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# **Project report**

# **Project title: CO<sub>2</sub> and amines**

# 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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1

# Preface

 $CO_2$  capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce  $CO_2$  emissions to the atmosphere, thus reducing the main contributor to global warming. A leading technology for  $CO_2$ capture is through the use of amines. The  $CO_2$  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  $CO_2$  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.

# Contents

		Page
Preface		
1 Literat	ure survey	5
1.1 Ki	netic data for the reaction of amines with OH radicals	6
1.1.1	$CH_3NH_2 + OH$	7
1.1.2	$(CH_3)_2NH + OH$	7
1.1.3	$(CH_3)_3N + OH$	
1.1.4	$CH_3CH_2NH_2 + OH$	
1.1.5	$(CH_3CH_2)_2NOH + OH$	
1.1.6	$(CH_3)_2NCH_2CH_2OH + OH$	
1.1.7	$(CH_3)_2C(NH_2)CH_2OH + OH$	
1.1.8	$(CH_3)_2 CNH_2 + OH$ .	
1.1.9	$CF_3CH_2NH_2 + OH$	
1.1.10	$N(CH_2CH_2)_3N + OH$	
1.2 Pr	oduct studies of amine + OH reactions	9
1.2.1	$(CH_3)_2NH + OH$	
1.2.2	$(CH_3)_2 N + OH$	
1.2.3	$(CH_2CH_2)_2NH + OH$	10
12.5	$(CH_2CH_2)_2N + OH$	11
13 01	ther relevant experimental studies	12
131	Photolysis of N-nitroso-Dimethylamine	12
132	Branching ratio in the $CH_2NH_2 + Cl$ reaction	13
133	Photolysis of aliphatic aldehydes	13
134	UV spectra of amides and imines	14
13.1	$CHONH_2 + OH$	14
1.3.5	$(CH_2)_2NNO + OH$	15
1.3.0	$(CH_3)_2 NNO_2 + OH$	15
13.7	Aerosol formation	15
1.5.6	ructure Activity Relationship (SAR)	16
	uantum chemistry studies	
1.5 Quite 1.6 Su	ummary of literature data	20
2  OCC t	oolbox for mechanistic elucidation	21
$2 \qquad \text{QCC}$	omputational Methods	21
2.1  Comparison	nermochemistry	21
2.2 II 2.3 Fr	$\mathbf{r}$	21
2.3 1	$CH_2NH_2$ (CH <sub>2</sub> ) <sub>2</sub> NH (CH <sub>2</sub> ) <sub>2</sub> N + OH	22
2.3.1	$R-N=CR'R'' + O_2$	23
2.3.2	R-N=CR'R''+OH	26
2.3.3 2 3 4	Atmospheric fate of $RN=CR'OH$	28
2.3.4	$NH_{0}CHO$ (and other amides) + OH	29
2.5.5	and Enthalpies and $OH$ reaction rate constants	30
2.4 DC	atical atmospheric degradation mechanisms	
31 H	NCH <sub>2</sub> CH <sub>2</sub> OH (MFA)	
211	Fate of the HaNCHaCHOH radical	
3.1.1 3.1.2	Fate of the HaNCHCH-OH radical	
$\begin{array}{c} \mathbf{J}.1.2 \\ 2 \ 1 \ 2 \end{array}$	Reactions following a possible hydrogon abstraction from	
J.1.J		
group	50	

3.1.4 Summary of the atmospheric MEA degradation	
$3.2 (CH_3)_2 C(NH_2) CH_2 OH (AMP)$	40
3.2.1 Fate of the $(CH_3)_2C(NH_2)\dot{C}HOH$ radical	40
3.2.2 Fate of the $(CH_3)(CH_2OH)C(NH_2)\dot{C}H_2$ radical	
3.2.3 Fate of the $(CH_3)_2(CH_2OH)CNH$ radical	
3.3 $CH_3N(CH_2CH_2OH)_2$ (MDEA)	
3.3.1 Fate of the $CH_3N(CH_2CH_2OH)CH_2\dot{C}HOH$ radical	
3.3.1.1 Fate of the $\dot{C}H_2N(CH_2CH_2OH)CH_2OH$ radical	50
3.3.1.2 Fate of the HOCH <sub>2</sub> $\dot{C}$ HN(CH <sub>3</sub> )CH <sub>2</sub> OH radical	53
3.3.1.3 Fate of the $(CH_3)N(CH_2\dot{C}HOH)CH_2OH$ radical	
3.3.2 Fate of the $CH_3N(CH_2CH_2OH)CHCH_2OH$ radical	
3.3.2.1 Fate of the $CH_3N(CH_2CH_2OH)CHOHCH_2O$ radical	60
3.3.2.2 Fate of the $\dot{C}H_2N(CH_2CH_2OH)CHOHCH_2OH$ radical	60
3.3.2.3 Fate of the HOCH <sub>2</sub> CHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH radical	
3.3.2.4 Fate of the $CH_3N(CH_2CHOH)CHOHCH_2OH$ radical	
3.3.3 Fate of the $CH_2N(CH_2CH_2OH)_2$ radical	69
3.3.3.1 Fate of the HOCH <sub>2</sub> N( $CH_2CH_2OH$ )CHCH <sub>2</sub> OH radical	69
3.3.3.2 Fate of the HOCH <sub>2</sub> N( $CH_2CH_2OH$ ) $CH_2CHOH$ radical	
3.4 $HN(CH_2CH_2)_2NH$ (PIPA)	
3.4.1 Fate of the <u>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>N</u> radical	
3.4.2 Fate of the $\overline{\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CHNH}}$ radical	
4 Summary	
5 Conclusions	
Appendix A Bond Enthalpies and CAS Registry Numbers, Formulas, Stru	ictures
and Names	
Literature	

# 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.<sup>1</sup> For the majority of gas-phase organic chemicals present in the troposphere, reaction with the OH radical is the dominant loss process.<sup>2</sup>

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<sub>2</sub>), 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<sub>2</sub>), peroxy nitrates (RC(=O)OONO<sub>2</sub>), 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).<sup>3</sup> 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.

Compound	Acronym	$k_{OH}$ /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	T /K	Ref.
		$1.02 \times 10^{-11} \times \exp\{(230 \pm 150)/T\}$		4
CH <sub>3</sub> NH <sub>2</sub>	MA	$(2.20 \pm 0.22) \times 10^{-11}$	298	4
5 2		$(1.73 \pm 0.11) \times 10^{-11}$	295	5
	DMA	$2.89 \times 10^{-11} \times \exp\{(245 \pm 150)/T\}$		6
$(CH_3)_2NH$	DMA	$(6.54 \pm 0.66) \times 10^{-11}$	298	6
		$(6.49 \pm 0.64) \times 10^{-11}$	295	5
(CH) N		$2.62 \times 10^{-11} \times \exp\{(250 \pm 150)/T\}$		6
(CH3)3IN	IMA	$(6.09 \pm 0.61) \times 10^{-11}$	298	6
		$(3.58 \pm 0.22) \times 10^{-11}$	295	5
CH.CH.NH.	ЕЛ	$1.47 \times 10^{-11} \times \exp\{(190 \pm 150)/T\}$		6
	LA	$(2.77\pm0.28) imes10^{-11}$	298	6
		$(2.38+0.5/-0.15) \times 10^{-11}$	295	5
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NOH	DEHA	$1.0 \times 10^{-10}$	308	7
(CH.)-NCH.CH.OH	DMAE	$(4.7 \pm 1.2) \times 10^{-11}$	300	8
(CI13)21\CI12CI12CI12OI1	DWIAL	$(9.0 \pm 2.0) \times 10^{-11} \times \exp(0/T)$		9
(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )CH <sub>2</sub> OH	AMP	$(2.8 \pm 0.5)  imes 10^{-11}$	300	8
(CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub>	TBA	$1.2 \times 10^{-11}$	298	10
CF <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	TFEA	$0.9 \times 10^{-12}$	298	10
N(CH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	DABCO	$2.2 \times 10^{-11}$	298	10

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

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  $\sim 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and with negative temperature dependencies equivalent to Arrhenius activation energies in the range of 1.5 to 2.0 kJ mol<sup>-1</sup>.

#### 1.1.1 CH<sub>3</sub>NH<sub>2</sub> + OH

Atkinson *et al.*<sup>4</sup> studied the kinetics of the OH radical reaction with CH<sub>3</sub>NH<sub>2</sub> (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<sub>2</sub>O while the MA concentration was determined indirectly from flow measurements. They reported a negative Arrhenius activation energy. Carl and Crowley<sup>5</sup> employed the flash photolysis method to generate OH radicals via two-photon absorption by NO<sub>2</sub> in the presence of H<sub>2</sub>. The room temperature result of Carl and Crowley<sup>5</sup> is ca. 30% below that of Atkinson *et al.*<sup>4</sup> depends on a calibrated gas whereas Carl and Crowley<sup>5</sup> 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 $(CH_3)_2NH + OH$

Atkinson et al.<sup>6</sup> studied the kinetics of the OH radical reaction with  $(CH_3)_2NH$  (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<sub>2</sub>O while the DMA concentration was determined

indirectly from flow measurements. A negative Arrhenius activation energy was observed. Carl and Crowley<sup>5</sup> employed the flash photolysis method to generate OH radicals via two-photon absorption by  $NO_2$  in the presence of  $H_2$ . The two room temperature determinations are in perfect agreement.

## 1.1.3 $(CH_3)_3N + OH$

Atkinson et al.<sup>6</sup> studied the kinetics of the OH radical reaction with  $(CH_3)_3N$  (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  $H_2O$  while the TMA concentration was determined indirectly from flow measurements. A negative Arrhenius activation energy was observed. Carl and Crowley<sup>5</sup> employed the flash photolysis method to generate OH radicals via two-photon absorption by NO<sub>2</sub> in the presence of  $H_2$ . The two room temperature determinations differ by a factor of 2. The absolute value of Atkinson *et al.*<sup>4</sup> depends on a calibrated gas whereas Carl and Crowley<sup>5</sup> 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 CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> + OH

Atkinson *et al.*<sup>4</sup> determined the rate constant for the reaction of OH radicals with  $CH_3CH_2NH_2$  (EA) over the temperature range 299-426 K by the flash photolysisresonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H<sub>2</sub>O. A negative Arrhenius activation energy was observed. Carl and Crowley<sup>5</sup> also employed the flash photolysis method to generate OH radicals. They used two-photon absorption by NO<sub>2</sub> in the presence of H<sub>2</sub> to generate the OH radicals. The two room temperature determinations agree within 10%.

# 1.1.5 $(CH_3CH_2)_2NOH + OH$

Gorse *et al.*<sup>7</sup> generated OH radicals by pulse radiolysis of  $H_2O$  and determined the rate constant for the reaction of OH radicals with  $(CH_3CH_2)_2NOH$  (DEHA) by following the OH pseudo first order decay by optical absorption spectrometry.

#### 1.1.6 $(CH_3)_2NCH_2CH_2OH + OH$

Harris and Pitts<sup>8</sup> determined the rate constant for the reaction of OH radicals with  $(CH_3)_2NCH_2CH_2OH$  (DMAE) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of H<sub>2</sub>O. Anderson and Stephens<sup>9</sup> 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 $(CH_3)_2C(NH_2)CH_2OH + OH$

Harris and Pitts<sup>8</sup> determined the rate constant for the reaction of OH radicals with  $(CH_3)_2C(NH_2)CH_2OH$  (AMP) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by the pulsed vacuum ultraviolet photolysis of  $H_2O$ .

#### 1.1.8 (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub> + OH

Koch et al.<sup>10</sup> determined the rate constant for the reaction of OH radicals with  $(CH_3)_3CNH_2$  (TBA) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N<sub>2</sub>O (ArF excimer laser at 193 nm) followed by  $O(^1D)+H_2O \rightarrow 2$  OH. The OH pseudo first order decay was followed by resonance fluorescence.

#### 1.1.9 CF<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> + OH

Koch et al.<sup>10</sup> determined the rate constant for the reaction of OH radicals with CF<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> (TFEA) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N<sub>2</sub>O (ArF excimer laser at 193 nm) followed by O(<sup>1</sup>D)+H<sub>2</sub>O  $\rightarrow$  2 OH. The OH pseudo first order decay was followed by resonance fluorescence.

#### 1.1.10 N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N + OH

Koch et al.<sup>10</sup> determined the rate constant for the reaction of OH radicals with  $N(CH_2CH_2)_3N$  (DABCO) at 300 K by the flash photolysis-resonance fluorescence technique. OH radicals were produced by photolysis of N<sub>2</sub>O (ArF excimer laser at 193 nm) followed by  $O(^1D)+H_2O \rightarrow 2$  OH. The OH pseudo first order decay was followed by resonance fluorescence.

#### **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 (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, (CH<sub>3</sub>(CH<sub>3</sub>)(CH<sub>3</sub>CH<sub>2</sub>)NH, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub>, and O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH.<sup>11</sup> Schade and Crutzen have presented even more detailed atmospheric degradation mechanisms for CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH and (CH<sub>3</sub>)<sub>3</sub>N in a study of the emission of aliphatic amines from animal husbandry and their reactions.<sup>12</sup> 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 (CH<sub>3</sub>)<sub>2</sub>NH + OH

Pitts *et al.*<sup>13</sup> carried out an exploratory study of the products formed when a mixture of 500 ppb  $(CH_3)_2NH + 80$  ppb NO + 160 ppb NO<sub>2</sub> was subjected to natural sunlight conditions. They found  $(CH_3)_2NNO_2$  (dimethyl nitramine) and CHON(H)CH<sub>3</sub> (N-methyl formamide) as gas phase products, but did not quantify the amounts formed. No  $(CH_3)_2NNO$  (dimethyl nitrosmine) 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:

$$(CH_3)_2NH + OH \rightarrow (CH_3)_2N + H_2O$$
 (1a)

$$\rightarrow (CH_3)N(H)CH_2 + H_2O$$
(1b)

$$(CH_3)_2N + NO_2 \rightarrow (CH_3)_2NNO_2$$
 (2)

$$(CH_3)N(H)CH_2 + O_2 \rightarrow (CH_3)N(H)CH_2O_2$$
(3)

$$(CH_3)N(H)CH_2O_2 + NO \rightarrow (CH_3)N(H)CH_2O + NO_2$$
(4)

$$(CH_3)N(H)CH_2O + O_2 \rightarrow (CH_3)N(H)CHO + HO_2$$
(5)

Lindley and Calvert reported the important branching ratio of the initial OH reaction with  $(CH_3)_2NH$  to be  $k_{(1a)} / (k_{(1a)} + k_{(1b)}) = 0.37 \pm 0.05$ .<sup>14</sup> An evaluation of the atmospheric *N*-nitrosamine formation in the degradation of dimethylamine has been presented by Glasson<sup>15</sup> and by Hanst *et al*.<sup>16</sup>

#### 1.2.2 (CH<sub>3</sub>)<sub>3</sub>N + OH

Pitts *et al.*<sup>13</sup> carried out an exploratory study of the products formed when a mixture of 500 ppb (CH<sub>3</sub>)<sub>3</sub>N + 80 ppb NO + 160 ppb NO<sub>2</sub> was subjected to natural sunlight conditions. They found (CH<sub>3</sub>)<sub>2</sub>NNO<sub>2</sub> (dimethylnitramine) and CHO-N(CH<sub>3</sub>)<sub>2</sub> (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 (CH<sub>3</sub>)<sub>2</sub>NNO (dimethylnitrosmine) was found. The aerosol formed contained ca. 3  $\mu$ g m<sup>-3</sup> (1.6 ppb) CHO-NH<sub>2</sub> (formamide) and another amide-like compound with M=87 was detected but not quantified. Schade and Crutzen<sup>12</sup> suggested that this mass could correspond to CHO-N(CH<sub>3</sub>)-CHO (N-formyl-N-methyl-formamide). The product formation is in accordance with the following mechanism:

$$(CH_3)_3N + OH \rightarrow (CH_3)_2N\dot{C}H_2 + H_2O$$
(6)

$$(CH_3)_2 N\dot{C}H_2 + O_2 \rightarrow (CH_3)_2 NCH_2 OO$$
(7)

$$(CH_3)_2NCH_2OO + NO \rightarrow (CH_3)_2NCH_2O + NO_2$$
 (8)

$$(CH_3)_2NCH_2O + O_2 \rightarrow (CH_3)_2N-CHO + HO_2$$
(9)

$$(CH_3)_2NCH_2O \rightarrow (CH_3)_2N + HCHO$$
 (10)

$$(CH_3)_2 N + NO_2 \rightarrow (CH_3)_2 N - NO_2$$
(11)

The reactivity of N,N-dimethylformamide formed in (9) is unknown, but assuming OH attack on one of the CH<sub>3</sub>-groups will lead to the suggested amide:

$$(CH_3)_2NCHO + OH \rightarrow (CH_3)N(CHO)\dot{C}H_2 + H_2O$$
 (12)

$$(CH_3)N(CHO)\dot{C}H_2 + O_2 \rightarrow (CH_3)N(CHO)CH_2OO$$
 (13)

$$(CH_3)N(CHO)CH_2OO+NO \rightarrow (CH_3)N(CHO)CH_2O+NO_2$$
 (14)

$$(CH_3)N(CHO)CH_2O + O_2 \rightarrow (CH_3)N(CHO)CHO + HO_2$$
(15)

#### 1.2.3 $(CH_3CH_2)_2NH + OH$

Pitts *et al.*<sup>13</sup> carried out a study of the products formed when a mixture of 500 ppb  $(CH_3CH_2)_2NH + 80$  ppb NO + 160 ppb NO<sub>2</sub> was subjected to natural sunlight conditions. They found the following molar conversion yields (taking into account the number of ethyl groups): 30% CH<sub>3</sub>CHO (acetaldehyde), 4% CH<sub>3</sub>CO(OO)NO<sub>2</sub> (PAN), 32% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NNO<sub>2</sub> (diethylnitramine), 1.4% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCHO (N,N-diethylformamide), 0.2% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NC(O)CH<sub>3</sub> (N,N-

diethylacetamide), and 2.4%  $CH_3CH_2NC(O)CH_3$  (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:

$(CH_3CH_2)_2NH + OH$	$\rightarrow$	$(CH_3CH_2)_2\dot{N} + H_2O$	(16a)
	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> NHĊHCH <sub>3</sub> + H <sub>2</sub> O	(16b)
$(CH_3CH_2)_2\dot{N} + NO$	$\rightarrow$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	(17)
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	$\xrightarrow{hv}$	$(CH_3CH_2)_2\dot{N} + NO$	(18)
$(CH_3CH_2)_2N + NO_2$	$\rightarrow$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>	(19a)
	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> N=CHCH <sub>3</sub> + HONO	(19b)
$(CH_3CH_2)_2N + O_2$	$\rightarrow$	$CH_3CH_2N=CHCH_3 + HO_2$	(20)
CH <sub>3</sub> CH <sub>2</sub> NHĊHCH <sub>3</sub> +O <sub>2</sub>	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> NHCH(OO)CH <sub>3</sub>	(21)
CH <sub>3</sub> CH <sub>2</sub> NHCH(OO)CH <sub>3</sub> + NO	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> NHCH(O)CH <sub>3</sub> + NO <sub>2</sub>	(22)
CH <sub>3</sub> CH <sub>2</sub> NHCH(O)CH <sub>3</sub> +O <sub>2</sub>	$\rightarrow$	$CH_3CH_2NHC(O)CH_3 + HO_2$	(23)
CH <sub>3</sub> CH <sub>2</sub> NHCH(O)CH <sub>3</sub>	$\xrightarrow{\Delta}$	$CH_3CH_2NHCHO + CH_3$	(24)
CH <sub>3</sub> CH <sub>2</sub> NHCH(O)CH <sub>3</sub>	$\xrightarrow{\Delta}$	CH <sub>3</sub> CH <sub>2</sub> NH + CH <sub>3</sub> CHO	(25)
CH <sub>3</sub> CH <sub>2</sub> N=CHCH <sub>3</sub> +O <sub>3</sub>	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub> + CH <sub>3</sub> CHO	(26)
$CH_3CHO + OH$	$\rightarrow$	$CH_3CO + H_2O$	(27)
$CH_3CO + O_2$	$\rightarrow$	CH <sub>3</sub> C(O)OO	(28)
$CH_3C(O)OO + NO_2$	$\leftrightarrow$	CH <sub>3</sub> C(O)OONO <sub>2</sub>	(29)
$CH_3C(O)OO + NO$	$\rightarrow$	$CH_3C(O)O + NO_2$	(30)
CH <sub>3</sub> C(O)O	$\xrightarrow{\Delta}$	$CH_3 + CO_2$	(31)

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 $(CH_3CH_3)_3N + OH$

Pitts *et al.*<sup>13</sup> carried out a study of the products formed when a mixture of 500 ppb  $(CH_3CH_2)_2NH + 80$  ppb NO + 160 ppb NO<sub>2</sub> was subjected to natural sunlight conditions. They found the following molar conversion yields (taking into account the number of ethyl groups): 47% CH<sub>3</sub>CHO (acetaldehyde), 5% CH<sub>3</sub>CO(OO)NO<sub>2</sub> (PAN), 1.8% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NNO (diethylnitrosamine), 7.4% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NNO<sub>2</sub> (diethylnitramine), 8.6% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCHO (diethylformamide), 0.6% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NC(O)CH<sub>3</sub> (diethylacetamide), 2.6% CH<sub>3</sub>CH<sub>2</sub>NC(O)CH<sub>3</sub> (ethylacetamide), 2.4% "unknown amide-like compound with M=87", and trace amounts of (CH<sub>3</sub>CO)<sub>2</sub>NH (diacetamide) in the gas phase. The aerosol formed contained ca. 8.7  $\mu$ g m<sup>-3</sup> CH<sub>3</sub>CONH<sub>2</sub> (acetamide) and 7.6  $\mu$ g m<sup>-3</sup> (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>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:

$(CH_3CH_2)_3N + OH$	$\rightarrow$	$(CH_3CH_2)_2NCHCH_3 + H_2O$	(32)
$(CH_3CH_2)_2NCHCH_3 + O_2$	$\rightarrow$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NCH(O <sub>2</sub> )CH <sub>3</sub>	(33)
$(CH_3CH_2)_2NCH(O_2)CH_3 + NO$	$\rightarrow$	$(CH_3CH_2)_2NCH(O)CH_3 + NO_2$	(34)
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NCH(O)CH <sub>3</sub>	$\xrightarrow{\Delta}$	$(CH_3CH_2)_2N + CH_3CHO$	(35a)
	$\xrightarrow{\Delta}$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NCHO + CH <sub>3</sub>	(35b)
$(CH_3CH_2)_2NCH(O)CH_3 + O_2$	$\rightarrow$	$(CH_3CH_2)_2NC(O)CH_3 + HO_2$	(36)
$(CH_3CH_2)_2N + NO_2$	$\rightarrow$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>	(37)
$(CH_3CH_2)_2N + NO$	$\rightarrow$	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	(38)
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	$\xrightarrow{h\nu}$	$(CH_3CH_2)_2N + NO$	(39)
$(CH_3CH_2)_2N + O_2$	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> N=CHCH <sub>3</sub> + HO <sub>2</sub>	(40)
CH <sub>3</sub> CH <sub>2</sub> N=CHCH <sub>3</sub> +O <sub>3</sub>	$\rightarrow$	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub> + CH <sub>3</sub> CHO	(41)
$CH_3CHO + OH$	$\rightarrow$	$CH_3CO + H_2O$	(42)
$CH_3CO + O_2$	$\rightarrow$	CH <sub>3</sub> C(O)OO	(43)
$CH_3C(O)OO + NO_2$	$\leftrightarrow$	CH <sub>3</sub> C(O)OONO <sub>2</sub>	(44)

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,<sup>17</sup> Lindley and Calvert,<sup>14</sup> and by Tuazon *et al.*<sup>18</sup> Stefan and Bolton reported the photolysis of NDMA in aqueous solutions at pH=3 and 7,<sup>19</sup> and found CH<sub>3</sub>NH<sub>2</sub>, HCHO, HCOOH, N<sub>2</sub>O, (CH<sub>3</sub>)<sub>2</sub>NH and CH<sub>2</sub>=NCH<sub>3</sub> as products. Tuazon *et al.*<sup>18</sup> determined the photolysis rate of NDMA relative to that of NO<sub>2</sub> to be  $j_{\text{NDMA}} / j_{\text{NO2}} = 0.53 \pm 0.03$ . 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.<sup>20</sup>

Lindley and Calvert studied the gas phase reactions of the  $(CH_3)_2N$  radical with O<sub>2</sub>, NO and NO<sub>2</sub> using FT-IR detection.<sup>14</sup> The products formed in the  $(CH_3)_2N$  radical reactions in an atmosphere containing NO and NO<sub>2</sub> were consistent with the following steps:

$$(CH_3)_2N-NO \xrightarrow{h\nu} (CH_3)_2N+NO$$
 (45)

$$(CH_3)_2N + O_2 \rightarrow CH_2 = N - CH_3 + HO_2$$
 (46)

$$(CH_3)_2N + NO \rightarrow (CH_3)_2N-NO$$
 (47)

$$(CH_3)_2N + NO_2 \rightarrow (CH_3)_2N - NO_2$$
 (48a)

$$\rightarrow$$
 CH<sub>2</sub>=N-CH<sub>3</sub> + HONO (48b)

Lindley and Calvert<sup>14</sup> 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  $k_{(48a)} / k_{(48a)} = 0.22 \pm 0.07$ . Tuazon *et al.*<sup>18</sup> did not observe CH<sub>2</sub>=NCH<sub>3</sub> in their photolysis studies where O<sub>3</sub> was present. Instead they found 33% CH<sub>3</sub>NO<sub>2</sub>, 38% HCHO and 2% CO in addition to 65% (CH<sub>3</sub>)<sub>2</sub>NNO<sub>2</sub> 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:

$$CH_2=N-CH_3+O_3 \rightarrow$$
 "Primary ozonide" (49)

"Primary ozonide" 
$$\rightarrow$$
 CH<sub>3</sub>NO<sub>2</sub> + HCHO (50)

In a later publication Tuazon and co-workers studied the reactions of amines with O<sub>3</sub> and showed that CH<sub>3</sub>N=CH<sub>2</sub> is essentially non-reactive towards O<sub>3</sub>.<sup>21</sup> Since the experiment, in which CH<sub>3</sub>N=CH<sub>2</sub> was found to react quickly, was such that NO<sub>3</sub> may be formed (NO, NO<sub>2</sub> and O<sub>3</sub> present) is the possible that the observed products may stem for the imine+NO<sub>3</sub> reaction. Lazarou *et al.*<sup>22</sup> studied the reactions of the (CH<sub>3</sub>)<sub>2</sub>N radical with NO and NO<sub>2</sub> 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<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. They also reported a third oxidation pathway in the (CH<sub>3</sub>)<sub>2</sub>N + NO<sub>2</sub> reaction:

$$(CH_3)_2N + NO_2 \rightarrow (CH_3)_2NO + NO$$
 (48c)

with a rate constant  $k_{(48c)} = (6.36 \pm 0.74) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . 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 CH<sub>3</sub>NH<sub>2</sub> + CI 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 spectrocopy with TOF MS detection.<sup>23</sup> 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 branced alkanals can be explained by a mechanism involving a primary dissociation step, which leads to the formation of free radicals (Norrish Type I):

$$RCHO \rightarrow R + CHO$$
(51)

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

$CH_3CH_2CH_2CH_2CHO \rightarrow$	$n-C_4H_9 + CHO$	(Norrish Type I)	(52)
$\rightarrow$	$n-C_4H_{10} + CO$		(53)
$\rightarrow$	$C_3H_6 + [CH_2=CHOH]$	(Norrish Type II)	(54)
$\rightarrow$	$CH_3 + C_3H_6CHO$		(55)

$$\rightarrow C_2H_5 + C_2H_4CHO \tag{56}$$

It was reported that for *n*-butanal the Norrish Type I reaction accounted for 78% while the Norrisch 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  $CH_2=NH$  in the region 235 to 260 nm showing a broad and structureless absorption with maximum near 250 nm.<sup>25</sup> 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 HCN + H<sub>2</sub>.<sup>25,26</sup>

The gas phase UV absorption cross-sections have been determined for a small series of amines: *NN*-dimethyl formamide, *N*,*N*-dimethyl acetamide, *N*,*N*-dimethyl propionamide and 1-methyl-2-pyrrolidone.<sup>27</sup> 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 CHONH<sub>2</sub> + OH

To the best of our knowledge there are no reports on the gas phase chemistry of CHONH<sub>2</sub> (formamide). Muñoz *et al.*<sup>28</sup> studied the CHONH<sub>2</sub> + OH reaction in an O<sub>2</sub> saturated aqueous solutions at pH = 4 and 11.3. They reported a value for the rate constant in the aqueous phase,  $k_{(57a)} + k_{(57b)} = 3.7 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> = 6.2 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. 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 ( $\tau_{OH}$ ) 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:

 $CHONH_2 + OH \quad \rightarrow \quad \dot{C}ONH_2 + H_2O \tag{57a}$ 

$$\rightarrow \quad \text{CHOŃH} + \text{H}_2\text{O} \tag{57b}$$

$$\dot{C}ONH_2 + O_2 \rightarrow \dot{O}O-CONH_2$$
 (58)

$$\text{ÓO-CONH}_2 \rightarrow \text{HO}_2 + \text{HOCN}$$
(59)

Muñoz *et al.*<sup>28</sup> reported that the main radical being formed is  $\text{CONH}_2$  (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 subtituted amides will have average global atmospheric lifetimes of less than 1 day.

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

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

#### 1.3.6 (CH<sub>3</sub>)<sub>2</sub>NNO + OH

Tuazon *et al.*<sup>18</sup> studied the atmospheric reactions of  $(CH_3)_2NNO$  (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 (CH<sub>3</sub>)<sub>2</sub>NNO<sub>2</sub> + OH

Tuazon *et al.*<sup>18</sup> studied the atmospheric reactions of  $(CH_3)_2NNO_2$  (DMN) initiated by reaction with OH radicals and found a reaction rate constant of  $k_{OH+NDMA} =$  $(4.5 \pm 0.5) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. The estimated atmospheric lifetime of DMN is around 3 days.

#### 1.3.8 Aerosol formation

Pitts *et al.*<sup>13</sup> studied the products formed when mixtures of 500 ppb  $(CH_3)_2NH$ ,  $(CH_3)_3N$ ,  $(CH_3CH_2)_2NH$ , or  $(CH_3CH_2)_3N + 80$  ppb NO + 160 ppb NO<sub>2</sub> 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.*<sup>31</sup> have studied the secondary aerosol formation from atmospheric reactions of aliphatic amines. They studied the OH initiated oxidation of  $CH_3NH_2$ ,  $(CH_3)_3N$ ,  $(CH_3CH_2)NH$ ,  $(CH_3CH_2)_3N$  and  $H_2NCH_2CH_2OH$  (MEA) in the presence of "seed" aerosol consisting of  $(NH_4)_2SO_4$  or  $NH_4NO_3$  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 radial interaction with –  $NH_2$ , >NH, and >N- groups.<sup>32</sup> In this SAR the total OH radical reaction rate constant is given by:

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

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

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

where  $k_{prim}$ ,  $k_{sec}$ , and  $k_{tert}$  are the rate constants per –CH<sub>3</sub>, -CH<sub>2</sub>-, and >CH- group for a "standard" substituent, X, Y, Z are the substituent groups; and F(X), F(Y), and F(Z) are the corresponding substituent factors. The standard substituent group is chosen to be  $X = Y = Z = -CH_3$ ,  $F(-CH_3) = 1.00$  by definition.<sup>33</sup> It was assumed that the majority of the initial OH radical reaction proceeds via OH radical addition to the N-atom,<sup>33</sup> followed by a number of decomposition reactions of the adduct leading to products. The following parameters for the amino-, nitrosamineand nitramine-groups were suggested:

Substituent Group X	F(X)
-NH <sub>2</sub> , -NH-, -N<, -NNO, -NNO <sub>2</sub>	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.*<sup>10</sup> studied 3 simple, commercially available amines (TBA, TFEA and DABCO) with different specialties to test the predictions of the Atkinson SAR<sup>32</sup> 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.<sup>34</sup> 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<sup>32,33,35</sup> 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  $-NNO_2$  groups actually enhance the reactivity of the neighboring C-H bonds by a factor of ~10 compared to an alkyl group:

Rate constant	$k_{OH}/10^{-12} cm^3 molecule^{-1} s^{-1}$	$ au_{OH}$
$k_{(OH + OxNN-CH3)}$	$1.3 \times 10^{-12}$	9 days
$k_{(OH + OxNN-CH2-)}$	$8.9 \times 10^{-12}$	1 day
$k_{(OH + OxNN-CH<)}$	$1.8  imes 10^{-11}$	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  $O_xNN-CH_2$ - 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	$k_{OH}/10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	$ au_{OH}$
$k_{(OH + >NC(=O)-CH3)}$	$1.0 \times 10^{-13}$	> 100 days
$k_{(OH + >NC(=O)CH2-)}$	$7.0  imes 10^{-13}$	17 days
$k_{(OH +>NC(=O)-CH<)}$	$1.5 \times 10^{-12}$	8 days

The predictions compare well with the experimental aqueous phase OH rate constant for formamide (HCONH<sub>2</sub>) of  $6.2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1.28</sup>

For the N-substituted amides the situations 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.

Rate constant	$k_{OH} / 10^{-12} cm^3 molecule^{-1} s^{-1}$	$ au_{OH}$
$k_{(OH + R-CH2OH)}$	$3.4 \times 10^{-12}$	3 days
$k_{(OH + RR'CHOH)}$	$8.9 \times 10^{-12}$	1.5 day
$k_{(OH + RR'R''COH)}$	$1.7 \times 10^{-13}$	>50 days

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

The OH-initiated oxidation reactions of intermediate products containing - CH<sub>2</sub>OH and >CHOH groups should therefore be included in the amine degradation schemes.

Carter and Atkinson<sup>36</sup> 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:  $^{36}$ 

$$E_{\rm a} = 50.2 + 0.70 \times \Delta_{\rm r} H/\rm{kJ} \ \rm{mol}^{-1}$$

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 Atkinson<sup>36</sup> also includes tables of estimated rate constants for 1,4- and 1,5- hydrogen shift reactions (RC-H•••OR' $\rightarrow$  RC•••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-Idaboy<sup>37</sup> presented their results for CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH and CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> 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 cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>):

$k_{\rm CH_3NH_2+OH}(\rm T) = 5.89 \times 10^{-11} e^{-757/\rm RT}$	$k_{\rm CH_3NH_2+OH}(298) = 5.2 \times 10^{-12}$
$k_{(CH_3)_2NH+OH}(T) = 2.72 \times 10^{-11} e^{200/RT}$	$k_{(CH_3)_2NH+OH}(298) = 5.2 \times 10^{-11}$
$k_{\text{CH}_3\text{CH}_2\text{NH}_2+\text{OH}}(\text{T}) = 1.39 \times 10^{-11} \text{ e}^{-49/\text{RT}}$	$k_{\rm CH_3CH_2NH_2+OH}(298) = 1.2 \times 10^{-11}$

which compares within a factor of 2 with the experimental values. However, the temperature dependence differs in sign for  $CH_3NH_2$  and  $CH_3CH_2NH_2$ . 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 Habstraction reactions. For  $CH_3NH_2$  they predict a branching ratio of C:N centered H-abstraction of 80:20; for  $(CH_3)_2NH$  their predicted branching ratio of C:N centered H-abstraction is 48:52; and for  $CH_3CH_2NH_2$  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  $(1-7) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. With an average global OH radical concentration of  $10^6$  molecules cm<sup>-3</sup> (5 × 10<sup>5</sup> molecules cm<sup>-3</sup> at 60° N) their lifetimes are the then  $\tau_{OH} = 4 - 28$  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<sub>3</sub>NH<sub>2</sub>, and probably also C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, H atom abstraction from the C-H bonds predominates, while for (CH<sub>3</sub>)<sub>2</sub>NH, H atom abstraction from the N-H bond is competitive with H atom abstraction from the C-H bonds.<sup>33</sup>

The experimental branching ratio of hydrogen abstraction by OH radicals from the CH<sub>3</sub> and NH groups in (CH<sub>3</sub>)<sub>2</sub>NH is 63:37,<sup>14</sup> which compares to 48:52 from a theoretical calculation.<sup>37</sup> 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.<sup>37</sup>

There are no experimental kinetic data for the reactions of aliphatic amines with other important atmospheric oxidants such as Cl atoms and NO<sub>3</sub> radicals. Although the OH radical is the most important oxidant Cl atoms and NO<sub>3</sub> radicals may account for as much as 10% of the atmospheric degradation in costal 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  $\tau_{UV} \sim$  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<sub>2</sub> but so fast with NO and NO<sub>2</sub> that their atmospheric fate under normal conditions is governed by reactions with the latter two.

The well established SAR by Atkinson and coworkers<sup>32,33,35</sup> 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 elucidation2.1 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<sup>-1</sup>) and good accuracy (mean absolute error is 3.6 kJ mol<sup>-1</sup>), with little penalty in computational speed.<sup>38</sup> We employed MP2<sup>39</sup> and CCSD(T)<sup>40</sup> 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.<sup>41</sup> 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)<sup>42,43</sup> 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.<sup>44,45</sup> 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<sup>-1</sup> (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:

$$R - X \longrightarrow R + X \tag{60}$$

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,<sup>46-48</sup> 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<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N + OH

The recent theoretical results by Galano and Alvarez-Idaboy<sup>37</sup> for the OH reactions with CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH and CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> 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. DFTcalculations 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<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>NH, and (CH<sub>3</sub>)<sub>3</sub>N 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<sup>-1</sup> below the reactant energy. Including the zero point energies the saddle points are found at 7.5 and 6.0 kJ mol<sup>-1</sup> 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  $CH_3NH_2 + OH$  reaction calculated at the 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-N=CR'R" + O<sub>3</sub>

Lindley and Calvert studied the gas phase reactions of the  $(CH_3)_2N$  radical with  $O_2$ , NO and  $NO_2$  and found  $CH_2=NCH_3$  among the products.<sup>14</sup> 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.*<sup>18</sup> did not observe the expected  $CH_2=NCH_3$  in their photolysis studies of  $(CH_3)_2NH$  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 methaneimine and N-methylene-methanamine are calculated to be exothermic by  $\Delta_r H = 140$  and 155 kJ mol<sup>-1</sup>, 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<sup>-1</sup> for the methaneimine 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 methaneimine and N-methylene-methanamine ozonides both dissociate as follows:

$$\Delta_{t}H = -140 \qquad CH_{2}=NH + O_{3} \rightarrow \left[ \begin{array}{c} & & & \\$$

$$\Delta_{r}H = \left[\begin{array}{c} & & & \\ & & & \\ & & & \\ +100 & & \\ &$$

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<sub>3</sub> radicals and NO.<sup>49,50</sup> Virtually nothing is known about the atmospheric fate of HNO; it reacts fast with O<sub>2</sub> with a rate constant  $k_{O2} = 8 \times 10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature,<sup>51</sup> 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<sub>2</sub> or N<sub>2</sub>O.

The fate of the excited Criegee biradical  $[H_2COO]^{\ddagger}$ , is well known and included in the MCM protocol:<sup>3</sup> 50% CO + H<sub>2</sub>O, 36% CH<sub>2</sub>OO, 13% HO<sub>2</sub> + CO + OH. The relaxed CH<sub>2</sub>OO subsequently reacts with H<sub>2</sub>O to for HCOOH and H<sub>2</sub>CO. 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:

57% 
$$[R-\dot{C}HO\dot{O}]^{\ddagger} \rightarrow RO\dot{O} + CO + OH$$
(64a)

$$12.5\% \longrightarrow \text{ROO} + \text{CO}_2 + \text{HO}_2 \tag{64b}$$

$$12.5\% \longrightarrow R-H+CO_2$$
(64c)

$$11\% \longrightarrow \text{R-COOH}$$
(64d)

$$7\% \rightarrow \text{R-CHO}$$
 (64e)

Thus, around 70% of the R-CHOO Criegee biradicals ends as alkyl peroxy radicals, ROÓ (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.<sup>18</sup> It is therefore comforting that the same authors later retract their postulated mechanism.<sup>21</sup> However, it is not obvious why the reaction between  $(CH_3)N=CH_2$  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<sub>2</sub>. 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<sup>-1</sup>.



*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.* 

,0From the experimental studies by Lindley and Calvert<sup>14</sup> and by Tuazon *et al.*<sup>18</sup> it is known that  $O_2$  reaction with N-based radicals is very slow but that reactions with NO and NO<sub>2</sub> are very fast. OH addition 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:

$\Delta_{\rm r}H = -121$	$HN=CH_2+OH$	$\rightarrow$	HŃ-CH <sub>2</sub> OH	(65)
$\Delta_{\rm r} H = -199$	$H\dot{N}$ - $CH_2OH + NO$	$\rightarrow$	ONNH-CH <sub>2</sub> OH	(66)
$\Delta_{\rm r}H$ =+199	ONN-CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$H\dot{N}$ - $CH_2OH + NO$	(67)
$\Delta_{\rm r}H = -221$	$H\dot{N}$ - $CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NNH-CH <sub>2</sub> OH	(68a)
$\Delta_{\rm r}H = -258$		$\rightarrow$	HN=CHOH + HONO	(68b)
$\Delta_{\rm r} H = -138$	$H\dot{N}$ - $CH_2OH + O_2$	$\rightarrow$	$\mathbf{HN=}\mathbf{CHOH}+\mathbf{HO}_{2}$	(69)

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.<sup>18</sup> The C-H bond enthalpies in

ONNHCH<sub>2</sub>OH and O<sub>2</sub>NNHCH<sub>2</sub>OH are very low ( $\Delta_r H = 313$  and 336 kJ mol<sup>-1</sup>, respectively) and hydrogen abstraction from the CH<sub>2</sub>-groups is expected to be fast

$\Delta_{\rm r}H = -185$	<b>ONNH-CH<sub>2</sub>OH</b> + OH	$\rightarrow$	$ONNH-\dot{C}HOH + H_2O$	(70)
$\Delta_{\rm r}H = -16$	$ONNH-\dot{C}HOH + O_2$	$\rightarrow$	<b>ONNH-CHO</b> + $HO_2$	(71)
$\Delta_{\rm r}H$ =+188	ONNH-CHO -	$\xrightarrow{hv}$	HŃCHO + NO	(72)
$\Delta_{\rm r}H = -77$	$\dot{HNCHO} + O_2$	$\rightarrow$	<b>HNCO</b> + $HO_2$	(73)
$\Delta_{\rm r}H = -162$	O <sub>2</sub> NNH-CH <sub>2</sub> OH + OH	$\rightarrow$	$O_2NNH-\dot{C}HOH + H_2O$	(74)
$\Delta_{\rm r}H = -23$	$O_2$ NNH-ĊHOH + $O_2$	$\rightarrow$	$O_2$ NNH-CHO + HO <sub>2</sub>	(75)

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,  $\Delta_r H \sim -121$  kJ mol<sup>-1</sup>, 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 H<sub>2</sub>NCHO (formamide):

$$\Delta_{\rm r} H = -200 \qquad \qquad {\rm H}_2 {\rm N} \cdot {\rm CH}_2 \acute{\rm O} + {\rm O}_2 \qquad \rightarrow \qquad {\rm H}_2 {\rm N} \cdot {\rm CH} {\rm O} + {\rm H} {\rm O}_2 \tag{77}$$

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(H<sub>2</sub>)-OH radical to H<sub>2</sub>N-CH<sub>2</sub>O is shown in Figure 2.3. The calculated barrier to the hydrogen shift is ca. 120 kJ mol<sup>-1</sup> 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<sup>-1</sup>) along the reaction coordinate for the 1,3-hydrogen shift reaction:  $HN-CH_2OH \rightarrow H_2NCH_2O$ . 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.  $\Delta_r H = -48$  HN=CHOH  $\leftarrow \overset{1,3}{\longrightarrow}$  H<sub>2</sub>N-CHO (78)

Figure 2.4 shows the electronic energy along the reaction coordinate. The barrier at the saddle point is  $145 \text{ kJ mol}^{-1}$  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:  $HN=CHOH \rightarrow H_2NCHO$ . Top: Results from B3LYP/aug-cc-pVDZ calculations. Bottom: Results from CAS(10e90)/cc-pVDZ and MRP2/cc-pVDZ calculations

#### 2.3.5 NH<sub>2</sub>CHO (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<sub>2</sub> (formamide) in particular. As a consequence, there is no SAR-data which can be applied to the -C(=O)-N< group. The kinetic study of the OH reaction with CHONH<sub>2</sub> in O<sub>2</sub> saturated aqueous solutions by Muñoz *et al.*<sup>28</sup> reports a value for the rate constant in the aqueous phase,  $k_{(57a)} + k_{(57b)} = 6.2 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and a branching ratio of  $k_{(57a)}/(k_{(57a)} + k_{(57b)}) = 0.90 \pm 0.05$ . Note that a rate constant of  $k_{OH} = 6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> corresponds to a lifetime  $\tau_{OH} \sim 20$  days assuming an average OH concentration of 10<sup>6</sup> radicals cm<sup>-3</sup>. The first steps of the gas phase degradation of formamide are expected to be the same as in the aqueous phase:

$$\Delta_{\rm r} H = -103 \qquad \qquad \text{CHONH}_2 + \text{OH} \quad \rightarrow \quad \dot{\text{CONH}}_2 + \text{H}_2\text{O} \tag{57a}$$

$$\Delta_{\rm r} H = -27 \qquad \rightarrow \quad {\rm CHO} {\rm \acute{N}H} + {\rm H}_2 {\rm O} \tag{57b}$$

The results from bond enthalpy calculations (see Sections 2.3 and 2.4) predict  $\Delta_{bond}H_{C-H} \sim 396$  and  $\Delta_{bond}H_{N-H} \sim 484$  kJ mol<sup>-1</sup> (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:

$$\Delta_{\rm r} H = -148 \qquad \dot{\rm C} ONH_2 + O_2 \quad \rightarrow \quad \dot{\rm O} OCONH_2 \qquad (79a)$$

$$\Delta_{\rm r} H = -77 \qquad \qquad \rightarrow \qquad {\rm HNCO + HO_2} \tag{79b}$$

$$\Delta_{\rm r} H = -108 \qquad \qquad \acute{\rm O}{\rm O}{\rm CONH}_2 + {\rm NO} \quad \rightarrow \quad {\rm NH}_2 + {\rm CO}_2 + {\rm NO}_2 \tag{80}$$

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  $\Delta_{bond}H_{C-H} \sim 397$ and  $\Delta_{bond}H_{N-H} \sim 484$  kJ mol<sup>-1</sup> (Table 5.2, page 86). Again, the only important oxidation reaction in the atmosphere is hydrogen abstraction from the CH<sub>3</sub> group leading to 2-oxo-acetamide:

$$\Delta_{\rm r} H = -85 \qquad \qquad \text{CH}_3 \text{CONH}_2 + \text{OH} \quad \rightarrow \quad \dot{\text{CH}}_2 \text{CONH}_2 + \text{H}_2 \text{O} \tag{81}$$

$$\Delta_{\rm r} H = -122 \qquad \dot{\rm CH}_2 {\rm CONH}_2 + {\rm O}_2 \quad \rightarrow \quad \dot{\rm OOCH}_2 {\rm CONH}_2 \qquad (82)$$

$$\Delta_{\rm r} H = -58 \qquad \qquad \acute{\rm O}{\rm O}{\rm CH}_2 {\rm C}{\rm O}{\rm N}{\rm H}_2 + {\rm N}{\rm O} \rightarrow \qquad \acute{\rm O}{\rm C}{\rm H}_2 {\rm C}{\rm O}{\rm N}{\rm H}_2 + {\rm N}{\rm O}_2 \tag{83}$$

$$\Delta_{\rm r}H = -130 \qquad \qquad \acute{\rm O}{\rm CH}_2{\rm CONH}_2 + {\rm O}_2 \quad \rightarrow \quad {\rm OHCCONH}_2 + {\rm HO}_2 \tag{84}$$

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

$$\Delta_{\rm r}H = +332$$
 OHCCONH<sub>2</sub>  $\xrightarrow{h\nu}$  ĊONH<sub>2</sub> + CHO (85)

$$\Delta_{\rm r} H = -104 \qquad \qquad OHCCONH_2 + OH \quad \rightarrow \quad O\dot{C}CONH_2 + H_2O \tag{86}$$

$$\Delta_{\rm r} H = -142 \qquad \qquad O\dot{\rm C}{\rm CONH}_2 + O_2 \quad \rightarrow \quad \acute{\rm O}{\rm O}{\rm C}({\rm O}){\rm CONH}_2 \tag{87}$$

$$\dot{OOC}(O)CONH_2 + NO_2 \rightarrow O_2NOOC(O)CONH_2$$
 (88)

$$O_2 NOOC(O) CONH_2 \xrightarrow{\Delta} OOC(O) CONH_2 + NO_2$$
 (89)

$$\Delta_{\rm r} H = -203 \qquad \acute{\rm OOC}({\rm O}){\rm CONH}_2 + {\rm NO} \rightarrow \acute{\rm CONH}_2 + {\rm CO}_2 + {\rm NO}_2 \qquad (90)$$

The SAR<sup>32,35</sup> predicts  $k_{OH} \sim 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CH<sub>3</sub>CONH<sub>2</sub> which, assuming an average OH concentration of 10<sup>6</sup> radicals cm<sup>-3</sup>, corresponds to a lifetime  $\tau_{OH} \sim 115$  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 relationship<sup>52</sup> 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:

$$\mathbf{E}_{\mathbf{a}} = \mathbf{a} + \mathbf{b} \times \boldsymbol{\Delta}_{react} \mathbf{H}$$
(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:  $k_{\text{OH}} \sim 0.5 \times \exp(-0.07 \times \Delta_{\text{bond}} \text{H})$ . 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 is it will not be possible to construct a general Structure-Activity Relationship for aliphatic amines as any such method is essentially is based on the same assumptions.



Figure 2.5: Plot of ln k<sub>OH</sub> 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, (25) ammonia, (26) methoxytbenzene, (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.<sup>33,36,53-56</sup> In the following mechanistic descriptions of the atmospheric degradation of the selected amines the following simplifications have been made:

• The atmospheric oxidation process of amimes is initiated by reaction with OH radicals. The annual average OH concentration at 60° N is ca.  $5 \times 10^5$  radicals cm<sup>-3</sup>.<sup>57</sup>

- RO<sub>2</sub> + RO<sub>2</sub> and RO<sub>2</sub> + HO<sub>2</sub> reactions have been neglected in setting up the routes.
- nitrate formation in the RO<sub>2</sub> + NO reactions has been disregarded
- only the radical channel in aldehyde photolysis, R-CHO  $\xrightarrow{h\nu}$  R + 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  $\tau_{OH} = (k_{OH}^*[OH]_{av})^{-1} > 3$  days are considered as "end products" in the degradation schemes

Intermediate products with lifetimes  $\tau_{OH} < 3$  days are highlighted in boldface. Products with lifetimes  $\tau_{OH} > 3$  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<sup>-3</sup> and a static RO<sub>2</sub> concentration of  $10^9$  radicals cm<sup>-3</sup> have been assumed. Reaction rate constants are taken from the Kwok and Atkinson SAR,<sup>35</sup> from Carter and Atkinson,<sup>36</sup> and from the MCM web-site.<sup>58</sup> In the lack of other information it has also been assumed that the initial NO and NO<sub>2</sub> 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  $3.5 \times 10^{-3}$  s<sup>-1</sup> (21% per minute) for 15 minutes. The NO and NO<sub>2</sub> concentrations in the mixing air is assumed to be 40 and 100 ppt, respectively.

# 3.1 $H_2NCH_2CH_2OH$ (MEA)

The systematic name of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH is 2-aminoethanol (CAS: 141-43-5).<sup>#</sup> The results from bond enthalpy calculations ( $\Delta_{bond}H_{O-H} \sim 448$ ,  $\Delta_{bond}H_{C-H} \sim 395$ , and  $\Delta_{bond}H_{N-H} \sim 442$  kJ mol<sup>-1</sup>, Table 5.2, page 86) suggest two major and equally important routes:

<sup>#</sup> 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.
$$\Delta_{\rm r}H = -103 \qquad \qquad \mathbf{H}_2 \mathbf{N} \mathbf{C} \mathbf{H}_2 \mathbf{C} \mathbf{H}_2 \mathbf{O} \mathbf{H} + \mathbf{O} \mathbf{H} \rightarrow \qquad \mathbf{H}_2 \mathbf{N} \mathbf{C} \mathbf{H}_2 \dot{\mathbf{C}} \mathbf{H} \mathbf{O} \mathbf{H} + \mathbf{H}_2 \mathbf{O} \qquad (92a)$$
$$\Delta_{\rm r}H = -105 \qquad \qquad \rightarrow \qquad \mathbf{H}_2 \mathbf{N} \dot{\mathbf{C}} \mathbf{H} \mathbf{C} \mathbf{H}_2 \mathbf{O} \mathbf{H} + \mathbf{H}_2 \mathbf{O} \qquad (92b)$$

$$\rightarrow H_2 N\dot{C} H C H_2 O H + H_2 O \tag{92b}$$

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  $NH_2$  group is considered later in Section 3.1.3.

# 3.1.1 Fate of the H<sub>2</sub>NCH<sub>2</sub>CHOH radical

The subsequent reactions of the R-CHOH radical are assumed to follow the degradation scheme for aliphatic alcohols leading to an aldehyde (H<sub>2</sub>NCH<sub>2</sub>CHO, amino-acetaldehyde) which may either photolyse or react with OH in aldehydic hydrogen abstraction in the same manner as in other aliphatic aldehydes.<sup>34</sup> Bond enthalpy calculations on amino-acetaldehyde predict an extremely low bond enthalpy for the methylene hydrogen,  $\Delta_{bond}H_{C-H2} = 310$  compared to  $\Delta_{bond}H_{C(O)-H}$ = 374, and  $\Delta_{\text{bond}}H_{\text{N-H2}}$  = 424 kJ mol<sup>-1</sup>. This suggests that also hydrogen abstraction from the CH<sub>2</sub> group in H<sub>2</sub>NCH<sub>2</sub>CHO may be an important route in the further degradation (see also bond enthalpies in Table 5.2).

$H_2NCH_2\dot{C}HOH + O_2$	$\rightarrow$	$\mathbf{H_2NCH_2CHO} + \mathbf{HO}_2$	(93)
H <sub>2</sub> NCH <sub>2</sub> CHO	$\xrightarrow{hv}$	$H_2N\dot{C}H_2+CHO$	(94)
$H_2NCH_2CHO + OH$	$\rightarrow$	$H_2NCH_2\dot{C}O+H_2O$	(95a)
	$\rightarrow$	$H_2N\dot{C}HCHO + H_2O$	(95b)
$H_2NCH_2\dot{C}O + O_2$	$\rightarrow$	H2NCH2C(O)OÓ	(96)
$H_2NCH_2C(O)OOO + NO_2$	$\rightarrow$	H <sub>2</sub> NCH <sub>2</sub> C(O)OONO <sub>2</sub>	(97)
H <sub>2</sub> NCH <sub>2</sub> C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$H_2NCH_2C(O)O\acute{O}+NO_2$	(98)
$H_2NCH_2C(O)OOO + NOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	$\rightarrow$	$H_2N\dot{C}H_2+CO_2+NO_2$	(99)
$H_2N\dot{C}H_2 + O_2$	$\rightarrow$	H <sub>2</sub> NCH <sub>2</sub> OÓ	(100a)
	$\rightarrow$	$HN=CH_2 + HO_2$	(100b)
$H_2NCH_2OO + NO$	$\rightarrow$	$H_2NCH_2\acute{O} + NO_2$	(101)
$H_2NCH_2OO + O_2$	$\rightarrow$	$H_2NCHO + HO_2$	(102)
H <sub>2</sub> NCH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	$HCHO + NH_2$	(103)
	$H_2NCH_2\dot{C}HOH + O_2$ $H_2NCH_2CHO$ $H_2NCH_2CHO + OH$ $H_2NCH_2\dot{C}O + O_2$ $H_2NCH_2C(O)O\dot{O} + NO_2$ $H_2NCH_2C(O)OONO_2$ $H_2NCH_2C(O)O\dot{O} + NO$ $H_2N\dot{C}H_2 + O_2$ $H_2NCH_2\dot{O} + NO$ $H_2N\dot{C}H_2 + O_2$ $H_2NCH_2\dot{O} + NO$ $H_2NCH_2\dot{O} + O_2$ $H_2NCH_2\dot{O} + O_2$ $H_2NCH_2\dot{O} + O_2$	$\begin{array}{ccc} H_2NCH_2\dot{C}HOH + O_2 & \rightarrow \\ H_2NCH_2CHO & \stackrel{h\nu}{\longrightarrow} \\ H_2NCH_2CHO + OH & \rightarrow \\ & & \rightarrow \\ H_2NCH_2CHO + OH & \rightarrow \\ H_2NCH_2\dot{C}O)O\dot{O} + NO_2 & \rightarrow \\ H_2NCH_2C(O)OONO_2 & \stackrel{\wedge}{\longrightarrow} \\ H_2NCH_2C(O)OONO_2 & \stackrel{\wedge}{\longrightarrow} \\ H_2NCH_2C(O)O\dot{O} + NO & \rightarrow \\ H_2NCH_2CO\dot{O} + NO & \rightarrow \\ H_2NCH_2\dot{O} & \stackrel{\wedge}{\longrightarrow} \\ H_2NCH_2\dot{O} & \stackrel{\wedge}{\longrightarrow} \\ \end{array}$	$\begin{array}{cccc} H_2NCH_2\dot{C}HOH + O_2 & \rightarrow & H_2NCH_2CHO + HO_2 \\ H_2NCH_2CHO & \stackrel{h\nu}{\longrightarrow} & H_2N\dot{C}H_2 + CHO \\ H_2NCH_2CHO + OH & \rightarrow & H_2NCH_2\dot{C}O + H_2O \\ & \rightarrow & H_2N\dot{C}HCHO + H_2O \\ H_2NCH_2\dot{C}O + O_2 & \rightarrow & H_2NCH_2C(O)OOO \\ H_2NCH_2C(O)OO + NO_2 & \rightarrow & H_2NCH_2C(O)OONO_2 \\ H_2NCH_2C(O)OONO_2 & \stackrel{A}{\longrightarrow} & H_2NCH_2C(O)OOO + NO_2 \\ H_2NCH_2C(O)OOO & \rightarrow & H_2NCH_2O \\ H_2NCH_2CO & \rightarrow & H_2NCH_2O \\ H_2NCH_2O & \rightarrow & H_2NCH_2O \\ \end{array}$

The threshold wavelength for photolysis channel (94) is 368 nm ( $\Delta_r H = +326$  kJ mol<sup>-1</sup>), which is at longer wavelength than the  $n \rightarrow \pi^*$  band of aliphatic aldehydes. The photolysis is thus feasible at tropospheric conditions. Reaction (99) is normally considered to be a two-step process:  $H_2NCH_2C(O)OO + NO \rightarrow$  $H_2N\dot{C}H_2C(O)\dot{O} + NO_2 \xrightarrow{\Lambda} H_2N\dot{C}H_2 + CO_2 + NO_2$ . 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  $CH_2OH + O_2 \rightarrow H_2C=O$  (there is no experimental evidence for such a reaction taking place). Note that the thermal dissociation of the  $H_2$ NCHÓ radical is endothermic.

The sequence of reactions initiated in (95b) by hydrogen abstraction from the  $CH_2$  group in amino-acetaldehyde is:

$$\Delta_{\rm r} H = -49 \qquad \qquad {\rm H}_2 {\rm N} \dot{\rm C} {\rm H} {\rm CHO} + {\rm O}_2 \quad \rightarrow \qquad {\rm H}_2 {\rm N} {\rm CH} ({\rm O} \dot{\rm O}) {\rm CHO} \qquad (104)$$

$$\Delta_{r}H = -57 \qquad H_2 \text{NCH}(OO) \text{CHO} + \text{NO} \rightarrow H_2 \text{NCH}(O) \text{CHO} + \text{NO}_2 \qquad (105)$$

$$\Delta_{\rm r} H = -205 \qquad \qquad {\rm H}_2 {\rm NCH}({\rm \dot{O}}) {\rm CHO} + {\rm O}_2 \quad \rightarrow \quad {\rm H}_2 {\rm NC}({\rm O}) {\rm CHO} + {\rm HO}_2 \qquad (106)$$

Note that the thermal decomposition in (108) is endothermic. The properties of the PAN-like molecule  $H_2NCH_2C(O)OONO_2$  (2-amino-peroxoacetylnitrate) formed in (97) is in many ways likely to resemble those of peroxoacetylnitrate (PAN). However, the bond enthalpy calculations suggest an enhanced reactivity of the CH<sub>2</sub> group ( $\Delta_{bond}H = 326$  kJ mol<sup>-1</sup>) and it may react just as fast with OH as the precursor amine itself:

	$H_2NCH_2C(O)OONO_2 + OH$	$\rightarrow$	$H_2N\dot{C}HC(O)OONO_2 + H_2O$	(109)
	$H_2N\dot{C}HC(O)OONO_2 + O_2$	$\rightarrow$	H <sub>2</sub> NCH(OÓ)C(O)OONO <sub>2</sub>	(110)
	H <sub>2</sub> NCH(OÓ)C(O)OONO <sub>2</sub> +NO	$\rightarrow$	$H_2NCH(\acute{O})C(O)OONO_2 + NO_2$	(111)
	H <sub>2</sub> NCH(Ó)C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$\mathbf{H_2NCHO} + \mathbf{CO} + \mathbf{NO}_2 + \mathbf{O}_2$	(112)
	$H_2NCH(O)C(O)OONO_2 + O_2$	$\rightarrow$	$\mathbf{H}_{2}\mathbf{NC}(\mathbf{O})\mathbf{C}(\mathbf{O})\mathbf{OONO}_{2} + \mathbf{HO}_{2}$	(113)
$\Delta_{\rm r}H$ =+131	$H_2NC(O)C(O)OONO_2$	$\xrightarrow{\Delta}$	$H_2NC(O)C(O)OOO + NO_2$	(114)
$\Delta_{\rm r}H = -203$	$H_2NC(O)C(O)OOO + NO$	$\rightarrow$	$H_2NC\acute{O}+CO_2+NO_2$	(115)
$\Delta_{\rm r}H$ =-148	$H_2NCO + O_2$	$\rightarrow$	H <sub>2</sub> NC(O)OÓ	(116a)
$\Delta_{\rm r} H = -77$		$\rightarrow$	$HNCO + HO_2$	(116b)
	$H_2NC(O)OOO + NO_2$	$\rightarrow$	$H_2NC(O)OONO_2$	(117)
	H <sub>2</sub> NC(0)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$H_2NC(O)OOO + NO_2$	(118)
$\Delta_{\rm r}H$ =-108	$H_2NC(O)OOO + NO$	$\rightarrow$	$H_2N+CO_2+NO_2 \\$	(119)

Although speculative considering the H:C:N:O ratio, the oxo-radical formed in (111) may in principle also undergo hydrogen abstraction by  $O_2$  resulting in H<sub>2</sub>NCOC(O)OONO<sub>2</sub> which is expected to be long-lived in the gas phase.

 $H_2NC(O)CHO$  (2-oxo-acetamide) formed in (106) is expected to undergo photolysis (threshold wavelength  $\lambda = 362$  nm) or react with OH radicals in an aldehydic hydrogen abstraction reaction, and eventually leading to the same products as above.

$\Delta_{\rm r}H = +332$	H <sub>2</sub> NC(O)CHO	$\xrightarrow{h\nu}$	$H_2N\dot{C}O + CHO$	(120	))
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$$\Delta_{\rm r} H = -104 \qquad \qquad \mathbf{H}_2 \mathbf{NC}(\mathbf{O}) \mathbf{C} \mathbf{H} \mathbf{O} + \mathbf{O} \mathbf{H} \quad \rightarrow \qquad \mathbf{H}_2 \mathbf{NC}(\mathbf{O}) \dot{\mathbf{C}} \mathbf{O} + \mathbf{H}_2 \mathbf{O} \tag{121}$$

$$H_2NC(O)C(O)OOO + NO_2 \rightarrow H_2NC(O)C(O)OONO_2$$
(123)

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

The other route (92b), initiated by hydrogen abstraction from MEA in C2position, is expected to proceed as follows

$\Delta_{\rm r}H = -105$	$H_2NCH_2CH_2OH + OH$	$\rightarrow$	$H_2N\dot{C}HCH_2OH + H_2O$	(92b)
$\Delta_{\rm r}H = -149$	$H_2N\dot{C}HCH_2OH + O_2$	$\rightarrow$	H2NCH(OÓ)CH2OH	(124)
$\Delta_{\rm r}H = -48$	$H_2NCH(OO)CH_2OH + NO$	$\rightarrow$	$H_2NCH(O)CH_2OH + NO_2$	(125)

The alkoxy radical formed in (125) may undergo abstraction of the  $\alpha$ -hydrogen by O<sub>2</sub>, bond scission reactions, and, in principle, also an 1,4-hydrogen shift between the two oxygen atoms:



**Scheme 3.1:** Atmospheric degradation of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (MEA) following initial hydrogen abstraction at C1.

$\Delta_{\rm r}H = -210$	$H_2NCH(O)CH_2OH + O_2$	$\rightarrow$	$\mathbf{H}_{2}\mathbf{NC}(\mathbf{O})\mathbf{CH}_{2}\mathbf{OH}+\mathbf{HO}_{2}$	(126)
$\Delta_{\rm r}H = -35$	H <sub>2</sub> NCH(Ó)CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$H_2NCHO + \dot{C}H_2OH$	(127a)
$\Delta_{\rm r}H = +39$		$\xrightarrow{\Delta}$	$\rm NH_2 + CHOCH_2OH$	(127b)
$\Delta_{\rm r}H = -1$	H2NCH(Ó)CH2OH	$\xleftarrow{1,4}$	H2NCH(OH)CH2Ó	(128)

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<sup>-1</sup> in the MP2 calculations, while the B3LYP calculations predicted a hydrogen shift barrier of around 60 kJ mol<sup>-1</sup> 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<sup>-1</sup>.

The dissociation reaction (127b) to give glycolaldehyde is calculated to be endothermic by 39 kJ mol<sup>-1</sup> and this route is therefore hardly relevant under atmospheric conditions considering that the precursor is formed with a maximum of 48 kJ mol<sup>-1</sup> 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 H<sub>2</sub>NCH(OH)CH<sub>2</sub>Ó radical may either dissociate, undergo H-abstraction by O<sub>2</sub> or, in principle, go through another 1,4-hydrogen shift from the N- to the O-atom

$\Delta_{\rm r}H = +42$	H <sub>2</sub> NCH(OH)CH <sub>2</sub> Ó	$\overset{\Delta}{\longrightarrow}$	$H_2N\dot{C}HOH + \textbf{HCHO}$	(129)
$\Delta_{\rm r}H = -161$	$H_2N\dot{C}HOH + O_2$	$\rightarrow$	$H_2NCHO + HO_2$	(130)
$\Delta_{\rm r}H = -132$	$H_2NCH(OH)CH_2OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	$\rightarrow$	$\textbf{H}_2\textbf{NCH(OH)CHO} + \textbf{HO}_2$	(131)
$\Delta_{\rm r}H = -18$	H <sub>2</sub> NCH(OH)CH <sub>2</sub> Ó	$\xleftarrow{1,4}$	HŃCH(OH)CH <sub>2</sub> OH	(132)

Although the dissociation reaction (129) is calculated to be endothermic by 42 kJ mol<sup>-1</sup> this route may be relevant under atmospheric conditions considering that the precursor is formed with up to 48 kJ mol<sup>-1</sup> excess energy. The barrier to the 1,4-hydrogen shift reaction (132) was estimated in QCC calculations to more than 70 kJ mol<sup>-1</sup>; the hydrogen shift reaction is therefore <u>not</u> feasible under atmospheric conditions considering that the available precursor energy is less than 48 kJ mol<sup>-1</sup>. Finally the N-centered radical, HNCH(OH)CH<sub>2</sub>OH, formed in (132) may react with O<sub>2</sub> and NO<sub>2</sub> by hydrogen abstraction, or react with NO and NO<sub>2</sub> to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during <u>daytime</u> (threshold wavelength  $\lambda = 641$  nm) to reform the N-centered radical.

$\Delta_{\rm r}H = -138$	$H\dot{N}CH(OH)CH_2OH + O_2$	$\rightarrow$	$HN=C(OH)CH_2OH + HO_2$	(133)
$\Delta_{\rm r}H = -258$	$H\dot{N}CH(OH)CH_2OH + NO_2$	$\rightarrow$	HN=C(OH)CH <sub>2</sub> OH + HONO	(134a)
$\Delta_{\rm r}H = -211$		$\rightarrow$	O <sub>2</sub> NNHCH(OH)CH <sub>2</sub> OH	(134b)
$\Delta_{\rm r}H = -187$	HŃCH(OH)CH <sub>2</sub> OH + NO	$\rightarrow$	ONNHCH(OH)CH <sub>2</sub> OH	(135)
$\Delta_{\rm r} H = +187$	ONNHCH(OH)CH <sub>2</sub> OH	$\xrightarrow{h_{\mathcal{V}}}$	HŃCH(OH)CH <sub>2</sub> OH + NO	(136)

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

$\Delta_{\rm r}H = +344$	H <sub>2</sub> NCH(OH)CHO	$\xrightarrow{h\nu}$	$H_2N\dot{C}HOH + CHO$	(138)
$\Delta_{\rm r}H = -113$	H <sub>2</sub> NCH(OH)CHO + OH	$\rightarrow$	$H_2NCH(OH)\dot{C}O + H_2O$	(139)
$\Delta_{\rm r}H = -150$	$H_2NCH(OH)\dot{C}O + O_2$	$\rightarrow$	H <sub>2</sub> NCH(OH)C(O)OÓ	(140)
$\Delta_{\rm r}H = -109$	$H_2NCH(OH)C(O)OOO + NO_2$	$\rightarrow$	H <sub>2</sub> NCH(OH)C(O)OONO <sub>2</sub>	(141)
$\Delta_{\rm r}H$ =+109	H <sub>2</sub> NCH(OH)C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$H_2NCH(OH)C(O)OOO + NO_2$	(142)
$\Delta_{\rm r}H = -181$	$H_2NCH(OH)C(O)OOO + NO$	$\rightarrow$	$H_2N\dot{C}HOH + CO_2 + NO_2$	(143)
$\Delta_{\rm r}H = -193$	$H_2NCH(OH)CHO + OH$	$\rightarrow$	$H_2N\dot{C}(OH)CHO + H_2O$	(144)
$\Delta_{\rm r}H = -66$	$H_2N\dot{C}(OH)CHO + O_2$	$\rightarrow$	$H_2NC(O)CHO + HO_2$	(145)

The threshold wavelength for photolysis channel (138) is 349 nm  $\Delta_r H = +344$  kJ mol<sup>-1</sup>), which is in the centre of the  $n \rightarrow \pi^*$  band of aliphatic aldehydes. The photolysis is thus feasible at tropospheric conditions. The H<sub>2</sub>NCHOH radical formed in (129), (138) and (143) is expected to react with O<sub>2</sub> (hydrogen abstraction from RO-H) resulting in the formation of H<sub>2</sub>NCHO (formamide).

$$\Delta_{\rm r} H = -161 \qquad \qquad {\rm H}_2 {\rm N} \dot{\rm C} {\rm HOH} + {\rm O}_2 \quad \rightarrow \quad {\rm H}_2 {\rm N} {\rm CHO} + {\rm HO}_2 \tag{146}$$

Summing up the feasible reactions following initial hydrogen abstraction from C2-position in MEA the products include  $NH_2CHO$  (formamide) and  $NH_2C(=O)CH_2OH$  (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  $NH_2CH(\acute{O})CH_2OH$  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 H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (MEA) following initial hydrogen abstraction at C2.

# 3.1.3 Reactions following a possible hydrogen abstraction from the NH<sub>2</sub> 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 calculation<sup>37</sup> 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<sub>2</sub> group. The following reactions may be envisaged following hydrogen abstraction from the amino-group in MEA:

$\Delta_{\rm r} H = -76$	$H_2NCH_2CH_2OH + OH$	$\rightarrow$	$HNCH_2CH_2OH + H_2O$	(147)
$\Delta_{\rm r}H = -191$	$H\dot{N}CH_2CH_2OH + NO$	$\rightarrow$	ON-NHCH <sub>2</sub> CH <sub>2</sub> OH	(148)
$\Delta_{\rm r}H = +191$	<b>ON-NHCH<sub>2</sub>CH<sub>2</sub>OH</b>	$\xrightarrow{h\nu}$	$\dot{HNCH_2CH_2OH} + NO$	(149)
$\Delta_{\rm r} H = -213$	$\dot{HNCH_2CH_2OH} + NO_2$	$\rightarrow$	O <sub>2</sub> N-NHCH <sub>2</sub> CH <sub>2</sub> OH	(150a)
$\Delta_{\rm r}H = -216$		$\rightarrow$	HN=CHCH <sub>2</sub> OH + HONO	(150b)
$\Delta_{\rm r}H = -97$	$\dot{HNCH_2CH_2OH} + O_2$	$\rightarrow$	$\mathbf{HN}{=}\mathbf{CHCH}_{2}\mathbf{OH}+\mathbf{HO}_{2}$	(151)

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)

	2
$\Delta_r H = +15$ HŃCHOHCH <sub>2</sub> OH $\leftarrow 1.3$ H <sub>2</sub> NCH	Ю́СН <sub>2</sub> ОН (153)
$\Delta_{\rm r} H = -209 \qquad \qquad {\rm H_2N-CHOCH_2OH} + {\rm O_2}  \rightarrow  {\rm H_2NC(CHOCH_2OH)} + {\rm O$	$\mathbf{O)CH}_{2}\mathbf{OH} + \mathrm{HO}_{2} $ (154)
$\Delta_{\rm r}H = -187$ HŃCHOHCH <sub>2</sub> OH + NO $\rightarrow$ ON-NH	<b>ICHOHCH<sub>2</sub>OH</b> (155)
$\Delta_r H = +187$ <b>ON-NHCHOHCH<sub>2</sub>OH</b> $\xrightarrow{h\nu}$ HŃCHO	$OHCH_2OH + NO$ (156)
$H\dot{N}CHOHCH_2OH + NO_2 \rightarrow O_2N-NI$	<b>НСНОНСН<sub>2</sub>ОН</b> (157а)
$\Delta_r H = -251 \qquad \rightarrow \qquad \text{HN}=C(0)$	$OH)CH_2OH + HONO \qquad (157b)$
$\Delta_{\rm r} H = -147 \qquad \qquad \text{HNCHOHCH}_2 \text{OH} + \text{O}_2  \rightarrow \qquad \text{HN=C}(0)$	$OH)CH_2OH + HO_2 $ (158)
$\Delta_{\rm r} H = -58 \qquad \qquad \mathbf{HN=C(OH)CH_2OH} \qquad \xleftarrow{1.3} \qquad \mathbf{H_2NC(OH)CH_2OH} \qquad \textcircled{1.3} \qquad \mathbf{H_2NC(OH)CH_2OH} \qquad (\mathbf{H_2NC(OH)CH_2OH} ) \qquad \mathbf{H_2NC(OH)CH_2OH} \qquad (\mathbf{H_2NC(OH)CH_2OH} ) \qquad \mathbf{H_2NC(OH)CH_2OH} \qquad (\mathbf{H_2NC(OH)CH_2OH} ) \qquad \mathbf{H_2NC(OH)CH_2OH} \qquad H_2N$	<b>O)CH<sub>2</sub>OH</b> (159)

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-NHCHOHCH<sub>2</sub>OH ((nitrosoamino)-glycol), O<sub>2</sub>N-(2-(nitroamino)-ethanol), O<sub>2</sub>N-NHCHOHCH<sub>2</sub>OH NHCH<sub>2</sub>CH<sub>2</sub>OH and ((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 as end up  $O_2NNHC(O)CH_2OH$  (N-nitramino-hydroxyacetamide). The atmospheric chemistry of the short-lived CHOCH<sub>2</sub>OH (glycolaldehyde) is well known and will not be elaborated on here.

$O_2$ N-NHCH <sub>2</sub> CH <sub>2</sub> OH + OH	$\rightarrow$	O <sub>2</sub> N-NHĊHCH <sub>2</sub> OH + H <sub>2</sub> O	(160)
$O_2N$ -NHĊHCH $_2OH + O_2$	$\rightarrow$	O2N-NHC(OÓ)HCH2OH	(161)
O <sub>2</sub> N-NHC(OÓ)HCH <sub>2</sub> OH + NO	$\rightarrow$	$O_2$ N-NHC(Ó)HCH <sub>2</sub> OH + NO <sub>2</sub>	(162)
$O_2$ N-NHC(Ó)HCH <sub>2</sub> OH + $O_2$	$\rightarrow$	$O_2$ N-NHC(O)CH <sub>2</sub> OH + HO <sub>2</sub>	(163)
$O_2$ N-NHCHOHCH <sub>2</sub> OH + OH	$\rightarrow$	$O_2$ N-NHĊ(OH)CH <sub>2</sub> OH + H <sub>2</sub> O	(164)
$O_2$ N-NHĊ(OH)CH <sub>2</sub> OH + $O_2$	$\rightarrow$	$O_2$ N-NHC(O)CH <sub>2</sub> OH + HO <sub>2</sub>	(165)

#### 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 H<sub>2</sub>NCHO (formamide) and NH<sub>2</sub>C(=O)CH<sub>2</sub>OH (2-hydroxy-acetamide) which are both expected to have  $\tau_{OH} > 3$  days. Other long-lived compounds are H<sub>2</sub>NC(O)C(O)OONO<sub>2</sub> (2-amino-2-oxo-peroxyacetyl-nitrate). Products with lifetimes  $\tau_{OH} < 3$  days include H<sub>2</sub>NCH<sub>2</sub>CHO, H<sub>2</sub>NC(O)CHO (2-oxo-acetamide), and H<sub>2</sub>NCH<sub>2</sub>C(O)OONO<sub>2</sub> (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 H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (MEA) following initial hydrogen abstraction from the amino group.

# 3.2 $(CH_3)_2C(NH_2)CH_2OH$ (AMP)

The systematic name of  $(CH_3)_2C(NH_2)CH_2OH$  is 2-amino-2-methyl-1-Propanol (CAS: 124-68-5).<sup>#</sup>

Bond enthalpy calculations ( $\Delta_{bond}H_{O-H} \sim 457$ ,  $\Delta_{bond}H_{C-H_3} \sim 433$ ,  $\Delta_{bond}H_{C-H_2} \sim 397$ , and  $\Delta_{bond}H_{N-H} \sim 426$  kJ mol<sup>-1</sup>, Table 5.2, page 86)) suggest that the initial reaction of AMP with OH should proceed entirely through H-abstraction from the CH<sub>2</sub> in the methanoyl group. However, the experimental rate constant for OH reaction with TBA (*tert*-butylamine) is  $k_{OH} = 1.2 \times 10^{-11}$  compared to  $k_{OH} = 2.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for AMP. The Atkinson SAR<sup>32,33,35</sup> predicts  $k_{OH} = 5 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for hydrogen abstraction from the -C(CH<sub>3</sub>)<sub>3</sub> group in alkanes. That is, either there are large errors in the measured rate constants or the reactivity of the -C(CH<sub>3</sub>)<sub>3</sub> and the NH<sub>2</sub>-group is larger than expected. Consequently, three reaction routes of the OH initiated degradation of AMP will be investigated.

$$\Delta_{\rm r}H = -101 \quad (CH_3)_2 C(NH_2) CH_2 OH + OH \rightarrow (CH_3)_2 C(NH_2) \dot{C}HOH + H_2 O \quad (166a)$$

$$\Delta_{\rm r}H = -65 \quad (CH_3)_2 C(NH_3) \dot{C}H + H_2 O \quad (166b)$$

$$\Delta_{\mathbf{r}}H = -05 \qquad \qquad \rightarrow \quad (CH_3)(CH_2OH)C(NH_2)CH_2 + H_2O \quad (1000)$$

$$\Delta_{\rm r} H = -72 \qquad \rightarrow \quad (\rm CH_3)_2(\rm CH_2\rm OH)\rm CNH + H_2O \qquad (166c)$$

# 3.2.1 Fate of the (CH<sub>3</sub>)<sub>2</sub>C(NH<sub>2</sub>)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-2propanal 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 that those of the other C-H and N-H bonds in the compound – see also Table 5.2):

$\Delta_{\rm r}H = -83$	$(CH_3)_2C(NH_2)\dot{C}HOH + O_2$	$\rightarrow$	$(CH_3)_2C(NH_2)CHO + HO_2$	(167)
$\Delta_{\rm r}H=+322$	(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )CHO	$\xrightarrow{h\nu}$	$(CH_3)_2\dot{C}(NH_2) + CHO$	(168)
$\Delta_{\rm r} H = -130$	$(CH_3)_2C(NH_2)CHO + OH$	$\rightarrow$	$(CH_3)_2C(NH_2)\dot{C}O + H_2O$	(169)
$\Delta_{\rm r} H = -141$	$(CH_3)_2C(NH_2)\dot{C}O + O_2$	$\rightarrow$	(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )C(O)OÓ	(170)
$\Delta_{\rm r} H = -104$	$(CH_3)_2C(NH_2)C(O)OOO + NO_2$	$\rightarrow$	(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	(171)
$\Delta_{\rm r}H$ =+104	(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	$(CH_3)_2C(NH_2)C(O)OOO + NO_2$	(172)
$\Delta_{\rm r}H = -188$	$(CH_3)_2C(NH_2)C(O)OOO + NO$	$\rightarrow$	$(CH_3)_2\dot{C}(NH_2) + CO_2 + NO_2$	(173)

The 2-amino-2-propyl radical formed in (168) and (173) will add  $O_2$  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:

<sup>&</sup>lt;sup>#</sup> 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.

$$\Delta_{\rm r} H = -162 \qquad (\rm CH_3)_2 \dot{\rm C}(\rm NH_2) + O_2 \quad \rightarrow \quad (\rm CH_3)_2 C(\rm NH_2) OO \qquad (174)$$

$$\Delta_{\rm r} H = -24 \qquad (\rm CH_3)_2 C(\rm NH_2) OO + \rm NO \rightarrow (\rm CH_3)_2 C(\rm NH_2) O + \rm NO_2 \qquad (175)$$

$$\Delta_{\rm r} H = +14 \qquad (\rm CH_3)_2 C(\rm NH_2) \acute{O} \xrightarrow{\Delta} (\rm CH_3)_2 CO + \rm NH_2 \qquad (176a)$$

Note that the formation of acetone in (176a) is endothermic. The atmospheric chemistry of acetone and of the NH<sub>2</sub> and CH<sub>3</sub> 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  $\tau_{OH} \sim 50$  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<sub>2</sub>-group in AMP are CH<sub>3</sub>C(O)NH<sub>2</sub> (acetamide) and  $(CH_3)_2C(NH_2)C(O)OONO_2$ . Scheme 3.4 summarizes the main atmospheric degradation routes of AMP following initial hydrogen abstraction from the CH<sub>2</sub>-group.



Scheme 3.4 The main atmospheric degradation routes of  $(CH_3)_2C(NH_2)CH_2OH$  (AMP) following initial hydrogen abstraction from the CH<sub>2</sub>-group.

## 3.2.2 Fate of the (CH<sub>3</sub>)(CH<sub>2</sub>OH)C(NH<sub>2</sub>)CH<sub>2</sub> 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.

$\Delta_{\rm r}H = -65$	$(CH_3)_2C(NH_2)CH_2OH + OH$	$\rightarrow$	$\dot{C}H_2C(CH_3)(NH_2)CH_2OH + H_2O$	(166b)
$\Delta_{\rm r} H = -147$	$\dot{C}H_2C(CH_3)(NH_2)CH_2OH + O_2$	$\rightarrow$	ÓOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	(177)
$\Delta_{\rm r}H = -51$	ÓOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH+ NO	$\rightarrow$	$\acute{O}CH_2C(CH_3)(NH_2)CH_2OH + NO_2$	(178)

#### $\Delta_{\mathbf{r}}H = -148 \quad \acute{\mathrm{O}}\mathrm{CH}_{2}\mathrm{C}(\mathrm{CH}_{3})(\mathrm{NH}_{2})\mathrm{CH}_{2}\mathrm{OH} + \mathrm{O}_{2} \rightarrow \mathrm{OHCC}(\mathrm{CH}_{3})(\mathrm{NH}_{2})\mathrm{CH}_{2}\mathrm{OH} + \mathrm{HO}_{2} \quad (179)$

The oxy radial formed in (178) may also undergo dissociation, three different 1,4hydrogen shift reactions ( $H_2CH....OCH_2$ ,  $HNH...OCH_2$ ,  $HOHCH...OCH_2$ ) and a 1,5-hydrogen shift reaction ( $H_2COH...OCH_2$ ). 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<sub>2</sub> we have included the subsequent reactions to check for the possible formation of carcinogenic compounds.

$\Delta_{\rm r}H = +19$	ÓCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$\dot{C}(CH_3)(NH_2)CH_2OH + HCHO$	(180a)
$\Delta_{\rm r}H = -23$		$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> C(ĊH <sub>2</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	(180b)

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)

$\Delta_{\rm r}H = -333$	OHCC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xrightarrow{h_{V}}$	$\dot{C}(CH_3)(NH_2)CH_2OH + CHO$	(181)
$\Delta_{\rm r} H = -114$	$OHCC(CH_3)(NH_2)CH_2OH+OH$	$\rightarrow$	$\dot{OCC}(CH_3)(NH_2)CH_2OH + H_2O$	(182)
	$\dot{OCC}(CH_3)(NH_2)CH_2OH + O_2$	$\rightarrow$	ÓO(O)CC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	(183)
	ÓO(O)CC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH+NO <sub>2</sub>	$\rightarrow$	O2NOO(O)CC(CH3)(NH2)CH2OH	(184)
	O2NOO(O)CC(CH3)(NH2)CH2OH	$\overset{\Delta}{\longrightarrow}$	$OO(O)CC(CH_3)(NH_2)CH_2OH + NO_2$	(185)
	ÓO(O)CC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH +NO	$\rightarrow$	$\dot{C}(CH_3)(NH_2)CH_2OH + CO_2 + NO_2$	(186)
$\Delta_{\rm r} H = -161$	$\dot{C}(CH_3)(NH_2)CH_2OH + O_2$	$\rightarrow$	ÓOC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	(187)
$\Delta_{\rm r} H = -48$	$OOC(CH_3)(NH_2)CH_2OH + NO$	$\rightarrow$	$\acute{OC}(CH_3)(NH_2)CH_2OH + NO_2$	(188)

The alkoxy radical formed in (188) may in principle may undergo three different dissociation reactions or yet another 1,4-hydrogen shift ( $H_2COH$ ....OC) reaction

$\Delta_{\rm r}H = -32$	ÓC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	CH <sub>3</sub> C(O)NH <sub>2</sub> + CH <sub>2</sub> OH	(189)
$\Delta_{\rm r}H = +34$		$\overset{\Delta}{\longrightarrow}$	$\mathbf{CH_3C(O)CH_2OH} + \mathrm{NH_2}$	(190)
$\Delta_{\rm r}H = -23$		$\xrightarrow{\Delta}$	NH <sub>2</sub> C(O)CH <sub>2</sub> OH + CH <sub>3</sub>	(191)
$\Delta_{\rm r}H = -{\rm xx}$		$\xleftarrow{1,4}$	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> Ó	(192)

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

$$HOC(CH_3)(NH_2)CH_2O \xrightarrow{\Delta} HOC(CH_3)(NH_2) + HCHO$$
 (193)

	$HOC(CH_3)(NH_2)CH_2\acute{O} + O_2$	$\rightarrow$	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )CHO +HO <sub>2</sub>	(194)
$\Delta_{\rm r}H = +344$	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )CHO	$\xrightarrow{hv}$	$HO\dot{C}(CH_3)(NH_2) + CHO$	(195)
$\Delta_{\rm r}H = -105$	$HOC(CH_3)(NH_2)CHO+OH$	$\rightarrow$	$HOC(CH_3)(NH_2)\dot{C}O + H_2O$	(196)
	$HOC(CH_3)(NH_2)\dot{C}O + O_2$	$\rightarrow$	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OÓ	(197)
	$HOC(CH_3)(NH_2)C(O)O\acute{O} + NO_2$	$\rightarrow$	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	(198)
	HOC(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	$HOC(CH_3)(NH_2)C(O)OOO + NO_2$	(199)
	$HOC(CH_3)(NH_2)C(O)OOO + NO$	$\rightarrow$	$HO\dot{C}(CH_3)(NH_2) + CO_2 + NO_2$	(200)
$\Delta_{\rm r} H = -164$	$HO\dot{C}(CH_3)(NH_2) + O_2$	$\rightarrow$	$CH_3C(O)NH_2 + HO_2$	(201)

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

ÓCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xleftarrow{1,4}$	HOCH <sub>2</sub> C(ĊH <sub>2</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	(180b)
$\dot{C}H_2C(CH_2OH)_2(NH_2)+O_2$	$\rightarrow$	ÓOCH2C(CH2OH)2(NH2)CH2OH	(202)
ÓOCH <sub>2</sub> C(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> ) + NO	$\rightarrow$	$\acute{O}CH_2C(CH_2OH)_2(NH_2) + NO_2$	(203)

In the above we have rewritten  $HOCH_2C(\dot{C}H_2)(NH_2)CH_2OH$  as  $\dot{C}H_2C(CH_2OH)_2(NH_2)$  for the sake of clarity. The alkoxy radical formed in (203) may either dissociate, undergo 2 different 1,4-hydrogen shift ( $H_2CO....HCHOH$ ,  $H_2CO...HCHOH$ ) or a 1,5-hydrogen shift reactions. However, the 1,5-hydrogen shift is between two identical radicals:

$$\acute{O}CH_2C(CH_2OH)_2(NH_2) \xrightarrow{\Delta} \acute{C}(CH_2OH)_2(NH_2) + HCHO$$
(204)

$$\xleftarrow{}^{1,4} \quad C(CH_2OH)_2(NH_2)\dot{C}HOH \tag{205}$$

$$\xleftarrow{1.4} C(CH_2OH)_3\dot{N}H$$
 (206)

The alkyl radical formed in the 1,4-hydrogen shift (205) will react with O<sub>2</sub> and form an aldehyde which will either undergo photolysis (threshold wavelength  $\lambda = 366 \text{ nm}$ ,  $\Delta_r H = 328 \text{ kJ mol}^{-1}$ ) or react with OH radicals in aldehydic hydrogen abstraction

	$(CH_2OH)_2(NH_2)C\dot{C}HOH + O_2$	$\rightarrow$	$(\mathbf{CH}_{2}\mathbf{OH})_{2}(\mathbf{NH}_{2})\mathbf{CCHO} + \mathbf{HO}_{2}$	(207)
$\Delta_{\rm r}H=+328$	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )CCHO	$\xrightarrow{h\nu}$	$(CH_2OH)_2(NH_2)\dot{C} + CHO$	(208)
	$(CH_2OH)_2(NH_2)CCHO + OH$	$\rightarrow$	$(CH_2OH)_2(NH_2)C\dot{C}O + H_2O$	(209)
	$(CH_2OH)_2(NH_2)C\dot{C}O + O_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )CC(O)OÓ	(210)
	$(CH_2OH)_2(NH_2)CC(O)O\acute{O} + NO_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )CC(O)OONO <sub>2</sub>	(211)
	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )CC(O)OONO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	$(CH_2OH)_2(NH_2)CC(O)OOO + NO_2$	(212)
	$(CH_2OH)_2(NH_2)CC(O)OOO + NO$	$\rightarrow$	$(CH_2OH)_2(NH_2)\dot{C} + CO_2 + NO_2$	(213)
	$(CH_2OH)_2(NH_2)\dot{C} + O_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )COÓ	(214)
	$(CH_2OH)_2(NH_2)COO + NO$	$\rightarrow$	$(CH_2OH)_2(NH_2)CO + NO_2$	(215)
	(CH <sub>2</sub> OH) <sub>2</sub> (NH <sub>2</sub> )CÓ	$\xrightarrow{\Delta}$	$(CH_2OH)_2CO + NH_2$	(216)

The alkoxy radical formed in (215) may undergo a 1,4-hydrogen shift (CO-----HOCH<sub>2</sub>)

$$\Delta_{r}H = -1 \qquad (CH_{2}OH)_{2}(NH_{2})C\acute{O} \quad \stackrel{1,4}{\longrightarrow} \quad (CH_{2}OH)(NH_{2})C(OH)CH_{2}\acute{O} \qquad (218)$$

$$(CH_{2}OH)(NH_{2})C(OH)CH_{2}\acute{O} \quad \stackrel{\Delta}{\longrightarrow} \quad (CH_{2}OH)(NH_{2})\dot{C}(OH) + \mathbf{HCHO} \qquad (219)$$

$$(CH_{2}OH)(NH_{2})\dot{C}(OH) + O_{2} \quad \rightarrow \qquad \mathbf{NH_{2}C(O)CH_{2}OH} + HO_{2} \qquad (220)$$

$$(CH_{2}OH)(NH_{2})C(OH)CH_{2}\acute{O} + O_{2} \quad \rightarrow \qquad (CH_{2}OH)(NH_{2})C(OH)CHO + HO_{2} \qquad (221)$$

$$(CH_{2}OH)(NH_{2})C(OH)CHO \quad \stackrel{h\nu}{\longrightarrow} \quad (CH_{2}OH)(NH_{2})\dot{C}OH + CHO \qquad (222)$$

$$(CH_{2}OH)(NH_{2})\dot{C}OH + O_{2} \quad \rightarrow \qquad \mathbf{NH_{2}C(O)CH_{2}OH} + HO_{2} \qquad (223)$$

Finally the N-centered radical,  $C(CH_2OH)_3$ NH, formed in (206) may react with NO and NO<sub>2</sub> to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during <u>daytime</u> (threshold wavelength  $\lambda = 641$  nm) to reform the N-centered radical. Alternatively, it may dissociate.

$\dot{N}HC(CH_2OH)_3 + NO$	$\rightarrow$	ONNHC(CH <sub>2</sub> OH) <sub>3</sub>	(224)
ONNHC(CH <sub>2</sub> OH) <sub>3</sub>	$\xrightarrow{h\nu}$	$\dot{N}HC(CH_2OH)_3 + NO$	(225)
$\dot{\text{NHC}}(\text{CH}_2\text{OH})_3 + \text{NO}_2$	$\rightarrow$	O <sub>2</sub> NNHC(CH <sub>2</sub> OH) <sub>3</sub>	(226)
ŃHC(CH <sub>2</sub> OH) <sub>3</sub>	$\xrightarrow{\Delta}$	HN=C(CH <sub>2</sub> OH) <sub>2</sub> + CH <sub>2</sub> OH	(227)

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

$$HN=C(CH_2OH)_2 + O_3 \rightarrow (CH_2OH)_2CO + HNO_2$$
(228)

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

ÓCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xleftarrow{1,4}$	HOCH <sub>2</sub> C(CH <sub>3</sub> )(ŃH)CH <sub>2</sub> OH	(180c)
$\dot{N}HC(CH_3)(CH_2OH)_2 + NO$	$\rightarrow$	ONNHC(CH <sub>3</sub> )(CH <sub>2</sub> OH) <sub>2</sub>	(229)
ONNHC(CH <sub>3</sub> )(CH <sub>2</sub> OH) <sub>2</sub>	$\xrightarrow{h\nu}$	ŃHC(CH <sub>3</sub> )(CH <sub>2</sub> OH) <sub>2</sub> + NO	(230)
$\dot{\text{NHC}}(\text{CH}_3)(\text{CH}_2\text{OH})_2 + \text{NO}_2$	$\rightarrow$	O <sub>2</sub> NNHC(CH <sub>3</sub> )(CH <sub>2</sub> OH) <sub>2</sub>	(231)
ŃHC(CH <sub>3</sub> )(CH <sub>2</sub> OH) <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	$HN=C(CH_2OH)_2+CH_3$	(232)
	$\overset{\Delta}{\longrightarrow}$	HN=C(CH <sub>3</sub> )(CH <sub>2</sub> OH) + CH <sub>2</sub> OH	(233)

For the sake of clarity we have rewritten  $HOCH_2C(CH_3)(\dot{N}H)CH_2OH$  as  $\dot{N}HC(CH_3)(CH_2OH)_2$  in the above equations. The imines formed in (232) and (233) will react with O<sub>3</sub> to give carbonyl compounds

$$HN=C (CH_2OH)_2 + O_3 \xrightarrow{\Delta} (CH_2OH)_2CO + HNO_2$$
(234)

$$HN=C(CH_3)(CH_2OH) + O_3 \xrightarrow{\Delta} CH_3C(O)CH_2OH + HNO_2$$
(235)

NILU OR 77/2008

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 $\Delta_{\rm r}H = -41$ 

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

ÓCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )ĊHOH	(180d)
$HOCH_2C(CH_3)(NH_2)\dot{C}HOH + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CHO + HO <sub>2</sub>	(236)



Scheme 3.5 The main atmospheric degradation routes of  $(CH_3)_2C(NH_2)CH_2OH$  (AMP) following initial hydrogen abstraction from the CH<sub>3</sub>-group.

HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )CHO	$\xrightarrow{h\nu}$	$HOCH_2\dot{C}(CH_3)(NH_2) + CHO$	(237)
$HOCH_2C(CH_3)(NH_2)CHO + OH$	$\rightarrow$	$HOCH_2C(CH_3)(NH_2)\dot{C}O + H_2O$	(238)
$HOCH_2C(CH_3)(NH_2)\dot{CO} + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OÓ	(239)
$HOCH_2C(CH_3)(NH_2)C(O)OOO + NO_2$	$\rightarrow$	HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	(240)
HOCH <sub>2</sub> C(CH <sub>3</sub> )(NH <sub>2</sub> )C(O)OONO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	$HOCH_2C(CH_3)(NH_2)C(O)OOO + NO_2$	(241)
$HOCH_2C(CH_3)(NH_2)C(O)OOO + NO$	$\rightarrow$	$HOCH_2\dot{C}(CH_3)(NH_2) + CO_2 + NO_2$	(242)
$HOCH_2\dot{C}(CH_3)(NH_2) + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(OÓ)(CH <sub>3</sub> )(NH <sub>2</sub> )	(243)
$HOCH_2C(OO)(CH_3)(NH_2) + NO$	$\rightarrow$	$HOCH_2C(O)(CH_3)(NH_2) + NO_2$	(244)
HOCH <sub>2</sub> C(Ó)(CH <sub>3</sub> )(NH <sub>2</sub> )	$\overset{\Delta}{\longrightarrow}$	$HOCH_2C(O)CH_3 + NH_2$	(245)
	$\overset{\Delta}{\longrightarrow}$	CH <sub>3</sub> C(O)NH <sub>2</sub> + CH <sub>2</sub> OH	(246)
	$\xrightarrow{\Delta}$	$HOCH_2C(O)NH_2 + CH_3$	(247)

We conclude that should H-abstraction take place at the  $CH_3$  group in AMP the products resulting would be  $CH_3C(O)NH_2$  (acetamide),  $CH_3C(O)CH_2OH$  (hydroxyacetone) and  $CH_2OHC(O)NH_2$  (hydroxylacetamide).

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

$\Delta_{\rm r}H = -73$	$(CH_3)_2C(NH_2)CH_2OH + OH$	$\rightarrow$	$\dot{N}HC(CH_3)_2CH_2OH + H_2O$	(248)
$\Delta_{\rm r} H = -196$	$\dot{N}HC(CH_3)_2CH_2OH + NO$	$\rightarrow$	ON-NHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH	(249)
$\Delta_{\rm r} H = +106$	ON-NHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	ŃHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH + NO	(250)
$\Delta_{\rm r}H = -{\rm xx}$	$\dot{N}HC(CH_3)_2CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> N-NHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH	(251)

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<sup>-1</sup>).

$$\Delta_{\rm r}H = +63 \qquad \qquad \dot{\rm N}HC(\rm CH_3)_2\rm CH_2\rm OH \xrightarrow{\Delta} HN=C(\rm CH_3)\rm CH_2\rm OH + \rm CH_3 \qquad (252a)$$

$$\Delta_{\rm r} H = +62 \qquad \qquad \qquad \stackrel{\Delta}{\longrightarrow} \quad {\rm HN=C(CH_3)_2 + CH_2OH} \qquad (252b)$$

The nitrosamine and nitramine formed in (249) and (251) have quite reactive CH<sub>2</sub>-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

$ON-NHC(CH_3)_2CH_2OH + OH$	$\rightarrow$	$ON-NHC(CH_3)_2\dot{C}HOH + H_2O$	(253)
$ON-NHC(CH_3)_2 \dot{C}HOH + O_2$	$\rightarrow$	$\textbf{ON-NHC(CH_3)_2CHO} + \text{HO}_2$	(254)
ON-NHC(CH <sub>3</sub> ) <sub>2</sub> CHO	$\xrightarrow{h\nu}$	ON-NHĊ(CH <sub>3</sub> ) <sub>2</sub> + CHO	(255)
$ON-NH\dot{C}(CH_3)_2+O_2$	$\rightarrow$	ON-NHC(OÓ)(CH <sub>3</sub> ) <sub>2</sub>	(256)
ON-NHC(OÓ)(CH <sub>3</sub> ) <sub>2</sub> + NO	$\rightarrow$	ON-NHC(Ó)(CH <sub>3</sub> ) <sub>2</sub> + NO <sub>2</sub>	(257)
ON-NHC(Ó)(CH <sub>3</sub> ) <sub>2</sub>	$\xrightarrow{\Delta}$	<b>ON-NHC(O)CH<sub>3</sub></b> +CH <sub>3</sub>	(258)
ON-NHC(O)CH <sub>3</sub>	$\xrightarrow{h\nu}$	$\dot{N}HC(O)CH_3 + NO$	(259)
$\dot{N}HC(O)CH_3 + NO$	$\rightarrow$	ON-NHC(O)CH <sub>3</sub>	(260)
$\dot{N}HC(O)CH_3 + NO_2$	$\rightarrow$	O <sub>2</sub> N-NHC(O)CH <sub>3</sub>	(261)
$O_2$ N-NHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH + NO	$\rightarrow$	O <sub>2</sub> N-NHC(CH <sub>3</sub> ) <sub>2</sub> ĊHOH	(262)
$O_2$ N-NHC(CH <sub>3</sub> ) <sub>2</sub> ĊHOH + $O_2$	$\rightarrow$	$O_2$ N-NHC(CH <sub>3</sub> ) <sub>2</sub> CHO + HO <sub>2</sub>	(263)
O <sub>2</sub> N-NHC(CH <sub>3</sub> ) <sub>2</sub> CHO	$\xrightarrow{hv}$	O <sub>2</sub> N-NHĊ(CH <sub>3</sub> ) <sub>2</sub> + CHO	(264)
$O_2$ N-NHĊ(CH <sub>3</sub> ) <sub>2</sub> + $O_2$	$\rightarrow$	O <sub>2</sub> N-NHC(OÓ)(CH <sub>3</sub> ) <sub>2</sub>	(265)
$O_2$ N-NHC(OÓ)(CH <sub>3</sub> ) <sub>2</sub> + NO	$\rightarrow$	$O_2$ N-NHC(Ó)(CH <sub>3</sub> ) <sub>2</sub> + NO <sub>2</sub>	(266)
O <sub>2</sub> N-NHC(Ó)(CH <sub>3</sub> ) <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	<b>O<sub>2</sub>N-NHC(O)CH<sub>3</sub> + CH<sub>3</sub></b>	(267)

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  $CH_3C(O)NHNO_2$  (N-nitro-formamide, CAS: 51883-27-3) The corresponding nitrosamine,  $CH_3C(O)NHNO$  (N-nitroso-Formamide, CAS: 675141-02-3) is expected to undergo rapid photolysis.



**Scheme 3.6** The main atmospheric degradation routes of (CH<sub>3</sub>)<sub>2</sub>C(NH<sub>2</sub>)CH<sub>2</sub>OH (AMP) following initial hydrogen abstraction from the NH<sub>2</sub>-group.

# 3.3 CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (MDEA)

The systematic name of  $CH_3N(CH_2CH_2OH)_2$  is 2,2'-(methylimino)bis-Ethanol (CAS: 105-59-9).<sup>#</sup>

Bond enthalpy calculations suggest that hydrogen abstraction by OH radicals is most likely to occur from the  $CH_2$  groups. However, hydrogen abstraction from the - $CH_3$  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

$CH_3N(CH_2CH_2OH)_2 + OH$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> ĊHOH+H <sub>2</sub> O	(268a)
	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)ĊHCH <sub>2</sub> OH+H <sub>2</sub> O	(268b)
	$\rightarrow$	$\dot{C}H_2N(CH_2CH_2OH)_2 + H_2O$	(268c)

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

# 3.3.1 Fate of the CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>ĊHOH 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.

$CH_3N(CH_2CH_2OH)CH_2\dot{C}HOH+O_2$	$\rightarrow$	$CH_{3}N(CH_{2}CH_{2}OH)CH_{2}CHO + HO_{2}$	(269)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> CHO	$\xrightarrow{h\nu}$	$CH_3N(CH_2CH_2OH)\dot{C}H_2+CHO$	(270)
$CH_{3}N(CH_{2}CH_{2}OH)CH_{2}CHO+OH$	$\rightarrow$	$CH_3N(CH_2CH_2OH)CH_2\dot{C}O + H_2O$	(271)
$CH_3N(CH_2CH_2OH)CH_2\dot{C}O+O_2$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ	(272)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ+ NO <sub>2</sub>	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	(273)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ+ NO <sub>2</sub>	(274)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ+ NO	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)Ó+NO <sub>2</sub>	(275)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)Ó	$\xrightarrow{\Delta}$	$CH_3N(CH_2CH_2OH)\dot{C}H_2+CO_2$	(276)
$CH_3N(CH_2CH_2OH)\dot{C}H_2+O_2$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(277)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OÓ+ NO	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> Ó+ NO <sub>2</sub>	(278)

The alkoxy radical formed in (278) may react with O<sub>2</sub> in a hydrogen abstraction reaction to form an amide or undergo one of two 1,4-hydrogen shift reactions ( $\underline{CH_3}$ .....OCH<sub>2</sub>, HOCH<sub>2</sub>CH<sub>2</sub>....OCH<sub>2</sub>) a 1,5-hydrogen shift reaction ( $\underline{CH_2}$ CH(OH)H.....OCH<sub>2</sub>), or alternatively it may dissociate.

<sup>&</sup>lt;sup>#</sup> 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; Jefftreat MS 100; MDEA; MDEA (diol); Methylbis(2-hydroxyethyl)amine; Methyldiethanolamine; Methyliminodiethanol; N,N-Bis(2-hydroxyethyl)methylamine; N,N-Di(2-hydroxyethyl)-N-methylamine; N,N-Di(2-hydroxy-ethyl)methylamine; N-(2-Hydroxyethyl)-N-methylethanolamine; N-Methyl-N,N-diethanolamine; N-Methylaminodiglycol; N-Methylbis(2-hydroxyethyl)amine; N-Methyldiethanolamine; N-Methyldiethanol; NSC 11690; NSC 49131; NSC 51500; ZC 10.

$(CH_3)N(CH_2CH_2OH)CH_2\acute{O}+O_2$	$\rightarrow$	$\mathbf{CH}_{3}\mathbf{N}(\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{OH})\mathbf{CHO} + \mathbf{HO}_{2}$	(279a)
CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\overset{1,4}{\longleftrightarrow}$	ĊH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(279b)
	$\xleftarrow{1,4}$	HOCH2CHN(CH3)CH2OH	(279c)

- $\xleftarrow{1.5} (CH_3)N(CH_2\dot{C}HOH)CH_2OH$ (279d)
- $\xrightarrow{\Delta} CH_3 \acute{N} CH_2 CH_2 OH + HCHO$ (280)

Although the 1,4-hydrogen shift reactions (279b) and (279c) are toos slow to be of importance compared to the hydrogen abstraction reaction by  $O_2$  (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  $O_2$  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 <u>daytime</u> to reform the Ncentered radical.

$CH_3\dot{N}CH_2CH_2OH + NO$	$\rightarrow$	ON-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	(281)
ON-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$CH_3 \acute{N} CH_2 CH_2 OH + NO$	(282)
$CH_3\dot{N}CH_2CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> N-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	(283a)
	$\rightarrow$	$CH_{3}N=CHCH_{2}OH+HONO$	(283b)
	$\rightarrow$	$CH_2 = NCH_2CH_2OH + HONO$	(283c)
$CH_3 \acute{N} CH_2 CH_2 OH + O_2$	$\rightarrow$	$\mathbf{CH}_{2} = \mathbf{NCH}_{2}\mathbf{CH}_{2}\mathbf{OH} + \mathbf{HO}_{2}$	(284a)
	$\rightarrow$	$\mathbf{CH}_{3}\mathbf{N} = \mathbf{CH}\mathbf{CH}_{2}\mathbf{OH} + \mathbf{HO}_{2}$	(284b)

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

$\mathbf{CH_3N}{=}\mathbf{CHCH_2OH}+\mathbf{OH}$	$\rightarrow$	CH <sub>3</sub> ŃCHOHCH <sub>2</sub> OH	(285)
$CH_3 \acute{N} CHOHCH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(286)
ONN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xrightarrow{h\nu}$	CH <sub>3</sub> ŃCHOHCH <sub>2</sub> OH + NO	(287)
$CH_3$ ŃCHOHCH_2OH + NO_2	$\rightarrow$	O <sub>2</sub> NN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(288a)
	$\rightarrow$	CH <sub>2</sub> =NCHOHCH <sub>2</sub> OH + HONO	(288b)
	$\rightarrow$	$CH_3N=C(OH)CH_2OH + HONO$	(288c)
$CH_3 \acute{N} CHOHCH_2 OH + O_2$	$\rightarrow$	$\mathbf{CH}_{2} = \mathbf{NCHOHCH}_{2}\mathbf{OH} + \mathbf{HO}_{2}$	(289a)
	$\rightarrow$	$\textbf{CH}_3\textbf{N=C(OH)CH}_2\textbf{OH} + \textbf{HO}_2$	(289b)
CH <sub>3</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CH <sub>3</sub> NHC(O)CH <sub>2</sub> OH	(290)
$\mathbf{CH}_{2} = \mathbf{NCHOHCH}_{2}\mathbf{OH} + \mathbf{O}_{3}$	$\rightarrow$	$O_2NCHOHCH_2OH + HCHO$	(291)

$\textbf{CH}_2 = \textbf{NCHOHCH}_2\textbf{OH} + \textbf{OH}$	$\rightarrow$	HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH	(292)
$HOCH_2 \dot{N}CHOHCH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(293)
ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$HOCH_2\dot{N}CHOHCH_2OH + NO$	(294)
$HOCH_2 \dot{N}CHOHCH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(295a)
	$\rightarrow$	HOCH=NCHOHCH <sub>2</sub> OH + HONO	(295b)
	$\rightarrow$	HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH +HONO	(295c)
$HOCH_2 \dot{N}CHOHCH_2 OH + O_2$	$\rightarrow$	$HOCH=NCHOHCH_2OH + HO_2$	(296a)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HO_2$	(296b)
HOCH=NCHOHCH2OH	$\xrightarrow{1,3}$	CHONHCHOHCH <sub>2</sub> OH	(297)
HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHC(O)CH <sub>2</sub> OH	(298)

# 3.3.1.1 Fate of the CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>OH radical.

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

CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\overset{1,4}{\longleftrightarrow}$	ĊH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(279b)
$\dot{C}H_2N(CH_2CH_2OH)CH_2OH+O_2$	$\rightarrow$	ÓOCH2N(CH2CH2OH)CH2OH	(299)
$\acute{O}OCH_2N(CH_2CH_2OH)CH_2OH + NO$	$\rightarrow$	ÓCH2N(CH2CH2OH)CH2OH+NO2	(300)
$\acute{O}CH_2N(CH_2CH_2OH)CH_2OH + O_2$	$\rightarrow$	OHCN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH+HO <sub>2</sub>	(301)

The alkoxy radical formed in (300) may also dissociate or undergo 1,4- and 1,5hydrogen shift reactions (the 1,4-hydrogen shift involving the N-CH<sub>2</sub>OH group will reform an identical radical).

ÓCH2N(CH2CH2OH)CH2OH	$\xrightarrow{\Delta}$	$ \dot{N}(CH_2CH_2OH)CH_2OH + HCHO $	(302a)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(302b)

 $\xleftarrow{1.5} \text{HOCH}_2\text{N}(\text{CH}_2\dot{\text{C}}\text{HOH})\text{CH}_2\text{OH}$ (302c)

The N-centered radical formed in (302a) 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 <u>daytime</u> to reform the N-centered radical.

$\dot{N}(CH_2CH_2OH)CH_2OH + O_2$	$\rightarrow$	$(CH_2OH)N=CHCH_2OH + HO_2$	(303a)
	$\rightarrow$	(CH <sub>2</sub> CH <sub>2</sub> OH)N=CHOH + HO <sub>2</sub>	(303b)
$\acute{N}(CH_2CH_2OH)CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(304)
ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{hv}$	$\dot{N}(CH_2CH_2OH)CH_2OH + NO$	(305)
$\dot{N}(CH_2CH_2OH)CH_2OH + NO_2$	$\rightarrow$	(CH <sub>2</sub> OH)N=CHCH <sub>2</sub> OH + HONO	(306a)
	$\rightarrow$	(CH <sub>2</sub> CH <sub>2</sub> OH)N=CHOH + HONO	(306b)
	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(306c)

HOCH <sub>2</sub> CH <sub>2</sub> N=CHOH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> CH <sub>2</sub> NHCHO	(307)
$(CH_2OH)N=CHCH_2OH+OH$	$\rightarrow$	(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH	(308)
(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH + NO	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(309)
ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{h\nu}$	(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH + NO	(310)
(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH + NO <sub>2</sub>	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(311a)
	,	$(CH_2OH)N=C(OH)CH_2OH +$	(311b)
	$\rightarrow$	HONO	(3110)
	$\rightarrow$	HOCH=NCHOHCH <sub>2</sub> OH + HONO	(311c)
$(CH_2OH)$ ŃCHOHCH_2OH + O <sub>2</sub>	$\rightarrow$	$(CH_2OH)N=C(OH)CH_2OH + HO_2$	(312a)
	$\rightarrow$	$HOCH=NCHOHCH_2OH + HO_2$	(312b)
(CH <sub>2</sub> OH)N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	(CH <sub>2</sub> OH)NHC(O)CH <sub>2</sub> OH	(313)
HOCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	<b>CHONHCHOHCH<sub>2</sub>OH</b>	(314)

The alkyl radical formed in the 1,4-hydrogen shift reaction (302b) will add  $O_2$  and eventually end as a new alkoxy radical which may dissociate or undergo H-shift reactions, or alternatively react with  $O_2$  in a hydrogen abstraction.

ÓCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(302b)
$(HOCH_2)_2N\dot{C}HCH_2OH + O_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCH(OÓ)CH <sub>2</sub> OH	(315)
$(HOCH_2)_2NCH(OO)CH_2OH + NO$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHÓCH <sub>2</sub> OH + NO <sub>2</sub>	(316)
(HOCH <sub>2</sub> ) <sub>2</sub> NCHÓCH <sub>2</sub> OH	$\xrightarrow{\Delta}$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHO + CH <sub>2</sub> OH	(317a)
	$\xrightarrow{\Delta}$	$(HOCH_2)_2 \dot{N} + CHOCH_2OH$	(317b)
	$\xleftarrow{1,4}$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHCH <sub>2</sub> Ó	(317c)
	$\xleftarrow{1,4}$	HOĊH(HOCH <sub>2</sub> )NCHOHCH <sub>2</sub> OH	(317d)
	$\xleftarrow{1,5}$	ÓCH2(HOCH2)NCHOHCH2OH	(317e)
$(HOCH_2)_2NCHOCH_2OH + O_2$	$\rightarrow$	$(\mathbf{HOCH}_2)_2\mathbf{NC}(\mathbf{O})\mathbf{CH}_2\mathbf{OH} + \mathbf{HO}_2$	(318)
$(HOCH_2)_2 \acute{N} + NO$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NNO	(319)
(HOCH <sub>2</sub> ) <sub>2</sub> NNO	$\xrightarrow{h\nu}$	$(HOCH_2)_2 \dot{N} + NO$	(320)
$(HOCH_2)_2 \dot{N} + NO_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>	(321a)
	$\rightarrow$	HOCH <sub>2</sub> N=CHOH + HONO	(321b)
$(HOCH_2)_2 \dot{N} + O_2$	$\rightarrow$	$\textbf{HOCH}_2\textbf{N}\textbf{=}\textbf{CHOH} + \textbf{HO}_2$	(322)
HOCH <sub>2</sub> N=CHOH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHCHO	(323)

The alkoxy radical formed in the hydrogen shift reaction (317c) may dissociate or react with  $O_2$  in a hydrogen abstraction resulting in the formation of an aldehyde which may undergo photolysis or reaction with OH in an aldehydic hydrogen abstraction

(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHCH <sub>2</sub> Ó	$\overset{\Delta}{\longrightarrow}$	(HOCH <sub>2</sub> ) <sub>2</sub> NĊHOH + <b>HCHO</b>	(324)
$(HOCH_2)_2N\dot{C}HOH + O_2$	$\rightarrow$	$(HOCH_2)_2NCHO + HO_2$	(325)
$(HOCH_2)_2NCHOHCH_2\acute{O} + O_2$	$\rightarrow$	$(HOCH_2)_2NCHOHCHO + HO_2$	(326)
(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHCHO	$\xrightarrow{h_{V}}$	(HOCH <sub>2</sub> ) <sub>2</sub> NĊHOH + CHO	(327)
$(HOCH_2)_2N\dot{C}HOH + O_2$	$\rightarrow$	$(HOCH_2)_2NCHO + HO_2$	(328)
$(HOCH_2)_2NCHOHCHO + OH$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHĊO + H <sub>2</sub> O	(329)
$(HOCH_2)_2NCHOH\dot{C}O + O_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHC(O)OÓ	(330)
$(HOCH_2)_2NCHOHC(O)OOO + NO_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHC(O)OONO <sub>2</sub>	(331)
(HOCH <sub>2</sub> ) <sub>2</sub> NCHOHC(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$(HOCH_2)_2NCHOHC(O)OOO + NO_2$	(332)
$(HOCH_2)_2NCHOHC(0)OOO + NO$	$\rightarrow$	$(HOCH_2)_2N\dot{C}HOH + CO_2 + NO_2$	(333)
$(HOCH_2)_2N\dot{C}HOH + O_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCHO + HO <sub>2</sub>	(334)

The alkyl radical formed in the 1,4-hydrogen shift reaction (317d) will undergo hydrogen abstraction by  $O_2$ 

(HOCH <sub>2</sub> ) <sub>2</sub> NCHÓCH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOĊH(HOCH <sub>2</sub> )NCHOHCH <sub>2</sub> OH	(317d)
$HO\dot{C}H(HOCH_2)NCHOHCH_2OH + O_2$	$\rightarrow$	CHON(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(335)

The alkoxy radical formed in the 1,5-hydrogen shift reaction (317e) may dissociate or react with  $O_2$  in a hydrogen abstraction reaction giving an amide.

(HOCH <sub>2</sub> ) <sub>2</sub> NCHÓCH <sub>2</sub> OH	$\xleftarrow{1,5}$	ÓCH <sub>2</sub> (HOCH <sub>2</sub> )NCHOHCH <sub>2</sub> OH	(317e)
ÓCH2(HOCH2)NCHOHCH2OH	$\xrightarrow{\Delta}$	(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH+ <b>HCHO</b>	(336)
$\dot{O}CH_2(HOCH_2)NCHOHCH_2OH + O_2$	$\rightarrow$	<b>CHON(CH<sub>2</sub>OH)CHOHCH<sub>2</sub>OH</b> +HO <sub>2</sub>	(337)

The N-centered radical formed in the dissociation (336) may undergo hydrogenabstraction 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.

(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH + NO	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(338)
ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{h_{V}}$	(CH <sub>2</sub> OH)ŃCHOHCH <sub>2</sub> OH + NO	(339)
$(CH_2OH)$ ŃCHOHCH_2OH + NO <sub>2</sub>	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(340a)
	$\rightarrow$	(CH <sub>2</sub> OH)N=C(OH)CH <sub>2</sub> OH+HONO	(340b)
	$\rightarrow$	OHCH=NCHOHCH <sub>2</sub> OH + HONO	(340c)
$(CH_2OH)$ ŃCHOHCH_2OH + O <sub>2</sub>	$\rightarrow$	(CH <sub>2</sub> OH)N=C(OH)CH <sub>2</sub> OH + HO <sub>2</sub>	(341a)
	$\rightarrow$	$OHCH=NCHOHCH_2OH + HO_2$	(341b)
(CH <sub>2</sub> OH)N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	(CH <sub>2</sub> OH)NHC(O)CH <sub>2</sub> OH	(342)
OHCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	<b>CHONHCHOHCH<sub>2</sub>OH</b>	(343)

The alkyl radical formed in the 1,5 hydrogen shift reaction (302c) is expected to undergo hydrogen abstraction by  $O_2$  resulting in the formation of an aldehyde which may undergo photolysis or reaction with OH in an aldehydic hydrogen abstraction.

ÓCH2N(CH2CH2OH)CH2OH	$\overset{1,5}{\longleftrightarrow}$	HOCH <sub>2</sub> N(CH <sub>2</sub> ĊHOH)CH <sub>2</sub> OH	(302c)
$(HOCH_2)_2NCH_2\dot{C}HOH + O_2$	$\rightarrow$	$(\mathbf{HOCH}_2)_2\mathbf{NCH}_2\mathbf{CHO} + \mathbf{HO}_2$	(344)
(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> CHO	$\xrightarrow{h_{V}}$	$(HOCH_2)_2N\dot{C}H_2 + CHO$	(345)
$(HOCH_2)_2NCH_2CHO + OH$	$\rightarrow$	$(HOCH_2)_2NCH_2\dot{C}O + H_2O$	(346)
$(HOCH_2)_2NCH_2\dot{C}O + O_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> C(O)OÓ	(347)
$(HOCH_2)_2NCH_2C(O)OOO+NO_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> C(O)OÓNO <sub>2</sub>	(348)
(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> C(O)OÓNO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> C(O)OÓ+ NO <sub>2</sub>	(349)
$(HOCH_2)_2NCH_2C(O)O\acute{O} + NO$	$\rightarrow$	$(HOCH_2)_2N\dot{C}H_2 + CO_2 + NO_2$	(350)
$(HOCH_2)_2N\dot{C}H_2 + O_2$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> OÓ	(351)
$(HOCH_2)_2NCH_2OO + NO$	$\rightarrow$	$(HOCH_2)_2NCH_2\acute{O} + NO_2$	(352)
$(HOCH_2)_2NCH_2\acute{O} + O_2$	$\rightarrow$	$(HOCH_2)_2NCHO + HO_2$	(353)

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  $O_2$  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 <u>daytime</u>.

(CH <sub>2</sub> OH) <sub>2</sub> NCH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	$(CH_2OH)_2\dot{N} + HCHO$	(354a)
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$\leftarrow^{1,4}$ (CH <sub>2</sub> OH) <sub>2</sub> N	СНОН (354)	b)
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$(\Pi \cup \Pi_2)_2 \Pi + \Pi \cup \rightarrow (\Pi \cup \Pi_2)_2 \Pi \Pi \cup (\Im, \Pi)$	$(HOCH_2)_2N + NO$	$\rightarrow$	(HOCH <sub>2</sub> ) <sub>2</sub> NNO	(35	55)
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$$(\text{HOCH}_2)_2 \text{NNO} \xrightarrow{h_{\nu}} (\text{HOCH}_2)_2 \acute{N} + \text{NO}$$
(356)

$$(HOCH_2)_2\dot{N} + NO_2 \rightarrow (HOCH_2)_2NNO_2$$
 (357a)

$$\rightarrow \text{HOCH}_2\text{N=CHOH} + \text{HONO}$$
(357b)

$$(HOCH_2)_2 \dot{N} + O_2 \longrightarrow HOCH_2 N = CHOH + HO_2$$
(358)

$$HOCH_2N=CHOH \xrightarrow{1,3} HOCH_2NHCHO$$
(359)

The alkyl radical formed in (354b) will react with  $O_2$  in a hydrogen abstraction reaction and form an amide.

 $(CH_2OH)_2N\dot{C}HOH + O_2 \rightarrow (CH_2OH)_2NCHO + HO_2$  (360)

# 3.3.1.2 Fate of the HOCH<sub>2</sub>ĊHN(CH<sub>3</sub>)CH<sub>2</sub>OH radical

The reactions following the 1,4-hydrogen shift reaction (279c) results in an alkyl radical which is expected to add O<sub>2</sub>. For the sake of readability we write  $(CH_3)N(CH_2CH_2OH)CH_2\acute{O}$  as  $HOCH_2CH_2N(CH_3)CH_2\acute{O}$ 

$$HOCH_2CH_2N(CH_3)CH_2O' \xrightarrow{1,4} HOCH_2CHN(CH_3)CH_2OH$$
 (279c)

$HOCH_2\dot{C}HN(CH_3)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> CH(OÓ)N(CH <sub>3</sub> )CH <sub>2</sub> OH	(361)
HOCH <sub>2</sub> CH(OÓ)N(CH <sub>3</sub> )CH <sub>2</sub> OH + NO	$\rightarrow$	HOCH <sub>2</sub> CH(Ó)N(CH <sub>3</sub> )CH <sub>2</sub> OH+NO <sub>2</sub>	(362)

The alkoxy radical formed in (362) may react with O<sub>2</sub> in a hydrogen abstraction leading to an amide, dissociate, or undergo two different 1,4 hydrogen shift reactions.

$HOCH_2CH(O)N(CH_3)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(O)N(CH <sub>3</sub> )CH <sub>2</sub> OH+HO <sub>2</sub>	(363)
HOCH <sub>2</sub> CH(Ó)N(CH <sub>3</sub> )CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$\mathbf{HOCH}_{2}\mathbf{CHO} + \mathbf{\acute{N}(CH_{3})CH}_{2}\mathbf{OH}$	(364a)
	$\xrightarrow{\Delta}$	CHON(CH <sub>3</sub> )CH <sub>2</sub> OH + CH <sub>2</sub> OH	(364b)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> CHOHN(CH <sub>3</sub> )ĊHOH	(364c)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)ĊH <sub>2</sub>	(364d)

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 <u>daytime</u> to reform the N-centered radical.

$\dot{N}(CH_3)CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>3</sub> )CH <sub>2</sub> OH	(365)
ONN(CH <sub>3</sub> )CH <sub>2</sub> OH	$\xrightarrow{hv}$	$\dot{N}(CH_3)CH_2OH + NO$	(366)
$\dot{N}(CH_3)CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>3</sub> )CH <sub>2</sub> OH	(367a)
	$\rightarrow$	$CH_2 = NCH_2OH + HONO$	(367b)
	$\rightarrow$	CH <sub>3</sub> N=CHOH + HONO	(367c)
$\acute{N}(CH_3)CH_2OH + O_2$	$\rightarrow$	$\textbf{CH}_2 = \textbf{NCH}_2 \textbf{OH} + HO_2$	(368a)
	$\rightarrow$	$\textbf{CH}_{\textbf{3}}\textbf{N}{=}\textbf{CHOH} + \text{HO}_2$	(368b)
CH <sub>2</sub> N=CHOH	<u>1,3</u>	<b>CH</b> <sub>3</sub> NHCHO	(369)
engi (=enton	,		(2 2 2 )
$CH_2 = NCH_2OH + OH$	$\rightarrow$	HOCH <sub>2</sub> ŃCH <sub>2</sub> OH	(370)
$CH_2 = NCH_2OH + OH$ $HOCH_2\dot{N}CH_2OH + NO$	$\rightarrow$ $\rightarrow$	HOCH <sub>2</sub> ŃCH <sub>2</sub> OH ONN(CH <sub>2</sub> OH) <sub>2</sub>	(370) (371)
$CH_2=NCH_2OH + OH$ $HOCH_2\dot{N}CH_2OH + NO$ $ONN(CH_2OH)_2$	$\xrightarrow{hv}$	HOCH <sub>2</sub> ŃCH <sub>2</sub> OH ONN(CH <sub>2</sub> OH) <sub>2</sub> HOCH <sub>2</sub> ŃCH <sub>2</sub> OH + NO	(370) (371) (372)
$CH_{2}=NCH_{2}OH + OH$ $HOCH_{2}\dot{N}CH_{2}OH + NO$ $ONN(CH_{2}OH)_{2}$ $HOCH_{2}\dot{N}CH_{2}OH + NO_{2}$	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \hline h\nu \\ \rightarrow \end{array} $	HOCH <sub>2</sub> ŃCH <sub>2</sub> OH ONN(CH <sub>2</sub> OH) <sub>2</sub> HOCH <sub>2</sub> ŃCH <sub>2</sub> OH + NO $O_2$ NN(CH <sub>2</sub> OH) <sub>2</sub>	(370) (371) (372) (373a)
$CH_{2}=NCH_{2}OH + OH$ $HOCH_{2}\dot{N}CH_{2}OH + NO$ $ONN(CH_{2}OH)_{2}$ $HOCH_{2}\dot{N}CH_{2}OH + NO_{2}$	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \hline h\nu \\ \rightarrow \\ \rightarrow \\ \rightarrow \end{array} $	HOCH <sub>2</sub> ŃCH <sub>2</sub> OH ONN(CH <sub>2</sub> OH) <sub>2</sub> HOCH <sub>2</sub> ŃCH <sub>2</sub> OH + NO $O_2$ NN(CH <sub>2</sub> OH) <sub>2</sub> HOCH=NCH <sub>2</sub> OH	(370) (371) (372) (373a) (373b)

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

$HOCH_2CHOHN(CH_3)\dot{C}HOH + O_2$	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>3</sub> )CHO+HO <sub>2</sub>	(375)
$HOCH_2CHOHN(CH_2OH)\dot{C}H_2+O_2$	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(376)
$HOCH_2CHOHN(CH_2OH)CH_2OO + NO$	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> Ó+NO <sub>2</sub>	(377)

The alkoxy radical formed in (377) may react with O<sub>2</sub> in a hydrogen abstraction reaction to form an amide, dissociate, or undergo 1,4- and 1,5-hydrogen shift reactions

$HOCH_2CHOHN(CH_2OH)CH_2\acute{O} + O_2$	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHO	(378)
HOCH2CHOHN(CH2OH)CH2Ó	$\xrightarrow{\Delta}$	$HOCH_2CHOH\acute{N}CH_2OH + \textbf{HCHO}$	(379a)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> CHOHN(ĊHOH)CH <sub>2</sub> OH	(379b)
	$\overset{1,4}{\longleftrightarrow}$	HOCH2Ċ(OH)N(CH2OH)CH2OH	(379c)
	$\overset{1,5}{\longleftrightarrow}$	HOĊHCHOHN(CH2OH)CH2OH	(379d)

The alkyl radicals formed in the 1,4-hydrogen shift reactions (379b) and (379c) will react with  $O_2$  in hydrogen abstraction reactions to form amides

$HOCH_2CHOHN(\dot{C}HOH)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)NCHO+HO <sub>2</sub>	(380)
$HOCH_2\dot{C}(OH)N(CH_2OH)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(O)N(CH <sub>2</sub> OH)CH <sub>2</sub> OH+HO <sub>2</sub>	(381)

The alkyl radical formed in the 1,5-hydrogen shift reaction (379d) will react with  $O_2$  in hydrogen abstraction reactions to form an aldehyde, which may undergo photolysis or reaction with OH radicals

$HO\dot{C}HCHOHN(CH_2OH)CH_2OH + O_2$	$\rightarrow$	$\mathbf{OHCCHOHN}(\mathbf{CH_2OH})\mathbf{CH_2OH} + \mathbf{HO}_2$	(382)
OHCCHOHN(CH2OH)CH2OH	$\xrightarrow{hv}$	HOĊHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH + CHO	(383)
$OHCCHOHN(CH_2OH)CH_2OH + OH$	$\rightarrow$	OĊCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH + H <sub>2</sub> O	(384)
$O\dot{C}CHOHN(CH_2OH)CH_2OH + O_2$	$\rightarrow$	ÓO(O)CCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH	(385)
ÓO(O)CCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH +NO <sub>2</sub>	$\rightarrow$	O <sub>2</sub> NOO(O)CCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH	(386)
O2NOO(O)CCHOHN(CH2OH)CH2OH	$\xrightarrow{\Delta}$	ÓO(O)CCHOHN(CH2OH)CH2OH +NO2	(387)
$OO(O)CCHOHN(CH_2OH)CH_2OH + NO$		$\acute{O}(O)$ CCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH + NO <sub>2</sub>	(388)
Ó(O)CCHOHN(CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	$HO\dot{C}HN(CH_2OH)CH_2OH + CO_2$	(389)
$HO\dot{C}HN(CH_2OH)CH_2OH + O_2$	$\rightarrow$	$CHON(CH_2OH)CH_2OH + HO_2$	(390)

The N-centered radical formed in (379a) may undergo hydrogen-abstraction by O<sub>2</sub> and NO<sub>2</sub>, or react with NO and NO<sub>2</sub> to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during <u>daytime</u> to reform the N-centered radical.

$HOCH_2CHOH\dot{N}CH_2OH + O_2$	$\rightarrow$	$\textbf{HOCH}_{2}\textbf{CHOHN}\textbf{=}\textbf{CHOH} + \textbf{HO}_{2}$	(391a)
	$\rightarrow$	$\mathbf{HOCH}_{2}\mathbf{C}(\mathbf{OH}) = \mathbf{NCH}_{2}\mathbf{OH} + \mathbf{HO}_{2}$	(391b)
$HOCH_2CHOH\acute{N}CH_2OH + NO_2$	$\rightarrow$	HOCH <sub>2</sub> CHOHN=CHOH+HONO	(392a)
	$\rightarrow$	HOCH <sub>2</sub> C(OH)=NCH <sub>2</sub> OH +HONO	(392b)
	$\rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)N-NO <sub>2</sub>	(392c)
HOCH <sub>2</sub> CHOHŃCH <sub>2</sub> OH + NO	$\rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)N-NO	(393)
HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)N-NO	$\xrightarrow{h\nu}$	HOCH <sub>2</sub> CHOHŃCH <sub>2</sub> OH + NO	(394)

HOCH <sub>2</sub> CHOHN=CHOH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> CHOHNHCHO	(395)
HOCH <sub>2</sub> C(OH)=NCH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> C(O)NHCH <sub>2</sub> OH	(396)

## 3.3.1.3 Fate of the (CH<sub>3</sub>)N(CH<sub>2</sub>ĊHOH)CH<sub>2</sub>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 (CH<sub>3</sub>)N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>Ó as HOCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>Ó

HOCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> Ó	$\xleftarrow{1,5}$	HOĊHCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	(279e)
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$HO\dot{C}HCH_2N(CH_3)CH_2OH + O_2$ —	<b>&gt;</b>	OHCCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH + HO <sub>2</sub>	(397)
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The aldehyde formed in (397) will either undergo photolysis or react with OH radicals

OHCCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$\dot{C}H_2N(CH_3)CH_2OH + CHO$	(398)
$\dot{C}H_2N(CH_3)CH_2OH+O_2$	$\rightarrow$	ÓOCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	(399)
$OOCH_2N(CH_3)CH_2OH + NO$	$\rightarrow$	ÓCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH + NO <sub>2</sub>	(400)
$OHCCH_2N(CH_3)CH_2OH + OH$	$\rightarrow$	$O\dot{C}CH_2N(CH_3)CH_2OH + H_2O$	(401)
$\dot{OCCH_2N(CH_3)CH_2OH} + O_2$	$\rightarrow$	$OO(O)CCH_2N(CH_3)CH_2OH + O_2$	(402)
$OO(O)CCH_2N(CH_3)CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NOO(O)CCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	(403)
O <sub>2</sub> NOO(O)CCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	$OO(O)CCH_2N(CH_3)CH_2OH + NO_2$	(404)
$OO(O)CCH_2N(CH_3)CH_2OH + NO$	$\rightarrow$	$\acute{O}(O)CCH_2N(CH_3)CH_2OH + NO_2$	(405)
Ó(O)CCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$\dot{C}H_2N(CH_3)CH_2OH + CO_2$	(406)
$\dot{C}H_2N(CH_3)CH_2OH+O_2$	$\rightarrow$	ÓOCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH	(407)
$OOCH_2N(CH_3)CH_2OH + NO$	$\rightarrow$	ÓCH <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> OH + NO <sub>2</sub>	(408)
$\acute{O}CH_2N(CH_3)CH_2OH + O_2$	$\rightarrow$	<b>OHCN(CH<sub>3</sub>)CH<sub>2</sub>OH</b> + HO <sub>2</sub>	(409)

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).

 $\acute{O}CH_2N(CH_3)CH_2OH \longrightarrow \acute{N}(CH_3)CH_2OH + HCHO$  (410a)

 $\xleftarrow{}^{1,4} \qquad \text{HOCH}_2\text{N}(\dot{\text{CH}}_2)\text{CH}_2\text{OH}$ (410b)

$$\xleftarrow{1.4} \text{HOCH}_2\text{N}(\text{CH}_3)\dot{\text{C}}\text{HOH}$$
(410c)

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<sub>2</sub> and subsequently end up as

 $HOCH_2N(\dot{C}H_2)CH_2OH + O_2 \rightarrow HOCH_2N(CH_2OO)CH_2OH$  (411)

$$HOCH_2N(CH_2OO)CH_2OH + NO \rightarrow HOCH_2N(CH_2O)CH_2OH + NO_2$$
 (412)



Scheme 3.7 The main routes to the atmospheric degradation of CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (MDEA) following initial hydrogen abstraction from one of the -CH<sub>2</sub>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

$HOCH_2N(CH_2\acute{O})CH_2OH + O_2$	$\rightarrow$	$(HOCH_2)_2NCHO + HO_2$	(413)
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 $HOCH_2N(CH_2\acute{O})CH_2OH \longrightarrow HOCH_2\acute{N}CH_2OH + HCHO$  (414)

$$\xleftarrow{}^{1,4} \quad \text{HOCH}_2\text{N}(\text{CH}_2\text{OH})\dot{\text{C}}\text{HOH}$$
(415)

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.

$$HOCH_2N(CH_2OH)\dot{C}HOH + O_2 \rightarrow (HOCH_2)_2NCHO + HO_2$$
 (416)

The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from one of the  $-CH_2OH$  groups are summarized in Scheme 3.7. The main products are the amides  $(CH_3)(CH_2CH_2OH)NCHO$  and  $(CH_3)(CH_2OH)NCHO$  and the PAN-like compounds  $(CH_3)(CH_2CH_2OH)NCH_2C(O)OONO_2$  and  $(CH_3)(CH_2OH)NCH_2C(O)OONO_2$ .

# 3.3.2 Fate of the CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)ĊHCH<sub>2</sub>OH radical

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

$CH_3N(CH_2CH_2OH)_2 + OH$	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NĊHCH <sub>2</sub> OH+H <sub>2</sub> O	(268b)
$CH_3(CH_2CH_2OH)N\dot{C}HCH_2OH+O_2$	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCH(OÓ)CH <sub>2</sub> OH	(417)
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCH(OÓ)CH <sub>2</sub> OH+NO	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCH(Ó)CH <sub>2</sub> OH+NO <sub>2</sub>	(418)

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.

$CH_3(CH_2CH_2OH)NCH(\acute{O})CH_2OH + O_2$	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NC(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(419)
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCH(Ó)CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	CH <sub>3</sub> ŃCH <sub>2</sub> CH <sub>2</sub> OH +CH(O)CH <sub>2</sub> OH	(420a)
	$\xrightarrow{\Delta}$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHO+CH <sub>2</sub> OH	(420b)
	$\xleftarrow{1,4}{}$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> Ó	(420c)
	$\overset{1,4}{\longleftrightarrow}$	ĊH2N(CH2CH2OH)CHOHCH2OH	(420d)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> ĊHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(420e)
	$\overset{1,5}{\longleftrightarrow}$	CH <sub>3</sub> N(CH <sub>2</sub> ĊHOH)CHOHCH <sub>2</sub> OH	(420f)

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 <u>daytime</u> to reform the N-centered radical.

$CH_3 \dot{N} CH_2 CH_2 OH + NO$	$\rightarrow$	ON-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	(421)
ON-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$CH_3\dot{N}CH_2CH_2OH + NO$	(422)
$CH_3 \acute{N} CH_2 CH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> N-N(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> OH	(423a)
	$\rightarrow$	CH <sub>2</sub> =NCH <sub>2</sub> CH <sub>2</sub> OH + HONO	(423b)
	$\rightarrow$	CH <sub>3</sub> N=CHCH <sub>2</sub> OH + HONO	(423c)
$CH_3 \acute{N} CH_2 CH_2 OH + O_2$	$\rightarrow$	$CH_2 = NCH_2CH_2OH + HO_2$	(424a)
	$\rightarrow$	CH <sub>3</sub> N=CHCH <sub>2</sub> OH + HO <sub>2</sub>	(424b

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

$CH_2 = NCH_2CH_2OH + OH$	$\rightarrow$	HOCH2ŃCH2CH2OH	(425)
HOCH <sub>2</sub> ŃCH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{1,3}$	ÓCH2NH(CH2CH2OH)	(426)
$\acute{O}CH_2NH(CH_2CH_2OH) + O_2$	$\rightarrow$	$\mathbf{CHONH}(\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{OH}) + \mathrm{HO}_{2}$	(427)
$HOCH_2 \dot{N}CH_2 CH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CH <sub>2</sub> CH <sub>2</sub> OH	(428)
ONN(CH <sub>2</sub> OH)CH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$OCH_2 \dot{N}CH_2 CH_2 OH + NO$	(429)

$HOCH_2 \acute{N}CH_2 CH_2 OH + NO_2$	$\rightarrow$	O2NN(CH2OH)CH2CH2OH	(430a)
	$\rightarrow$	$HOCH=NCH_2CH_2OH + HONO$	(430b)
	$\rightarrow$	$HOCH_2N=CHCH_2OH + HONO$	(430c)
$HOCH_2 \acute{N}CH_2 CH_2 OH + O_2$	$\rightarrow$	$\textbf{HOCH=NCH}_2\textbf{CH}_2\textbf{OH} + HO_2$	(431a)
	$\rightarrow$	$HOCH_2N=CHCH_2OH + HO_2$	(431b)
HOCH=NCH2CH2OH	$\xrightarrow{1,3}$	CHONH(CH <sub>2</sub> CH <sub>2</sub> OH)	(432)
$HOCH_2N=CHCH_2OH + OH$	$\rightarrow$	HOCH2ŃCH(OH)CH2OH	(433)
HOCH2ŃCH(OH)CH2OH	$\xrightarrow{1,3}$	ÓCH2NHCH(OH)CH2OH	(434)
$\acute{O}CH_2NHCH(OH)CH_2OH + O_2$	$\rightarrow$	<b>CHONHCH(OH)CH<sub>2</sub>OH</b> + $HO_2$	(435)
$HOCH_2\dot{N}CH(OH)CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CH(OH)CH <sub>2</sub> OH	(436)
ONN(CH <sub>2</sub> OH)CH(OH)CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$HOCH_2 NCH(OH)CH_2OH + NO$	(437)
$HOCH_2 \dot{N}CH(OH)CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CH(OH)CH <sub>2</sub> OH	(438a)
	$\rightarrow$	HOCH=NCH(OH)CH <sub>2</sub> OH+HONO	(438b)
	$\rightarrow$	HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH +HONO	(438c)
$HOCH_2 \acute{N}CH(OH)CH_2OH + O_2$	$\rightarrow$	$HOCH=NCH(OH)CH_2OH + HO_2$	(439a)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HO_2$	(439b)
HOCH=NCH(OH)CH2OH	$\xrightarrow{1,3}$	CHONHCH(OH)CH <sub>2</sub> OH	(440)
HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CHON(CH <sub>2</sub> OH) <sub>2</sub>	(441)

The imine formed in (423c) and (424b) is expected to undergo the following reactions  $% \left( \frac{1}{2} \right) = 0$ 

CH <sub>3</sub> N=CHCH <sub>2</sub> OH + OH	$\rightarrow$	CH₃ŃCHOHCH₂OH	(442)
CH <sub>3</sub> ŃCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	CH <sub>3</sub> NHCH(Ó)CH <sub>2</sub> OH	(443)
$CH_3NHCH(O)CH_2OH + O_2$	$\rightarrow$	$\mathbf{CH_3NHC}(\mathbf{O})\mathbf{CH_2OH} + \mathbf{O}_2$	(444)
CH <sub>3</sub> ŃCHOHCH <sub>2</sub> OH + NO	$\rightarrow$	ONN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(445)
ONN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xrightarrow{hv}$	CH <sub>3</sub> ŃCHOHCH <sub>2</sub> OH + NO	(446)
$CH_3$ ŃCHOHCH_2OH + NO_2	$\rightarrow$	O <sub>2</sub> NN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(447a)
	$\rightarrow$	CH <sub>3</sub> N=C(OH)CH <sub>2</sub> OH + HONO	(447b)
	$\rightarrow$	CH <sub>2</sub> =NCHOHCH <sub>2</sub> OH + HONO	(447c)
$CH_3\dot{N}CHOHCH_2OH + O_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(448a)
	$\rightarrow$	$CH_3N=C(OH)CH_2OH + HO_2$	(448b)
	$\rightarrow$	CH <sub>2</sub> =NCHOHCH <sub>2</sub> OH + HO <sub>2</sub>	(448c)
CH <sub>3</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CH <sub>3</sub> (H)NC(O)CH <sub>2</sub> OH	(449)
CH <sub>2</sub> =NCHOHCH <sub>2</sub> OH + OH	$\rightarrow$	HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH	(450)
HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	ÓCH2N(H)CHOHCH2OH	(451)
ÓCH <sub>2</sub> N(H)CHOHCH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	<b>CHON(H)CHOHCH<sub>2</sub>OH</b> + HO <sub>2</sub>	(452)

# 3.3.2.1 Fate of the CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CHOHCH<sub>2</sub>Ó radical

We will first consider 1,4-hydrogen shift (420c) within the  $-CH(O)-CH_2OH$  moiety.

CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCH(Ó)CH <sub>2</sub> OH	$\xleftarrow{1,4}$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHCH <sub>2</sub> Ó	(420c)
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHCH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NĊHOH + HCHO	(453)
$CH_3(CH_2CH_2OH)N\dot{C}HOH+O_2$	$\rightarrow$	<b>CH<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>OH)NCHO</b> + HO <sub>2</sub>	(454)
$CH_{3}N(CH_{2}CH_{2}OH)CHOHCH_{2}\acute{O}+O_{2}$	$\rightarrow$	$\textbf{CH}_{\textbf{3}}\textbf{N}(\textbf{CH}_{\textbf{2}}\textbf{CH}_{\textbf{2}}\textbf{OH})\textbf{CHOHCHO} + \textbf{HO}_{2}$	(455)
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHCHO	$\xrightarrow{h_{V}}$	CHN(CH <sub>2</sub> CH <sub>2</sub> OH)NĊHOH + CHO	(456)
$CH_3(CH_2CH_2OH)N\dot{C}HOH+O_2$	$\rightarrow$	$\mathbf{CH}_{3}(\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{OH})\mathbf{NCHO} + \mathbf{HO}_{2}$	(457)
$CH_3(CH_2CH_2OH)NCHOHCHO + OH$	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHĊO + H <sub>2</sub> O	(458)
$CH_3N(CH_2CH_2OH)CHOH\dot{C}O+O_2$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHC(O)OÓ	(459)
$CH_3(CH_2CH_2OH)NCHOHC(O)O\acute{O}+NO_2$	$\rightarrow$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHC(O)OÓNO <sub>2</sub>	(460)
H <sub>3</sub> C(CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHC(O)OÓNO <sub>2</sub>	$\xrightarrow{\Delta}$	CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHC(O)OÓ+NO <sub>2</sub>	(461)
CH <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> OH)NCHOHC(O)OÓ+NO	$\rightarrow$	$CH_3(CH_2CH_2OH)N\dot{C}HOH+CO_2+NO_2$	(462)
$CH_3(CH_2CH_2OH)N\dot{C}HOH+O_2$	$\rightarrow$	<b>CH<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>OH)NCHO</b> + HO <sub>2</sub>	(463)

# 3.3.2.2 Fate of the CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CHOHCH<sub>2</sub>OH radical

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

CH <sub>3</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH(Ó)CH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	ĊH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(420d)
$\dot{C}H_2N(CH_2CH_2OH)CHOHCH_2OH+O_2$	$\rightarrow$	ÓOCH2N(CH2CH2OH)CHOHCH2OH	(464)
ÓOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+NO	$\rightarrow$	ÓCH2N(CH2CH2OH)CHOHCH2OH+NO2	(465)

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

ÓCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+O <sub>2</sub>	$\rightarrow$	CH(O)N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(466)
ÓCH2N(CH2CH2OH)CHOHCH2OH	$\xrightarrow{\Delta}$	$\acute{\mathrm{N}}(\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{OH})\mathrm{CHOHCH}_{2}\mathrm{OH}+\mathbf{HCHO}$	(467a)
	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(CHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(467b)
	$\xleftarrow{1,4}$	ÓCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)ĊOHCH <sub>2</sub> OH	(467c)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> ĊHOH)CHOHCH <sub>2</sub> OH	(467d)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHĊHOH	(467e)

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 <u>daytime</u> to reform the N-centered radical.

$HOCH_2CH_2\dot{N}CHOHCH_2OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(468)
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59)
Da)
)b)
)c)
la)
lb)
72)

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

HOCH <sub>2</sub> CH=NCHOHCH <sub>2</sub> OH+OH	$\rightarrow$	Ń(CHOHCH <sub>2</sub> OH) <sub>2</sub>	(473)
$\dot{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + NO	$\rightarrow$	ONN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	(474)
ONN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	$\xrightarrow{h_{\mathcal{V}}}$	$\dot{N}(CHOHCH_2OH)_2 + NO$	(475)
$\acute{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + NO <sub>2</sub>	$\rightarrow$	O <sub>2</sub> NN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	(476a)
	$\rightarrow$	HOCH <sub>2</sub> C(OH)=NCHOHCH <sub>2</sub> OH+HONO	(476b)
$\dot{N}(CHOHCH_2OH)_2 + O_2$	$\rightarrow$	HOCH <sub>2</sub> C(OH)=NCHOHCH <sub>2</sub> OH + HO <sub>2</sub>	(477)
HOCH <sub>2</sub> C(OH)=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> C(O)NHCHOHCH <sub>2</sub> OH	(478)

The alkyl radical formed in (467b) will first add  $O_2$  and subsequently form an alkoxy radical, which may react with  $O_2$  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.

ÓCH2N(CH2CH2OH)CHOHCH2OH	$\xleftarrow{1,4}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(467b)
$HOCH_2N(\dot{C}HCH_2OH)CHOHCH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH(OÓ)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(479)
HOCH <sub>2</sub> N(CH(OÓ)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+NO	$\rightarrow$	HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+NO <sub>2</sub>	(480)
HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+O <sub>2</sub>	$\rightarrow$	$HOCH_2C(O)N(CH_2OH)CHOHCH_2OH + HO_2$	(481)
HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH + CHOCH <sub>2</sub> OH	(482a)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> Ó)CHOHCH <sub>2</sub> OH	(482b)
	$\xleftarrow{1,4}$	HOĊHN(CHOHCH2OH)CHOHCH2OH	(482c)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)ĊOHCH <sub>2</sub> OH	(482d)
	$\overset{1,5}{\longleftrightarrow}$	ÓCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(482e)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHĊHOH	(482f)

The N-centered radical formed in (482a) 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 <u>daytime</u> to reform the N-centered radical.

$HOCH_2 NCHOHCH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(483)
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ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{h_{V}}$	$HOCH_2 \dot{N}CHOHCH_2 OH + NO$	(484)
$HOCH_2 \dot{N}CHOHCH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(485)
	$\rightarrow$	HOCH=NCHOHCH <sub>2</sub> OH + HONO	
	$\rightarrow$	HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH + HONO	
$HOCH_2 \dot{N}CHOHCH_2 OH + O_2$	$\rightarrow$	$\textbf{HOCH=NCHOHCH}_2\textbf{OH} + HO_2$	(486)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HO_2$	
HOCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	<b>CHONHCHOHCH<sub>2</sub>OH</b>	(487)
HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHC(O)CH <sub>2</sub> OH	(488)

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

$HOCH_2N(CHOHCH_2\acute{O})CHOHCH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCHO)CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(489)
HOCH <sub>2</sub> N(CHOHCHO)CHOHCH <sub>2</sub> OH	$\xrightarrow{h\nu}$	HOCH <sub>2</sub> N(ĊHOH)CHOHCH <sub>2</sub> OH + CHO	(490)
$\textbf{HOCH}_2\textbf{N}\textbf{(CHOHCHO)CHOHCH}_2\textbf{OH} + \textbf{OH}$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHĊO + H <sub>2</sub> O	(491)
$HOCH_2N(CHOHCH_2OH)CHOH\dot{C}O + O_2$	$\rightarrow$	HOCH2N(CHOHCH2OH)CHOHC(O)OÓ	(492)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ+NO <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓNO <sub>2</sub>	(493)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓNO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ+NO <sub>2</sub>	(494)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ+NO	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)Ó+NO <sub>2</sub>	(495)
HOCH2N(CHOHCH2OH)CHOHC(O)Ó	$\overset{\Delta}{\longrightarrow}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)ĊHOH + CO <sub>2</sub>	(496)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> Ó)CHOHCH <sub>2</sub> OH	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(ĊHOH)CHOHCH <sub>2</sub> OH + <b>HCHO</b>	(497)
$HOCH_2N(\dot{C}HOH)CHOHCH_2OH + O_2$	$\rightarrow$	<b>CHON(CH<sub>2</sub>OH)CHOHCH<sub>2</sub>OH</b> + HO <sub>2</sub>	(498)

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

HOĊHN(CHOHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+O <sub>2</sub> →	$\mathbf{CHON}(\mathbf{CHOHCH}_{2}\mathbf{OH})_{2} + \mathrm{HO}_{2}$	(499)
$HOCH_2N(CHOHCH_2OH)\dot{C}OHCH_2OH+O_2 \rightarrow$	HOCH <sub>2</sub> (CHOHCH <sub>2</sub> OH)NC(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(500)

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 <u>daytime</u> to reform the N-centered radical.

$OCH_2N(CHOHCH_2OH)CHOHCH_2OH + O_2$	$\rightarrow$	$\mathbf{CHON}(\mathbf{CHOHCH}_{2}\mathbf{OH})_{2} + \mathrm{HO}_{2}$	(501)
ÓCH2N(CHOHCH2OH)CHOHCH2OH	$\xrightarrow{\Delta}$	$\dot{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + <b>HCHO</b>	(502)
$\dot{N}(CHOHCH_2OH)_2 + NO$	$\rightarrow$	ONN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	(503)
ONN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	$\xrightarrow{h\nu}$	$\dot{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + NO	(504)
$\dot{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + NO <sub>2</sub>	$\rightarrow$	O <sub>2</sub> NN(CHOHCH <sub>2</sub> OH) <sub>2</sub>	(505)
	$\rightarrow$	HOCH <sub>2</sub> C(OH)=ŃCHOHCH <sub>2</sub> OH +HONO	

$\dot{N}(CHOHCH_2OH)_2 + O_2$	$\rightarrow$	$\mathbf{HOCH_2C(OH)=} \mathbf{\acute{N}CHOHCH_2OH} + \mathrm{HO}_2$	(506)
HOCH <sub>2</sub> C(OH)=ŃCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH₂C(O)ŃHCHOHCH₂OH	(507)

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:

$HOCH_2N(CHOHCH_2OH)CHOH\dot{C}HOH + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHCHO+HO <sub>2</sub>	(508)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHCHO	$\xrightarrow{h\nu}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)ĊHOH + CHO	(509)
$HOCH_2N(CHOHCH_2OH)CHOHCHO + OH$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHĊO + H <sub>2</sub> O	(510)
$HOCH_2N(CHOHCH_2OH)CHOH\dot{C}O + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ	(511)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ+NO <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	(512)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)OÓ+NO <sub>2</sub>	(513)
HOCH2N(CHOHCH2OH)CHOHC(O)OÓ+NO	$\rightarrow$	$HOCH_2N(CHOHCH_2OH)CHOHC(O)O' + NO_2$	(514)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CHOHC(O)Ó	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)ĊHOH + CO <sub>2</sub>	(515)
$HOCH_2N(CHOHCH_2OH)\dot{C}HOH + O_2$	$\rightarrow$	HOCH <sub>2</sub> (CHOHCH <sub>2</sub> OH)NCHO + HO <sub>2</sub>	(516)

## 3.3.2.3 Fate of the HOCH<sub>2</sub>ĊHN(CH<sub>3</sub>)CHOHCH<sub>2</sub>OH radical

The third 1,4-hydrogen shift reaction of the alkoxy radical formed in (418) involves the other ethanol group.<sup>#</sup> 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

HOCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )CH(Ó)CH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> ĊHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(420e)
$HOCH_2\dot{C}HN(CH_3)CHOHCH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> CH(OÓ)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(517)
HOCH <sub>2</sub> CH(OÓ)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH+NO	$\rightarrow$	HOCH <sub>2</sub> CH(Ó)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH+NO <sub>2</sub>	(518)
$HOCH_2CH(\acute{O})N(CH_3)CHOHCH_2OH+O_2$	$\rightarrow$	HOCH <sub>2</sub> C(O)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(519)
HOCH <sub>2</sub> CH(Ó)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	Ń(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + HOCH <sub>2</sub> CHO	(520a)
	$\xrightarrow{\Delta}$	CH(O)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + CH <sub>2</sub> OH	(520b)
	$\overset{1,4}{\longleftrightarrow}$	ÓCH2CHOHN(CH3)CHOHCH2OH	(520c)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> CHOHN(ĊH <sub>2</sub> )CHOHCH <sub>2</sub> OH	(520d)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> CHOHN(CH <sub>3</sub> )ĊOHCH <sub>2</sub> OH	(520e)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> CHOHN(CH <sub>3</sub> )CHOĊHOH	(520f)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> CHOHN(CH <sub>3</sub> )CHÓHCHOH	(520g)

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 <u>daytime</u> to

<sup>&</sup>lt;sup>#</sup> For the sake of readability we re-write  $CH_3N(CH_2CH_2OH)CH(\acute{O})CH_2OH$  as  $HOCH_2CH_2N(CH_3)CH(\acute{O})CH_2OH$ 

$ \dot{N}(CH_3)CHOHCH_2OH + NO $	$\rightarrow$	ON-N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(521)
ONN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xrightarrow{hv}$	$\dot{N}(CH_3)CHOHCH_2OH + NO$	(522)
$\acute{N}(CH_3)CHOHCH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> N-N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(523a)
	$\rightarrow$	CH <sub>2</sub> =NCHOHCH <sub>2</sub> OH + HONO	(523c)
	$\rightarrow$	CH <sub>3</sub> N=C(OH)CH <sub>2</sub> OH + HONO	(523c)
$\dot{N}(CH_3)CHOHCH_2OH + O_2$	$\rightarrow$	$\mathbf{CH}_2 \texttt{=} \mathbf{NCHOHCH}_2\mathbf{OH} + \mathbf{HO}_2$	(524a)
	$\rightarrow$	$\mathbf{CH_3N=C(OH)CH_2OH} + \mathbf{HO}_2$	(524b)
CH <sub>3</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CH <sub>3</sub> NHC(O)CH <sub>2</sub> OH	(525)
$\textbf{CH}_2 = \textbf{NCHOHCH}_2\textbf{OH} + \textbf{O}_3$	$\rightarrow$	$O_2NCHOHCH_2OH + HCHO$	(526)
$\mathbf{CH}_2 \texttt{=} \mathbf{NCHOHCH}_2\mathbf{OH} + \mathbf{OH}$	$\rightarrow$	$HOCH_2 \dot{N}CHOHCH_2 OH + H_2 O$	(527)
$HOCH_2 \acute{N}CHOHCH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(528)
ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{h_{V}}$	$HOCH_2 \dot{N}CHOHCH_2 OH + NO$	(529)
$HOCH_2 \acute{N}CHOHCH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(530a)
	$\rightarrow$	HOCH=NCHOHCH <sub>2</sub> OH+HONO	(530b)
	$\rightarrow$	HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH+HONO	(530c)
$HOCH_2 \acute{N}CHOHCH_2 OH + O_2$	$\rightarrow$	$\textbf{HOCH=NCHOHCH}_2\textbf{OH} + HO_2$	(531a)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HO_2$	(531b)
HOCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	<b>CHONHCHOHCH<sub>2</sub>OH</b>	(532)
HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NC(O)CH <sub>2</sub> OH	(533)

reform the N-centered radical. The imines formed are assumes 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  $O_2$  in a hydrogen abstraction reaction leading to an aldehyde, which may then undergo photolysis or hydrogen abstraction by OH

ÓCH2CHOHN(CH3)CHOHCH2OH	$\xrightarrow{\Delta}$	$\dot{C}HOHN(CH_3)CHOHCH_2OH + HCHO$	(534)
$OCH_2CHOHN(CH_3)CHOHCH_2OH + O_2$	$\rightarrow$	OHCCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(535)
OHCCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xrightarrow{h_{V}}$	ĊHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + CHO	(536)
$OHCCHOHN(CH_3)CHOHCH_2OH + OH$	$\rightarrow$	OĊCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + H <sub>2</sub> O	(537)
OĊCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	ÓO(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	(538)
ÓO(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH +NO <sub>2</sub>	$\rightarrow$	O2NÓO(O)CCHOHN(CH3)CHOHCH2OH	(539)
O <sub>2</sub> NÓO(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xrightarrow{\Delta}$	ÓO(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH +NO <sub>2</sub>	(540)
$OO(O)CCHOHN(CH_3)CHOHCH_2OH + NO$	$\rightarrow$	Ó(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + NO <sub>2</sub>	(541)
Ó(O)CCHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	ĊHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + CO <sub>2</sub>	(542)
ĊHOHN(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	CHON(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH + HO <sub>2</sub>	(543)

The alkyl radical formed in the 1,4-hydrogen shift reaction (520d) will first add  $O_2$  and subsequently become an alkoxy radical, which may react with  $O_2$  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.

HOCH <sub>2</sub> CH(Ó)N(CH <sub>3</sub> )CHOHCH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> CHOHN(ĊH <sub>2</sub> )CHOHCH <sub>2</sub> OH	(520d)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> )CHOHCH <sub>2</sub> OH+O <sub>2</sub>	$\rightarrow$	HOCH2CHOHN(CH2OÓ)CHOHCH2OH	(544)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OÓ)CHOHCH <sub>2</sub> OH+NO	$\rightarrow$	HOCH2CHOHN(CH2Ó)CHOHCH2OH+NO2	(545)
$HOCH_2CHOHN(CH_2\acute{O})CHOHCH_2OH+O_2$	$\rightarrow$	<b>CHON(CHOHCH<sub>2</sub>OH)</b> <sub>2</sub> + HO <sub>2</sub>	(546a)
	$\xrightarrow{\Delta}$	$\dot{N}$ (CHOHCH <sub>2</sub> OH) <sub>2</sub> + <b>HCHO</b>	(546b)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)ĊOHCH <sub>2</sub> OH	(546c)
	$\xleftarrow{1,5}$	HOCH2CHOHN(CH2OH)CHÓCH2OH	(546d)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHĊHOH	(546e)

The reactions of the N-centered radical  $\dot{N}$ (CHOHCH<sub>2</sub>OH)<sub>2</sub> 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<sub>2</sub> to form an amide. The same reaction applies to the alkoxy radical formed in the 1,5hydrogen shift reaction (546d).

$HOCH_2CHOHN(CH_2OH)\dot{C}OHCH_2OH+O_2 \rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)NC(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(547)
$HOCH_2CHOHN(CH_2OH)CHOCH_2OH+O_2 \rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)NC(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(548)

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

$HOCH_{1}CHOHN(CH_{1}OH)CHOHCHOH + O_{2}$	_	HOCH.CHOHN(CH.OH)CHOHCHO+HO.	(549)
hoen2enonik(en2on)enonenoni + 02	$\rightarrow$		(34))
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHCHO	$\xrightarrow{h\nu}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)ĊHOH + CHO	(550)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHCHO +OH	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHĊO + H <sub>2</sub> O	(551)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHĊO + O <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)OÓ	(552)
HOCH2CHOHN(CH2OH)CHOHC(O)OÓ+NO2	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	(553)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)OÓ+NO <sub>2</sub>	(554)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)OÓ+NO	$\rightarrow$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)CHOHC(O)Ó+NO <sub>2</sub>	(555)
HOCH2CHOHN(CH2OH)CHOHC(O)Ó	$\overset{\Delta}{\longrightarrow}$	HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)ĊHOH + CO <sub>2</sub>	(556)
HOCH <sub>2</sub> CHOHN(CH <sub>2</sub> OH)ĊHOH + O <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> CHOH(CH <sub>2</sub> OH)NCHO + HO <sub>2</sub>	(557)

# 3.3.2.4 Fate of the CH<sub>3</sub>N(CH<sub>2</sub>ĊHOH)CHOHCH<sub>2</sub>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.

 $CH_{3}N(CH_{2}CH_{2}OH)CH(\acute{O})CH_{2}OH \xleftarrow{1.5} CH_{3}N(CH_{2}\dot{C}HOH)CHOHCH_{2}OH$ (420f)

$\rightarrow$	$\mathbf{CH_{3}N(CH_{2}CHO)CHOHCH_{2}OH} + \mathbf{HO}_{2}$	(558)
$\xrightarrow{hv}$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)ĊH <sub>2</sub> + CHO	(559)
$\rightarrow$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(560)
$\rightarrow$	$CH_3N(CHOHCH_2OH)CH_2\acute{O} + NO_2$	(561)
$\rightarrow$	$CH_3N(CHOHCH_2OH)CH_2C\acute{O} + H_2O$	(562)
$\rightarrow$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ	(563)
$\rightarrow$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	(564)
$\xrightarrow{\Delta}$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ+NO <sub>2</sub>	(565)
$\rightarrow$	$CH_3N(CHOHCH_2OH)CH_2C(O)\acute{O} + NO_2$	(566)
$\xrightarrow{\Delta}$	$CH_3N(CHOHCH_2OH)\dot{C}H_2 + CO_2$	(567)
$\rightarrow$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(568)
$\rightarrow$	$CH_3N(CHOHCH_2OH)CH_2OH + NO_2$	(569)
	$ \begin{array}{c} \rightarrow \\ & \stackrel{h\nu}{\longrightarrow} \\ \rightarrow \\ $	$\rightarrow$ CH <sub>3</sub> N(CH <sub>2</sub> CHO)CHOHCH <sub>2</sub> OH) $\dot{C}$ H <sub>2</sub> OH $h\nu$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH) $\dot{C}$ H <sub>2</sub> + CHO $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ + NO <sub>2</sub> $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ + H <sub>2</sub> OO $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CO)OÓ $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CO)OÓ $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CO)OÓ + NO <sub>2</sub> $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CO)Ó + NO <sub>2</sub> $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CO)Ó + NO <sub>2</sub> $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÚ $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÚ $\rightarrow$ CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÚ

The alkoxy radical formed in (561) and (569) may react with  $O_2$  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  $O_2$  and the 1,5-hydrogen shift reactions. The same is expected for the 1,4-hydrogen shift reactions.

$CH_3N(CHOHCH_2OH)CH_2\acute{O} + O_2$	$\rightarrow$	CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CHO+HO <sub>2</sub>	(570)
CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	$CH_{3}\acute{N}CHOHCH_{2}OH + \textbf{HCHO}$	(571a)
	$\xleftarrow{1,4}$	ĊH2N(CHOHCH2OH)CH2OH	(571b)
	$\xleftarrow{1,4}$	CH <sub>3</sub> N(ĊOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(571c)
	$\xleftarrow{1,5}$	CH <sub>3</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	(571d)
	$\xleftarrow{1,5}$	CH <sub>3</sub> N(CHOHĊHOH)CH <sub>2</sub> OH	(571e)

The amide formed in (570), CH<sub>3</sub>N(CHOHCH<sub>2</sub>OH)CHO, has an activated >CHOH group which is expected to react relatively fast with OH radicals:

$CH_3N(CHOHCH_2OH)CHO + OH$	$\rightarrow$	$CH_3N(\dot{C}OHCH_2OH)CHO + H_2O$	(572)
$CH_{3}N(\dot{C}OHCH_{2}OH)CHO+O_{2}$	$\rightarrow$	$CH_3N(C(O)CH_2OH)CHO + HO_2$	(573)

The N-centered radical formed in (571a) 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 <u>daytime</u> 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  $O_2$  and subsequently become a new alkoxy radical, which may react with  $O_2$  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  $\dot{C}H_2N(CHOHCH_2OH)_2$  formed in (520d), see page 65, and  $\dot{C}H_2N(CHOHCH_2OH)CH_2CH_2OH$  formed in (420d), see page 60, and are at present not be 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

CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\overset{1,5}{\longleftrightarrow}$	CH <sub>3</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	(571d)
$CH_3N(CHO{CH_2OH})CH_2OH + O_2$	$\rightarrow$	CH <sub>3</sub> N(C(O)CH <sub>2</sub> OH)CH <sub>2</sub> OH+HO <sub>2</sub>	(574)
CH <sub>3</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	CH <sub>3</sub> (CH <sub>2</sub> OH)NCHO + CH <sub>2</sub> OH	(575a)
	$\xrightarrow{\Delta}$	$CH_3 \acute{N} CH_2 OH + CHOCH_2 OH$	(575b)

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 <u>daytime</u> to reform the N-centered radical.

$CH_3\dot{N}CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>3</sub> )CH <sub>2</sub> OH	(576)
ONN(CH <sub>3</sub> )CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$CH_3\dot{N}CH_2OH + NO$	(577)
$CH_3 \acute{N} CH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>3</sub> )CH <sub>2</sub> OH	(578a)
	$\rightarrow$	CH <sub>2</sub> =NCH <sub>2</sub> OH + HONO	(578b)
	$\rightarrow$	CH <sub>3</sub> N=CHOH + HONO	(578c)
$CH_3\dot{N}CH_2OH + O_2$	$\rightarrow$	$CH_2 = NCH_2OH + HO_2$	(579a)
	$\rightarrow$	$CH_3N=CHOH + HO_2$	(579b)
CH <sub>3</sub> N=CHOH	$\xrightarrow{1,3}$	CH <sub>3</sub> NHCHO	(580)
CH <sub>2</sub> =NCH <sub>2</sub> OH + OH	$\rightarrow$	HOCH <sub>2</sub> NCH <sub>2</sub> OH	(581)
HOCH <sub>2</sub> ŃCH <sub>2</sub> OH	$\xrightarrow{1,3}$	ÓCH2NHCH2OH	(582)
$\acute{O}CH_2NCH_2OH + O_2$	$\rightarrow$	$CHONHCH_2OH + HO_2$	(583)

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 aldehydig hydrogen abstraction.

CH <sub>3</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xleftarrow{1,5}$	CH <sub>3</sub> N(CHOHĊHOH)CH <sub>2</sub> OH	(571e)
$CH_{3}N(CHOH\dot{C}HOH)CH_{2}OH+O_{2}$	$\rightarrow$	$CH_3N(CHOHCHO)CH_2OH + HO_2$	(584)
CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHCHO	$\xrightarrow{h\nu}$	CH <sub>3</sub> N(CH <sub>2</sub> OH)ĊHOH + CHO	(585)
$CH_3N(CH_2OH)CHOHCHO + OH$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHĊO + H <sub>2</sub> O	(586)
$CH_3N(CH_2OH)CHOH\dot{C}O+O_2$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHC(O)OÓ	(587)
$CH_3N(CH_2OH)CHOHC(O)OOO + NO_2$	$\rightarrow$	CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	(588)
CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	CH <sub>3</sub> N(CH <sub>2</sub> OH)CHOHC(O)OÓ +NO <sub>2</sub>	(589)
$CH_3N(CH_2OH)CHOHC(O)OOO + NO$	$\rightarrow$	$CH_3N(CH_2OH)CHOHC(O)OOO + NO_2$	(590)

$$CH_{3}N(CH_{2}OH)CHOHC(O)\acute{O} \xrightarrow{\Delta} CH_{3}N(CH_{2}OH)\dot{C}HOH + CO_{2}$$
(591)

$$CH_{3}N(CH_{2}OH)\dot{C}HOH+O_{2} \rightarrow CH_{3}(CH_{2}OH)NCHO+HO_{2}$$
(592)

The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from one of the -CH<sub>2</sub>-(CH<sub>2</sub>OH) groups are summarized in Scheme main products 3.8. The are the amides (CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH)NC(O)CH<sub>2</sub>OH, (CH<sub>3</sub>)(CH<sub>2</sub>OH)NC(O)CH<sub>2</sub>OH, (CH<sub>3</sub>)(CHOHCH<sub>2</sub>OH)NCHO, (CH<sub>3</sub>)(C(O)CH<sub>2</sub>OH)NCHO and (CH<sub>3</sub>)(CH<sub>2</sub>OH)NCHO. Two **PAN-like** compounds (CH<sub>3</sub>)(CHOHCH<sub>2</sub>OH)NCH<sub>2</sub>C(O)OONO<sub>2</sub> and (CH<sub>3</sub>)(CH<sub>2</sub>OH)NCHOHC(O)OONO<sub>2</sub> are expected as intermediates. In addition, two thermal dissociation reactions leading to N-based radicals are expected to be relevant: (I) N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH and (II) N(CH<sub>3</sub>)CH<sub>2</sub>OH. The atmospheric reactions of these radicals leads to nitrosamines such as ONN(CH<sub>3</sub>)CH<sub>2</sub>OH and ONN(CH<sub>2</sub>OH)<sub>2</sub> as well as the corresponding nitramines and to CH<sub>3</sub>NHCHO (Nmethyl-formamide) and (CH<sub>2</sub>OH)NHCHO N-hydroxymethyl-formamide.



Scheme 3.8. The main routes to the atmospheric degradation of CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (MDEA) following initial hydrogen abstraction from one of the –CH<sub>2</sub>-(CH<sub>2</sub>OH) groups. The further atmospheric reactions of the N-centered radicals N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH (I) and N(CH<sub>3</sub>)CH<sub>2</sub>OH (II) are discussed in the text.
#### 3.3.3 Fate of the CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> radical

The first steps following hydrogen abstraction from the CH<sub>3</sub>-group in MDEA are expected to be:

$\rightarrow$	$\dot{C}H_2N(CH_2CH_2OH)_2 + H_2O$	(268c)
$\rightarrow$	ÓOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	(593)
$\rightarrow$	$\acute{O}CH_2N(CH_2CH_2OH)_2 + NO_2$	(594)
$\rightarrow$	$OHCNCHOHCH_2OH + HO_2$	(595)
$\xrightarrow{\Delta}$	$\acute{N}(CH_2CH_2OH)_2 + HCHO$	(596a)
$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)ĊHCH <sub>2</sub> OH	(596b)
$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> ĊHOH	(596c)
	$ \begin{array}{c} \rightarrow \\ \rightarrow \\ \rightarrow \\ \hline \rightarrow \\ \hline \rightarrow \\ \hline \leftarrow \\ \downarrow \downarrow$	$ \rightarrow \dot{C}H_2N(CH_2CH_2OH)_2 + H_2O  \rightarrow \dot{O}OCH_2 N(CH_2CH_2OH)_2  \rightarrow \dot{O}CH_2N(CH_2CH_2OH)_2 + NO_2  \rightarrow OHCNCHOHCH_2OH + HO_2  \rightarrow \dot{N}(CH_2CH_2OH)_2 + HCHO  \leftarrow 1.4 + HOCH_2N(CH_2CH_2OH)\dot{C}HCH_2OH  \leftarrow 1.5 + HOCH_2N(CH_2CH_2OH)CH_2\dot{C}HOH $

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 <u>daytime</u> to reform the N-centered radical.

$N(CH_2CH_2OH)_2 + NO$	$\rightarrow$	ONN(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	(597)
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ONN(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	$\xrightarrow{h\nu}$	$\dot{N}(CH_2CH_2OH)_2 + NO$	(598)
	,		

 $\dot{N}(CH_2CH_2OH)_2 + NO_2 \rightarrow O_2NN(CH_2CH_2OH)_2$ (599a)

	$\rightarrow$	$HOCH_2CH=NCH_2CH_2OH + HONO$	(599b)
$\dot{N}(CH_2CH_2OH)_2 + O_2$	$\rightarrow$	$HOCH_2CH=NCH_2CH_2OH + HO_2$	(600)

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

$HOCH_2CH=NCH_2CH_2OH + OH$	$\rightarrow$	HOCH <sub>2</sub> CHOH-NCH <sub>2</sub> CH <sub>2</sub> OH	(601)
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HOCH <sub>2</sub> CHOH-NCH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> CHONH(CH <sub>2</sub> CH <sub>2</sub> OH)	(602)
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$HOCH_2CHONH(CH_2CH_2OH) + O_2$	$\rightarrow$	$HOCH_2CONH(CH_2CH_2OH) + HO_2$	(603)
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#### **3.3.3.1** Fate of the HOCH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)ĊHCH<sub>2</sub>OH radical

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

ÓCH2N(CH2CH2OH)2	$\xleftarrow{1,4}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)ĊHCH <sub>2</sub> OH	(596b)
$HOCH_2N(CH_2CH_2OH)\dot{C}HCH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH(OÓ)CH <sub>2</sub> OH	(604)
HOCH2N(CH2CH2OH)CH(OÓ)CH2OH+NO	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH+NO <sub>2</sub>	(605)
$HOCH_2N(CH_2CH_2OH)CH\acute{O}CH_2OH+O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)C(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(606)

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  $O_2$  and the 1,5-hydrogen shift reactions to be important:

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH	$\overset{\Delta}{\longrightarrow}$	$HOCH_2 \acute{N}CH_2 CH_2 OH + CHOCH_2 OH$	(607a)
	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHO +CH <sub>2</sub> OH	(607b)
	$\xleftarrow{1,4}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> Ó	(607c)
	$\overset{1,4}{\longleftrightarrow}$	HOHĊ-N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(607d)
	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(607e)
	$\overset{1,5}{\longleftrightarrow}$	HOCH <sub>2</sub> N(CH <sub>2</sub> ĊHOH)CHOHCH <sub>2</sub> OH	(607f)
	$\overset{1,5}{\longleftrightarrow}$	ÓCH2N(CH2CH2OH)CHOHCH2OH	(607g)

The N-centered radical formed in (607a) 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 <u>daytime</u> to reform the N-centered radical.

$HOCH_2\dot{N}CH_2CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)(CH <sub>2</sub> CH <sub>2</sub> OH)	(608)
ONN(CH <sub>2</sub> OH)(CH <sub>2</sub> CH <sub>2</sub> OH)	$\xrightarrow{hv}$	$HOCH_2 \dot{N}CH_2 CH_2 OH + NO$	(609)
$HOCH_2 \acute{N}CH_2 CH_2 OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)(CH <sub>2</sub> CH <sub>2</sub> OH)	(610a)
	$\rightarrow$	$HOCH_2N=CHCH_2OH + HONO$	(610b)
	$\rightarrow$	HOCH=NCH <sub>2</sub> CH <sub>2</sub> OH + HONO	(610c)
$HOCH_2 \dot{N}CH_2 CH_2 OH + O_2$	$\rightarrow$	$\textbf{HOCH}_2\textbf{N}\textbf{=}\textbf{CHCH}_2\textbf{OH} + \textbf{HO}_2$	(611a)
	$\rightarrow$	$\textbf{HOCH=NCH}_{2}\textbf{CH}_{2}\textbf{OH} + \textbf{HO}_{2}$	(611b)

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:

HOCH=NCH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CHONH(CH <sub>2</sub> CH <sub>2</sub> OH)	(612)
$HOCH_2N=CHCH_2OH + OH$	$\rightarrow$	HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH	(613)
$HOCH_2 \acute{N}CHOHCH_2 OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(614)
ONN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{hv}$	$HOCH_2 \acute{N}CHOHCH_2 OH + NO$	(615)
$HOCH_2\dot{N}CHOHCH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(616a)
	$\rightarrow$	$HOCH=NCHOHCH_2OH + HONO$	(616b)
	$\rightarrow$	$HOCH_2N=COHCH_2OH + HONO$	(616c)
$HOCH_2 \dot{N}CHOHCH_2 OH + O_2$	$\rightarrow$	$\textbf{HOCH=NCHOHCH}_2\textbf{OH} + HO_2$	(617a)
	$\rightarrow$	$\textbf{HOCH}_2\textbf{N}\textbf{=}\textbf{COHCH}_2\textbf{OH} + \textbf{HO}_2$	(617b)
HOCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	CHO=NH(CHOHCH <sub>2</sub> OH)	(618)
HOCH <sub>2</sub> N=COHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHC(O)HCH <sub>2</sub> OH	(619)

The alcoxy radical formed in the 1,4-hydrogen shift reaction (607c) may dissociate or undergo hydrogen abstraction by  $O_2$  to form an aldehyde, which in turn will undergo photolysis or react with OH in an aldehydic hydrogen abstraction:

HOCH <sub>2</sub> N(C	H <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH2N(CH2CH2OH)CHOHCH2Ó	(607c)
HOCH <sub>2</sub> N(C	H <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	$HOCH_2N(CH_2CH_2OH)\dot{C}HOH + \textbf{HCHO}$	(620)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH	$H_2OH)CHOHCH_2OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	$\rightarrow$	$HOCH_2N(CH_2CH_2OH)CHOHCHO+HO_2$	(621)
HOCH <sub>2</sub> N(Cl	H <sub>2</sub> CH <sub>2</sub> OH)CHOHCHO	$\xrightarrow{h\nu}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)ĊHOH + CHO	(622)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH	I2OH)CHOHCHO+OH	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHĊO + H <sub>2</sub> O	(623)
HOCH <sub>2</sub> N(CH <sub>2</sub>	CH <sub>2</sub> OH)CHOHĊO + O <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHC(O)OÓ	(624)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> C	DH)CHOHC(O)OÓ+NO <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHC(O)OONO <sub>2</sub>	(625)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub>	OH)CHOHC(O)OONO <sub>2</sub>	$\overset{\Delta}{\longrightarrow}$	HOCH2N(CH2CH2OH)CHOHC(O)OÓ+NO2	(626)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> C	DH)CHOHC(O)OÓ +NO	$\rightarrow$	$HOCH_2N(CH_2CH_2OH)CHOHC(O)\acute{O} + NO_2$	(627)
HOCH <sub>2</sub> N(Cl	H <sub>2</sub> CH <sub>2</sub> OH)CHOHC(O)Ó	$\xrightarrow{\Delta}$	$HOCH_2N(CH_2CH_2OH)\dot{C}HOH + CO_2$	(628)
HOCH <sub>2</sub> N(	$CH_2CH_2OH)\dot{C}HOH + O_2$	$\rightarrow$	$\mathbf{HOCH}_{2}(\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{OH})\mathbf{NCHO} + \mathbf{HO}_{2}$	(629)

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  $O_2$  to form an amide:

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOHĊ-N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(607d)
HOHĊ-N(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+O <sub>2</sub>	$\rightarrow$	$CHON(CH_2CH_2OH)CHOHCH_2OH + HO_2$	(630)
	$\overset{\Delta}{\longrightarrow}$	$\acute{N}(CH_{2}CH_{2}OH)CHOHCH_{2}OH + \textbf{HCHO}$	(631)

The N-centered radical formed in (631) 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 <u>daytime</u> to reform the N-centered radical. Note that the rate of (631) is slow compared to that of the hydrogen abstraction reaction by  $O_2$ .

$ \dot{N}(CH_2CH_2OH)CHOHCH_2OH + NO $	$\rightarrow$	ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(632)
ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	$\xrightarrow{hv}$	$\acute{N}(CH_2CH_2OH)CHOHCH_2OH + NO$	(633)
$\dot{N}(CH_2CH_2OH)CHOHCH_2OH + NO_2$	$\rightarrow$	O2NN(CH2CH2OH)CHOHCH2OH	(634a)
	$\rightarrow$	$(CH_2CH_2OH)N=C(OH)CH_2OH + HONO$	(634b)
	$\rightarrow$	(CHOHCH <sub>2</sub> OH)N=CHCH <sub>2</sub> OH + HONO	(634c)
$\acute{N}(CH_{2}CH_{2}OH)CHOHCH_{2}OH + O_{2}$	$\rightarrow$	$(\mathbf{CH_2CH_2OH})\mathbf{N}{=}\mathbf{C}(\mathbf{OH})\mathbf{CH_2OH} + \mathbf{HO}_2$	(635a)
	$\rightarrow$	$(CHOHCH_2OH)N=CHCH_2OH + HO_2$	(635b)

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:

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(CH_2CH_2OH)N=C(OH)CH_2OH \xrightarrow{1,3} (CH_2CH_2OH)NHC(O)CH_2OH (636)
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(CHOHCH <sub>2</sub> OH)N=CHCH <sub>2</sub> OH +OH	$\rightarrow$	$(CHOHCH_2OH)N\dot{C}HOHCH_2OH + OH$	(637)
(CHOHCH2OH)NCHOHCH2OH	$\xrightarrow{1,3}$	(CHOHCH2OH)NHCHÓCH2OH	(638)
(CHOHCH2OH)NHCHÓCH2OH+O2	$\rightarrow$	(CHOHCH <sub>2</sub> OH)NHC(O)CH <sub>2</sub> OH+HO <sub>2</sub>	(639)

The alkyl radical formed in the 1,4-hydrogen shift reaction (607e) will first O<sub>2</sub>:

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH	(607e)
$HOCH_2N(\dot{C}HCH_2OH)CHOHCH_2OH + O_2$	$\rightarrow$	HOCH2N(CH(OÓ)CH2OH)CHOHCH2OH	(640)
HOCH <sub>2</sub> N(CH(OÓ)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+NO	$\rightarrow$	HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+NO <sub>2</sub>	(641)
HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+O <sub>2</sub>	$\rightarrow$	HOCH <sub>2</sub> N(C(O)CH <sub>2</sub> OH)CHOHCH <sub>2</sub> OH+HO <sub>2</sub>	(642)

The alkyl radical formed in the 1,5-hydrogen shift reaction (607f) will undergo hydrogen abstraction by  $O_2$  to form an aldehyde which in turn may undergo photolysis or aldehydic hydrogen abstraction by OH:

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CHÓCH <sub>2</sub> OH	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> ĊHOH)CHOHCH <sub>2</sub> OH	(607f)
$HOCH_2N(CH_2\dot{C}HOH)CHOHCH_2OH + O_2$	$\rightarrow$	$HOCH_2N(CHOHCH_2OH)CH_2CHO + HO_2$	(643)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> CHO	$\xrightarrow{h_{V}}$	$HOCH_2N(CHOHCH_2OH)\dot{C}H_2 + CHO$	(644)
$HOCH_2N(CHOHCH_2OH)CH_2CHO + OH$	$\rightarrow$	$HOCH_2N(CHOHCH_2OH)CH_2\dot{C}O + H_2O$	(645)
$HOCH_2N(CHOHCH_2OH)CH_2\dot{C}O+O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ	(646)
$HOCH_2N(CHOHCH_2OH)CH_2C(O)O\acute{O} + \\$	$\rightarrow$	HOCH_N(CHOHCH_OH)CH_C(O)OONO	(647)
$NO_2$			(017)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ+ NO <sub>2</sub>	(648)
$HOCH_2N(CHOHCH_2OH)CH_2C(O)O\acute{O} + NO$	$\rightarrow$	$HOCH_2N(CHOHCH_2OH)\dot{C}H_2+CO_2$	(649)
$HOCH_2N(CHOHCH_2OH)\dot{C}H_2+O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(650)
$HOCH_2N(CHOHCH_2OH)CH_2OOO + NO$	$\rightarrow$	$HOCH_2N(CHOHCH_2OH)CH_2\acute{O}+NO_2$	(651)
$HOCH_2N(CHOHCH_2OH)CH_2\acute{O}+O_2$	$\rightarrow$	$\mathbf{HOCH_2N(CHOHCH_2OH)CHO} + \mathrm{HO}_2$	(652)

In addition to the hydrogen abstraction by  $O_2$ , 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  $O_2$  and the 1,5-hydrogen shift reactions.

HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xrightarrow{\Delta}$	$HOCH_2\dot{N}(CHOHCH_2OH) + HCHO$	(653a)
	$\xleftarrow{1,4}{}$	HOĊHN(CHOHCH2OH)CH2OH	(653b)
	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(ĊOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(653c)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	(653d)
	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CHOHĊHOH)CH <sub>2</sub> OH	(653e)

The N-centered radical formed in (653a) 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 <u>daytime</u> to reform the N-centered radical.

HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\overset{\Delta}{\longrightarrow}$	$HOCH_2 \acute{N}(CHOHCH_2OH) + HCHO$	(653a)
$HOCH_2 \dot{N}(CHOHCH_2OH) + NO$	$\rightarrow$	ONN(CHOHCH <sub>2</sub> OH)(CH <sub>2</sub> OH)	(654)
ONN(CHOHCH <sub>2</sub> OH)(CH <sub>2</sub> OH)	$\xrightarrow{h\nu}$	$HOCH_2 \acute{N}(CHOHCH_2OH) + NO$	(655)
$HOCH_2\dot{N}(CHOHCH_2OH) + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CHOHCH <sub>2</sub> OH)(CH <sub>2</sub> OH)	(656a)
	$\rightarrow$	HOCH=N(CHOHCH <sub>2</sub> OH) + HONO	(656b)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HONO$	(656c)
$HOCH_2 \dot{N}(CHOHCH_2OH) + O_2$	$\rightarrow$	HOCH=N(CHOHCH <sub>2</sub> OH) + HONO	(657a)
	$\rightarrow$	$HOCH_2N=C(OH)CH_2OH + HONO$	(657b)
HOCH=N(CHOHCH <sub>2</sub> OH)	$\xrightarrow{1,3}$	CHONH(CHOHCH <sub>2</sub> OH)	(658)
HOCH <sub>2</sub> N=C(OH)CH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHC(O)CH <sub>2</sub> OH	(659)

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:

HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xleftarrow{1,4}{}$	HOĊHN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(653b)
HOĊHN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	CHON(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH +HO <sub>2</sub>	(660)

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:

HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> O	$\xleftarrow{1,4}{}$	HOCH <sub>2</sub> N(COHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(653c)
$HOCH_2N(\dot{C}OHCH_2OH)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> NC(O)CH <sub>2</sub> OH)CH <sub>2</sub> OH +HO <sub>2</sub>	(661)

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.

HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	(653d)
$HOCH_2N(CHO{O}CH_2OH)CH_2OH + O_2$	$\rightarrow$	$(CH_2OH)_2NC(O)CH_2OH + HO_2$	(662)
HOCH <sub>2</sub> N(CHÓCH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$\dot{N}(CH_2OH)_2 + CHOCH_2OH$	(663)
$\dot{N}(CH_2OH)_2 + NO$	$\rightarrow$	ONN(CH <sub>2</sub> OH) <sub>2</sub>	(664)
ONN(CH <sub>2</sub> OH) <sub>2</sub>	$\xrightarrow{h_{V}}$	$\dot{N}(CH_2OH)_2 + NO$	(665)
$\dot{N}(CH_2OH)_2 + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> OH) <sub>2</sub>	(666)
	$\rightarrow$	$HOCH_2N=CHOH + HONO$	(667)
$\dot{N}(CH_2OH)_2 + O_2$	$\rightarrow$	$HOCH_2N=CHOH + HO_2$	(668)

#### $HOCH_2N=CHOH \xrightarrow{1,3} HOCH_2NHCHO$ (669)

The alkyl radical formed in the 1,5-hydrogen shift reaction (653e) will react with  $O_2$  in a hydrogen abstraction reaction to yield an aldehyde which may either photolysereact with OH in an aldehydic hydrogen abstraction:

$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CHOHĊHOH)CH <sub>2</sub> OH	(653e)
$\rightarrow$	HOCH <sub>2</sub> N(CHOHCHO)CH <sub>2</sub> OH +HO <sub>2</sub>	(670)
$\xrightarrow{hv}$	HOCH <sub>2</sub> N(CH <sub>2</sub> OH)ĊHOH + CHO	(671)
$\rightarrow$	$(CH_2OH)_2NCHO + HO_2$	(672)
$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NCHOHĊO + H <sub>2</sub> O	(673)
$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NCHOHC(O)OÓ	(674)
$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NCHOHC(O)OONO <sub>2</sub>	(675)
$\xrightarrow{\Delta}$	$(CH_2OH)_2NCHOHC(O)OOO + NO_2$	(676)
$\rightarrow$	$(CH_2OH)_2NCHOHC(O)\acute{O} + NO_2$	(677)
$\rightarrow$	$(CH_2OH)_2N\dot{C}HOH+CO_2$	(678)
$\rightarrow$	$(CH_2OH)_2NCHO + HO_2$	(679)
	$\begin{array}{c} \xleftarrow{1.5} \\ \rightarrow \\ \hline \\ h\nu \\ \rightarrow \\ $	$ \begin{array}{ccc} \overset{1.5}{\leftarrow} & HOCH_2N(CHOH\dot{C}HOH)CH_2OH \\ & HOCH_2N(CHOHCHO)CH_2OH \\ & +HO_2 \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & h\nu \\ & hOCH_2N(CH_2OH)\dot{C}HOH + CHO \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & hOCH_2OH)_2NCHO + HO_2 \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & hOCH_2OH)_2NCHOH\dot{C}O + H_2O \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & hOCH_2OH)_2NCHOHCO)OO \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & hoch \\ & hoch \\ \end{array} \\ \begin{array}{ccc} & h\nu \\ & hoch \\ & hoch \\ & hoch \\ \end{array} \\ \begin{array}{ccc} & hoch \\ & h$

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 HOCH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>ĊHOH radical

The alkyl radical formed in the 1,5-hydrogen shift reaction (596c) will undergo hydrogen abstraction by  $O_2$  forming an aldehyde which may photolyse or react with OH in an aldehydic hydrogen abstraction reaction.

ÓCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> ĊHOH	(596c)
$HOCH_2N(CH_2CH_2OH)CH_2\dot{C}HOH+O_2$	$\rightarrow$	$\textbf{HOCH}_2\textbf{N}(\textbf{CH}_2\textbf{CH}_2\textbf{OH})\textbf{CH}_2\textbf{CHO} + \textbf{HO}_2$	(680)
HOCH2N(CH2CH2OH)CH2CHO	$\xrightarrow{hv}$	$HOCH_2N(CH_2CH_2OH)\dot{C}H_2+CHO$	(681)
$HOCH_2N(CH_2CH_2OH)CH_2CHO + OH$	$\rightarrow$	$HOCH_2N(CH_2CH_2OH)CH_2\dot{C}O + H_2O$	(682)
$HOCH_2N(CH_2CH_2OH)CH_2\dot{C}O+O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ	(683)
$HOCH_2N(CH_2CH_2OH)CH_2C(O)O\acute{O} + NO_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	(684)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)OÓ +NO <sub>2</sub>	(685)
$HOCH_2N(CH_2CH_2OH)CH_2C(O)O\acute{O} + NO$	$\rightarrow$	$HOCH_2N(CH_2CH_2OH)CH_2C(O)\acute{O} + NO_2$	(686)
HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> C(O)Ó	$\xrightarrow{\Delta}$	$HOCH_2N(CH_2CH_2OH)\dot{C}H_2+CO_2$	(687)
$HOCH_2N(CH_2CH_2OH)\dot{C}H_2+O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OÓ	(688)
$HOCH_2N(CH_2CH_2OH)CH_2O\acute{O} + NO$	$\rightarrow$	$HOCH_2N(CH_2CH_2OH)CH_2\acute{O} + NO_2$	(689)
$HOCH_2N(CH_2CH_2OH)CH_2\acute{O} + O_2$	$\rightarrow$	$\mathbf{HOCH_2N(CH_2CH_2OH)CHO} + \mathbf{HO_2}$	(690)

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:

- $HOCH_2N(CH_2CH_2OH)CH_2O \longrightarrow HOCH_2N(CH_2CH_2OH) + HCHO$ (691a)
  - $\leftarrow$  <sup>1,4</sup> HOĊHN(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>OH (691b)
    - $\leftarrow$  <sup>1,4</sup> HOCH<sub>2</sub>N(ĊHCH<sub>2</sub>OH)CH<sub>2</sub>OH (691c)
    - $\leftarrow$  <sup>1,5</sup> HOCH<sub>2</sub>N(CH<sub>2</sub>ĊHOH)CH<sub>2</sub>OH (691d)

The N-centered radical formed in (691a) will undergo hydrogen abstraction by O<sub>2</sub> and NO<sub>2</sub>, or react with NO and NO<sub>2</sub> to form the respective nitrosamines or nitramines. The nitrosamine, in turn, undergoes fast photolysis during daytime to reform the N-centered radical.

$\dot{N}(CH_2CH_2OH)CH_2OH + NO$	$\rightarrow$	ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(691a)
ONN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$\dot{N}(CH_2CH_2OH)CH_2OH + NO$	(692)
$\dot{N}(CH_2CH_2OH)CH_2OH + NO_2$	$\rightarrow$	O <sub>2</sub> NN(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> OH	(693a)
	$\rightarrow$	$\textbf{HOCH=NCH}_2\textbf{CH}_2\textbf{OH} + \textbf{HONO}$	(693b)
	$\rightarrow$	HOCH <sub>2</sub> N=CHCH <sub>2</sub> OH + HONO	(693c)
$\acute{N}(CH_2CH_2OH)CH_2OH + O_2$	$\rightarrow$	$\textbf{HOCH=NCH}_2\textbf{CH}_2\textbf{OH} + \textbf{HO}_2$	(694a)
	$\rightarrow$	$HOCH_2N=CHCH_2OH + HO_2$	(694b)
HOCH=NCH <sub>2</sub> CH <sub>2</sub> OH	$\xrightarrow{1,3}$	CHONHCH <sub>2</sub> CH <sub>2</sub> OH	(695)

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

$HOCH_2N=CHCH_2OH + OH$	$\rightarrow$	HOCH <sub>2</sub> ŃCHOHCH <sub>2</sub> OH	(696)
HOCH2ŃCHOHCH2OH _	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHCH(Ó)CH <sub>2</sub> OH	(697)
$HOCH_2NHCH(O)CH_2OH + O_2$	$\rightarrow$	$HOCH_2NHC(O)CH_2OH + HO_2$	(698)

The alkyl radical formed in the 1,4-hydrogen shift reaction (691b) will undergo hydrogen abstraction by O<sub>2</sub> and form amide:

- $HOCH_2N(CH_2CH_2OH)CH_2O \leftarrow \stackrel{1,4}{\longrightarrow} HOCHN(CH_2CH_2OH)CH_2OH$ (691b)
- $HO\dot{C}HN(CH_2CH_2OH)CH_2OH + O_2 \rightarrow CHON(CH_2CH_2OH)CH_2OH + HO_2$ (699)

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

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\overset{1,4}{\longleftrightarrow}$	HOCH <sub>2</sub> N(ĊHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(691c)
$HOCH_2N(\dot{C}HCH_2OH)CH_2OH + O_2$	$\rightarrow$	HOCH <sub>2</sub> N(CH(OÓ)CH <sub>2</sub> OH)CH <sub>2</sub> OH	(700)
HOCH <sub>2</sub> N(CH(OÓ)CH <sub>2</sub> OH)CH <sub>2</sub> OH+NO	$\rightarrow$	HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CH <sub>2</sub> OH+NO <sub>2</sub>	(701)

 $HOCH_2N(CH(\acute{O})CH_2OH)CH_2OH + O_2 \rightarrow HOCH_2N(C(O)CH_2OH)CH_2OH + HO_2$  (702)

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:

$HOCH_2N(CH(\acute{O})CH_2OH)CH_2OH \longrightarrow HOCH_2\acute{N}CH_2OH + CH$	$(OCH_2OH)$ (703a)
---	--------------------

- $\xleftarrow{}^{1.4} HOCH_2N(CHOHCH_2\acute{O})CH_2OH$ (703b)
- $\leftarrow^{1,4} HO\dot{C}HN(CHOHCH_2OH)CH_2OH$ (703c)
- $\xleftarrow{1.5} \acute{OCH}_2N(CHOHCH_2OH)CH_2OH$ (703d)

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 alcoxy radical formed in the 1,4-hydrogen shift reaction (703b) may dissociate or undergo hydrogen abstraction by  $O_2$  to form an aldehyde, which may subsequently undergo photolysis or aldehydic hydrogen abstraction:

$HOCH_2N(CH(\acute{O})CH_2OH)CH_2OH \leftarrow$	<u>1,4</u> →	HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> Ó)CH <sub>2</sub> OH	(703b)
HOCH <sub>2</sub> N(CHOHCH <sub>2</sub> Ó)CH <sub>2</sub> OH -	$\xrightarrow{\Delta}$	$HOCH_2N(\dot{C}HOH)CH_2OH + HCHO$	(704)
$HOCH_2N(\dot{C}HOH)CH_2OH + O_2$	$\rightarrow$	$(CH_2OH)_2NCHO + HO_2$	(705)
$HOCH_2N(CHOHCH_2\acute{O})CH_2OH + O_2$	$\rightarrow$	$(CH_2OH)_2NCHOHCHO + HO_2$	(706)
(CH <sub>2</sub> OH) <sub>2</sub> NCHOHCHO –	$\xrightarrow{hv}$	(CH <sub>2</sub> OH) <sub>2</sub> NĊHOH + CHO	(707)
$(CH_2OH)_2N\dot{C}HOH + O_2$	$\rightarrow$	$(CH_2OH)_2NCHO + HO_2$	(708)

The alkyl radical formed in the 1,4-hydrogen shift reaction (703c) will undergo hydrogen abstraction by  $O_2$  forming an amide:

HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\overset{1,4}{\longleftrightarrow}$	HOĊHN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(703c)
HOĊHN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	CHON(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH +HO <sub>2</sub>	(709)

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  $O_2$ :

HOCH <sub>2</sub> N(CH(Ó)CH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xleftarrow{1,5}$	ÓCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(703d)
ÓCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	<b>CHON(CHOHCH<sub>2</sub>OH)CH<sub>2</sub>OH</b> +HO <sub>2</sub>	(710)

The N-centered radical formed in (703a) 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 <u>daytime</u> to reform the N-centered radical.

ÓCH <sub>2</sub> N(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{\Delta}$	$\dot{N}$ (CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + HCHO	(703a)
$\dot{N}$ (CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + NO	$\rightarrow$	ONN(CHOHCH2OH)CH2OH	(711)

ONN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	$\xrightarrow{h\nu}$	$\acute{N}(CHOHCH_2OH)CH_2OH + NO$	(712)
$\dot{N}$ (CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + NO <sub>2</sub>	$\rightarrow$	O <sub>2</sub> NN(CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH	(713a)
	$\rightarrow$	$HOCH_2N=COHCH_2OH + HONO$	(713b)
		HOCH=NCHOHCH <sub>2</sub> OH + HONO	(713c)
$\dot{N}$ (CHOHCH <sub>2</sub> OH)CH <sub>2</sub> OH + O <sub>2</sub>	$\rightarrow$	$\textbf{HOCH}_2\textbf{N}\textbf{=}\textbf{COHCH}_2\textbf{OH} + \textbf{HO}_2$	(714a)
	$\rightarrow$	$\textbf{HOCH=NCHOHCH}_2\textbf{OH} + HO_2$	(714b)
HOCH=NCHOHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	CHONHCHOHCH <sub>2</sub> OH	(715)
HOCH <sub>2</sub> N=COHCH <sub>2</sub> OH	$\xrightarrow{1,3}$	HOCH <sub>2</sub> NHC(O)CH <sub>2</sub> OH	(716)

The alkyl radical formed in the 1,5-hydrogen shift reaction (691d) will undergo hydrogen abstraction by  $O_2$  to form an aldehyde which, in turn, will undergo photolysis ot aldehydic hydrogen abstraction by OH:

HOCH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)CH <sub>2</sub> Ó	$\xleftarrow{1,5}$	HOCH <sub>2</sub> N(CH <sub>2</sub> ĊHOH)CH <sub>2</sub> OH	(691d)
$HOCH_2N(CH_2\dot{C}HOH)CH_2OH + O_2$	$\rightarrow$	$\mathbf{HOCH_2N(CH_2CHO)CH_2OH} + \mathbf{HO_2}$	(717)
HOCH <sub>2</sub> N(CH <sub>2</sub> CHO)CH <sub>2</sub> OH	$\xrightarrow{hv}$	$(CH_2OH)_2N\dot{C}H_2 + CHO$	(718)
$HOCH_2N(CH_2CHO)CH_2OH + OH$	$\rightarrow$	$(CH_2OH)_2NCH_2\dot{C}O + H_2O$	(719)
$(CH_2OH)_2NCH_2\dot{C}O + O_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NCH <sub>2</sub> C(O)OÓ	(720)
$(CH_2OH)_2NCH_2C(O)OOO + NO_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NCH <sub>2</sub> C(O)OONO <sub>2</sub>	(721)
(CH <sub>2</sub> OH) <sub>2</sub> NCH <sub>2</sub> C(O)OONO <sub>2</sub>	$\xrightarrow{\Delta}$	$(CH_2OH)_2NCH_2C(O)OO + NO_2$	(722)
$(CH_2OH)_2NCH_2C(O)OOO + NO$	$\rightarrow$	$(CH_2OH)_2NCH_2C(O)\acute{O} + NO_2$	(723)
(CH <sub>2</sub> OH) <sub>2</sub> NCH <sub>2</sub> C(O)Ó	$\xrightarrow{\Delta}$	$(CH_2OH)_2N\dot{C}H_2+CO_2$	(724)
$(CH_2OH)_2N\dot{C}H_2 + O_2$	$\rightarrow$	(CH <sub>2</sub> OH) <sub>2</sub> NĊH <sub>2</sub> OÓ	(725)
(CH <sub>2</sub> OH) <sub>2</sub> NĊH <sub>2</sub> OÓ+ NO	$\rightarrow$	$(CH_2OH)_2NCH_2\acute{O} + NO_2$	(726)
$(CH_2OH)_2NCH_2OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO$	$\rightarrow$	$(CH_2OH)_2NCHO + HO_2$	(727)

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  $O_2$ . 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).

$$(CH_2OH)_2NCH_2O' \xrightarrow{\Delta} N(CH_2OH)_2 + HCHO$$
 (728)

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

$$(CH_2OH)_2NCH_2O' \xleftarrow{1,4} (CH_2OH)_2NCHOH$$
 (729)

$$(CH_2OH)_2N\dot{C}HOH + O_2 \rightarrow (CH_2OH)_2NCHO + HO_2$$
 (730)

The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from the  $CH_3$  group is summarized in Scheme 3.9. The

main products are amides:  $(CH_2CH_2OH)_2NCHO$  (N,N-diethanol-formamide),  $(CH_2CH_2OH)(CH_2OH)NCHO$  (N-methanol, N-ethanol-formamide),  $(CH_2OH)_2NCHO$  (N,N-dimethanol-formamide). In addition two PAN-like compounds are predicted as intermediates:

 $(CH_2OH)(CH_2CH_2OH)NCH_2C(O)OONO_2$  and  $(CH_2OH)_2NCH_2C(O)OONO_2$ .



**Scheme 3.9.** The main routes to the atmospheric degradation of CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (MDEA) following initial hydrogen abstraction from the CH<sub>3</sub>–group.

### 3.4 $HN(CH_2CH_2)_2NH$ (PIPA)

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

The results of the bond enthalpy calculations ( $\Delta_{bond}H_{C-H} \sim 392$ , and  $\Delta_{bond}H_{N-H} \sim 404 \text{ kJ mol}^{-1}$ , 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 adressed here.

$$CH_2CH_2NHCH_2CH_2NH + OH \rightarrow CH_2CH_2NHCH_2CH_2N + H_2O$$
(731a)

$$\rightarrow CH_2CH_2NHCH_2\dot{C}HNH + H_2O$$
(731b)

### 3.4.1 Fate of the CH2CH2NHCH2CH2Ń radical

We first consider reactions following hydrogen abstraction from the amino groups

$CH_2CH_2NHCH_2CH_2\dot{N} + NO$	$\rightarrow$	CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NNO	(732)
CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NNO	$\xrightarrow{h\nu}$	CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> Ń + NO	(733)
$CH_2CH_2NHCH_2CH_2\dot{N} + NO_2$	$\rightarrow$	CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NNO <sub>2</sub>	(734a)
	$\rightarrow$	CH2CH2NHCH2CH=N + HONO	(734b)
$CH_2CH_2NHCH_2CH_2N + O_2$	$\rightarrow$	CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH=N + HO <sub>2</sub>	(735)

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

$$CH_{2}CH_{2}NHCH_{2}CH=N + OH \rightarrow CH_{2}CH_{2}NHCH_{2}CHOH-N$$
(736)

$$CH_2CH_2NHCH_2CHOH-N \xrightarrow{1,3} CH_2CH_2NHCH_2CHO-NH$$
(737)

$$CH_2CH_2NHCH_2CHO-NH + O_2 \rightarrow CH_2CH_2NHCH_2CO-NH + HO_2$$
(738)

The amide formed in (738) still has activated  $CH_2$ -groups which will react readily with OH radicals. These reactions will be not be addressed in the present report.

### 3.4.2 Fate of the GH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CHNH radical

We next consider the subsequent reactions of the  $CH_2CH_2NHCH_2CHNH$  radical which will first add  $O_2$ 

<sup>&</sup>lt;sup>#</sup> 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 Wurmirazin.

$$\begin{array}{cccc} CH_{2}CH_{2}NHCH_{2}\dot{C}HNH &+ O_{2} &\rightarrow & CH_{2}CH_{2}NHCH_{2}C(OO)HNH & (739) \\ CH_{2}CH_{2}NHCH_{2}C(OO)HNH &+ NO &\rightarrow & CH_{2}CH_{2}NHCH_{2}C(O)HNH &+ NO_{2} & (740) \end{array}$$

$$CH_{2}CH_{2}NHCH_{2}C(O)HNH + O_{2} \rightarrow CH_{2}CH_{2}NHCH_{2}CO-NH + HO_{2}$$
(741)

$$\overset{\text{CH}_2\text{CH}_2\text{NHCH}_2\text{C}(\text{O})\text{HNH}}{\longrightarrow} \quad \overset{\Delta}{\longrightarrow} \quad \text{CHONHCH}_2\text{CH}_2\text{NHCH}_2 \tag{742}$$

$$\xrightarrow{\Delta} \dot{\text{NHCH}}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$$
(743)

The alkyl radical formed in (742) will first add  $O_2$  and eventually end up as a diamide.

$$\begin{array}{rcl} CHONHCH_{2}CH_{2}NH\dot{C}H_{2}+O_{2} & \rightarrow & CHONHCH_{2}CH_{2}NHCH_{2}OO&(744)\\ CHONHCH_{2}CH_{2}NHCH_{2}OO&+NO & \rightarrow & CHONHCH_{2}CH_{2}NHCH_{2}O&+NO_{2}&(745)\\ CHONHCH_{2}CH_{2}NHCH_{2}O&+O_{2} & \rightarrow & CHONHCH_{2}CH_{2}NHCHO&+HO_{2}&(746) \end{array}$$

The N-centered radical formed in (743) 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 <u>daytime</u> to reform the N-centered radical.

$\dot{N}HCH_2CH_2NHCH_2CHO + NO$	$\rightarrow$	ONNHCH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CHO	(747)
ONNHCH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CHO	$\xrightarrow{h\nu}$	ŃHCH2CH2CHCH2CH2CHO+NO	(748)
$\dot{M}HCH_2CH_2NHCH_2CHO + NO_2$	$\rightarrow$	O2NNHCH2CH2NHCH2CHO	(749)
	$\rightarrow$	HN=CHCH2NHCH2CHO + HONO	(750)
$\acute{N}HCH_{2}CH_{2}NHCH_{2}CHO + O_{2}$	$\rightarrow$	$\textbf{HN=CHCH}_2\textbf{NHCH}_2\textbf{CHO} + \textbf{HO}_2$	(751)

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

$\textbf{HN=CHCH}_2\textbf{NHCH}_2\textbf{CHO}+\textbf{OH}$	$\rightarrow$	HŃCHOHCH <sub>2</sub> NHCH <sub>2</sub> CHO	(752)
HŃCHOHCH <sub>2</sub> NHCH <sub>2</sub> CHO	$\xrightarrow{1,3}$	H2NCH(Ó)CH2NHCH2CHO	(753)
$H_2NCH(\acute{O})CH_2NHCH_2CHO + O_2$	$\rightarrow$	H <sub>2</sub> NC(O)CH <sub>2</sub> NHCH <sub>2</sub> CHO + HO <sub>2</sub>	(754)

The products formed in reactions (731)-(754) have in many cases active  $CH_2$ 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  $CH_2CH_2NHCH_2CO-NH$ 

(2-Piperazinone), CHONHCH<sub>2</sub>CH<sub>2</sub>NHCHO (N,N'-1,2-ethanediylbis-formamide), an amine/amide/aldehyde (H<sub>2</sub>NC(O)CH<sub>2</sub>NHCH<sub>2</sub>CHO) not listed in CAS. In addition there will be formed a nitrosamine (ONNHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CHO) and a nitramine (O<sub>2</sub>NNHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CHO) 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  $H_2NCH_2CH_2OH$  (MEA, 2aminoethanol), (CH<sub>3</sub>)<sub>2</sub>C(NH<sub>2</sub>)CH<sub>2</sub>OH (AMP, 2-amino-2-methyl-1-Propanol), and CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (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  $\tau_{OH} < 3$  days are highlighted in boldface. Products with lifetimes  $\tau_{OH} > 3$  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 af 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 5.1C-H and N-H bond enthalpies  $(\Delta_{bond}H/kJmol^1)$  from CBS-QB3<br/>calculations for amines included in the OH radical rate constant<br/>correlation.

Compound		$\Delta_{bond}H$ /kJ mol <sup>-1</sup>	$k_{298}$ /10 <sup>-11</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
	CBS-QB3	Experimental	Experimental
CH <sub>3</sub> NH <sub>2</sub>	419	$416.7$ , <sup>48</sup> $431 \pm 8$ <sup>46</sup>	17.2
CH <sub>3</sub> NH <sub>2</sub>	391	$390.62$ , <sup>48</sup> $396 \pm 8$ <sup>47</sup>	17.5
$(CH_3)_2NH$	395	$398 \pm 8^{46}$	65 3
$(CH_3)_2NH$	389		05.5
	• • •		
$(CH_3)_3N$	389		35.8
CH.CH.NH.	128	414 2 <sup>48</sup>	
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	386	376.81 <sup>48</sup>	23.8
CH <sub>3</sub> CH <sub>2</sub> IVII <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	380 A19	413 0 <sup>48</sup>	25.0
	417	415.0	
(CH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH			
$(CH_2)_2NCH_2CH_2OH$			
$(CH_2)_2 NCH_2 CH_2 OH$			
$(CH_2)_2 NCH_2 CH_2 OH$			
(0113)/21 (0112/0112/0112			
$(CH_3)_2C(NH_2)CH_2OH$	433		
$(CH_3)_2C(NH_2)CH_2OH$	426		20
$(CH_3)_2C(NH_2)CH_2OH$	397		28
$(CH_3)_2C(NH_2)CH_2OH$	457		
$(CH_3)_3CNH_2$	424	406.6 48	12.0
$(CH_3)_3CNH_2$	43		12.0
$CF_3CH_2NH_2$	427		0.9
$CF_3CH_2NH_2$	387		
	111		22
$N(CH_2CH_2)_3N$	414		22
HN(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH	400		
$HN(CH_2CH_2)_2NH$	392		
H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	448		
$H_2NCH_2CH_2OH$	395		
H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	394		
H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	442		

	A TT	0 1	A 11
Compound	$\Delta_{bond}$ H	Compound	$\Delta_{bond} \mathbf{H}$
NH <sub>2</sub> CHO	396	$H_2NC(O)CH_2OH$	355
NH <sub>2</sub> CHO	484	$H_2NC(O)CH_2OH$	449
		$H_2NC(O)CH_2OH$	482
(CH <sub>3</sub> ) <sub>2</sub> C(NH <sub>2</sub> )CHO	378	NH <sub>2</sub> CHOHC <mark>H</mark> O	392
$(CH_3)_2C(NH_2)CHO$	430	NH <sub>2</sub> CHOHCHO	313
$(CH_3)_2C(NH_2)CHO$	427	NH <sub>2</sub> CHOHCHO	437
		NH <sub>2</sub> CHO <mark>H</mark> CHO	453
$(CH_3)_2C(NH_2)CH_2OH$	433		
$(CH_3)_2C(NH_2)CH_2OH$	426		
$(CH_3)_2C(NH_2)CH_2OH$	397	NH <sub>2</sub> CH <sub>2</sub> CHO	424
$(CH_3)_2C(NH_2)CH_2OH$	457	NH <sub>2</sub> CH <sub>2</sub> CHO	310
		NH <sub>2</sub> CH <sub>2</sub> CHO	374
$CH_3CONH_2$	484		
CH <sub>3</sub> CONH <sub>2</sub>	397		
ONNHC <mark>H</mark> 2OH	313		
O <sub>2</sub> NNHC <mark>H</mark> <sub>2</sub> OH	336		

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

## **CAS Registry Numbers, Formulas, Structures and Names**

Registry Number	Formula	Structure	Name
12385-13-6	Н	н	Hydrogen atom
3352-57-6	НО	НО	Hydroxide radical
7732-18-5	H2 O	Н <sub>2</sub> О	Water
3170-83-0	H O2	о— он	Hydrogen dioxide radical
7722-84-1	H2 O2	но — он	Hydrogen peroxide
10102-43-9	NO	N O	Nitrogen monoxide
10102-44-0	N O2	о−и≡о	Nitrogen oxide
12033-49-7	N O3	o <u>_</u> ∎_o	Nitrate radical
14332-28-6	ΗΝΟ	HN — O	Nitrosyl hydride
7782-77-6	H NO2	о — и — он	Nitrous acid
7697-37-2	H N O3	о <u>  </u> о — и — он	Nitric acid
7782-44-7	O2	o <u> </u>	Oksygen
10028-15-6	O3	o— o— o	Ozone

Table 5.3 Inorganic compounds included in the CAS Register.

Registry Number	Formula	Structure	Name
75-13-8	СНИО		Isocyanic acid
675141-02-3	C H2 N2 O2	0 <u>— CH</u> – NH – N <u>—</u> O	Formamide, N-nitroso-
51883-27-3	C H2 N2 O3	OHC — NH — NO $_2$	Formamide, N-nitro-
56077-92-0	C H2 O2	н <sub>2</sub> с-о-о	Methyl, dioxy-
2053-29-4	C H3 N	H 2 C NH	Methanimine
60100-09-6	C H3 N O	ни — сн — он	Methanimidic acid
865-40-7	C H3 N O	н <sub>3</sub> с- м — о	Nitrosomethane
75-12-7	C H3 N O	н <sub>2</sub> №— сн <del>—</del> о	Formamide
64768-29-2	C H4 N2 O	н <sub>3</sub> с− NH − N <del>—</del> О	Methanamine, N- Nitroso-
598-57-2	C H4 N2 O2	о    о — NH — CH 3	Methanamine, N-nitro-
598-57-2	C H4 N2 O2	о    о nh — сн <sub>3</sub>	Methanamine, N-Nitro-
67-56-1	C H4 O	н <sub>3</sub> с—он	Methanol
107-22-2	C2 H2 O2	о <u>— сн</u> — сн <u>—</u> о	Ethanedial
298-12-4	C2 H2 O3	о Но — с — сн — о	Acetic acid, 2-oxo-
60939-21-1	C2 H3 N O2	о    H <sub>2</sub> N-с-сн — о	Acetamide, 2-oxo-
107031-65-2	C2 H3 O2	но-сн <sub>2</sub> -с <u></u> о	Ethyl, 2-hydroxy-1-oxo-
246506-71-8	C2 H4 N O2	он   H <sub>2</sub> N — CH — C — о	Ethyl, 2-amino-2- hydroxy-1-oxo-
141-46-8	C2 H4 O2	но — сн <sub>2</sub> — сн <u>—</u> о	Acetaldehyde, hydroxy-
79-14-1	C2 H4 O3	о    но -с-сн <sub>2</sub> -он	Acetic acid, 2-hydroxy-
1761-67-7	C2 H5 N	н <sub>3</sub> с- м — сн <sub>2</sub>	N-methylene- Methanamine
6542-88-7	C2 H5 N O	$H_2 N - CH_2 - CH = 0$	Acetaldehyde, amino-

Table 5.4Organic compounds included in the CAS Register.

60-35-5	C2 H5 N O	о    н <sub>2</sub> n — с — сн <sub>3</sub>	Acetamide
123-39-7	C2 H5 N O	о <u> — сн — мн — сн </u> 3	Formamide, N-Metyl-
734507-86-9	C2 H5 N O	но-сн <sub>2</sub> -n=сн <sub>2</sub>	Methanol, (methyleneamino)-
598-42-5	C2 H5 N O2	$ \begin{array}{c} 0 \\ \  \\ H_2 N - C - CH_2 - OH \end{array} $	Acetamide, 2-Hydroxy-
62-75-9	C2 H6 N2 O	м <u></u> о   н <sub>3</sub> с−м−сн <sub>3</sub>	Methanamine, N- Methyl-N-nitroso-
98033-27-3	C2 H6 N2 O2	HO - CH $_2$ - CH $_2$ - NH - NO	Ethanol, 2- (nitrosoamino)-
4164-28-7	C2 H6 N2 O2	NO 2   Me - N - Me	Methanamine, N- Methyl-N-nitro-
74386-82-6	C2 H6 N2 O3	но -сн 2 -сн 2 - мн - мо 2	Ethanol, 2-(nitroamino)-
32818-80-7	C2 H6 N2 O3	NO <sub>2</sub>   ме — N — СН <sub>2</sub> — ОН	Methanol, (methylnitroamino)-
141-43-5	C2 H7 N O	$H_2 N - CH_2 - CH_2 - OH$	Ethanol, 2-amino-
18197-25-6	C3 H5 N O2	Ме   ОНС—— N—— СНО	Formamide, N-Formyl- N-Metyl-
344549-61-7	C3 H6 N O	но-сн <sub>2</sub> -с <u></u> п-сн <sub>3</sub>	Ethyl, 2-hydroxy-1- (methylimino)-
67-64-1	C3 H6 O	о    н <sub>3</sub> с-с-сн <sub>3</sub>	2-Propanone
38697-07-3	C3 H7 N	№Н    н <sub>3</sub> с—с—сн <sub>3</sub>	2-Propanimine
68-12-2	C3 H7 N O	сн <sub>3</sub>   н <sub>3</sub> с-м-сн—о	Formamide, N,N- Dimetyl-
79-16-3	C3 H7 N O	Me-N-Me	Acetamide, N-Metyl-
13010-54-3	C3 H7 N O	HO-CH2-CH2-N-CH2	Ethanol, 2- (methyleneamino)-
20546-32-1	C3 H7 N O2	Ме   онс-N-сн <sub>2</sub> -он	Formamide, N- (hydroxymethyl)-N- methyl-

42499-46-7	C3 H8 N 2O3	$Me = N - CH_2 - CH_2 - OH$	Ethanol, 2- (methylnitroamino)-
26921-68-6	C3 H8 N2 O2	NO │ Me — N— CH <sub>2</sub> — CH <sub>2</sub> — OH	Ethanol, 2- (methylnitrosoamino)-
55-18-5	C4 H10 N2 O	NO   EtEt	Etanamine, N-Etyl-N- Nitroso-
7119-92-8	C4 H10 N2 O2	NO <sub>2</sub>   EtEt	Etanamine, N-Etyl-N- Nitro-
127-19-5	C4 H9 N O	Me I Me—N—Ac	Acetamide, N,N- Dimetyl-
1590-50-7	C4 H9 N O2	Ме   онс — N— сн <sub>2</sub> — сн <sub>2</sub> — он	Formamide, N-(2- hydroxyethyl)-N-methyl-
124-68-5	C4 H11 N O	ИН 2   ме -с-сн <sub>2</sub> -он   ме	1-Propanol, 2-amino-2- methyl-
617-84-5	C5 H11 N O	CHO I Et—N—Et	Formamide, N,N-Dietyl-
17236-38-3	C5 H11 N O3	Ме о      но-сн <sub>2</sub> -сн <sub>2</sub> -м-с-сн <sub>2</sub> -он	Glycolamide, N-(2- hydroxyethyl)-N-methyl-
105-59-9	C5 H13 N O2	Ме   но -сн <sub>2</sub> -сн <sub>2</sub> - м- сн <sub>2</sub> - сн <sub>2</sub> - он	Ethanol, 2,2'- (methylimino)bis-
685-91-6	C6 H13 N O	Ac I Et—N—Et	Acetamide, N,N-Dietyl-

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REPORT PREPARED FOR Gassnova SF Statoil Hydro ASA Shell Technology Norway AS ABSTRACT Amines emitted into the atmosphere will undergo a series of chemical and physical processes. Compounds with liquid-phase vapour pressures > 10 <sup>-6</sup> 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 <sub>3</sub> and NO <sub>3</sub> . In marine areas reactions with C1 atoms may also constitute an important sink. The types of radical generated following initiation processes include peroxy (RO <sub>2</sub> ), 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 <sub>2</sub> ), peroxy nitrates (RC(=O)OONO <sub>2</sub> ), hydroperoxides (ROOH), percarboxylic acids (RC(=O)OOH) and carboxylic acids (RC(=O)OH). A literature survey was carried out and theoretical degradation mechanisms for selected amines have been developed on the basis of experimental findings. NORWEGIAN TITLE			
KEYWORDS			
$CO_2$ capture	Amines	Gas phase	e chemistry

#### 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<sub>3</sub> og NO<sub>3</sub>. I marine område kan også reaksjonar med Cl-atom vere eit viktig sluk. Typen av radikalar som vert danna etter initieringsprosessane inkluderer peroksy (RO<sub>2</sub>), 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<sub>2</sub>), peroksynitrat (RC(=O)OONO<sub>2</sub>), hydroperoksid (ROOH), perkarboksylsyrer RC(=O)OOH) og karboksylsyrer (RC(=O)OH).

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

* Classification	Α	Unclassified (can be ordered from NILU)
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