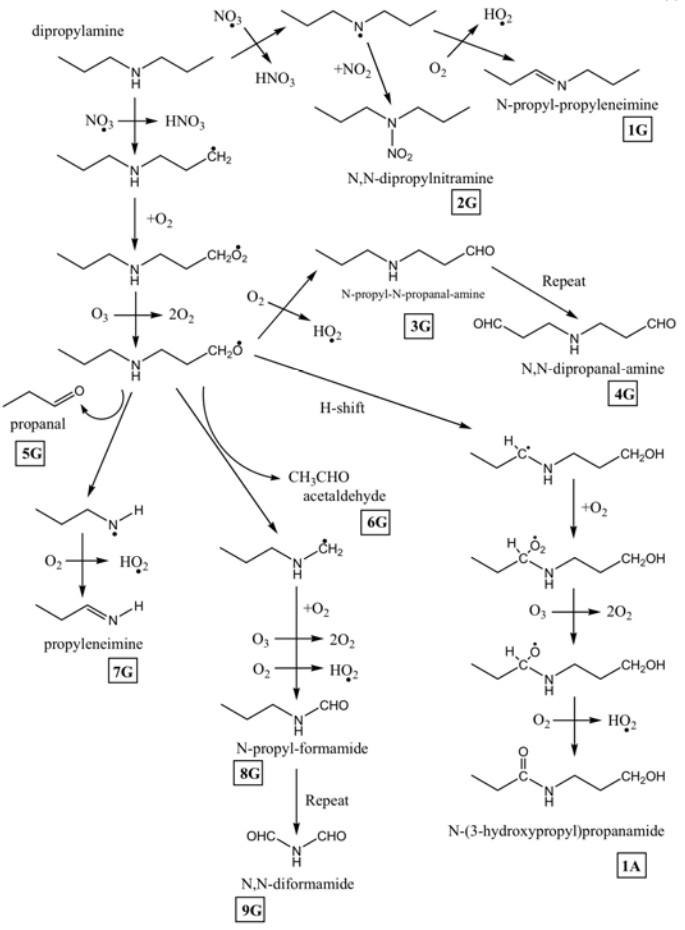
Erupe *et al.*[10] also reported ion peaks from the aerosol: low mass peaks include *m/z* 44.052 ($C_2H_6N^+$), *m/z* 58.065 ($C_3H_8N^+$), *m/z* 72.082 ($C_4H_{10}N^+$) and *m/z* 86.095 ($C_5H_{12}N^+$) that represent fragments from the amine back-bone. Other ions detected are *m/z* 72.046 ($C_3H_6NO^+$), *m/z* 86.068 ($C_4H_8NO^+$), *m/z* 102.05 ($C_4H_8NO_2^+$) and *m/z* 146.07 ($C_6H_{12}NO_3^+$). In each of these cases, one, two, or three oxygen atoms have been added representing oxidized amine fragments. Apart from a short burst shortly after NO injection, nitrate salt formation was generally minimal.

2.7 $(CH_3CH_2CH_2)_2NH$

In a recent investigation of the NO_3 radical initiated atmospheric oxidation of $(CH_3CH_2CH_2)_2NH$ Derek Price[8] suggests the following interpretation of the major PTR-MS ion signals $[MH]^+$: *m/z* 31, CH_2O (formaldehyde); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 58, $HNCHCH_2CH_3$ (propyleneimine); *m/z* 60, $(CH_3)_3N$ (trimethylamine) and/or CH_3CH_2NO (nitrosoethane); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol); *m/z* 74,

$HN(CHO)_2$ (diformamide) and/or $H_2NC(O)CH_2CH_3$ (propanamide); *m/z* 75, $CH_3CH_2CH_2CH_2OH$ (butanol); *m/z* 88, $CH_3CH_2CH_2NHCHO$ (propyl-formamide); *m/z* 100, $CH_3CH_2CH_2N{=}CHCH_2CH_3$ (propyl-propyleneimine); *m/z* 130, $HN(C(O)CH_2CH_3)_2$ (dipropanamide); *m/z* 130, $(CH_3CH_2CH_2)_2NNO_2$ (dipropyl-nitramine). There are some inconsistencies between the chemical formulae and the names given in the thesis, and there is no attempt to relate the compounds mentioned to any specific degradation mechanism. In the above the chemical formulas have been corrected to reflect the chemical names stated in the thesis.

The observed gas phase products and the aerosol composition were rationalized in terms of the suggested reaction pathways shown in Scheme 2.7.



Scheme 2.7. Proposed amine/Ozone/NOx reaction pathways with dipropylamine as the initial amine. G = gas phase, A = aerosol phase. (From Price, Ref. 8).

2.8 $(CH_3CH_2CH_2CH_2)_2NH$

In a recent investigation of the NO_3 radical initiated atmospheric oxidation of $(CH_3CH_2CH_2CH_2)_2NH$ (DPA) Derek Price[8] suggests the following interpretation of the major PTR-MS ion signals $[MH]^+$: *m/z* 31, CH_2O (formaldehyde); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 47, HCOOH (formic acid and/or CH_3OH (ethanol); *m/z* 55, $CH_2CHCHCH_2$ (1,3-butadiene); *m/z* 59, $(CH_3)_2CO$ (acetone) and/or CH_3CH_2CHO (propanal); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol); *m/z* 73, $CH_3CH_2CH_2CHO$ (butanal); *m/z* 74, CH_3CH_2NHCHO (ethyl-formamide) and/or $H_2NC(O)CH_2CH_3$ (propanamide); *m/z* 88, $H_2NC(O)CH_2CH_2CH_3$ (butanamide); *m/z* 100, $CH_3CH_2CH_2N{=}CHCH_2CH_3$ (propyl-propyleneimine); *m/z* 102, $CH_3CH_2CH_2NHCHO$ (butyl-formamide) and/or

$CH_3CH_2NHCH_2CH_2CH_2CH_3$ (*N*-ethyl-butylamine). There are some inconsistencies between the chemical formulae and the names given in the thesis, and there is no attempt to relate the compounds mentioned to any specific degradation mechanism. In the above the chemical formulas have been corrected to reflect the chemical names stated in the thesis.

The major ion fragment peaks observed during the DPA reaction can be seen in the HR-TOF-AMS includes the amine backbone fragments (*m/z* 30.034, *m/z* 44.050, *m/z* 58.066, *m/z* 86.099, and *m/z* 100.113). Higher mass fragment ions include *m/z* 114.096 ($C_6H_{12}NO^+$), *m/z* 130.091 ($C_6H_{12}NO_2^+$), and 146.082 ($C_6H_{12}NO_3^+$). These represent fragments that have been oxidized by one, two, or three oxygen atoms. These fragment patterns were observed in the tertiary amine experiments, and are most likely formed by the isomerization of an amino-alkoxy radical to form hydroxyl-substituted amides. These amides were not detected in the gas phase by the PTR-MS as they have very low vapour pressures. Also observed was a higher mass oxidized fragment at *m/z* 191.07 ($C_6H_{11}N_2O_5^+$).

2.9 $(CH_3CH_2CH_2CH_2)_3NH$

Erupe *et al.*[10] investigated the secondary organic aerosol formation from reaction of tributhylamine with nitrate radicals, produced *in situ* by adding NO to a mixture of tributhylamine with excess O_3 under dark condition, and followed the gas phase VOCs by PTR-MS. Their interpretation of the major ion masses $[MH]^+$ were as follows: *m/z* 31, HCHO (formaldehyde); *m/z* 45, CH_3CHO (acetaldehyde); *m/z* 47, HCOOH (formic acid) and/or CH_3OH (methanol); *m/z* 59, $(CH_3)_2CO$ (acetone) and/or CH_3CH_2CHO (propanal); *m/z* 61, CH_3COOH (acetic acid) and/or $CH_3CH_2CH_2OH$ (propanol); *m/z* 73, $CH_3CH_2CH_2CHO$ (butanal); *m/z* 74, $CH_3CH_2CH_2CH_2OH$ (butanol); *m/z* 100, $CH_3CH_2CH_2CH_2NO_2$ (nitro-buthane); *m/z* 128, $C_4H_9N{=}CHCH_2CH_2CH_3$ (butylimine); *m/z* 159, $(C_4H_9)_2NNO$ (dibuthyl-nitrosamine); *m/z* 175, $(C_4H_9)_2NNO_2$ (dibuthylnitramine); *m/z* 189, $(C_4H_9)_3N$ (tributylamine); *m/z* 200, $(C_4H_9)_2NC(O)CH_2CH_2CH_3$ (dibutylbutanamide).

Erupe *et al.*[10] also reported ion peaks in the AMS mass of the aerosol: high intensity ion peaks were detected at *m/z* 44.052 ($C_2H_6N^+$), *m/z* 58.065 ($C_3H_8N^+$), *m/z* 72.082 ($C_4H_{10}N^+$), *m/z* 86.095 ($C_5H_{12}N^+$) and *m/z* 126 ($C_8H_{16}N^+$). The oxygenated fragments from TBA reaction were m/z 100 ($C_5H_{10}NO^+$), *m/z* 142 ($C_8H_{16}NO^+$), *m/z* 174 ($C_8H_{16}NO_3^+$) and *m/z* 230 ($C_{12}H_{24}NO_3^+$).

2.10 $(CH_3CH_2)_2NOH$

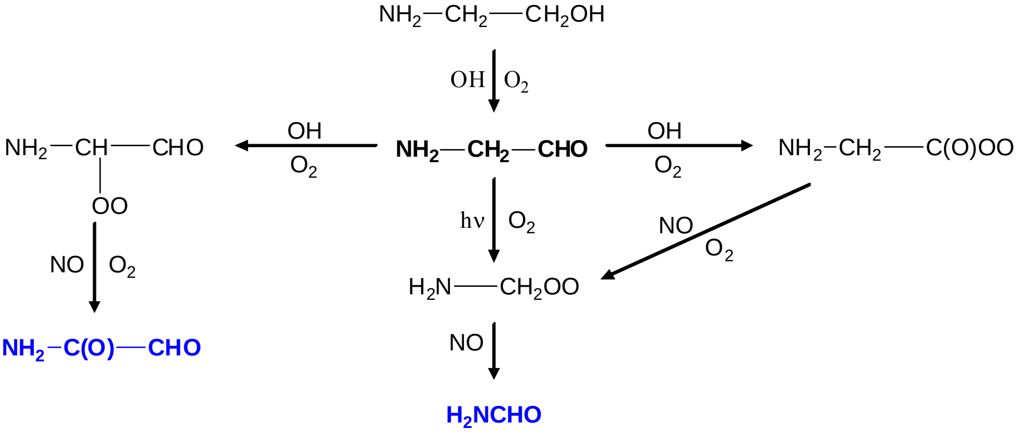
Gorse *et al.*[27] generated OH radicals by pulse radiolysis of H_2O and determined the rate constant for the reaction of OH radicals with $(CH_3CH_2)_2NOH$ by following the OH pseudo first order decay by optical absorption spectrometry. The reaction is extremely fast, $kOH = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 308 K. There are no data on the products formed in the photo-oxidation of $(CH_3CH_2)_2NOH$.

2.11 $NH_2CH_2CH_2OH$ - MEA

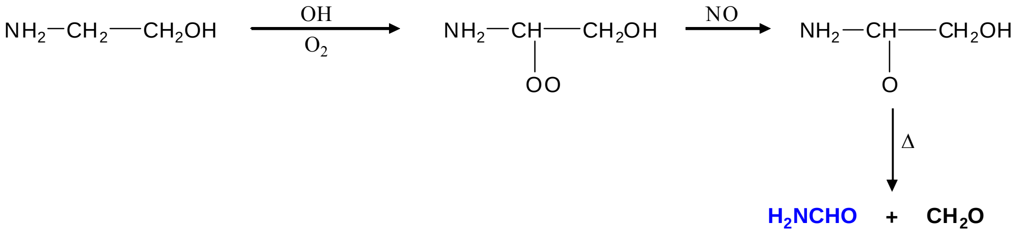
The ADA-2009 project reported results from atmospheric gas phase photo-oxidation of 2-aminoethanol ($NH_2CH_2CH_2OH$, MEA) at the European Photochemical Reactor, EUPHORE, in Valencia, Spain.[7] The photo-oxidation was monitored in situ by FT-IR and on-line by PTR-TOF-MS, and samples were collected on various adsorbents for subsequent off-line analysis. The formation of particles was monitored by SMPS and AMS on-line instruments and filter sampling followed by analysis with LC/HRMS(TOF). All major photo-oxidation products were identified and quantified, and limits to the branching ratios in the initial H-abstraction reaction obtained. Based on the results from on-line and in situ instrumentation it is found that more than 80 % of the reaction between MEA and OH radicals takes place at $–CH_2–$, while less than 10 % occurs at $-NH_2$, and less than 10 % at $–CH_2OH$. The major products (>80 %) in the photo-oxidation are formamide (NH_2CHO) and formaldehyde (CH_2O), of which the latter has a short atmospheric lifetime. Minor products (<10 %) are the short-lived amino acetaldehyde (NH_2CH_2CHO) and the longer lived 2-oxo acetamide ($NH_2C(O)CHO$).

The MEA-nitrosamine, $ONNHCH_2CH_2OH$, was not detected in any of the experiments. The nitramine, $O_2NNHCH_2CH_2OH$, was confirmed as product in the experiments. The yield depends upon the mixing ratio of NOx. For rural regions with NOx levels of 0.2-10 ppbV, less that 3 ‰ of emitted MEA will end up as the nitramine.

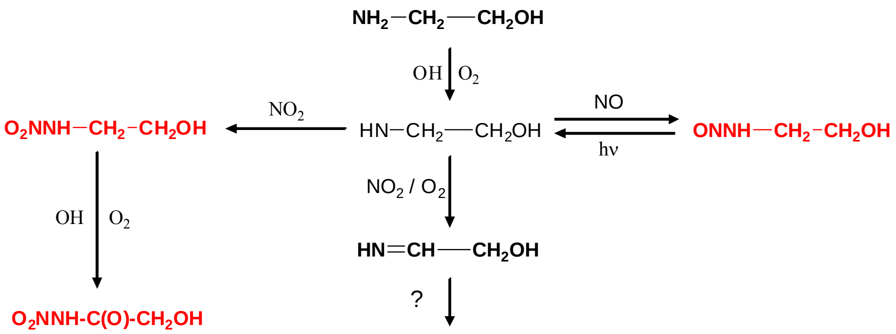
The photo-oxidation of MEA was found to give rise to ozone and significant formation of particles. Aerosols were formed immediately after the exposure of the chamber to sunlight; simulations of the chamber experiments show that, depending on the initial conditions, between 20 and 50 % of MEA removal from the gas-phase is due to reaction with OH radicals, between 10 and 40 % is converted into particle mass (gas-to-particle conversion) during the photo-oxidation experiments, while the remaining 30 to 70 % of the initial MEA amount is lost to the walls or by dilution through replenishment flow. The theoretical photo-oxidation schemes from Bråthen *et al.*[5] were modified to concord with the experimental observations, see Schemes 2.8-2.10.



Scheme 2.8. Atmospheric photo-oxidation of MEA following hydrogen abstraction from the $-CH_2OH$ group. (From Nielsen *et al.*, Ref. 7).



Scheme 2.9. Atmospheric photo-oxidation of MEA following hydrogen abstraction from the $-CH_2-$ group. (From Nielsen *et al.*, Ref. 7).



Scheme 2.10. Atmospheric photo-oxidation of MEA following hydrogen abstraction from the $-NH_2$ group. (From Nielsen *et al.*, Ref. 7).

2.12 $(CH_3)_2NCH_2CH_2OH$

Harris and Pitts[28] determined the rate constant for the reaction of OH radicals with $(CH_3)_2NCH_2CH_2OH$ (DMAE) to be $k_{OH} = (4.7 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H_2O. Anderson and Stephens[29] investigated the temperature dependence of the rate of the reaction over the temperature range 234-364 K by the same method and found that the reaction proceeds essentially with no temperature dependence. Their room temperature rate constant was $k_{OH} = (10.3 \pm 2.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and they suggest a value of $k_{OH} = (9.0 \pm 2.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} will best describe the reaction over the entire temperature range. The two room temperature determinations, however, differ by a factor of 2. No explanation to this discrepancy is offered by the authors. Anderson and Stephens[29] apportioned the reactivity of OH radicals with DMAE such that 55 % of the H atom abstraction will occur from the methyl hydrogens, while about 35 % occurs from the methylene hydrogens next to the amine N. The remaining 10 % of the OH radical reactivity is expected to occur away from the amine N. They suggest the following main reactions to occur at atmospheric conditions:

$$\begin{array}{rcll}
(CH_3)_2NCH_2CH_2OH + OH & \rightarrow & (CH_3)_2NCHCH_2OH + H_2O\ \ (35\%) & (3)\\
 & \rightarrow & (CH_3)(CH_2)NCH_2CH_2OH + H_2O\ \ (55\%) & (4)\\
(CH_3)_2NCHCH_2OH + O_2 & \rightarrow & (CH_3)_2NCH(OO)CH_2OH & (5)\\
(CH_3)_2NCH(OO)CH_2OH + NO & \rightarrow & (CH_3)_2NCH(O)CH_2OH + NO_2 & (6)\\
(CH_3)_2NCH(O)CH_2OH & \rightarrow & (CH_3)_2NCHO + CH_2OH & (7)\\
 & \rightarrow & (CH_3)_2N + CHOCH_2OH & (8)\\
(CH_3)_2NCH(O)CH_2OH + O_2 & \rightarrow & (CH_3)_2NC(O)CH_2OH + HO_2 & (9)
\end{array}$$

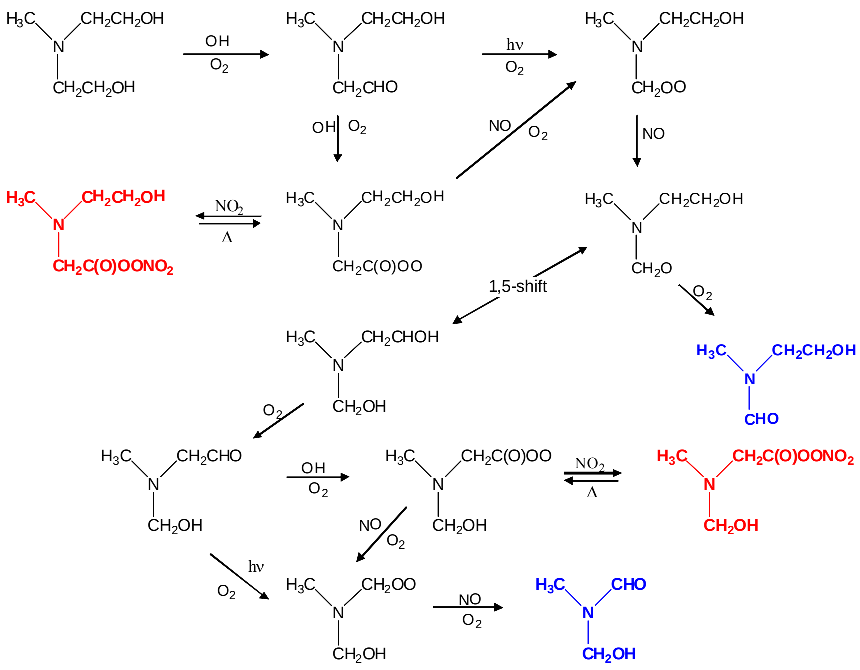
The dimethyl amino radical formed in (8) will subsequently lead to the formation of dimethylnitrosamine and dimethylnitramine.

Tuazon *et al.*[13] have determined the rate constant for reaction of DMAE with O_3 to be $k_{O3} = (6.76 \pm 0.83) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K. They observed CH_2O in a yield of 30-45% and an unidentified amide, tentatively assigned to be $(CH_3)_2NC(O)CH_2OH$.

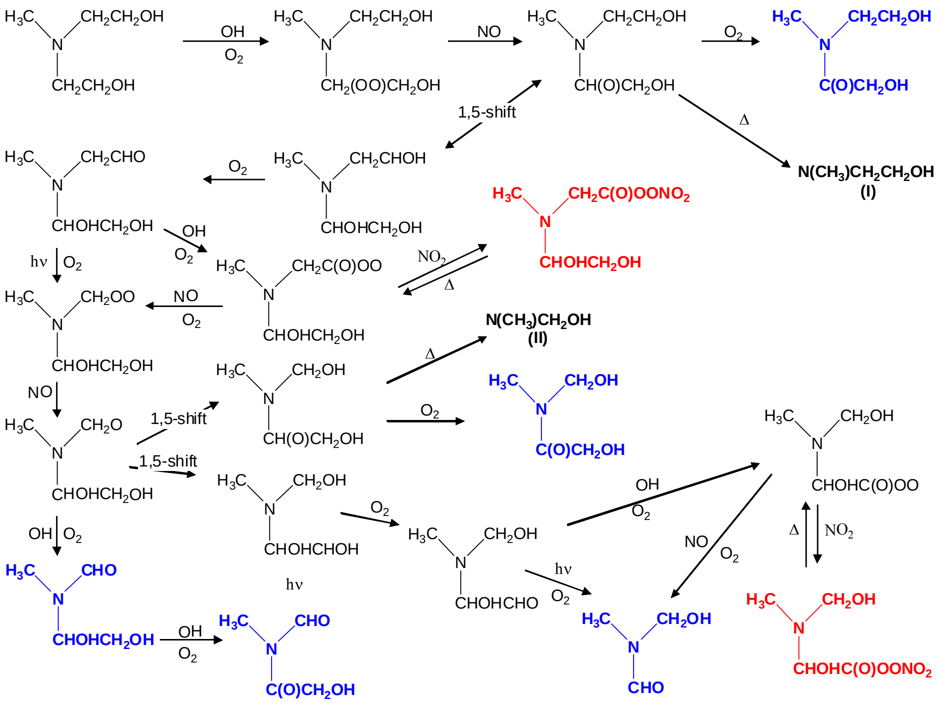
2.13 $CH_3N(CH_2CH_2OH)_2$ - MDEA

There are no experimental data for the atmospheric photo-oxidation of MDEA. The only information available stems from Bråthen *et al.*[5] who derived at theoretical scheme for the OH initiated photo-oxidation, Schemes 2.11-2.13. For the sake of brevity, the further atmospheric reactions of the N-centered radicals $N(CH_3)CH_2CH_2OH$ (I) and $N(CH_3)CH_2OH$

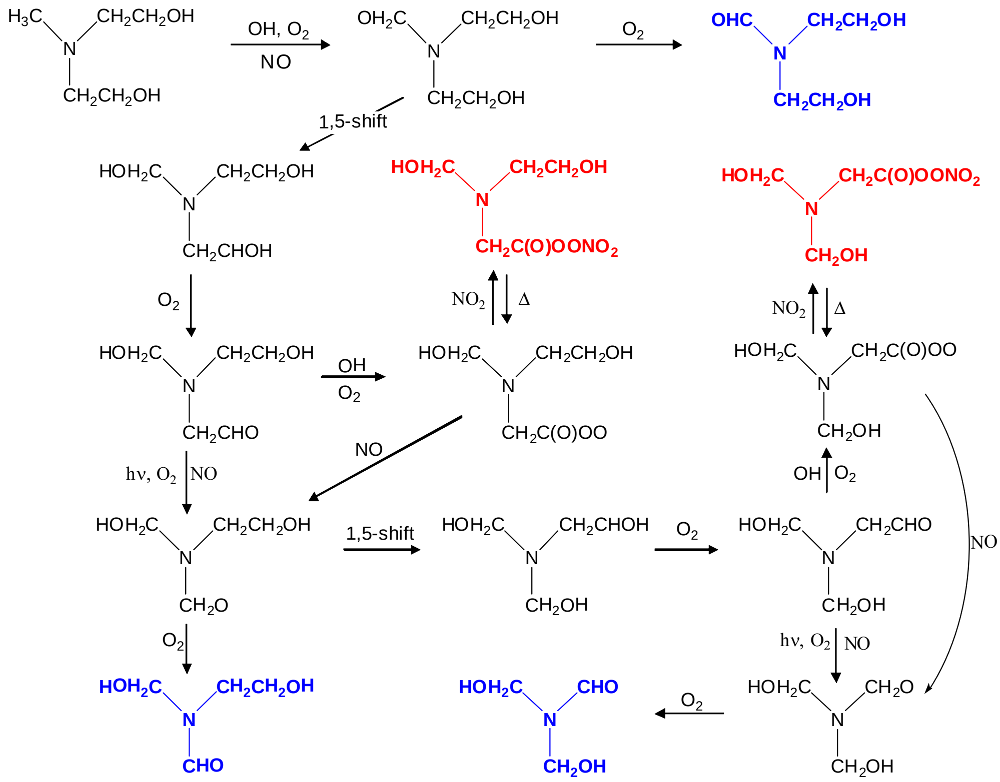
(II) in Scheme 2.12 are are not included in the present text; the reader should consult Bråthen *et al.*[5] for further details.



Scheme 2.11. The main routes to the atmospheric degradation of $CH_3N(CH_2CH_2OH)_2$ (MDEA) following initial hydrogen abstraction from one of the $–CH_2OH$ groups. (From Bråthen *et al.*, Ref. 5).



Scheme 2.12. The main routes to the atmospheric degradation of $CH_3N(CH_2CH_2OH)_2$ (MDEA) following initial hydrogen abstraction from one of the $–CH_2-(CH_2OH)$ groups. (From Bråthen *et al.*, Ref. 5).



Scheme 2.13. The main routes to the atmospheric degradation of $CH_3N(CH_2CH_2OH)_2$ (MDEA) following initial hydrogen abstraction from the CH_3–group. (From Bråthen *et al.*, Ref. 5).

2.14 $(CH_3)_2C(NH_2)CH_2OH$ - AMP

Harris and Pitts[28] determined the rate constant for the reaction of OH radicals with AMP to be $k_{OH} = (2.8 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H_2O. The authors suggest that the AMP reaction with OH radicals most likely will proceed by H-abstraction from the primary amino group followed either by reaction with NO_2 to give the nitramine or, alternatively, by C-C bond scission:

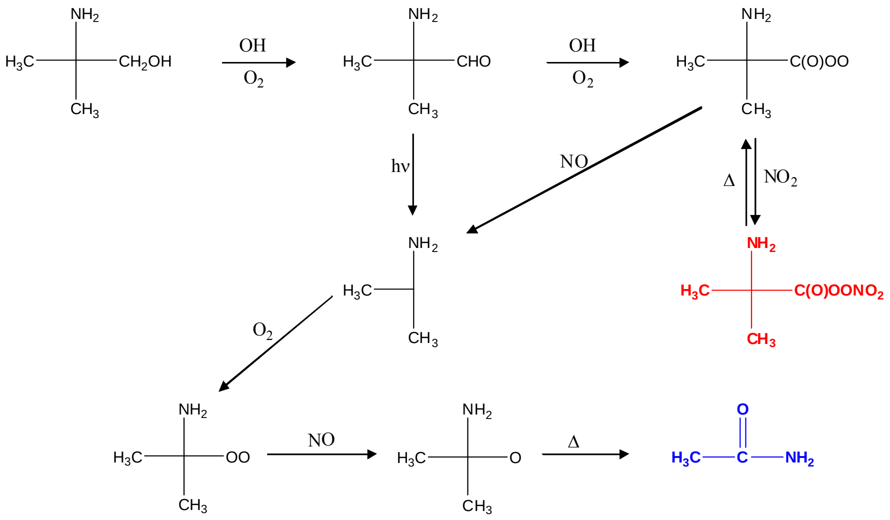
$$(CH_3)_2C(NH_2)CH_2OH + OH \rightarrow (CH_3)_2C(NH)CH_2OH + H_2O \quad (10)$$

$$(CH_3)_2C(NH)CH_2OH + NO_2 \rightarrow (CH_3)_2C(CH_2OH)NHNO_2 \quad (11)$$

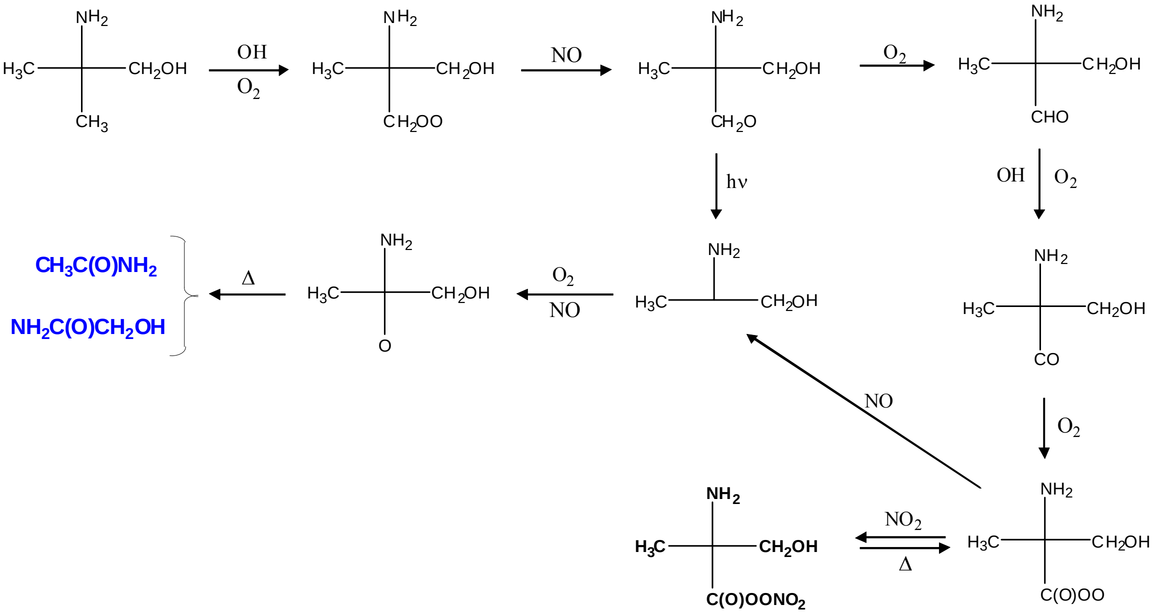
$$(CH_3)_2C(NH)CH_2OH \rightarrow CH_3C(CH_2OH){=}NH + CH_3 \quad (12)$$

$$\rightarrow (CH_3)_2C{=}NH + CH_2OH \quad (13)$$

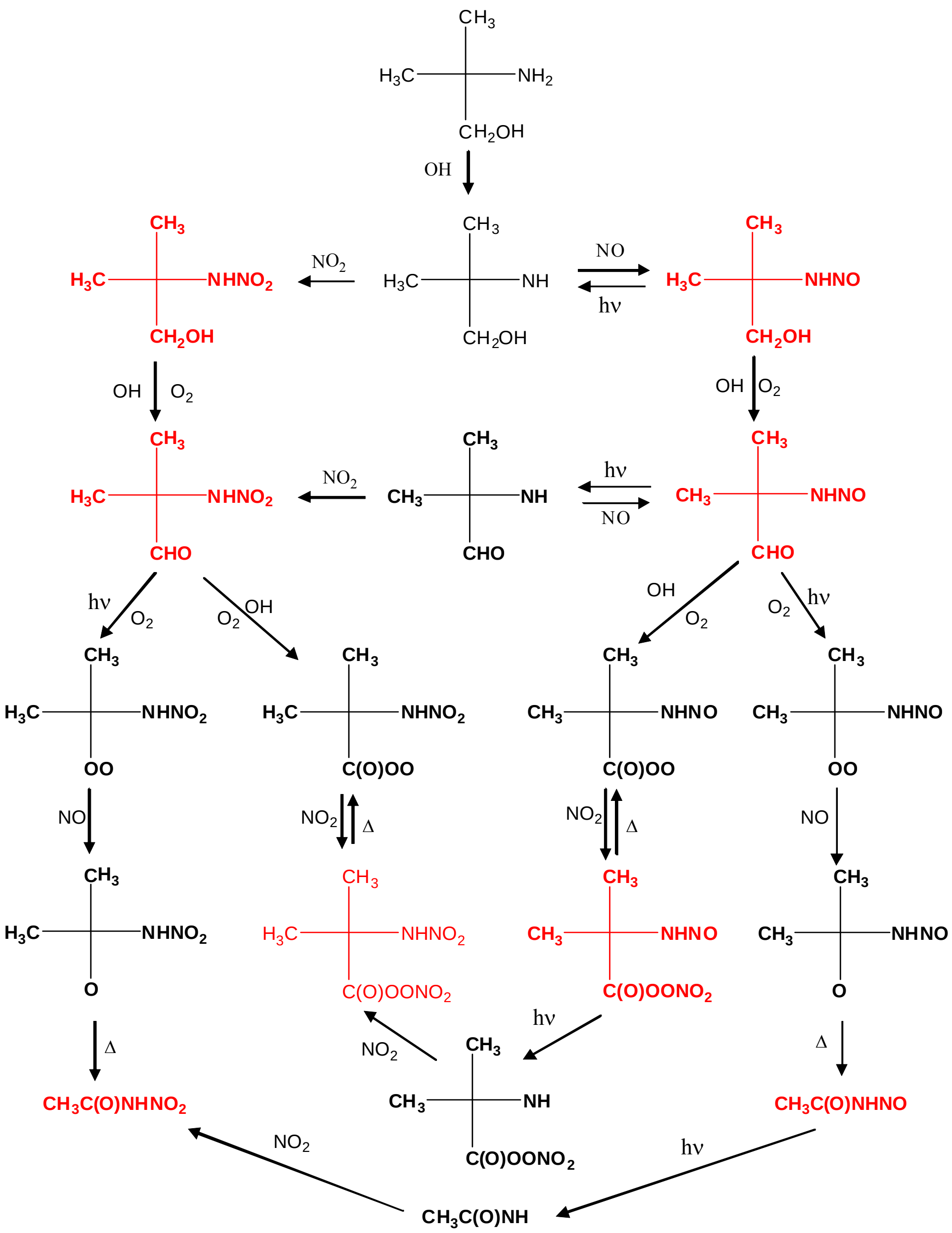
Bråthen *et al.*[5] derived theoretical schemes for the OH initiated photo-oxidation of AMP, Schemes 2.14-2.16.



Scheme 2.14. The main atmospheric degradation routes of $(CH_3)_2C(NH_2)CH_2OH$ (AMP) following initial hydrogen abstraction from the CH_2-group. (From Bråthen *et al.*, Ref. 5).



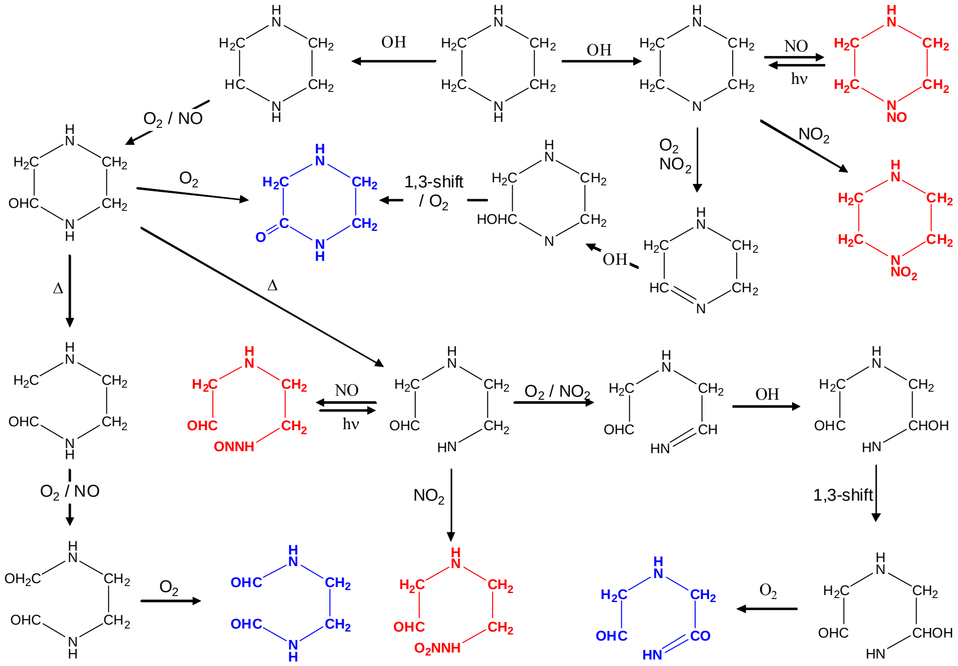
Scheme 2.15. The main atmospheric degradation routes of $(CH_3)_2C(NH_2)CH_2OH$ (AMP) following initial hydrogen abstraction from the CH_3-group. (From Bråthen *et al.*, Ref. 5).



Scheme 2.16. The main atmospheric degradation routes of $(CH_3)_2C(NH_2)CH_2OH$ (AMP) following initial hydrogen abstraction from the NH_2-group. (From Bråthen *et al.*, Ref. 5).

2.15 $HN(CH_2CH_2)_2NH$ - PZ

There are no experimental data available for the gas phase photo-oxidation of piperazine. The only public available atmospheric photo-oxidation scheme for piparazine stems from the teoretical work reported by Bråthen *et al.*, [5] see Scheme 2.17.



Scheme 2.17. The main atmospheric degradation routes of $HN(CH_2CH_2)_2NH$ (PZ) (From Bråthen *et al.*, Ref. 5).

2.16 $(CH_3)_3CNH_2$

Koch *et al.*[30] determined the rate constant for the reaction of OH radicals with $(CH_3)_3CNH_2$ by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N_2O (ArF excimer laser at 193 nm) followed by $O(^1D)+H_2O \rightarrow 2\ OH$. The OH pseudo first order decay was followed by resonance fluorescence. They found $k_{OH} = (1.2 \pm 0.1) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ and at 298 K, and a *negative* Arrhenius activation energy $E_a/R = (-230 \pm 100)$ K. No products of the reaction were reported.

2.17 $CF_3CH_2NH_2$

Koch *et al.*[30] determined the rate constant for the reaction of OH radicals with $CF_3CH_2NH_2$ at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N_2O (ArF excimer laser at 193 nm) followed by $O(^1D)+H_2O \rightarrow 2\ OH$. The OH pseudo first order decay was followed by resonance fluorescence. They found $k_{OH} = (0.9 \pm 0.2) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ and at 298 K, and a positive Arrhenius activation energy $E_a/R = (+450 \pm 150)$ K. No products of the reaction were reported.

2.18 $N(CH_2CH_2)_3N$

Koch *et al.*[30] determined the rate constant for the reaction of OH radicals with $N(CH_2CH_2)_3N$ at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N_2O (ArF excimer laser at 193 nm) followed by $O(^1D)+H_2O \rightarrow 2$ OH. The OH pseudo first order decay was followed by resonance fluorescence. They found $k_{OH} = (2.2 \pm 0.2) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ and at 298 K, and a *negative* Arrhenius activation energy $E_a/R = (-150 \pm 100)$ K. No products of the reaction were reported.

3 Summary of the present knowledge about atmospheric gas phase chemistry of amines

The amine reactions with OH radicals are fast, with room-temperature rate constants being in the range ~10^{-11} cm^3 $molecule^{-1}$ s^{-1}, Table 3.1. The corresponding O_3 reactions are slower, but these reactions may, however, be relevant under extreme conditions.

The *average global lifetimes* of amines with respect to reaction with OH radicals will therefore be of the order of one day or less. The atmospheric lifetimes of amines in the Mongstad area will be addressed in section 9.

Table 3.1. Summary of experimental rate constants at 295-300 K (/cm^3 $molecule^{-1}$ s^{-1}) for the reactions of OH radicals and O_3 with amines.

Compound	k_{OH}	Ref.	k_{O3}	Ref.
CH_3NH_2	$(2.20 \pm 0.22) \times 10^{-11}$	11	$(7.4 \pm 2.4) \times 10^{-21}$	13
	$(1.73 \pm 0.11) \times 10^{-11}$	12		
$(CH_3)_2NH$	$(6.54 \pm 0.66) \times 10^{-11}$	19	$(1.67 \pm 0.20) \times 10^{-18}$	13
	$(6.49 \pm 0.64) \times 10^{-11}$	12		
$(CH_3)_3N$	$(6.09 \pm 0.61) \times 10^{-11}$	19	$(7.84 \pm 0.87) \times 10^{-18}$	13
	$(3.58 \pm 0.22) \times 10^{-11}$	12		
$CH_3CH_2NH_2$	$(2.77 \pm 0.28) \times 10^{-11}$	19		
	$(2.38+0.5/-0.15) \times 10^{-11}$	12		
$(CH_3CH_2)_2NH$			$(1.33 \pm 0.15) \times 10^{-17}$	6
$(CH_3CH_2)_3N$			$(8.20 \pm 1.01) \times 10^{-17}$	6
$(CH_3CH_2)_2NOH$	1.0×10^{-10}	27		
$(CH_3)_2NCH_2CH_2OH$	$(4.7 \pm 1.2) \times 10^{-11}$	28	$(6.76 \pm 0.83) \times 10^{-18}$	13
	$(9.0 \pm 2.0) \times 10^{-11}$	29		
$(CH_3)_2C(NH_2)CH_2OH$	$(2.8 \pm 0.5) \times 10^{-11}$	28		
$(CH_3)_3CNH_2$	1.2×10^{-11}	30		
$CF_3CH_2NH_2$	0.9×10^{-12}	30		
$N(CH_2CH_2)_3N$	2.2×10^{-11}	30		

There are only two experimental reports on the branching ratio in the initial OH reaction with amines – dimethylamine[25] and MEA.[7] The initial amine reaction with OH radicals constitutes the rate-limiting step in the formation of nitrosamines, nitramines and imines. The branching ratios in these reactions are addressed in section 4.4.

There are no experimental kinetic data for the reactions of Cl atoms and NO_3 radicals with amines. There is, however, an unfortunate misunderstanding in the literature relating to a study by Aschmann and Atkinson,[31] who presented kinetic data for the reaction of NO_3 with *N*-methyl-2- pyrrolidinone. *N*-methyl-2-pyrrolidinone is not an amine, but a cyclic amide (5-membered lactam structure).

The two aerosol formation studies in which NO_3 radicals were used to initiate the degradation of amines[10,8] show many of the same types of products as found in the OH-initiated photo-oxidation studies, *i.e.* amides, nitrosamines and nitramines. It can be concluded that the nighttime gas phase degradation of amines will result in the same compounds as the daytime photo-oxidation. However, the relative amounts of the different products may be different.

The NO_3 radical is not a gas phase nitrosation agent. It reacts with saturated compounds through H-abstraction, forming nitric acid, and with unsaturated compounds through addition, see e.g. the reviews by Atkinson[32] and by Wayne *et al.*[33]

4 Summary of the present knowledge about the atmospheric chemistry of amine photo-oxidation products

4.1 Amides

Amides are found as major products in the gas phase amine oxidation; Table 4.1 summarizes the amides reported in the various experiments.

Table 4.1. Amides reported as products in amine gas phase oxidation.

Parent amine	Oxidant	Amides reported		Ref.
		Gas phase	Aerosol	
$(CH_3)_2NH$	OH	CH_3NHCHO		20
$(CH_3)_2NH$	O_3	CH_3NHCHO		13
$(CH_3)_3N$	OH	$(CH_3)_2NCHO$	$CHONH_2$ $CH_3N(CHO)_2$	20
$(CH_3)_3N$	O_3	$(CH_3)_2NCHO$		13
$(CH_3)_3N$	O_3/NO	$(CH_3)_2NCHO$ $CH_3N(CHO)_2$ $CH_2OH(CH_3)NCHO$ $(CHO)_3N$		10
$(CH_3CH_2)_2NH$	OH	$CH_3CH_2NC(O)CH_3$ $(CH_3CH_2)_2NCHO$ $(CH_3CH_2)_2NC(O)CH_3$	$CH_3C(O)NH_2$	20
$(CH_3CH_2)_2NH$	O_3/NOx	CH_3CH_2NHCHO $CH_3CH_2NHC(O)CH_3$		8
$(CH_3CH_2)_3N$	OH	$(CH_3CH_2)_2NCHO$ $(CH_3CH_2)_2NC(O)CH_3$ $CH_3CH_2NC(O)CH_3$ $(CH_3CO)_2NH$	$CH_3C(O)NH_2$	20
$(CH_3CH_2)_3N$	O_3/NOx	CH_3CH_2NHCHO $(CH_3CH_2)_2NC(O)CH_3$		10
$(CH_3CH_2CH_2)_2NH$	O_3/NOx	$(CHO)_2NH$ $CH_3CH_2C(O)NH_2$ $CH_3CH_2CH_2NHCHO$ $(CH_3CH_2C(O))_2NH$		8
$(CH_3CH_2CH_2CH_2)_2NH$	O_3/NOx	CH_3CH_2NHCHO $CH_3CH_2C(O)NH_2$ $CH_3CH_2CH_2C(O)NH_2$ $CH_3CH_2CH_2NHCHO$		8
$(CH_3CH_2CH_2CH_2)_3N$	O_3/NOx	$(C_4H_9)_2NC(O)CH_2CH_2CH_3$		10
$NH_2CH_2CH_2OH$	OH	NH_2CHO $NH_2C(O)CHO$		7
$(CH_3)_2NCH_2CH_2OH$	O_3	$(CH_3)_2NC(O)CH_2OH$		13

Amides do not absorb light in the actinic region and will therefore not undergo photolysis in the troposphere.

There are three kinetic studies of OH radical reactions with amides. Koch *et al.*[34] studied 4 amides with the aim of testing/extending a commonly used structure-activity relationship (SAR)[3] for prediction of OH rate constants. The reactions were found to show *negative* Arrhenius temperature dependencies and to conflict with the SAR predictions. Solignac *et al.*[35] studied the OH and Cl reaction kinetics of 3 amides; the results support that the reactivity of amides deviate from the SAR predictions. Finally, Aschmann and Atkinson[31] studied the reactions of 1-methyl-2-pyrolidone at 296 K and proposed a scheme for the reactions.

There are two kinetic studies of NO_3 radical reaction with amides. Aschmann and Atkinson[31] studied the reactions of 1-methyl-2-pyrolidone at 296 K, Dib and Chakir[36] studied the temperature dependence of the NO_3 reaction with 4 amides. The available kinetic results are summarized in Table 3.2.

The amide-OH reactions are relatively fast, and the *average global lifetimes* of amides with respect to reaction with OH radicals will be of the order of a few days. Although the reactions of amides with Cl atoms are faster that the corresponding OH reactions, the average global atmospheric concentration of OH radicals is so much higher than that of Cl atoms that the atmospheric amide loss is dominated by OH reactions. The atmospheric lifetimes of amines in the Mongstad area will be addressed in section 9.

There is only one report in the open literature of products in the reactions between OH radicals and amides; Aschmann and Atkinson[31] report the formation of N-methylsuccinimide and 1-formyl-2-pyrrolidinone from the OH reaction with 1-methyl-2-pyrrolidinone and essentially only 1-formyl-2-pyrrolidinone from the NO_3 reaction. Unpublished results by Geraldine Solignac[37] show $HN(CHO)_2$, CH_3NCO and $CH_3NHC(O)OONO_2$ in the photo-oxidation of CH_3NHCHO, and $CH_3N(CHO)_2$ and $(CH_3)_2NC(O)OONO_2$ in the photo-oxidation of $(CH_3)_2NCHO$.

Table 4.2. Rate constants at 298-300 K (/cm^3 molecule^{-1} s^{-1}) and activation energies (/K) for the reaction of OH radicals with amides.

Compound	k_{OH} /10^{-11}	E$_a$/R	k_{Cl} /10^{-11}	k_{NO3} /10^{-14}	E$_a$/R
$CH_3NHC(O)CH_3$	0.52 [a]	-490			
$CH_3NHC(O)CH_2CH_3$	0.76 [a]	-400			
$(CH_3)_2NC(O)CH_3$	1.36 [a] 1.9 ± 0.3 [b]	-630	25 ± 4 [b]	4.9 ± 1.8 [d]	1900 ± 200 [d]
$(CH_3)_2NC(O)CH_2CH_3$	2.07 [a]	-530		1.6 ± 4 [d]	2700 ± 300 [d]
CH_3NHCHO	0.86 ± 0.24 [b]		9.7 ± 1.7 [b]		
$(CH_3)_2NCHO$	1.4 ± 0.3 [b]		19 ± 3 [b]	4.5 ± 1.1 [d]	1600 ± 300 [d]
1-Methyl-2-pyrrolidinone	2.15 ± 0.36 [c]			12.6 ± 0.4 [c] 16.6 ± 1.1 [d]	1500 ± 100 [d]

[a] From Koch *et al.*, Ref. 34. [b] From Solignac *et al.*, Ref. 35. [c] From Aschmann and Atkinson, Ref. 31. [c] From Dib and Chakir, Ref 36.

4.2 Aldehydes

Aldehydes, such as HCHO (formaldehyde) and CH_3CHO (acetaldehyde), are also among the major products reported in gas phase amine photo-oxidation experiments. The react fast with OH radicals, and in addition they undergo photolysis. The atmospheric chemistry of this class of compounds, including their reactions with Cl atoms and NO_3 radicals, is well established and detailed reaction schemes are included in MCM.[4] Table 4.3 summarizes the recommended rate constants at 298 K for the reactions HCHO, CH_3CHO and CH_3CH_2CHO with OH, Cl, NO_3 and O_3.

Table 4.3. Recommended rate constants at 298 K (/cm^3 molecule^{-1} s^{-1}) for the reactions of OH, Cl, NO_3 and O_3 with simple aldehydes.

Compound	k_{OH} [a]	k_{Cl} [a]	k_{NO3} [a]	k_{O3}
HCHO	8.5×10^{-12}	7.2×10^{-11}	5.5×10^{-16}	2.1×10^{-24} [b]
CH_3CHO	1.5×10^{-11}	8.0×10^{-11}	2.7×10^{-15}	6.0×10^{-21} [c]
CH_3CH_2CHO	1.9×10^{-11}	1.3×10^{-10}	6.3×10^{-15}	No data

[a]From Ref. 38. [b]From Ref. 39. [c]From Ref. 40.

4.3 Imines

Imines, $R_1N{=}CR_2R_3$, are reported as major products in amine gas phase photo-oxidation experiments. There are no experimental data available for the gas phase reactions of imines. They are, however, known to hydrolyse in aqueous solution resulting in amines and carbonyle compounds:[41]

$$R_1N{=}CR_2R_3 + H_2O(l) \quad \rightarrow \quad R_1NH_2 + R_2R_3CO \qquad (14)$$

4.4 Nitrosamines and nitramines

Experiments show that the atmospheric oxidation of secondary and tertiary amines results in the formation on photo-labile *N*-nitroso amines (nitrosamines) and photo-stable *N*-nitro amines (nitramines). There are no reports of nitrosamines being formed in the gas phase from primary amines. Tuazon *et al.*[42] studied the reactions of OH radicals with $(CH_3)_2NNO$ (NDMA) and $(CH_3)_2NNO_2$ (DMN) by long-path FTIR employing CH_3OCH_3 as reference and found $k_{OH+NDMA}/k_{OH+CH3OCH3} = 0.85 \pm 0.05$ and $k_{OH+DMN}/k_{OH+CH3OCH3} = 1.29 \pm 0.05$. Taking todays recommended absolute value for $k_{OH+CH3OCH3} = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K,[43] places $k_{OH+NDMA} = (2.4 \pm 0.4) \times 10^{-12}$ and $k_{OH+DMN} = (3.6 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Later Zabarnick *et al.*[44] reported a 50% higher rate constant for dimethylnitrosamine reaction with OH radicalsfrom experiments employing the two-laser photolysis/LIF probe technique, $k_{OH+NDMA} = (3.6 \pm 0.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K. The average global atmospheric lifetimes of NMDA and DMN with respect to reaction with OH are of the order of days. The atmospheric lifetimes of nitrosamines and nitramines with respect to reaction with OH in the Mongstad area will be addressed in section 9.

The gas phase photolysis of *N*-nitrosodimethylamine (NDMA) was studied by Bamford,[45] Lindley *et al.*,[25] Geiger *et al.*,[46] Geiger and Huber[47] and by Tuazon *et al.*,[42] who determined the photolysis rate of NDMA relative to that of NO_2 to be $j_{NDMA}/j_{NO2} = 0.53 \pm 0.03$. Geiger *et al.*[47,46] report a quantum yield to photo-dissociation of NDMA following $S_1(n\pi^*) \leftarrow S_0$ excitation to be 1 ± 0.1. Photolysis of NDMA (and presumably also of other nitrosamines) is therefore fast and NDMA has an atmospheric lifetime of less than 1 hour during summer.

Tuazon *et al.*[42] found 33% CH_3NO_2, 38% HCHO and 2% CO in addition to 65% $(CH_3)_2NNO_2$ and could account for ~100% of the carbon and ~95% of the nitrogen and states that the amount of $(CH_3)_2NNO_2$ formed in the photolysis experiment is in agreement with the relative rates k_{28}/k_{30} and k_{31}/k_{30} determined by Lindley *et al.*[25], see below.[#] It should be noted, however, that they employed a large excess O_3 in their photolysis experiments to prevent back-reaction of NO with the dimethylamino radical, see reactions (15)-(20). This was at a time when it was not realized that the NO_3 radical is formed under such conditions and that this radical might also contribute to the loss of NDMA. Their result for j_{NDMA}/j_{NO2} is therefore an *upper* limit to the nitrosamine relative photolysis rate.

$$\begin{array}{rcll}
\mathrm{(CH_3)_2NNO} & \xrightarrow{h\nu} & \mathrm{(CH_3)_2N + NO} & (15) \\
\mathrm{(CH_3)_2N + NO} & \xcancel{\longrightarrow} & \mathrm{(CH_3)_2NNO} & (16) \\
\mathrm{NO + O_3} & \rightarrow & \mathrm{NO_2 + O_2} & (17) \\
\mathrm{(CH_3)_2N + NO_2} & \rightarrow & \mathbf{(CH_3)_2NNO_2} & (18) \\
\mathrm{NO_2 + O_3} & \rightarrow & \mathrm{NO_3 + O_2} & (19) \\
\mathrm{(CH_3)_2NNO + NO_3} & \rightarrow & \mathrm{Products} & (20)
\end{array}$$

Lindley *et al.*[25] studied the gas phase reactions of the $(CH_3)_2N$ radical following photolysis of NDMA with O_2, NO and NO_2, and also derived the relative rates $k_{28}/k_{29} = (1.48 \pm 0.07) \times 10^{-6}$, $k_{28}/k_{30} = (3.90 \pm 0.28) \times 10^{-7}$ and $k_{31}/k_{30} = 0.22 \pm 0.06$. Lazarou *et al.*[48] studied the reactions of the $(CH_3)_2N$ radical with NO and NO_2 by the Very Low Pressure Reactor (VLPR) technique and reported absolute rates of reaction $k_{29} = (8.53 \pm 1.42) \times 10^{-14}$, $k_{23} = (3.18 \pm 0.48) \times 10^{-13}$, and $k_{32} = (6.36 \pm 0.74) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K.

The products observed were explained at the time by the following series of reactions:

$$\begin{array}{rcll}
\mathrm{(CH_3)_2NH + OH} & \rightarrow & \mathrm{(CH_3)_2N + H_2O} & (21) \\
 & \rightarrow & \mathrm{(CH_3)N(H)CH_2 + H_2O} & (22) \\
\mathrm{(CH_3)_2N + NO_2} & \rightarrow & \mathbf{(CH_3)_2NNO_2} & (23) \\
\mathrm{(CH_3)N(H)CH_2 + O_2} & \rightarrow & \mathrm{(CH_3)N(H)CH_2O_2} & (24) \\
\mathrm{(CH_3)N(H)CH_2O_2 + NO} & \rightarrow & \mathrm{(CH_3)N(H)CH_2O + NO_2} & (25) \\
\mathrm{(CH_3)N(H)CH_2O + O_2} & \rightarrow & \mathbf{(CH_3)N(H)CHO} + \mathrm{HO_2} & (26) \\
\mathrm{(CH_3)_2N\text{-}NO} & \rightarrow & \mathrm{(CH_3)_2N + NO} & (27) \\
\mathrm{(CH_3)_2N + O_2} & \rightarrow & \mathbf{CH_2{=}N\text{-}CH_3} + \mathrm{HO_2} & (28) \\
\mathrm{(CH_3)_2N + NO} & \rightarrow & \mathbf{(CH_3)_2N\text{-}NO} & (29) \\
\mathrm{(CH_3)_2N + NO_2} & \rightarrow & \mathbf{(CH_3)_2N\text{-}NO_2} & (30) \\
 & \rightarrow & \mathbf{CH_2{=}N\text{-}CH_3} + \mathrm{HONO} & (31) \\
 & \rightarrow & \mathrm{(CH_3)_2NO + NO} & (32)
\end{array}$$

Nitramines, such as DMN, do not undergo photolysis in the troposphere, and virtually nothing is known about their environmental fate. Nitramines have been reported as products in the studies of secondary and tertiary amines, but results from ADA-2009 [7] also show that nitramines are also formed in photo-oxidation of primary aliphatic amines. From a theoretical point of view, the photo-oxidation of nitramines should result in the formation of *N*-nitro amides, R-C(O)-N(R')NO_2, for which no atmospheric chemistry data exist.

[#] Under atmospheric conditions the branching between reactions (28)-(31) will differ from those observed in laboratory experiments. In a polluted area one may have average NOx-values as high as 100 ppbV NO_2 and 50 ppbV NO. Under such conditions (p° = 1 atm) the branching of reactions (28)-(31) will be: $r_{28} : r_{29} : r_{30} : r_{31} = k_{28} \times p_{O2} : k_{29} \times p_{NO} : k_{30} \times p_{NO2} : k_{31} \times p_{NO2}$ which results in a formation ratio of imine : nitrosamine : nitramine ≈ 47 : 6 : 47.

It should be noted that there is only kinetic information for one, single nitramine – DMN. It should also be noted that there is only gas phase photolysis rate data for one, single nitrosamine – NDMA.

5 Summary of the present knowledge about particle formation during the atmospheric oxidation of amines

Gas phase aliphatic amines may play a significant role in secondary aerosol formation via photo-oxidation and gas-to-particle conversion in regions with high amine concentrations.[26,18] Both oxidation reactions of amines with the OH radical and acid-base reactions between amines and acids commonly present in the atmosphere (i.e. nitric acid and sulphuric acid) and in the emissions appear to play roles in the formation and chemistry of organic nitrogen-containing particle phase species. Currently, data on the chemical composition of particles obtained from chamber experiments is very uncertain and at best qualitative.

Amines are basic compounds that can react with HNO_3, H_2SO_4 and organic acids forming low-vapour pressure amine salts that will partition into the aerosol phase, making the amine unavailable for reaction in the gas phase. However, these reactions are reversible and equilibrium exists between the salt, and the amine and acids. This means that under sufficiently low amine or acid concentrations, or if other basic species such as NH_3 are present to compete for the acids, or there are other important loss processes for the amine or acids, then the salt formation may be less important in affecting the availability of the amine to react in the gas phase. The equilibrium constants for amine salt formation are not available in the literature. Aerosol amine salt formation from reactions of amines with HNO_3 in environmental chamber experiments under simulated atmospheric conditions all show that aerosol amine salt formation occurs rapidly when the gas-phase amine and HNO_3 are present at concentrations of ~100 ppb. However, the studies also show that the amine salt aerosol formation eventually declined relatively under conditions where the amine is removed from the gas phase by other reactions. This suggests that re-volatilization may be important under atmospheric conditions, and because of the relatively high gas phase reactivity of the amines, the amine salt formation may not be a permanent sink for the amine under conditions where O_3 formation can occur. In addition, if excess NH_3 (which essentially is unreactive towards OH radicals) is present in the environment, it may compete with the amine for nitrate salt formation, making loss of the amine to salt formation less important.

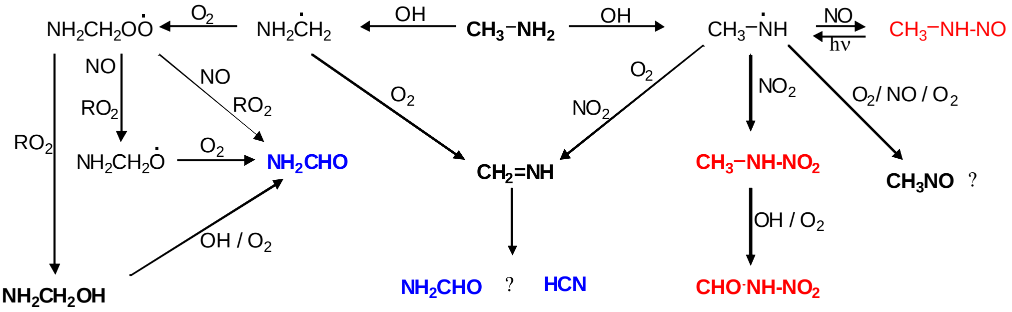
It may be argued that most chamber experiments are not useful for assessing whether loss of amines due to reaction with HNO_3 may be important under atmospheric conditions.[9] The impact in the real atmosphere depends on the magnitudes of acid sources and sinks, the amounts of other amines or ammonia present to compete with the acids, and the amine salt equilibrium constants, which are unknown. At present, there is insufficient information available to quantify these impacts, or even to assess which of these extremes is most likely to be representative of the situation at Mongstad.

6 Update of theoretical gas phase degradation schemes

There is no new mechanistic information in the literature concerning the atmospheric photo-oxidation of amines. Consequently, there is no sound fundament for updating gas phase degradation schemes in general. However, detailed quantum chemical calculations have been carried out for the OH-initiated gas phase photo-oxidation of methylamine, dimethylamine and trimethylamine. For the sake of brevity the details of these calculations are not included here.

6.1 CH_3NH_2

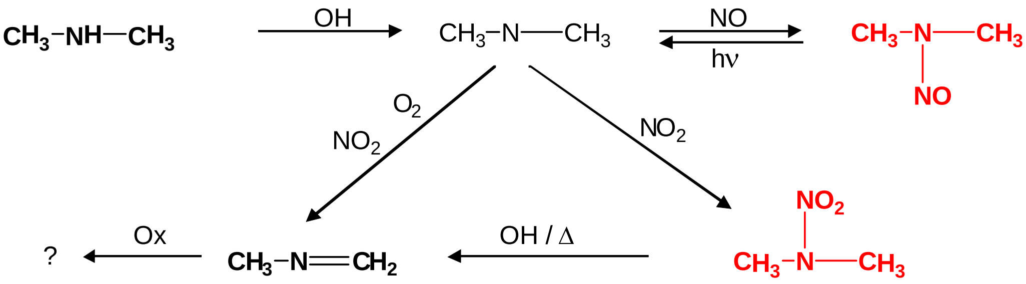
The atmospheric degradation mechanism for the OH initiated photo-oxidation of CH_3NH_2 by Schade and Crutzen[17] has been further elaborated in a systematic quantum chemistry study; the main routes in the atmospheric photo-oxidation following initial reaction with OH radicals are summarized in Scheme 6.1. The remaining "unknows" in the atmospheric photo-oxidation of methylamine are linked to the fate of methanimine and to a possible formation of nitrosomethane.



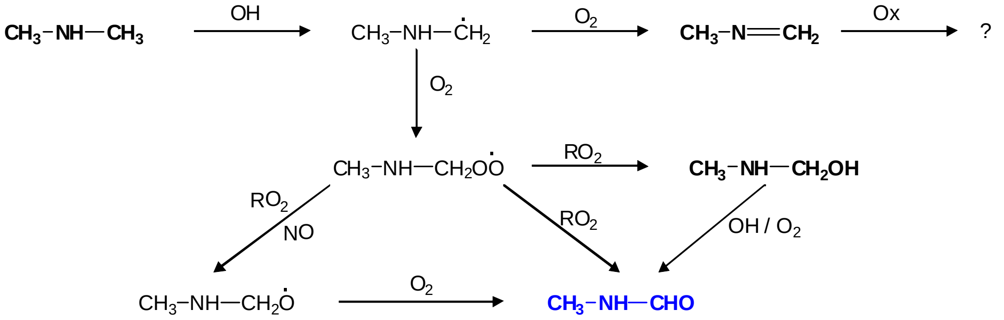
Scheme 6.1. Main routes of the atmospheric methylamine photo-oxidation.

6.2 $(CH_3)_2NH$

Grosjean outlined the mechanism for atmospheric photo-oxidation of $(CH_3)_2NH$, in 1991.[24] The scheme has been further elaborated in a systematic quantum chemistry study; the main routes in the atmospheric photo-oxidation of $(CH_3)_2NH$ following initial reaction with OH radicals are presented in Schemes 6.2 and 6.3. The remaining "unknows" in the atmospheric photo-oxidation of dimethylamine are linked to the fate of methylmethanimine and N-methyl formamide.



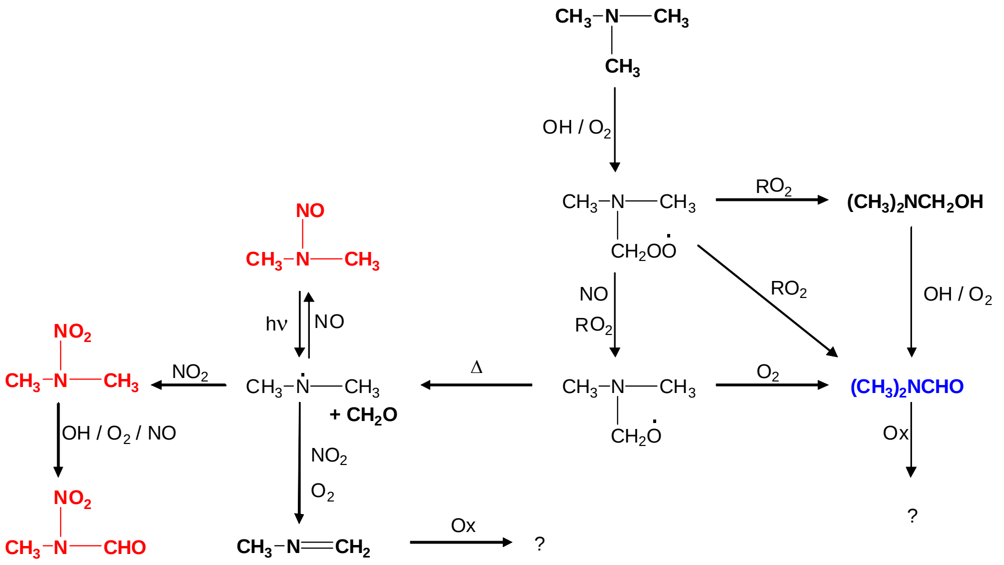
Scheme 6.2. Updated atmospheric photo-oxidation scheme for $(CH_3)_2NH$ following initial hydrogen abstraction from the amino group.



Scheme 6.3. Atmospheric photo-oxidation of $(CH_3)_2NH$ following initial hydrogen abstraction from the CH_3 group.

6.3 $(CH_3)_3N$

The atmospheric degradation mechanism for the OH initiated photo-oxidation of $(CH_3)_3N$ by Schade and Crutzen[17] has been further elaborated in a systematic quantum chemistry study; the main routes in the atmospheric photo-oxidation following initial reaction with OH radicals are summarized in Scheme 6.4. For the sake of brevity the details of the quantum chemistry calculations are not included here. The remaining "unknows" in the atmospheric photo-oxidation of trimethylamine are linked to the fate of methylmethanimine and to fate of *N*,*N*-dimethyl formamide.



Scheme 6.4. Atmospheric photo-oxidation of $(CH_3)_3N$ following initial hydrogen abstraction from the methyl group.

7 Atmospheric aqueous phase chemistry assessment

7.1 Tasks

Describing the atmospheric fate of amines used in CO_2 capturing processes based on an literature survey of aqueous phase kinetic and mechanistic data. Of particular interest are radical oxidation reactions, atmospheric lifetimes and the possible formation of nitrosamines as degradation products. Furthermore, the distribution of the investigated amines in between the atmospheric gas and aqueous phase should be described based on available Henry's law constants.

7.2 Overview

Today's understanding of our troposphere implies that this environmental compartment is not a pure gas phase reactor but a so-called multiphase system, because particles are dispersed in the gas phase establishing solid but, to a large extend liquid aqueous systems. The atmospheric aqueous phase consists of water-containing aerosol particles, and, of course, the droplets of cloud, fog and rain. Tropospheric aerosol particles can have lifetimes in the range of a week in the size regime about a micrometer and a typical tropospheric air parcel is expected to be cloud processed a few times during any day for about 10 – 20 min while moving on its trajectory.

Table 7.1 gives an overview on properties of aqueous particles, for more details see Herrmann (2003)[49] and references therein.

Table 7.1. Characteristics of different atmospheric water-containing particles, after Herrmann (2003)[49]

Particle or Drop	Radius r µm	LWC $cm^3\ m^{-3}$	pH	Ionic Strength I $mol\ l^{-1}$
Rain	200 - 2000	0.1 - 1	4 - 5	10^{-4}
Remote cloud	10	0.1 - 3	4 - 6	$(0.75 - 7.5) \cdot 10^{-4}$
Polluted cloud	10	0.1 - 3	2 - 5	$(0.5 - 1.0) \cdot 10^{-2}$
Polluted fog	10	0.02 - 0.2	3 - 7	$(0.07 - 4) \cdot 10^{-2}$
Marine aerosol	1.5 - 2.5	$(0.01 - 1)\cdot 10^{-3}$	$\approx 8^{(a)}$	6.1
Haze	0.03	$10^{-5} - 10^{-4}$	1 - 8	≈ 1
Urban aerosol	≤10	$(2.5 - 4) \cdot 10^{-5(b,d)}$	$3.4 - 3.7^{(c,d)}$	$8.0 – 18.6^{(c,d)}$

Remarks to Table 7.1:
(a) Value for fresh seaspray
(b) LWC (Liquid water content) when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_{Ka} = 0$, and $x_{Mg} = 0$ in mol / 1000 g of H_2O and the sum of electrolyte concentration is between 15 $\mu g \cdot m^{-3}$ and 25 $\mu g \cdot m^{-3}$.
(c) pH and Ionic strength when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_{Ka} = 0$, and $x_{Mg} = 0$ in mol / 1000 g of H_2O.
(d) Parameters for this given case study, measurements in the Los Angeles area in 1973.

The physical properties of this multiphase system have consequences for tropospheric chemistry because particles and aqueous particles may take up substances from the gas phase. While such phase transfer is not expected to be important for fully non-polar species, compounds with higher polarity and of a more hydrophilic character might very efficiently be taken up into aqueous particles and drops. It should be noted that less volatile reaction products might also evaporate back from aqueous particles, *e.g.* when water is evaporating at the rims of a cloud.

Then, in these particles chemical reactions can take place, which could have very different characteristics compared to gas phase reactions and which might also lead to much different products. Preferably, these degradation products need to be elucidated by product studies according to the analytical state-of-the art. Chemical reactions in the atmosphere are often triggered by free radicals in all phases. Typical aqueous phase radical oxidant concentrations are given in Table 7.2.

The elucidation of the atmospheric chemistry of the aqueous particle phase is a process which started in the mid 1980s and is still heavily ongoing. Aqueous phase chemistry is a complement to gas phase oxidation reactions because polar products will phase partition and an atmospheric chemical degradation scheme for a give compound cannot be regarded complete when only gas phase processes are being described.

Table 7.2. Calculated OH, NO_3, and SO_4^- radical concentrations in clouds and deliquescent particles using the CAPRAM 3.0i multiphase mechanism. Mean concentrations are averaged values over three simulation days.

OH radical									
	urban case [OH] in mol L^{-1}			remote case [OH] in mol L^{-1}			maritime case [OH] in mol L^{-1}		
	mean	*max*	*min*	*mean*	*max*	*min*	*mean*	*max*	*min*
cloud droplets	$3.5\cdot10^{-15}$	$1.6\cdot10^{-14}$	$2.9\cdot10^{-16}$	$2.2\cdot10^{-14}$	$6.9\cdot10^{-14}$	$4.8\cdot10^{-15}$	$2.0\cdot10^{-12}$	$5.3\cdot10^{-12}$	$3.8\cdot10^{-14}$
deliquescent Particles	$4.4\cdot10^{-13}$	$1.9\cdot10^{-12}$	$1.4\cdot10^{-16}$	$3.0\cdot10^{-12}$	$8.0\cdot10^{-12}$	$5.5\cdot10^{-14}$	$1.0\cdot10^{-13}$	$3.3\cdot10^{-12}$	$4.6\cdot10^{-15}$
NO_3 radical									
	urban case [NO_3] in mol L^{-1}			remote case [NO_3] in mol L^{-1}			maritime case [NO_3] in mol L^{-1}		
	mean	*max*	*min*	*mean*	*max*	*min*	*mean*	*max*	*min*
cloud droplets	$1.4\cdot10^{-13}$	$2.7\cdot10^{-13}$	$4.7\cdot10^{-14}$	$5.1\cdot10^{-15}$	$1.7\cdot10^{-14}$	$1.1\cdot10^{-15}$	$6.9\cdot10^{-15}$	$2.0\cdot10^{-14}$	$1.9\cdot10^{-15}$
deliquescent Particles	$8.6\cdot10^{-14}$	$2.1\cdot10^{-13}$	$2.4\cdot10^{-14}$	$3.5\cdot10^{-13}$	$1.0\cdot10^{-12}$	$8.0\cdot10^{-16}$	$1.9\cdot10^{-15}$	$6.7\cdot10^{-15}$	$1.6\cdot10^{-16}$
SO_4^- radical									
	urban case [SO_4^-] in mol L^{-1}			remote case [SO_4^-] in mol L^{-1}			maritime case [SO_4^-] in mol L^{-1}		
	mean	*max*	*min*	*mean*	*max*	*min*	*mean*	*max*	*min*
cloud droplets	$1.1\cdot10^{-14}$	$2.8\cdot10^{-14}$	$6.5\cdot10^{-15}$	$2.4\cdot10^{-14}$	$1.8\cdot10^{-13}$	$4.0\cdot10^{-15}$	$2.3\cdot10^{-15}$	$5.7\cdot10^{-14}$	$5.5\cdot10^{-17}$
deliquescent particles	$9.3\cdot10^{-15}$	$4.8\cdot10^{-14}$	$4.5\cdot10^{-16}$	$3.6\cdot10^{-13}$	$9.1\cdot10^{-13}$	$1.6\cdot10^{-15}$	$1.2\cdot10^{-14}$	$1.2\cdot10^{-13}$	$7.4\cdot10^{-17}$

Deliquescence = A process by which a substance (for example a salt particle) absorbs moisture from the atmosphere until it dissolves in the absorbed water and forms a solution. Therefore, a deliquescent particle should by considered as an aqueous particle of a concentrated solution.

It should be noted that the physico-chemical concepts for phase transfer treatment being applied in CAPRAM/SPACCIM model runs and elsewhere, i.e. the so-called resistance model, as a kinetic description of gas uptake by particles and droplets goes back to the concepts known from chemical engineering.

7.3 Literature review and development of theoretical aqueous phase degradation schemes

7.3.1 Introduction

Theoretical aqueous phase degradation schemes have been developed for the following target compounds **dimethylamine (DMA), 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA), monoethanolamin (MEA)** and **piperazine (PZ).** The literature research comprised a search for kinetic data on radical reactions, prefered reaction sites and product formations of the target compounds and their degradation products. As long as kinetic data were measured or could be estimated, atmospheric lifetimes of the target compounds have been calculated (Table 11.1). The reaction schemes and the associated discussions presented in the following include information on available references describing the single reaction steps. However, not all reaction rates and products included in the schemes are based on experimental studies, due to a restricted number of studies. In such cases reaction sites and potential reaction products have been estimated based on data of similar/comparable systems or by analogy. Colored boxes in the reaction schemes indicate the level of confidence of the proposed reaction sites and products.

In summary, it can be stated that experimental studies on the kinetics and the reactions products of amine oxidation reactions are very sparse and restricted to certain compounds or compound classes (e.g., alkyl amines). During the literature research and the assembly of the degradation schemes the following main problems occurred.

1) It has to be stated that the protonation of the amine group has a strong influence on the reaction kinetics and the preferred reaction sites. This clearly limits the transferability of gas phase kinetic data and reaction schemes. Based on the work of Getoff and Schwörer[50,51] as well as Simic et al.[52] an H-abstraction reaction by the electrophilic OH radical at the protonated amino group was ruled out under atmospheric conditions.
2) The influence of the protonation on the reactivity and the reaction sites is systematically investigated and characterized for the target compounds and their reaction products. Within the proposed degradation schemes it was tried to describe the chemistry of amines for the pH range of 4-7, which is the most relevant one for atmospheric conditions. Under these conditions the amino group is protonated in the target compounds. However, under slightly acidic or neutral conditions one of the amino groups in the piperazine molecule remains non-protonated.
3) Furthermore, it has to be mentioned that kinetic and mechanistic studies on other important atmospheric free radicals than OH, such as the night-time oxidants NO_3 and ozone, are almost completely missing. This is a serious limitation to describe the chemistry and lifetime of amines and their degradation products in particular at low actinic fluxes or during the night hours.
4) Experimental data on functionalized, branched or cyclic amines as well as data on secondary or tertiary amines with different alkyl chains are very sparse in aqueous solution. Accordingly, estimated kinetic data and assumed reaction products can contain large uncertainties. In particular the preferred reaction site in these rather complex molecules is often not clear and could be only assumed in some cases.

5) Amines can be converted in nitrosamines in acidic solution in the presence of nitrite ions. Probabilities and yields of these processes are not clear for all target compounds and depend strongly on the conditions (e.g., pH). Furthermore, it is not clear to what extend these nitrosation reactions can compete with the fast radical processes. Therefore, formation routes of nitrosamines in the degradation schemes below should be considered as a potential pathway only.
Nitrite concentrations in the atmospheric aqueous phase are extremely variable and are much influenced by the local NOx regime and other conditions. They should be derived from a multiphase box model calculation for a given scenario. CAPRAM in its current version predicts nitrite concentrations in the range 0.4 - 3 nmol/l for clouds and 0.01 to 0.1 nmol/l for the aerosol particle case depending on scenarios. Nitrite is expected to evaporate from acidified particles as HONO that explain the lower aqueous particle concentrations. Note: These concentrations refer to the aqueous solution, not gas volume

6) The chemistry and photolysis of N-nitrosodimethylamine (NDMA) is well characterized by several studies in the past. Also photolysis processes of other nitrosamines have been recently investigated [53,54]. All nitrosamines studied by these two groups are rapidly photolysed in aqueous solution. Half-lifetimes of some nitrosamines are in the order of a few minutes only depending on the solar radiation level. However, aside from the radiation level also the nature of the side groups influences the efficiency of these photolysis processes. Therefore it was only assumed in the following that all the nitrosamines formed are easily photolysed.
In contrast to photolysis processes, radical oxidation reactions of nitrosamines in aqueous solution are much less investigated and the reactivity and reaction products might differ significantly from NDMA. This means that the atmospheric lifetimes and the fates of nitrosamines in aqueous solution are highly uncertain in particular during the night hours.

7.3.2 Oxidation of dimethylamine (DMA) in aqueous solution

There is **one aqueous phase rate constant available** describing the reaction between OH and protonated DMA in aqueous solution ($k_{2nd} = 6{\cdot}10^7\ M^{-1}s^{-1}$ at pH 7[55]). This rate constant is significantly lower than the rate constants for the protonated forms of methylamine ($k_{2nd} = 1.2{\cdot}10^8\ M^{-1}s^{-1}$;[50]) and trimethylamine ($k_{2nd} = 4.4{\cdot}10^8\ M^{-1}s^{-1}$;[52]). Therefore, the rate constant should be remeasured in order to verify or correct this number.

(I) Dimethylamine (pK = 10.64) is protonated in the tropospheric aqueous phase. It was shown by Getoff and Schwörer (1973) that H-abstraction reactions of protonated aliphatic amines takes place at positions distant from the $–NH_3^+$ group[51]. In presence of oxygen the corresponding organic peroxy radical (2) is formed after the H-abstraction by OH at one of the methyl groups in DMA.

(II) Following the chemistry suggested by von Sonntag and Schuchmann[56] two of these primary peroxy radicals recombine ($k_{2nd} \approx 2{\cdot}10^8\ M^{-1}s^{-1}$) to form N-methylaminomethanol (3) and N-methylformamide (4). N-methylaminomethanol (3) is most likely further oxidized to N-methylformamide (4) by OH radical reactions and $HO_2{\cdot}$ elimination in presence of oxygen. However, the possibility of an H-abstraction at the $-CH_3$ group of (3) cannot be ruled out.

(III) H-abstraction at the $-CH_3$ group leads to the organic primary peroxy radical (5). Recombination of this peroxy radical lead to the formation of alkanol amines and amides. This highly functionalized amines and amides formed are either further oxidized by OH to the corresponding amino acids or decompose by a C-N cleavage.

(IV) Also N-methylformamide (4) is further oxidized by OH radicals. This reaction ($k_{2nd} = 1.2 \cdot 10^9$ $M^{-1}s^{-1}$;[57]) is about one order of magnitude faster than the reaction of OH with dimethylamine. In carbonyl compounds the H-abstraction would take place at the carbonyl group due to the lower C-H bond strength in comparison with a methyl group. However, it was demonstrated by Hayon et al. (1970)[57] as well as by Misik and Riesz (1996)[58] that the H-abstraction takes preferentially place at the $–CH_3$ group in the N-methylformamide molecule. Accordingly the organic peroxy radical (6) is formed. The recombination reaction of two peroxy radicals ($k_{2nd} \approx 2 \cdot 10^8$ $M^{-1}s^{-1}$;[56]) should yield (7) and (8).

(V) The two amides (7) and (8) are most likely further oxidized to an amino acid. Another possibility for the highly functionalized amides (7,8) as well as potentially formed α-amino acids is the cleavage of the C-N bond leading to a products such as amines, amides, carbonyls, NH_3 and CO_2. The oxidation of (7) and (8) and their oxidation products by OH surely competes with the C-N cleavage process.

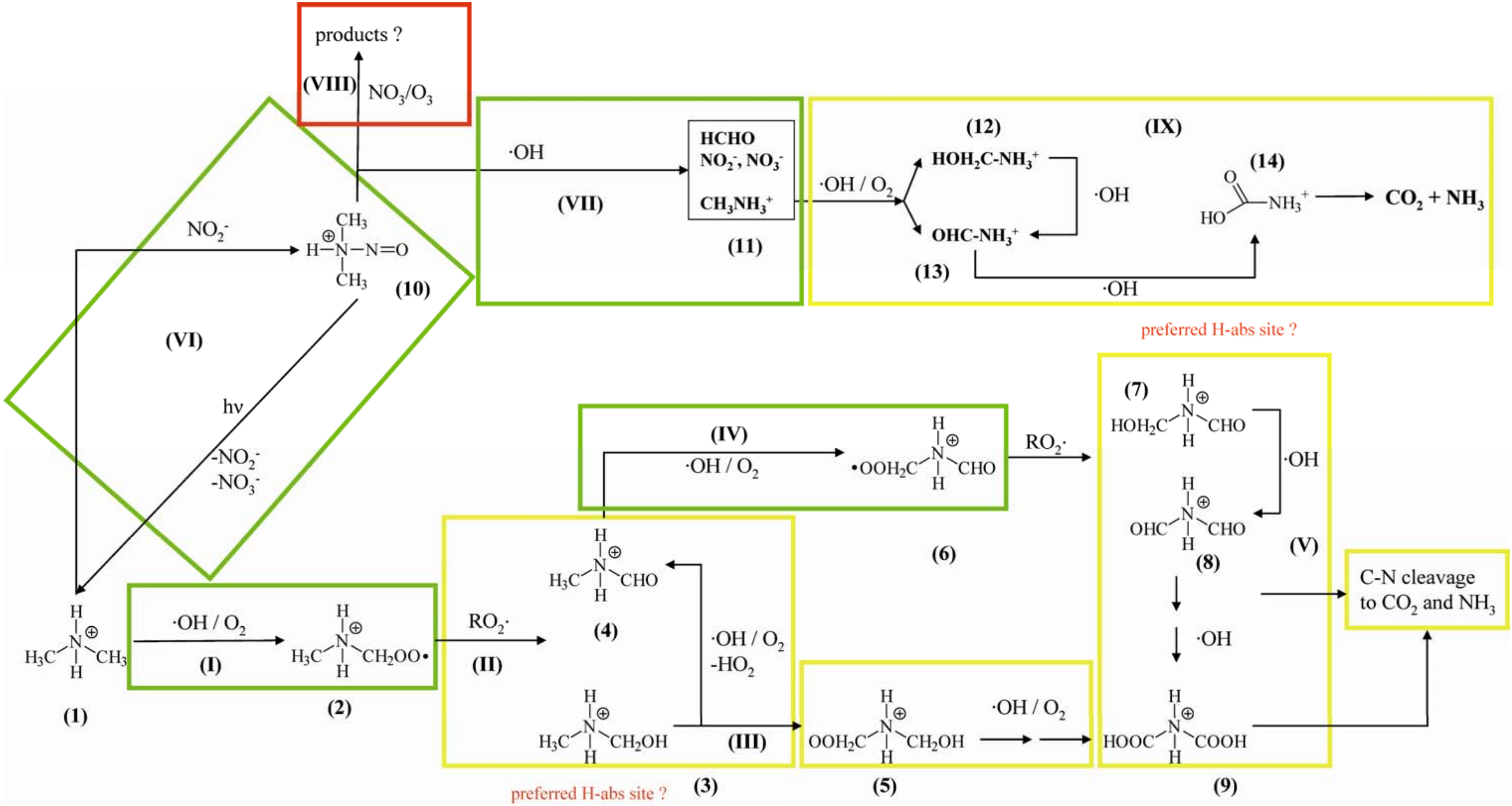


Figure 7.1. Proposed atmospheric oxidation scheme for dimethylamine (DMA) in aqueous solution. Green boxes indicate reaction paths that are verified by experimental evidence. Yellow boxes indicate estimated reaction paths with a great level of confidence according to the known aqueous phase chemistry. Red boxes indicate highly speculative reaction paths.

(VI) N-nitrosodimethylamine (NDMA, 10) is formed by the reaction of dimethylamine with nitrite ions in acidic solution [5961]. Keefer and Roller showed in 1973 that the N-nitrosation of secondary amines is catalyzed by HCHO and can also take place in basic solution[62]. The degradation of NDMA has been the subject of several investigations. Stefan and Bolton (2002) investigated the photolysis of NDMA in acidic and neutral aqueous solution[63]. They found dimethylamine, nitrite and nitrate ions as major degradation products. Photolysis processes in the presence and absence of either O_3 or H_2O_2 have been also studied by other groups [6466,53,54]. Hanst et al. (1977)[21] and later also Tuazon and co-workers in 1984[42] as well as Chen et al. (2010)[54] report a half-lifetime of NDMA under sunlight of a few minutes only. Therefore, Hanst and co-workers concluded their study that the destruction of NDMA by sunlight prevents a day-to-day accumulation of this compound. But, this conclusion should be taken with care since the lifetimes depends strongly on the radiation level. With regards to the radiation conditions at the Mongstad site the lifetime of this nitrosamine and can be completely different in the summer and winter time.

(VII) Mezyk and co-workers[67] measured also the reaction kinetics of NDMA + OH in aqueous solution. Their value of $k_{2nd} = (4.3\pm0.12)\cdot10^8\ M^{-1}s^{-1}$ confirms other values from Wink et al. in 1991[68] of $k_{2nd} = (3.3\pm0.4)\cdot10^8\ M^{-1}s^{-1}$ and Lee et al. in 2007[69] of $k_{2nd} = (4.5\pm0.2)\cdot10^8\ M^{-1}s^{-1}$. The calculated tropospheric lifetimes of NDMA towards OH radicals in clouds and deliquescent particles ranges from 1.4 hours up to 8.2 days. Heur and co-workers (1989)[70], Lee et al. (2007)[69] and Xu et al. (2009)[71] measured also the products formed in the oxidation of NDMA by OH radicals. Heur et al. used in their study the Fenton reaction as a source for OH in aqueous solution and described nitrite, nitrate, HCHO and methylamine (11) as degradation products. These findings were later confirmed by Lee in 2007 and Xu in 2009.

(VIII) Kinetic data on the reactivity of NDMA towards NO_3 in aqueous solution are completely missing in the literature. The reaction with ozone is extremely slow ($0.052\pm0.0016\ M^{-1}\ s^{-1}$;[69]). Therefore, the atmospheric fate and lifetime of NDMA during the night hours remains highly speculative. NO_3 reactions are usually much slower than the corresponding OH reactions. This means that it is very likely that the lifetimes of NDMA are significantly longer during the night.

(IX) Methylamine (11) is further oxidized in aqueous solution ($k_{2nd} = 1.2\cdot10^8\ M^{-1}s^{-1}$;[50,51]) to aminomethanol (12) and formamide (13). Formamide is oxidized by OH ($k_{2nd} = 3.7\cdot10^8\ M^{-1}s^{-1}$;[72]) to the very instable carbamic acid (14) which further decays to CO_2 and NH_3.

7.3.3 Oxidation of monoethanolamine (MEA) in aqueous solution

Kishore et al. (2004) studied the kinetics of the reaction between MEA and OH radicals in aqueous solution[73]. They report a rate constant of $\mathbf{k_{2nd} = 3.0\cdot10^8\ M^{-1}s^{-1}}$ (pH = 7) and $\mathbf{k_{2nd} = 2.9\cdot10^9\ M^{-1}s^{-1}}$ (pH = 11), respectively.

(I) Monoethanolamine ($pK_A = 9.4$;[73]) is protonated in the troposphere. It was shown by Foster and West (1973, 1974)[74,75] that H-abstraction reactions of protonated alcohol amines takes place preferentially at the $–CH_2OH$ group (β-carbon). However, an H-abstraction at the $-CH_2$ group (α-carbon) cannot be ruled out. Accordingly, the organic peroxy radical (2) is the main reaction product.

(II) The loss of HO_2 leads to the formation of an amide (amino acetaldehyde, 3) which is further oxidized by OH radicals in the presence of oxygen to the amino acid glycine (4).

(III) Glycine reacts in his protonated form relatively slow with OH radicals ($k_{2nd} = 1.0\cdot10^7\ M^{-1}s^{-1}$; pH = 5.9;[76]). Products of these reactions were analyzed by Berger and co-workers in 1999 at pH = 8[77]. They identified oxalic acid as the main degradation product.

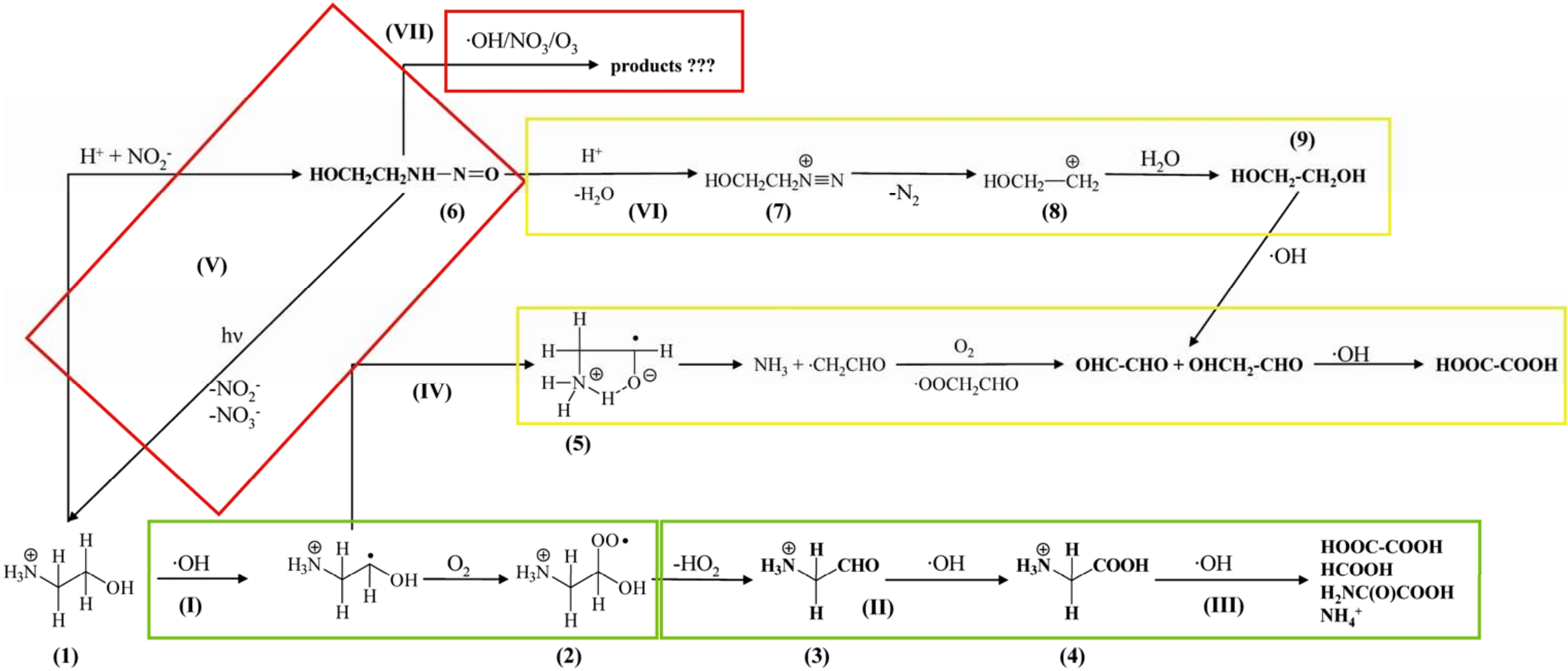


Figure 7.2. Proposed atmospheric oxidation scheme for monoethanolamine (MEA) in aqueous solution. Green boxes indicate reaction paths that are verified by experimental evidence. Yellow boxes indicate estimated reaction paths with a great level of confidence according to the known aqueous phase chemistry. Red boxes indicate highly speculative reaction paths.

Furthermore, other compounds such as formic acid, oxamic acid and NH_4^+ could be identified as additional reaction products. Mönig et al. (1985)[78] showed that the OH radical induced decarboxylation of α-amino acids by OH radical is effective when the amino group is unprotonated. However, in case of glycine this should be only of minor importance in the atmosphere (pK value for $–NH_3^+/-NH_2 = 9.6$). Similar MEA reaction products have been also described by Takasaki and Harada (1985)[79] for the oxidation of monoethanolamine in aqueous solution. They studied the oxidation of amines and amino alcohols in aqueous solution induced by argon arc plasma. Also Takasaki and Harada described the formation of aminoacetaldehyde (3) glycine (4), oxalic acid and formic acid in acidic or neutral conditions. Furthermore, they report the formation of glycolaldehyde, glycolic acid and glyoxylic acid.

(IV) Petryaev et al. (1984)[80] studied the deamination of amino alcohols in aqueous solution. At pH 5-6 the hydroxyl group of MEA begins to dissociate and a five membered transition state (5) can be formed out of the hydroxyalkyl radical. This transient compound decomposes to NH_3 and $\cdot CH_2CHO$. Addition of O_2 and recombination of the formed peroxy radicals leads most likely to the formation of glyoxal and glycolaldehyde. Both aldehydes are further oxidized in aqueous solution to oxalic acid.

(V) To the best of the author's knowledge there is no direct study available showing the formation of N-nitrosoethanolamine (6) in acidic aqueous solution in the presence of nitrite. However, it is known from organic chemistry textbooks that primary amines can undergo nitrosation reaction under such conditions. It is not clear from the existing literature if the formed nitrosamine (6) is as easily photolysed as other nitrosoalkylamines[54]. Therefore, it is only assumed in the scheme that it is photolysed and that MEA, nitrate and nitrite are formed in analogy to NDMA.

(VI) Primary nitrosamines form in acidic solutions a diazonium cation (7) which easily eliminates nitrogen to form a carbenium ion (8). Stabilization of the carbenium ion in water results in the formation of ethylene glycol (9). The further oxidation of ethylene glycol gives glycolaldehyde, glycolic acid and finally oxalic acid.

(VII) N-nitrosoethanolamine will also react with OH radicals in aqueous solution. However, there is no experimental study available measuring the kinetics as well as the products of this reaction. There is also no study available measuring the reactivity of N-nitrosoethanolamine towards ozone and NO_3 radicals. That means the atmospheric lifetime and fate of this nitrosamine is highly uncertain.

7.3.4 Oxidation of 2-amino-2-methyl-1-propanol (AMP) in aqueous solution

There is **no kinetic study available** measuring the reactivity of OH radicals towards AMP. Since there are several possible reaction sites for OH in the molecule it is not possible to estimate an reliable H-abstraction rate constant. **It is only assumed by the authors that** the prefered reaction site is located at the $–CH_2OH$ group as in other alkanolamines too. If this is a valid assumption, the **reactivity** of AMP should be very **similar to MEA.**

(I) Abstracting a hydrogen atom by OH at the $–CH_2OH$ group in AMP ($pK_A = 9.7$) leads to the formation of (2). This alkyl radical reacts to the corresponding peroxy radical (3) in presence of oxygen.

(II) The peroxy radical will eliminate HO_2 to form the amide (4). The preferred site for the H-abstraction by OH in the amide is also not clear. However, the authors assume that it takes preferentially place at the carbonyl group to form the amino acid 2-methylalanine (5).

(III) The rate constant for the oxidation 2-methylalanine (5) by OH was measured by Goldstein et al. in 1992[81] ($k_{2nd} = (1.2 \pm 0.1) \cdot 10^8\ M^{-1}s^{-1}$) at pH = 3. However, there is no product study available in the literature. Therefore, it is only speculated that compounds such as acetone, formic acid and primary amines could be formed.

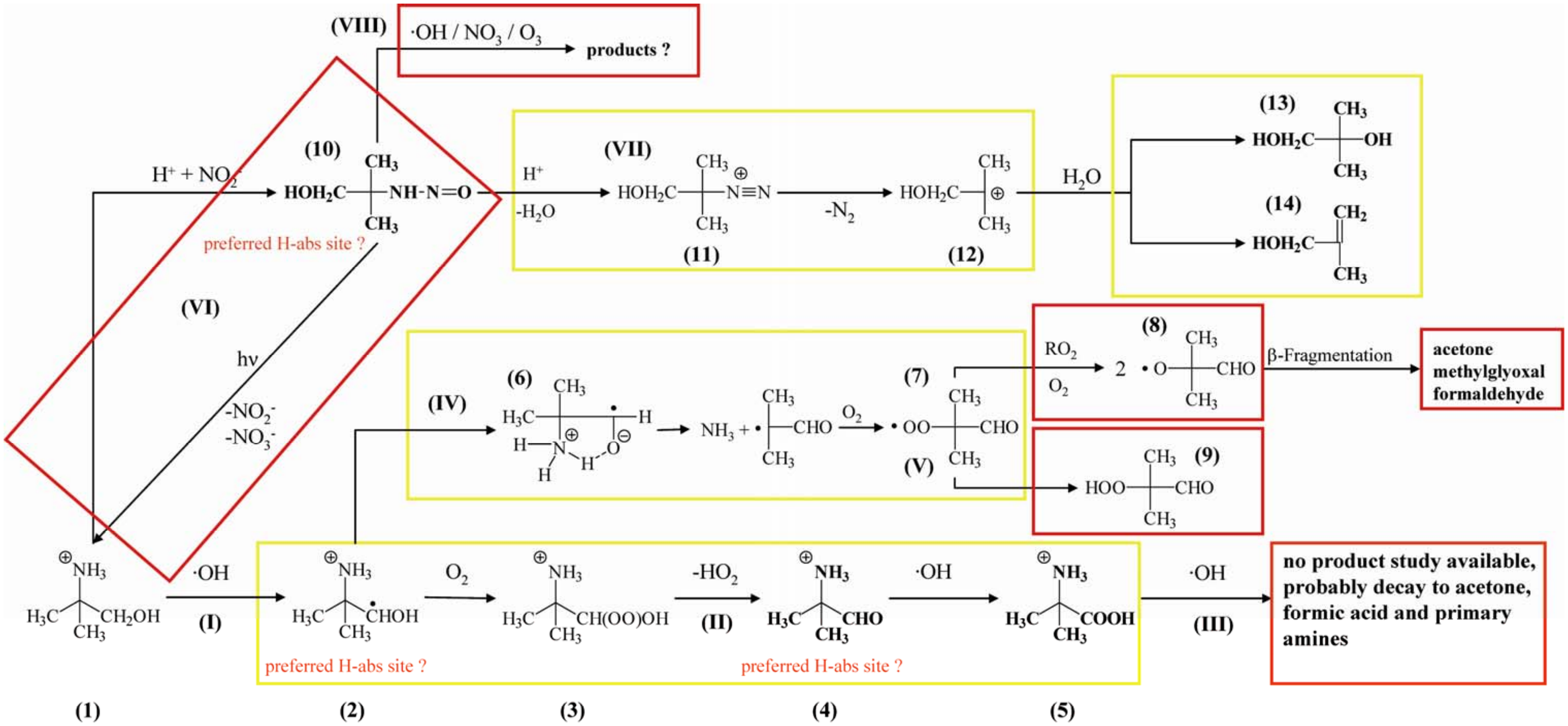


Figure 7.3. Proposed atmospheric oxidation scheme for 2-amino-2-methyl-1-propanol (AMP) in aqueous solution. Green boxes indicate reaction paths that are verified by experimental evidence. Yellow boxes indicate estimated reaction paths with a great level of confidence according to the known aqueous phase chemistry. Red boxes indicate highly speculative reaction paths.

(IV) Additionally, there is also the option that the alkyl radical (2) forms a a five membered transition state (6) similar to MEA[80]. The decay of the transient forms an alkyl radical which further reacts with O_2 to a tertiary peroxy radical (7).

(V) Recombination reactions of two tertiary peroxy radicals form most likely the alkoxy radical (8)[56]. Alkoxy radicals can undergo a β-fragmentation leading to carbonyls such as acetone, methylglyoxal or formaldehyde. However, it is also possible that an organic hydroperoxide (9) is formed in the complex atmospheric aqueous phase.

(VI) There is no study available showing the formation of the corresponding N-nitrosamine (10) in acidic aqueous solution in presence of nitrite. However, it is suggested that also this primary amine will undergo a nitrosation reaction under such conditions. It is not clear from the existing literature if the formed nitrosamine (10) is as easily photolysed as NDMA. Therefore, it is only assumed in the scheme that it is photolysed and that AMP, nitrate and nitrite are formed.

(VII) As primary nitrosamines it is expected that this compound is converted in acidic solutions in a diazonium cation (11) which easily eliminates nitrogen forming a carbenium ion (12). The carbenium ion is stabilized in water forming an alcohol (13) and probably an alkene (14). Both compounds will be oxidized quickly by atmospheric free radicals leading to mono- and dicarboxylic acids.

(VIII) The N-nitrosamine (10) will also react with OH radicals. However, there is no experimental study available measuring the kinetics and products of this reaction. There is also no study available measuring the reactivity of this nitrosamine towards ozone and NO_3 radicals. That means the atmospheric lifetime and fate of this compound is highly uncertain.

7.3.5 Oxidation of methyldiethanolamine (MDEA) in aqueous solution

There is **one kinetic study** available measuring the reactivity of OH radicals towards MDEA ($k_{2nd} = 4.7 \cdot 10^8$ $M^{-1}s^{-1}$; pH = 7;[55]) in aqueous solution. This rate constant is similar to the one for the protonated diethanolamine $k_{2nd} = 4.5 \cdot 10^8$ $M^{-1}s^{-1}$; pH = 7 [73]. Therefore, it was assumed that an H-abstraction at the $–CH_3$ can be neglected.

(I) Abstracting a hydrogen atom by OH at the $–CH_2OH$ group in MDEA ($pK_A = 8.5$) leads to the formation of the hydroxyalkyl radical (2) and to the peroxy radical (3) in presence of O_2. The peroxy radical (2) will eliminate HO_2 to form the amide (3).

(II) The preferred site for the H-abstraction by OH in the amide (3) is not clear at all. There are five different possible reaction sites in the molecule. Since, there are no experimental data on bond strengths available authors assumed that the H-abstraction takes place at the carbonyl group. This assumption is based on the fact that the C-H bonding in an –CHO group is usually rather weak. However, this has to be considered as very speculative at this point. H-abstraction at the carbonyl group in presence of oxygen will form the corresponding amino acid (5).

(III) The further oxidation of this amino acid is again very speculative. No product or kinetic studies of this reaction or of comparable reactants have been found in the literature and the site for the OH radical attack is unclear.

(IV) Another possibility for the radical (2) is the formation of the five membered transition state (4) as suggested by Petryaev[80] for MEA. The decay of this transient forms the alkyl radical $·CH_2CHO$ and MEA.

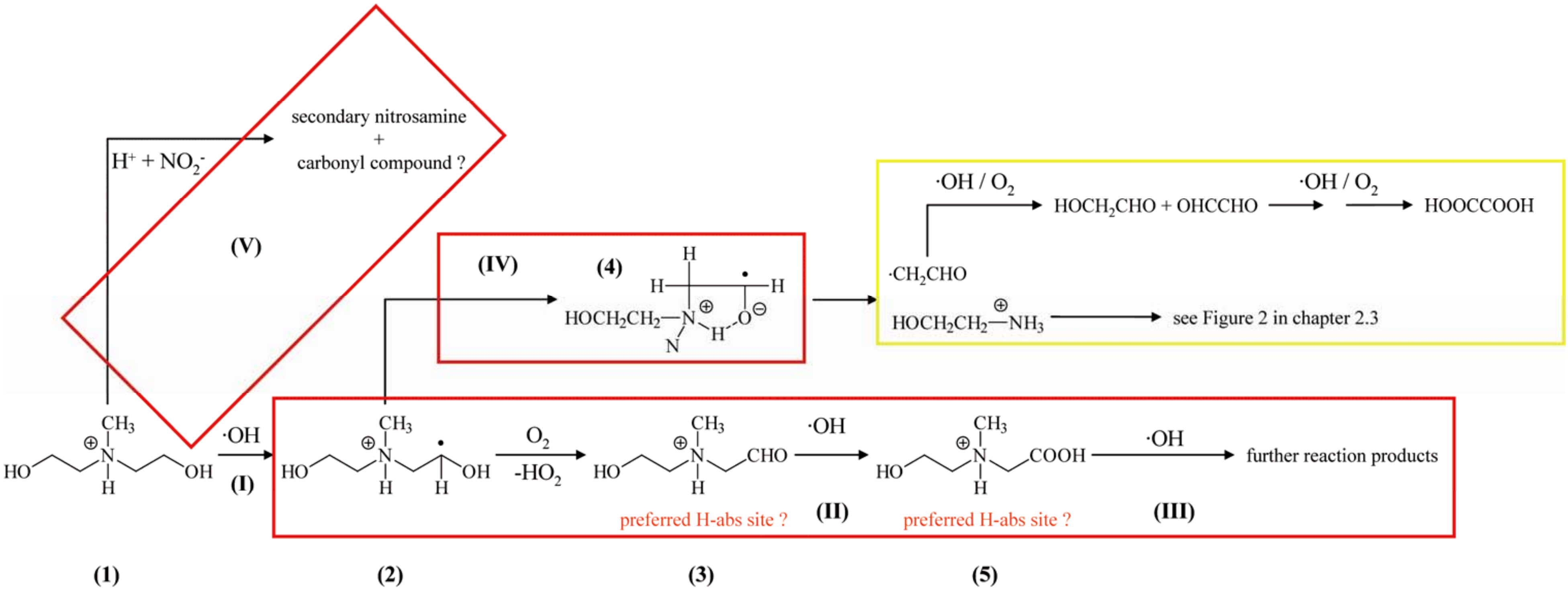


Figure 7.4: Proposed atmospheric oxidation scheme for methyldiethanolamine (MDEA) in aqueous solution. Green boxes indicate reaction paths that are verified by experimental evidence. Yellow boxes indicate estimated reaction paths with a great level of confidence according to the known aqueous phase chemistry. Red boxes indicate highly speculative reaction paths.

The further chemistry of MEA is already discussed before and results in the formation of glycolic acid, glycolaldehyde, glyoxylic acid, glycine, aminoacetaldehyde, oxalic acid and formic acid (see chapter 2.3 and Figure 2).

(V) Tertiary amines can also react with aqueous nitrous acid by dealkylation. This reaction result in the formation of a carbonyl compound and a secondary nitrosamine[82]. However, the nitrosation of tertiary amines under atmospherically relevant conditions is extremely slow and requires elevated temperatures[83,84]. Therefore, it is not clear and remains speculative if and to what extend tertiary amines such as DMEA are nitrosated in the atmosphere

A remark on Alkanolamines: The literature was earched for the agreed-upon target compounds AMP and MDEA and the authors refer to the references given for these compound in the above chapters 5.3.4. and 5.3.5.According to our knowledge, we know about studies on other Alkanolamines which are included in the cited work by Kishore et al. (2004)[73] e.g. for mono-, di -., and triethanolamine, by Foster and West (1973, 1974)[74,75] for a number of β-amino alcohols and and by Takasaki and Harada (1985)[79] for 2-aminoethanol, 3-amino-1-propanol and 2-amino-1-propanol.

7.3.6 Oxidation of piperazine (PZ) in aqueous solution

There is **no kinetic and mechanistic study available** measuring the reactivity of OH radicals towards PZ in aqueous solution. Therefore, all the discussions in the following are highly speculative in nature. The pK values of piperazine are 5.68 and 9.82 which means that under typical atmospheric conditions both the fully protonated as well as the mono protonated form of piperazine are present.

(I) The presence of an non protonated amino group offers an additional reaction site for OH radicals in aqueous solution. An hydrogen atom abstraction reaction directly at the nitrogen atom in piperazine could be another way to form nitrosamines in the atmosphere. It was shown by Dey and Kishore (2003)[85] that the protonated form of morpholine reacts fast with OH radicals ($k_{2nd} = (1.0 \pm 0.05) \cdot 10^9\ M^{-1}s^{-1}$) in aqueous solution. The same authors showed that the non-protonated form of morpholine reacts even faster with OH ($k_{2nd} = (1.0 \pm 0.05) \cdot 10^{10}\ M^{-1}s^{-1}$) and close to the diffusion limit. As mentioned above, the piperazine molecule has probably a non protonated as well as an protonated amino group under atmospheric conditions. Therefore, one could speculate that the overall rate constant under atmospheric conditions is probably in between the two morpholine rate constants ($k_{2nd} \approx 5 \cdot 10^9\ M^{-1}s^{-1}$). However, this number should be taken as a rough estimation only.

Dey and Kishore (2003)[85] investigated also the reactions sites of OH radicals at the morpholine molecule. They found for the non protonated form of morpholine both H-abstraction at the $-CH_2$ groups and H-abstraction at the –NH group. Accordingly, several reaction sites (1-3) are also expected for the mono protonated form of piperazine. The radicals (1) and (3) will add O_2 forming the organic peroxy radicals (4) and (5). Recombination reactions of these peroxy radicals leads to the formation of (6-9). A further oxidation of these highly functionalized piperazines leads probably to an ring opening forming amines and carbonyl compounds.

(II) Reactions of (2) with NO results similar to the gas phase in the formation of mononitrosopiperazine (11). Furthermore, there is also the possibility that mononitrosopiperazine and dinitrosopiperazine (11) are formed by the reaction of piperazine with nitrite. Keefer and Roller[62] demonstrated that cyclic secondary amines (e.g. pyrrolidine and piperidine) are easily converted into nitrosamines under such conditions. However, no informations on the degradation of this nitrosamine have been found in the literature. Chen and co-workers[54] stated in their paper that cyclic nitrosamines tends to be better photolysed in aqueous solution than aliphatic nitrosamines.

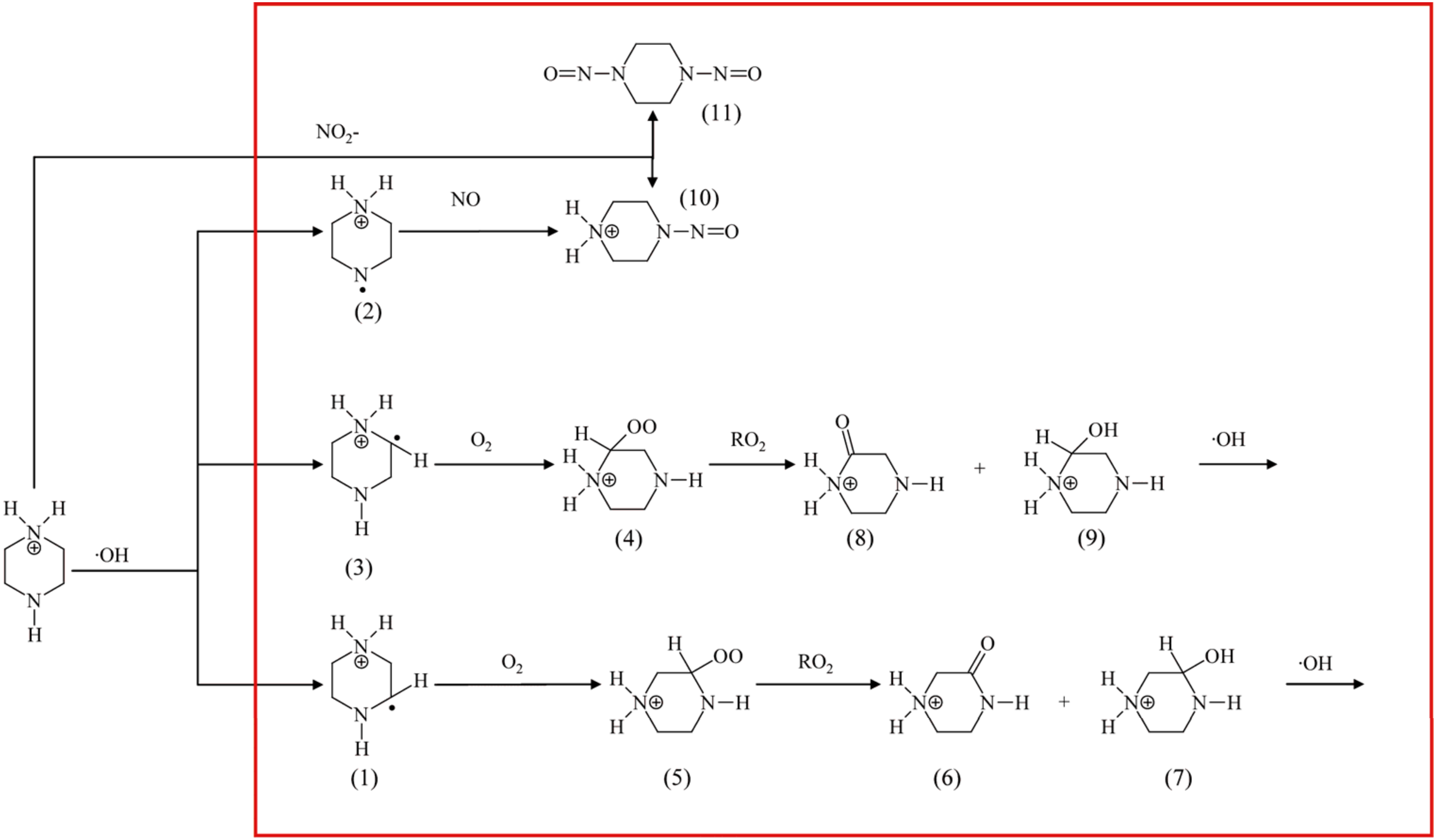


Figure 7.5. Possible degradation reaction for piperazine (PZ)

7.3.7 Identification of important uncertainties

Based on the results of the literature research, the lifetime calculations and the formulation of the degradation schemes the following main uncertainties were identified in the project.

Nitrosamines

In the case of MEA, AMP and 3-aminopropanol it has been shown[86], that under acidic deamination conditions a secondary reaction may form oxazolidine derivatives, which, as secondary amines, will ultimatly form a stable nitrosamine. However, studies by Pedersen et al.[87] identified N-nitroso-diethanolamine when exposing MEA to NOx in a pilot plant or a batch reactor. See also the nitrosamine chapter in the wp-1 part of the report.

Reactions of amines with nitrite in acidic or neutral solution is a possible route to form nitrosamines in the atmosphere. There is only very limited knowledge with regards to kinetics and mechanisms of these reactions . Therefore, the atmospheric importance of this formation pathway could not be specified within this project. Sinks for nitrosamines are photolysis processes as well as radical oxidation reactions. The data indicate that nitrosamines are easily photolysed in aqueous solution. However, direct measurements for the nitrosamines formed from the target compounds in this study are missing with the exception of N-nitrosodimethylamine. Also the reactivity of nitrosamines with other atmospheric radicals (such as the night time oxidant NO_3) and ozone is not known. Therefore, the fate and the lifetime of many nitrosamines during the night hours are very uncertain at this point.

Partitioning of amines and degradation products

The partitioning of amines and their degradation products remains very speculative due to the restricted number of phase transfer parameter available and the fact that most of them are estimated values. Furthermore, the found Henry's law coefficients are thermodynamic parameter which do not reflect reactive uptake processes. Therefore, reliable conclusions on the partitioning of amines and the most important degradation products needs further laboratory and theoretical studies.

Reaction sites and products

Reaction sites in functionalized or branched secondary and tertiary amines and amides are highly uncertain. Therefore, conclusions on the products, their yields and their distribution are often uncertain and need experimental evidence. In particular the aqueous phase chemistry of the cyclic amine piperazine is not investigated and very uncertain due to the large number of potential reaction sites and possible ring opening reactions.

Reactivity

Aqueous phase rate constants of some target compounds and important degradation products are missing. Even if the kinetics of some OH radical reactions with amines, amides and nitrosamines have been measured, the rate constants for NO_3, SO_4^- and ozone reactions are almost completely missing. Furthermore, effects of the pH (protonation of the amino group) and the temperature on the reaction rate constants are often completely missing even for most of the investigated OH reactions.

8 Atmospheric gas phase photolysis lifetimes of nitrosamines

8.1 Estimated NO_2 photolysis rate in the Mongstad area

The calculated NO_2 photolysis rate at Mongstad (60°N 5°E) is shown in Figure 8.1. The calculations are based on an idealized situation with clear sky conditions, a stratospheric ozone layer of 300 DU and a local albedo of 0.1.[88]

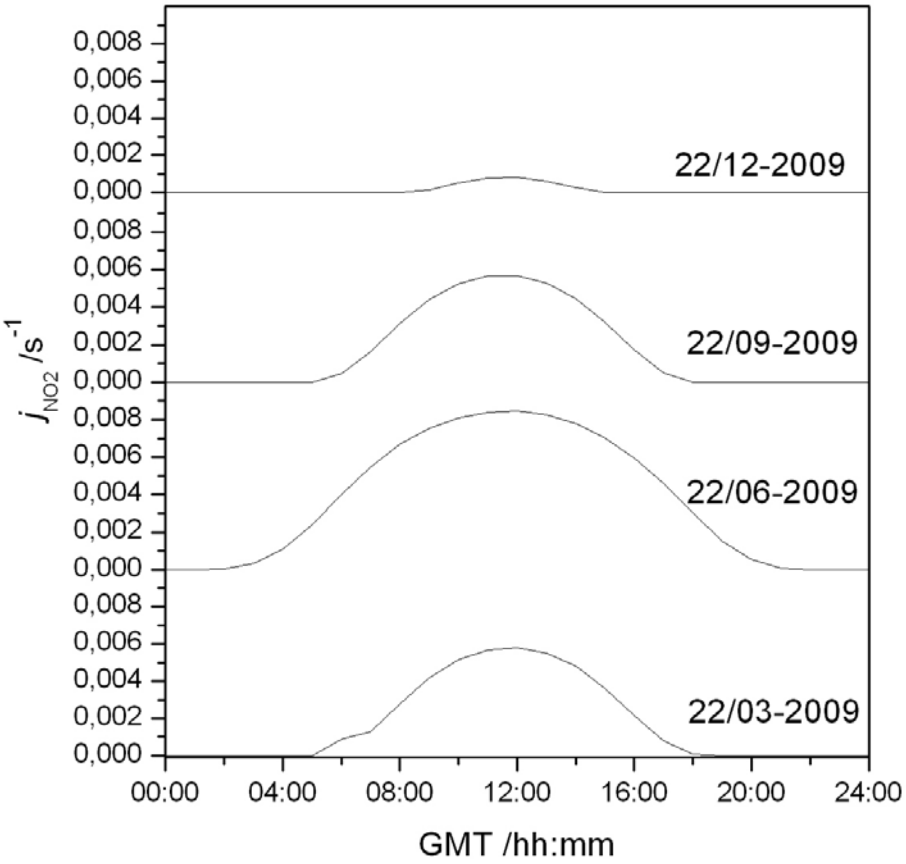


Figure 8.1. Calculated NO_2 photolysis rate at Mongstad (60°N 5°E**).**

The annual average clear sky NO_2 photolysis rate at Mongstad (ground level) is estimated to be $\langle j_{NO2} \rangle_y \approx 1.9 \times 10^{-3}\ s^{-1}$, which corresponds to an average NO_2 photolysis lifetime of around 9 min. The extremes, see Figure 1, are the mid-summer lifetime of around 4 min. and the mid-winter lifetime of about 2 hours.

Cloudy conditions will reduce the actinic flux density and thereby the NO_2 and nitrosamine photolysis rates. The available information about cloud cover in the Mongstad area is plotted in Figure 8.2.[#]

[#] Data for cloudiness are available from Hellisøy Lighthouse for the period 01.01.1970 – 31.07.1992. Cloudiness is the fraction of the sky covered by clouds and is normally given as the discrete values n/8 where n takes the values 0, 1, 2, …, 8. The amount of time (unit: days) each month with cloudiness equal to the distinct values is given in Table 6.1. It is possible that the cloudiness at Mongstad will exceed that at Hellisøy to some extent due to the more inland location and the higher surrounding topography. It is not easy to obtain a measure of the degree of this bias.

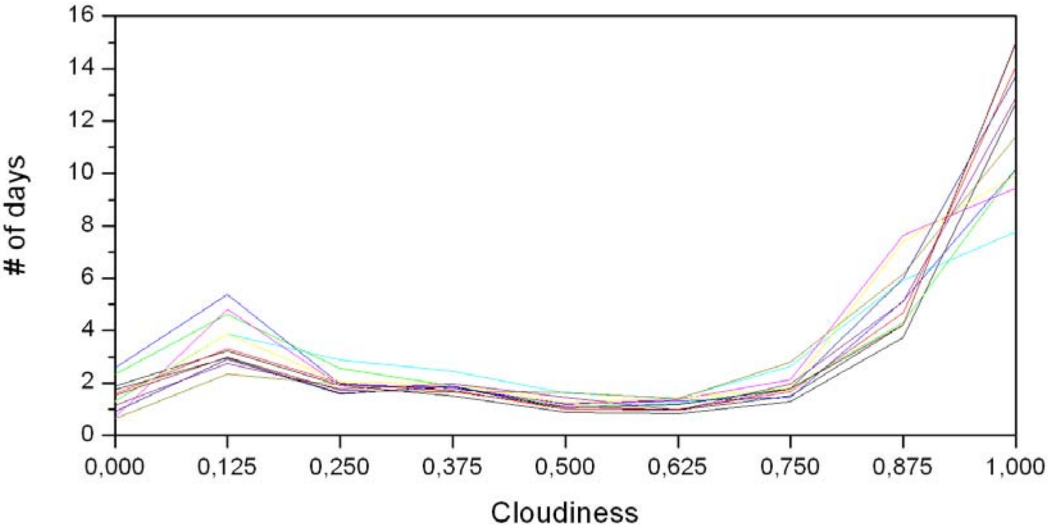


Figure 8.2. Monthly amount of time (days) with distinct values of cloudiness at Hellisøy Lighthouse, Based on data from Hellisøy Lighthouse for the period 1970 – 1992. Data are colour coded by month.

There is no information about the cloud type and it is not possible to derive the true actinic flux density from the available data. As a first approximation it is therefore assumed that a cloudiness of 1 will attenuate the actinic flux density by 50% and that less cloudiness reduces the actinic flux density in proportion. This is in rough accordance with the results of the INSPECTRO Campaign in 2008.[89]

The cloudiness in the Mongstad area will therefore reduce the cloud-free actinic flux density by around 34% to give an average effective $<j_{NO2}>_{y,eff} \approx 1.25 \times 10^{-3}$ s^{-1}, corresponding to an annual average NO_2 photolysis lifetime of around 13 min.

8.2 Nitrosamine gas phase photolysis rates and lifetimes in the Mongstad area

Taking the relative photolysis for nitrosodimethylamine, NDMA, to be $j_{NDMA}/j_{NO2} = 0.53 \pm 0.03$,[42] the 1-year average photolysis lifetime of NDMA in the Mongstad area is estimated to be 25 min.

The calculations indicate the extreme photolysis lifetimes to be ≈ 8 min. at mid-summer (average around 12 min during the summer half-year), and ≈ 4 hours at mid-winter (average around 35 min during the winter half-year). It should be noted, again, that the Tuazon *et al.*[42] result for $j_{NDMA}/j_{NO2} = 0.53 \pm 0.03$ is an *upper* limit to the nitrosamine relative photolysis rate, and that the true value could be as much as 50% lower. If this is the case then the photolysis lifetimes of NDMA in the Mongstad area could be two times longer than the estimates values given above.

There is only one experimental study quantifying the gas phase photolysis rate of nitrosamines in the literature. It is expected that the gas phase UV spectra of all aliphatic nitrosamines without other substituent groups will be "identical" and that their absorption efficiencies will also be "identical". However, differences in structure will result in different efficiencies to the internal relaxation processes and thereby to different quantum efficiencies to photo-dissociation.

Differences in molecular structure will also influence the rate of gas phase formation of nitrosamines. An energy plot of stationary points in NDMA formation illustrates this effect, Figure 8.3.

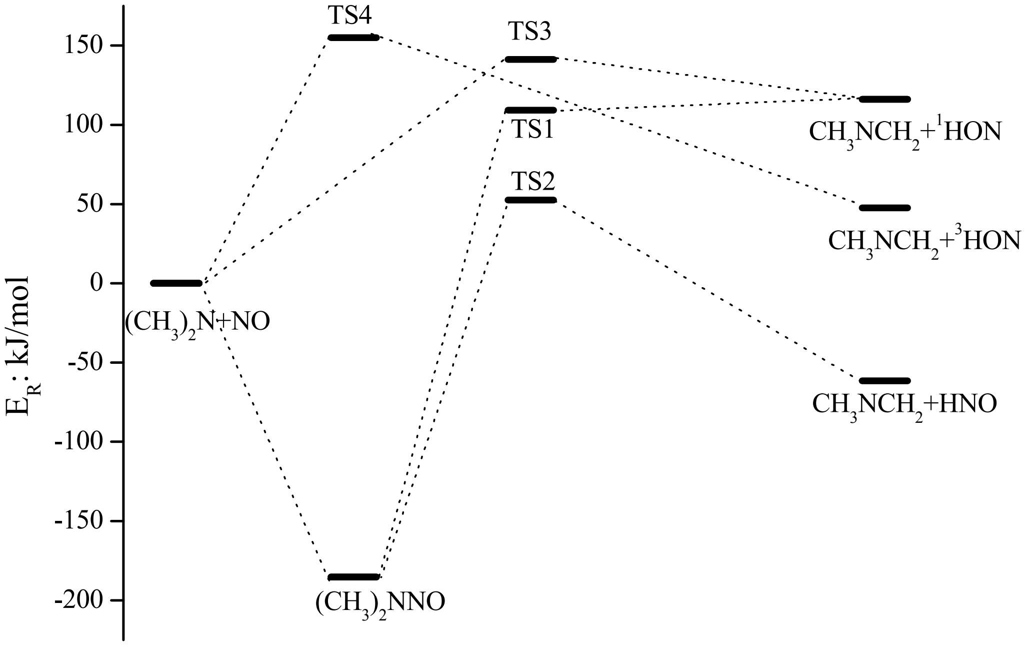


Figure 8.3. Stationary points of the $(CH_3)_2N$ +NO singlet of triplet reaction surfaces calculated at the G4 level. (From Tang *et al.*, Ref. [90]).

The $(CH_3)_2N$ + NO → $(CH_3)_2NNO$ reaction is exothermic by around 180 kJ mol^{-1}. This excess energy has to be dissipated or re-distributed to internal degrees of freedom to prevent back-dissociation before quenching by collisions with the bath gas (N_2 and O_2). The time between collisions at atmospheric pressure is typically 10^{-9} s in the troposphere, which is 5 orders of magnitude longer than the radiation-less intra-molecular transitions. Systematic calculations on larger systems show very little variation in the energetics. Obviously, larger molecules than NDMA will have more degrees of freedom to distribute excess energy and their effective rates of nitrosamine formation are therefore expected to be larger than that of NDMA.

The formation rate for reaction of larger amino radicals with NO is expected from theoretical considerations to be larger than that of the dimethylamino radical. At the same time the gas phase quantum yield to photo-dissociation is expected to be smaller than that of NDMA. In conclusion, for the gas phase the atmospheric lifetimes of larger nitrosamines are expected to be *longer* than that of NDMA. Considering that nitrosamines absorb around 340 nm, which corresponds to photon energies around 350 kJ mol^{-1}, and that the R_1R_2N—NO bond enthalpy is around 180 kJ mol^{-1}, the lifetimes of the excited S_1 states cannot differ much among the various nitrosamines.

9 Gas phase chemical lifetimes of amines and amine photo-oxidation products

9.1 Structure Activity Relationship (SAR)

On the basis of kinetic information available in 1987 Atkinson proposed at Structure-Activity Relationship (SAR) including the OH radial interaction with $–NH_2$, >NH, and >N- groups.[91] In this SAR the total OH radical reaction rate constant is given by:

$$\begin{aligned} k_{total} = {} & k(\text{H-atom abstraction from C-H and O-H bonds}) \\ & + k(\text{OH radical addition to >C=C< and –C≡C- bonds}) \\ & + k(\text{OH radical addition to aromatic rings}) \\ & + k(\text{OH radical interaction with –NH}_2\text{, >NH, >N-, -SH and –S- groups}) \end{aligned}$$

The calculation of overall H-atom abstraction rate constants is based upon the estimation of $-CH_3$, $-CH_2-$, >CH-, and –OH group rate constants. The $–CH_3$, $-CH_2-$, and >CH- group rate constants depend on the identity of the substituents around those groups, with

$$k(CH_3\text{-X}) = k_{prim} \cdot F(X)$$
$$k(\text{X-}CH_2\text{-Y}) = k_{sec} \cdot F(X) \cdot F(Y)$$
$$k(\text{X-CH(Y)-Z}) = k_{tert} \cdot F(X) \cdot F(Y) \cdot F(Z)$$

where k_{prim}, k_{sec}, and k_{tert} are the rate constants per $–CH_3$, $-CH_2-$, and >CH- group for a "standard" substituent, X, Y, Z are the substituent groups; and $F(X)$, $F(Y)$, and $F(Z)$ are the corresponding substituent factors. The standard substituent group is chosen to be $X = Y = Z = -CH_3$, $F(-CH_3) = 1.00$ by definition.[3] It was assumed that the majority of the initial OH radical reaction proceeds via OH radical addition to the N-atom,[3] followed by a number of decomposition reactions of the adduct leading to products. The following parameters for the amino-, nitrosamine- and nitramine-groups were suggested and later slightly modified:[92]

Substituent Group X	$F(X)$
$-NH_2$, -NH-, -N<, -NNO, $-NNO_2$	9.3

Group	k_{298} /10^{-12} cm^3 $molecule^{-1}$ s^{-1}
RNH_2	21
R_1R_2NH	63
$R_1R_2R_3N$	66
R_1R_2NNO	0
$R_1R_2NNO_2$	1.3

It should be noted that the available database is not sufficient to allow anything more than estimates of some of the necessary parameters to be made. The calculated and experimental room-temperature rate constants for the reaction of OH radicals with amines and related compounds, for which data are available, agree within a factor of 2. However, kinetic data for a wider series of such organics are needed, together with studies of the dynamics of the reactions, before a more accurate estimation technique can be developed for this general class of organic compounds.

Koch *et al.*[30] studied 3 simple, commercially available amines $(CH_3)_3CNH_2$ (TBA), $CF_3CH_2NH_2$ (TFEA) and $N(CH_2CH_2)_3N$ (DABCO) with different specialties to test the predictions of the Atkinson SAR[91] and to explore the ground for improvements. The discrepancy between observed and predicted rate constants was more than a factor of 20 for TFEA and a factor of 6 for DABCO. On this basis the authors concluded that the predictive power of the SAR for amines appears to be extremely poor. In particular the SAR does not give a sound indication to where the hydrogen abstraction actually takes place in the molecule. The apparent failure of the amine-OH SAR is linked to the fact that the reaction involves a pre-reaction adduct.[5] Consequently, the SAR cannot be improved by further measurements.

Koch *et al.*[34] make a similar point in their kinetic study of 4 simple amides *N*-methyl acetamide, *N*,*N*-dimethyl acetamide, *N*-methyl propylamide and *N*,*N*-dimethyl propylamide. There is no SAR for the amides.

9.2 Estimates of atmospheric lifetimes of amines in the Mongstad area

The diurnal average OH concentration at 60 °N vary from around 10^5 cm^{-3} in the winter to 10^6 cm^{-3} at summer.[93] The daily average mixing ratio of surface ozone in summer are between 30 and 50 ppbV in rural areas of Europe, during winter the surface ozone mixing ratio in rural areas is likely to be 10-20 ppbV.[94] Table 9.1 summarizes the atmospheric lifetimes of amines with respect to reaction with the oxidants OH and O_3 under “normal” atmospheric conditions, $\tau_{Ox} = (k_{Ox} \times [Ox])^{-1}$, and are based on the reported reaction rate constants at 298 K in Table 1. Taking the temperature dependency of the reaction rate constants into consideration makes little difference in the results. The conclusion to be drawn is that amine gas phase reaction with O_3 will not constitute an important sink in the rural environment. Further, it is likely that other processes may dominate in removing amines emitted from the atmosphere during the winter period. It should also be noted that amine reactions with Cl atoms and NO_3 radicals are not included in the lifetime estimates. This means that the actual lifetimes will be shorter.

Table 9.1. Estimated atmospheric lifetimes of amines with respect to reaction with OH radicals and O_3 during the summer and winter periods in the Mongstad area.

Compound	Abbreviation	τ_{OH} (Summer)[a]	τ_{O3} (Summer)[b]	τ_{OH} (Winter)[c]	τ_{O3} (Winter)[d]
CH_3NH_2		12 – 16 h	3 – 6 y	5 – 7 d	8 – 17 y
$(CH_3)_2NH$		4 h	5 – 9 d	2 d	14 – 28 d
$(CH_3)_3N$		4 – 8 h	1 – 2 d	2 – 3 d	3 – 6 d
$CH_3CH_2NH_2$		10 – 12 h		4 – 5 d	
$(CH_3CH_2)_2NH$			17 – 28 h		2 – 4 d
$(CH_3CH_2)_3N$			3 – 5 h		7 – 14 h
$(CH_3CH_2)_2NOH$	DEHA	3 h		1 d	
$(CH_3)_2NCH_2CH_2OH$	DMAE	3 – 6 h	1 – 2 d	1 – 3 d	3 – 7 d
$(CH_3)_2C(NH_2)CH_2OH$	AMP	10 h		4 d	
$(CH_3)_3CNH_2$	TBA	23 h		10 d	
$CF_3CH_2NH_2$	TFEA	13 d		4 m	
$N(CH_2CH_2)_3N$	DABCO	13 h		5 d	

[a] Assuming a diurnal OH concentration during summer of 10^6 cm^{-3}. [b] Assuming a diurnal O_3 mixing ratio during summer of 30 – 50 ppbV. [c] Assuming a diurnal OH concentration during winter of 10^5 cm^{-3}. [d] Assuming a diurnal O_3 mixing ratio during summer of 10 – 20 ppbV.

The reactivity of relevant amines, for which no experimental kinetic data are available, has been estimated using the Kwok-Atkinson SAR.[92] The predicted rate constants for reaction with OH radicals are listed in Table 9.2 together with the estimated atmospheric lifetimes during the summer and winter periods in the Mongstad area.

Table 9.2. Predicted rate constants at 298 K for the reaction of amines with OH radicals ($/10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}), and estimated atmospheric lifetimes of amines with respect to reaction with OH radicals and O_3 during the summer and winter periods in the Mongstad area.

Compound	Abbreviation	k_{OH}	τ_{OH} (Summer)[a]	τ_{OH} (Winter)[b]
$H_2NCH_2CH_2OH$	MEA	3.6	7 – 8 h	3 d
$CH_3NHCH_2CH_2OH$	MAE	7.9	3 – 4 h	1 – 2 d
$HN(CH_2CH_2OH)_2$	DEA	9.3	3 h	1 d
$H_2NCH_2CH_2NHCH_2CH_2OH$	HEEDA	11.6	2 – 3 h	1 d
$CH_3NHC(CH_3)_2CH_2OH$	MAMP	6.9	4 h	2 d
$HN(CH_2CH_2)_2NH$	PZ	10.6	2 – 3 h	1 d
$H_2NCH_2CH_2NH_2$	EDA	6.3	4 – 5 h	2 d

[a] Assuming a diurnal OH concentration during summer of 10^6 cm^{-3}. [b] Assuming a diurnal OH concentration during winter of 10^5 cm^{-3}.

9.3 Estimates of atmospheric lifetimes of amides in the Mongstad area

The estimated atmospheric lifetimes of amides with respect to Cl atoms, and OH and NO_3 radicals are summarized in Table 9.3 for summer conditions at Mongstad. The average nocturnal NO_3 mixing ratio is assumed to be around 20 ppt as was measured in vicinity of Vancouver,[95] and the Cl atom concentration around 6×10^4 cm^{-3}, which is representative for the polluted North Atlantic air mass.[96] Clearly, all three loss processes should be taken into account in an environmental impact assessment.

It is expected that most other amides will have similar atmospheric lifetimes.

Table 9.3. Estimated atmospheric lifetimes of amides with respect to reaction with OH and NO_3 radicals and Cl atoms during the summer period in the Mongstad area.

Compound	τ_{OH} [a]	τ_{NO3} [b]	τ_{Cl} [c]
$CH_3NHC(O)CH_3$	2 d		
$CH_3NHC(O)CH_2CH_3$	2 d		
$(CH_3)_2NC(O)CH_3$	1 d	1 d	2 d
$(CH_3)_2NC(O)CH_2CH_3$	1 d	3 d	
CH_3NHCHO	1 d	1 d	4 d
$(CH_3)_2NCHO$	1 d	7 – 9 h	2 d

[a] Assuming a diurnal OH concentration of 10^6 cm^{-3}. [b] Assuming a 12 h nocturnal NO_3 concentration of 20 pptV. [a] Assuming a diurnal Cl concentration of 6×10^4 cm^{-3}.

9.4 Estimates of atmospheric lifetimes of nitramines in the Mongstad area

It is stressed again that there are only one kinetic study of nitramines in the literature. Tuazon *et al.*[42] studied the reactions of OH radicals with $(CH_3)_2NNO_2$ (DMN) and found $k_{OH+NDMA}$= k_{OH+DMN} = (3.6 ± 0.4) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K. The atmospheric lifetime of DMN with respect to reaction with OH is therefore quite long at 60 °N. Assuming a diurnal OH concentration during summer of 10^6 cm^{-3} and a diurnal OH concentration during winter of 10^5 cm^{-3} in the Mongstad area, the estimated atmospheric lifetime of DMN is estimated to be τ_{OH}(Summer) ≈ 3 days and τ_{OH}(Winter) ≈ 4 weeks.

The nitramines predicted to be produced post emission of amines emissions to the atmosphere are summarized in Table 9.4. The Table also includes the estimate rate constants for reaction with OH radicals at 298 K. The estimation is based on the Kwok-Atkinson SAR,[92] which does not include kinetic information from primary nitramines, R_1NHNO_2. There are no data for primary nitramines, and it has been assumed that the group rate constant for $-NHNO_2$ is the same as that for $>NNO_2$.

Table 9.4. Estimated rate constants (/10^{-12} cm^3 $molecule^{-1}$ s^{-1}) for reaction of nitramines with OH radicals at 298 K, and estimated atmospheric lifetimes in the Mongstad area with respect to reaction with OH radicals.

Abbreviation	Amine precursor	Nitramine	k_{OH}	τ_{OH} (Summer)[b]	τ_{OH} (Winter)[c]
	CH_3NH_2	CH_3NHNO_2	2.6	4 d	45 d
	$(CH_3)_2NH$ $(CH_3)_3N$	$(CH_3)_2NNO_2$	3.6[a]	3 d	32 d
	$CH_3CH_2NH_2$	$CH_3CH_2NHNO_2$	10	1 d	12 d
	$(CH_3CH_2)_2NH$ $(CH_3CH_2)_3N$	$(CH_3CH_2)_2NNO_2$	19	15 h	6 d
MEA	$H_2NCH_2CH_2OH$	$O_2NNHCH_2CH_2OH$	16	17 h	7 d
MAE	$CH_3NHCH_2CH_2OH$	$CH_3N(NO_2)CH_2CH_2OH$	17	16 h	7 d
HEEDA	$H_2NCH_2CH_2NHCH_2CH_2OH$	$O_2NNHCH_2CH_2NHCH_2CH_2OH$	101	3 h	1 d
		$H_2NCH_2CH_2N(NO_2)CH_2CH_2OH$	59	5 h	2 d
		$O_2NNHCH_2CH_2N(NO_2)CH_2CH_2OH$	39	7 h	3 d
MDEA	$CH_3N(CH_2CH_2OH)_2$	$CH_3N(NO_2)CH_2CH_2OH$	17	16 h	7 d
		$O_2NN(CH_2CH_2OH)_2$	31	9 h	4 d
DMAE	$(CH_3)_2NCH_2CH_2OH$	$CH_3N(NO_2)CH_2CH_2OH$	17	16 h	7 d
		$(CH_3)_2NNO_2$	3.6	3 d	32 d
DEA	$HN(CH_2CH_2OH)_2$	$O_2NN(CH_2CH_2OH)_2$	31	9 h	4 d
AMP	$H_2NC(CH_3)_2CH_2OH$	$O_2NNHC(CH_3)_2CH_2OH$	5.8	2 d	20 d
MAMP	$CH_3NHC(CH_3)_2CH_2OH$	$CH_3N(NO_2)C(CH_3)_2CH_2OH$	7.1	2 d	16 d
PZ	$HN(CH_2CH_2)_2NH$	$HN(CH_2CH_2)_2NNO_2$	107	3 h	1 d
		$O_2NN(CH_2CH_2)_2NNO_2$	45	6 h	3 d
EDA	$H_2NCH_2CH_2NH_2$	$H_2NCH_2CH_2NHNO_2$	44	3 h	3 d
		$O_2NNHCH_2CH_2NHNO_2$	24	12 h	5 d

[a] Experimental value (From Tuazon *et al.*, Ref. [42]). [b] Assuming a diurnal OH concentration during summer of 10^6 cm^{-3}. [c] Assuming a diurnal OH concentration during winter of 10^5 cm^{-3}.

9.5 Estimates of atmospheric lifetimes of aldehydes in the Mongstad area

Aldehydes have relatively short lifetimes in the atmosphere. In addition to reactions with radicals (OH, Cl, NO_3) they also undergo photolysis. To a first approximation the photolysis rates of formaldehyde, acetaldehyde and propanal scale roughly to that of NO_2 by factors of 6×10^{-3}, 6×10^{-4} and 3×10^{-3}, respectively.[97] The estimated, yearly averaged, atmospheric lifetimes of the three aldehydes (HCHO, CH_3CHO and CH_3CH_2CHO) with respect to Cl, OH and NO_3 radicals, O_3 and photolysis are summarized in Table 9.5.

Table 9.5. Estimated, yearly averaged atmospheric lifetimes of simple aldehydes with respect to reaction with OH and NO_3 radicals and Cl atoms, and photolysis in the Mongstad area..

Compound	τ_{OH} [a]	τ_{Cl} [b]	τ_{NO3} [c]	τ_{O3} [d]	$\tau_{\mathrm{photolysis}}$ [e]
HCHO	2.7 d	16 d	86 d	>1 y	1.5 d
CH_3CHO	1.5 d	15 d	17 d	>1 y	15 d
CH_3CH_2CHO	1.2 d	9 d	8 d		3 d

[a] Assuming an average OH concentration of 5×10^5 cm^{-3}. [b] Assuming an average Cl concentration of 1×10^4 cm^{-3}. [c] Assuming an average 12 h nocturnal NO_3 mixing ratio of 20 pptV. [c] Assuming an average O_3 mixing ratio of 20 ppbV. [c] Assuming an average $j_{\mathrm{NO2}} = 1.25\times10^{-3}\ s^{-3}$.

It can be seen from Table 9.5 that the major atmospheric loss prosess for aldehydes are reaction with OH and photolysis. Taking the temperature dependency of the reaction rate constants into consideration makes little difference in the results.

10 Describing phase transfer parameters between aqueous and gas phase

In order to describe the partitioning of compounds in between the aqueous and gas phase, transfer parameter such as the uptake coefficient and the mass accommodation coefficient needs to be known. Another, usually easily available phase parameter is the Henry's law constant (H). However, H is a purely thermodynamic constant and conclusions on the partitioning based on this parameter only can be misleading. Chemical reactions of an compound in both phases can change the distribution of this compound significantly. Accordingly, the chemistry of this compound in both of the phases needs to be considered in order to get really reliable information on the partitioning of the compound. Therefore, conclusions drawn in the following on the partitioning of the target compounds should be taken only as a rough orientation since they are based on Henry coefficients. Furthermore, most of the Henry coefficients found in the literature (see Table 10.1) are estimated values which are not verified by experimental studies. Accordingly, the estimated H values can contain large uncertainties. Therefore, the numbers in Table 10.1 should not be considered as exact numbers but rather as an hint on the distribution of these compounds in the atmosphere. Exact conclusions on the distribution of these compounds are only possible based on experimental studies of mass accommodation and uptake coefficients.

Table 10.1. Compilation of Henry's law constants (H) for amines and degradation products found in the literature. Colored circles indicate the level of confidence. green = great confidence; yellow = less confidence; red = uncertain

compound		**H** **M atm^{-1}**	**reference**		
dimethylamine	DMA	31	Wilhelm *et al.*, 1977 [98]	🟢	experimental
		57	Christie and Crisp, 1967 [99]	🟢	experimental
		60	Hilal *et al.*, 2008 [100]	🟢	calculated
monoethanolamine	MEA	$6.2\cdot10^{6}$	Bone *et al.*, 1983 [101]	🟡	experimental
		$2.3\cdot10^{5}$	Hilal *et al.*, 2008 [100]	🟡	calculated
		$3.1\cdot10^{4}$	Howard and Meylan, 1997 [102]	🟡	estimated
diethanolamine	DEA	$2.6\cdot10^{7}$	Howard and Meylan, 1997 [102]	🔴	estimated
N-methyldiethanolamine	MDEA	$3.2\cdot10^{7}$	Howard and Meylan, 1997 [102]	🔴	estimated
2-amino-2-methyl-1-propanol	AMP	$1.5\cdot10^{6}$	Howard and Meylan, 1997 [102]	🔴	estimated
piperazine	PZ	$4.5\cdot10^{5}$	Howard and Meylan, 1997 [102]	🔴	estimated
piperidine	PIP	$2.2\cdot10^{2}$	Cabani *et al.*, 1971 [103]	🟡	experimental
pyrrolidine	PYR	$4.2\cdot10^{2}$	Cabani *et al.*, 1971 [103]	🟡	experimental
N-nitrosodimethylamine	NDMA	$9.6\cdot10^{2}$	Hilal *et al.*, 2008 [100]	🟡	calculated
		$5.5\cdot10^{2}$	Mirvish *et al.*, 1976 [104]	🟢	experimental
N-nitrosodiethanolamine	NDEA	$2.1\cdot10^{8}$	Howard and Meylan, 1997 [102]	🔴	estimated
N-nitrosopiperazine	NPZ	$3.7\cdot10^{6}$	Howard and Meylan, 1997 [102]	🔴	estimated
formamide	FA	$7.2\cdot10^{5}$	Howard and Meylan, 1997 [102]	🔴	estimated
glycine	GLY	$9.0\cdot10^{7}$	Saxena and Hildemann,1996[105]	🟢	experimental
alanine	ALA	$6.0\cdot10^{7}$	Saxena and Hildemann,1996[105]	🟢	experimental

In order to account for the limited data set available the literature research was extended to Henry coefficients of similar compounds. This gives at least a better idea on the distribution of certain compound classes in between the aqueous and gas phase. Conclusions for six relevant compound classes (unsubstituted alkyl amine, cyclic alkyl amines, alkanol amines, amides, nitrosamines and amino acids) are discussed in the following.

Unsubstituted alkyl amines

Unsubstituted alkyl amines such as methylamine (36-140 mol L^{-1} atm^{-1}), ethylamine (35-100 mol L^{-1} atm^{-1}) or dimethylamine (see Table) have usually Henry coefficients below 150 mol L^{-1} atm^{-1}. Henry coefficients of unsubstituted alkyl amines are further decreasing with the chain length and the number of site groups. Accordingly, such compounds will preferentially react in the gas phase and only a small part is oxidized in aqueous solution.

Cyclic amines

Henry coefficients of cyclic amines have been measured by Cabani et al. in 1971[103]. Cabani and co workers measured relatively low Henry coefficents for cyclic amines with only one nitrogen atom in the ring such as pyrrolidine (420 mol L^{-1} atm^{-1}) and piperidine (220 mol L^{-1} atm^{-1}). However, the estimated Henry coeffcient of piperazine in the Table above is three orders of magnitude higher. Based on these data it is assume by the authors that cyclic amines with only one nitrogen atom in the ring will be preferentially oxidized in the gas phase. Cyclic amines with more than one nitrogen atom will be oxidized also in aqueous solution.

Alkanol amines

Introducing an OH function in the alkyl chain of an amine increases the Henry coefficient dramatically. In case of MEA the Henry coefficient is 4-5 orders of magnitude higher (see Table) than the one for ethylamine (35-100 mol L^{-1} atm^{-1}). The Henry coefficent is even significantly higher than the values reported for mono alcohols ($\approx 10^2$ mol L^{-1} atm^{-1}) and in the same order of magnitude than dialcohols ($\approx 10^5$-10^6 mol L^{-1} atm^{-1}). Also the values for MDEA ($3.2 \cdot 10^7$ mol L^{-1} atm^{-1}) and AMP ($1.5 \cdot 10^6$ mol L^{-1} atm^{-1}) have been estimated (see Table) and are in the same order of magnitude. Therefore, it can be assumed that alkanol amines will preferentially react in the atmospheric aqueous phase.

Amides

Henrys law constants of almost all the amides proposed in the oxidation schemes above have not been found in the literature. However, it is not possible, based on the estimated value for formamide only, to give any conclusion on the partitioning of amides.

Nitrosamines

The available estimated data for Nitrosamines indicate that the nitroso group increases the Henrys law constant by an factor of ten. This means that the distribution of the nitrosamines in between the two phases is probably comparable to the corresponding amines.

Amino acids

Amino acids represent most likely an important fraction of amine degradation products in aqueous solution. These compounds have very high Henry coefficients ($\geq 10^7$ mol L^{-1} atm^{-1}). This means that they will be degraded almost solely in aqueous solution.

11 Aqueous phase kinetics and atmospheric lifetimes overview

Table 11.1 summarizes the kinetic data found in the literature for the target compounds and their degradation products. If no experimental kinetic data were available it was tried to estimate rate constants. Estimated kinetic data are indicated in the Table. Based on the kinetic data atmospheric lifetimes of the compounds in Table 9.1 have been calculated using equation 1. OH radical concentrations for the lifetime calculations have been taken from a modeling study applying the Chemical Aqueous Phase Radical Mechanism (CAPRAM 3.0) in its current version. Lifetimes were calculated in clouds and in deliquescent particles for a rural (less polluted) scenario. OH radical concentrations taken in the following are averaged values over three simulation days differing between cloud and deliquescent particle conditions. Since the applied OH radical concentrations are calculated values and strongly depends on the local radiation conditions as well as the local sources and sinks **the calculated lifetimes should considered as rough estimations only**.

$$\tau = \frac{1}{k_{2nd} \cdot [OH]} \qquad \text{(Eq. 1)}$$

Table 11.1. Summary of OH radical rate constants (T = 298 K) and calculated lifetimes in clouds and deliquescent particles for an rural scenario. Colored circles indicate the level of confidence. green = great confidence; yellow = less confidence; red = uncertain

compound		k_{2nd} [$M^{-1}s^{-1}$]		τ_{cloud} [h]	$\tau_{deliquescent\ particle}$ [h]
				[OH] = $2.2 \cdot 10^{-14}$ M	[OH] = $3.0 \cdot 10^{-12}$ M
dimethylamine	**1**	**$6 \cdot 10^7$**	**Lee et al., 2007** 🟡[55]	**210.4**	**1.5**
N-methylaminomethanol	3	< $3.0 \cdot 10^8$	estimated [a], 🔴	< 42.1	< 0.3
N-methylformamide	4	$1.2 \cdot 10^9$	Hayon et al., 1970 🟢[57]	10.5	0.1
N-nitrosodimethylamine	10	$4.3 \cdot 10^8$	Mezyk et al., 2004 🟢[67]	29.4	0.2
methylamine	11	$1.2 \cdot 10^8$	Getoff and Schwörer, 1971 🟢[50]	105.2	0.8
formamide	13	$3.7 \cdot 10^8$	Munoz et al., 2000 🟢[72]	34.1	0.3
monoethanolamine	**1**	**$3.0 \cdot 10^8$**	**Kishore et al., 2004** 🟢[73]	**42.1**	**0.3**
amino acetaldehyde	3	$3.6 \cdot 10^9$	estimated [b], 🔴	3.5	0.03
glycine	4	$1.7 \cdot 10^7$	Scholes et al., 1965 🟢[76]	742.7	5.4
ethylene glycol		$1.7 \cdot 10^9$	Hoffmann et al. 2009 🟢[106]	7.4	0.1
glycolaldehyde		$1.2 \cdot 10^9$	estimated [c], 🔴	10.5	0.1
glyoxal		$1.1 \cdot 10^9$	Buxton et al., 1997 🟢[107]	11.5	0.1
oxalic acid		$5.5 \cdot 10^7$	Ershov et al., 2008 🟢[108]	229.6	1.7
formic acid		$1.3 \cdot 10^8$	Buxton et al., 1988 🟢[109]	97.1	0.7
N-nitrosoethanolamine		-	-	-	-
2-amino-2-methyl-1-propanol	**1**	**$3.0 \cdot 10^8$**	**estimated [a],** 🔴	**42.1**	**0.3**
2-methylpropanalamine	4	$2.8 \cdot 10^9$	estimated [d], 🔴	4.5	0.03
2-methylalanine	5	$1.2 \cdot 10^8$	Goldstein et al., 1992 🟢[81]	105.2	0.8
acetone		$1.0 \cdot 10^8$	Buxton et al., 1988 🟢[109]	126.3	0.9
methylglyoxal		$5.3 \cdot 10^8$	Monod et al., 2005 🟢[110]	23.8	0.2
formaldehyde		$1.0 \cdot 10^9$	Buxton et al., 1988 🟢[109]	12.6	0.1

nitrosamine	10	-	-	-	-
methyldiethanolamine	**1**	**$4.7\cdot10^{8}$**	**Lee et al., 2007 🟢 [55]**	**26.9**	**0.2**
piperazine	**1**	**$>1.0\cdot10^{9}$**	**estimated [e], 🔴**	**-**	**-**

a) like monoethanolamine; b) like acetaldehyde; c) like $CH_3CH(OH)_2$; d) like propanal; e) assumed to be similar to morpholine

Lifetimes of the compounds in clouds are longer than in deliquescent particles due to the lower [OH] concentrations. Lifetimes of amines in clouds are usually in the range of one day or longer. However, the lifetimes towards other atmospheric oxidants such as NO_3 and ozone were not calculated due to missing kinetic data. Usually, the reactivity of NO_3 and ozone is significantly smaller compared to OH. Therefore, it is expected that the lifetimes of the compounds in Table 1 is longer during the night. This could lead to an enrichment and deposition of these compounds in particular during the winter time. In order to verify this conclusion the kinetics of NO_3 and ozone reactions should be measured.

12 Research recommendations

12.1 Gas phase

The knowledge database concerning gas phase amine oxidation has improved since the previous review by Bråthen *et al.*[5] Most of the new information is, however, of qualitative nature, and there is still a lack of quantitative information concerning the product distribution. This situation will improve considerably by the end of 2010 when the on-going ADA-2010 project will publish data from gas phase photo-oxidation studies of methylamine, dimethylamine and trimethylamine. There are no kinetic data on amine reactions with Cl atoms (marine boundary layer chemistry) and NO_3 radicals (night-time chemistry). Considering the geographical location of Mongstad, amine reactions with Cl and NO_3 could be very important.

- ***It is recommended that quantitative product studies of OH radical reactions with simple aliphatic amines are continued***
- ***It is recommended that kinetic studies of Cl and NO_3 reactions with methylamine, dimethylamine and trimethylamine be initiated.***
- ***It is recommended that kinetic and product studies of OH, Cl and NO_3 reactions with simple nitramines be initiated***
- ***It is recommended that the data base for Cl and NO_3 reactions with simple amides be supplemented***

12.2 Phase transfer

All available product data from amine gas phase oxidation studies indicate that amides constitute the main products. There are no experimental data on the subsequent atmospheric fate of amides. The on-going ADA-2010 project will supply some data for the atmospheric OH radical initiated gas phase degradation of formamide, *N*-methylformamide and *N,N*-dimethylformamide by the end of 2010 and this will improve the situation considerably. The vapour pressures of the smaller amides are high enough to prevent their partitioning to existing particles. There are no experimental data on the Henry´s Law coefficients for amides and it is therefore uncertain if they will undergo further oxidation in the gas phase or in aqueous solution.

- ***It is recommended to initiate experimental studies of the Henry´s Law coefficients for amides.***

Various nitrosamines may either be emitted directly from a post-combustion CO_2-capture facility or result from atmospheric photo-oxidation of amines post-emission. The on-going ADA-2010 project will supply some new data on nitrosamine gas phase photolysis. Considering the relatively long atmospheric lifetime of nitrosamines during the winter season at 60 °N, their partitioning into the aqueous phase may be important. There are very few experimental Henry´s Law constants available for nitrosamines.

- ***It is recommended to initiate experimental studies of the Henry´s Law coefficients for simple nitrosamines.***

Nitramines will result from atmospheric photo-oxidation of amines. There is only kinetic information for the atmospheric oxidation of one nitramine (dimethylnitramine), and there are no data on the products of atmospheric nitramine oxidation. The on-going ADA-2010 project will supply some new data on nitramine gas phase chemistry. However, the available information, including the projected results from ADA-2010 is insufficient to establish a SAR for general prediction of the atmospheric lifetimes of nitramines. Considering the relatively long atmospheric lifetime of nitramines at 60 °N, their possible partitioning into the aqueous phase may also be important. There are no experimental Henry´s Law constants available for nitramines.

- ***It is recommended to initiate experimental kinetic and product studies of atmospheric nitramine oxidation, and to initiate experimental studies of the Henry´s Law coefficients for simple nitramines***.

Amines can react with HNO_3, H_2SO_4 and organic acids reversibly forming low-vapour pressure amine salts that will partition into the aerosol phase. Equilibrium constants for amine salt formation are not available in the literature and re-volatilization may be important under atmospheric conditions.

- ***It is recommended to initiate experimental studies of amine/acid salt vapour pressure and formation enthalpy***.

Beyond the non-satisfying data on Henry constants for the compounds in questions, phase transfer can be treated by the kinetic resistance model after Steve Schwarz and hence the phase transfer of mother compounds as well degradation product can be quantified for atmospheric conditions where equilibrium considerations might be misleading.

- ***It is recommended that, as an extension of the Henry coefficient measurements, partitioning of amines and resulting products should be better described by the determination of mass accommodation and uptake coefficients of target compounds and key products***

12.3 Atmospheric aqueous phase studies and modeling

Due to the restricted number of experimental data available most of the conclusions that have been drawn in this report should be taken with care. In order to increase the level of confidence more experimental data on both oxidation and phase transfer processes are needed. More experimental evidence of the proposed oxidation schemes will strongly substantiate the conclusions. Based on the experiences of the authors and the uncertainties listed above the following studies are suggested.

Formation and Degradation of nitrosamines in aqueous solution

- ***Measuring the yields of radicalic and non-radicalic formation reactions***
- ***Measuring the reactivity towards OH, NO_3 and ozone***
- ***Characterizing photolysis processes and quantum yields***

Nitrosamine formation and degradation pathways will be experimentally assessed and kinetics and mechanisms available.

Measuring kinetics of target compounds (amines, amides) in aqueous solution (OH, NO_3 and O_3) as a function of temperature and pH (protonation)

The key rate constants and most important product from the radical-initiated degradation and conversion reactions will be available. Thus, chemical schemes will be on a much better basis and ready to be implemented into a multiphase model

Modeling studies (0-D-box model)

- ***Modeling the atmospheric fate of amines in the multiphase system based on literature data and newly obtained experimental results***
- ***Calculation of fluxes and phase ratios under different environmental conditions***

The model studies suggested here (0D-box model) will enable to quantitatively assess the main conversion, phase transfer and degradation pathways of the mother compound in questions and their derivatives when based on preceding laboratory studies. The model runs will yield reliable phase ratios of the compounds treated for the aerosol and the cloud case. It needs to be noted that such model runs will only lead to improved knowledge when based on a better experimental basis.

Note for dispersion modeling:
A dispersion model needs to be carefully set-up with proper process descriptions, preferably based on laboratory estimations of key processes. It could then be possible to model not only the chemical conversions in the gas and the aqueous phase but also the deposition of compounds and hence the input into ecosystems as such. The assessment of how this input then affects surface waters and then, finally, 'drinking water' is a subsequent step. Once the deposition fluxes are know from a model, the flux into surface waters (Lakes, rivers) will be available.

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13 Literature

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