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Final report on a theoretical study on the atmospheric degradation of selected amines

**Hanne Birgitte Bråten, Arne Joakim Bunkan,
Lihn Bache-Andreassen, Mohammad Solimannejad
and Claus Jørgen Nielsen**

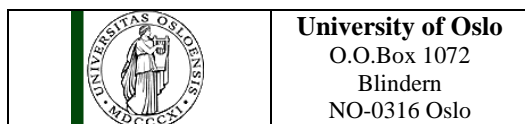
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Project report

Project title: CO₂ and amines

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Preface

CO₂ capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO₂ emissions to the atmosphere, thus reducing the main contributor to global warming. A leading technology for CO₂ capture is through the use of amines. The *CO₂ and Amines Screening Project* began with *Phase I* in May 2008. The project was initiated by NILU based on the results of an expert meeting in October 2007, and discussions with SFT. The expert meeting and the following Phase I project is based upon the concern that the emissions from CO₂ capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC)
Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric degradation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.

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Final report on a theoretical study on the atmospheric degradation of selected amines (Task 3)

1 Literature survey

Chemicals emitted into the atmosphere will undergo a series of chemical and physical processes. Gas phase organic chemicals are removed from the atmosphere by wet and dry deposition, photolysis, and chemical reaction. Compounds with liquid-phase vapor pressures $> 10^{-6}$ Torr at the ambient atmospheric temperature will to a large extent undergo reactions in the gas phase.¹ For the majority of gas-phase organic chemicals present in the troposphere, reaction with the OH radical is the dominant loss process.²

In general the degradation is initiated by reaction with OH and, where appropriate, direct photolysis and the reactions with O_3 and NO_3 . In marine areas reactions with Cl atoms may also constitute an important sink. The types of radical generated following initiation processes include peroxy (RO_2), oxy (RO) and excited and stabilized Criegee ($R'R''COO$) species, which each have a number of possible reactions which may be competitive under tropospheric conditions. The complex initiation and radical chemistry leads to the generation of many different products. Some are species which themselves have primary emissions, such as simple alcohols, aldehydes and ketones; others include complex (multifunctional) carbonyls, nitrates ($RONO_2$), peroxy nitrates ($RC(=O)OONO_2$), hydroperoxides ($ROOH$), percarboxylic acids ($RC(=O)OOH$) and carboxylic acids ($RC(=O)OH$). To describe the complete tropospheric degradation of the VOC, these products are

in turn degraded resulting, eventually in the final degradation products CO_2 and H_2O . Figure 1.1 shows the complexity of the atmospheric degradation scheme for a simple hydrocarbon, C_4H_{10} , as it is currently included in the Master Chemical Mechanism (MCM).³ The complete oxidation to CO_2 and H_2O includes 171 different species and 538 different reactions.

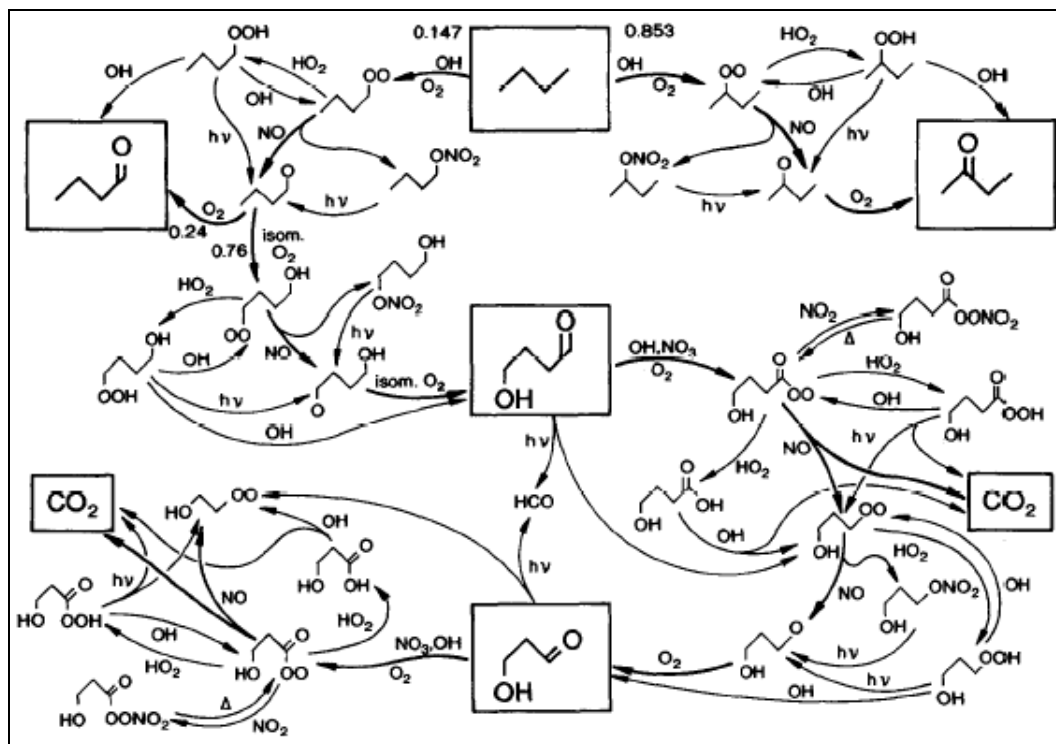


Figure 1.1: The MCM atmospheric degradation scheme for butane, Ref. 3.

Ideally a similar degradation scheme for the amines under investigation should be constructed.

1.1 Kinetic data for the reaction of amines with OH radicals

Amines are polar and hygroscopic; they have a high affinity to surfaces and present many difficulties to the experimentalist. Consequently there are only relatively few experimental studies of OH radical reactions with amines. Table 1.1 summarizes the data available in the literature.

Table 1.1: Kinetic data for the reaction of OH radicals with amines.

Compound	Acronym	$k_{\text{OH}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T /K	Ref.
CH_3NH_2	MA	$1.02 \times 10^{-11} \times \exp\{(230 \pm 150)/T\}$		4
		$(2.20 \pm 0.22) \times 10^{-11}$	298	4
		$(1.73 \pm 0.11) \times 10^{-11}$	295	5
$(\text{CH}_3)_2\text{NH}$	DMA	$2.89 \times 10^{-11} \times \exp\{(245 \pm 150)/T\}$		6
		$(6.54 \pm 0.66) \times 10^{-11}$	298	6
		$(6.49 \pm 0.64) \times 10^{-11}$	295	5
$(\text{CH}_3)_3\text{N}$	TMA	$2.62 \times 10^{-11} \times \exp\{(250 \pm 150)/T\}$		6
		$(6.09 \pm 0.61) \times 10^{-11}$	298	6
		$(3.58 \pm 0.22) \times 10^{-11}$	295	5
$\text{CH}_3\text{CH}_2\text{NH}_2$	EA	$1.47 \times 10^{-11} \times \exp\{(190 \pm 150)/T\}$		6
		$(2.77 \pm 0.28) \times 10^{-11}$	298	6
		$(2.38 + 0.5 / - 0.15) \times 10^{-11}$	295	5
$(\text{CH}_3\text{CH}_2)_2\text{NOH}$	DEHA	1.0×10^{-10}	308	7
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$	DMAE	$(4.7 \pm 1.2) \times 10^{-11}$	300	8
		$(9.0 \pm 2.0) \times 10^{-11} \times \exp(0/T)$		9
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	AMP	$(2.8 \pm 0.5) \times 10^{-11}$	300	8
$(\text{CH}_3)_3\text{CNH}_2$	TBA	1.2×10^{-11}	298	10
$\text{CF}_3\text{CH}_2\text{NH}_2$	TFEA	0.9×10^{-12}	298	10
$\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$	DABCO	2.2×10^{-11}	298	10

As shown in Table 1.1, the OH radical reactions with the aliphatic amines are rapid, with room-temperature rate constants being in the range $\sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and with negative temperature dependencies equivalent to Arrhenius activation energies in the range of 1.5 to 2.0 kJ mol^{-1} .

1.1.1 $\text{CH}_3\text{NH}_2 + \text{OH}$

Atkinson *et al.*⁴ studied the kinetics of the OH radical reaction with CH_3NH_2 (MA) over the temperature range 299-426 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H_2O while the MA concentration was determined indirectly from flow measurements. They reported a negative Arrhenius activation energy. Carl and Crowley⁵ employed the flash photolysis method to generate OH radicals via two-photon absorption by NO_2 in the presence of H_2 . The room temperature result of Carl and Crowley⁵ is ca. 30% below that of Atkinson *et al.*⁴ The absolute value of Atkinson *et al.*⁴ depends on a calibrated gas whereas Carl and Crowley⁵ used the UV cross section of the amine for calibration, and they suggest that the earlier results suffer from a calibration error.

1.1.2 $(\text{CH}_3)_2\text{NH} + \text{OH}$

Atkinson *et al.*⁶ studied the kinetics of the OH radical reaction with $(\text{CH}_3)_2\text{NH}$ (DMA) over the temperature range 299-426 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H_2O while the DMA concentration was determined

indirectly from flow measurements. A negative Arrhenius activation energy was observed. Carl and Crowley⁵ employed the flash photolysis method to generate OH radicals via two-photon absorption by NO₂ in the presence of H₂. The two room temperature determinations are in perfect agreement.

1.1.3 (CH₃)₃N + OH

Atkinson *et al.*⁶ studied the kinetics of the OH radical reaction with (CH₃)₃N (TMA) over the temperature range 299-426 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H₂O while the TMA concentration was determined indirectly from flow measurements. A negative Arrhenius activation energy was observed. Carl and Crowley⁵ employed the flash photolysis method to generate OH radicals via two-photon absorption by NO₂ in the presence of H₂. The two room temperature determinations differ by a factor of 2. The absolute value of Atkinson *et al.*⁴ depends on a calibrated gas whereas Carl and Crowley⁵ used the UV cross section of the amine for calibration, and they suggest that the earlier results suffer from a calibration error.

1.1.4 CH₃CH₂NH₂ + OH

Atkinson *et al.*⁴ determined the rate constant for the reaction of OH radicals with CH₃CH₂NH₂ (EA) over the temperature range 299-426 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H₂O. A negative Arrhenius activation energy was observed. Carl and Crowley⁵ also employed the flash photolysis method to generate OH radicals. They used two-photon absorption by NO₂ in the presence of H₂ to generate the OH radicals. The two room temperature determinations agree within 10%.

1.1.5 (CH₃CH₂)₂NOH + OH

Gorse *et al.*⁷ generated OH radicals by pulse radiolysis of H₂O and determined the rate constant for the reaction of OH radicals with (CH₃CH₂)₂NOH (DEHA) by following the OH pseudo first order decay by optical absorption spectrometry.

1.1.6 (CH₃)₂NCH₂CH₂OH + OH

Harris and Pitts⁸ determined the rate constant for the reaction of OH radicals with (CH₃)₂NCH₂CH₂OH (DMAE) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H₂O. Anderson and Stephens⁹ 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. The two room temperature determinations, however, differ by a factor of 2. No explanation to this discrepancy was offered by the authors.

1.1.7 (CH₃)₂C(NH₂)CH₂OH + OH

Harris and Pitts⁸ determined the rate constant for the reaction of OH radicals with (CH₃)₂C(NH₂)CH₂OH (AMP) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H₂O.

1.1.8 (CH₃)₃CNH₂ + OH

Koch et al.¹⁰ determined the rate constant for the reaction of OH radicals with (CH₃)₃CNH₂ (TBA) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N₂O (ArF excimer laser at 193 nm) followed by O(¹D)+H₂O → 2 OH. The OH pseudo first order decay was followed by resonance fluorescence.

1.1.9 CF₃CH₂NH₂ + OH

Koch et al.¹⁰ determined the rate constant for the reaction of OH radicals with CF₃CH₂NH₂ (TFEA) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N₂O (ArF excimer laser at 193 nm) followed by O(¹D)+H₂O → 2 OH. The OH pseudo first order decay was followed by resonance fluorescence.

1.1.10 N(CH₂CH₂)₃N + OH

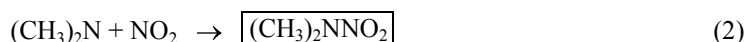
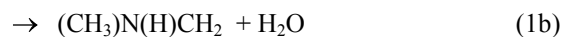
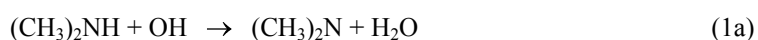
Koch et al.¹⁰ determined the rate constant for the reaction of OH radicals with N(CH₂CH₂)₃N (DABCO) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N₂O (ArF excimer laser at 193 nm) followed by O(¹D)+H₂O → 2 OH. The OH pseudo first order decay was followed by resonance fluorescence.

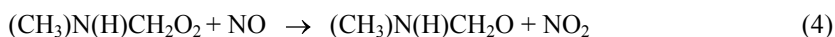
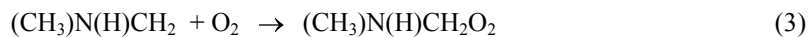
1.2 Product studies of amine + OH reactions

There are also few reports of products identified in the reactions of amines with OH radicals. Grosjean outlined detailed mechanisms for the atmospheric reactions of (CH₃)₂NH, (CH₃)₃N, (CH₃CH₂)₃N, (CH₃CH₂)₃N, (CH₃)(CH₃CH₂)NH, (CH₃CH₂)₂NCH₃, and O(CH₂CH₂)₂NH.¹¹ Schade and Crutzen have presented even more detailed atmospheric degradation mechanisms for CH₃NH₂, (CH₃)₂NH and (CH₃)₃N in a study of the emission of aliphatic amines from animal husbandry and their reactions.¹² The mechanistic suggestions in the following are based on the individual reports and in accordance with today's generally accepted understanding of atmospheric degradation processes. The reported products are highlighted in frames.

1.2.1 (CH₃)₂NH + OH

Pitts *et al.*¹³ carried out an exploratory study of the products formed when a mixture of 500 ppb (CH₃)₂NH + 80 ppb NO + 160 ppb NO₂ was subjected to natural sunlight conditions. They found (CH₃)₂NNO₂ (dimethyl nitramine) and CHON(H)CH₃ (N-methyl formamide) as gas phase products, but did not quantify the amounts formed. No (CH₃)₂NNO (dimethyl nitrosamine) was found. No formation of HCHO (formaldehyde) was reported. Aerosol was formed during the degradation. However, it was not analyzed. The product formation is in accordance with the following mechanism:

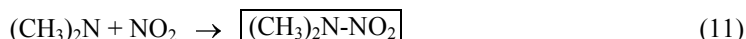
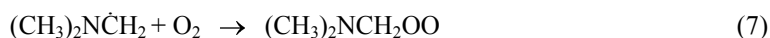
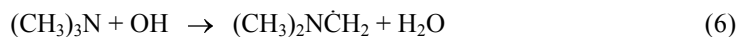




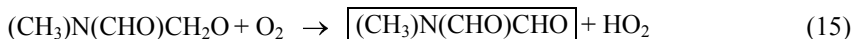
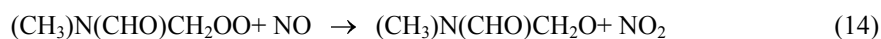
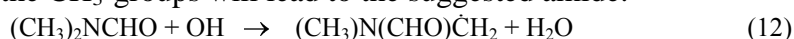
Lindley and Calvert reported the important branching ratio of the initial OH reaction with $(\text{CH}_3)_2\text{NH}$ to be $k_{(1a)} / (k_{(1a)} + k_{(1b)}) = 0.37 \pm 0.05$.¹⁴ An evaluation of the atmospheric *N*-nitrosamine formation in the degradation of dimethylamine has been presented by Glasson¹⁵ and by Hanst *et al.*¹⁶

1.2.2 $(\text{CH}_3)_3\text{N} + \text{OH}$

Pitts *et al.*¹³ carried out an exploratory study of the products formed when a mixture of 500 ppb $(\text{CH}_3)_3\text{N}$ + 80 ppb NO + 160 ppb NO_2 was subjected to natural sunlight conditions. They found $(\text{CH}_3)_2\text{NNO}_2$ (dimethylnitramine) and $\text{CHO-N}(\text{CH}_3)_2$ (N,N-dimethylformamide) as gas phase products, but did not quantify the amounts formed. Large amounts (370 ppb) of HCHO (formaldehyde) was detected in the gas phase. No $(\text{CH}_3)_2\text{NNO}$ (dimethylnitrosamine) was found. The aerosol formed contained ca. $3 \mu\text{g m}^{-3}$ (1.6 ppb) CHO-NH_2 (formamide) and another amide-like compound with $M=87$ was detected but not quantified. Schade and Crutzen¹² suggested that this mass could correspond to $\text{CHO-N}(\text{CH}_3)\text{-CHO}$ (N-formyl-N-methyl-formamide). The product formation is in accordance with the following mechanism:



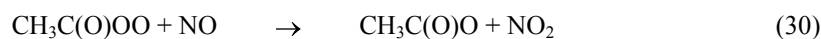
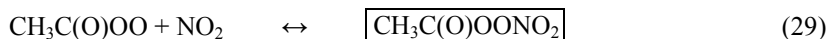
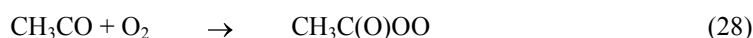
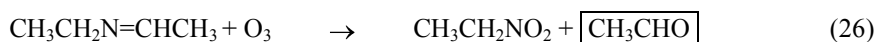
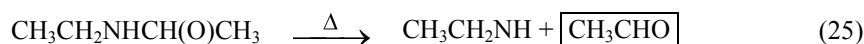
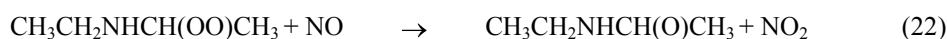
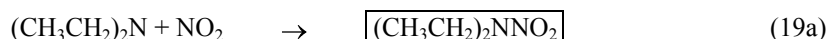
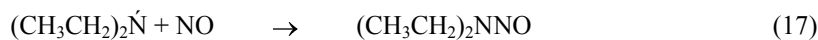
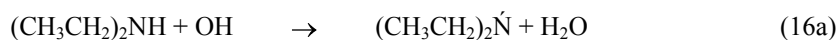
The reactivity of N,N-dimethylformamide formed in (9) is unknown, but assuming OH attack on one of the CH_3 -groups will lead to the suggested amide:



1.2.3 $(\text{CH}_3\text{CH}_2)_2\text{NH} + \text{OH}$

Pitts *et al.*¹³ carried out a study of the products formed when a mixture of 500 ppb $(\text{CH}_3\text{CH}_2)_2\text{NH}$ + 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% $\text{CH}_3\text{CO}(\text{OO})\text{NO}_2$ (PAN), 32% $(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$ (diethylnitramine), 1.4% $(\text{CH}_3\text{CH}_2)_2\text{NCHO}$ (N,N-diethylformamide), 0.2% $(\text{CH}_3\text{CH}_2)_2\text{NC}(\text{O})\text{CH}_3$ (N,N-

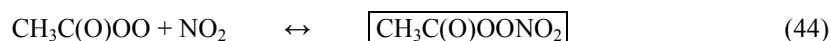
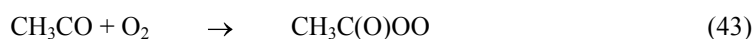
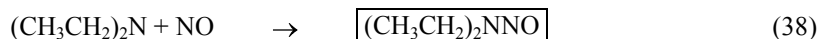
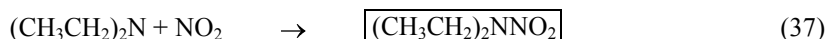
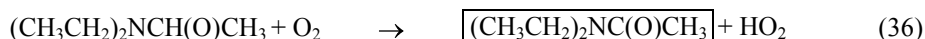
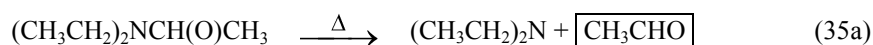
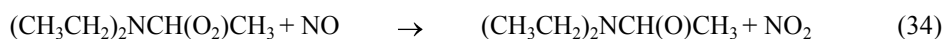
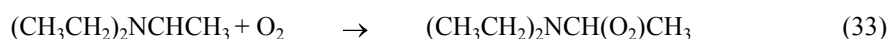
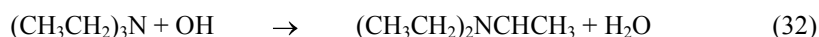
diethylacetamide), and 2.4% $\text{CH}_3\text{CH}_2\text{NC}(\text{O})\text{CH}_3$ (N-ethylacetamide) in the gas phase. In addition they found small amounts of CH_3CONH_2 (acetamide) in the aerosol phase. The mass balance reported was 46% for nitrogen and 69% for carbon. The product formation is in accordance with the following mechanism:



The finding of diethylformamide and diethylacetamide among the products is somewhat unexpected and remain unexplained because the carbon number in the oxidation product is larger than in the precursor.

1.2.4 $(\text{CH}_3\text{CH}_2)_3\text{N} + \text{OH}$

Pitts *et al.*¹³ carried out a study of the products formed when a mixture of 500 ppb $(\text{CH}_3\text{CH}_2)_2\text{NH} + 80$ ppb $\text{NO} + 160$ 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% $\text{CH}_3\text{CO}(\text{OO})\text{NO}_2$ (PAN), 1.8% $(\text{CH}_3\text{CH}_2)_2\text{NNO}$ (diethylnitrosamine), 7.4% $(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$ (diethylnitramine), 8.6% $(\text{CH}_3\text{CH}_2)_2\text{NCHO}$ (diethylformamide), 0.6% $(\text{CH}_3\text{CH}_2)_2\text{NC}(\text{O})\text{CH}_3$ (diethylacetamide), 2.6% $\text{CH}_3\text{CH}_2\text{NC}(\text{O})\text{CH}_3$ (ethylacetamide), 2.4% “unknown amide-like compound with $M=87$ ”, and trace amounts of $(\text{CH}_3\text{CO})_2\text{NH}$ (diacetamide) in the gas phase. The aerosol formed contained ca. $8.7 \mu\text{g m}^{-3}$ CH_3CONH_2 (acetamide) and $7.6 \mu\text{g m}^{-3}$ $(\text{CH}_3\text{CH}_2)_2\text{NOH}$ (diethylhydroxylamine). The mass balance reported was 59% for nitrogen and 69% for carbon. The remaining product formation is in accordance with the following mechanism:



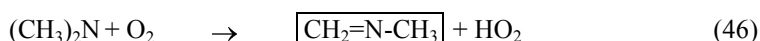
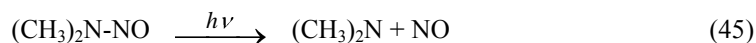
The formation of diacetamide in the gas phase (trace amounts) remains unexplained. A very speculative explanation involves a N-centred radical and intramolecular 1,2-hydrogen transfer.

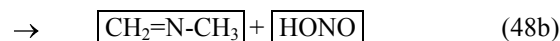
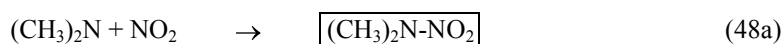
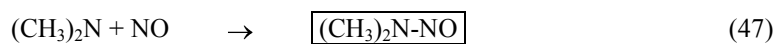
1.3 Other relevant experimental studies

1.3.1 Photolysis of N-nitroso-Dimethylamine

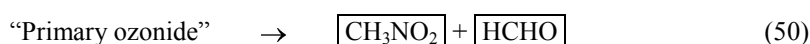
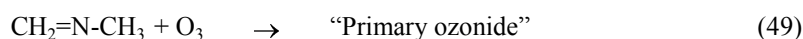
The gas phase photolysis of N-nitrosodimethylamine (NDMA) has been studied by Bamford,¹⁷ Lindley and Calvert,¹⁴ and by Tuazon *et al.*¹⁸ Stefan and Bolton reported the photolysis of NDMA in aqueous solutions at pH=3 and 7,¹⁹ and found CH_3NH_2 , HCHO , HCOOH , N_2O , $(\text{CH}_3)_2\text{NH}$ and $\text{CH}_2=\text{NCH}_3$ as products. Tuazon *et al.*¹⁸ determined the photolysis rate of NDMA relative to that of NO_2 to be $j_{\text{NDMA}} / j_{\text{NO}_2} = 0.53 \pm 0.03$. That is photolysis of NDMA (and presumably also of other nitrosamines) is extremely fast with a lifetime only minutes. The fast photolysis corresponds to a quantum yield of ~ 1 at wavelengths ≥ 290 nm, in agreement with the value of 1.03 ± 0.10 determined by Geiger and Huber at 363.5 nm.²⁰

Lindley and Calvert studied the gas phase reactions of the $(\text{CH}_3)_2\text{N}$ radical with O_2 , NO and NO_2 using FT-IR detection.¹⁴ The products formed in the $(\text{CH}_3)_2\text{N}$ radical reactions in an atmosphere containing NO and NO_2 were consistent with the following steps:

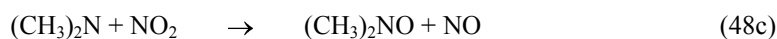




Lindley and Calvert¹⁴ also derived the following relative rates: $k_{(46)} / k_{(47)} = (1.48 \pm 0.07) \times 10^{-6}$, $k_{(46)} / k_{(48a)} = (3.90 \pm 0.28) \times 10^{-7}$, and $k_{(48a)} / k_{(48b)} = 0.22 \pm 0.07$. Tuazon *et al.*¹⁸ did not observe $\text{CH}_2=\text{NCH}_3$ in their photolysis studies where O_3 was present. Instead they found 33% CH_3NO_2 , 38% HCHO and 2% CO in addition to 65% $(\text{CH}_3)_2\text{NNO}_2$ and could account for ~100% of the carbon and ~95% of the nitrogen. Their observations were at the time explained by a fast reaction with ozone:



In a later publication Tuazon and co-workers studied the reactions of amines with O_3 and showed that $\text{CH}_3\text{N}=\text{CH}_2$ is essentially non-reactive towards O_3 .²¹ Since the experiment, in which $\text{CH}_3\text{N}=\text{CH}_2$ was found to react quickly, was such that NO_3 may be formed (NO , NO_2 and O_3 present) is the possible that the observed products may stem for the imine+ NO_3 reaction. Lazarou *et al.*²² studied the reactions of the $(\text{CH}_3)_2\text{N}$ radical with NO and NO_2 by the VLPR technique and reported $k_{(48a)} = (3.18 \pm 0.48) \times 10^{-13}$ and $k_{(47)} = (8.53 \pm 1.42) \times 10^{-14}$ cm^3 molecule⁻¹ s⁻¹. They also reported a third oxidation pathway in the $(\text{CH}_3)_2\text{N} + \text{NO}_2$ reaction:



with a rate constant $k_{(48c)} = (6.36 \pm 0.74) \times 10^{-13}$ cm^3 molecule⁻¹ s⁻¹. The rate constant for reaction (48b) could not be determined in their experiment due to overlapping signals of ions in the mass spectrometer.

1.3.2 Branching ratio in the $\text{CH}_3\text{NH}_2 + \text{Cl}$ reaction.

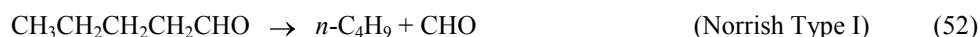
The dynamics of the Cl atom reaction with CH_3NH_2 , CD_3NH_2 , CH_3ND_2 and CD_3ND_2 has been studied by REMPI spectroscopy with TOF MS detection.²³ The results indicate branching ratios for C-H:N-H and C-D:N-D abstraction of 0.48:0.52 and 0.58:0.42. Since OH radicals and Cl atoms very often show similar selectivity in their reactions, one may expect that also hydrogen abstraction in primary amines by OH will occur from both C and N.

1.3.3 Photolysis of aliphatic aldehydes

A systematic study on the photolysis of aliphatic aldehydes was carried out under the RADICAL project. The results show that the major products resulting from photolysis of acetaldehyde, propanal and branched alkanals can be explained by a mechanism involving a primary dissociation step, which leads to the formation of free radicals (Norrish Type I):



Photolysis of *n*-butanal, *n*-pentanal and *n*-hexanal can theoretically occur through several ways.²⁴ Taking pentanal as example



It was reported that for *n*-butanal the Norrish Type I reaction accounted for 78% while the Norrish Type II reaction accounted for 22%. For *n*-pentanal the numbers were ca. 20% and 60%, respectively.

1.3.4 UV spectra of amides and imines.

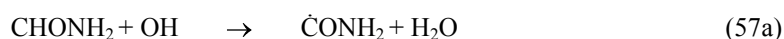
There is a single study of the electronic spectrum of $\text{CH}_2=\text{NH}$ in the region 235 to 260 nm showing a broad and structureless absorption with maximum near 250 nm.²⁵ There is no information concerning the spectrum in the region of relevance to tropospheric chemistry ($\lambda > 300$ nm). It is possible, however, that the absorption band stretches into this region such that photolysis may occur in the troposphere in which case the product is $\text{HCN} + \text{H}_2$.^{25,26}

The gas phase UV absorption cross-sections have been determined for a small series of amines: *NN*-dimethyl formamide, *NN*-dimethyl acetamide, *NN*-dimethyl propionamide and 1-methyl-2-pyrrolidone.²⁷ The spectra are structureless and show low absorption cross-sections beyond 270 nm. Consequently, tropospheric photolysis of amines will not be an important loss process.

1.3.5 $\text{CHONH}_2 + \text{OH}$

To the best of our knowledge there are no reports on the gas phase chemistry of CHONH_2 (formamide). Muñoz *et al.*²⁸ studied the $\text{CHONH}_2 + \text{OH}$ reaction in an O_2 saturated aqueous solutions at pH = 4 and 11.3. They reported a value for the rate constant in the aqueous phase, $k_{(57a)} + k_{(57b)} = 3.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 6.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To a first approximation one may assume that the gas phase rate constant for reaction with OH is the same as that of the aqueous phase. That is the lifetime (τ_{OH}) of formamide in the gasphase is more than 10 days.

The first steps of the gas phase degradation of formamide are expected to be the same as in the aqueous phase:



Muñoz *et al.*²⁸ reported that the main radical being formed is CONH₂ (85-95%), while the CHONH radical is formed in 5-15% yield.

Results from kinetic studies of OH radical reactions with a series of amides are available. The reactions show negative Arrhenius temperature dependencies. The results are summarized in Table 1.2. It can be seen from Table 1.2 that mono-*N* substituted amides will have average global atmospheric lifetimes of around 1.5 days (> 3 days at 60° N) and that di-*N* substituted amides will have average global atmospheric lifetimes of less than 1 day.

Table 1.2: Kinetic data for the reaction of OH radicals with amides.

Compound	Acronym	$k_{OH}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T /K	Ref.
CH ₃ NHC(O)CH ₃	MAA	$5.2 \times 10^{-12} \times \exp\{490/T\}$		29
CH ₃ NHC(O)CH ₂ CH ₃	MPA	$7.6 \times 10^{-12} \times \exp\{400/T\}$		29
(CH ₃) ₂ NC(O)CH ₃	DMAA	$1.36 \times 10^{-11} \times \exp\{630/T\}$ 1.9×10^{-11}	298	29 30
(CH ₃) ₂ NC(O)CH ₂ CH ₃	DMPA	$2.07 \times 10^{-11} \times \exp\{530/T\}$		29
CH ₃ NHCHO		8.6×10^{-12}	298	30
(CH ₃) ₂ NCHO		1.4×10^{-11}	298	30

1.3.6 (CH₃)₂NNO + OH

Tuazon *et al.*¹⁸ studied the atmospheric reactions of (CH₃)₂NNO (NDMA) initiated by reaction with OH radicals and found a reaction rate constant of $k_{OH+NDMA} = (3.0 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The estimated atmospheric lifetime of DMN is around 4 days.

1.3.7 (CH₃)₂NNO₂ + OH

Tuazon *et al.*¹⁸ studied the atmospheric reactions of (CH₃)₂NNO₂ (DMN) initiated by reaction with OH radicals and found a reaction rate constant of $k_{OH+NDMA} = (4.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The estimated atmospheric lifetime of DMN is around 3 days.

1.3.8 Aerosol formation

Pitts *et al.*¹³ studied the products formed when mixtures of 500 ppb (CH₃)₂NH, (CH₃)₃N, (CH₃CH₂)₂NH, or (CH₃CH₂)₃N + 80 ppb NO + 160 ppb NO₂ were subjected to natural sunlight conditions. In all cases they found aerosol formation – the most was formed during the oxidation of the tertiary amines. Murphy *et al.*³¹ have studied the secondary aerosol formation from atmospheric reactions of aliphatic amines. They studied the OH initiated oxidation of CH₃NH₂, (CH₃)₃N, (CH₃CH₂)NH, (CH₃CH₂)₃N and H₂NCH₂CH₂OH (MEA) in the presence of “seed” aerosol consisting of (NH₄)₂SO₄ or NH₄NO₃ and found that only the tertiary amines formed significant amounts of non-salt organic aerosol.

1.4 Structure Activity Relationship (SAR)

On the basis of kinetic information available in 1987 Atkinson proposed at Structure-Activity Relationship (SAR) including the OH radical interaction with -NH_2 , >NH , and >N- groups.³² In this SAR the total OH radical reaction rate constant is given by:

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

The calculation of overall H-atom abstraction rate constants is based upon the estimation of -CH_3 , $\text{-CH}_2\text{-}$, >CH- , and -OH group rate constants. The -CH_3 , $\text{-CH}_2\text{-}$, and >CH- group rate constants depend on the identity of the substituents around those groups, with

$$\begin{aligned}
 k(\text{CH}_3\text{-X}) &= k_{prim} \cdot F(X) \\
 k(\text{X-CH}_2\text{-Y}) &= k_{sec} \cdot F(X) \cdot F(Y) \\
 k(\text{X-CH(Y)-Z}) &= k_{tert} \cdot F(X) \cdot F(Y) \cdot F(Z)
 \end{aligned}$$

where k_{prim} , k_{sec} , and k_{tert} are the rate constants per -CH_3 , $\text{-CH}_2\text{-}$, 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 $X = Y = Z = \text{-CH}_3$, $F(\text{-CH}_3) = 1.00$ by definition.³³ It was assumed that the majority of the initial OH radical reaction proceeds via OH radical addition to the N-atom,³³ 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:

Substituent Group X	F(X)
-NH_2 , -NH- , -N< , -NNO , -NNO_2	10

Group	$k_{298} / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
-NH_2	20
>NH	60
>N-	60

Citing Atkinson: “The available database is not sufficient to allow anything more than estimates of some of the necessary parameters to be made”. Further, “...the calculated and experimental room-temperature rate constants for the reaction of OH radicals with the series of amines and related compounds for which data are available again 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.*¹⁰ studied 3 simple, commercially available amines (TBA, TFEA and DABCO) with different specialties to test the predictions of the Atkinson SAR³² 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.

A somewhat similar problem with the SAR predictions is encountered for aldehydes. In this class of compounds, however, the bond enthalpy of the aldehydic hydrogen is significantly lower than those of the other C-H bonds and abstraction of the aldehydic hydrogen is completely dominant.³⁴ To be discussed later (Section 2.3, page 22) the inadequacy of the SAR is in both cases linked to “negative activation energies”. For other classes of compounds the predictive power of the SAR is well documented.

The Atkinson SAR^{32,33,35} is at present the best tool for estimating the atmospheric lifetimes of the degradation products of amines. The nitrosamines and nitramines are of prime concern. There are few experimental data available and a bold estimate of the reactivity of nitrosamine and nitramines, but according to the data available the -NNO and -NNO₂ groups actually enhance the reactivity of the neighboring C-H bonds by a factor of ~10 compared to an alkyl group:

Rate constant	$k_{\text{OH}} / 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	τ_{OH}
$k_{(\text{OH} + \text{O}_x\text{NN-CH}_3)}$	1.3×10^{-12}	9 days
$k_{(\text{OH} + \text{O}_x\text{NN-CH}_2\text{-})}$	8.9×10^{-12}	1 day
$k_{(\text{OH} + \text{O}_x\text{NN-CH}<)}$	1.8×10^{-11}	15 h

Until experimental data are available the best estimate of the OH reaction rate constants indicates that OH radical reactions with nitrosamines and nitramines of the general formulas O_xNN-CH₂- and O_xNN-CH< should be included in the amine degradation schemes.

Experiments have shown amides (RC(=O)NR'R'') as products in the atmospheric amine degradation. As there are no experimental gas phase data available the SAR prediction is not reliable but to a first approximation one may estimate the following group rate reaction constants:

Rate constant	$k_{\text{OH}} / 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	τ_{OH}
$k_{(\text{OH} + >\text{NC}(=\text{O})\text{-CH}_3)}$	1.0×10^{-13}	> 100 days
$k_{(\text{OH} + >\text{NC}(=\text{O})\text{CH}_2\text{-})}$	7.0×10^{-13}	17 days
$k_{(\text{OH} + >\text{NC}(=\text{O})\text{-CH}<)}$	1.5×10^{-12}	8 days

The predictions compare well with the experimental aqueous phase OH rate constant for formamide (HCONH₂) of $6.2 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.²⁸

For the N-substituted amides the situation is the same as for the amines: no projection is available. A conservative estimate is to place the substituent factor at a value less than that of the amine group, in which case the group lifetime of any N-substituted amide will be more than 2 days.

For alcohols the estimated group reaction rate constants ($R = -CH_3$) and the associated lifetimes are approximately:

Rate constant	$k_{OH}/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	τ_{OH}
$k_{(OH + R-CH_2OH)}$	3.4×10^{-12}	3 days
$k_{(OH + RR'CHOH)}$	8.9×10^{-12}	1.5 day
$k_{(OH + RR'R''COH)}$	1.7×10^{-13}	>50 days

The OH-initiated oxidation reactions of intermediate products containing $-CH_2OH$ and $>CHOH$ groups should therefore be included in the amine degradation schemes.

Carter and Atkinson³⁶ have reviewed the atmospheric chemistry of alkanes and presented generic rate constants for decomposition and isomerisation reactions of alkoxy radicals. Many of these constants may, at least to a first approximation, also be used for the alkoxy radicals formed during the degradation of aliphatic amines.

For the alkoxy radical decomposition the experimental activation energies correlate well with the enthalpy change of reaction, see Figure 1.2. The correlation derived is:³⁶

$$E_a = 50.2 + 0.70 \times \Delta_r H / \text{kJ mol}^{-1}$$

Assuming Arrhenius behavior of the unimolecular decomposition, the A factor is given by: $A = n \times 8 \times 10^{14} \text{ s}^{-1}$ where n is the reaction path degeneracy.

The publication by Carter and Atkinson³⁶ also includes tables of estimated rate constants for 1,4- and 1,5- hydrogen shift reactions ($RC-H\bullet\bullet\bullet OR' \rightarrow RC\bullet\bullet\bullet HOR'$), but these tables will not be included here. Suffice to say that the 1,4-hydrogen shift reactions in general are too slow compared to competing reactions to be of importance.

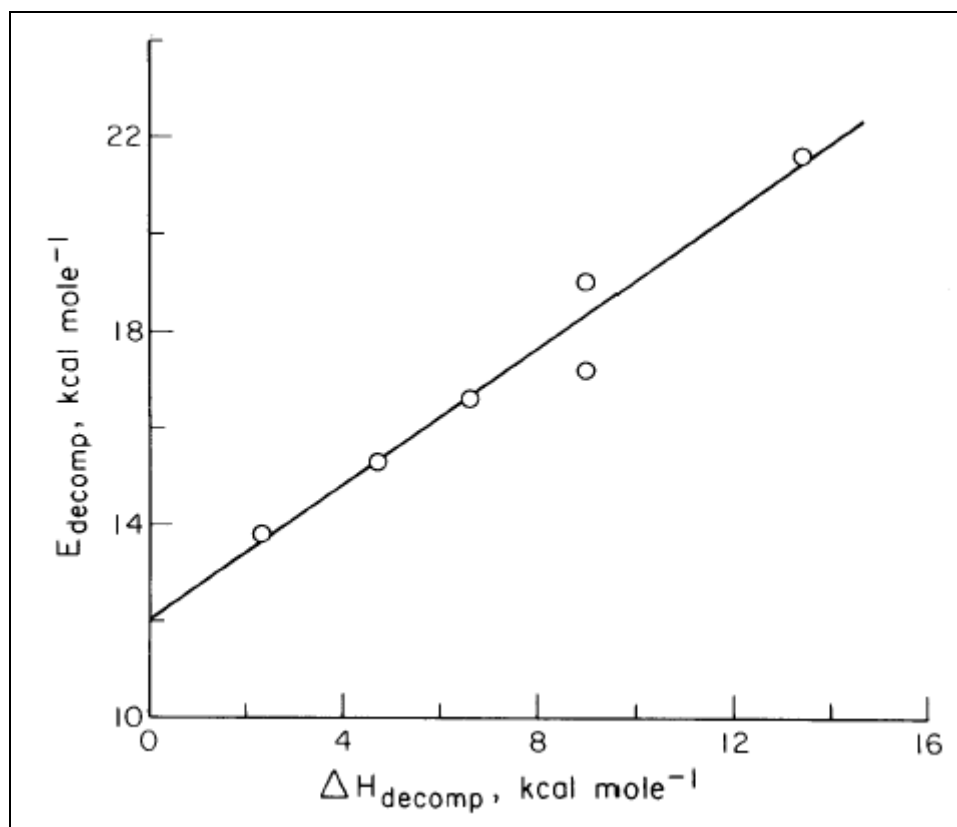


Figure 1.2: Correlation between the experimental energy of activation for alkoxy radical decomposition and calculated enthalpy of reaction. (From Ref. 36).

1.5 Quantum chemistry studies

There is only one quantum chemical study on the OH reaction with aliphatic amines published. Galano and Alvarez-Idaboy³⁷ presented their results for CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $\text{CH}_3\text{CH}_2\text{NH}_2$ from BHandHLYP/6-311++G(2d,2p) calculations of the potential surfaces, and from CCSD(T) single-point energies of the stationary points. Intrinsic Reaction Coordinate (IRC) calculations were carried out at the DFT-level and the reactions rate constants were calculated using Canonical Variational Theory (CVT). They report (in unites of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$):

$$\begin{aligned}
 k_{\text{CH}_3\text{NH}_2+\text{OH}}(\text{T}) &= 5.89 \times 10^{-11} e^{-757/\text{RT}} & k_{\text{CH}_3\text{NH}_2+\text{OH}}(298) &= 5.2 \times 10^{-12} \\
 k_{(\text{CH}_3)_2\text{NH}+\text{OH}}(\text{T}) &= 2.72 \times 10^{-11} e^{200/\text{RT}} & k_{(\text{CH}_3)_2\text{NH}+\text{OH}}(298) &= 5.2 \times 10^{-11} \\
 k_{\text{CH}_3\text{CH}_2\text{NH}_2+\text{OH}}(\text{T}) &= 1.39 \times 10^{-11} e^{-49/\text{RT}} & k_{\text{CH}_3\text{CH}_2\text{NH}_2+\text{OH}}(298) &= 1.2 \times 10^{-11}
 \end{aligned}$$

which compares within a factor of 2 with the experimental values. However, the temperature dependence differs in sign for CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$. A closer inspection of the methodology employed in calculating the reaction rates reveals that the authors have used inconsistent methods and that the apparent agreement at room temperature is accidental.

Galano and Alvarez-Idaboy also presented branching ratios for the different H-abstraction reactions. For CH_3NH_2 they predict a branching ratio of C:N centered H-abstraction of 80:20; for $(\text{CH}_3)_2\text{NH}$ their predicted branching ratio of C:N centered H-abstraction is 48:52; and for $\text{CH}_3\text{CH}_2\text{NH}_2$ their predicted branching ratios of C2:C1:N centered H-abstractions are 0 : 98 : 2. Again, any resemblance to experimental values is merely accidental.

1.6 Summary of literature data

Aliphatic amines react very fast in the atmosphere with OH radical rate constants in the range $(1-7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. With an average global OH radical concentration of $10^6 \text{ molecules cm}^{-3}$ ($5 \times 10^5 \text{ molecules cm}^{-3}$ at 60° N) their lifetimes are then $\tau_{\text{OH}} = 4 - 28 \text{ h}$. For the methyl-substituted amines, the trend of the room-temperature rate constants suggests that these reactions proceed via abstraction from the C-H bonds and, where possible, the N-H bonds. From the rate constants and the C-H and N-H bond enthalpies (see later), it has been suggested that for CH_3NH_2 , and probably also $\text{C}_2\text{H}_5\text{NH}_2$, H atom abstraction from the C-H bonds predominates, while for $(\text{CH}_3)_2\text{NH}$, H atom abstraction from the N-H bond is competitive with H atom abstraction from the C-H bonds.³³

The experimental branching ratio of hydrogen abstraction by OH radicals from the CH_3 and NH groups in $(\text{CH}_3)_2\text{NH}$ is 63:37,¹⁴ which compares to 48:52 from a theoretical calculation.³⁷ There are no other experimental branching ratios available and there are no thorough studies of the products resulting from the reaction between OH radicals and primary amides. A theoretical study suggests a branching ratio of C:N centered H-abstraction of 80:20. Although the theoretical study leaves many open questions, one should clearly not disregard the possibility that a significant fraction of the initial hydrogen abstraction takes place from the amino group as suggested by the theoretical calculations.³⁷

There are no experimental kinetic data for the reactions of aliphatic amines with other important atmospheric oxidants such as Cl atoms and NO_3 radicals. Although the OH radical is the most important oxidant Cl atoms and NO_3 radicals may account for as much as 10% of the atmospheric degradation in coastal areas. There are, however, experimental results for branching ratio in CH_3NH_2 for the C-H:N-H abstraction of 0.48:0.52. Since OH radicals and Cl atoms very often show similar selectivity in their reactions, one may expect that also hydrogen abstraction in primary amines by OH will occur from both C and N.

The few product studies report amides, nitrosamines, nitramines, aldehydes, PAN, imines, and nitro compounds among the products formed in the degradation of aliphatic amines. Of these classes of compounds the nitrosamines undergo rapid photolysis during daytime with a lifetime $\tau_{\text{UV}} \sim \text{minutes}$. All products are in concord with today's understanding of standard atmospheric degradation mechanisms. N-centered radicals are special in the sense that they react slowly with O_2 but so fast with NO and NO_2 that their atmospheric fate under normal conditions is governed by reactions with the latter two.

The well established SAR by Atkinson and coworkers^{32,33,35} does not work well for amines and, in addition, it does not give a sound indication to where the hydrogen abstraction actually takes place in the molecule.

The best estimate of OH rate constants for reaction with nitrosamines and nitramines of the general formulas O_xNN-CH_2- and $O_xNN-CH<$ indicates that OH radical reactions with should be included in the amine degradation schemes.

The best estimate of OH rate constants for reaction with amides and N-substituted amides of the general formulas $H_2NC(=O)-R$, $RHNC(=O)-R'$ and $RR'NC(=O)-R''$ indicates that their lifetimes with respect to reaction with OH radicals are > 2 days and that they can be considered as end products in the amine degradation schemes.

The best estimate of OH rate constants for reaction with compounds containing $-CH_2OH$ and $>CHOH$ groups should be included in the amine degradation schemes.

2 QCC toolbox for mechanistic elucidation

2.1 Computational Methods

We have used the complete basis set model chemistry, CBS-QB3, for thermochemistry calculations. The CBS-QB3 method uses B3LYP hybrid density functional geometries and frequencies, and gives both high reliability (maximum error for the reference G2 test set is only 11.7 kJ mol⁻¹) and good accuracy (mean absolute error is 3.6 kJ mol⁻¹), with little penalty in computational speed.³⁸ We employed MP2³⁹ and CCSD(T)⁴⁰ calculations for accurate calculations of stationary states on the potential energy surface of reaction between selected amines and the OH radical. All calculations were carried out with the Gaussian 03 program.⁴¹ Unrestricted wavefunctions were used to describe open shell systems and bond breaking processes; singlet ground state structures were calculated using a restricted wavefunction. The core electrons were kept frozen in the calculations. Dunning's correlation-consistent aug-cc-pVXZ ($X = D, T$)^{42,43} basis sets were employed in the MP2 and CCSD(T) calculations.

The minimum energy path (MEP) connecting reactants and products were computed at the MP2/aug-cc-pVDZ level of theory using the intrinsic reaction coordinate (IRC) method of Gonzales and Schlegel.^{44,45} The IRC calculations were carried out in mass-weighted Cartesian coordinates using a step size of 0.02 u^{1/2} bohr.

2.2 Thermochemistry

We have calculated the thermo-chemistry of relevant reactions in CBS-QB3 calculations, which we consider reliable within ca. 5 kJ mol⁻¹ (see above). In many cases both the reactants and products under investigation have several

conformational energy minima. In these cases the minimum energy conformation has always been used for calculating the thermodynamic functions.

The enthalpy of a chemical bond R—X is defined by the reaction:



Bond enthalpies are therefore a special case of the general reaction enthalpy. However, they are always positive. There are only few experimental bond enthalpies available for amines,⁴⁶⁻⁴⁸ and in most cases they have large uncertainties. Table 5.1 in the Annex (page 85) includes calculated and observed bond enthalpies for the relevant amines. Table 5.2 in the Annex (page 86) summarises the calculated bond enthalpies for various intermediates predicted in the atmospheric degradation of the amines under investigation.

Calculated reaction enthalpies are, in many cases, included in the detailed mechanistic description of the atmospheric degradation.

2.3 Energetics and mechanisms from QCC

2.3.1 CH_3NH_2 , $(CH_3)_3NH$, $(CH_3)_3N + OH$

The recent theoretical results by Galano and Alvarez-Idaboy³⁷ for the OH reactions with CH_3NH_2 , $(CH_3)_2NH$ and $CH_3CH_2NH_2$ were based on BHandHLYP/6-311++G(2d,2p) DFT-calculations of the potential surfaces, combined with CCSD(T) single-point energies of the stationary points. DFT-calculations can be very misleading for low-barrier cases and it was decided to carry out a systematic study of the potential energy surfaces of reaction between OH and CH_3NH_2 , $(CH_3)_3NH$, and $(CH_3)_3N$ at the CCSD(T)//MP2 level of theory. The potential energy hyper-surfaces were first scanned in MP2/aug-cc-pVDZ calculations; the stationary points were located and geometry optimized in MP2/aug-cc-pVTZ calculations, and single point energies obtained in CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ calculations. Figure 2.1 shows the energetics of the $CH_3NH_2 + OH$ reaction. Apparently the reaction proceeds via a pre-reaction adduct ca. 25 kJ mol⁻¹ below the reactant energy. Including the zero point energies the saddle points are found at 7.5 and 6.0 kJ mol⁻¹ below the reactants energy for the N-H and the C-H hydrogen abstractions, respectively. That is the reaction is unusual by having a “negative barrier”. It should be noted that calculations employing smaller basis sets result in a positive barrier to reaction.

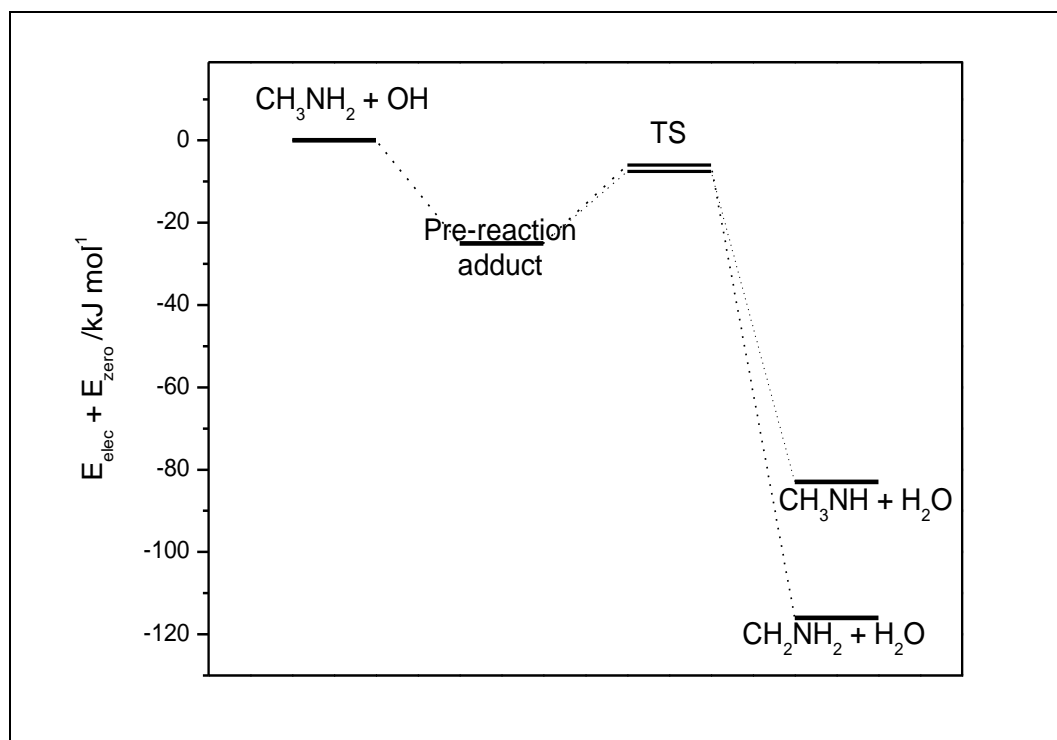
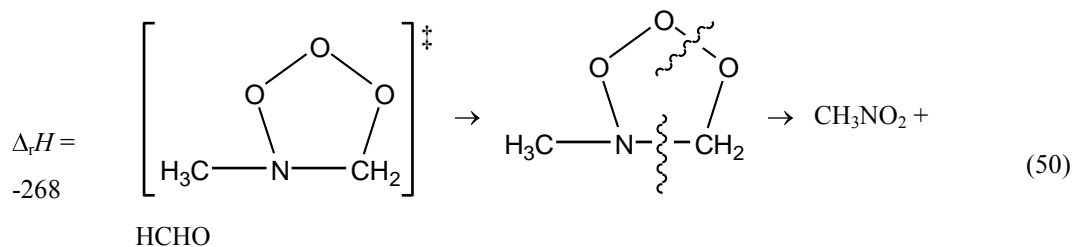
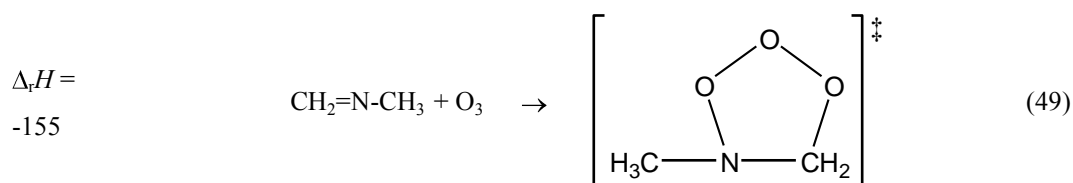


Figure 2.1: Energetics of the $\text{CH}_3\text{NH}_2 + \text{OH}$ reaction calculated at the $\text{CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ}$ level.

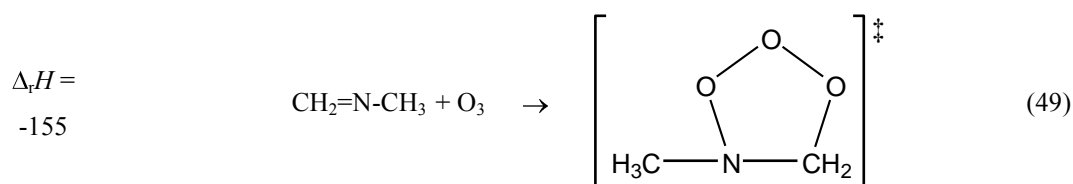
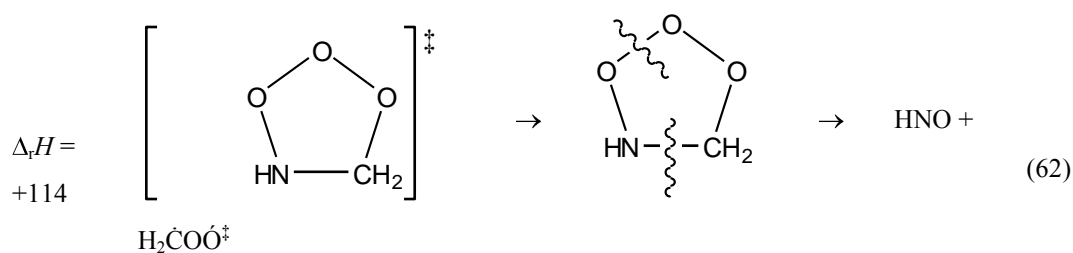
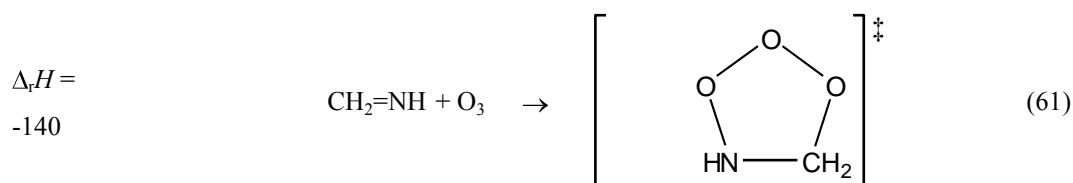
It is difficult to calculate the rates of reactions with negative barriers; the main problem is linked to the width of the dynamical bottleneck for the reaction. We are currently calculating the rates by RRKM theory and results from these calculations will be communicated as soon as possible.

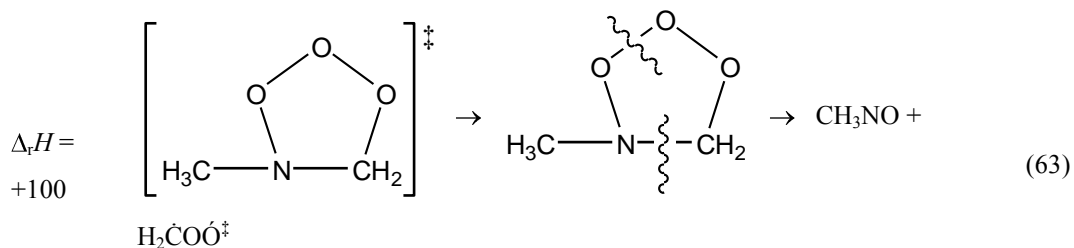
2.3.2 $R\text{-N=CR'R''} + \text{O}_3$

Lindley and Calvert studied the gas phase reactions of the $(\text{CH}_3)_2\text{N}$ radical with O_2 , NO and NO_2 and found $\text{CH}_2=\text{NCH}_3$ among the products.¹⁴ Imines are unstable compounds and difficult to synthesize, and this is the only experimental observation of an imine being formed in the atmospheric degradation of amines. There is little doubt, however, that imines are formed in general during the atmospheric degradation of amines – most likely they simply react so fast with oxidants that they have evaded detection. Tuazon *et al.*¹⁸ did not observe the expected $\text{CH}_2=\text{NCH}_3$ in their photolysis studies of $(\text{CH}_3)_2\text{NH}$ where also O_3 was present. Instead they found CH_3NO_2 and HCHO being formed and suggested a fast ozonolysis reaction (49)-(50) to account for the loss of N-methylene-methanamine and the formation of nitromethane. Unsaturated hydrocarbons react with O_3 in an addition reaction to form a primary ozonide, which dissociates into a carbonyl compound and a biradical Criegee-intermediate. Virtually nothing is known about the analogous reactions of imines.



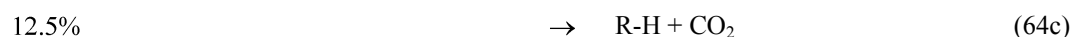
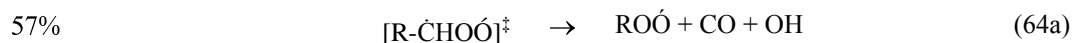
To elucidate the atmospheric fate of imines the ozonolysis reaction was investigated in B3LYP/aug-cc-pVDZ calculations. The formation of the primary ozonides of methanimine and N-methylene-methanamine are calculated to be exothermic by $\Delta_r H = 140$ and 155 kJ mol^{-1} , respectively. The barriers to dissociation of the primary ozonides were estimated from B3LYP/aug-cc-pVDZ calculations by elongating the N-C distance while relaxing structure. The barriers were found to be around 105 and 115 kJ mol^{-1} for the methanimine and N-methylene-methanamine ozonides, respectively, and the highly excited ozonides have more than sufficient energy to dissociate. However, the QCC calculations suggest that the methanimine and N-methylene-methanamine ozonides both dissociate as follows:





The atmospheric fate of nitrosomethane and presumably also other nitrosoalkanes is photolysis after excitation in the visible band around 600-700 nm. The prevailing reaction of the photolysis is the C-N bond breaking to yield CH_3 radicals and NO .^{49,50} Virtually nothing is known about the atmospheric fate of HNO ; it reacts fast with O_2 with a rate constant $k_{\text{O}_2} = 8 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature,⁵¹ that is its lifetime is less than 1 min at atmospheric pressure. The product of the reaction is unknown but is likely to be either NO , NO_2 or N_2O .

The fate of the excited Criegee biradical $[\text{H}_2\text{COO}]^{\ddagger}$, is well known and included in the MCM protocol:³ 50% $\text{CO} + \text{H}_2\text{O}$, 36% CH_2OO , 13% $\text{HO}_2 + \text{CO} + \text{OH}$. The relaxed CH_2OO subsequently reacts with H_2O to form HCOOH and H_2CO . For the longer-chain Criegee biradicals the mechanisms and product distributions are more complex; the pattern varies slightly but the general branching (non stoichiometric reactions) is:



Thus, around 70% of the R-CHOO Criegee biradicals ends as alkyl peroxy radicals, ROO (which eventually will end as carbonyl compounds), 12% as saturated compounds, RH , 11% as carboxylic acids, and only 7% as the corresponding aldehyde, R-CHO .

Conclusion: The route predicted from first principles predicts other products than those originally postulated by Tuazon and co-workers.¹⁸ It is therefore comforting that the same authors later retract their postulated mechanism.²¹ However, it is not obvious why the reaction between $(\text{CH}_3)\text{N}=\text{CH}_2$ and O_3 is slow.

2.3.3 $R-N=CR'R'' + OH$

Unsaturated hydrocarbons also react with the OH radical in an addition reaction followed by addition of O_2 to the other carbon atom to form a peroxy radical. We have investigated the analogous imine reaction. Figure 2.2 shows the potential energy curves for addition of an OH radical to $HN=CH_2$. The addition to the N atom is not stable enough to secure a lifetime in the order of 10^{-9} s, which is a typical time between collisions at atmospheric pressure. The C atom is, as expected, clearly the preferred reaction site being exothermic by 130 kJ mol^{-1} .

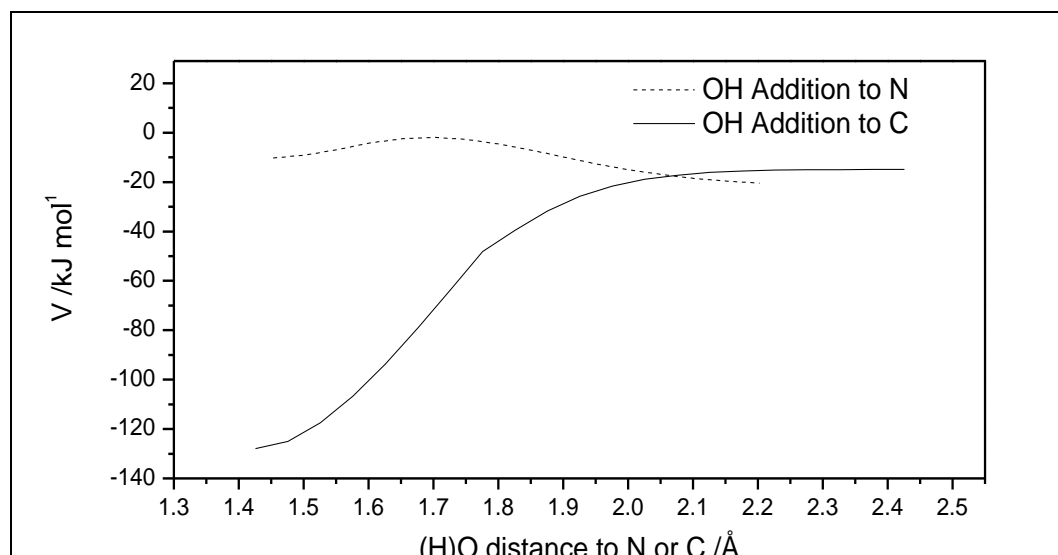
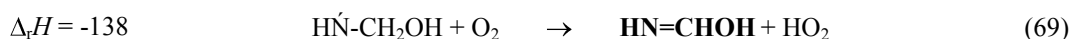
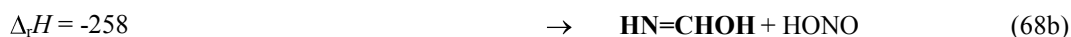
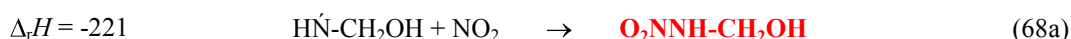
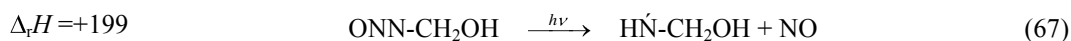
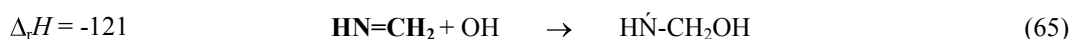


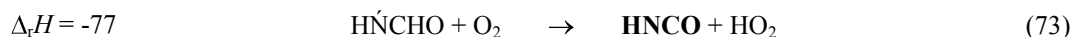
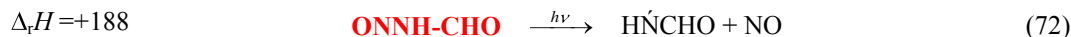
Figure 2.2: Potential energy curve for the addition of an OH radical to $HN=CH_2$ as resulting from B3LYP/aug-cc-pVDZ calculations.

From the experimental studies by Lindley and Calvert¹⁴ and by Tuazon *et al.*¹⁸ it is known that O_2 reaction with N-based radicals is very slow but that reactions with NO and NO_2 are very fast. OH addition to the carbon atom in an imine, $RN-C(R'R'')-OH$, may therefore result in the formation of nitrosamines, nitramines and new enol-like imines (the possible fate of such enol-like compounds will be discussed below). Taking methanimine as the example:



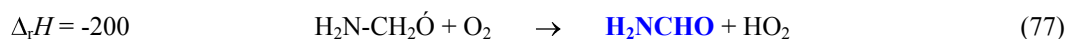
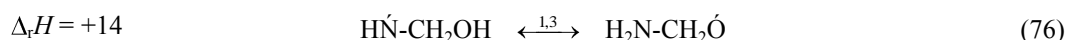
According to the bond enthalpy calculations the threshold wavelength for photolysis of the nitrosamine formed in (66) is the 604 nm in accordance with the short photolysis lifetime determined by experiment.¹⁸ The C-H bond enthalpies in

ONNHCH₂OH and O₂NNHCH₂OH are very low ($\Delta_r H = 313$ and 336 kJ mol^{-1} , respectively) and hydrogen abstraction from the CH₂-groups is expected to be fast



The N-nitroso-formamide formed in (71) is expected to undergo photolysis like the nitrosamines and the threshold wavelength is calculated to be 640 nm.

Because the imine-OH adduct formation (65) is highly exothermic, $\Delta_r H \sim -121 \text{ kJ mol}^{-1}$, it may be feasible for the excited adduct to overcome the internal barrier to 1,3-hydrogen shift which would lead to the formation of H₂NCHO (formamide):



Such an internal rearrangement may take place with a rate which is orders of magnitudes faster than any bimolecular chemical reaction. The results from a B3LYP/aug-cc-pVDZ scan of the energy surface in the hydrogen shift from the HN-C(H₂)-OH radical to H₂N-CH₂O is shown in Figure 2.3. The calculated barrier to the hydrogen shift is ca. 120 kJ mol^{-1} and this suggests that the reaction (76) is feasible. However, the reaction is slightly endothermic which suggests that it may not be a dominant atmospheric route following OH addition to the imine.

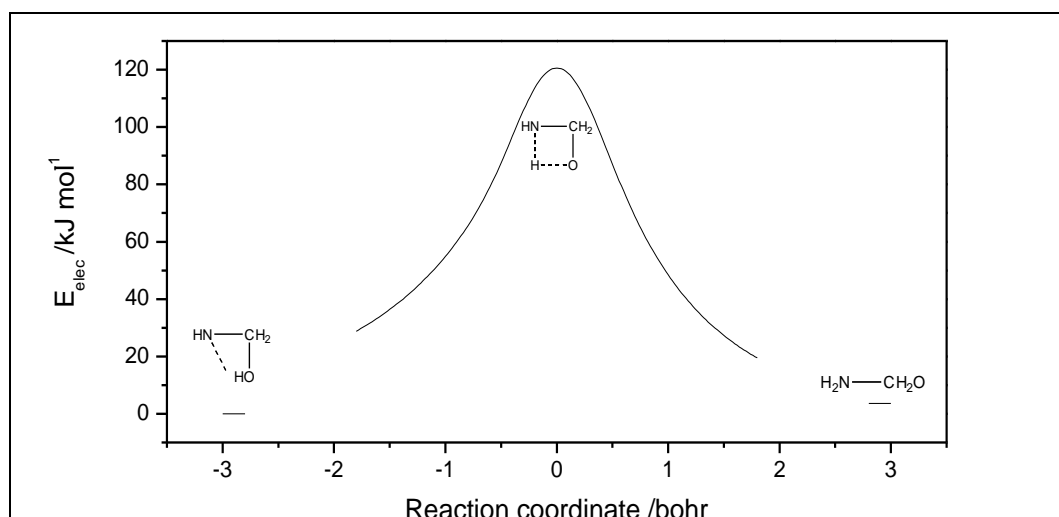


Figure 2.3. Electronic energy (kJ mol^{-1}) along the reaction coordinate for the 1,3-hydrogen shift reaction: $\text{HN-CH}_2\text{OH} \rightarrow \text{H}_2\text{NCH}_2\text{O}$. Results from B3LYP/aug-cc-pVDZ calculations.

2.3.4 Atmospheric fate of $RN=CR'OH$

The enol-imine resulting in (68b) and (69) is highly energized when formed and isomerization to the corresponding amide (1,3-hydrogen shift) is conceivable.

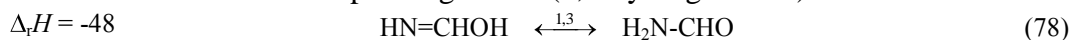


Figure 2.4 shows the electronic energy along the reaction coordinate. The barrier at the saddle point is 145 kJ mol^{-1} above the energy of HN=CHOH (methaneimidic acid) calculated at the B3LYP/aug-cc-pVDZ level. Advanced CASPT2-calculations confirm this number. We conclude that the internal 1,3-hydrogen shift in HN=CHOH is feasible and that this will be the major atmospheric route of such enol-imines formed in the atmospheric degradation of amines.

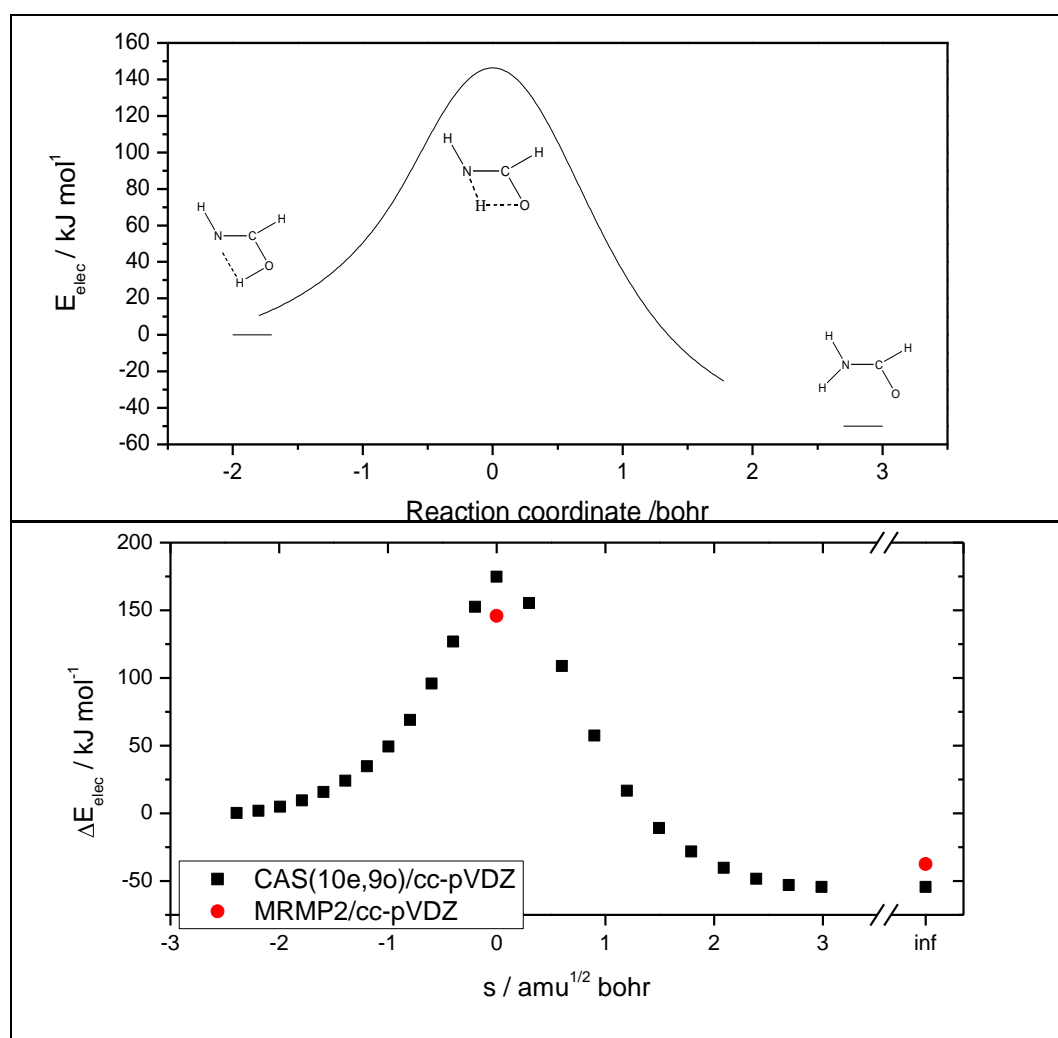


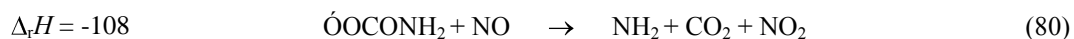
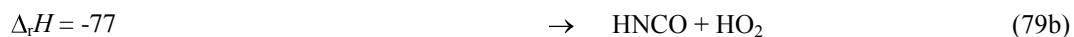
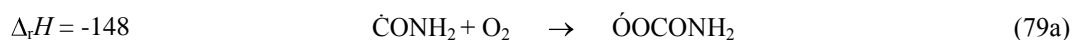
Figure 2.4. Electronic energy (kJ mol^{-1}) along the reaction coordinate for the 1,3-hydrogen shift reaction: $\text{HN=CHOH} \rightarrow \text{H}_2\text{NCHO}$. Top: Results from B3LYP/aug-cc-pVDZ calculations. Bottom: Results from CAS(10e9o)/cc-pVDZ and MRMP2/cc-pVDZ calculations

2.3.5 NH_2CHO (and other amides) + OH

In amides the N atom is best described as being sp^2 -hybridised whereas the N atom in amines is best described by being sp^3 -hybridised. This makes an enormous difference in the reactivity of these classes of compounds towards OH radicals. As mentioned in Section 1.3 there are no reports on the gas phase chemistry of amides in general and CHONH_2 (formamide) in particular. As a consequence, there is no SAR-data which can be applied to the $-\text{C}(=\text{O})-\text{N}<$ group. The kinetic study of the OH reaction with CHONH_2 in O_2 saturated aqueous solutions by Muñoz *et al.*²⁸ reports a value for the rate constant in the aqueous phase, $k_{(57a)} + k_{(57b)} = 6.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a branching ratio of $k_{(57a)}/(k_{(57a)} + k_{(57b)}) = 0.90 \pm 0.05$. Note that a rate constant of $k_{\text{OH}} = 6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ corresponds to a lifetime $\tau_{\text{OH}} \sim 20$ days assuming an average OH concentration of 10^6 radicals cm^{-3} . The first steps of the gas phase degradation of formamide are expected to be the same as in the aqueous phase:

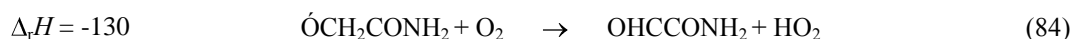
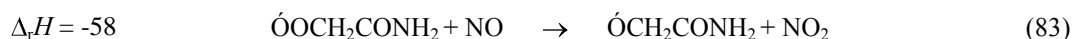
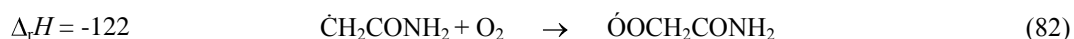
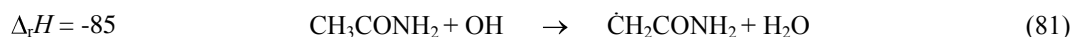


The results from bond enthalpy calculations (see Sections 2.3 and 2.4) predict $\Delta_{\text{bond}} H_{\text{C-H}} \sim 396$ and $\Delta_{\text{bond}} H_{\text{N-H}} \sim 484 \text{ kJ mol}^{-1}$ (Table 5.2, page 86) which suggest that for the gas phase oxidation of formamide only C-based hydrogen abstraction (57a) is important. The reactions following the initial hydrogen abstractions are expected to be:

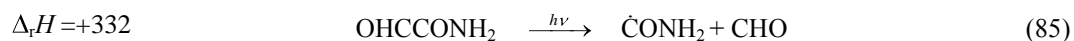


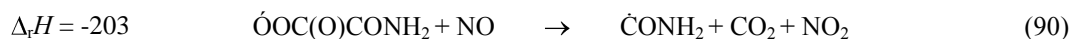
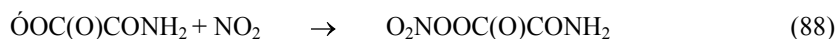
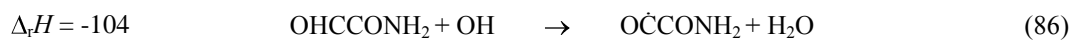
The atmospheric chemistry of HNCO (isocyanic acid) is well known and will not be elaborated on here.

Acetamide, CH_3CONH_2 is another possible product in the degradation of aliphatic amines. For this molecule the bond enthalpy calculations predict $\Delta_{\text{bond}} H_{\text{C-H}} \sim 397$ and $\Delta_{\text{bond}} H_{\text{N-H}} \sim 484 \text{ kJ mol}^{-1}$ (Table 5.2, page 86). Again, the only important oxidation reaction in the atmosphere is hydrogen abstraction from the CH_3 group leading to 2-oxo-acetamide:



2-Oxo-acetamide will undergo photolysis (threshold wavelength = 362 nm) to give $\dot{\text{C}}\text{ONH}_2$ radicals, see reactions (79a)-(80) above, or react with OH radicals:





The SAR^{32,35} predicts $k_{\text{OH}} \sim 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CH_3CONH_2 which, assuming an average OH concentration of $10^6 \text{ radicals cm}^{-3}$, corresponds to a lifetime $\tau_{\text{OH}} \sim 115 \text{ days}$.

2.4 Bond Enthalpies and OH reaction rate constants

Rate data for hydrogen abstraction reactions of radicals often show a linear relationship between the logarithm of the rate constant per abstractable H atom and the bond dissociation energy of the broken bond in the substrate. This rather empirical correlation is a simplified form of the Evans-Polanyi relationship⁵² between the activation energy, E_a , and the reaction enthalpy, $\Delta_{\text{react}}H$, for a particular process, in this case the abstraction of an H atom by the OH radical:

$$E_a = \mathbf{a} + \mathbf{b} \times \Delta_{\text{react}}H \quad (91)$$

Assuming in the Arrhenius expression the same pre-exponential factor for each relevant H atom, the logarithm of the rate constant is a measure of the activation energy and the bond dissociation energy is directly related to the exothermicity of the reaction, since the bond formed (H-OH), is the same. In the present case, however, we have 2 types of abstractable H atoms: C bonded and N bonded. We have 2 classes of activation energies and thus need to consider a 2-dimensional correlation. With a data base containing only 10 rate data attempts to extract sensible information becomes nearly futile.

The bond enthalpy – rate constant correlation approach works well for many other systems. Figure 2.5 shows the correlation for a collection of rather diverse compounds: $k_{\text{OH}} \sim 0.5 \times \exp(-0.07 \times \Delta_{\text{bond}}H)$. However, when the saddle points to reactions are below the energy of the entrance channel the basic assumptions behind the Evans-Polanyi relationship becomes invalid. We conclude that it will not be possible to establish a bond enthalpy – rate constant correlation for aliphatic amines. We also conclude that it will not be possible to construct a general Structure-Activity Relationship for aliphatic amines as any such method is essentially based on the same assumptions.

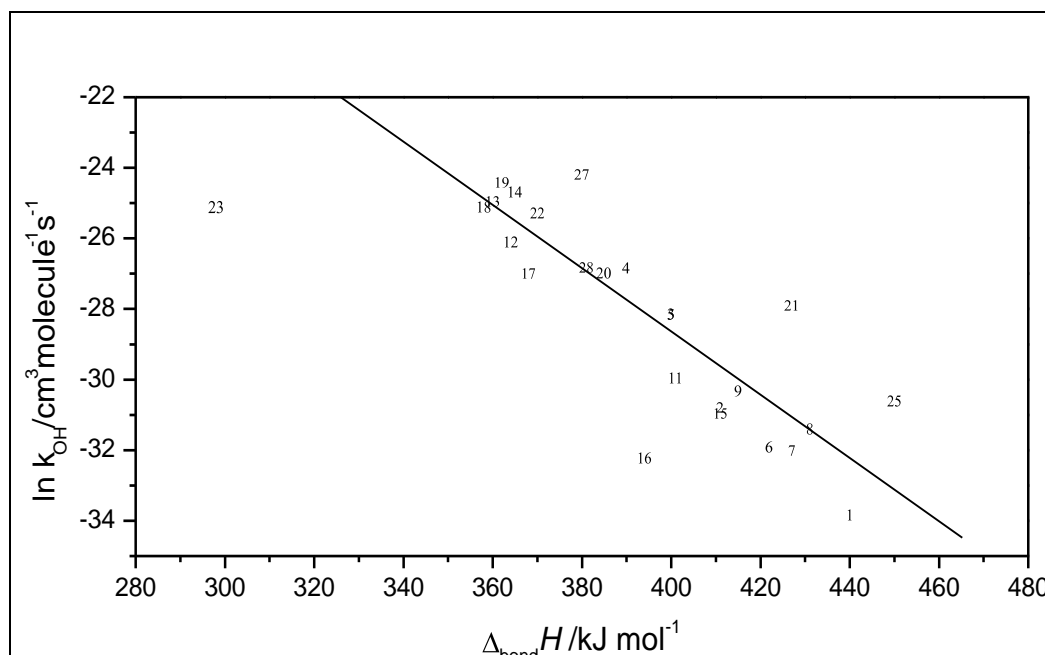


Figure 2.5: Plot of $\ln k_{OH}$ per abstractable hydrogen atom versus bond enthalpy. Data: (1) methane, (2) ethane, (3) *n*-butane, (4) methyl propane, (5) cyclohexane, (6) methyl chloride, (7) methyl bromide, (8) methyl iodide, (9) methylene chloride, (10) methylene iodide, (11) chloroform, (12) formaldehyde, (13) acetaldehyde, (14) acrolein, (15) acetone, (16) methanol, (17) toluene, (18) benzaldehyde, (19) phenol, (20) tetrahydrofuran, (21) hydrogen chloride, (22) hydrogen bromide, (23) hydrogen iodide, (24) hydrogen peroxide, (25) ammonia, (26) methoxybenzene, (27) methylmercaptan, (28) hydrogen sulphide.

3 Theoretical atmospheric degradation mechanisms

As mentioned in Section 0 the atmospheric chemistry of organics comprises many intricate reactions and intermediates. In essence, however, most of all these exotic reactions are just detours on the way to the very same products one arrives at in a little more naïve way, see Figure 1.1. Thus, when the objective is to screen for main products and a few specific classes of products in the degradation process, one may to a first approximation neglect most of the radical-radical reactions.

The theoretical mechanistic descriptions of the atmospheric degradations of $H_2NCH_2CH_2OH$, $(CH_3)_2C(NH_2)CH_2OH$, $CH_3N(CH_2CH_2OH)_2$ and $HN(CH_2CH_2)_2NH$ presented in the present report are based on results from laboratory studies of amines (see Section 2) and on well established sequences of elementary reactions in the atmospheric degradation of hydrocarbons.^{33,36,53-56} In the following mechanistic descriptions of the atmospheric degradation of the selected amines the following simplifications have been made:

- The atmospheric oxidation process of amines is initiated by reaction with OH radicals. The annual average OH concentration at 60° N is ca. 5×10^5 radicals cm^{-3} .⁵⁷

- $\text{RO}_2 + \text{RO}_2$ and $\text{RO}_2 + \text{HO}_2$ reactions have been neglected in setting up the routes.
- nitrate formation in the $\text{RO}_2 + \text{NO}$ reactions has been disregarded
- only the radical channel in aldehyde photolysis, $\text{R-CHO} \xrightarrow{h\nu} \text{R} + \text{CHO}$, is included
- OH radical reaction with alcohols is known from experiment to proceed >95% through C-based hydrogen abstraction and O-based hydrogen abstraction is not considered
- Compounds with estimated lifetimes $\tau_{\text{OH}} = (k_{\text{OH}} * [\text{OH}]_{\text{av}})^{-1} > 3$ days are considered as “end products” in the degradation schemes

Intermediate products with lifetimes $\tau_{\text{OH}} < 3$ days are highlighted in boldface. Products with lifetimes $\tau_{\text{OH}} > 3$ days are highlighted in boldface blue colour – both classes are included in the list of CAS Registry numbers in Table 5.4 on page 88 in the Annex. Possible nitrosamines and nitramines formed in the atmospheric degradation of amines are highlighted in boldface red colour and included in the list of CAS Registry whenever the entry exists.

The bond enthalpy concept is used as a guiding tool for establishing specially reactive sites in the different molecules. Reaction enthalpies (kJ mol^{-1}) from CBS-QB3 calculations (see Section 1.5, page 19) are included on the left-hand side of the individual steps in the degradation.

In modeling the atmospheric degradation a static OH concentration of 10^6 radicals cm^{-3} and a static RO_2 concentration of 10^9 radicals cm^{-3} have been assumed. Reaction rate constants are taken from the Kwok and Atkinson SAR,³⁵ from Carter and Atkinson,³⁶ and from the MCM web-site.⁵⁸ In the lack of other information it has also been assumed that the initial NO and NO_2 concentrations in the plume are comparable to that estimated for the gas power plant, that is 100 and 50 ppb, respectively. The emitted plume is assumed to contain 1 ppm of an amine and is expanding with a rate of $3.5 \times 10^{-3} \text{ s}^{-1}$ (21% per minute) for 15 minutes. The NO and NO_2 concentrations in the mixing air is assumed to be 40 and 100 ppt, respectively.

3.1 $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (MEA)

The systematic name of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ is 2-aminoethanol (CAS: 141-43-5).[#]

The results from bond enthalpy calculations ($\Delta_{\text{bond}}H_{\text{O-H}} \sim 448$, $\Delta_{\text{bond}}H_{\text{C-H}} \sim 395$, and $\Delta_{\text{bond}}H_{\text{N-H}} \sim 442 \text{ kJ mol}^{-1}$, Table 5.2, page 86) suggest two major and equally important routes:

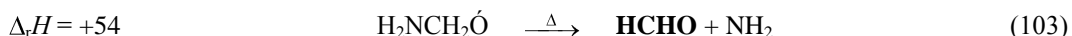
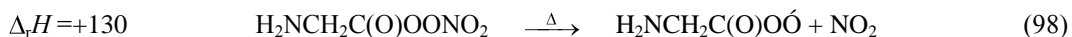
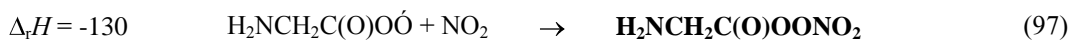
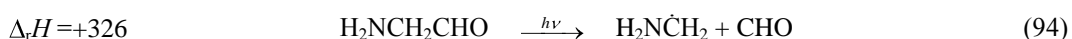
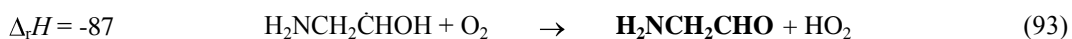
[#] The list of trivial- and trade names are plenty: β -Aminoethanol; β -Aminoethyl alcohol; β -Ethanolamine; β -Hydroxyethylamine; 1-Amino-2-hydroxyethane; 2-Amino-1-ethanol; 2-Aminoethanol; 2-Aminoethyl alcohol; 2-Ethanolamine; 2-Hydroxyethanamine; 2-Hydroxyethylamine; Aminoethanol; Colamine; ETA; Envision Conditioner PDD 9020; Ethanolamine; Ethylolamine; Glycinol; MEA; MEA (alcohol); MEA-LCI; Mealan; Monoethanolamine; Olamine; Seramine.



It is an open question if hydrogen abstraction also takes place from the amino group in primary amines. In the literature this route has been assumed to be negligible. However, there is no experimental evidence that this is really the case. The reactions following possible hydrogen abstraction from the NH₂ group is considered later in Section 3.1.3.

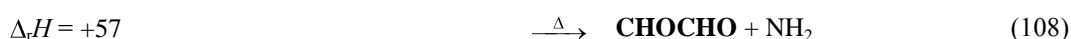
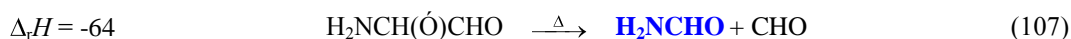
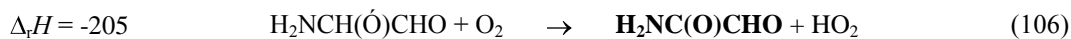
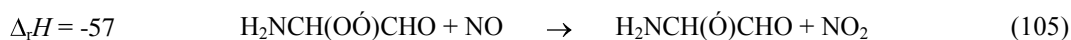
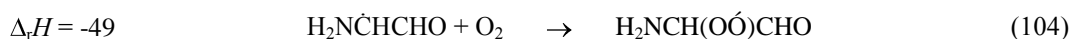
3.1.1 Fate of the $\mathbf{H_2NCH_2\dot{C}HOH}$ radical

The subsequent reactions of the R- $\dot{C}HOH$ radical are assumed to follow the degradation scheme for aliphatic alcohols leading to an aldehyde ($\mathbf{H_2NCH_2CHO}$, amino-acetaldehyde) which may either photolyse or react with OH in aldehydic hydrogen abstraction in the same manner as in other aliphatic aldehydes.³⁴ Bond enthalpy calculations on amino-acetaldehyde predict an extremely low bond enthalpy for the methylene hydrogen, $\Delta_{\text{bond}}H_{\text{C-H}_2} = 310$ compared to $\Delta_{\text{bond}}H_{\text{C(O)-H}} = 374$, and $\Delta_{\text{bond}}H_{\text{N-H}_2} = 424$ kJ mol⁻¹. This suggests that also hydrogen abstraction from the CH₂ group in $\mathbf{H_2NCH_2CHO}$ may be an important route in the further degradation (see also bond enthalpies in Table 5.2).

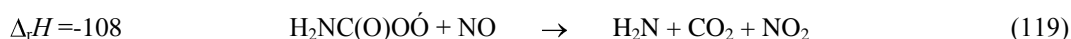
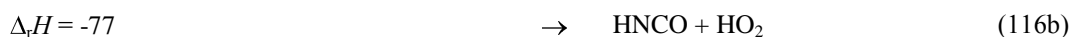
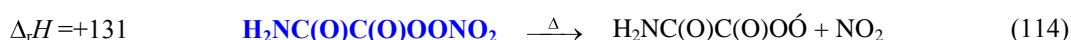
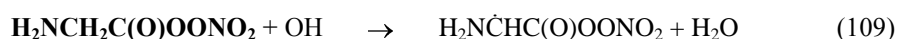


The threshold wavelength for photolysis channel (94) is 368 nm ($\Delta_r H = +326$ kJ mol⁻¹), which is at longer wavelength than the n→π* band of aliphatic aldehydes. The photolysis is thus feasible at tropospheric conditions. Reaction (99) is normally considered to be a two-step process: $\mathbf{H_2NCH_2C(O)O\dot{O}} + \text{NO} \rightarrow \mathbf{H_2N\dot{C}H_2C(O)\dot{O}} + \text{NO}_2 \xrightarrow{\Delta} \mathbf{H_2N\dot{C}H_2} + \text{CO}_2 + \text{NO}_2$. However, the quantum chemical calculations show that the intermediate acyl radical does not correspond to a local energy minimum. Reaction (100b) is speculative and based on the analogy with $\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{H}_2\text{C=O}$ (there is no experimental evidence for such a reaction taking place). Note that the thermal dissociation of the $\mathbf{H_2NCH\dot{O}}$ radical is endothermic.

The sequence of reactions initiated in (95b) by hydrogen abstraction from the CH₂ group in amino-acetaldehyde is:

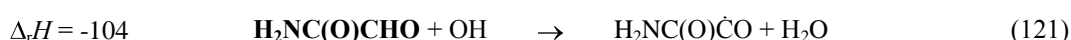
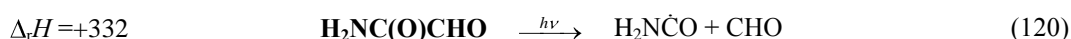


Note that the thermal decomposition in (108) is endothermic. The properties of the PAN-like molecule H₂NCH₂C(O)OONO₂ (2-amino-peroxyacetylnitrate) formed in (97) is in many ways likely to resemble those of peroxyacetylnitrate (PAN). However, the bond enthalpy calculations suggest an enhanced reactivity of the CH₂ group ($\Delta_{\text{bond}}H = 326 \text{ kJ mol}^{-1}$) and it may react just as fast with OH as the precursor amine itself:



Although speculative considering the H:C:N:O ratio, the oxo-radical formed in (111) may in principle also undergo hydrogen abstraction by O₂ resulting in H₂NCOC(O)OONO₂ which is expected to be long-lived in the gas phase.

H₂NC(O)CHO (2-oxo-acetamide) formed in (106) is expected to undergo photolysis (threshold wavelength $\lambda = 362 \text{ nm}$) or react with OH radicals in an aldehydic hydrogen abstraction reaction, and eventually leading to the same products as above.

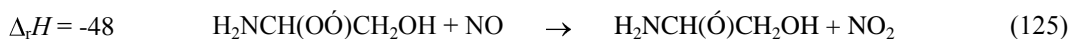
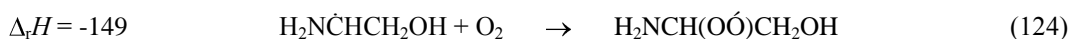
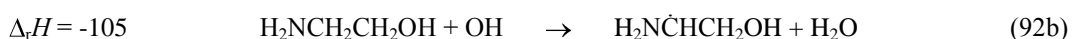


In summary, the products with lifetimes $\tau_{\text{OH}} > 3$ days expected to follow from an initial hydrogen abstraction from C1-position in MEA include H_2NCHO (formamide) and $\text{H}_2\text{NC(O)C(O)OONO}_2$ (2-amino-2-oxo-peroxyacetyl-nitrate). Products with lifetimes $\tau_{\text{OH}} < 3$ days include $\text{H}_2\text{NCH}_2\text{CHO}$, $\text{H}_2\text{NC(O)CHO}$ (2-oxo-acetamide), and $\text{H}_2\text{NCH}_2\text{C(O)OONO}_2$ (2-amino-peroxyacetyl-nitrate). The atmospheric chemistry of the possible product $\text{HN}=\text{CH}_2$ (methaneimine) is discussed in Sections 2.3.2 and 2.3.3.

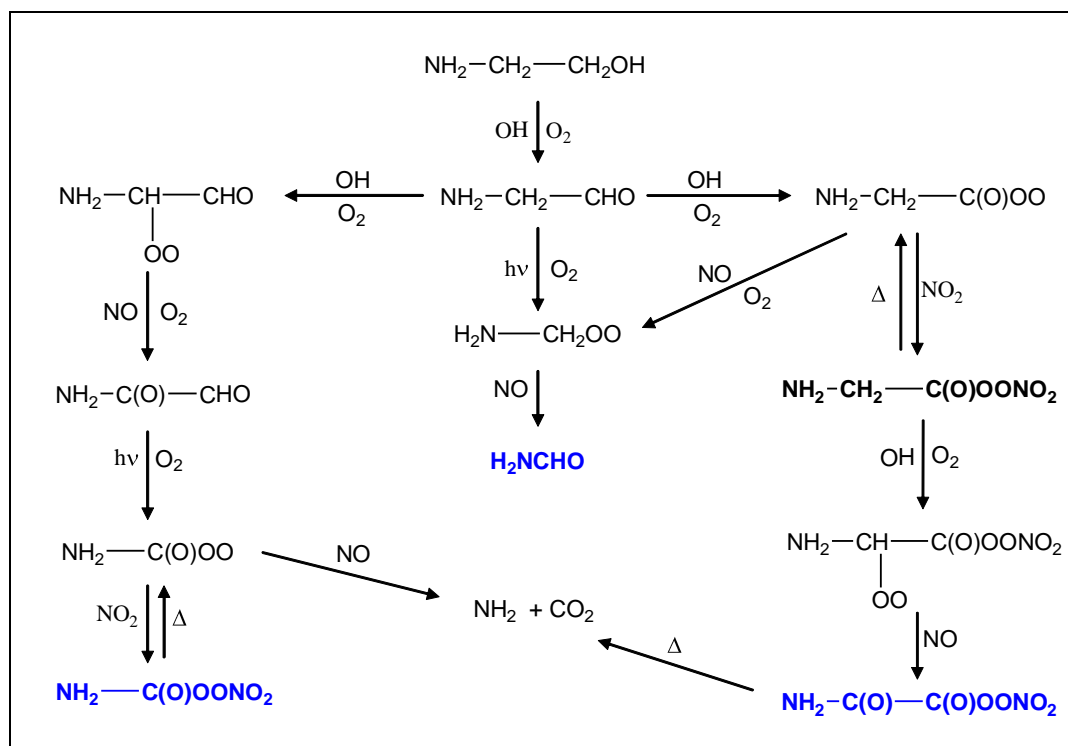
The atmospheric chemistry of the CHO and NH_2 radicals, as well as of HCHO and CHOCHO are well known and will not be elaborated on here – they are all short-lived species. The atmospheric chemistry of H_2NCHO (formamide) is discussed in Section 0. The main routes to atmospheric degradation of MEA following hydrogen abstraction from C1 are summarized in Scheme 3.1.

3.1.2 Fate of the $\text{H}_2\text{N}\dot{\text{C}}\text{HCH}_2\text{OH}$ radical

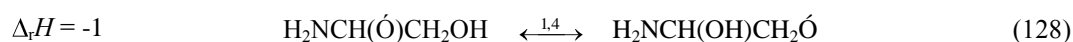
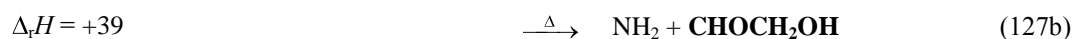
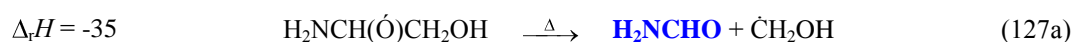
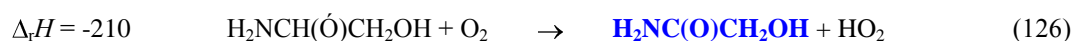
The other route (92b), initiated by hydrogen abstraction from MEA in C2-position, is expected to proceed as follows



The alkoxy radical formed in (125) may undergo abstraction of the α -hydrogen by O_2 , bond scission reactions, and, in principle, also an 1,4-hydrogen shift between the two oxygen atoms:



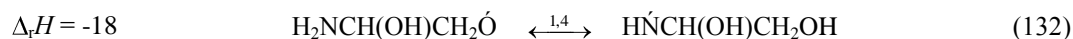
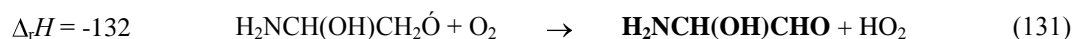
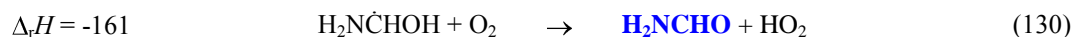
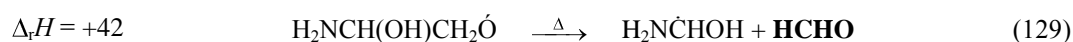
Scheme 3.1: Atmospheric degradation of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (MEA) following initial hydrogen abstraction at C1.



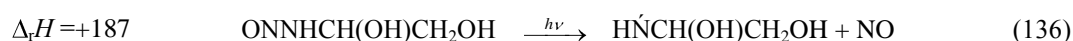
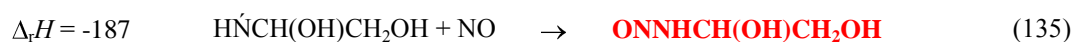
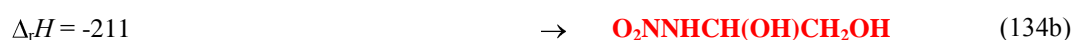
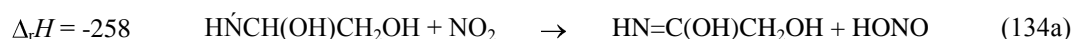
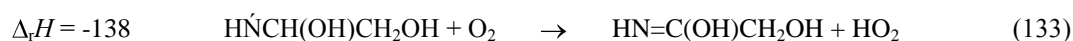
The 1,4-hydrogen shift reaction (128), which is nearly thermo-neutral, was studied in B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ calculations. The barrier was predicted to be around 150 kJ mol⁻¹ in the MP2 calculations, while the B3LYP calculations predicted a hydrogen shift barrier of around 60 kJ mol⁻¹ concerted by C-C dissociation. We conclude that the hydrogen shift reaction is not feasible under atmospheric conditions considering that the available precursor energy is less than 48 kJ mol⁻¹.

The dissociation reaction (127b) to give glycolaldehyde is calculated to be endothermic by 39 kJ mol⁻¹ and this route is therefore hardly relevant under atmospheric conditions considering that the precursor is formed with a maximum of 48 kJ mol⁻¹ excess energy.

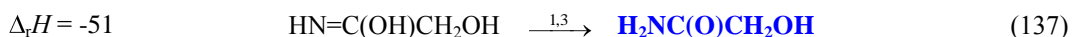
Although the formation of the in the 1,4-hydrogen shift reaction (128) is predicted unfeasible we have followed this route to map possible products. The H₂NCH(OH)CH₂Ó radical may either dissociate, undergo H-abstraction by O₂ or, in principle, go through another 1,4-hydrogen shift from the N- to the O-atom



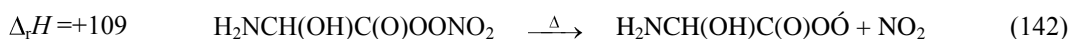
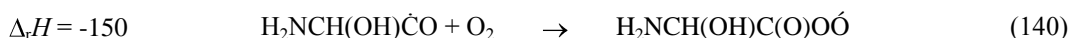
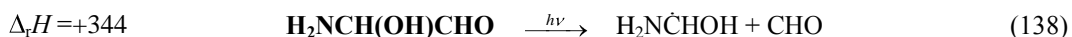
Although the dissociation reaction (129) is calculated to be endothermic by 42 kJ mol⁻¹ this route may be relevant under atmospheric conditions considering that the precursor is formed with up to 48 kJ mol⁻¹ excess energy. The barrier to the 1,4-hydrogen shift reaction (132) was estimated in QCC calculations to more than 70 kJ mol⁻¹; the hydrogen shift reaction is therefore not feasible under atmospheric conditions considering that the available precursor energy is less than 48 kJ mol⁻¹. Finally the N-centered radical, H $\dot{\text{N}}$ CH(OH)CH₂OH, formed in (132) may react with O₂ and NO₂ by hydrogen abstraction, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime (threshold wavelength $\lambda = 641$ nm) to reform the N-centered radical.



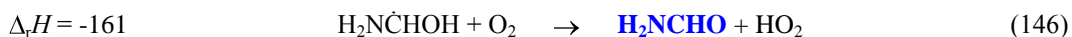
The enol-imine formed in (133) and (134a) will, according to the theoretical calculations, undergo 1,3-hydrogen shift to form the corresponding amide, see Section 2.3.3.



The 2-amino-2-hydroxy acetaldehyde ($\text{H}_2\text{NC}(\text{O})\text{CH}_2\text{OH}$) formed in (131) will either undergo photolysis or react with OH in a hydrogen abstraction. The results from bond enthalpy calculations ($\Delta_{\text{bond}}H_{\text{O-H}} \sim 453$, $\Delta_{\text{bond}}H_{\text{C-H}} \sim 313$, $\Delta_{\text{bond}}H_{\text{C}(\text{O})-\text{H}} \sim 392$, and $\Delta_{\text{bond}}H_{\text{N-H}} \sim 437$ kJ mol⁻¹, Table 5.2, page 86) suggest two major chemical routes

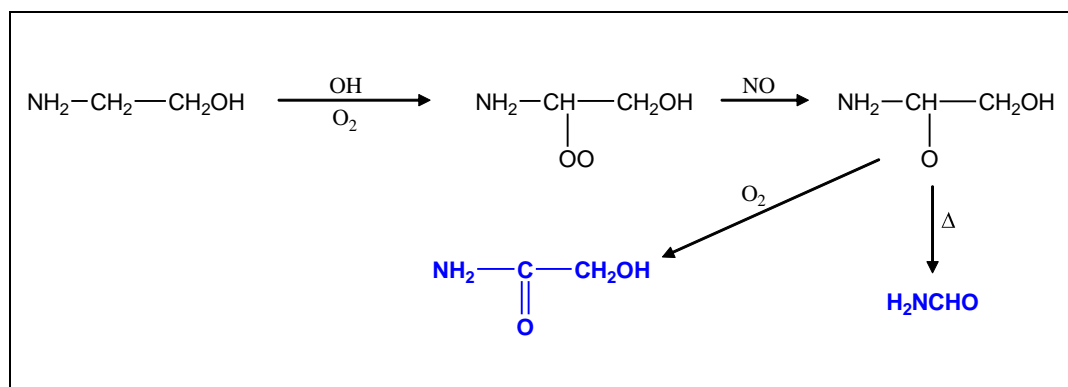


The threshold wavelength for photolysis channel (138) is 349 nm ($\Delta_r H = +344$ kJ mol⁻¹), which is in the centre of the $n \rightarrow \pi^*$ band of aliphatic aldehydes. The photolysis is thus feasible at tropospheric conditions. The $\text{H}_2\text{N}\dot{\text{C}}\text{HOH}$ radical formed in (129), (138) and (143) is expected to react with O_2 (hydrogen abstraction from RO-H) resulting in the formation of H_2NCHO (formamide).



Summing up the feasible reactions following initial hydrogen abstraction from C2-position in MEA the products include NH_2CHO (formamide) and $\text{NH}_2\text{C}(=\text{O})\text{CH}_2\text{OH}$ (2-hydroxy-acetamide). Both nitrosamines and nitramines could in principle be formed in the above reaction sequence. However, the QCC calculations place the 1,4-hydrogen shift between the two oxygen atoms in $\text{NH}_2\text{CH}(\dot{\text{O}})\text{CH}_2\text{OH}$ to be thermoneutral and with a high barrier, and the reactions following are therefore not feasible under atmospheric conditions. More important, the formation of nitrosamines and nitramines follow an additional 1,4-hydrogen transfer between N- and O-atoms, and the barrier to this reaction far exceeds the available reaction enthalpy of the precursor. One may therefore conclude that nitrosamines and nitramines will not result from reactions following hydrogen abstraction for C2-position in MEA.

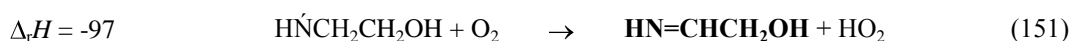
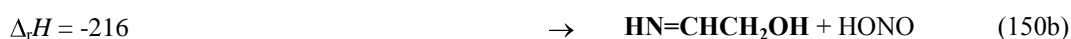
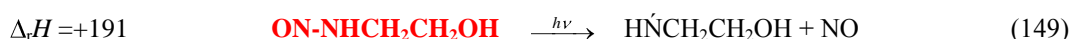
The main routes to the atmospheric degradation of MEA following hydrogen abstraction in C2-position are therefore very simple, Scheme 3.2



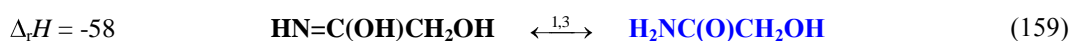
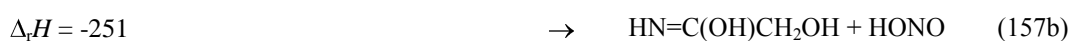
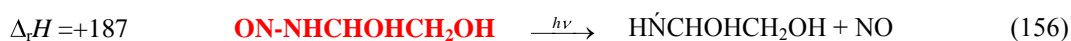
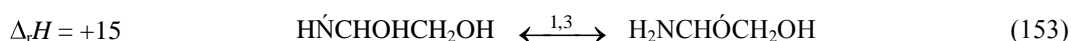
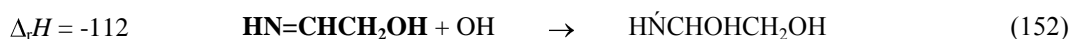
Scheme 3.2 Atmospheric degradation of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (MEA) following initial hydrogen abstraction at C2.

3.1.3 Reactions following a possible hydrogen abstraction from the NH_2 group

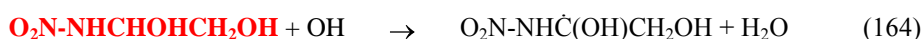
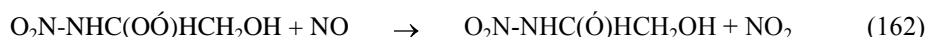
As mentioned in Section 1.6 (page 20) there are no thorough studies on the products resulting from reaction between OH radicals and primary amines. More important, there is no experimental branching ratio of C- versus N-based hydrogen abstraction in primary amines by OH radicals. As mentioned in Section 1.5 one should regard the theoretical calculation³⁷ of the C- to N-based hydrogen abstraction branching ratio with some skepticism. However, one should clearly not disregard the possibility that a significant fraction of the initial hydrogen abstraction could take place from the NH_2 group. The following reactions may be envisaged following hydrogen abstraction from the amino-group in MEA:



The imines formed in (150b) and (151) may react with O_3 (see section 2.3.2) or OH radicals (see Section 2.3.3)

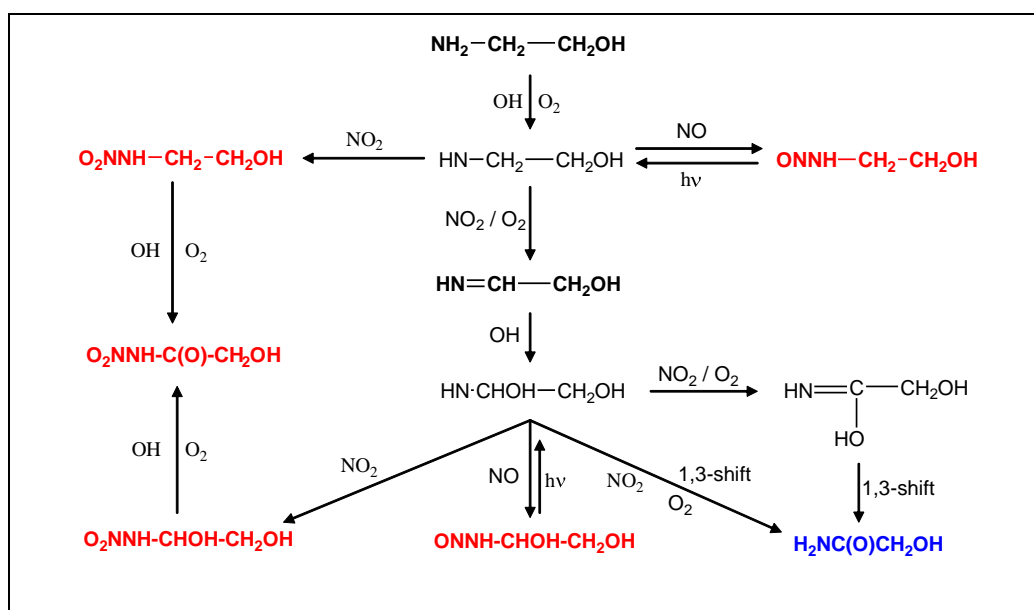


The best estimate of possible products formed as a result of an initial hydrogen abstraction from the amino group in MEA include ON-NHCH₂CH₂OH (2-(nitrosoamino)-ethanol), ON-NHCHOHCH₂OH ((nitrosoamino)-glycol), O₂N-NHCH₂CH₂OH (2-(nitroamino)-ethanol), and O₂N-NHCHOHCH₂OH ((nitroamino)-glycol) of which the former two will undergo rapidly photolysis during the daytime. Bond enthalpy calculations suggest that all of the nitramines will react relatively fast with OH radicals and, through a series of reactions both end up as O₂NNHC(O)CH₂OH (N-nitramino-hydroxyacetamide). The atmospheric chemistry of the short-lived CHOCH₂OH (glycolaldehyde) is well known and will not be elaborated on here.



3.1.4 Summary of the atmospheric MEA degradation

Initial hydrogen abstraction at C1- and C2-position in MEA by OH radicals will eventually lead to the formation of H₂NCHO (formamide) and NH₂C(=O)CH₂OH (2-hydroxy-acetamide) which are both expected to have $\tau_{\text{OH}} > 3$ days. Other long-lived compounds are H₂NC(O)C(O)OONO₂ (2-amino-2-oxo-peroxyacetyl-nitrate). Products with lifetimes $\tau_{\text{OH}} < 3$ days include H₂NCH₂CHO, H₂NC(O)CHO (2-oxo-acetamide), and H₂NCH₂C(O)OONO₂ (2-amino-peroxyacetyl-nitrate). Hydrogen abstraction from the amino group, however, will lead to the formation of various nitrosamines and nitramines in addition to amides. The ratio of hydrogen abstraction from C- to N-atoms is unknown. It is generally assumed in the literature that hydrogen abstraction takes place at the C-atoms, but there is no experimental evidence to support this assumption.

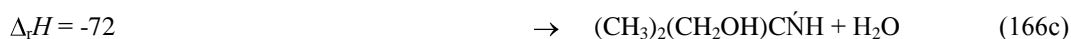
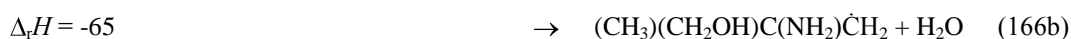
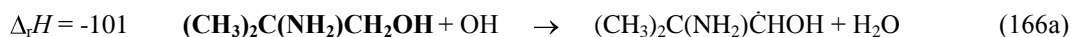


Scheme 3.3 Atmospheric degradation of H₂NCH₂CH₂OH (MEA) following initial hydrogen abstraction from the amino group.

3.2 (CH₃)₂C(NH₂)CH₂OH (AMP)

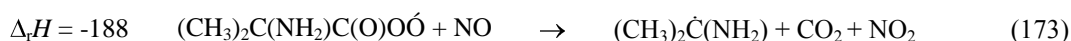
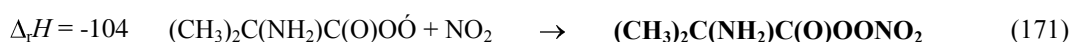
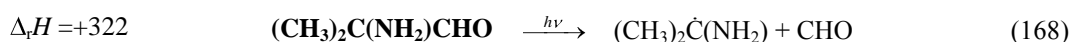
The systematic name of (CH₃)₂C(NH₂)CH₂OH is 2-amino-2-methyl-1-Propanol (CAS: 124-68-5).[#]

Bond enthalpy calculations ($\Delta_{\text{bond}}H_{\text{O-H}} \sim 457$, $\Delta_{\text{bond}}H_{\text{C-H}_3} \sim 433$, $\Delta_{\text{bond}}H_{\text{C-H}_2} \sim 397$, and $\Delta_{\text{bond}}H_{\text{N-H}} \sim 426$ kJ mol⁻¹, Table 5.2, page 86)) suggest that the initial reaction of AMP with OH should proceed entirely through H-abstraction from the CH₂ in the methanoyl group. However, the experimental rate constant for OH reaction with TBA (*tert*-butylamine) is $k_{\text{OH}} = 1.2 \times 10^{-11}$ compared to $k_{\text{OH}} = 2.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for AMP. The Atkinson SAR^{32,33,35} predicts $k_{\text{OH}} = 5 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ for hydrogen abstraction from the -C(CH₃)₃ group in alkanes. That is, either there are large errors in the measured rate constants or the reactivity of the -C(CH₃)₃ and the NH₂-group is larger than expected. Consequently, three reaction routes of the OH initiated degradation of AMP will be investigated.



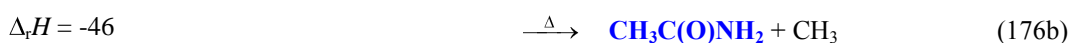
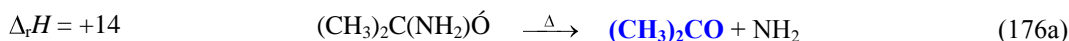
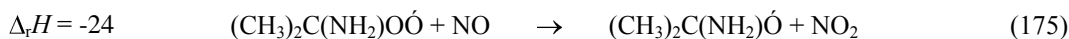
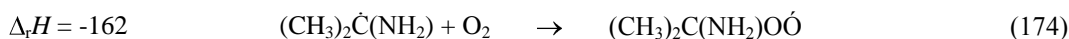
3.2.1 Fate of the (CH₃)₂C(NH₂)ĊHOH radical

The first step of the atmospheric degradation of AMP following (166a) is expected to be analogous to the reactions of aliphatic alcohols. 2-Amino-2-propanal formed in (167) will then either undergo photolysis (threshold wavelength $\lambda = 373$ nm) or react with OH in the same manner as other aliphatic aldehydes (the bond enthalpy of the aldehydic C-H is considerably lower than those of the other C-H and N-H bonds in the compound – see also Table 5.2):



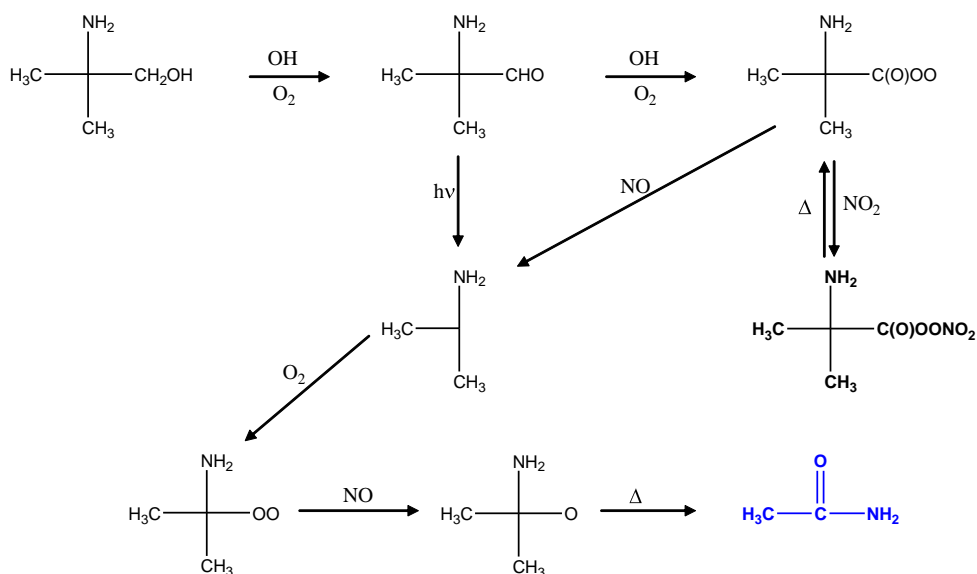
The 2-amino-2-propyl radical formed in (168) and (173) will add O₂ and eventually end as the corresponding 2-amino-2-oxy-propan radical, which can undergo cleavage of the either one of the C-C bonds to give acetamide, or of the C-N bond to give acetone:

[#] The list of trivial- and trade names include: β -Aminoisobutanol; 1,1-Dimethyl-2-hydroxyethylamine; 2,2-Dimethylethanolamine; 2-Amino-1-hydroxy-2-methylpropane; 2-Amino-2,2-dimethylethanol; 2-Amino-2-methyl-1-propanol; 2-Amino-2-methylpropanol; 2-Aminoisobutanol; 2-Hydroxy-1,1-dimethylethylamine; 2-Hydroxymethyl-2-propylamine; 2-Methyl-2-amino-1-propanol; 2-Methyl-2-aminopropanol; AMP; AMP (thinner); AMP 75; AMP 90; AMP 90 (amine); AMP 95; AMP Regular; Corrguard 75; Hydroxy-*tert*-butylamine; Isobutanol-2-amine; KV 5088; NSC 441; Pamabron.



Note that the formation of acetone in (176a) is endothermic. The atmospheric chemistry of acetone and of the NH_2 and CH_3 radicals are well known and will not be dealt with here. The atmospheric reactions of acetamide formed in (176b) are discussed in Section 0. Acetone has a lifetime $\tau_{\text{OH}} \sim 50$ days and acetamide is expected to have an even longer lifetime with respect to OH.

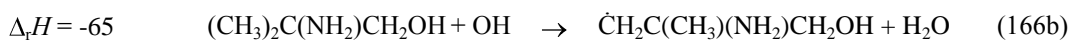
In summary, the primary products formed following hydrogen-abstraction from the CH_2 -group in AMP are $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ (acetamide) and $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{C}(\text{O})\text{OONO}_2$. Scheme 3.4 summarizes the main atmospheric degradation routes of AMP following initial hydrogen abstraction from the CH_2 -group.



Scheme 3.4 The main atmospheric degradation routes of $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$ (AMP) following initial hydrogen abstraction from the CH_2 -group.

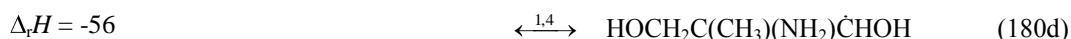
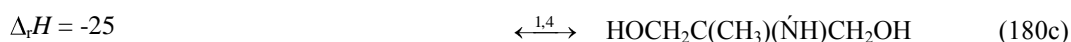
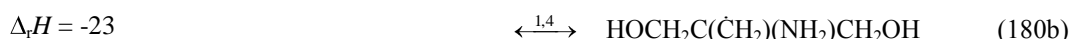
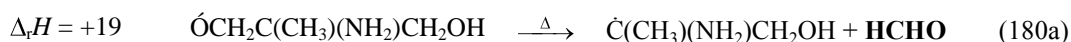
3.2.2 Fate of the $(\text{CH}_3)(\text{CH}_2\text{OH})\text{C}(\text{NH}_2)\dot{\text{C}}\text{H}_2$ radical

It is not expected that the initial hydrogen abstraction will take place from one of the methyl groups in AMP. As mentioned above experimental data, however, suggest that the reactivity of the methyl groups may be higher than predicted by SAR.

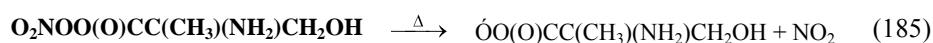
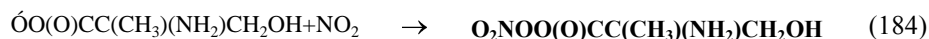
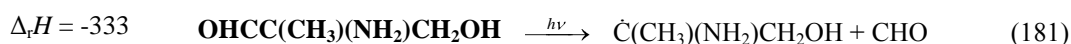




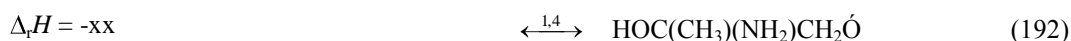
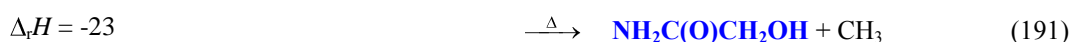
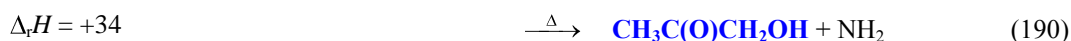
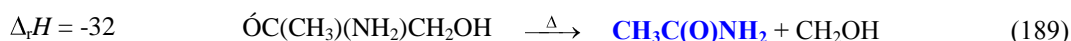
The oxy radical formed in (178) may also undergo dissociation, three different 1,4-hydrogen shift reactions ($\text{H}_2\text{C}\dot{\text{H}}\text{---}\text{OCH}_2$, $\text{HNH}\dot{\text{H}}\text{---}\text{OCH}_2$, $\text{HOH}\dot{\text{C}}\text{H}\text{---}\text{OCH}_2$) and a 1,5-hydrogen shift reaction ($\text{H}_2\text{C}\dot{\text{O}}\text{H}\text{---}\text{OCH}_2$). However, the 1,5-hydrogen shift reaction is between two identical radicals. Although the rates of the 1,4-hydrogen shift reactions and the thermal decomposition reaction (180) are insignificant relative to that of the hydrogen abstraction by O_2 we have included the subsequent reactions to check for the possible formation of carcinogenic compounds.



We will first consider the aldehyde formed in (179) which will either undergo photolysis or aldehydic hydrogen abstraction by OH radicals, and eventually end up as the same alkyl radical also formed in the dissociation reaction (180a)

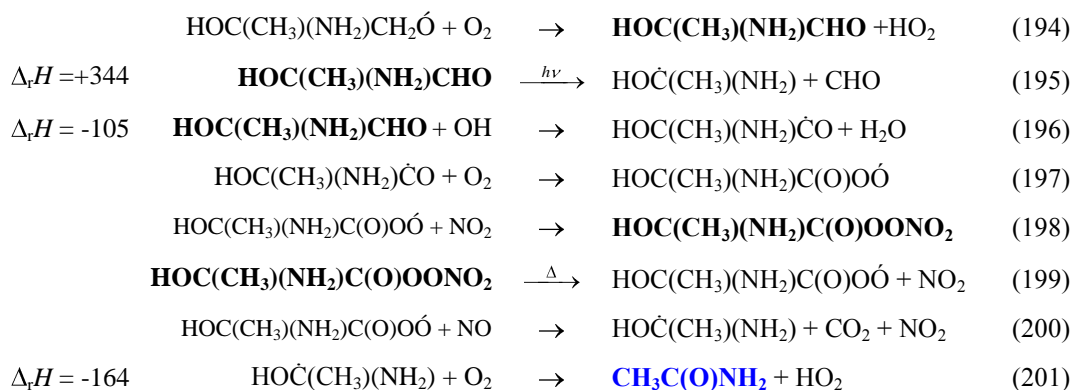


The alkoxy radical formed in (188) may in principle may undergo three different dissociation reactions or yet another 1,4-hydrogen shift ($\text{H}_2\text{C}\dot{\text{O}}\text{H}\text{---}\text{OC}$) reaction

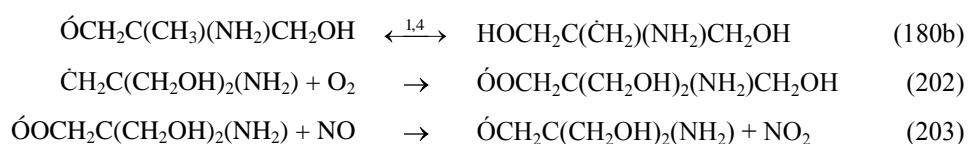


The new oxy-radical resulting from the 1,4-hydrogen shift in (192) may also dissociate or undergo hydrogen abstraction by O_2 which leads to an aldehyde that may undergo photolysis or react with OH in an aldehydic hydrogen abstraction

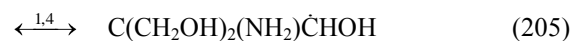
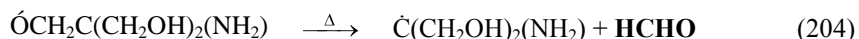




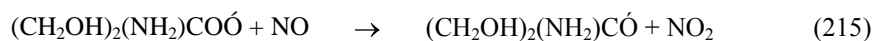
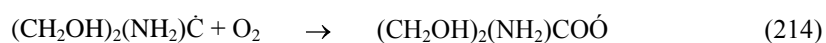
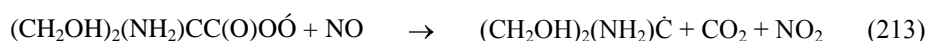
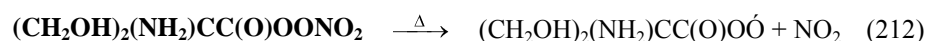
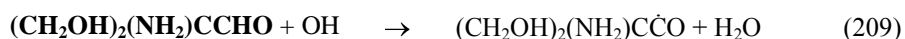
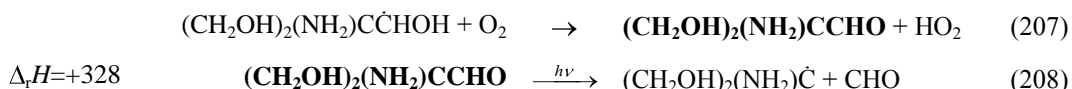
The reactions following the 1,4-hydrogen shift reaction (180b) are:



In the above we have rewritten $\text{HOCH}_2\text{C}(\dot{\text{C}}\text{H}_2\text{)(NH}_2\text{)CH}_2\text{OH}$ as $\dot{\text{C}}\text{H}_2\text{C(CH}_2\text{OH)}_2\text{(NH}_2\text{)}$ for the sake of clarity. The alkoxy radical formed in (203) may either dissociate, undergo 2 different 1,4-hydrogen shift ($\text{H}_2\text{C}\text{---}\text{C}\text{---}\text{HCHOH}$, $\text{H}_2\text{C}\text{---}\text{C}\text{---}\text{HN}$) or a 1,5-hydrogen shift reactions. However, the 1,5-hydrogen shift is between two identical radicals:

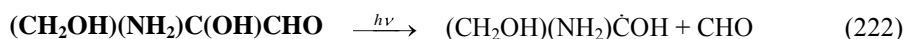
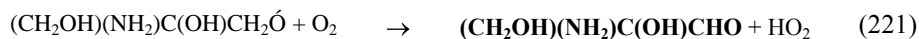
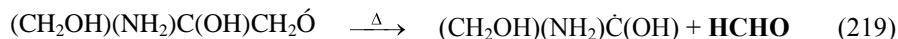
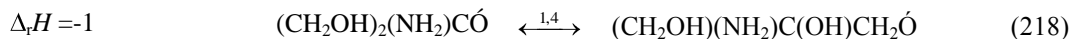


The alkyl radical formed in the 1,4-hydrogen shift (205) will react with O_2 and form an aldehyde which will either undergo photolysis (threshold wavelength $\lambda = 366$ nm, $\Delta_r H = 328$ kJ mol⁻¹) or react with OH radicals in aldehydic hydrogen abstraction





The alkoxy radical formed in (215) may undergo a 1,4-hydrogen shift ($\text{C}\cdots\text{HOCH}_2$)



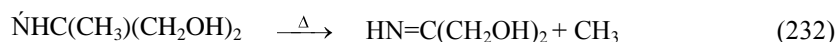
Finally the N-centered radical, $\text{C}(\text{CH}_2\text{OH})_3\dot{\text{N}}\text{H}$, formed in (206) may react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime (threshold wavelength $\lambda = 641$ nm) to reform the N-centered radical. Alternatively, it may dissociate.



The imine formed in (227) may react with O_3 to form the corresponding ketone



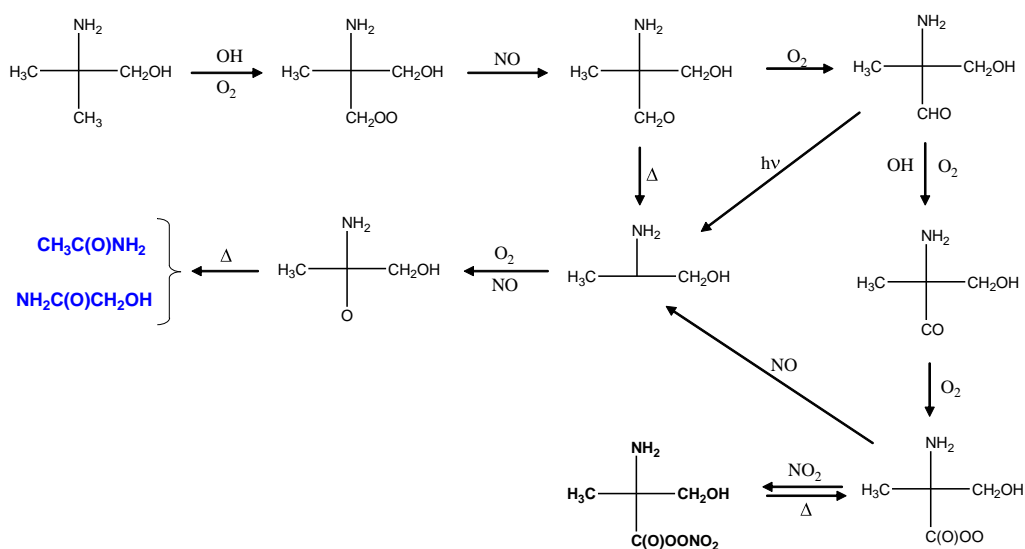
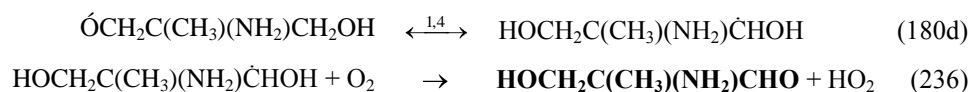
The reactions following the 1,4-hydrogen shift reaction (180c) leading to a N-centered radical are:



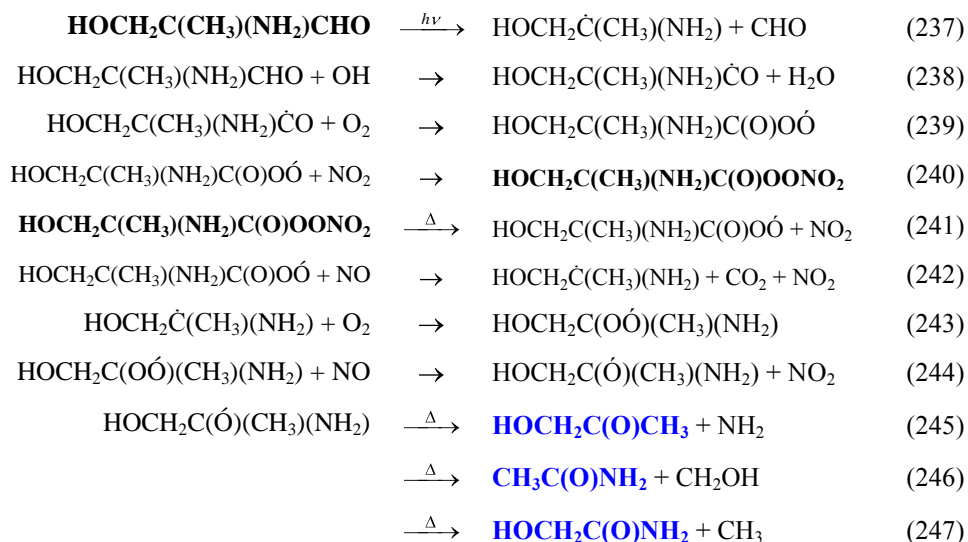
For the sake of clarity we have rewritten $\text{HOCH}_2\text{C}(\text{CH}_3)(\dot{\text{N}}\text{H})\text{CH}_2\text{OH}$ as $\dot{\text{N}}\text{HC}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ in the above equations. The imines formed in (232) and (233) will react with O_3 to give carbonyl compounds



Finally the alkoxy radical formed in the 1,4-hydrogen shift (180d) will react as follows:



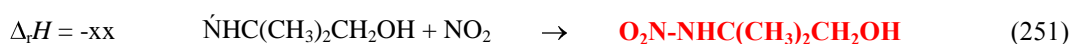
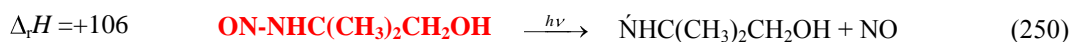
Scheme 3.5 The main atmospheric degradation routes of $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$ (AMP) following initial hydrogen abstraction from the CH_3 -group.



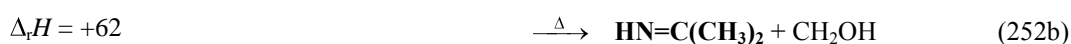
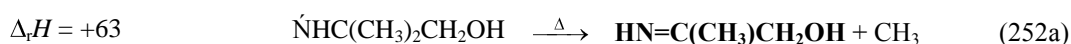
We conclude that should H-abstraction take place at the CH_3 group in AMP the products resulting would be $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ (acetamide), $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$ (hydroxyacetone) and $\text{CH}_2\text{OHC}(\text{O})\text{NH}_2$ (hydroxylacetamide).

3.2.3 Fate of the $(\text{CH}_3)_2(\text{CH}_2\text{OH})\dot{\text{C}}\text{NH}$ radical

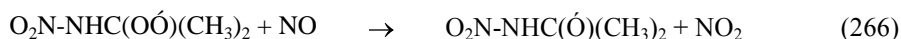
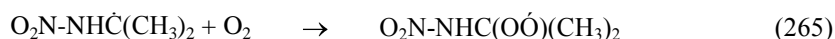
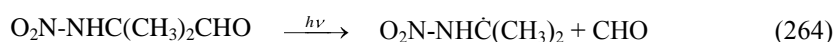
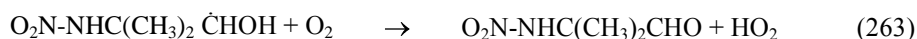
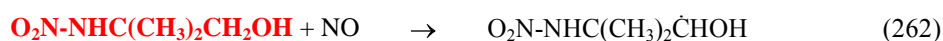
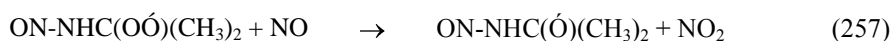
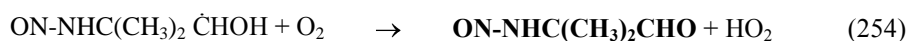
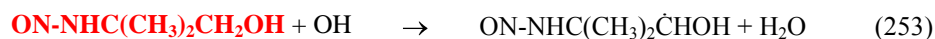
Considering the trends in bond enthalpies it is more likely that hydrogen abstraction by OH will take place from the NH_2 -group than from the CH_3 -groups in AMP



The N-centered radical may also be envisaged to undergo two different dissociation reactions resulting in the formation of imines. However, both of these reactions are endothermic and therefore of little relevance considering the maximal energy available to reaction in the precursor (73 kJ mol^{-1}).

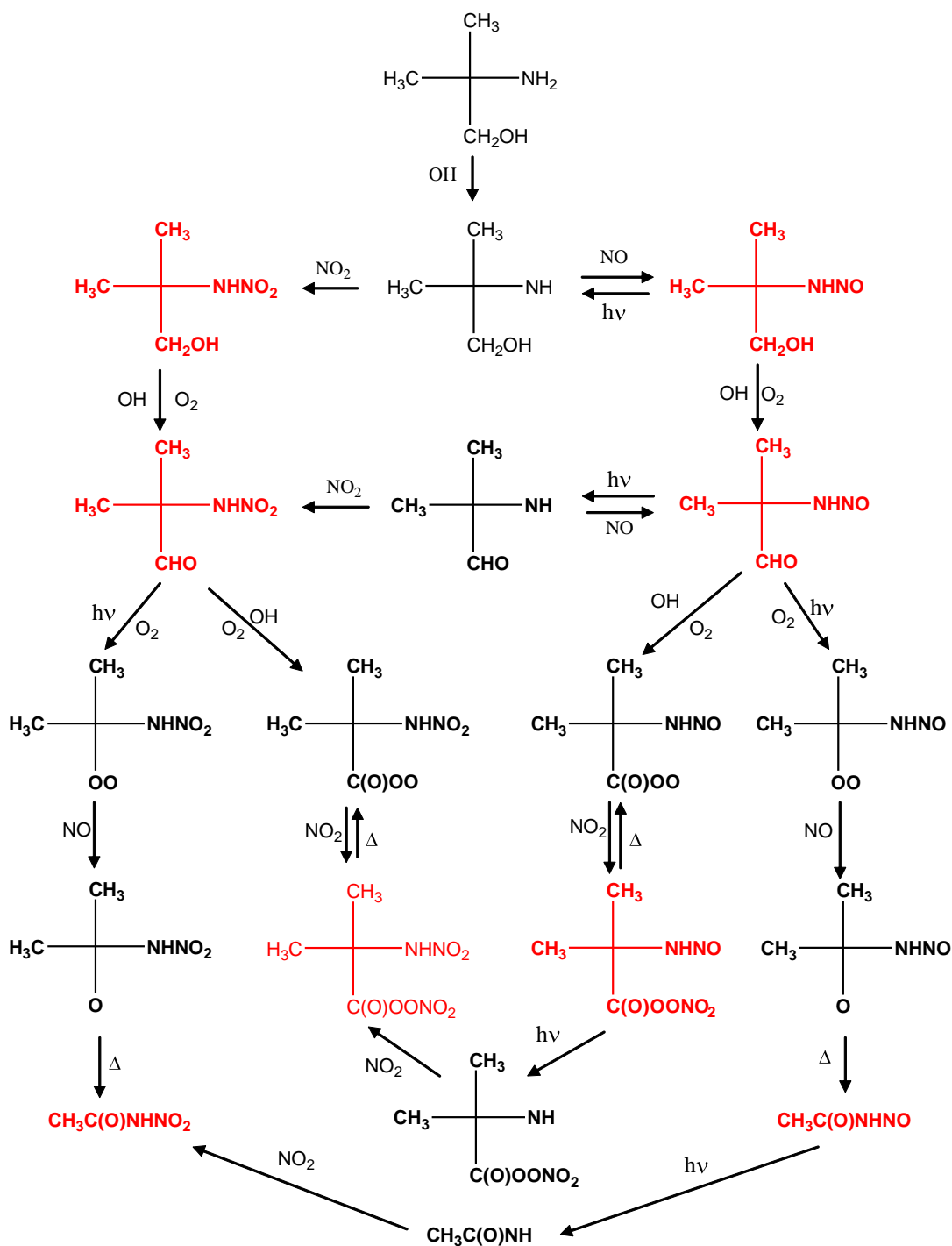


The nitrosamine and nitramine formed in (249) and (251) have quite reactive CH_2 -groups and are therefore expected to react fast with OH radicals to the corresponding aldehyde, which, in turn will undergo photolysis or react with OH radical in aldehydic hydrogen abstraction



The main atmospheric degradation routes of AMP following initial hydrogen abstraction from the NH_2 -group is shown in Scheme 3.6. In summary: an initial hydrogen abstraction from the amine group in AMP will lead to several

nitrosamines and nitramines. The expected end-product during daytime oxidation is $\text{CH}_3\text{C}(\text{O})\text{NHNO}_2$ (N-nitro-formamide, CAS: 51883-27-3) The corresponding nitrosamine, $\text{CH}_3\text{C}(\text{O})\text{NHNO}$ (N-nitroso-Formamide, CAS: 675141-02-3) is expected to undergo rapid photolysis.

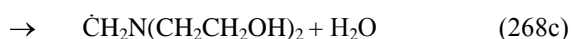


Scheme 3.6 The main atmospheric degradation routes of $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$ (AMP) following initial hydrogen abstraction from the NH_2 -group.

3.3 CH₃N(CH₂CH₂OH)₂ (MDEA)

The systematic name of CH₃N(CH₂CH₂OH)₂ is 2,2'-(methylimino)bis-Ethanol (CAS: 105-59-9).[#]

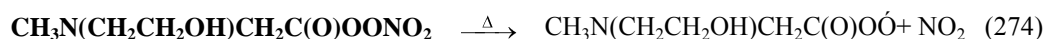
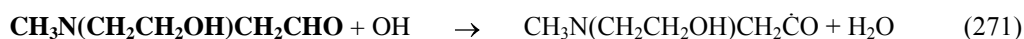
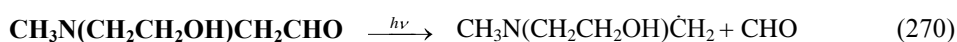
Bond enthalpy calculations suggest that hydrogen abstraction by OH radicals is most likely to occur from the CH₂ groups. However, hydrogen abstraction from the -CH₃ group cannot be ruled out. In general reaction enthalpies are not included – the calculations are too time consuming. The initial step can in principle take place as shown



The three routes of initial attack by OH will be dealt with separately below.

3.3.1 Fate of the CH₃N(CH₂CH₂OH)CH₂ĊHOH radical

The main route of atmospheric oxidation of aliphatic alcohols leads to the corresponding aldehyde which may undergo photolysis or hydrogen abstraction from the aldehyde group by OH radicals.



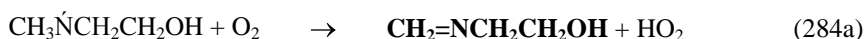
The alkoxy radical formed in (278) may react with O₂ in a hydrogen abstraction reaction to form an amide or undergo one of two 1,4-hydrogen shift reactions ($\text{CH}_3\text{---}\text{N---}\text{OCH}_2$, $\text{HOCH}_2\text{---}\text{CH}_2\text{---}\text{N---}\text{OCH}_2$) a 1,5-hydrogen shift reaction ($\text{CH}_2\text{CH}(\text{OH})\text{H---}\text{N---}\text{OCH}_2$), or alternatively it may dissociate.

[#] Other Names includes: Ethanol, 2,2'-(methylimino)di- (6CI,8CI); 2,2'-(Methylimino)bis[ethanol]; 2,2'-(Methylimino)diethanol; 2-[(2-Hydroxyethyl)(methyl)amino]ethanol; Amino Alcohol MDA; Diethanolmethylamine; Eve; Gas Spec CS 2000; Jeffreat MS 100; MDEA; MDEA (diol); Methylbis(2-hydroxyethyl)amine; Methyl-diethanolamine; Methyliminodiethanol; N,N-Bis(2-hydroxyethyl)methylamine; N,N-Di(2-hydroxyethyl)-N-methylamine; N,N-Di(2-hydroxyethyl)methylamine; N-(2-Hydroxyethyl)-N-methylethanolamine; N-Methyl-N,N-diethanolamine; N-Methylaminodiglycol; N-Methylbis(2-hydroxyethyl)amine; N-Methyl-diethanolamine; N-Methyliminodiethanol; NSC 11690; NSC 49131; NSC 51500; ZC 10.



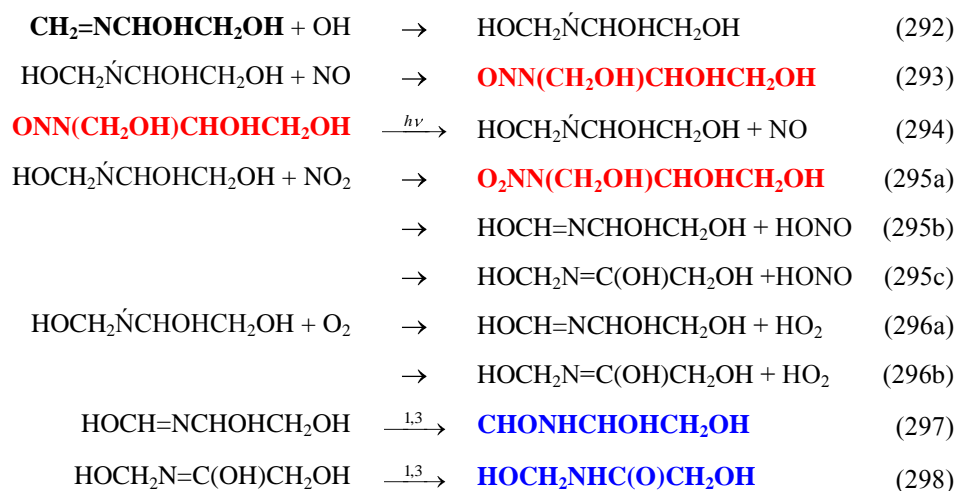
Although the 1,4-hydrogen shift reactions (279b) and (279c) are too slow to be of importance compared to the hydrogen abstraction reaction by O₂ (279a) and the 1,5-hydrogen shift reaction (279d) we include the reactions following these shift-reactions. Also the rate constant for dissociation reaction (280) is too small for this route to be important. Again, the reaction following this dissociation is included to map the possible products.

The dissociation reaction in (280) leads to a N-centered radical which may undergo hydrogen-abstraction from the neighboring carbon atoms by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



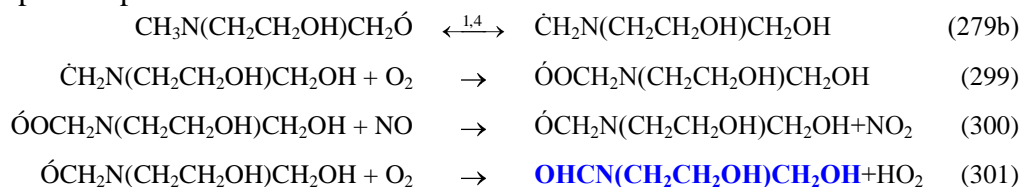
The imines formed in (283) and (284) are expected to undergo the following reactions (see Section 2.3)



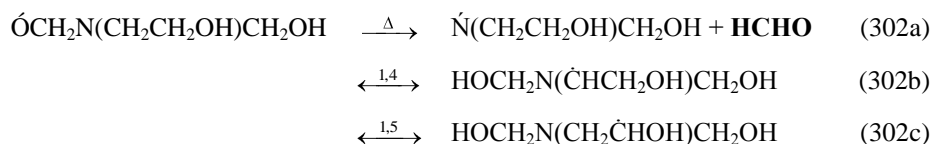


3.3.1.1 Fate of the $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\text{CH}_2\text{OH}$ radical.

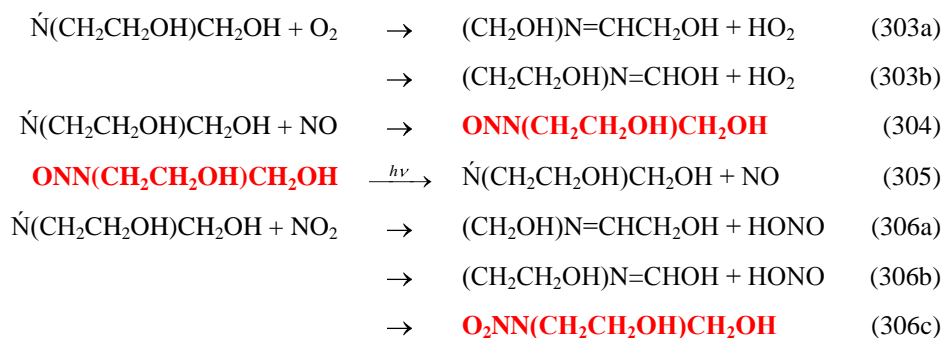
The reactions following the 1,4-hydrogen shift in (279b) involving the methyl group are expected to be



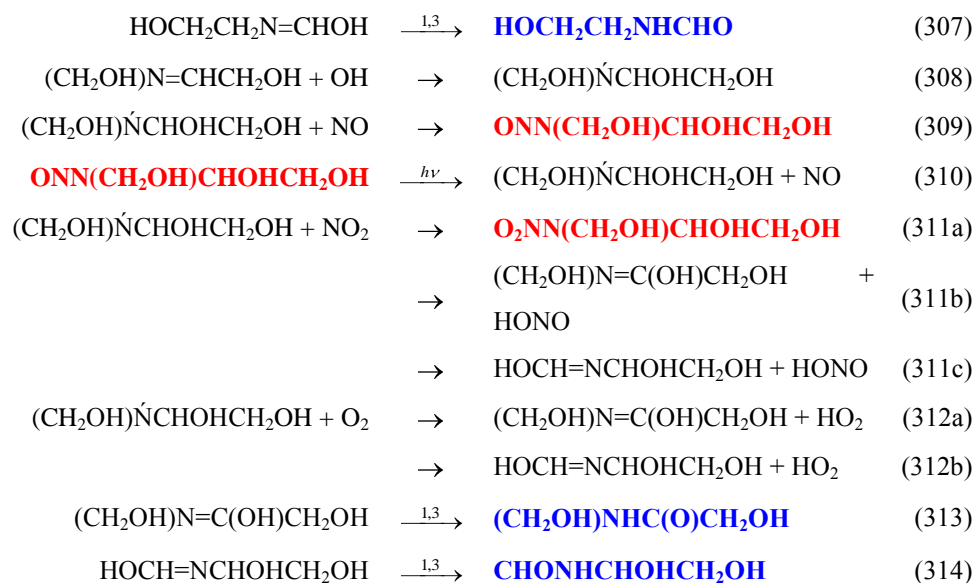
The alkoxy radical formed in (300) may also dissociate or undergo 1,4- and 1,5-hydrogen shift reactions (the 1,4-hydrogen shift involving the N-CH₂OH group will reform an identical radical).



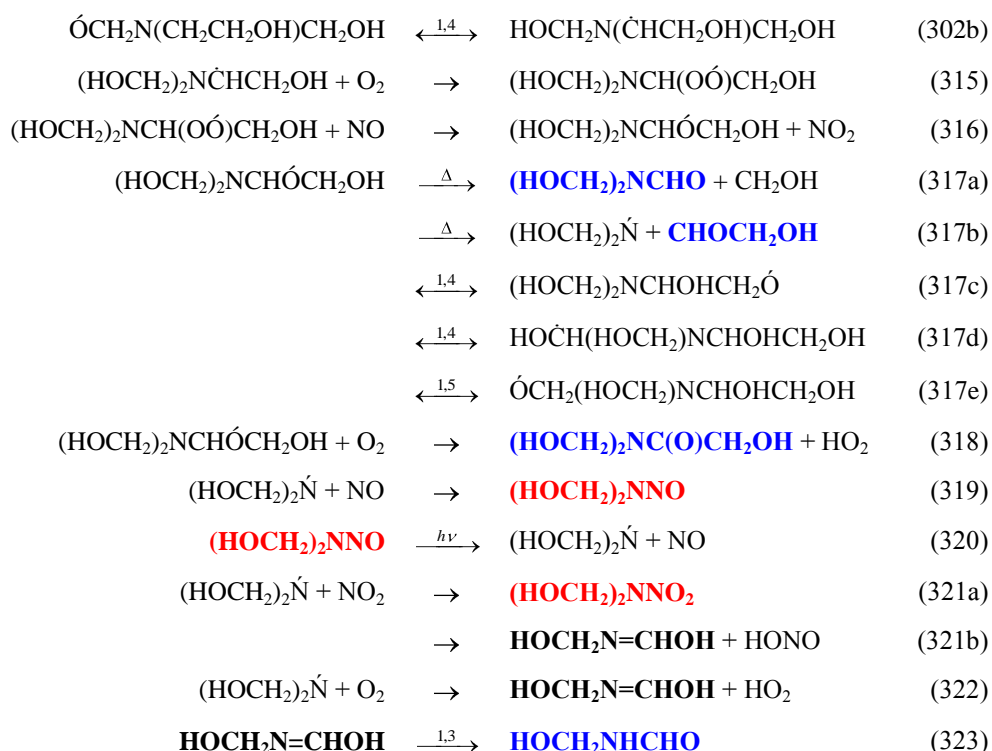
The N-centered radical formed in (302a) may undergo hydrogen-abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



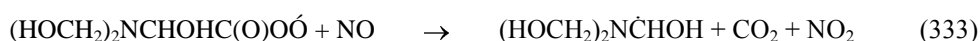
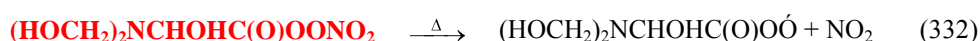
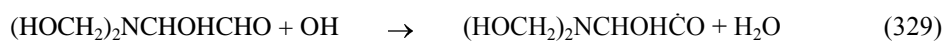
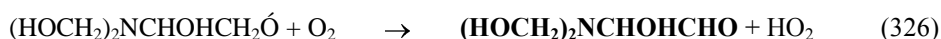
The imines formed in (303) and (306) are expected to undergo the following reactions (see Section 2.3)



The alkyl radical formed in the 1,4-hydrogen shift reaction (302b) will add O₂ and eventually end as a new alkoxy radical which may dissociate or undergo H-shift reactions, or alternatively react with O₂ in a hydrogen abstraction.



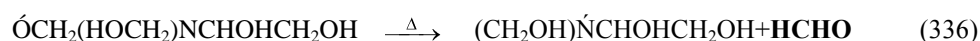
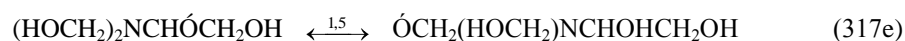
The alkoxy radical formed in the hydrogen shift reaction (317c) may dissociate or react with O₂ in a hydrogen abstraction resulting in the formation of an aldehyde which may undergo photolysis or reaction with OH in an aldehydic hydrogen abstraction



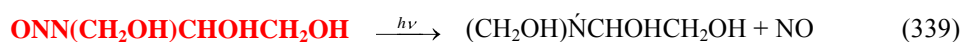
The alkyl radical formed in the 1,4-hydrogen shift reaction (317d) will undergo hydrogen abstraction by O₂



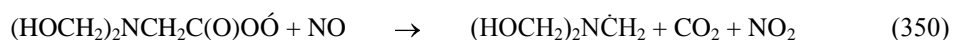
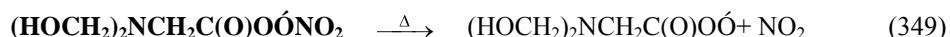
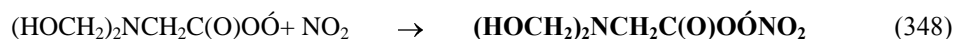
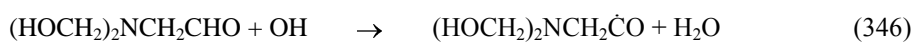
The alkoxy radical formed in the 1,5-hydrogen shift reaction (317e) may dissociate or react with O₂ in a hydrogen abstraction reaction giving an amide.



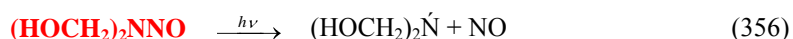
The N-centered radical formed in the dissociation (336) may undergo hydrogen-abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



The alkyl radical formed in the 1,5 hydrogen shift reaction (302c) is expected to undergo hydrogen abstraction by O₂ resulting in the formation of an aldehyde which may undergo photolysis or reaction with OH in an aldehydic hydrogen abstraction.



The alkoxy radical formed in (352) may also dissociate or undergo a 1,4-hydrogen shift reaction to give a new alkoxy radical which can only react with O₂ in a hydrogen abstraction leading to an amide. The N-centred radical so formed in the dissociation will form an imine, nitramine or nitrosamine in subsequent reactions. The nitrosamine will photolyse fast during daytime.



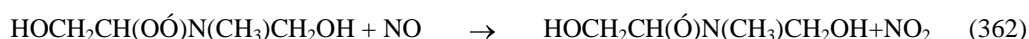
The alkyl radical formed in (354b) will react with O₂ in a hydrogen abstraction reaction and form an amide.



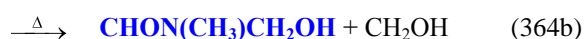
3.3.1.2 Fate of the HOCH₂ĈHN(CH₃)CH₂OH radical

The reactions following the 1,4-hydrogen shift reaction (279c) results in an alkyl radical which is expected to add O₂. For the sake of readability we write (CH₃)N(CH₂CH₂OH)CH₂Ċ as HOCH₂CH₂N(CH₃)CH₂Ċ

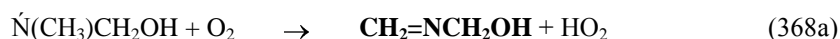
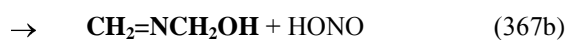
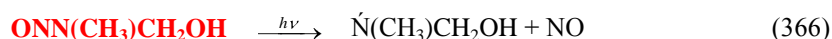




The alkoxy radical formed in (362) may react with O_2 in a hydrogen abstraction leading to an amide, dissociate, or undergo two different 1,4 hydrogen shift reactions.



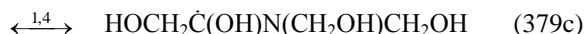
The N-centered radical formed in (364a) may undergo hydrogen-abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



The alkyl radical formed in 1,4-hydrogen shift reaction (364c) will undergo hydrogen abstraction by O_2 and form an amide. The alkyl radical formed in 1,4-hydrogen shift reaction (364d) will add O_2 and end as new alkoxy radical



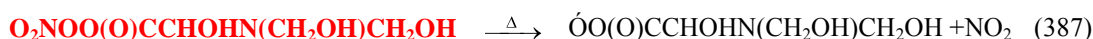
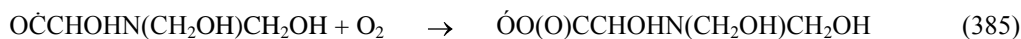
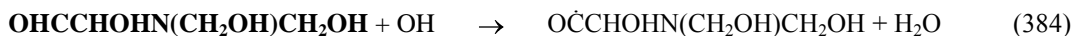
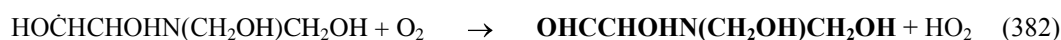
The alkoxy radical formed in (377) may react with O₂ in a hydrogen abstraction reaction to form an amide, dissociate, or undergo 1,4- and 1,5-hydrogen shift reactions



The alkyl radicals formed in the 1,4-hydrogen shift reactions (379b) and (379c) will react with O₂ in hydrogen abstraction reactions to form amides



The alkyl radical formed in the 1,5-hydrogen shift reaction (379d) will react with O₂ in hydrogen abstraction reactions to form an aldehyde, which may undergo photolysis or reaction with OH radicals



The N-centered radical formed in (379a) may undergo hydrogen-abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



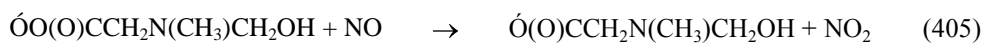
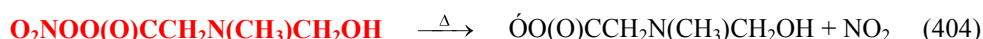
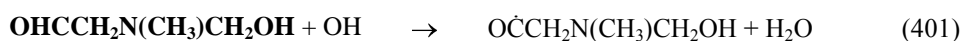
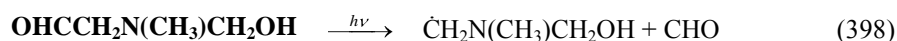


3.3.1.3 Fate of the $(\text{CH}_3)\text{N}(\text{CH}_2\dot{\text{C}}\text{HOH})\text{CH}_2\text{OH}$ radical

We now consider the subsequent reactions of the alkoxy radical formed in the 1,5-hydrogen shift reaction (279d). For the sake of readability we write the alkoxy radical $(\text{CH}_3)\text{N}(\text{CH}_2\text{CH}_2\text{OH})\text{CH}_2\dot{\text{O}}$ as $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\dot{\text{O}}$



The aldehyde formed in (397) will either undergo photolysis or react with OH radicals

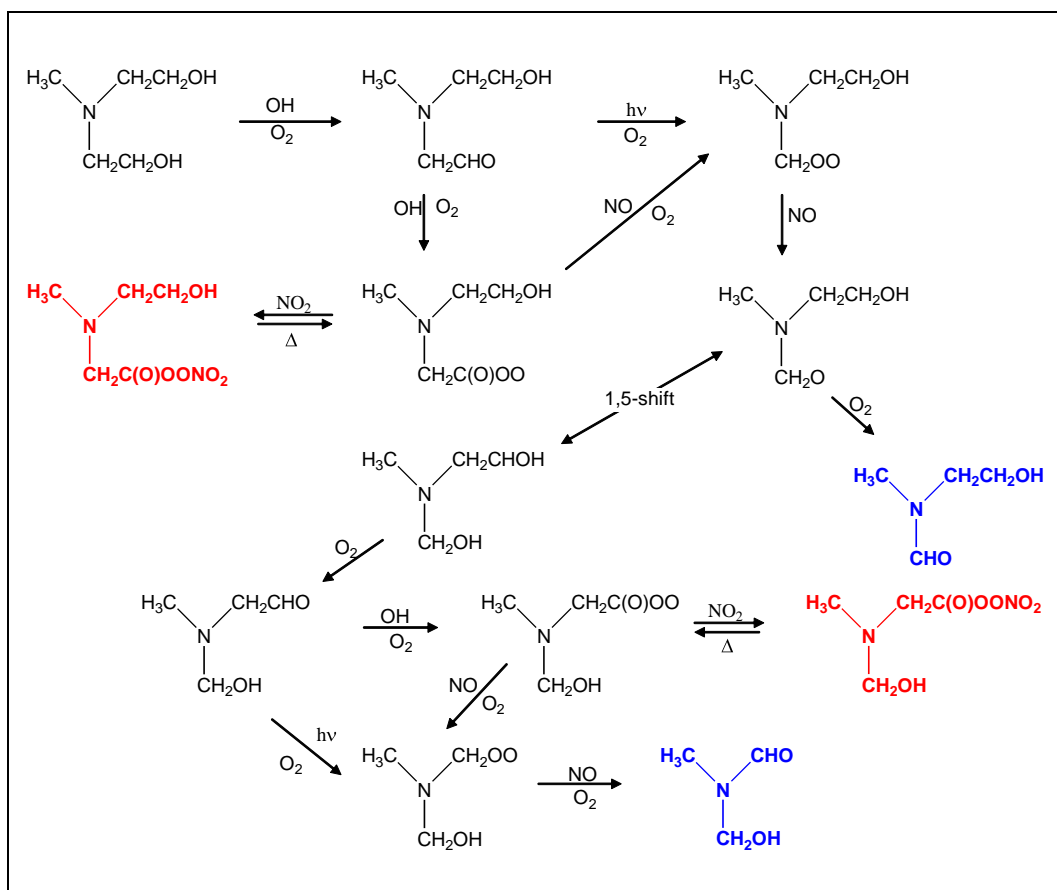


The alkoxy radical formed in (400) and (408) may also dissociate, undergo two different 1,4-hydrogen shift reactions which are all too slow to be of importance compared to the hydrogen abstraction by O_2 (409).



The N-centered radical formed in (410a) is the same as that formed in (364a) and its further reactions has already been outlined. The alkyl radical formed in (410b) will add O_2 and subsequently end up as





Scheme 3.7 The main routes to the atmospheric degradation of $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ (MDEA) following initial hydrogen abstraction from one of the $-\text{CH}_2\text{OH}$ groups.

The alkoxy radical formed in xx may react with O_2 in a hydrogen abstraction to form an amide, dissociate, or undergo a 1,4-hydrogen shift reaction



The N-centred radical formed in (413) is the same as that formed in (370) and its further reactions has already been outlined. The alkyl radical formed in the 1,4-hydrogen shift reaction will undergo hydrogen abstraction by O_2 and form an amide.



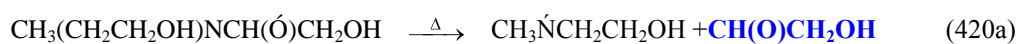
The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from one of the $-\text{CH}_2\text{OH}$ groups are summarized in Scheme 3.7. The main products are the amides $(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OH})\text{NCHO}$ and $(\text{CH}_3)(\text{CH}_2\text{OH})\text{NCHO}$ and the PAN-like compounds $(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{OH})\text{NCH}_2\text{C}(\text{O})\text{OONO}_2$ and $(\text{CH}_3)(\text{CH}_2\text{OH})\text{NCH}_2\text{C}(\text{O})\text{OONO}_2$.

3.3.2 Fate of the $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})\dot{\text{C}}\text{HCH}_2\text{OH}$ radical

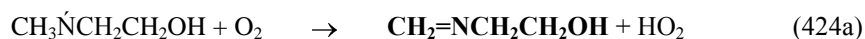
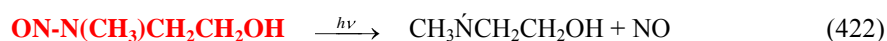
We now turn to the second possible path in the initial OH reaction with MDEA.



The alkoxy radical formed in (418) may react with O_2 in a hydrogen abstraction reaction, dissociate or undergo 1,4- or 1,5-hydrogen shift reactions. Note, again, that the 1,4-hydrogen shift reactions are too slow to be of importance in comparison to the hydrogen abstraction reaction by O_2 and the 1,5-hydrogen shift reaction.

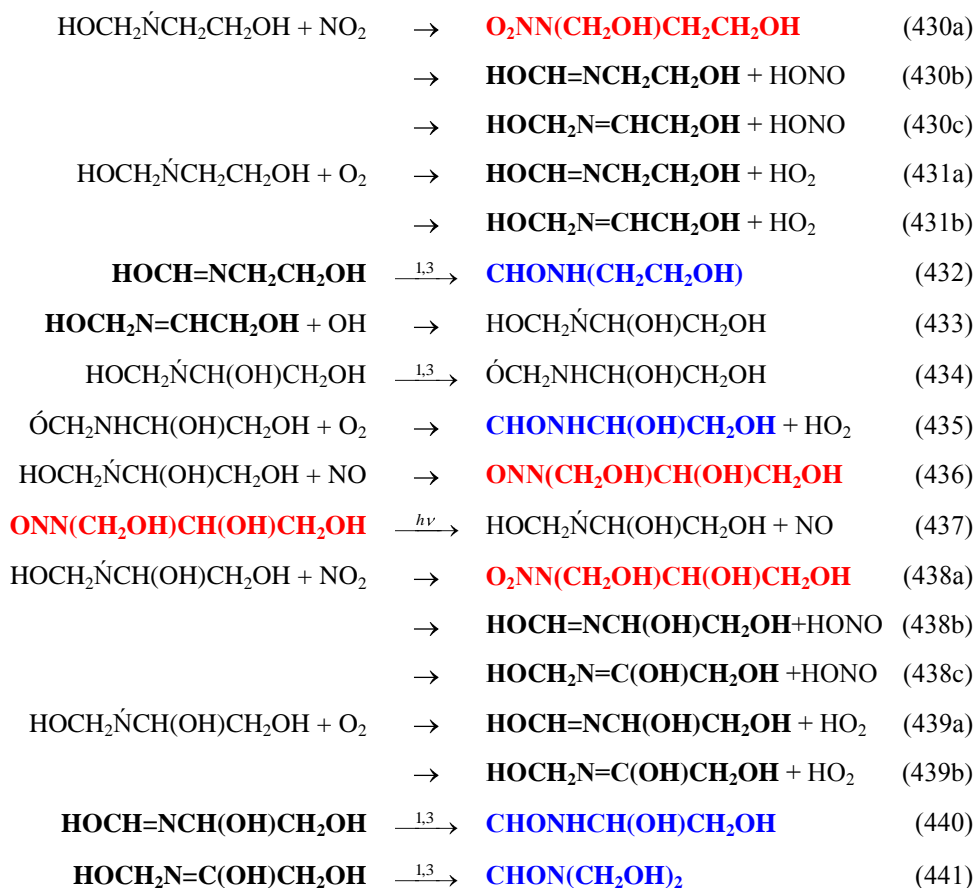


The N-centered radical formed in (420a) will undergo hydrogen-abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.

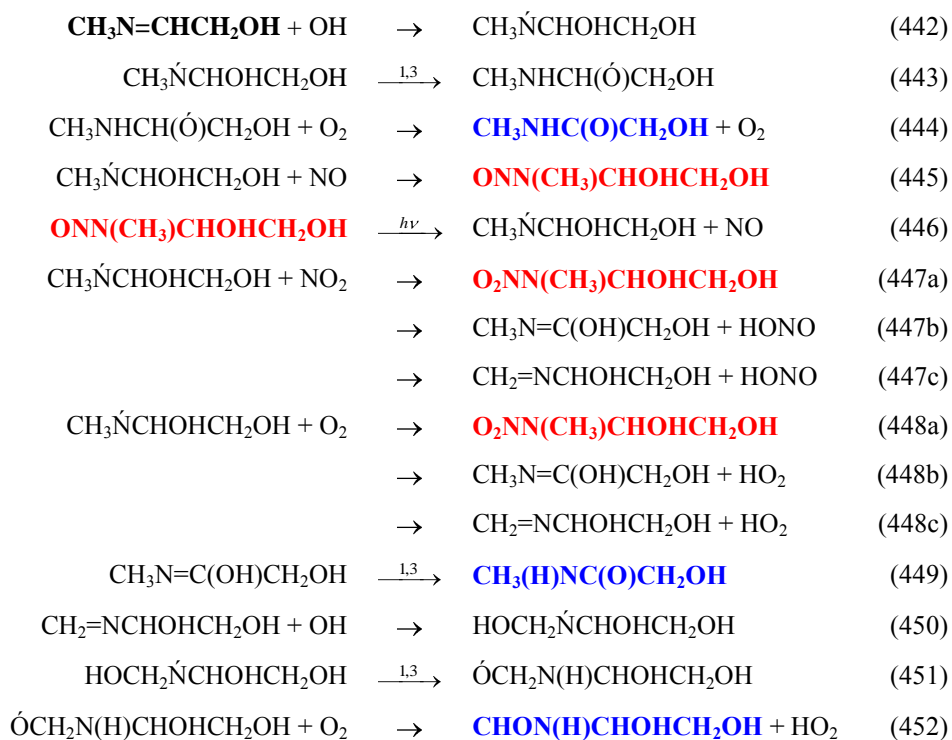


The imine formed in (423b) and (424a) is expected to undergo the following reactions



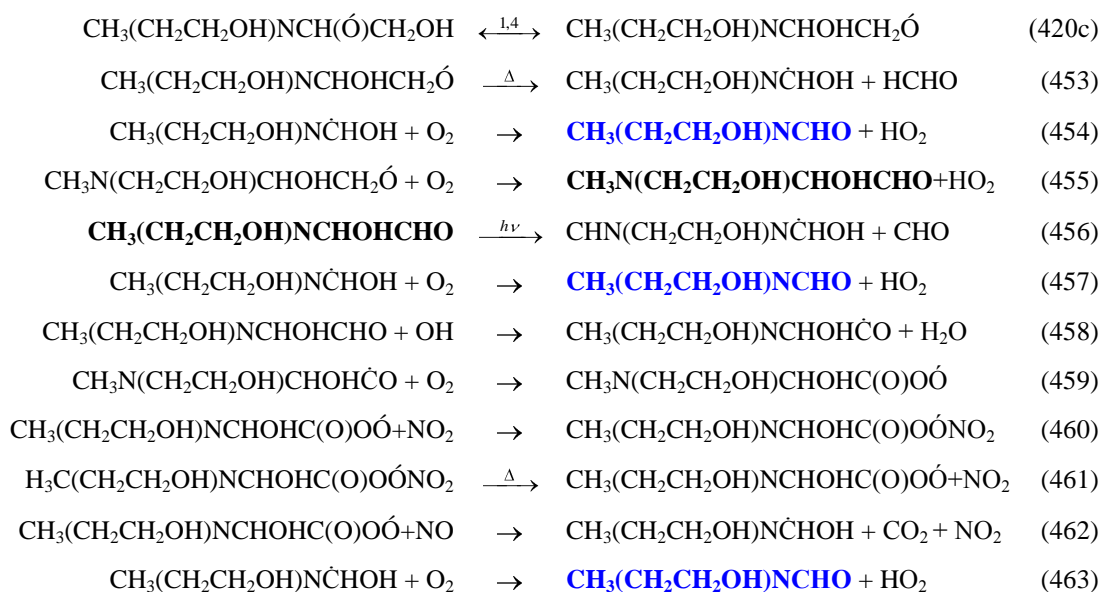


The imine formed in (423c) and (424b) is expected to undergo the following reactions



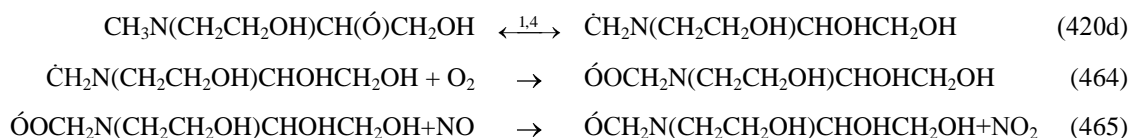
3.3.2.1 Fate of the $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})\text{CHOHCH}_2\dot{\text{O}}$ radical

We will first consider 1,4-hydrogen shift (420c) within the $-\text{CH}(\dot{\text{O}})-\text{CH}_2\text{OH}$ moiety.

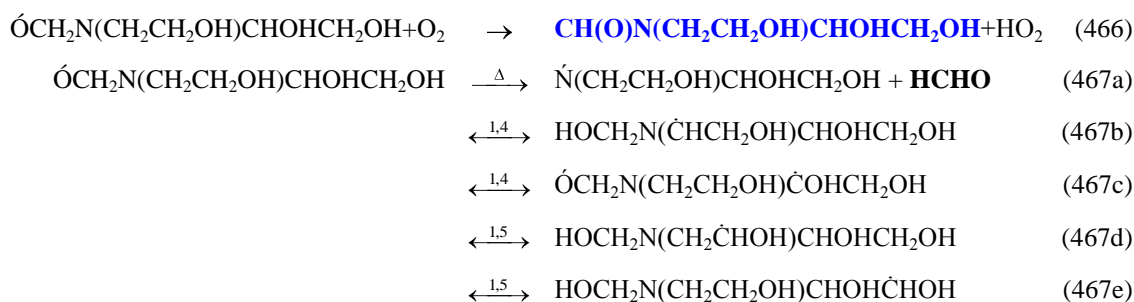


3.3.2.2 Fate of the $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\text{CHOHCH}_2\text{OH}$ radical

The alkyl radical formed in the 1,4-hydrogen shift in (420d) is expected to react as follows

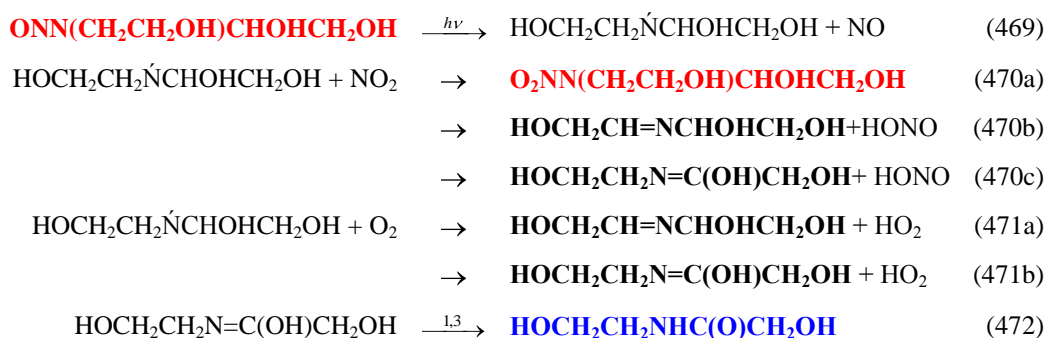


The alkoxy radical formed in (465) undergo hydrogen abstraction by O_2 , dissociation or 1,4- or 1,5-hydrogen shift reactions

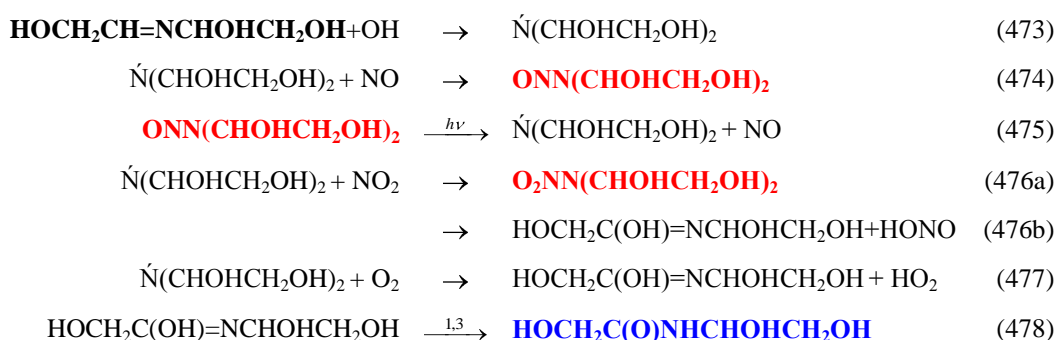


The N-centered radical formed in (467a) will undergo hydrogen-abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.

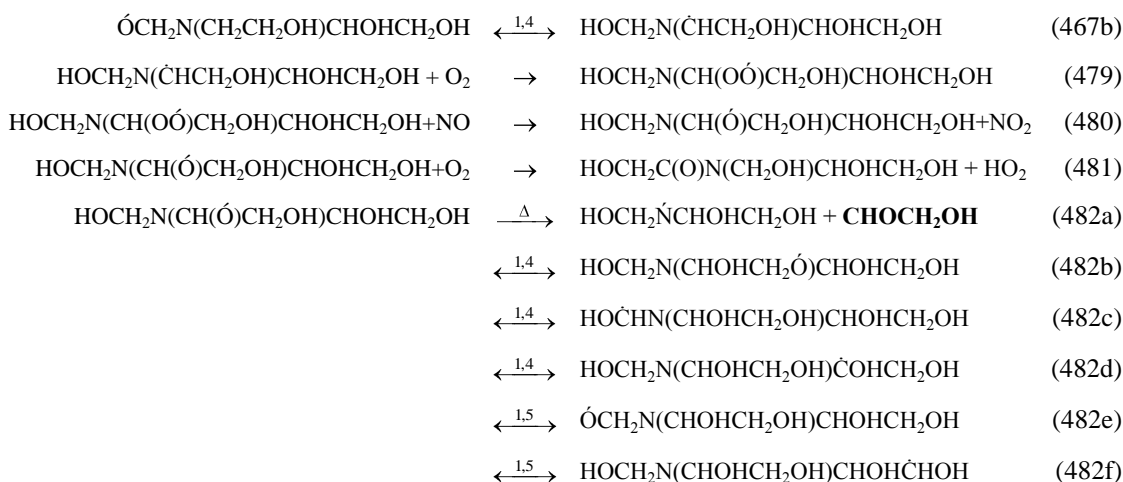




The imine formed in (470b) and (471a) is expected to react as outlined in Section 2.3

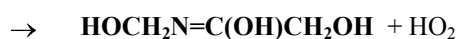
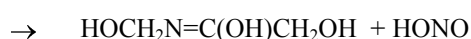


The alkyl radical formed in (467b) will first add O₂ and subsequently form an alkoxy radical, which may react with O₂ in a hydrogen abstraction reaction to form an amide, dissociate, or undergo one of three 1,4-hydrogen shift reactions or two 1,5-hydrogen shift reactions.

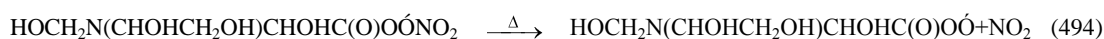


The N-centered radical formed in (482a) will undergo hydrogen-abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.





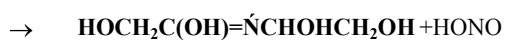
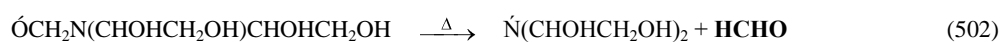
The alkoxy radical formed in (482b) may either undergo hydrogen abstraction by O_2 to form an aldehyde, which may then undergo photolysis or reaction with OH , or dissociate



The alkyl radicals formed in the 1,4-hydrogen shift reactions (482c) and (482d) will undergo hydrogen abstraction by O_2 to form amides.

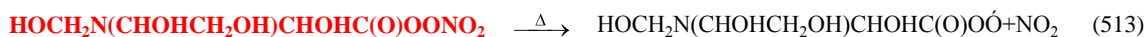


The alkyl radical formed in the 1,5-hydrogen shift reaction (482e) may undergo hydrogen abstraction to form an amide or dissociate to form an N-centered radical, which will undergo hydrogen-abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



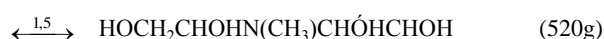
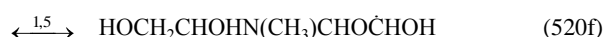
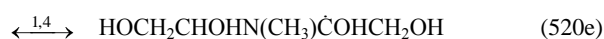
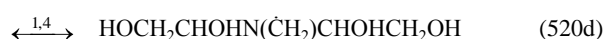
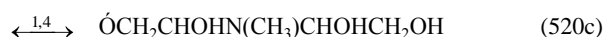
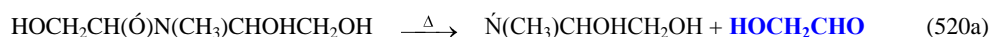


The alkyl radical formed in the 1,5-hydrogen shift reaction (482f) may undergo hydrogen abstraction to form an aldehyde, which may undergo photolysis of hydrogen abstraction by OH:



3.3.2.3 Fate of the $\text{HOCH}_2\dot{\text{C}}\text{HN}(\text{CH}_3)\text{CHOHCH}_2\text{OH}$ radical

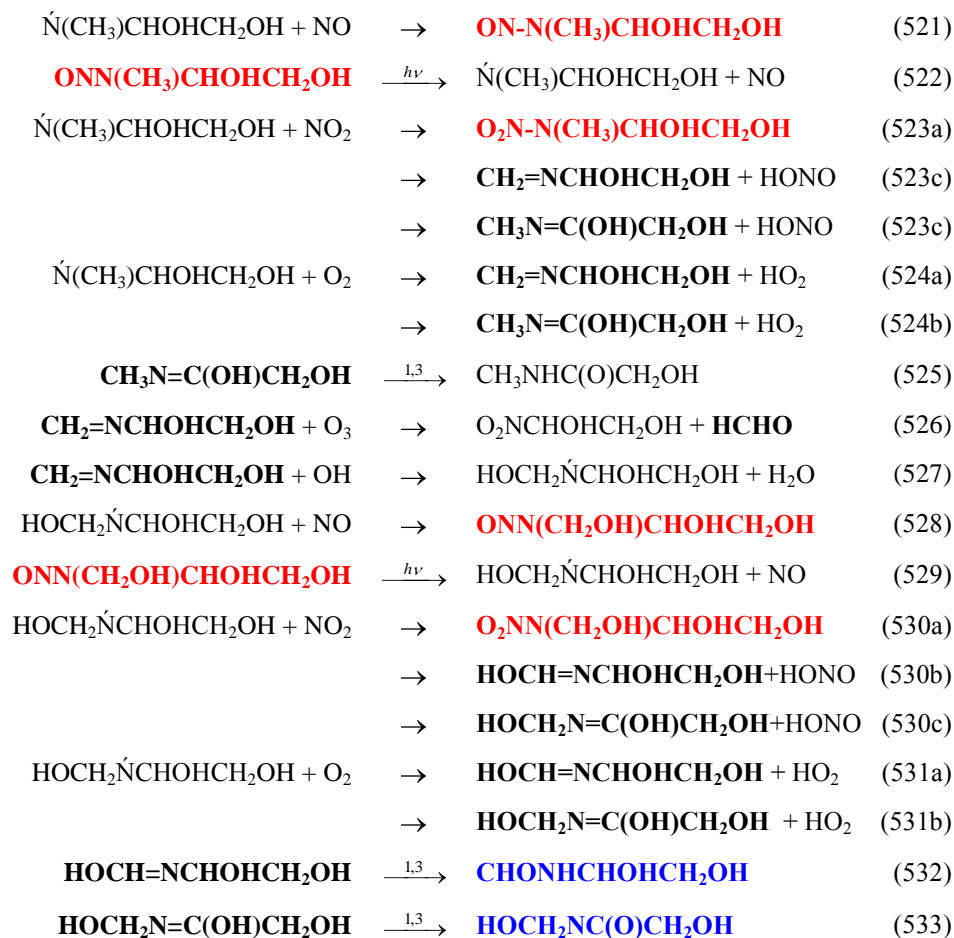
The third 1,4-hydrogen shift reaction of the alkoxy radical formed in (418) involves the other ethanol group.[#] The alkyl radical formed will first add O_2 and eventually become a new alkoxy radical, which may then either undergo hydrogen abstraction by O_2 and end up as an amide, dissociate, or undergo one of three 1,4-hydrogen shift reactions or two 1,5-hydrogen shift reactions



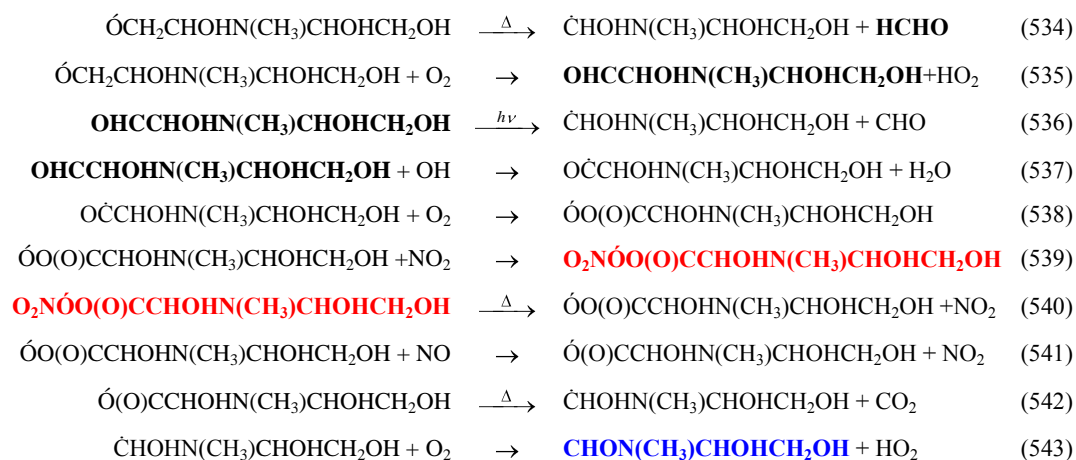
The N-centered radical formed in (520a) will undergo hydrogen-abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to

[#] For the sake of readability we re-write $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})\text{CH}(\dot{\text{O}})\text{CH}_2\text{OH}$ as $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}(\dot{\text{O}})\text{CH}_2\text{OH}$

reform the N-centered radical. The imines formed are assumed to react as outlined in Section 2.3.

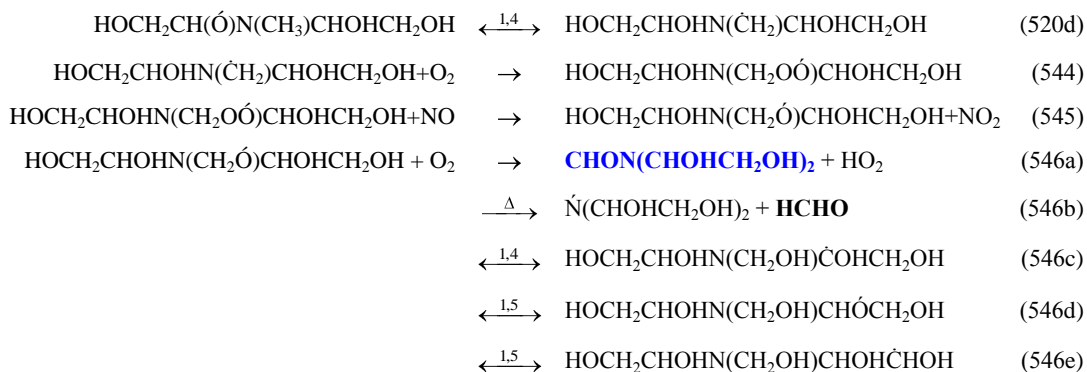


The alkoxy radical formed in the 1,4-hydrogen shift reaction (520c) may dissociate or react with O₂ in a hydrogen abstraction reaction leading to an aldehyde, which may then undergo photolysis or hydrogen abstraction by OH



The alkyl radical formed in the 1,4-hydrogen shift reaction (520d) will first add O₂ and subsequently become an alkoxy radical, which may react with O₂ in a

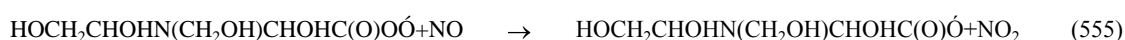
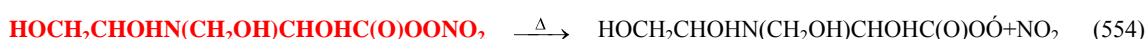
hydrogen abstraction to form an amide, dissociate, or undergo a 1,4-hydrogen shift reaction or one of two 1,5-hydrogen shift reactions.



The reactions of the N-centered radical $\dot{\text{N}}(\text{CHOHCH}_2\text{OH})_2$ formed in (546b) have already been in (473) and subsequent equations. The alkyl radical formed in the 1,4-hydrogen shift reaction (546c) will undergo hydrogen abstraction by O_2 to form an amide. The same reaction applies to the alkoxy radical formed in the 1,5-hydrogen shift reaction (546d).



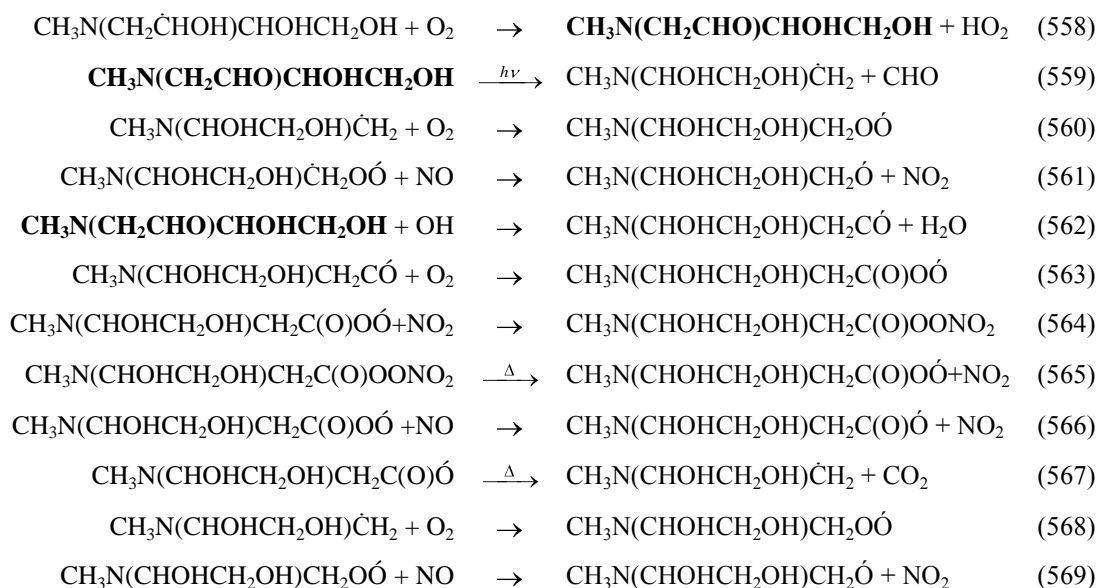
The alkoxy radical formed in the 1,5-hydrogen shift reaction (546e) will undergo hydrogen abstraction by O_2 to form an aldehyde, which may subsequently undergo photolysis or reaction with OH



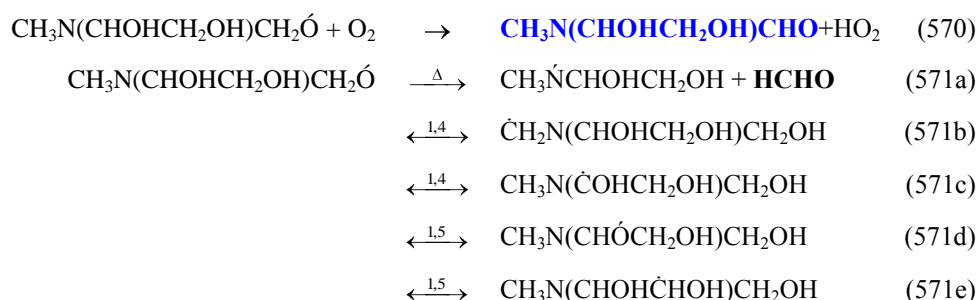
3.3.2.4 Fate of the $\text{CH}_3\text{N}(\text{CH}_2\dot{\text{C}}\text{HOH})\text{CHOHCH}_2\text{OH}$ radical

We next consider the fate of the alkoxy radical formed in (418) as it undergoes 1,5-hydrogen shift reaction involving the other ethanol group. The resulting alkyl radical will undergo hydrogen abstraction by O_2 forming an aldehyde, which may photolyse during daytime or react with OH.

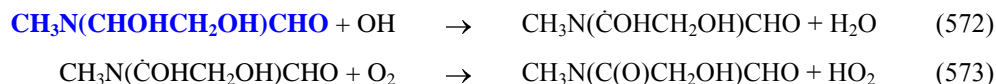




The alkoxy radical formed in (561) and (569) may react with O₂ in a hydrogen abstraction leading to an amide, dissociate, or undergo one of two 1,4-hydrogen shift reactions and two 1,5-hydrogen shift reactions. The thermal dissociation rate is expected to be too low to be of importance in comparison with the hydrogen abstraction by O₂ and the 1,5-hydrogen shift reactions. The same is expected for the 1,4-hydrogen shift reactions.



The amide formed in (570), CH₃N(CHOHCH₂OH)CHO, has an activated >CHOH group which is expected to react relatively fast with OH radicals:

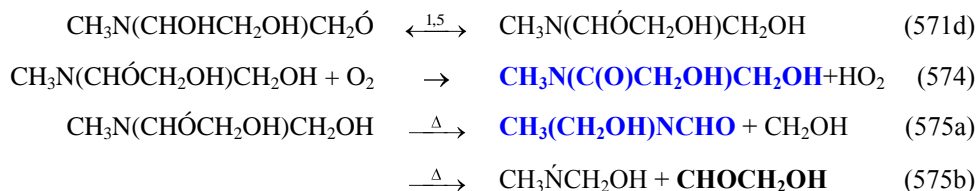


The N-centered radical formed in (571a) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical. The reaction sequence is already outlined in reactions (285) – (298) on page 49.

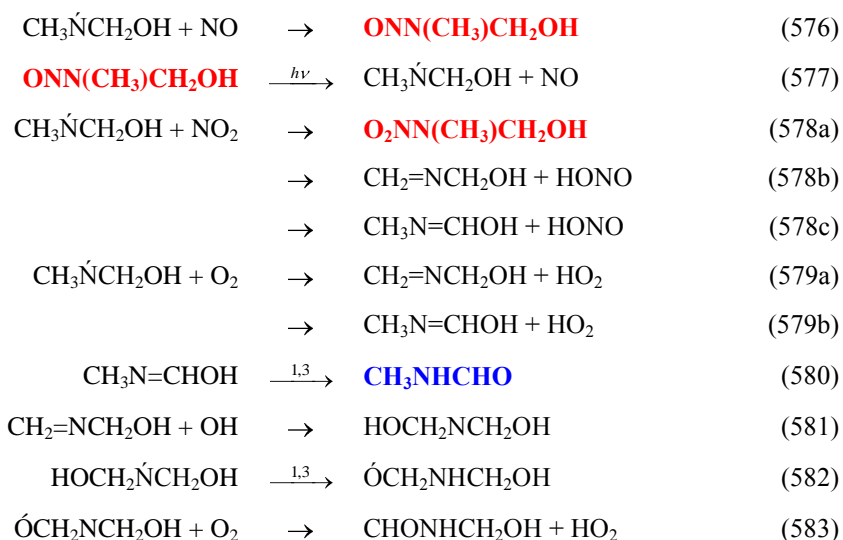
The alkyl radical formed in the 1,4-hydrogen shift reaction (571b) add O₂ and subsequently become a new alkoxy radical, which may react with O₂ in a hydrogen abstraction to form an amide. Alternative paths includes dissociation and hydrogen shift reactions and will essentially follow the routes outlined for the

similar alkyl radicals $\dot{\text{C}}\text{H}_2\text{N}(\text{CHOHCH}_2\text{OH})_2$ formed in (520d), see page 65, and $\dot{\text{C}}\text{H}_2\text{N}(\text{CHOHCH}_2\text{OH})\text{CH}_2\text{CH}_2\text{OH}$ formed in (420d), see page 60, and are at present not included for the reasons stated above.

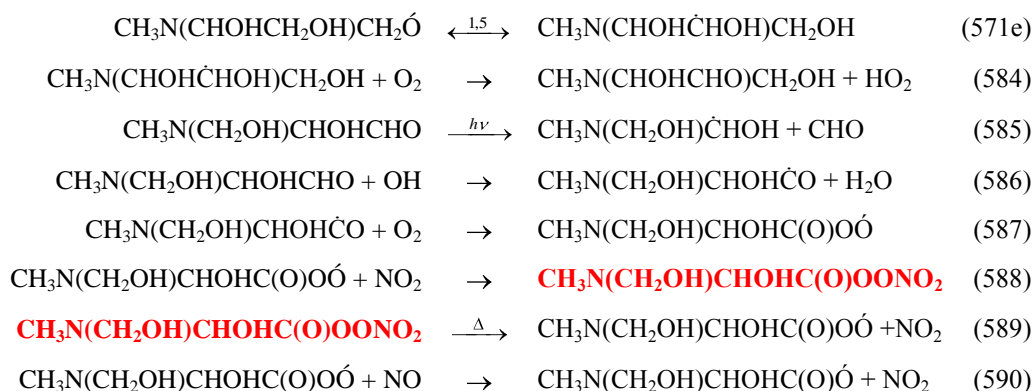
The alkoxy radical formed in the 1,5-hydrogen shift reaction (571d) will react with O_2 in a hydrogen abstraction reaction and form an amide or alternatively dissociate



The N-centered radical formed in (575b) will undergo hydrogen abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.

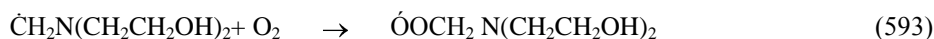


The other alkoxy radical formed in the 1,5-hydrogen shift reaction (571e) will react with O_2 in a hydrogen abstraction reaction to form an aldehyde, which may either photolyse or react with OH in an aldehydic hydrogen abstraction.



3.3.3 Fate of the $\dot{\text{C}}\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ radical

The first steps following hydrogen abstraction from the CH_3 -group in MDEA are expected to be:



The rate of the thermal dissociation reaction leading to the N-centered radical in (596a) is slow compared to the hydrogen abstraction by O_2 and the 1,5-hydrogen shift reaction. In any case, the N-centered radical will undergo hydrogen abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.

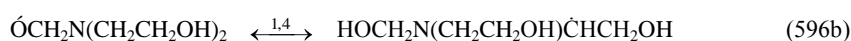


The imine formed (599b) and (600) is assumed to react as outlined in Section 2.3 leading to an amide.

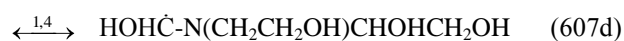
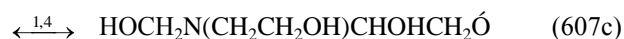


3.3.3.1 Fate of the $\text{HOCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\dot{\text{C}}\text{HCH}_2\text{OH}$ radical

The alkyl radical formed in the 1,4-hydrogen shift reaction in (596b) will first add O_2 :



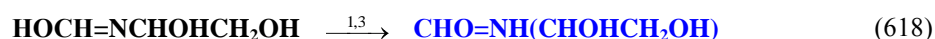
The alkoxy radical formed in (605) may also undergo dissociation reactions and a number of 1,4- and 1,5-hydrogen shift reactions of which the 1,4-hydrogen shift reactions are too slow compared to hydrogen abstraction by O₂ and the 1,5-hydrogen shift reactions to be important:



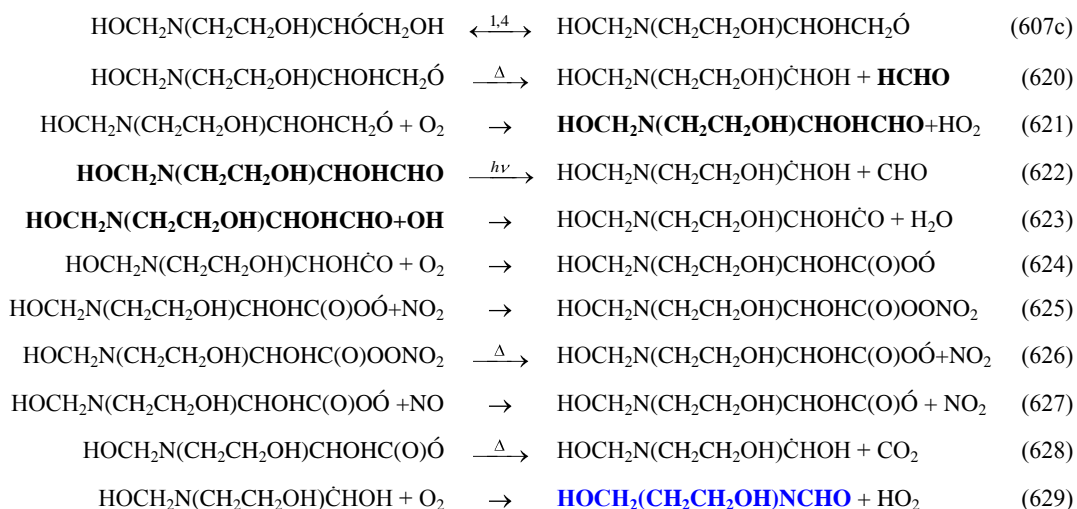
The N-centered radical formed in (607a) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



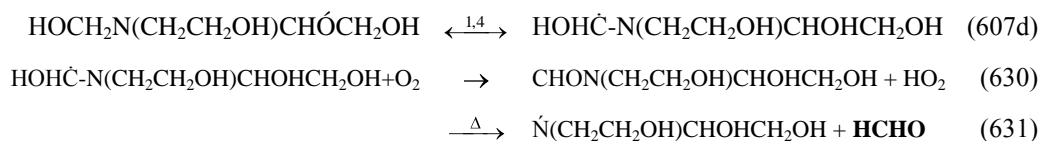
The imine formed in (610c) and (611b) will undergo 1,3-hydrogen shift to form an amide directly while the imine formed in (610b) and (611a) may react with OH radicals in an addition reaction:



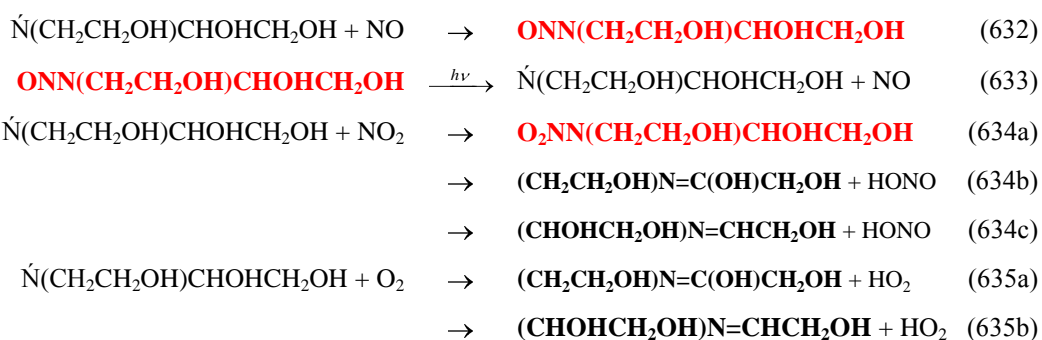
The alkoxy radical formed in the 1,4-hydrogen shift reaction (607c) may dissociate or undergo hydrogen abstraction by O₂ to form an aldehyde, which in turn will undergo photolysis or react with OH in an aldehydic hydrogen abstraction:



The alkyl radical formed in the 1,4-hydrogen shift reaction (607d) may dissociate to form an N-centered radical or undergo hydrogen abstraction by O₂ to form an amide:

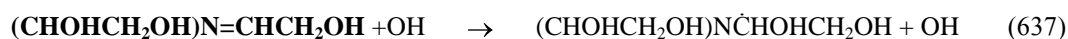


The N-centered radical formed in (631) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical. Note that the rate of (631) is slow compared to that of the hydrogen abstraction reaction by O₂.

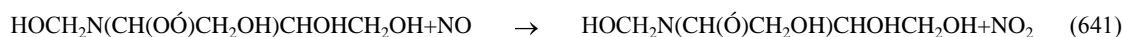


The imines formed in and will undergo 1,3-hydrogen shift reaction to form an amide while the imines formed in and may first add OH, undergo 1,3-hydrogen shift and subsequent hydrogen abstraction to form other amides:

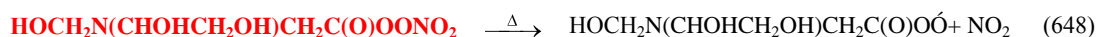
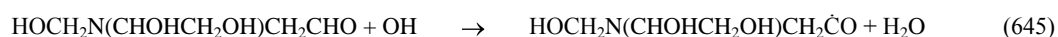
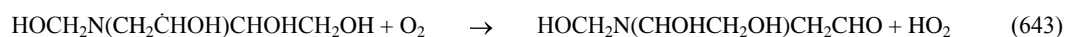




The alkyl radical formed in the 1,4-hydrogen shift reaction (607e) will first O₂:



The alkyl radical formed in the 1,5-hydrogen shift reaction (607f) will undergo hydrogen abstraction by O₂ to form an aldehyde which in turn may undergo photolysis or aldehydic hydrogen abstraction by OH:



In addition to the hydrogen abstraction by O₂, the alkoxy radical formed in (651) may also undergo dissociation and two 1,4-hydrogen and two 1,5-hydrogen shift reactions. Note that the dissociation and the 1,4-hydrogen shift reactions are too slow to compete with the hydrogen abstraction by O₂ and the 1,5-hydrogen shift reactions.



The N-centered radical formed in (653a) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or

nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



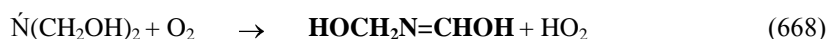
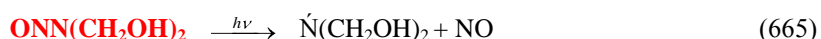
The alkyl radical formed in the 1,4-hydrogen shift reaction in (653b) will react with O_2 in a hydrogen abstraction reaction to yield an amide:



The alkyl radical formed in 1,4-hydrogen shift reaction in (653c) will react with O_2 in a hydrogen abstraction reaction to yield an amide:

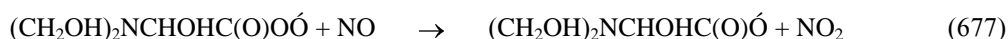
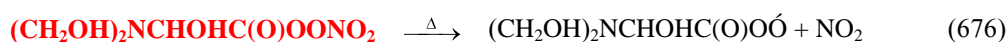
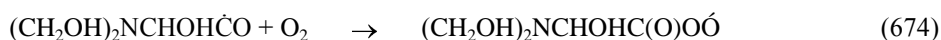
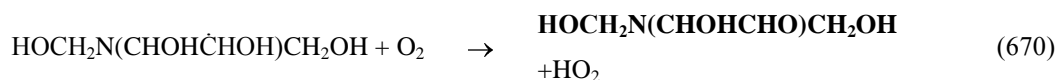


The alkoxy radical formed in the 1,5-hydrogen shift reaction between oxygen atoms in (653d) will react with O_2 in a hydrogen abstraction reaction to yield an amide or dissociate to give an N-centered radical formed in which may undergo hydrogen abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.





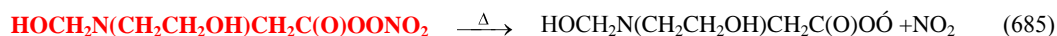
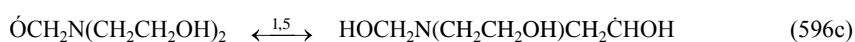
The alkyl radical formed in the 1,5-hydrogen shift reaction (653e) will react with O₂ in a hydrogen abstraction reaction to yield an aldehyde which may either photolysereact with OH in an aldehydic hydrogen abstraction:



Alternatively the alkoxy radical formed in (679) may dissociate to give the same N-centered radical as formed in (663) and whose reactions were discussed in (664) to (669).

3.3.3.2 Fate of the HOCH₂N(CH₂CH₂OH)CH₂ĊHOH radical

The alkyl radical formed in the 1,5-hydrogen shift reaction (596c) will undergo hydrogen abstraction by O₂ forming an aldehyde which may photolyse or react with OH in an aldehydic hydrogen abstraction reaction.



The alkoxy radical formed in (690) may also dissociate to form an N-centered radical (slow reaction because it is a small oxo compound that is formed), or undergo two 1,4-hydrogen shift reactions (slow) and a 1,5-hydrogen shift reaction:



The N-centered radical formed in (691a) will undergo hydrogen abstraction by O_2 and NO_2 , or react with NO and NO_2 to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



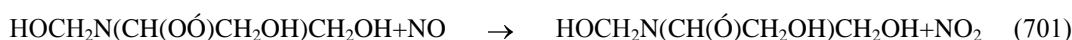
The imine formed in (693c) and (694b) is expected to react as outlined in Section 2.3.



The alkyl radical formed in the 1,4-hydrogen shift reaction (691b) will undergo hydrogen abstraction by O_2 and form amide:



The alkyl radical formed in the 1,4-hydrogen shift reaction (691c) will first add O_2

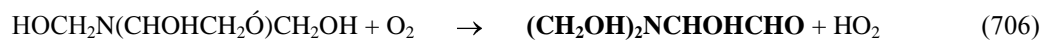


The alkoxy radical formed in (701) may also undergo two 1,4-hydrogen shift reactions, a 1,5-hydrogen shift reaction between two oxygen atoms, or dissociate to form an N-centered radical:



The N-centered radical formed in (703a) is the same as that formed in (663) and whose reactions were discussed in (664) to (669).

The alkoxy radical formed in the 1,4-hydrogen shift reaction (703b) may dissociate or undergo hydrogen abstraction by O₂ to form an aldehyde, which may subsequently undergo photolysis or aldehydic hydrogen abstraction:



The alkyl radical formed in the 1,4-hydrogen shift reaction (703c) will undergo hydrogen abstraction by O₂ forming an amide:

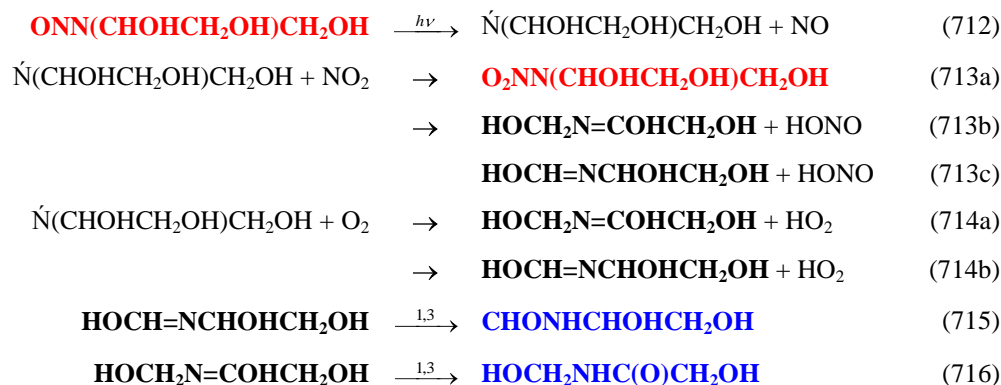


The alkoxy radical formed in the 1,5-hydrogen shift reaction between two oxygen atoms (703d) may dissociate (slow because the oxo compound formed is small) or undergo hydrogen abstraction by O₂:

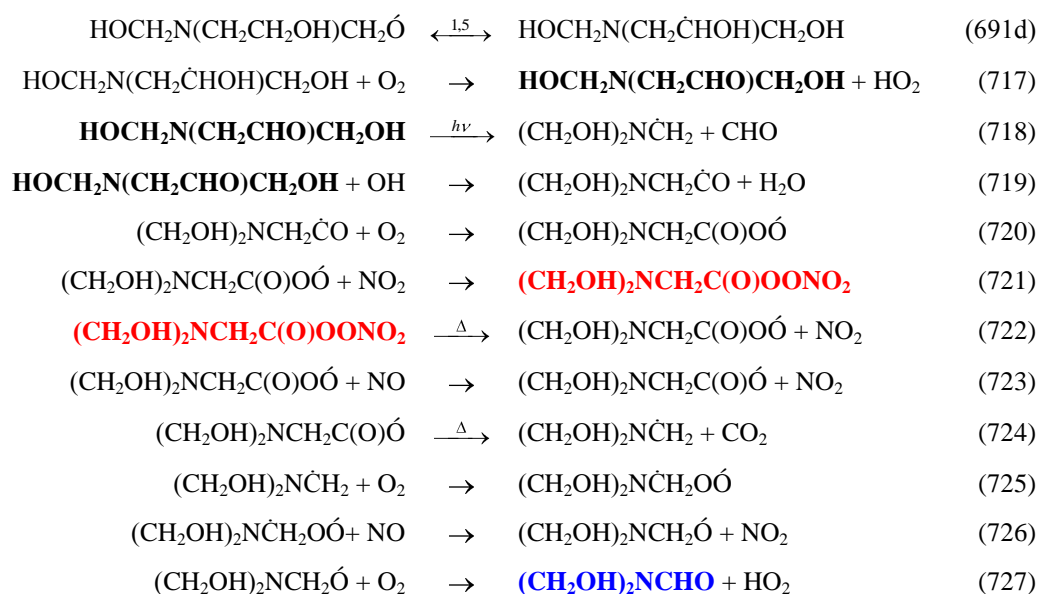


The N-centered radical formed in (703a) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.





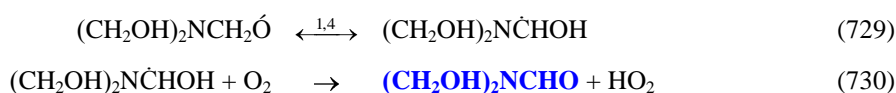
The alkyl radical formed in the 1,5-hydrogen shift reaction (691d) will undergo hydrogen abstraction by O₂ to form an aldehyde which, in turn, will undergo photolysis or aldehydic hydrogen abstraction by OH:



The alkoxy radical formed in (726) may also dissociate or undergo a 1,4-hydrogen shift reactions. Both of these reactions are slow compared to the hydrogen abstraction by O₂. In any case, the dissociation reaction will lead to the same N-centered radical as formed in (703a) and (663) and whose reactions were discussed in (664) to (669).

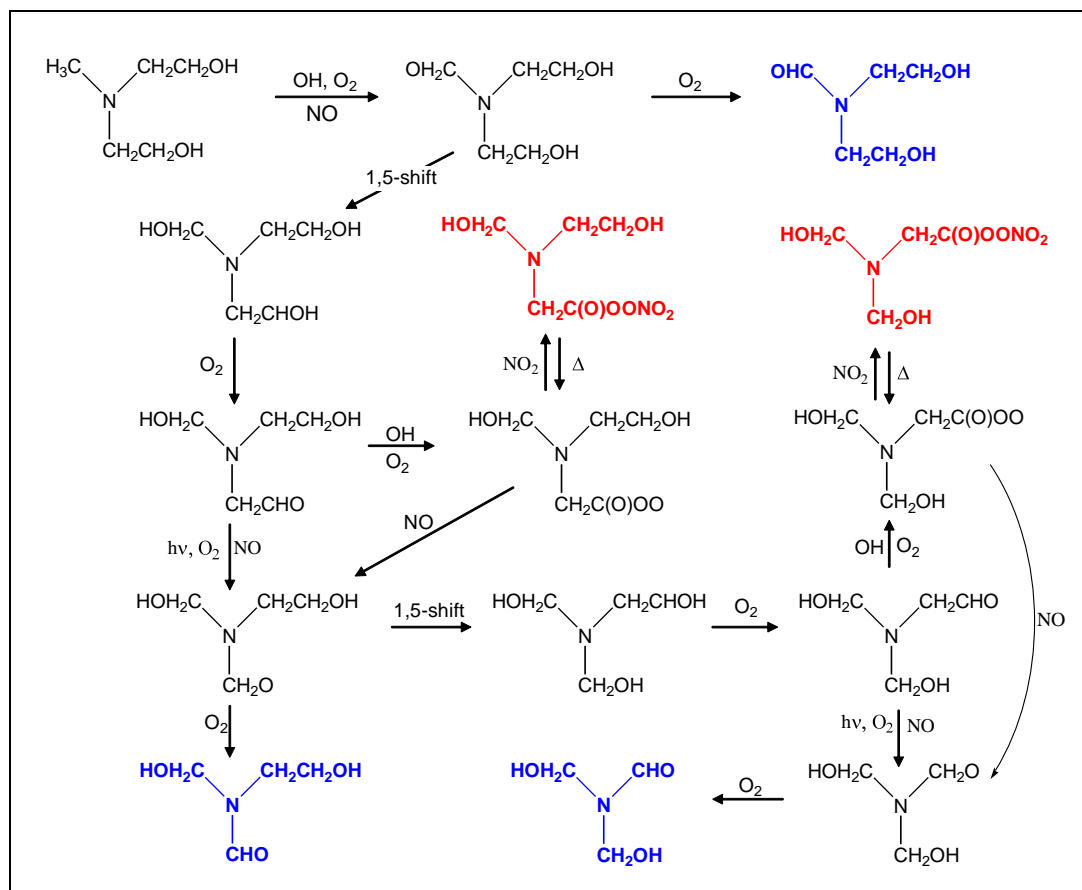


The alkyl radical formed in the 1,4-hydrogen shift reaction undergo hydrogen abstraction and form an amide:



The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from the CH₃ group is summarized in Scheme 3.9. The

main products are amides: $(\text{CH}_2\text{CH}_2\text{OH})_2\text{NCHO}$ (N,N-diethanol-formamide), $(\text{CH}_2\text{CH}_2\text{OH})(\text{CH}_2\text{OH})\text{NCHO}$ (N-methanol, N-ethanol-formamide), $(\text{CH}_2\text{OH})_2\text{NCHO}$ (N,N-dimethanol-formamide). In addition two PAN-like compounds are predicted as intermediates: $(\text{CH}_2\text{OH})(\text{CH}_2\text{CH}_2\text{OH})\text{NCH}_2\text{C}(\text{O})\text{OONO}_2$ and $(\text{CH}_2\text{OH})_2\text{NCH}_2\text{C}(\text{O})\text{OONO}_2$.

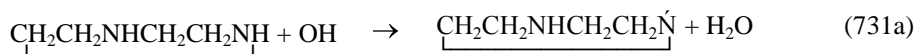


Scheme 3.9. The main routes to the atmospheric degradation of $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ (MDEA) following initial hydrogen abstraction from the CH_3 -group.

3.4 HN(CH₂CH₂)₂NH (PIPA)

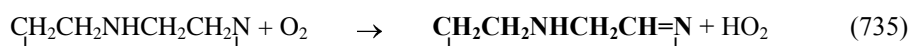
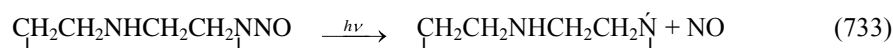
The systematic name of piperazin is 1,4-Diazacyclohexane (CAS: 110-85-0).[#]

The results of the bond enthalpy calculations ($\Delta_{\text{bond}}H_{\text{C-H}} \sim 392$, and $\Delta_{\text{bond}}H_{\text{N-H}} \sim 404$ kJ mol⁻¹, Table 5.2, page 86) suggest that the (C)H- and (N)H-abstraction routes in the initial OH reaction with piperazine are both important. The reaction routes are very complex and only the very major routes are addressed here.

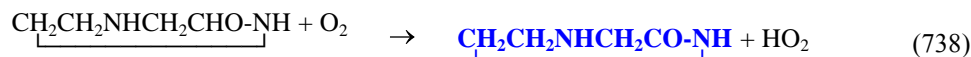
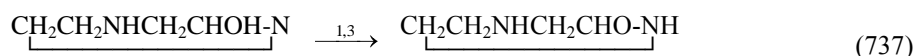
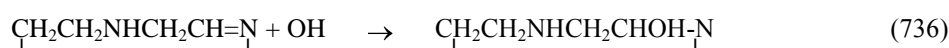


3.4.1 Fate of the $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\dot{\text{N}}$ radical

We first consider reactions following hydrogen abstraction from the amino groups



The imine formed in (734b) and (735) may react with OH radicals (see Section 2.3) leading to the formation of a cyclic amide.

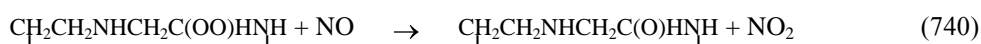
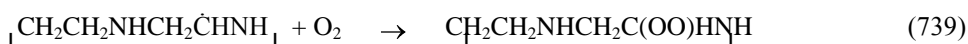


The amide formed in (738) still has activated CH₂-groups which will react readily with OH radicals. These reactions will not be addressed in the present report.

3.4.2 Fate of the $\text{CH}_2\text{CH}_2\text{NHCH}_2\dot{\text{C}}\text{HNH}$ radical

We next consider the subsequent reactions of the $\text{CH}_2\text{CH}_2\text{NHCH}_2\dot{\text{C}}\text{HNH}$ radical which will first add O₂

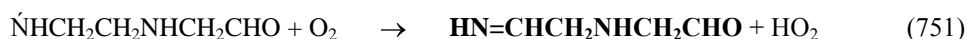
[#] Other tradenames include: 1,4-Piperazine; Antiren; Diethylenediamine; Dispermine; Eraverm; Hexahydropyrazine; Lumbrical; NSC 474; Piperazidine; Pipersol; Pyrazine hexahydride; Pyrazine, hexahydro-; Uvilon; Vermex; Worm-A-Ton; and Wurmiazin.



The alkyl radical formed in (742) will first add O₂ and eventually end up as a di-amide.



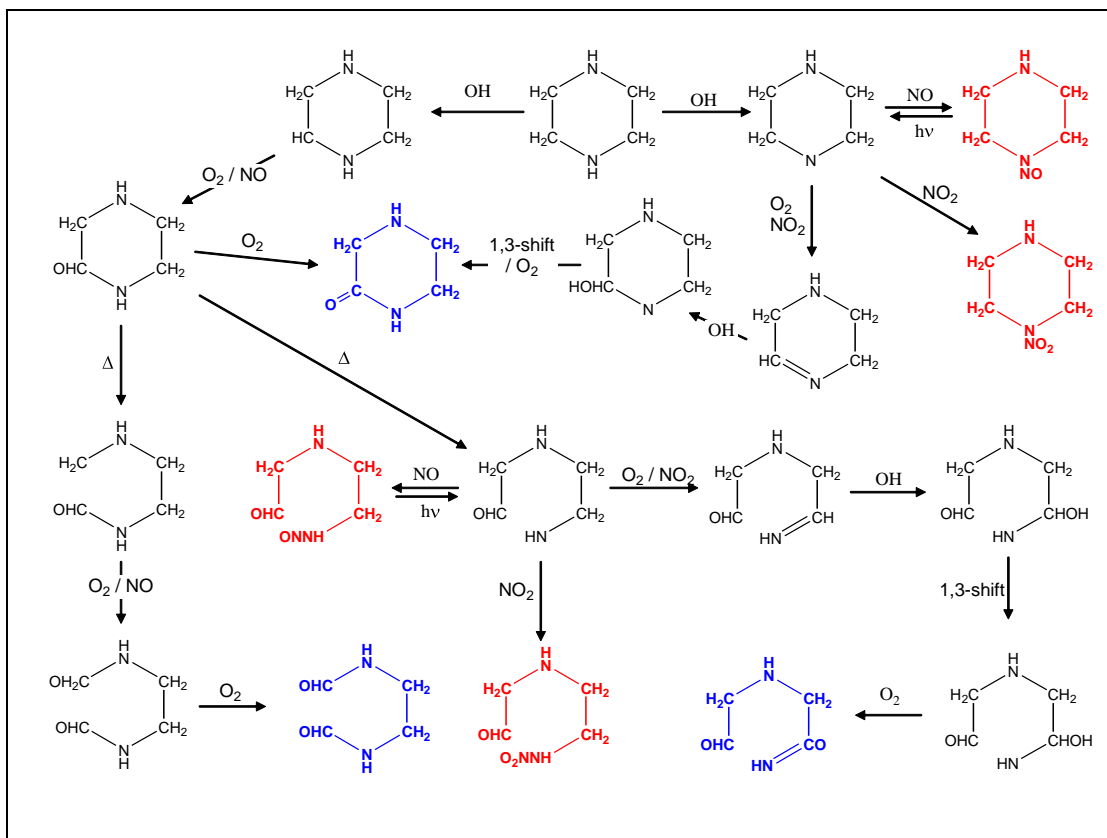
The N-centered radical formed in (743) will undergo hydrogen abstraction by O₂ and NO₂, or react with NO and NO₂ to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.



The imine formed in (750) and (751) is assumed to react as outlined in Section 2.3



The products formed in reactions (731)-(754) have in many cases active CH₂-groups and numerous subsequent reactions are possible. The main routes of the atmospheric degradation of piperazine are shown in Scheme 3.10. The main products from the initial reaction with OH radicals includes CH₂CH₂NHCH₂CO-NH (2-Piperazinone), CHONHCH₂CH₂NHCHO (N,N'-1,2-ethanediybis-formamide), an amine/amide/aldehyde (H₂NC(O)CH₂NHCH₂CHO) not listed in CAS. In addition there will be formed a nitrosamine (ONNHCH₂CH₂NHCH₂CHO) and a nitramine (O₂NNHCH₂CH₂NHCH₂CHO) in the atmospheric degradation of piperazine.



Scheme 3.10 The main atmospheric degradation routes of piperazine.

4 Summary

Detailed schemes for the atmospheric degradation of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (MEA, 2-aminoethanol), $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$ (AMP, 2-amino-2-methyl-1-Propanol), and $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ (MDEA, 2,2'-(methylimino)bis-Ethanol) have been developed based on laboratory data from the literature and quantum chemical calculations. An approximate degradation scheme has been developed for piperazin.

The objective has been to screen for main products and a few specific classes of products in the degradation process, and most of the atmospheric radical-radical reactions have been neglected in the development. Intermediate products with lifetimes $\tau_{\text{OH}} < 3$ days are highlighted in boldface. Products with lifetimes $\tau_{\text{OH}} > 3$ days are highlighted in boldface blue colour – both classes are included in the list of CAS Registry numbers in Table 5.4 on page 88 in the Annex. Possible nitrosamines and nitramines formed in the atmospheric degradation of amines are highlighted in boldface red colour and included in the list of CAS Registry whenever the entry exists.

5 Conclusions

The screening shows that the main products of the atmospheric degradation are different amides, but that a number nitrosamines and nitramines also will result. There is no certain way to assess the relative amounts of nitrosamines and nitramines formed in the atmospheric degradation of amines – there is a serious lack of experimental data. It is recommended that the atmospheric degradation of every amine should be studied in detail before use in industrial scale.

Appendix A

**Bond Enthalpies and
CAS Registry Numbers, Formulas, Structures and
Names**

Bond Enthalpies

Table 5.1 C-H and N-H bond enthalpies ($\Delta_{\text{bond}}H / \text{kJ mol}^{-1}$) from CBS-QB3 calculations for amines included in the OH radical rate constant correlation.

Compound	$\Delta_{\text{bond}}H / \text{kJ mol}^{-1}$		k_{298}
	CBS-QB3	Experimental	$/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
CH_3NH_2	419	416.7^{48} 431 ± 8^{46}	17.3
CH_3NH_2	391	390.62^{48} 396 ± 8^{47}	
$(\text{CH}_3)_2\text{NH}$	395	398 ± 8^{46}	65.3
$(\text{CH}_3)_2\text{NH}$	389		
$(\text{CH}_3)_3\text{N}$	389		35.8
$\text{CH}_3\text{CH}_2\text{NH}_2$	428	414.2^{48}	23.8
$\text{CH}_3\text{CH}_2\text{NH}_2$	386	376.81^{48}	
$\text{CH}_3\text{CH}_2\text{NH}_2$	419	413.0^{48}	
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$			
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$			
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$			
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$			
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	433		28
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	426		
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	397		
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	457		
$(\text{CH}_3)_3\text{CNH}_2$	424	406.6^{48}	12.0
$(\text{CH}_3)_3\text{CNH}_2$	43		
$\text{CF}_3\text{CH}_2\text{NH}_2$	427		0.9
$\text{CF}_3\text{CH}_2\text{NH}_2$	387		
$\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$	414		22
$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$	400		
$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$	392		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	448		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	395		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	394		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	442		

Table 5.2 C-H and N-H bond enthalpies ($\Delta_{\text{bondH}}/\text{kJ mol}^{-1}$) from CBS-QB3 calculations.

Compound	Δ_{bondH}	Compound	Δ_{bondH}
NH ₂ CHO	396	H ₂ NC(O)CH ₂ OH	355
NH ₂ CHO	484	H ₂ NC(O)CH ₂ OH	449
		H ₂ NC(O)CH ₂ OH	482
(CH ₃) ₂ C(NH ₂)CHO	378	NH ₂ CHOHCHO	392
(CH ₃) ₂ C(NH ₂)CHO	430	NH ₂ CHOHCHO	313
(CH ₃) ₂ C(NH ₂)CHO	427	NH ₂ CHOHCHO	437
		NH ₂ CHOHCHO	453
(CH ₃) ₂ C(NH ₂)CH ₂ OH	433		
(CH ₃) ₂ C(NH ₂)CH ₂ OH	426	NH ₂ CH ₂ CHO	424
(CH ₃) ₂ C(NH ₂)CH ₂ OH	397	NH ₂ CH ₂ CHO	310
(CH ₃) ₂ C(NH ₂)CH ₂ OH	457	NH ₂ CH ₂ CHO	374
CH ₃ CONH ₂	484		
CH ₃ CONH ₂	397		
ONNHCH ₂ OH	313		
O ₂ NNHCH ₂ OH	336		

CAS Registry Numbers, Formulas, Structures and Names

Table 5.3 Inorganic compounds included in the CAS Register.

Registry Number	Formula	Structure	Name
12385-13-6	H	H	Hydrogen atom
3352-57-6	H O	HO	Hydroxide radical
7732-18-5	H ₂ O	H ₂ O	Water
3170-83-0	H O ₂	o — OH	Hydrogen dioxide radical
7722-84-1	H ₂ O ₂	HO — OH	Hydrogen peroxide
10102-43-9	N O	N = O	Nitrogen monoxide
10102-44-0	N O ₂	o — N = O	Nitrogen oxide
12033-49-7	N O ₃	$\begin{array}{c} \text{O} \\ \\ \text{O} = \text{N} - \text{O} \end{array}$	Nitrate radical
14332-28-6	H N O	HN = O	Nitrosyl hydride
7782-77-6	H NO ₂	O = N — OH	Nitrous acid
7697-37-2	H N O ₃	$\begin{array}{c} \text{O} \\ \\ \text{O} = \text{N} - \text{OH} \end{array}$	Nitric acid
7782-44-7	O ₂	o = o	Oksygen
10028-15-6	O ₃	o — o — o	Ozone

Table 5.4 Organic compounds included in the CAS Register.

Registry Number	Formula	Structure	Name
75-13-8	C H N O	$\text{HN}=\text{C}=\text{O}$	Isocyanic acid
675141-02-3	C H ₂ N ₂ O ₂	$\text{O}=\text{CH}-\text{NH}-\text{N}=\text{O}$	Formamide, N-nitroso-
51883-27-3	C H ₂ N ₂ O ₃	$\text{OHC}-\text{NH}-\text{NO}_2$	Formamide, N-nitro-
56077-92-0	C H ₂ O ₂	$\text{H}_2\text{C}-\text{O}-\text{O}$	Methyl, dioxy-
2053-29-4	C H ₃ N	$\text{H}_2\text{C}=\text{NH}$	Methanimine
60100-09-6	C H ₃ N O	$\text{HN}=\text{CH}-\text{OH}$	Methanimidic acid
865-40-7	C H ₃ N O	$\text{H}_3\text{C}-\text{N}=\text{O}$	Nitrosomethane
75-12-7	C H ₃ N O	$\text{H}_2\text{N}-\text{CH}=\text{O}$	Formamide
64768-29-2	C H ₄ N ₂ O	$\text{H}_3\text{C}-\text{NH}-\text{N}=\text{O}$	Methanamine, N-Nitroso-
598-57-2	C H ₄ N ₂ O ₂	$\begin{array}{c} \text{O} \\ \\ \text{O}=\text{N}-\text{NH}-\text{CH}_3 \end{array}$	Methanamine, N-nitro-
598-57-2	C H ₄ N ₂ O ₂	$\begin{array}{c} \text{O} \\ \\ \text{O}=\text{N}-\text{NH}-\text{CH}_3 \end{array}$	Methanamine, N-Nitro-
67-56-1	C H ₄ O	$\text{H}_3\text{C}-\text{OH}$	Methanol
107-22-2	C ₂ H ₂ O ₂	$\text{O}=\text{CH}-\text{CH}=\text{O}$	Ethanedial
298-12-4	C ₂ H ₂ O ₃	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{C}-\text{CH}=\text{O} \end{array}$	Acetic acid, 2-oxo-
60939-21-1	C ₂ H ₃ N O ₂	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}=\text{O} \end{array}$	Acetamide, 2-oxo-
107031-65-2	C ₂ H ₃ O ₂	$\text{HO}-\text{CH}_2-\text{C}=\text{O}$	Ethyl, 2-hydroxy-1-oxo-
246506-71-8	C ₂ H ₄ N O ₂	$\begin{array}{c} \text{OH} \\ \\ \text{H}_2\text{N}-\text{CH}-\text{C}=\text{O} \end{array}$	Ethyl, 2-amino-2-hydroxy-1-oxo-
141-46-8	C ₂ H ₄ O ₂	$\text{HO}-\text{CH}_2-\text{CH}=\text{O}$	Acetaldehyde, hydroxy-
79-14-1	C ₂ H ₄ O ₃	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{C}-\text{CH}_2-\text{OH} \end{array}$	Acetic acid, 2-hydroxy-
1761-67-7	C ₂ H ₅ N	$\text{H}_3\text{C}-\text{N}=\text{CH}_2$	N-methylene-Methanamine
6542-88-7	C ₂ H ₅ N O	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}=\text{O}$	Acetaldehyde, amino-

60-35-5	C2 H5 N O	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_3 \end{array}$	Acetamide
123-39-7	C2 H5 N O	$\text{O}=\text{CH}-\text{NH}-\text{CH}_3$	Formamide, N-Methyl-
734507-86-9	C2 H5 N O	$\text{HO}-\text{CH}_2-\text{N}=\text{CH}_2$	Methanol, (methyleneamino)-
598-42-5	C2 H5 N O2	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{OH} \end{array}$	Acetamide, 2-Hydroxy-
62-75-9	C2 H6 N2 O	$\begin{array}{c} \text{N}=\text{O} \\ \\ \text{H}_3\text{C}-\text{N}-\text{CH}_3 \end{array}$	Methanamine, N- Methyl-N-nitroso-
98033-27-3	C2 H6 N2 O2	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{NO}$	Ethanol, 2- (nitrosoamino)-
4164-28-7	C2 H6 N2 O2	$\begin{array}{c} \text{NO}_2 \\ \\ \text{Me}-\text{N}-\text{Me} \end{array}$	Methanamine, N- Methyl-N-nitro-
74386-82-6	C2 H6 N2 O3	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{NO}_2$	Ethanol, 2-(nitroamino)-
32818-80-7	C2 H6 N2 O3	$\begin{array}{c} \text{NO}_2 \\ \\ \text{Me}-\text{N}-\text{CH}_2-\text{OH} \end{array}$	Methanol, (methylnitroamino)-
141-43-5	C2 H7 N O	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$	Ethanol, 2-amino-
18197-25-6	C3 H5 N O2	$\begin{array}{c} \text{Me} \\ \\ \text{OHC}-\text{N}-\text{CHO} \end{array}$	Formamide, N-Formyl- N-Methyl-
344549-61-7	C3 H6 N O	$\text{HO}-\text{CH}_2-\text{C}=\text{N}-\text{CH}_3$	Ethyl, 2-hydroxy-1- (methylimino)-
67-64-1	C3 H6 O	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	2-Propanone
38697-07-3	C3 H7 N	$\begin{array}{c} \text{NH} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	2-Propanimine
68-12-2	C3 H7 N O	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{N}-\text{CH}=\text{O} \end{array}$	Formamide, N,N- Dimethyl-
79-16-3	C3 H7 N O	$\begin{array}{c} \text{O} \\ \\ \text{Me}-\text{N}-\text{H}-\text{Me} \end{array}$	Acetamide, N-Methyl-
13010-54-3	C3 H7 N O	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2$	Ethanol, 2- (methyleneamino)-
20546-32-1	C3 H7 N O2	$\begin{array}{c} \text{Me} \\ \\ \text{OHC}-\text{N}-\text{CH}_2-\text{OH} \end{array}$	Formamide, N- (hydroxymethyl)-N- methyl-

42499-46-7	C3 H8 N 2O3	$\begin{array}{c} \text{NO}_2 \\ \\ \text{Me}-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	Ethanol, 2-(methylnitroamino)-
26921-68-6	C3 H8 N2 O2	$\begin{array}{c} \text{NO} \\ \\ \text{Me}-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	Ethanol, 2-(methylnitrosoamino)-
55-18-5	C4 H10 N2 O	$\begin{array}{c} \text{NO} \\ \\ \text{Et}-\text{N}-\text{Et} \end{array}$	Etanamine, N-Etyl-N-Nitroso-
7119-92-8	C4 H10 N2 O2	$\begin{array}{c} \text{NO}_2 \\ \\ \text{Et}-\text{N}-\text{Et} \end{array}$	Etanamine, N-Etyl-N-Nitro-
127-19-5	C4 H9 N O	$\begin{array}{c} \text{Me} \\ \\ \text{Me}-\text{N}-\text{Ac} \end{array}$	Acetamide, N,N-Dimethyl-
1590-50-7	C4 H9 N O2	$\begin{array}{c} \text{Me} \\ \\ \text{OHC}-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	Formamide, N-(2-hydroxyethyl)-N-methyl-
124-68-5	C4 H11 N O	$\begin{array}{c} \text{NH}_2 \\ \\ \text{Me}-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{Me} \end{array}$	1-Propanol, 2-amino-2-methyl-
617-84-5	C5 H11 N O	$\begin{array}{c} \text{CHO} \\ \\ \text{Et}-\text{N}-\text{Et} \end{array}$	Formamide, N,N-Diethyl-
17236-38-3	C5 H11 N O3	$\begin{array}{c} \text{Me} \quad \text{O} \\ \quad \\ \text{HO}-\text{CH}_2-\text{CH}_2-\text{N}-\text{C}-\text{CH}_2-\text{OH} \end{array}$	Glycolamide, N-(2-hydroxyethyl)-N-methyl-
105-59-9	C5 H13 N O2	$\begin{array}{c} \text{Me} \\ \\ \text{HO}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	Ethanol, 2,2'-(methylimino)bis-
685-91-6	C6 H13 N O	$\begin{array}{c} \text{Ac} \\ \\ \text{Et}-\text{N}-\text{Et} \end{array}$	Acetamide, N,N-Diethyl-

Literature

- (1) Bidleman, T. F. (1988) Atmospheric processes - wet and dry deposition of organic-compounds are controlled by their vapor particle partitioning. *Environ. Sci. Technol.*, 22, 361-67.
- (2) Finlayson-Pitts, B. J. and Pitts, J. N. (1986) *Atmospheric chemistry: fundamentals and experimental techniques*. New York, Wiley.
- (3) Jenkin, M. E., Saunders, S. M. and Pilling, M. J. (1997) The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmos. Environ.*, 31, 81-104.
- (4) Atkinson, R., Perry, R. A. and Pitts, J. N., Jr. (1977) Rate constants for the reaction of the hydroxyl radical with methanethiol and methylamine over the temperature range 299-426 DegK. *J. Phys. Chem.*, 66, 1578-81.
- (5) Carl, S. A. and Crowley, J. N. (1998) Sequential two (blue) photon absorption by NO₂ in the presence of H₂ as a source of OH in pulsed photolysis kinetic studies: Rate constants for reaction of OH with CH₃NH₂, (CH₃)₂NH, (CH₃)₃N, and C₂H₅NH₂ at 295 K. *J. Phys. Chem. A*, 102, 8131-41.
- (6) Atkinson, R., Perry, R. A. and Pitts, J. N., Jr. (1978) Rate constants for the reactions of the hydroxyl radical with dimethylamine, trimethylamine, and ethylamine over the temperature range 298-426 K. *J. Phys. Chem.*, 68, 1850-3.
- (7) Gorse, R. A., Jr., Lii, R. R. and Saunders, B. B. (1977) Hydroxyl radical reactivity with diethylhydroxylamine. *Science*, 197, 1365-7.
- (8) Harris, G. W. and Pitts, J. N. (1983) Rates of reaction of hydroxyl radicals with 2-(dimethylamino)ethanol and 2-amino-2-methyl-1-propanol in the gas-phase at 300 ± 2 K. *Environ. Sci. Technol.*, 17, 50-51.
- (9) Anderson, L. G. and Stephens, R. D. (1988) Kinetics of the reaction of hydroxyl radicals with 2-(dimethylamino)ethanol from 234-364-K. *Intern. J. Chem. Kinet.* 20, 103-10.
- (10) Koch, R., Kruger, H. U., Elend, M., Palm, W. U. and Zetzsch, C. (1996) Rate constants for the gas-phase reaction of OH with amines: tert-Butyl amine, 2,2,2-trifluoroethyl amine, and 1,4-diazabicyclo[2.2.2]octane. *Intern. J. Chem. Kinet.*, 28, 807-15.
- (11) Grosjean, D. (1991) Atmospheric chemistry of toxic contaminants. 6. Nitrosamines: dialkyl nitrosamines and nitrosomorpholine. *J. Air Waste Manage. Ass.*, 41, 306-11.
- (12) Schade, G. W. and Crutzen, P. J. (1995) Emission of aliphatic-amines from animal husbandry and their reactions - potential source of N₂O and HCN. *J. Atmos. Chem.*, 22, 319-46.
- (13) Pitts, J. N., Grosjean, D., Vancauwenberghe, K., Schmid, J. P. and Fitz, D. R. (1978) Photo-oxidation of aliphatic-amines under simulated atmospheric conditions - formation of nitrosamines, nitramines, amides, and photo-chemical oxidant. *Environ. Sci. Technol.*, 12, 946-53.
- (14) Lindley, C. R. C., Calvert, J. G. and Shaw, J. H. (1979) Rate studies of the reactions of the (CH₃)₂n radical with O₂, NO, and NO₂. *Chem. Phys. Letters*, 67, 57-62.
- (15) Glasson, W. A. (1979) An experimental evaluation of atmospheric nitrosamine formation. *Environ. Sci. Technol.*, 13, 1145-46.

- (16) Hanst, P. L., Spence, J. W. and Miller, M. (1977) Atmospheric chemistry of N-nitroso dimethylamine. *Environ. Sci. Technol.*, *11*, 403-05.
- (17) Bamford, C. H. (1939) A study of the photolysis of organic nitrogen compounds - Part I: Dimethyl- and diethyl-nitrosoamines. *J. Chem. Soc.*, 12-17.
- (18) Tuazon, E. C., Carter, W. P. L., Atkinson, R., Winer, A. M. and Pitts, J. N. (1984) Atmospheric reactions of N-nitrosodimethylamine and dimethylnitramine. *Environ. Sci. Technol.*, *18*, 49-54.
- (19) Stefan, M. I. and Bolton, J. R. (2002) UV direct photolysis of N-nitrosodimethylamine (NDMA): kinetic and product study. *Helvetica Chimica Acta*, *85*, 1416-26.
- (20) Geiger, G. and Huber, J. R. (1981) Photolysis of dimethylnitrosamine in the gas-phase. *Helvetica Chimica Acta*, *64*, 989-95.
- (21) Tuazon, E. C., Atkinson, R., Aschmann, S. M. and Arey, J. (1994) Kinetics and products of the gas-phase reactions of O₃ with amines and related-compounds. *Res. Chem. Intermed.*, *20*, 303-20.
- (22) Lazarou, Y. G., Kambanis, K. G. and Papagiannakopoulos, P. (1994) Gas-phase reactions of (CH₃)₂N radicals with NO and NO₂. *J. Phys. Chem.*, *98*, 2110-15.
- (23) Rudic, S., Murray, C., Harvey, J. N. and Orr-Ewing, A. J. (2003) The product branching and dynamics of the reaction of chlorine atoms with methylamine. *Phys. Chem. Chem. Phys.*, *5*, 1205-12.
- (24) Calvert, J. G. and Pitts, J. N. (1966) Photochemistry. N.Y., Wiley.
- (25) Teslja, A., Nizamov, B. and Dagdigian, P. J. (2004) The electronic spectrum of methyleneimine. *J. Phys. Chem. A*, *108*, 4433-39.
- (26) Nguyen Minh, T., Sengupta, D. and Ha, T.-K. (1996) Another look at the decomposition of methyl azide and methanimine: How is HCN formed? *J. Phys. Chem.*, *100*, 6499-503.
- (27) Chakir, A., Solignac, B., Mellouki, A. and Daumont, D. (2005) Gas phase UV absorption cross-sections for a series of amides. *Chem. Phys. Letters*, *404*, 74-78.
- (28) Munoz, F., Schuchmann, M. N., Olbrich, G., and von Sonntag, C. (2000) Common intermediates in the OH-radical-induced oxidation of cyanide and formamide. *J. Chemical Soc.-Perkin Transact.*, *2*, 655-59.
- (29) Koch, R., Palm, W. U. and Zetzsch, C. (1997) First rate constants for reactions of OH radicals with amides. *Internat. J. Chem. Kinet.*, *29*, 81-87.
- (30) Solignac, G., Mellouki, A., Le Bras, G., Barnes, I. and Benter, T. (2005) Kinetics of the OH and Cl reactions with N-methylformamide, N,N-dimethylformamide and N,N-dimethylacetamide. *J. Photochem. Photobiol., A - Chemistry*, *176*, 136-42.
- (31) Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C. and Seinfeld, J. H. (2007) Secondary aerosol formation from atmospheric reactions of aliphatic amines. *Atmos. Chem. Phys.*, *7*, 2313-37.
- (32) Atkinson, R. (1987) A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic-compounds. *Internat. J. Chem. Kinet.*, *19*, 799-828.
- (33) Atkinson, R. (1986) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic-compounds under atmospheric conditions. *Chem. Rev.*, *86*, 69-201.

- (34) D'Anna, B., Andresen, W., Gefen, Z. and Nielsen, C. J. (2001) Kinetic study of OH and NO₃ radical reactions with 14 aliphatic aldehydes. *Phys. Chem. Chem. Phys.*, *3*, 3057-63.
- (35) Kwok, E. S. C. and Atkinson, R. (1995) Estimation of hydroxyl radical reaction-rate constants for gas-phase organic-compounds using a structure-reactivity relationship - an update. *Atmos. Environ.*, *29*, 1685-95.
- (36) Carter, W. P. L. and Atkinson, R. (1985) Atmospheric chemistry of alkanes. *J. Atmos. Chem.*, *3*, 377-405.
- (37) Galano, A. and Alvarez-Idaboy, J. R. (2008) Branching ratios of aliphatic amines + OH gas-phase reactions: A variational transition-state theory study. *J. Chem. Theor. Comput.*, *4*, 322-27.
- (38) Montgomery, J. A., Frisch, M. J., Ochterski, J. W. and Petersson, G. A. (1999) A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. *J. Chem. Phys.*, *110*, 2822-27.
- (39) Møller, C. and Plesset, M. S. (1934) Note on a approximation treatment for many-electron systems. *Phys. Rev.*, *46*, 618-22.
- (40) Raghavachari, K., Trucks, G. W., Pople, J. A. and Head-Gordon, M. (1989) A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Letters*, *157*, 479-83.
- (41) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Jr., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W.; Gonzalez, C., Pople, J. A. (2003) *Gaussian 03, Revision B.03*. Pittsburgh, PA., Gaussian Inc.
- (42) Dunning, T. H., Jr. (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.*, *90*, 1007-23.
- (43) Kendall, R. A., Dunning, T. H., Jr. and Harrison, R. J. (1992) Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.*, *96*, 6796-806.
- (44) Gonzalez, C. and Schlegel, H. B. (1989) An improved algorithm for reaction path following. *J. Chem. Phys.*, *90*, 2154-61.
- (45) Gonzalez, C. and Schlegel, H. B. (1990) Reaction path following in mass-weighted internal coordinates. *J. Phys. Chem.*, *94*, 5523-7.
- (46) Golden, D. M., Gac, N. A., Solly, R. K. and Benson, S. W. (1972) Very low-pressure pyrolysis .5. Benzylamine, N-methylbenzylamine, and N,N-dimethylbenzylamine and heat of formation of amino, methylamino, and dimethylamino radicals. *J. Am. Chem. Soc.*, *94*, 363-&.

- (47) Colussi, A. J. and Benson, S. W. (1977) Very low-pressure pyrolysis of 2-phenylethylamine - enthalpy of formation of aminomethyl radical. *Internat. J. Chem. Kinet.*, *9*, 307-16.
- (48) Takhistov, V. V. (1990) *Organic mass spectrometry*. Leningrad, Nauka. (in Russian).
- (49) McCoustra, M. R. S. and Pfab, J. (1990) Free-jet studies of the visible spectroscopy of some perhalonitrosomethanes. *Spectrochim. Acta, Part A-Mol. Biomol. Spectrosc.*, *46*, 937-55.
- (50) Toniolo, A. and Persico, M. (2001) A theoretical study of spectroscopy and predissociation dynamics in nitrosoalkanes. *J. Chem. Phys.*, *115*, 1817-27.
- (51) Bryukov, M. G., Kachanov, A. A., Timonnen, R., Seetula, J., Vandoren, J. and Sarkisov, O. M. (1993) Kinetics of Hno reactions with O₂ and HNO. *Chem. Phys. Letters*, *208*, 392-98.
- (52) Evans, M. G. and Polanyi, M. (1938) Inertia and driving force of chemical reactions. *Transact. Faraday Society*, *34*, 0011-23.
- (53) Atkinson, R. (1989) *Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds*. Wash. DC, Am. Chem. Soc. and Am. Inst. Phys. (Journal of physical and chemical reference data, Monograph, 1).
- (54) Atkinson, R. (1990) Gas-phase tropospheric chemistry of organic compounds: a review. *Atmos. Environ.*, *24A*, 1-41.
- (55) Atkinson, R. (1994) *Gas-phase tropospheric chemistry of organic compounds*. Wash. DC, Am. Chem. Soc. and Am. Inst. Phys. (Journal of physical and chemical reference data, Monograph, 2).
- (56) Atkinson, R. and Arey, J. (2003) Atmospheric degradation of volatile organic compounds. *Chem. Rev.*, *103*, 4605-38.
- (57) Hein, R., Crutzen, P. J. and Heimann, M. (1997) An inverse modeling approach to investigate the global atmospheric methane cycle. *Global Biogeochem. Cycles*, *11*, 43-76.
- (58) The Master Chemical Mechanism.
URL: <http://mcm.leeds.ac.uk/MCM/home.htm>.



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ABSTRACT <p>Amines emitted into the atmosphere will undergo a series of chemical and physical processes. Compounds with liquid-phase vapour pressures $> 10^{-6}$ Torr at the ambient atmospheric temperature will to a large extent undergo reactions in the gas phase. For the majority of gas-phase organic chemicals present in the troposphere, reaction with the OH radical is the dominant loss process. In general the degradation is initiated by reaction with OH and, where appropriate, direct photolysis and the reactions with O_3 and NO_3. In marine areas reactions with Cl atoms may also constitute an important sink. The types of radical generated following initiation processes include peroxy (RO_2), oxy (RO) and excited and stabilized Criegee ($R'R''COO$) species, which each have a number of possible reactions which may be competitive under tropospheric conditions. The complex initiation and radical chemistry leads to the generation of many different products. Some are species which themselves have primary emissions, such as simple alcohols, aldehydes and ketones; others include complex (multifunctional) carbonyls, nitrates ($RONO_2$), peroxy nitrates ($RC(=O)OONO_2$), hydroperoxides (ROOH), percarboxylic acids ($RC(=O)OOH$) and carboxylic acids ($RC(=O)OH$).</p> <p>A literature survey was carried out and theoretical degradation mechanisms for selected amines have been developed on the basis of experimental findings.</p>			
NORWEGIAN TITLE Sluttrapport til ein teoretisk studie av den atmosfæriske nedbrytinga av utvalte amin			
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ABSTRACT (in Norwegian)

Amin som vert sleppt ut i atmosfæren vil inngå i ei rekkje kjemiske og fysiske prosessar. Kjemiske stoff i væskefase med damptrykk $> 10^{-6}$ Torr ved temperaturen til atmosfæren i omgivnaden, vil for det meste gjennomgå reaksjonar som skjer i gassfase. For storparten av dei organiske stoffa som ein finn i gassfase i troposfæren, vil reaksjon med OH-radikalet være den dominerande tapsprosessen. Generelt vil nedbrytinga starte med reaksjon med OH og, der kor det er høveleg, direkte fotolyse og reaksjonar med O_3 og NO_3 . I marine område kan også reaksjonar med Cl-atom vere eit viktig sluk. Typen av radikalar som vert danna etter initieringsprosessane inkluderer peroksy (RO_2), oksy (RO) og eksiterte og stabiliserte Criegee-sambindingar ($R'R''COO$), som kvar kan ha ei rekkje mulige reaksjonar som kan konkurrere med kvarandre under troposfæriske forhold. Den komplekse initierings- og radikalkjemien fører til at mange forskjellige produkt vert danna. Nokre er stoff som sjølve har primære utsleppskjelder som enkle alkoholar, aldehyd og keton; andre inkluderer komplekse (multifunksjonelle) karbonyl, nitrat ($RONO_2$), peroksynitrat ($RC(=O)OONO_2$), hydroperoksid ($ROOH$), perkarboksylsyrer $RC(=O)OOH$ og karboksylsyrer ($RC(=O)OH$).

Ein litteraturstudie har blitt utført og teoretiske nedbrytingsmekanismar for utvalte amin har blitt utvikla på grunnlag av eksperimentelle funn.

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