

## Literature Review of Nitrosamine and Nitramine Formation Chemistry Relevant to Carbon Capture

### Table of Contents

1.0 Introduction	2
2.0 Summary evaluation	2
2.1 Risks associated with amine/amino acid selection	2
2.2 Risks associated with formation scenario	3
2.2.1 Capture unit	3
2.2.2 Dark atmosphere	4
2.2.3 Sunlit atmosphere	4
3.0 Background material	6
3.1 Formation of nitrosating/nitrating species	6
3.1.1 Formation pathways in the atmosphere	6
3.1.2 Mass transport effects	10
3.1.3 Importance of species in the gas vs. liquid phases	11
3.2 Stability of nitrosamines and nitramines	11
3.3 Amine/amino acid nitrosation and nitration pathways	15
3.3.1 Aqueous reactions	15
3.3.1.1 Amines	16
3.3.1.2 Amino acids	20
3.3.1.3 Additional factors	22
3.3.2 Gas phase reactions	23
3.3.2.1 Importance of HONO and NO <sub>3</sub> * in the dark	23
3.3.2.2 Importance of OH* and NO <sub>x</sub> in sunlight	23
3.4 Pathways for removal in the atmosphere	27
3.4.1 Reactions with atmospheric species	28
3.4.2 Nitrosamine sunlight photolysis	28
3.4.2.1 Kinetics	28
3.4.2.2 Byproduct formation	30
References	32
List of compounds	37

## 1.0 Introduction

This report reviews literature on nitrosamine and nitramine formation pathways relevant to amine- and amino acid-based carbon capture in the atmosphere downwind of carbon capture units, as well as within the units themselves. We note that very few studies have been conducted that are directly relevant to amine- or amino acid-based carbon capture. Many studies have been conducted on nitrosation reactions in other fields, particularly nitrosation *in vivo* by nitrite under the acidic conditions of the stomach. A subset of these studies bear relevance to the conditions found in amine-based carbon capture, but these studies were often side projects conducted by groups focusing on *in vivo* conditions, and many were conducted as long ago as the 1970s. This situation somewhat limits our ability to draw firm conclusions regarding the propensity of amine-based carbon sequestration technology to promote the formation of nitrosamines/nitramines. Rather than an exhaustive summary of previous research, this report targets a critical literature review that comments on the relative importance of different pathways with regard to nitrosamine/nitramine formation during amine-based carbon capture.

Below is a summary evaluation of the relative risks associated with amine selection and environmental scenario. Following this summary is a critical literature review providing the background upon which this summary evaluation was based. This background section summarizes relevant reaction pathways including:

1. Formation of nitrosating/nitrating species
2. Stability of nitrosamines/nitramines
3. Reactions of nitrosating/nitrating species with amines relevant to:
  - a. The capture unit
  - b. The atmosphere downwind of capture units in the presence or absence of sunlight
4. Pathways for the destruction of nitrosamines/nitramines in the environment

## 2.0 Summary evaluation of the nitrosamine/nitramine risks associated with amine/amino acid selection and formation scenario

2.1 Risks associated with amine/amino acid selection: The risk associated with nitrosamine formation is anticipated to increase in the order: primary amine  $\ll$  tertiary amine  $<$  secondary amine. Secondary amines, like piperazine, can form stable nitrosamines directly, and are likely to be form significant concentrations of stable nitrosamines.  $\text{NO}_x$ -fostered dealkylation of tertiary amines, like MDEA, is necessary to form a secondary amine precursor suitable for stable nitrosamine formation. In the case of primary amines, formation of a secondary amine precursor for formation of stable nitrosamines requires substantial amine concentrations (e.g., levels typical of amine-based solvents) to permit reaction of the primary amine with the carbocation product of primary nitrosamine decay. This requirement is likely to significantly limit nitrosamine formation from primary amines. However, the purity of the primary amine reagent may be critical. The solvent should be screened for levels of secondary and tertiary amine impurities.

Less information is available regarding the risk of nitramine formation. However, the risk from tertiary amines is likely to be significantly less than for secondary amines, because, as for nitrosation, dealkylation is required to form a secondary amine suitable for stable nitramine formation. However, primary nitramines are stable. Current research is

insufficient to compare the propensity of secondary and primary amines to form stable nitramines.

The other critical factor for amine selection is the polarity of the amine. Polar amines with alcohol functional groups, such as monoethanolamine and MDEA, are likely to form polar nitrosamines (e.g., N-nitrosodiethanolamine) that are less likely to volatilize from the solvent. In contrast, nitrosated piperazines might be comparable to the relatively volatile N-nitrosomorpholine. However, as the vapor pressures at 25 °C of piperazine (4.05 mm Hg) and monoethanolamine (0.46 mm Hg) are similar, experimental determinations of the Henry's Law constants for these amines and their nitrosated and nitrated byproducts is needed.

Based on these principles, it is anticipated that the risks posed by common generic solvents would be 30% MEA << 25% MDEA and 5% MEA < 25% AMP and 15% PZ. The 30% MEA solvent features a primary amine that is polar, thus minimizing nitrosamine formation, and volatility of the amine itself. However, it is possible that low yields of more volatile amines (e.g., methylamine and oxazolidone) might form from MEA degradation. The 25% MDEA and 5% MEA solvent includes the tertiary amine, MDEA. This amine is more likely to form nitrosamines than MEA alone. Additionally, one of the potential amine fragmentation products, methylethanolamine, is likely to be more volatile than MEA. The 25% AMP and 15% PZ solvent contains the primary amine AMP and the secondary amine PZ. PZ is likely to be more volatile than MEA or MDEA, and could directly form nitrosamines and nitramines at both nitrogens in the molecule.

Amino acids have been considered as alternatives to amines for CO<sub>2</sub> capture. They are believed to be more resistant to degradation by oxygen, and are considered less volatile due to the negative charge on the carboxylate group under typical CO<sub>2</sub> capture pH conditions (Aronu et al., 2010). However, the tendency of amino acids to undergo nitrosation may be similar to, or greater than that of amines. Indeed, the electron-donating nature of the carboxylate group may enhance nitrosation of the  $\alpha$ -terminal amine group. Among amino acids, those with secondary amine functionalities, including proline and sarcosine, will form stable nitrosamine products. Among primary amino acids, increasing distance between the amine group, and the carboxylate group reduces nitrosation, as well as the formation of secondary amine intramolecular cyclization byproducts from the carbocation intermediates of primary nitrosamine decay. Additionally, increasing distance between the amine and carboxylate groups increases the resistance of the amino acids to decarboxylation under heat, a process which would produce more volatile products. For these reasons, the tendency of amino acids to form nitrosamines would be secondary > primary, and  $\alpha$ -amino acid >  $\beta$ -amino acid >  $\gamma$ -amino acid amongst primary amino acids.

## 2.2 Risks associated with formation scenarios

**2.2.1 Capture unit:** The greatest risk for nitrosamine/nitramine formation is likely to occur in the capture unit. However, remedial techniques may be applied to clean the exhaust prior to release. Compared to the atmosphere, in which NO<sub>x</sub> concentrations vary from ppb to ppt levels, the flue gas entering the absorber unit contains a much higher concentration of NO<sub>x</sub> (ppm level). Amine concentrations in the solvent are substantial (e.g., ~5 M). Moreover, the turbulence in the absorber unit enhances mass transfer of amine to the gas phase, enabling reactions in either phase. Reactions related to sunlight, including photolytic destruction, are

not applicable. Alternatively, sunlight-driven formation reactions, including  $\text{OH}^*$ -initiated reactions, are also not applicable. At present, it is not possible to predict the relative importance of nitrosamine/nitramine formation in the capture unit.

The amine-based  $\text{CO}_2$  capture system consists of two major units - absorber and desorber. Concerning nitrosamine and nitramine formation, the absorber is characterized by the presence of  $\text{NO}_x$  and associated nitrosating and nitrating agents in the gas phase. As a result, mass transfer from the gas to liquid phases as well as reaction mechanisms must be considered. Although exhibiting comparable amine levels to the adsorber unit, the desorber is characterized by its higher operating temperature, and a negligible level of  $\text{NO}_x$  and associated nitrosating and nitrating agents. Preliminary results in our laboratory also indicate substantial formaldehyde concentrations in washwater, suggesting that it also occurs in significant concentrations in the solvent. In the desorber, the high nitrite concentration, one of the end products of nitrosating and nitrating agents, may play a significant role. The extreme temperature and pH conditions, elevated amine and formaldehyde concentrations, may promote substantial degradation of amines, potentially forming volatile amines and associated nitrosamines/nitramines (e.g., oxazolidone formation from monoethanolamine).

*2.2.2 Formation in the dark atmosphere:* This scenario is likely to present a lower risk than in the capture unit. Amine and  $\text{NO}_x$  concentrations in the atmosphere would be lower than in the capture unit. In the absence of sunlight, the nitrosating agent HONO may be the most important, although reactions initiated by  $\text{NO}_3^*$  may play a role. Nitrating agents would not be important. In the case of primary amines, unstable primary nitrosamines would form. The carbocation products of their decay would be unlikely to react with another primary amine to form a secondary amine precursor of a stable secondary nitrosamine. The level of secondary and tertiary amine impurities in the solvent would be particularly important. Where secondary and tertiary amines are used as solvents, stable nitrosamine formation from HONO reactions would occur, but at lower levels than in the capture unit. However, any formation may be of concern, as the nitrosamine products would already be in the environment.

*2.2.3 Formation in the sunlit atmosphere:* This pathway is likely to represent the lowest threat of the three pathways. Although nitramine formation would still be important, sunlight photolysis of nitrosamines would reduce the overall formation of byproducts. Formation of nitrosamines and nitramines would be dominated by sunlight-generated hydroxyl radicals ( $\text{OH}^*$ ). H-atom removal from N-H groups in amines forms amino radicals with which  $\text{NO}^*$  and  $\text{NO}_2^*$  can combine to form nitrosamines and nitramines, respectively. Photolysis would reduce the observed concentrations of nitrosamines. However, recent research indicates that significant concentrations of nitrosamines can persist in aerosols/fogs, potentially due to light shielding by nitrite or nitrate. In contrast, nitramines are not photolabile, and may accumulate in the atmosphere. Additionally, for primary amine-based solvents, primary nitramines are more stable than primary nitrosamines.

It is likely that nitramines may be more important than nitrosamines, although further research is needed to validate this hypothesis. If atmospheric emissions from the capture unit are controlled, and if nitramine formation in the atmosphere emerges as the dominant risk, the advantage exhibited by primary amines of reduced nitrosamine formation potential no longer applies. Accordingly, it is possible that secondary or tertiary

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University

amines could exhibit a lower tendency than a comparable primary amine to form nitramines, but further research would be necessary to examine this possibility.

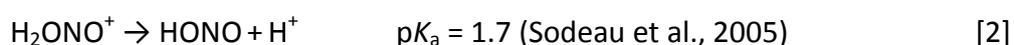
### 3.0 Background Material

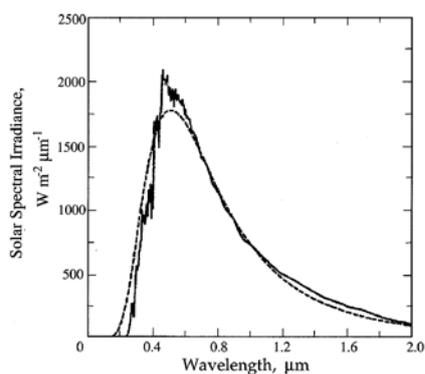
#### 3.1 Formation of nitrosating/nitrating species

A number of nitrosating/nitrating species are relevant to nitrosamine/nitramine formation during amine-based carbon capture. These species can be found in both the gaseous and aqueous phases, and include  $\text{HONO}_{(g,l)}$ ,  $\text{H}_2\text{ONO}^+_{(l)}$ ,  $\text{NO}_2^*$ ,  $\text{NO}^*$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_3$ . Evaluating their concentrations can be challenging due to a number of key factors. These factors include the fact that 1) the formation pathways of these species are complex and often interrelated, 2) some species as well as other atmospheric contaminants (e.g.,  $\text{HNO}_3/\text{NO}_3^-$ ) are photoactive and can generate additional reactive byproducts, and 3) they can undergo mass transfer between different phases. This section discusses each of these areas in detail. This discussion is designed to provide a comprehensive background of their chemistry to help understand their potential impact as nitrosating and nitrating agents, with a particular reference to the atmosphere, where the greatest variety of these species is expected.

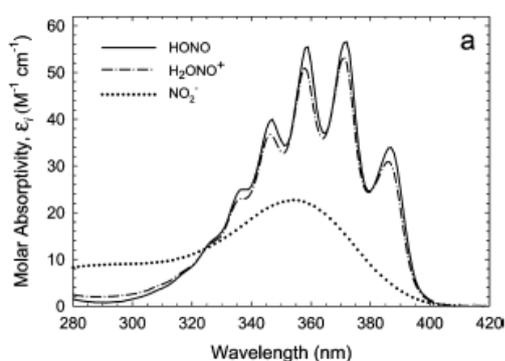
**3.1.1 Formation Pathways in the Atmosphere:** The nitrosating agent,  $\text{NO}^*$ , and the nitrating agent,  $\text{NO}_2^*$ , are components of  $\text{NO}_x$  in the flue gas, or may be present in the ambient atmosphere from various combustion sources. The solar spectrum emits wavelengths of light from 290 nm (UVA) to the visible/IR range (Figure 1). Many compounds can absorb light over this range, including compounds that can photolyze to form  $\text{NO}_x$ . One set of such compounds includes  $\text{NO}_2^-$  and its related conjugate acids,  $\text{HONO}_{(g,l)}$  and  $\text{H}_2\text{ONO}^+_{(l)}$ , whose equilibria are described in equations 1-2. The molar absorption spectra for all three of these compounds overlap with the solar spectrum in the UVA range (290-400 nm) and are plotted in Figure 2. The  $\text{NO}_2^-$  adsorption spectrum indicates a maximum molar absorption coefficient at 360 nm ( $\epsilon_{360\text{nm}} = 22.5 \text{ M}^{-1} \text{ cm}^{-1}$  (Mack and Bolton, 1999)). By comparison, the  $\text{HONO}_{(g,l)}$  and  $\text{H}_2\text{ONO}^+_{(l)}$  spectra are quite different from  $\text{NO}_2^-$  but very similar to each other, exhibiting molar absorption coefficients that are at least two times greater than  $\text{NO}_2^-$  between 330 to 400 nm (Anastasio and Chu, 2009).

The products formed from photolysis of  $\text{NO}_2^-$  and its conjugate acids,  $\text{HONO}_{(g,l)}$  and  $\text{H}_2\text{ONO}^+_{(l)}$ , are quite similar in that, when illuminated, they form  $\text{NO}^*$  and  $\text{OH}^*$  (Table 1). Interestingly, the quantum yield ( $\Phi = \text{moles of product formed/moles of photons}$ ) of  $\text{OH}^*$  for  $\text{HONO}$  is 0.19, ~ twice as much as  $\text{NO}_2^-$  and  $\text{H}_2\text{ONO}^+_{(l)}$  (Table 1). As the nitrosating agent,  $\text{NO}^*$ , is the other product of this photolysis, these quantum yields should apply to it as well. These quantum yields suggest that the speciation of  $\text{NO}_2^-$  can have a significant effect on the level of nitrosating agents formed during sunlight photolysis. The hydroxyl radical ( $\text{OH}^*$ ) in turn can react with  $\text{NO}_2^-$  to form the nitrating species,  $\text{NO}_2^*$ , at close to diffusion-controlled reaction rates ( $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) (Table 1).



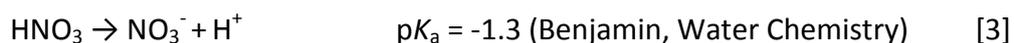


**Figure 1.** Solar spectrum ( $\text{W}/\text{m}^2/\mu\text{m}$ ) at the top of the Earth's atmosphere (solid line) (taken from Seinfeld and Pandis, 1998).

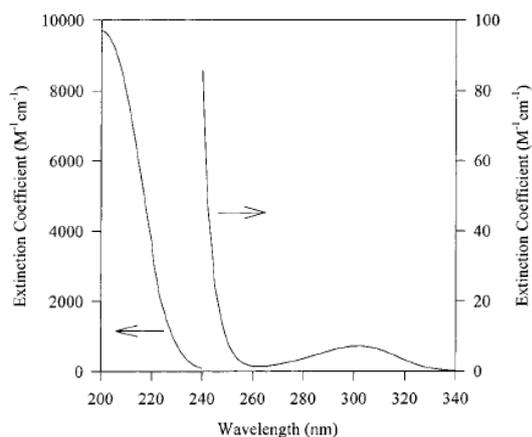


**Figure 2.** Molar absorption spectra of  $\text{NO}_2^-$ , HONO, and  $\text{H}_2\text{ONO}^+$  from 280-400 nm (Anastasio and Chu, 2009).

Another compound of interest is  $\text{HNO}_{3(\text{g})}$  which, as one of the major oxidation products of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), can readily partition into the aqueous phase ( $H_{\text{HNO}_3}$  in Table 2 (Seinfeld and Pandis, 1998)). There it deprotonates to form  $\text{NO}_3^-$  since it is a strong acid (see equation 3). The direct photolysis of  $\text{HNO}_{3(\text{g})}$  in the troposphere has been observed to be quite slow in comparison to its photolysis when deposited on the ground or vegetation surfaces, where the rate increases by one to two orders of magnitude and HONO is formed (Zhu et al., 2010). Alternatively, in the aqueous phase,  $\text{NO}_3^-$  is also photoactive and absorbs light in the UVA region (300-400 nm) (Figure 3). The  $\text{NO}_3^-$  adsorption spectrum indicates a maximum molar absorption coefficient at 310 nm ( $\epsilon_{310\text{nm}} = 7.4 \text{ M}^{-1}\text{cm}^{-1}$  (Mack and Bolton, 1999)) where  $\text{NO}_3^-$  photolyzes to the nitrating agent,  $\text{NO}_2^*$ , as well as to  $\text{NO}_2^-$ , with quantum yields at 305 nm of 0.001 and 0.009, respectively (Table 1).



Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University



**Figure 3.** Molar absorption spectra of  $\text{NO}_3^-$  (l) from 200-340 nm (Sharpless and Linden, 2001)

$\text{NO}^*$  and  $\text{NO}_2^*$  participate in a wide range of reactions causing them to interchange into a variety of species, many of which are also nitrosating and nitrating agents (Table 1). Among these are the nitrosating agents  $\text{N}_2\text{O}_3$  and  $\text{ONOOH}$ , and the nitrating and nitrosating agent  $\text{N}_2\text{O}_4$ .  $\text{N}_2\text{O}_4$  occurs in two tautomeric forms, the nitrating agent  $\text{O}_2\text{N}-\text{NO}_2$ , and the nitrosating agent,  $\text{ONO}-\text{NO}_2$ .

**Table 1.** Photolytic and other relevant reactions for species in the atmosphere

Reactions	Phase	$k_{forward}$ (aq) ( $M^{-2}s^{-1}/M^{-1}s^{-1}/s^{-1}$ )	$k_{reverse}$ (aq) ( $M^{-1}s^{-1}$ )	$K_{eq}$ ( $M^{-1}/atm^{-1}$ )	$\Phi$ Quantum Yield
$NO_3^- + hv \rightarrow NO_2^* + O^{*-}$	aq				$\Phi_{O^*}$ (305 nm) = 0.001 <sup>b</sup>
$NO_3^- + hv \rightarrow NO_2^- + O^*$	aq				$\Phi_{OH^*}$ (305 nm) = 0.009 <sup>b</sup>
$NO_2^- + hv \rightarrow NO^* + O^{*-}$	aq				$\Phi_{OH^*}$ (351 nm) = 0.027 <sup>b</sup>
$HONO + hv \rightarrow NO^* + OH^*$	aq				$\Phi_{OH^*}$ (366 nm) = 0.19 <sup>c</sup>
$H_2ONO^+ + hv \rightarrow NO^* + OH^* + H^+$	aq				$\Phi_{OH^*}$ (366 nm) = 0.024 <sup>c</sup>
$NO^* + HO^* \rightarrow HONO$	aq	$1.0 \times 10^{10b}$			
$NO^* + NO_2^* + H_2O \rightarrow 2 HONO$	gas			$10^{-5.82h}$	
$HO^* + NO_2^- \rightarrow NO_2^* + OH^-$	aq	$1.0 \times 10^{10b}$			
$O^{*-} + H_2O^+ \rightarrow HO^* + OH^-$	aq	$1.7 \times 10^{6b}$	$1.7 \times 10^{10b}$	$10^{-11.9b}$	
$2 NO_2^* \rightarrow N_2O_4$	gas			$6.7^e$	
$2 NO_2^* \rightarrow N_2O_4$	aq	$4.5 \times 10^{8b}$		$6.5 \times 10^{4e}$	
$NO^* + NO_2^* \rightarrow N_2O_3$	aq	$1.1 \times 10^{9b}$		$1.4 \times 10^{4e}$	
$NO^* + NO_2^* \rightarrow N_2O_3$	gas			$0.41^e$	
$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^-$	aq	$1.0 \times 10^{3b}$			
$2 NO_2^* \rightarrow N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^-$	aq	$3.0 \times 10^{7i}$			
$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^-$	aq	$5.3 \times 10^{2b}$ $1.6 \times 10^{3g}$	$5.6^g$		
$2NO^* + O_2 \rightarrow N_2O_4$	aq				
$2NO + O_2 \rightarrow 2NO_2$	aq	$6.4 \times 10^{6f}$			
$N_2O_4 \rightarrow ONO-NO_2$	aq				
$HOONO \rightarrow NO_3^- + H^+$	aq	$0.9^a$			
$NO_2^* + HO^* \rightarrow HOONO$	aq	$1.3 \times 10^{9b}$	$0.35^a$		
$HOONO \rightarrow H^+ + OONO^-$	aq			$10^{-6.5b}$	
$HOONO \rightarrow NO_3^- + H^+$	aq	$1.4^b$			
$ONOO^- + HO^* \rightarrow ONOO^* + OH^-$	aq	$5.0 \times 10^{9b}$			
$ONOO^- \rightarrow NO^* + O_2^{*-}$	aq	$0.023^a$	$5 \times 10^{9a}$		
$ONOO^- + CO_{2(aq)} \rightarrow NO_3^-$	aq	$3 \times 10^{4a}$			
$ONOO^- + NO_2^- \rightarrow NO_3^- + NO_2^{-d}$	aq				

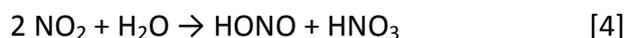
<sup>a</sup>Goldstein and Rabani, 2007, <sup>b</sup>Mack and Bolton, 1999, <sup>c</sup>Anastasio and Chu, 2009, <sup>d</sup>Lee et al., 2005, <sup>e</sup>Challis and Krytopoulos, 1979, <sup>f</sup>Pires et al., 1994, <sup>g</sup>Lewis et al., 1995; <sup>h</sup>ppm<sup>-1</sup> (Hanst et al., 1977); <sup>i</sup>overall observed rate constant at 293 K (Cheung et al., 2000); aq = aqueous, s = solid

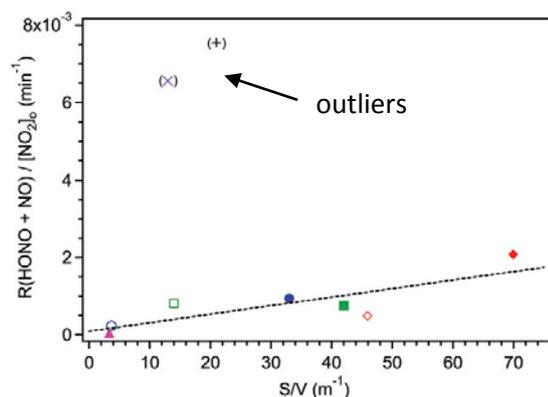
**3.1.2 Mass Transport Effects:** For mass transport between the gas-liquid phases, one quantitative way of assessing the desire for a specific compound to reside in either phase is by evaluating the Henry's Law constant,  $H$ , defined as the aqueous phase concentration (moles/L = M) divided by the gas phase concentration (atm). The  $H$  values for various atmospheric species (Table 2) indicate that  $\text{NO}^*$  and  $\text{NO}_2^*$  are orders of magnitude less soluble than many other species.

**Table 2.** Henry's Law constants for important reactive species in the atmosphere.

Reactive Species	$H$ (M atm <sup>-1</sup> )	Temp (K)	Reference
$\text{NO}^*$	$1.9 \times 10^{-3}$	298	Seinfeld and Pandis, 1998
$\text{NO}_2^*$	$1.4 \times 10^{-2}$	293	Cheung et al., 2000
	$2.3 \times 10^{-2}$	276	Cheung et al., 2000
$\text{N}_2\text{O}_4$	$\sim 10^2 \times \text{NO}_2$		Finlayson-Pitts et al., 2003
$\text{O}_3$	$1.13 \times 10^{-2}$	298	Seinfeld and Pandis, 1998
$\text{HO}^*$	25	298	Seinfeld and Pandis, 1998
$\text{HNO}_2$	49	298	Seinfeld and Pandis, 1998
$\text{HNO}_3$	$2.1 \times 10^5$	298	Seinfeld and Pandis, 1998

Mass transport between the gas and solid phases can also be important as many reactions can take place on solid airborne particles such as sea salts, windblown dust, and aerosol particles that can act as condensation nuclei for cloud and fog formation in urban areas (Finlayson-Pitts et al., 2003). One study found that the reaction rate of  $\text{NO}_2$  to form HONO (equation 4), which is a major source of  $\text{HO}^*$  ( $\text{HONO} + h\nu \rightarrow \text{NO}^* + \text{OH}^*$ ) in polluted urban atmospheres, can increase linearly when in greater contact with surfaces. This trend is presented in Figure 4 where the formation rates of HONO and  $\text{NO}^*$  (the other reaction product of HONO) are normalized to the different initial  $\text{NO}_2$  and water vapor concentrations (y-axis) and plotted against different surface-to-volume ratios used in the reaction cells (x-axis). Each point represents a set of experimental results from different studies. This type of study suggests that mass transport onto solid phases can greatly impact atmospheric reaction chemistry and byproduct distribution.





**Figure 4.** Measured formation rates of HONO + NO in reaction cells exhibiting various surface-to-volume ratios (Finlayson-Pitts et al., 2003).

**3.1.3 Importance of nitrosating and nitrating species in the gas and liquid phases:** Using the data presented above, we can compare the relative concentrations of nitrosating and nitrating species in different phases. Employing just the equilibrium constants in Table 1, and the Henry's Law constants from Table 2, Table 3 presents concentrations in each phase for the following two situations:

1. Absorber unit experiencing 20 ppm  $\text{NO}^*$ , 2 ppm  $\text{NO}_2^*$ , and 70,000 ppm  $\text{H}_2\text{O}_{(\text{gas})}$
2. Atmosphere containing 100 ppb  $\text{NO}^*$ , 50 ppb  $\text{NO}_2^*$ , and 13,000 ppm  $\text{H}_2\text{O}_{(\text{gas})}$

**Table 3.** Concentrations of nitrosating and nitrating species in the gas and liquid phases.

	Absorber		Atmosphere		Species Type
	Gas ppm	Liquid M	Gas ppm	Liquid M	
NO	20	3.80E-08	0.1	1.90E-10	Nitrosating
NO <sub>2</sub>	2	4.60E-08	0.05	1.15E-09	Nitrating
HONO	2	9.80E-05	0.01	4.90E-07	Nitrosating
N <sub>2</sub> O <sub>3</sub>	1.67E-05	2.39E-11	2.08E-09	2.99E-15	Nitrosating
N <sub>2</sub> O <sub>4</sub>	6.10E-07	1.40E-10	3.8E-10	8.74E-14	Nitrosating/Nitrating

Note that  $\text{NO}^*$ ,  $\text{NO}_2^*$ , and HONO are important species in all of these systems. However, the relative importance of HONO,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  increases in the aqueous phase compared to  $\text{NO}^*$  and  $\text{NO}_2^*$ . The relative importance of nitrosation and nitration in the different phases remains unclear.

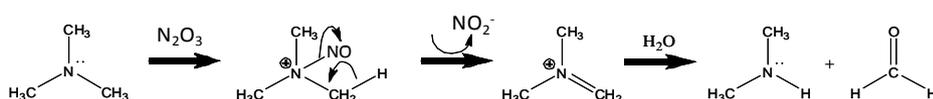
### 3.2 Stability of Nitrosamines and Nitramines

Where secondary amines are employed for carbon dioxide capture (e.g., piperazine), the secondary nitrosamine and nitramine products are chemically stable. Accordingly, secondary amines have been a focus for nitrosation and nitration research. In the case of tertiary amines (e.g., MDEA), reaction with  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  oxidants leads to dealkylation to form a secondary amine and an aldehyde (Figure 5 for tertiary nitrosamine decay) (Loeppky

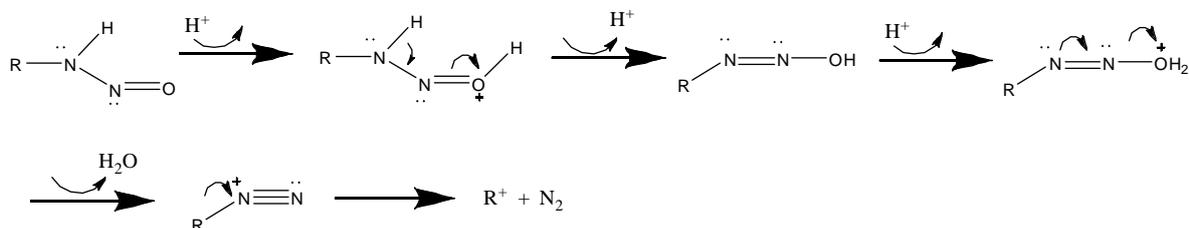
et al., 1998). The secondary amine can then form stable nitrosamine or nitramine products. In the case of primary amines (e.g., MEA or AMP), primary nitrosamines (e.g., nitrosomonoethanolamine) are unstable in the presence of water, rapidly decaying to nitrogen gas and a carbocation ( $R^+$ ; Figure 6; Ridd, 1961). Due to this rapid decay, primary nitrosamines are too unstable to synthesize. The pathway requires acidity and therefore it would seem to require aqueous phases. Nonetheless, the polar nitroso group renders all nitrosamines highly soluble, and would readily partition into any available aqueous phase, and subsequently decay. In contrast, primary nitramines are stable enough to be synthesized and isolated (Hassel et al., 1991).

The carbocations formed during primary nitrosamine decay are short-lived species that react rapidly with nucleophiles. The high amine concentrations with the absorber unit (e.g., 30% monoethanolamine or  $\sim 5$  M or roughly 1 in 10 molecules) render it likely that the carbocation may react with another amine. The product would be a secondary amine, that could then form stable secondary nitrosamines and nitramines (Figure 7; Obiedzinski et al., 1980). It has been shown that N-nitrosodimethylamine and N-nitrosodibutylamine are formed from methylamine and butylamine, respectively, from acid-catalyzed nitrosation by nitrite (Obiedzinski et al., 1980; Warthesen et al., 1975). However, the low amine concentrations in the atmosphere downwind of the capture plant renders this type of secondary amine formation unlikely.

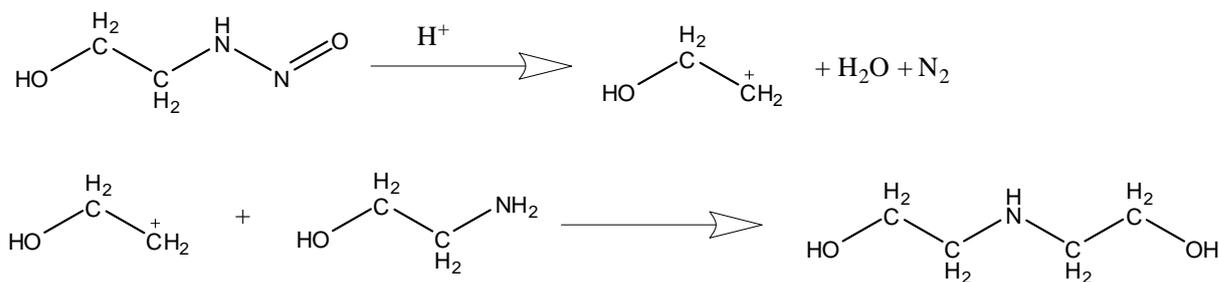
From this discussion of the stability of nitrosamines, one would predict that the tendency of amines to be nitrosated within the capture unit, or in the atmosphere would be: primary  $\ll$  tertiary < secondary. Regarding nitramines, tertiary amines would be less likely to undergo nitration than secondary amines. However, primary nitramines are stable, and there has not been sufficient research to indicate the relative potential of primary amines to undergo nitration compared to secondary and tertiary amines.



**Figure 5:** Tertiary nitrosamine decay pathway.



**Figure 6:** Primary nitrosamine decay pathway.



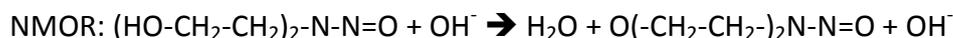
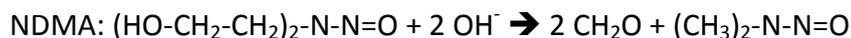
**Figure 7:** Diethanolamine formation from monoethanolamine.

Additional structural characteristics of amines must be considered. For the  $\text{OH}^*$ -driven nitrosation and nitration processes described below relevant to the atmosphere, nitrosation/nitration should be minimally subject to structural variations in the amine, as  $\text{OH}^*$  is a non-selective oxidant. For reactions with nitrosating and nitrating agents like  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ , which are far more selective oxidants, rates are much more likely to depend on amine structure. Amine basicity, as measured by the  $\text{pK}_a$  of the amine, has been considered a critical factor in the rates of aqueous nitrosation reactions, as the reaction involves the nucleophilic attack of the unprotonated amine lone pair on these agents. Amines with electron-donating alkyl chains exhibit higher basicity. The pH of the amine solution in the absorber is usually higher than the  $\text{pK}_a$  of the amine, such that the amine lone pair is also available for complex formation with  $\text{CO}_2$ . However, the lower the  $\text{pK}_a$ , the less nucleophilic are the lone pair of electrons. Therefore, amines with lower  $\text{pK}_a$ s are expected to be less prone to nitrosation. This effect was observed in Challis et al. (1979) for amines with  $\text{pK}_a < 4$ . However, the nitrosation of amines with higher  $\text{pK}_a$ s decreased with increasing  $\text{pK}_a$ , as less of the amine was in the active, deprotonated form (Challis et al., 1979; Mirvish 1975). In contrast, nitramine formation increased with increasing amine  $\text{pK}_a$  over the entire  $\text{pK}_a$  range from 0 to 11 (Challis et al., 1979; Masuda et al., 2000; Cooney et al., 1987). Accordingly, the nitramine/nitrosamine product ratio increased with basicity (Cooney et al., 1987).

In addition to basicity, steric hindrance is also important, because the lone pair of electrons on the nitrogen atom may be shielded from nitrosating and nitrating agents. At neutral and alkaline pH, nitrosation by nitrite catalyzed by formaldehyde increased as steric hindrance decreased (pyrrolidine  $\sim$  piperidine  $\sim$  dimethylamine  $>$  diethylamine  $>$  diisopropylamine) (Keefer and Roller, 1973). Moreover, the formation rate constant for the intermediate carbinolamine in this aldehyde-catalyzed pathway was higher for the less sterically-hindered amine (Casado et al., 1984).

As indicated previously, primary nitrosamines are unstable, and decay to release nitrogen gas and a carbocation. Among the primary amines, monoethanolamine is of special interest as it is the most widely used carbon capture solvent on an industrial scale (Strazisar et al., 2003). After unstable N-nitrosomonoethanolamine is formed, it can form N-nitrosodiethanolamine via diethanolamine (Figure 7). However,  $\beta$ -hydroxynitrosamines, such as N-nitrosodiethanolamine, undergo base-induced carbon-carbon bond scission. In the case of N-nitrosodiethanolamine, formaldehyde and N-nitrosomethylethanolamine, or even N-nitrosodimethylamine, would form (Loepky et al., 1979). Alternatively, elimination

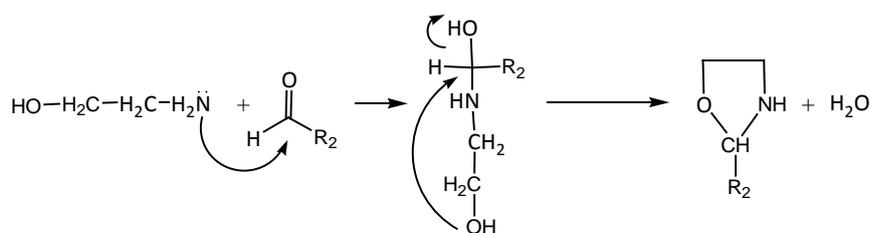
of water under heat, catalyzed by base, forms the cyclic nitrosomorpholine (NMOR) (Loeppky et al., 1979):



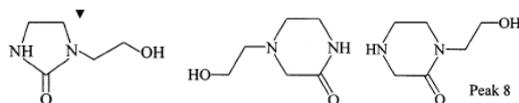
Nitrosomorpholine and NDMA are significantly more volatile than nitrosodiethanolamine. Although not yet studied, these transformations are also likely relevant to nitroethanolamines.

In addition to their relevance to nitrosamine and nitramine formation during amine-based carbon capture, these mechanisms have important implications for sample handling. As described below, sample storage at low pH bears the risk of artifactual nitrosamine formation from nitrite, perhaps with aldehyde catalysis (Casado et al., 1984). However, sample storage at high pH (perhaps even the native pH around 10.5 of monoethanolamine-based washwater or solvent mixtures) risks transformation of nitroso/nitroethanolamines into nitroso/nitromorpholines and nitroso/nitrodimethylamines.

One active field of study for monoethanolamine-based CO<sub>2</sub> capture technology is the oxidative degradation of monoethanolamine. While this review does not focus on the monoethanolamine loss, secondary amine formation is of concern, because secondary amines are important precursors for stable nitrosamines. For example, the presence of aldehydes may trigger another pathway for the transformation of the primary amine, monoethanolamine, into oxazolidones, which are secondary amines (Figure 8; Saavedra, 1981). Figure 9 provides the structures of additional byproducts of the oxidation degradation of monoethanolamine. In some cases, stable secondary nitrosamines could form from these precursors. However, the electron-withdrawing nature of carbonyl groups in the alpha position to the amine nitrogen would reduce their tendency to react with nitrosating and nitrating agents.



**Figure 8:** Oxazolidone formation from monoethanolamine in the presence of aldehydes.



**Figure 9:** Additional products of the oxidative degradation of monoethanolamine.

When using a mixture of amines for CO<sub>2</sub> capture, a nitrosamine may transfer its nitroso group to another amine, potentially forming a more volatile nitrosamine product. Such transnitrosation reactions have been reported between aliphatic cyclic amines (e.g., between N-nitroso-4-methylpiperazine and morpholine (Singer, 1978)). Protonation of the nitrosyl oxygen forms a hydroxylamine. A nucleophilic attack by nucleophiles (X<sup>-</sup>), like Cl<sup>-</sup>, on the hydroxylamine nitrogen liberates the amine and the nitrosating agent, XNO. XNO can

react with the other amine to form a nitrosamine. Although no transnitrosation reactions have been documented for straight chain amines, the proposed pathway does not require a cyclic structure. Though low pH is required for this reaction, catalysis by nucleophilic anions (e.g.,  $\text{Cl}^-$  and  $\text{Br}^-$ ) may play a role (Singer, 1978). The effect of temperature on transnitrosation is not reported.

Amino acids are being considered for carbon capture. Previous research indicated that structural characteristics relevant to amino acids affect the stability of their respective nitrosamines; nitrated amino acids have not been a focus of research. Comparing the stability at 110 °C of the nitrosated alkylamine, N-nitrosodimethylamine, with the nitrosated amino acids, N-nitrososarcosine and N-nitrosoproline, Fan and Tannenbaum (1972) found that the  $\alpha$ -carboxylic acid on the amino acids accelerated nitrosamine decay by a factor of 1000 at  $\text{pH} < 4$ . However, comparing the decay of N-nitrosodimethylamine to the cyclic alkyl nitrosamine, N-nitrosopyrrolidine, the decay of the cyclic nitrosamine was 100 times faster at alkaline pH. Regarding the nitrosated amino acids, decay of N-nitrososarcosine decreased with increasing pH, while the decay of N-nitrosoproline increased with pH.

In all cases, nitrite was the major inorganic product detected; organic products were inadequately characterized. A major concern for nitrosated amino acids regards the possibility of decarboxylation, because loss of the polar carboxylic acid would form more volatile products. In the Fan and Tannenbaum study (1972), no decarboxylation of N-nitrosoproline or N-nitrososarcosine was observed at 110 °C over  $\text{pH} 2.2\text{-}12.5$ . However, studies conducted at higher temperatures and pressures (e.g., 310-330 °C and 275 bar) indicate that decarboxylation of non-nitrosated amino acids follows the order:  $\alpha$ -amino acid  $>$   $\beta$ -amino acid  $\gg$   $\gamma$ -amino acid (Li and Brill, 2003). Of additional concern is the possibility of a concerted nitrosation and decarboxylation of amino acids during reaction with nitrosating agents. In such a reaction, the nitrosation of an  $\alpha$ -amino group is coupled with decarboxylation. Although research has not evaluated the importance of these reactions in solution, in cigarette smoke, the volatile alkyl nitrosamine, N-nitrosopyrrolidine, formed at 0.0005% yield from a concerted nitrosation and decarboxylation of proline by reaction with  $\text{NO}_x$  (Tricker and Preussman, 1992).

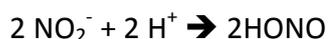
### 3.3 Amine and Amino Acid Nitrosation and Nitration Pathways

The purpose of this section is to help identify which specific types of amines or nitrosating/nitrating agents dominate formation under four different reaction conditions, including both the gas and aqueous phase as well as with and without solar irradiation.

#### 3.3.1 Aqueous Reactions

**3.3.1.1 Amines:** Nitrite, the end product of many nitrosating and nitrating agents, may be involved in nitrosation. Many studies have evaluated nitrosation by nitrite at the acidic pH characteristic of the human stomach. Under acidic conditions, formation of the nitrosating agent,  $\text{N}_2\text{O}_3$ , occurs in a reaction that is second order in nitrite (Mirvish, 1975), and involves HONO as an intermediate. However, for most secondary amines, previous research has indicated that the formation of  $\text{N}_2\text{O}_3$  is the rate limiting step, suggesting that  $\text{N}_2\text{O}_3$  is the responsible nitrosating agent. HONO has not been considered as the active nitrosating agent; however, more recent research suggests that HONO might be the active nitrosating agent

for nitrosation of phenols in aqueous systems (Vione et al., 2004). Further research is needed to identify the most important nitrosating species.



A nucleophilic attack by the lone electron pair of the amine on  $\text{N}_2\text{O}_3$  forms the nitrosamine. The dual requirement for acidified nitrite and the deprotonated amine results in an optimal pH for this reaction near 3.4 (Fan and Tannenbaum, 1973). For most amines, the formation rate is given by (Mirvish, 1975):

$$\text{Rate} = k[\text{R}_2\text{NH}][\text{HNO}_2]^2$$

These absolute rate constants varied by only a factor of 34 among 14 secondary amines ranging from dimethylamine ( $\text{pK}_a = 10.7$ ) to N-methylaniline ( $\text{pK}_a = 4.9$ ). However, note that the rate is written in terms of the deprotonated secondary amine. Accordingly, the observed rate at a particular pH varies dramatically with higher rates for those amines with lower  $\text{pK}_a$ s, due to the greater fraction of the amine in the deprotonated form. For example, Table 4 provides data for a subset of these secondary amines, including both the absolute rate constant ( $k_1$ ; i.e., speciating the amine and nitrite) and the observed rate constants ( $k_2$ ; not speciating the amine and nitrite) near pH 2.5-3.5. Note that despite the similarities in absolute rate constants, amines like morpholine and piperazine will be nitrosated at orders of magnitude faster rates than dimethylamine at a particular pH because a significantly higher fraction of these amines will be in the active deprotonated form. Note that these rate constants often reflect  $\text{N}_2\text{O}_3$  formation from acidification of nitrite as a rate-limiting step, and hence rates are enhanced at low pH. During carbon capture,  $\text{N}_2\text{O}_3$  formation from  $\text{NO}_x$  may be less dependent on acidic pH conditions; during capture,  $\text{N}_2\text{O}_3$  could form directly from the reaction of  $\text{NO}^*$  and  $\text{NO}_2^*$ , rather than forming by the acidification of nitrite. Note that many of these amines and amino acids are relevant to carbon capture, including morpholine, N-methylethanolamine, piperazine, and 1-nitrosopiperazine.

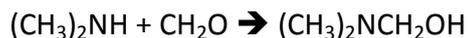
**Table 4:** Nitrosation rates of amines and amino acids.

Amine	$\text{pK}_a$	$k_1 (\text{M}^{-2} \text{s}^{-1})$	$k_2 (\text{M}^{-2} \text{s}^{-1})$
Piperidine	11.2	$1.4 \times 10^5$	0.00045
Dimethylamine	10.7	$1.5 \times 10^5$	0.0017
N-methylethanolamine	9.5	$0.62 \times 10^5$	0.01
Proline	-	$1.4 \times 10^5$	0.037
Sarcosine	-	$2.6 \times 10^5$	0.23
Propylglycine	8.97	$5.0 \times 10^5$	0.25
Morpholine	8.7	$2.3 \times 10^5$	0.42
1-nitrosopiperazine	6.8	$0.83 \times 10^5$	6.7
Piperazine	5.57	$0.62 \times 10^5$	83

This dependency of nitrosation rate on the  $\text{pK}_a$  of the amine enables a structure activity relationship to be developed. Mirvish (1975) provides an excellent correlation

between the  $pK_a$  of secondary amines and their observed nitrosation rates at a particular pH.

According to this scheme, no nitrosation from nitrite would be expected at neutral or alkaline pH, where  $\text{NO}_2^-$  would predominate over  $\text{HONO}$ . However, formaldehyde has been found to catalyze nitrosation by nitrite, enabling significant formation at neutral and even alkaline pH (Roller and Keefer, 1973). For example, a reaction between dimethylamine and formaldehyde forms a carbinolamine (Casado et al., 1984). Protonation of the carbinolamine, followed by dehydration, forms an iminium ion. The iminium ion reacts with nitrite to form a nitrosamine, releasing formaldehyde for further reactions.



In this case, the formation rate is first order in nitrite concentration. The importance of other aldehydes is unclear. Due to the high concentrations of aldehydes anticipated to be present in the absorbent solution and in the washwater, and because nitrite occurs in washwater, this pathway is likely to be a significant pathway for nitrosamine formation. Figure 10 presents modeled nitrosation rates (M/s) of 10 mM dimethylamine by 100 mM nitrite in the absence or presence of 10 mM formaldehyde as a function of pH; dimethylamine was selected because rate constants for its nitrosation were available by both pathways (Mirvish, 1975; Casado et al., 1984). Catalysis of nitrosation by formaldehyde increased nitrosation rates by at least 9 orders of magnitude across the range of pH. Additionally, the nitrosation rate was nearly constant from pH 1-9, but dropped by an order of magnitude for each pH unit thereafter. At pH 10.5, this rate translates to the formation of 257  $\mu\text{M}$  after 5 d.

Fewer studies have been conducted with tertiary amines. However several studies have indicated that nitrosation rates of tertiary amines via acidified nitrite are  $\sim 4$  orders of magnitude slower than for their analogous secondary amines (Mirvish, 1975), likely due to the requirement to undergo dealkylation. The studies are limited, and often under unusual conditions (e.g., 100 °C), rendering their direct comparison to secondary amines difficult.

Amides may feature as functional groups within certain amino acids. In amides, although the nitrogen is adjacent to an electron-withdrawing carbonyl group, nitrosation rates can be more rapid than for certain secondary amines (e.g., dimethylamine) for two reasons (Mirvish, 1975). First, these compounds feature lower  $pK_a$ s ( $\sim 1$ ) due to the carbonyl group, and so nearly all of the compound is in the active deprotonated form. Second, the rate is first order in nitrite, and so may proceed under lower nitrite concentrations:

$$\text{Rate} = k[\text{amide}][\text{HONO}][\text{H}^+]$$

However, nitrosated amides may hydrolyze rapidly and so are less likely to accumulate in the environment.

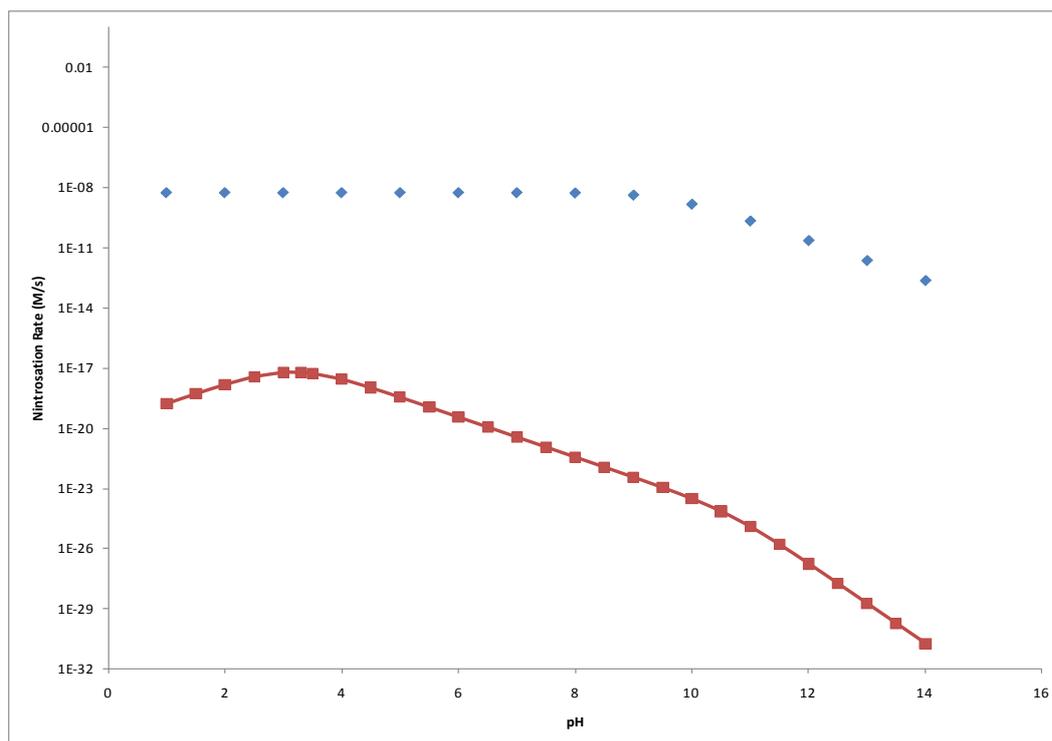
No nitration by nitrite has been reported. In fact, nitrite inhibited nitration by  $\text{N}_2\text{O}_4$  by reversing the reaction through the mass action effect (Figure 10; Cooney et al., 1987).

For reactions involving  $\text{NO}_x$ , NO and  $\text{NO}_2$  are considered to dissolve into the aqueous phase, and then form other nitrosating or nitrating species (Table 1). There have been limited studies conducted on heterogeneous  $\text{NO}_x$ -amine systems. For these studies, results are often interpreted as a serial process of mass transfer followed by reaction in the aqueous phase (Challis and Kyrtopoulos, 1979; Cooney et al., 1987; Lewis et al., 1995; Caulfield et al., 1996). Previous research indicated that direct heterogeneous reactions on the gas-liquid interface are not important (Cheung et al., 2000).

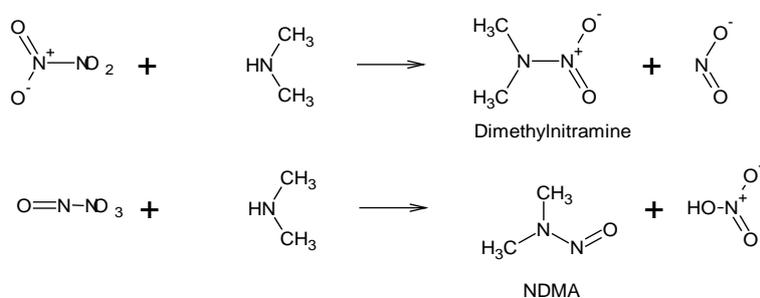
A study attempting to control  $\text{NO}_x$  pollution using primary aromatic and aliphatic amines demonstrated that NO alone does not react efficiently with primary amines (Kobayashi et al., 1980).  $\text{NO}_2$  reactions with amines were significantly faster. The presence of  $\text{NO}_2$  significantly enhanced the reaction of NO with amines, even though the rate was still slower than the  $\text{NO}_2$  reaction. Similarly, when  $\text{NO}^*$  was introduced into the gaseous headspace above an acetonitrile solution containing amines, nitrosation was negligible in the absence of oxygen, but significant in its presence. These results suggest that daughter nitrosating and nitrating species of  $\text{NO}_x$  could be more important nitrosating and nitrating agents than  $\text{NO}^*$  or  $\text{NO}_2^*$ .  $\text{NO}^*$  is a poor nitrosating agent in solution, because of a low potential to remove an electron from the amine to form amino radical intermediates. In the presence of oxygen,  $\text{NO}_2^*$  formation (via  $2 \text{NO}^* + \text{O}_2 \rightarrow 2 \text{NO}_2^*$ ) enables  $\text{N}_2\text{O}_3$  formation in solution; as an even-electron oxidant, nitrosation can proceed directly without an amino radical intermediate.

Overall,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  are among the most important nitrosating and nitrating agents are  $\text{N}_2\text{O}_3$ , an active nitrosating agent, and  $\text{N}_2\text{O}_4$ , which exists in two tautomeric forms, one a nitrosating agent, and the other a nitrating agent (Figure 11). However, in aqueous solution, nitrosation/nitration of amines competes with hydrolysis of  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ . Previous research indicated that between pH 6.9 and 13, ~10% of ~ 10 mM  $\text{N}_2\text{O}_3$  nitrosated ~ 1mM amines in aqueous solution, while the rest hydrolyzed (Challis and Kyrtopoulos, 1979).

The dependency of nitrosation and nitration on other reaction conditions has not been completely defined. When diluting  $\text{N}_2\text{O}_4$  from 0.083 atm to 0.001 atm at alkaline pH, the yield of N-nitrosopiperidine decreased as expected, but the yield of N-nitropiperidine increased dramatically (Challis and Kyrtopoulos, 1979). However, when  $\text{N}_2\text{O}_3$  was diluted from 0.05 atm to 0.001 atm, the yield of N-nitrosopiperidine remained constant, and only traces of N-nitropiperidine were detected. The increase in N-nitropiperidine with decreasing  $\text{N}_2\text{O}_4$  seems to contradict another study which reported an increase in nitration rate with  $\text{NO}_2$  concentration (Cooney et al., 1987). However, the reaction rate order with respect to  $\text{NO}_2$  declined as  $\text{NO}_2$  concentration increased above 30 ppm (Cooney et al., 1987). A later study isolated the rate constant for the reaction of  $\text{N}_2\text{O}_3$  and morpholine to be  $6.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (Lewis et al., 1995). As the earlier study indicated that rate constants for reaction of gaseous  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  with amines in 0.1 N sodium hydroxide solution were  $10^6$ - $10^7 \text{ M}^{-1} \text{ s}^{-1}$  (Challis and Kyrtopoulos, 1979), the results indicate that mass transfer from the gas to liquid phase is essentially diffusion-controlled.

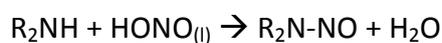


**Figure 10:** Nitrosation rates vs. pH for 100 mM nitrite, 10 mM dimethylamine in the absence (red) or presence (blue) of 10 mM formaldehyde.



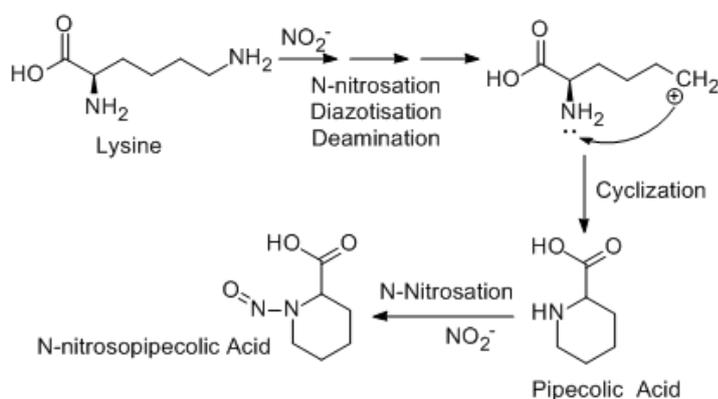
**Figure 11:** Nitrosating and nitration of dimethylamine by  $\text{N}_2\text{O}_4$ .

Atmospheric aqueous conditions differ from capture units, especially with regard to the pH which is typically between pH 3-6, as opposed to the higher pH 10.5 typical of the adsorber/desorber units. This indicates that along with the other nitrosating agents considered for the adsorber (e.g.,  $\text{N}_2\text{O}_4$ ,  $\text{ONO-NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$ ), the nitrosating ability of  $\text{HONO}$  and  $\text{H}_2\text{ONO}^+$ , which are formed from  $\text{NO}_2^-$  at lower pH conditions (equations 1 and 2) also need to be considered. Numerous studies have previously documented that  $\text{HONO}_{(l)}$  and  $\text{H}_2\text{ONO}^+_{(l)}$  can nitrosate amines (Anastasio and Chu, 2009):

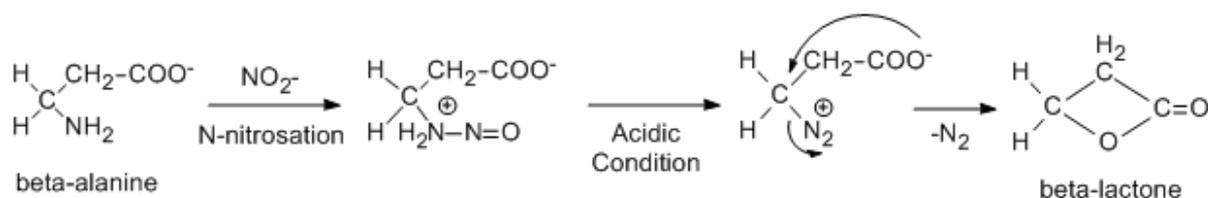


However, one study in particular has assessed their potential reactivity in water-soluble aerosol extracts (dissolved organic carbon (DOC) = 2.0 mg C/L) (Hutchings et al., 2010). This study found that upon addition of 5.0 mg/L dimethylamine and 5.0 mg/L nitrite between pH 3 to 6 to such water soluble aerosol extracts, N-nitrosodimethylamine (NDMA) formation up to 5.5  $\mu\text{g/L}$  (0.16% product yield) was observed (Hutchings et al., 2010). Given that the dimethylamine and nitrite concentrations were atypically high, model simulations were performed at more likely atmospheric concentrations to evaluate NDMA formation. The gas phase HONO and dimethylamine concentrations were set between 1-4 ppb and 10 ppt, respectively. Model simulations predicted NDMA concentrations in the aqueous fog phase between 70 to 220 ng/L (Hutchings et al., 2010), a significant level of formation even at low precursor concentrations. The model indicated that most formation occurred within the gas phase from reaction of HONO and dimethylamine, followed by dissolution of NDMA into the aerosols; aqueous phase nitrosation was negligible. However, inclusion of HONO formation by heterogeneous reactive uptake of gas phase  $\text{NO}_2^*$  at the aerosol interface would increase modeled NDMA concentrations in the fogwater by several orders of magnitude; further research is needed to evaluate the importance of this heterogeneous uptake mechanism.

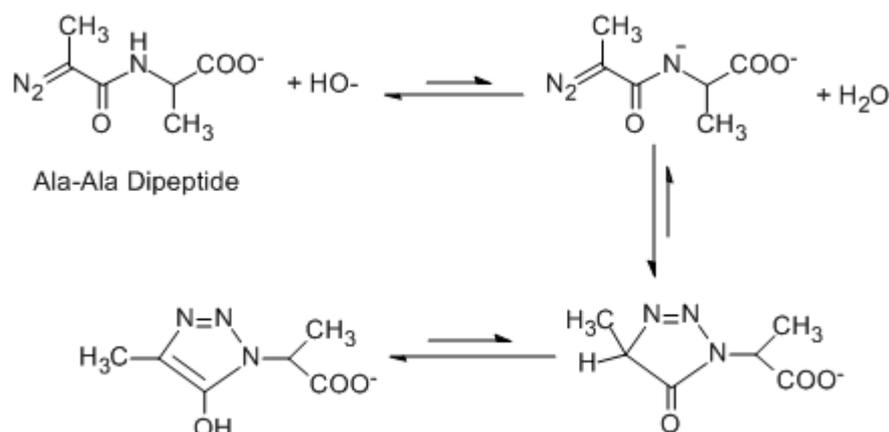
**3.3.1.2 Amino Acids:** Most amino acids feature an  $\alpha$ -terminal primary amine and a carboxylic acid functional group. Reaction of nitrosating agents formed by the acidification of nitrite or by exposure to gaseous  $\text{NO}_2$  form unstable primary nitrosamines (Challis et al., 1994). Like other primary nitrosamines, these nitrosamines decay by deamination via formation of a diazonium ion, which releases  $\text{N}_2$  gas and a carbocation. As for other primary amines, the carbocation intermediate may react with  $\alpha$ -terminal primary amines in adjacent amino acids to form dimers (Warthesen et al., 1975). In certain cases, intramolecular attacks of other functional groups on the carbocation intermediates may form cyclic products. For example, nitrosation of ornithine and lysine form the cyclic secondary amines, proline and pipercolic acid (Figure 12), respectively (Warthesen et al., 1975). Under acidic conditions, attack of the carboxylic acid on the carbocation intermediate can form lactones (Figure 13), which are alkylating agents that are likely mutagenic (Garcia-Santos et al., 2001). At alkaline pH, for dipeptides, the diazotized dipeptide may form a cyclized triazole compound (Figure 14; Challis et al., 1994). In contrast, nitrosation of the secondary amines sarcosine and proline forms stable nitrosamines.



**Figure 12:** Nitrosopipecolic acid formation from nitrosation of lysine.

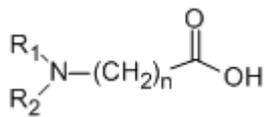


**Figure 13:** Lactone formation from amino acid-based carbocations



**Figure 14:** Triazole formation from dipeptide-based carbocations

In the case of nitrosation by acidification of nitrite, nitrosation is considered to occur by a reaction of  $\text{N}_2\text{O}_3$  with the unprotonated amine group, and generally the reaction is second order in nitrite (Garcia-Santos et al., 2002). At very low pH, a first order dependence in nitrite can be observed, indicative of reaction via a  $\text{NO}^+$  nitrosating agent (Casado et al., 1985); however, it is postulated that nitrosation of the carboxylate group (i.e.,  $-\text{COONO}$ ), followed by an intramolecular attack on the  $\alpha$ -terminal amine could partially explain this dependence. It is important to note that there are different rate constants for reaction of the nitrosating agent  $\text{N}_2\text{O}_3$  with the protonated (i.e.,  $-\text{COOH}$ ) and unprotonated (i.e.,  $-\text{COO}^-$ ) carboxylic acid (Garcia-Santos et al., 2002), resulting in a more complex picture than provided in Table 1. The rate constants for reaction with the deprotonated carboxylic acid are generally an order of magnitude higher, because these are electron-donating substituents that stabilize the carbocation intermediates (Challis et al., 1994; Garcia-Santos et al., 2002). For example, the pH-independent rate constant for the reaction of N with morpholine is  $6.4 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  (Lewis et al., 1995), compared to  $44 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  for  $\beta$ -alanine (Garcia-Santos et al., 2002). Regarding acidic nitrosation by nitrite, the third order rate constants follow the order  $\alpha$ -amino acid  $>$   $\beta$ -amino acid  $>$   $\gamma$ -amino acid (Gil et al., 1994). Structural characteristics of these amino acids are provided in Figure 15, where  $n = 1$  for  $\alpha$ -amino acids, 2 for  $\beta$ -amino acids and 3 for  $\gamma$ -amino acids. The higher rate constants for  $\alpha$ -amino acids may reflect the proximity of the electron-donating  $-\text{COO}^-$  group. However, experimental results are insufficient to elucidate the importance of this trend. However, these results, combined with those in Table 4, indicate that nitrosation of amino acids would be at least as rapid as for alkylamines. However, most experiments have been conducted at low pH, so it is difficult to extrapolate to the higher pH conditions relevant to absorber units.



**Figure 15:**  $\alpha$ -,  $\beta$ - and  $\gamma$ -amino acid structures.

**3.3.1.3 Additional factors:** Impurity anions are commonly present in industrial-scale capture facilities, as well as atmospheric aerosols. These anions include chloride, bromide, nitrate, nitrite, phosphate and bicarbonate (Strazisar et al., 2003). At acidic pH, chloride, bromide, and sulfate enhanced nitrosation by nitrite. The enhancement was more significant for anions, like bromide, that are stronger nucleophiles and bases of stronger acids (Fan and Tannenbaum, 1973). Anions (X<sup>-</sup>) can form the nitrosating species XNO via a nucleophilic attack on other species, including N<sub>2</sub>O<sub>3</sub> (Fan and Tannenbaum, 1973). The nitrosation rate in the presence of anions can be expressed as (Mirvish, 1975):

$$\text{Rate} = k[\text{R}_2\text{NH}][\text{HONO}][\text{H}^+][\text{X}^-]$$

Because this rate expression is only first order in nitrous acid, anions may be important under acidic conditions where nitrite concentrations are low, and the second order nature of the reaction in the absence of anions is unimportant.

At circumneutral pH, bromide only enhanced nitrosation of morpholine by NO<sub>2</sub><sup>\*</sup> at high concentrations (i.e., >2 mM bromide, 99 ppm NO<sub>2</sub><sup>\*</sup>, and 10 mM morpholine (Cooney et al., 1987)). As a weaker nucleophile, chloride did not affect nitrosation by NO<sub>2</sub><sup>\*</sup>, even at 100 mM chloride (Cooney et al., 1987). In contrast, during nitrosation of morpholine by NO at the presence of O<sub>2</sub>, 40 mM chloride reduced N-nitrosomorpholine formation by 30% (Lewis et al., 1995), presumably by forming NOCl from N<sub>2</sub>O<sub>3</sub> ( $k = 1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ). NOCl rapidly hydrolyzes at mid pH to nitrite. The net result is a significant reduction in the concentration of nitrosating agents. Since chloride concentrations up to 1,600 ppm have been measured in absorber solutions (Strazisar et al., 2003), the impact of anions can be important. Whether anions promote or reduce nitrosation may depend on the anion concentrations. While nitrate was not observed to affect nitrosation, one study found that it increased nitration, potentially by reacting with N<sub>2</sub>O<sub>4</sub> to form N<sub>2</sub>O<sub>5</sub> (Cooney et al., 1987):



Lastly, metals may catalyze nitrosation via formation of NO-metal complexes (Challis and Kyrtopoulos, 1979).

In a CO<sub>2</sub> capture system, carbonates may be particularly important. The inhibitory effect of carbonates on nitrosation by N<sub>2</sub>O<sub>3</sub> is greater than that by N<sub>2</sub>O<sub>4</sub> (Caulfield et al., 1996; Lewis et al., 1995). The inhibitory effect is thought to arise from complex formation between the amine and CO<sub>2</sub> (Kirsch et al., 2000). The resulting carbamate is much less susceptible to attack by nitrosating and nitrating agents.

Although not present in significant concentrations in absorber solutions (Strazisar et al., 2003), phosphate is commonly used as a buffer in lab studies. The inhibitory effect of phosphate has been observed for both nitrosation and nitration (Challis and Kyrtopoulos, 1979; Cooney et al., 1987; Lewis et al., 1995), while the effect on nitration was more significant (Cooney et al., 1987). The responsible phosphate species is unclear, but Lewis et al. (1995) quantified an observed reaction rate constant total phosphate reaction with N<sub>2</sub>O<sub>3</sub>

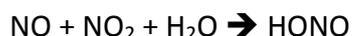
as  $6.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , a value that can be used to account for the inhibitory effect of phosphate used in laboratory buffers.

Temperature may be particularly important. Most studies on nitrosamine and nitramine formation were related to medical applications, and so were conducted at room temperature or body temperature (37 °C). Extrapolation to the significantly higher temperatures encountered in desorber units (e.g., ~120 °C for monoethanolamine) is difficult. One limited study found that nitration of morpholine by  $\text{NO}_2^*$  increased to a greater degree than nitrosation as the temperature increased to 50 °C (Cooney et al., 1987). These results may indicate that formation of the nitrating tautomer,  $\text{O}_2\text{N-NO}_2$  may require a higher activation energy than the nitrosating  $\text{ONO-NO}_2$  tautomer. Another relevant finding was that the phosphate inhibition of nitrosation was higher at 37 °C than 25 °C (Lewis et al., 1995), suggesting that phosphate may be a poor choice for a laboratory buffer. Additionally, initial results in our laboratory indicate a significant enhancement in nitrosation of amines by nitrite as temperatures increase above 100 °C. The underlying reaction mechanisms are unclear, but these results bear particular relevance to desorber units, where nitrite forming as a  $\text{NO}_x$  end product of nitrosating/nitrating species in the absorber unit, is heated in the presence of amines to temperature up to ~120 °C.

The stability of nitrosamines and nitramines may also be affected by temperature. At 110 °C and alkaline pH (8.5 to 12.5), cyclic nitrosamines decayed 100 times faster than straight chain nitrosamines (Fan and Tannenbaum, 1972). Moreover, the decay rate of cyclic nitrosamines increased with pH, while that of straight chain nitrosamines decreased with pH (Fan and Tannenbaum, 1972). However, the fact that less than a molar equivalent of nitrite formed per nitrosamine lost (Fan and Tannenbaum, 1972) indicated that alkyl chain scission may occur, potentially producing smaller, more volatile nitrosamines.

### 3.3.2 Gas Phase Reactions

3.3.2.1 Importance of  $\text{HONO}_{(g)}$  and  $\text{NO}_3^*$  in the Dark: Previous research has suggested that nitrosamines may form downwind from reactions of ambient  $\text{NO}_x$  with amines released with the flue gas. In the dark, nitrous acid (HONO) formed from reaction of  $\text{NO}_x$  with water vapor reacts with amines to form nitrosamines (Hanst et al., 1977):



It is possible that gas phase  $\text{N}_2\text{O}_3$  could also nitrosate gas-phase amines via:



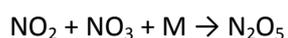
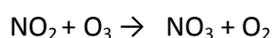
However, the second order dependence on HONO concentrations for  $\text{N}_2\text{O}_3$  renders this pathway less likely. Although  $\text{N}_2\text{O}_3$  could also form from the reaction of  $\text{NO}^*$  and  $\text{NO}_2^*$ , the equilibrium favors  $\text{NO}^*$  and  $\text{NO}_2^*$  in the gas phase.

The first study to observe the importance of the HONO reaction was conducted by Hanst et al. (1977). In this study, a series of experiments were performed in a cylindrical glass reaction chamber where either (1) 1 ppm dimethylamine + 1 ppm  $\text{NO}_2^*$  + 4 ppm  $\text{NO}^*$  were added together in  $\text{N}_2$  or (2) 1 ppm dimethylamine + 2 ppm  $\text{NO}_2^*$  + 2 ppm  $\text{NO}^*$  + 13,000 ppm  $\text{H}_2\text{O}_{(g)}$  were added together in air. Amine loss was found to be 1%/min for the

experiment in N<sub>2</sub> but 4% for the experiment in humidified air. Assuming amine loss was proportional to nitrosamine increase, these findings suggested that HONO<sub>(g)</sub> formation from the reaction of NO<sub>x</sub> and H<sub>2</sub>O (Table 1) lead to greater nitrosamine formation compared to NO<sub>x</sub> alone, presumably due to the formation of HONO. Because both NO<sub>x</sub> constituents (NO\* and NO<sub>2</sub>\*) are radicals, their direct reaction with amines to form a stable (even-electron) product would require that an electron be removed from the amine prior to the interaction with NO<sub>x</sub>. As an even electron reactant, this requirement does not apply to HONO. The second study to confirm the importance of HONO<sub>(g)</sub> was conducted by Pitts et al. (1978). In that study, 0.48 ppm of the secondary amine, diethylamine, was mixed with 0.08 ppm NO\* + 0.17 NO<sub>2</sub>\* in a reaction chamber containing 31-51% relative humidity. The maximum diethylnitrosamine concentration was achieved within 10 min at a concentration of 14 ppb (2.8% conversion of the amine). The nitrosation of DEA was linked to reactions of HONO<sub>(g)</sub>. Within this same experiment, diethylnitramine did not form at any appreciable level over 2 h, suggesting that NO<sub>x</sub> alone is unable to nitrate secondary amines such as diethylamine in the dark; HONO<sub>(g)</sub> is a nitrosating agent, but not a nitrating agent.

For tertiary amines (R<sub>3</sub>N), the study by Pitts et al. (1978) similarly evaluated the reaction of 0.35 ppm triethylamine mixed with 0.08 ppm NO\* + 0.16 NO<sub>2</sub>\* in a reaction chamber containing 24-41% relative humidity, but diethylnitrosamine conversion was only 0.8%, while no diethylnitramine formation was observed. The results suggest that tertiary amines are less readily nitrosated than secondary amines by HONO<sub>(g)</sub>. For primary amines (R<sub>1</sub>NH<sub>2</sub>), no known studies to date have evaluated their nitrosation potential in the presence of NO<sub>x</sub> or HONO under dark conditions. These results are in accordance with the inability to form stable nitrosamines, and the requirement to first dealkylate tertiary amines and then nitrosate the secondary amine product.

The nitrate radical (NO<sub>3</sub>) can play a dual role in formation of nitrosamines and nitramines in the atmosphere. First, NO<sub>3</sub> can serve as a nighttime reservoir for the nitrating agent, NO<sub>2</sub>, which can thus lessen the overall level of amine nitration. NO<sub>2</sub> can be captured either through the reaction of NO<sub>2</sub> with O<sub>3</sub> to form NO<sub>3</sub> directly or NO<sub>3</sub> can react with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub> (Seinfeld and Pandis, 1998; Chameides, 1986). During the day, NO<sub>3</sub> is rapidly photolyzed under sunlight to form NO<sub>2</sub> or NO. NO<sub>3</sub> can also react with the photolysis-generated NO to form NO<sub>2</sub> (Seinfeld and Pandis, 1998). Thus, NO<sub>3</sub> in the atmosphere is more stable at night than the day. A typical NO<sub>3</sub> concentration at night is ~ 2 x 10<sup>9</sup> molecules/cm<sup>3</sup> (3.3 ppt; (Atkinson et al., 1984)), which is ~ 3 orders of magnitude greater than the typical daytime OH concentration (Table 5).



**Table 5.** Typical NO<sub>3</sub> and OH concentrations in the atmosphere.

Radical Species	Conditions	Typical concentrations
OH	gas phase, daytime, summer	$5-10 \times 10^6$ molecules/cm <sup>3</sup> <sup>a</sup>
OH	gas phase, daytime, winter	$1-5 \times 10^6$ molecules/cm <sup>3</sup> <sup>a</sup>
OH	gas phase, nighttime, winter	$\leq 2 \times 10^6$ molecules/cm <sup>3</sup> <sup>a</sup>
NO <sub>3</sub>	gas phase, nighttime	$\sim 2 \times 10^9$ molecules/cm <sup>3</sup> <sup>b</sup>
NO <sub>3</sub>	aqueous phase, nighttime	$10^{12}$ M <sup>c</sup>

<sup>a</sup> Seinfeld and Pandis, <sup>b</sup> Atkinson 1984, <sup>c</sup> Chameides 1986

The second way NO<sub>3</sub><sup>\*</sup> can affect nitrosamine and nitramine formation is similar to the OH<sup>\*</sup> reaction in sunlight (see section 3.3.2.2). NO<sub>3</sub><sup>\*</sup> abstracts a hydrogen from the N-H group of amines, forming an amino radical (Malloy et al., 2009). The amino radical can then react with NO<sub>x</sub> to form nitrosamines/nitramines. However, previous kinetic studies with ammonia suggest that its reaction rate (*k*) with NO<sub>3</sub><sup>\*</sup> is quite slow ( $< 5.99 \times 10^{-16}$  molecules/cm<sup>3</sup>/s; Cantrell et al., 1987), nearly four orders of magnitude slower than the reaction of ammonia with OH<sup>\*</sup> ( $1.83 \times 10^{-12}$  molecules/cm<sup>3</sup>/s; Clark et al., 2008). These *k* values along with those related to reactions with trimethylamine are provided in Table 6.

**Table 6.** Amine reaction rates with NO<sub>3</sub> and OH.

Radical Species	Amine	<i>k</i> (cm <sup>3</sup> /molecule/s)
NO <sub>3</sub>	ammonia	$< 5.99 \times 10^{-16}$ <sup>a</sup>
OH	ammonia	$1.83 \times 10^{-12}$ <sup>b</sup>
NO <sub>3</sub>	trimethylamine	$> 4.4 \times 10^{-16}$ <sup>c</sup>
OH	trimethylamine	$3.58 \pm 0.22 \times 10^{-11}$ <sup>d</sup>

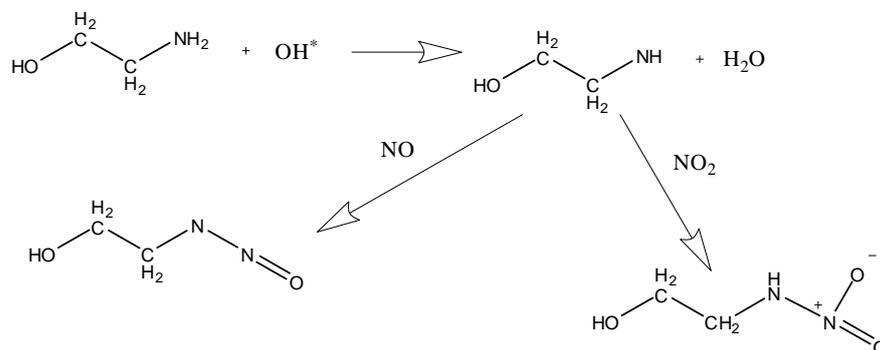
<sup>a</sup> Cantrell et al. 1987, <sup>b</sup> Clark et al. 2008, <sup>c</sup> Silva et al. 2008, <sup>d</sup> Carl and Crowley 1998

The relative importance of NO<sub>3</sub><sup>\*</sup> reactions with amines at night compared to OH<sup>\*</sup> reactions with amines during the day can be assessed by multiplying typical concentrations of these radicals with their rate constants. For the reactions of NO<sub>3</sub><sup>\*</sup> with ammonia during the night, this value was  $< 1.2 \times 10^{-6} \text{ s}^{-1}$ . For the reaction of OH<sup>\*</sup> with ammonia during the day, the value was  $1.83 \times 10^{-6} - 1.83 \times 10^{-5} \text{ s}^{-1}$ . Accordingly, the importance of the OH<sup>\*</sup> reaction may be slightly greater, although their importance appears to be comparable. Rate constants with amines are needed to further evaluate the relative importance of the pathways.

Once the amino radical is formed, nitration and nitrosation ultimately depend on the nitrosating/nitrating agent concentration (e.g.,  $\text{NO}_x$ ) present in the atmosphere. For nitramines, the presence of  $\text{NO}_3^*$  corresponds to a sink for  $\text{NO}_2^*$ , suggesting that nitration is more likely to occur during the day through the  $\text{OH}^*$ -dependent pathway rather than through the nighttime  $\text{NO}_3^*$ -dependent pathway; however, this may not be true for nitrosamine formation given that the nitrosating agent,  $\text{NO}^*$ , is not affected in the same manner, and thus both reaction pathways at both day and night may play a role.

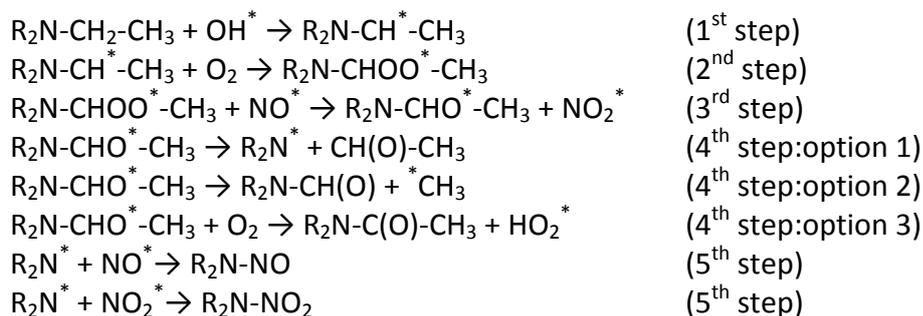
3.3.2.2 Importance of  $\text{OH}^*$  and  $\text{NO}_x$  in the Presence of Sunlight: Both a secondary amine (diethylamine) and a tertiary amine (triethylamine) were exposed to  $\text{NO}_x$  in air containing 31-51% humidity while being irradiated for up to 4 h with outdoor sunlight (Pitts et al., 1978). The results indicated that when diethylamine (0.48 ppm) was mixed with 0.08 ppm  $\text{NO}^* + 0.17 \text{NO}_2^*$ , the diethylnitrosamine concentration decreased over time from 9 ppb to ~1.7 ppb after 2 h while the diethylnitramine concentration increased from 0 to 162 ppb (32% conversion). Alternatively, when triethylamine (0.35 ppm) was mixed with 0.08 ppm  $\text{NO}^* + 0.16 \text{NO}_2^*$ , the diethylnitrosamine concentration slightly increased from 4 to 9 ppb in 1 h while the diethylnitramine concentration increased from 0 to 37 ppb (7.4% conversion) (Pitts et al., 1978). These results suggest that nitrosation was at best only slightly enhanced, and perhaps reduced, in the presence of sunlight. However, nitration was greatly enhanced in the presence of sunlight. This could be due a number of effects. First, because  $\text{HONO}$  rapidly photolyzes in sunlight (Table 1), this reaction is not important during the day (Hanst et al., 1977; Pitts et al., 1978). Second, as discussed below, nitrosamines are subject to sunlight photolysis, while nitramines do not absorb sunlight. Nitration may also have been promoted because higher  $\text{NO}_2^*$  concentrations were employed than  $\text{NO}^*$  concentrations.

For secondary amines, nitrosamine and nitramine formation is likely initiated by the hydroxyl radical ( $\text{OH}^*$ ), which can be generated from  $\text{HONO}_{(g)}$  photolysis (Table 1).  $\text{OH}^*$  can remove a H-atom from C-H, O-H, or N-H bonding units within amines. H-atom removal from C-H or O-H groups forms relatively harmless byproducts, including amides (NILU, 2009). H-atom removal from N-H bonding units forms diamino radicals  $(\text{R})_2\text{N}^*$ , which in turn reacts with  $\text{NO}_x$  to form nitrosamines or nitramines (Figure 16; Pitts et al., 1978). Although the amine radical can also react with oxygen, previous research indicates that reactions with  $\text{NO}_x$  components are sufficiently fast that nitrosamine/nitramine formation can occur despite the high oxygen: $\text{NO}_x$  ratio in air (Pitts et al., 1978).



**Figure 16:** NO-MEA and NO<sub>2</sub>-MEA formation from hydroxyl radical reactions with MEA.

However, the reaction mechanisms hypothesized for tertiary amines are more complicated since the OH\* can no longer undergo hydrogen abstraction at the amine N. This may explain why, in general, tertiary amines do not appear to undergo nitrosation and nitration as rapidly as secondary amines. The complex set of reactions mechanisms is described below (Pitts et al., 1978):



Overall, this study suggests that nitrosamine and nitramine formation can occur for both secondary and tertiary amines in the presence of NO<sub>x</sub>, but that the reaction needs to be initiated by a radical species capable of abstracting amine hydrogens. The radical could be OH\*, but other radicals (e.g., Cl\*) may participate. However, for primary amines (R<sub>1</sub>NH<sub>2</sub>), no known studies have evaluated their nitrosation and nitration potential in the presence of NO<sub>x</sub> during solar irradiance. Nitrosation is unlikely given the instability of primary nitrosamines, but nitration is possible.

### 3.4 Pathways for removal in the atmosphere: nitrosamine/nitramine photolysis and reactions with atmospheric species

Nitrosamines and nitramines have the potential to degrade either through sunlight-driven direct photolysis reactions or by reacting with other atmospheric species. This section discusses the potential for such reactions to occur by evaluating the kinetic reaction rates and/or quantum yields while also discussing byproduct reaction pathways. This

information will in turn help to better understand how long such compounds may exist in the atmosphere.

**3.4.1 Reactions with atmospheric species:** In the gas phase, reactions with O<sub>3</sub> were evaluated by mixing 4 ppm N-nitrosodimethylamine (NDMA) or N-nitrodimethylamine (DMNA) with 12 ppm O<sub>3</sub> in a rectangular vessel where NDMA/DMNA loss was monitored over 3 h. Both reaction rates were found to be slow (Table 4) (Tuazon et al., 1984). In the same vessel, the reaction rates of NDMA and DMNA with OH\* were determined using competition kinetics where NDMA/DMNA and the competing organic compound, CH<sub>3</sub>OCH<sub>3</sub>, both reacted with OH\* generated in situ. Reaction rates for both compounds were greater with OH\* than compared to O<sub>3</sub> (Table 7) (Tuazon et al., 1984). Corresponding half-life (τ<sub>1/2</sub>) measurements for typical O<sub>3</sub> and OH\* concentrations in the atmosphere suggest that 50% removal of NDMA or DMNA will take ≥ 2 days, and would be dominated by OH\* reactions.

**Table 7.** Rate constants and half-lives (τ<sub>1/2</sub>) for NDMA and DMNA reactions with O<sub>3</sub> and OH\* in the gas phase (Tuazon et al., 1984).

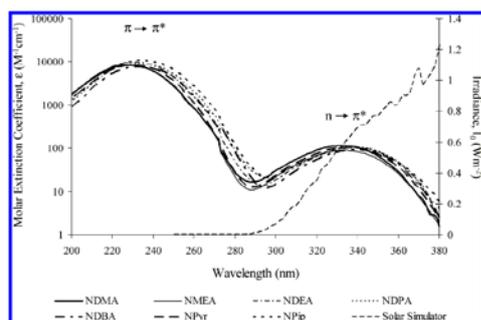
Reactions	k (cm <sup>3</sup> /molecule/s)	Half-life (  )
NDMA + O <sub>3</sub>	< 1.0 × 10 <sup>-20</sup>	≥ 2 years*
DMNA + O <sub>3</sub>	≤ 3.0 × 10 <sup>-21</sup>	≥ 7 years*
NDMA + OH*	3.0±0.4 × 10 <sup>-12</sup>	3 days**
DMNA + OH*	4.5±0.5 × 10 <sup>-12</sup>	2 days**

\* approximated using [O<sub>3</sub>] = 1 × 10<sup>12</sup> cm<sup>-3</sup>, the background tropospheric concentration

\*\* [OH\*] = 8 × 10<sup>5</sup> cm<sup>-3</sup>

### 3.4.2 Nitrosamine Sunlight Photolysis:

**3.4.2.1 Kinetics:** Nitramines do not typically adsorb at wavelengths > 290 nm due to their lack of a n → π\* transition and are therefore unreactive to sunlight. Nitrosamines adsorb at wavelengths > 290 nm as they exhibit a n → π\* transition and can undergo sunlight photolysis. For example, NDMA and other select nitrosamines adsorb light at 330 nm with maximum molar absorption coefficients (ε<sub>305nm</sub>) ranging from 85-100 M<sup>-1</sup>s<sup>-1</sup> (Figure 17; Plumlee and Reinhard, 2007).



**Figure 17.** Molar absorption spectra of NDMA and other nitrosamines from 200-380 nm (Plumlee and Reinhard, 2007).

The efficiency of nitrosamine photolysis under sunlight can be measured by evaluating its loss over time. This loss can be simply measured as a function of time in the form of a time-based rate constant ( $k$ ) or measuring a half-life ( $\tau_{1/2}$ ). Alternatively the loss can be normalized to the photon flux in the form of the quantum yield ( $\Phi = \text{moles reacted/moles of photons}$ ). Studies have evaluated these different values in both the gas and aqueous phase by exposing various nitrosamines to black light (300-400 nm) or a solar simulator (290  $< \lambda < \sim 800$  nm) and measuring reaction kinetics under different experimental conditions. The results and values obtained in such studies are listed in Table 5.

In the gas phase, nitrosamines such as NDMA were found to photolyze rapidly with a half-life of  $\sim 5.0$  min (Table 6; Tuazon et al., 1984). In the aqueous phase, nitrosamine photolysis in pure deionized water was found to be similarly fast with half-lives of  $\sim 15$  min and quantum yields ranging from 0.4-0.6 (Table 8; Plumlee and Reinhard, 2007). Reaction kinetics for NDMA were also not influenced by the presence of  $O_2$ . Previous research involving irradiation of NDMA at lower wavelengths (254 nm) in the presence of  $O_2$  had observed up to a  $\sim 50\%$  increase in the quantum yield between pH 5.5-10 due to the presence of  $O_2$  (Lee et al., 2005). The aqueous results were then used to develop a model prediction for NDMA loss in surface water exposed to typical solar irradiance values. Model predictions suggested that half-lives at a water depth of 10 cm ranged from 40-230 min depending on the earth's latitude (Table 6; Plumlee and Reinhard, 2007).

In an alternative study relevant to atmospheric aerosols, NDMA photolysis was evaluated in DI water containing water-soluble aerosol extracts (DOC = 2.0 mg C/L) using a xenon lamp to simulate solar illumination of atmospheric cloud and fog droplets (Hutchings et al., 2010). In this case, both dimethylamine and  $NO_2^-$  were added at 1.0 mg/L at pH 4.5 to form NDMA in the dark, but then the solution was illuminated to assess photolysis rates. Interestingly, no significant level of NDMA loss was observed upon illumination. The authors attributed the lack of NDMA photolysis to significant light-shielding by  $NO_2^-$ , as it competes for sunlight photons (Figure 2) (Hutchings et al., 2010).

It is unclear to what extent the high nitrite concentration employed (1 mg/L) is relevant to atmospheric aerosols. A number of studies have previously evaluated nitrosamine concentrations in the atmosphere, particularly in the gas phase where NDMA concentrations have been reported to range from 8-25  $ng/m^3$  in various parts of the US (Fine et al., 1976, 1977a,b; Pellizzari et al., 1976). However, only recently have nitrosamine concentrations in the atmospheric aqueous phase been reported at up to 500  $ng/L$  (Herckes

et al., 2007; Hutchings et al., 2010). These results would indicate that a similar shielding effect may be relevant to actual atmospheric aerosols. The identity of the compounds competing for sunlight photons is unclear, but may include nitrate. The importance of such shielding requires further research. If shielding turns out to be significant, the data in Table 6 may underestimate nitrosamine half-lives in aerosols. On the other hand, no studies to date have assessed nitramine concentrations in either the gas or aqueous phases of the atmosphere.

**Table 8.** Nitrosamine reaction rate constants ( $k$ ), half-lives ( $\tau_{1/2}$ ), and quantum yields ( $\Phi$ ) for direct photolysis under sunlight (Plumlee and Reinhard, 2007; Tuazon et al., 1984).

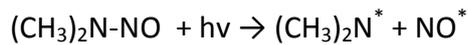
Nitrosamine	$k$ ( $\text{min}^{-1}$ )	$\tau_{1/2}$ (min)	$\Phi$	Lamp	Phase	Other Conditions
NDMA	0.04	16±0.8	0.41	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NMEA	0.049	15±0.8	0.61	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NDEA	0.045	15±1	0.43	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NDPA	0.050	14±1	0.46	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NDBA	0.048	15±0.3	0.52	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NPYR	0.055	14±1	0.55	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NPIP	0.057	12±0.5	0.51	ss	aqueous	DI water; pH 6; 765 W/m <sup>2</sup>
NDMA		40-80		sunlight	aqueous	model prediction in surface water; depth=10 cm; 33°N latitude
NDMA		50-230		sunlight	aqueous	model prediction in surface water; depth=10 cm; 51°N latitude
NDMA		~ 40		sunlight	aqueous	model prediction in surface water; depth=10 cm; 2°S latitude
NDMA*	0.240		1.0	bl	gas	in excess O <sub>3</sub> ; photon flux not reported
NDMA		~ 5.0		sunlight	gas	model prediction based equinox at 34°N latitude; zenith angle of 0

NMEA = nitrosomethylethylamine; NDEA = nitrosodiethylamine; NDPA= nitrosodi-*n*-propylamine; NDBA = nitrosodi-*n*-butylamine; NPYR = nitrosopyrrolidine; NPIP = nitropiperidine; ss = solar simulator; bl = black light.  
 \* experiment conducted in excess O<sub>3</sub> in order to quench NO, one of the byproducts formed; therefore,  $k$  represents only the forward reaction and excludes the reverse reaction. (NDMA +  $h\nu$  → (CH<sub>3</sub>)<sub>2</sub>N\* + NO (forward reaction); NO + O<sub>3</sub> → NO<sub>2</sub> + O<sub>2</sub>)

**3.4.2.2 Byproduct Formation:** In the gas phase, two studies have evaluated byproduct formation after sunlight photolysis of nitrosamines. The studies have conducted

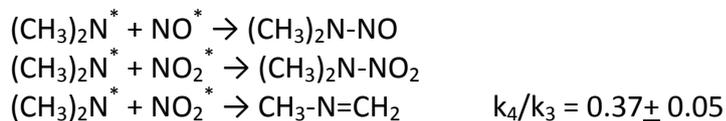
Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University

experiments either 1) in the presence of excess O<sub>3</sub> (4 ppm NDMA; 12 ppm O<sub>3</sub>; black light; Tuazon et al., 1984) or 2) in the presence of NO<sub>x</sub> (12 ppm NDMA; 0.2-5 ppm NO<sub>2</sub>; 0-5 ppm NO; black light; Lindsay et al., 1979). In the Tuazon et al. (1984) study, NDMA irradiation for 10 min led to 65% N-nitrodimethylamine, 33% methylnitramine, and 38% formaldehyde (Tuazon et al., 1984). In the Lindsay et al. (1979) study, NDMA irradiation for 50 min formed N-nitrodimethylamine, NDMA, and methylmethyleamine (CH<sub>2</sub>=N-CH<sub>3</sub>). The reaction pathways were similar. The initial reaction occurs through homolytic bond cleavage of the N-N bond to form the dimethylamino radical (CH<sub>3</sub>)<sub>2</sub>N\* and NO\*:

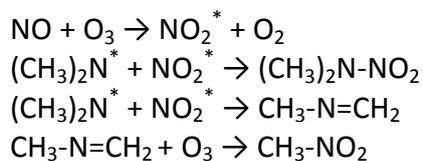


Further reaction of the dimethylamino radical depends on the reactive species present in the gas phase (NO<sub>x</sub>, O<sub>3</sub>, or O<sub>2</sub>) leading to the series of reactions shown below (Lindsay et al., 1979; Tuazon et al., 1984):

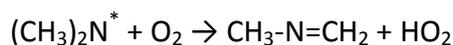
if NO<sub>x</sub> is present:



if O<sub>3</sub> is present:



if O<sub>2</sub> is present:



It is interesting to note that if significant levels of NO<sub>x</sub> and/or O<sub>3</sub> are present in the atmosphere, NDMA can undergo photolysis to either form its nitrated counterpart, N-nitrodimethylamine, or revert to NDMA. This information was used in Lindsay et al. (1979) to estimate the potential steady-state concentration of NDMA in a polluted, sunlight irradiated atmosphere (Z = 40°) with typical NO<sub>x</sub> concentrations of [NO] = 0.1 ppm and [NO<sub>2</sub>] / [NO] = 1 (Lindsay et al., 1979). The steady-state concentration as a function of amine dose was determined to be:

$$[\text{NDMA}]_{ss} = (4.0 \times 10^{-3}) * [\text{dimethylamine}]$$

In addition, the increase in N-nitrodimethylamine (DMNA) formation could be modeled as a function of time through the equation below (Lindsay et al., 1979):

$$d[\text{DMNA}]/dt = 3.58 \times 10^{-3} \text{ min}^{-1} * [\text{dimethylamine}] / (3.9 \times 10^{-7} * ([\text{O}_2]/[\text{NO}_2]) + 1.22)$$

In the aqueous phase, one study assessed byproduct formation by irradiating 500 µg/L NDMA in deionized water (pH 6) using a solar simulator (765 W/m<sup>2</sup>) for 1 hr (Plumlee and Reinhard, 2007). The products formed included methylamine, dimethylamine, nitrate, nitrite, and formate, but of these, methylamine and nitrite were the dominant compounds formed. The nitrogen mass balance was complete while the carbon mass balance achieved 80-90%, possibly due to formaldehyde formation that was not monitored in the experiment. These results suggest that N-nitrodimethylamine formation and NDMA reformation is unlikely in the aqueous phase, such that NDMA photolysis will lead to less toxic byproducts. Additional studies of NDMA photolysis have also been conducted in water, generating similar byproducts. However, they were performed using either low-pressure ( $\lambda = 254$  nm) or medium-pressure ( $200 < \lambda < \text{visible light}$ ) lamps. These studies included NDMA photolysis within the lower UV range ( $\lambda_{\text{max}} = 228$  nm;  $\epsilon_{\text{max}} = 7378 \text{ M}^{-1}\text{cm}^{-1}$ ;  $\pi \rightarrow \pi^*$ ) which is not relevant under atmospheric conditions (Stefan and Bolton, 2002; Lee et al., 2005; Lee et al., 2005b).

## References

- Anastasio, C.; Chu, L. **2009**. Photochemistry of Nitrous Acid (HONO) and Nitrous Acidium Ion (H<sub>2</sub>ONO<sup>+</sup>) in Aqueous Solution and Ice. *Environ.Sci.Tech.* 43, 1108-1114.
- Aronu U.E.; Svendsen H.F.; Hoff K.A. **2010**. Investigation of Amine Amino Acid Salts for Carbon Dioxide Absorption. *International Journal of Greenhouse Gas Control*, 4, 771-775.
- Atkinson, R.; Plum, C.N.; Carter, W.P.L.; Winer, A.M. Pitts, J.N. **1984**. Rate constants for the gas-phase reactions of nitrate radicals with a series of organics in air at  $298 \pm 1$ K, *J. Phys. Chem.* 88 (6), 1210-1215.
- Benjamin, M.M. *Water Chemistry*, McGraw-Hill, New York, **2002**.
- Cantrell, C.A.; Davidson, J.A.; Shetter, R.E.; Anderson, B.A.; Calvert, J.G. **1987**. Reactions of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> with molecular-species of atmospheric interest, *J. Phys Chem.* 91(23), 6017-6021.
- Carl, S.A., Crowley, J.N., **1998**. Sequential two (blue) photon absorption by NO<sub>2</sub> in the presence of H<sub>2</sub> as a source of OH in pulsed photolysis kinetic studies: rate constants for reaction of OH with CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N, and C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> at 295 K. *Journal of Physical Chemistry A* 102, 8131-8141.
- Casado, J.; Mosquera, M.; Paz, L.C.; Prieto, M.F.R., Tato, J.V. **1984**. Nitrite Ion as a Nitrosating Reagent. Nitrosation of Morpholine and Diethylamine in the Presence of Formaldehyde. *Journal of the Chemical Society-Perkin Transactions 2*, 12, 1963-1966.
- Casado J.; Castro A.; Leis J.R.; Mosquera M.; Pena, M.E. **1985**. The Mechanism of the Nitrosation of  $\alpha$ -Amino Acids: Evidence for an Intramolecular Pathway. *Journal of the Chemical Society-Perkin Transactions 2*, 12, 1859-1864.
- Caulfield, J.L.; Singh, S.P.; Wishnok, J.S.; Deen, W.M.; Tannenbaum, S.R. **1996**. Bicarbonate inhibits N-nitrosation in oxygenated nitric oxide solutions. *Journal of Biological Chemistry*, 271, 25859-25863.

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University

Challis, B.C.; Kyrtopoulos, S.A. **1979**. Chemistry of Nitroso-Compounds. 11. Nitrosation of Amines by the 2-Phase Interaction of Amines in Solution with Gaseous Oxides of Nitrogen. *Journal of the Chemical Society-Perkin Transactions 1*, 2, 299-304.

Challis B.C.; Carman, N.; Fernandes, M.H.R.; Glover, B.R.; Latif, F.; Patel, P.; Sandhu, J.S.; Shuja, S. **1994**. Peptide Nitrosations. Nitrosamines and Related N-Nitroso Compounds - Chemistry and Biochemistry, ACS Symposium Series, 553, 74-92.

Chameides, W.L. **1986**. Possible role of NO<sub>3</sub> in the nighttime chemistry of a cloud, *Journal of Geophysical Research* 91, 5331-5337.

Cheung, J.L.; Li, Q.Y.; Boniface, J.; Shi, Q.; Davidovits, P.; Worsnop, D.R.; Jayne, J.T.; Kolb, C.E. **2000**. Heterogeneous interactions of NO<sub>2</sub> with aqueous surfaces. *J. Phys. Chem. A* 104 (12), 2655-2662.

Clark, K.; Edge, R.; Johnson, V.; Land, E.J., Navaratnam, S.; Truscott, T.G. **2008**. Direct observation of NH<sub>2</sub> circle reactions with oxygen, amino acids, and melanins. *Journal of Physical Chemistry A* 112, 1234-1237.

Cooney, R.V.; Ross, P.D.; Bartolini, G.L.; Ramseyer, J. **1987**. N-Nitrosoamine and N-Nitroamine Formation: Factors Influencing the Aqueous Reactions of Nitrogen-Dioxide with Morpholine. *Environmental Science & Technology*, 21, 77-83

Fan, T.Y.; Tannenbaum, S.R. **1972**. Stability Of N-Nitroso Compounds. *Journal Of Food Science*, 37, 274-276.

Fan, T.Y.; Tannenbaum, S.R. **1973**. Factors Influencing Rate of Formation of Nitrosomorpholine from Morpholine and Nitrite: Acceleration by Thiocyanate and Other Anions. *Journal of Agricultural and Food Chemistry*, 21, 237-240.

Fine, D. H.; Rounbehler, D. P.; Belcher, N. M.; Epstein, S.S. **1976**. N-Nitroso compounds detection in ambient air. *Science*, 192, 1328–1330.

Fine, D. H.; Rounbehler, D. P.; Rounbehler, A.; Silvergleid, A.; Sawicki, E.; Krost, K.; Demarrais, G. A. **1977**. Determination of dimethylnitrosamine in air, water, and soil by thermal-energy analysis measurements in Baltimore, Md. *Environ. Sci. Technol.*, 11, 581–584.

Fine, D. H.; Rounbehler, D. P.; Sawicki, E.; Krost, K. **1977b**. Determination of dimethylnitrosamine in air and water by thermal energy analysis validation of analytical procedures. *Environ.Sci. Technol.*, 11, 577–580.

Finlayson-Pitts, B.J.; Wingen, L.M.; Sumner, A.L.; Syomin, D.; Ramazan, K.A. **2003**. The heterogeneous hydrolysis of NO<sub>2</sub> in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism. *Phys. Chem. Chem. Phys.*, 5, 223-242.

Garcia-Santos, M.D.; Gonzalez-Mancebo, S.; Hernandez-Benito, J.; Calle, E.; Casado, J. **2002**. Reactivity of Amino Acids in Nitrosation Reactions and Its Relation to the Alkylating Potential of Their Products. *Journal of The American Chemical Society*, 124, 2177-2182.

Gil, R.; Casado, J.; Izquierdo, C. **1997**. Structural Effects on the N-nitrosation of Amino Acids. *International Journal of Chemical Kinetics*, 39, 495-504.

Gil, R.; Casado, J.; Izquierdo, C. **1994**. The Nitrosation of Amino Acids. *International Journal of Chemical Kinetics*, 26, 1167-1178.

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University

- Goldstein, S.; Rabini, J. **2007**. Mechanism of Nitrite Formation by Nitrate Photolysis in Aqueous Solutions: The Role of Peroxynitrite, Nitrogen Dioxide, and Hydroxyl Radical. *JACS*. 129, 10597-10601.
- Hanst, P.L.; Spence, J.W.; Miller, M. **1977**. Atmospheric chemistry of N-nitrosodimethylamine. *Environ.Sci.Tech.* 11, 403-405.
- Hassel, M.; Frei, E.; Streeter, A.J.; Wiessler, M. **1990**. Pharmacokinetics of N-Nitrodimethylamine and N-Nitromethylamine in the Rat. *Carcinogenesis*, 11, 357-360.
- Hutchings, J.W.; Ervens, B.; Straub, D.; Herckes, P.N. **2010**. Nitrosodimethylamine occurrence, formation, and cycling in clouds and fogs. *Environ.Sci.Tech.* 41, 393-399.
- Herckes, P.; Leenheer, J.A.; Collet, J.L. **2007**. Comprehensive characterization of atmospheric organic matter in Fresno, California fog water. *Environ.Sci.Tech.* 44, 8128-8133.
- Keefer, L.K.; Roller, P.P. **1973**. N-Nitrosation by Nitrite Ion in Neutral and Basic Medium. *Science*, 181, 1245-1247.
- Kirsch, M.; Korth, H.G.; Sustmann, R.; De Groot, H. **2000**. Carbon Dioxide but Not Bicarbonate Inhibits N-Nitrosation of Secondary Amines. Evidence for Amine Carbamates as Protecting Entities. *Chemical Research In Toxicology*, 13, 451-461
- Kobayashi, H.; Takezawaa, N.; Nikia, T. **1980**. Removal of Nitrogen Oxides with Organic Amines and Metal Complexes. *Environment International*, 4, 273-275.
- Lee, C.; Choi, W.; Yoon, J. **2005**. UV photolytic mechanism of N-Nitrosodimethylamine in water: roles of dissolved oxygen and solution pH. *Environ.Sci.Tech.* 39, 9702-9709.
- Lee, C.; Choi, W.; Kim, Y.G.; Yoon, J. **2005b**. UV photolytic mechanism of N-nitrosodimethylamine in water: dual pathways to methylamine versus dimethylamine. *Environ. Sci. Technol.* 39, 2101-2106.
- Lewis, R.S.; Tannenbaum, S.R.; Deen, W.M. **1995**. Kinetics of N-Nitrosation in Oxygenated Nitric Oxide Solutions at Physiological pH - Role of Nitrous Anhydride and Effects of Phosphate and Chloride. *Journal of the American Chemical Society*, 117, 3933-3939.
- Li, J.; Brill, T.B. **2003**. Spectroscopy of Hydrothermal Reactions, Part 26: Kinetics of Decarboxylation of Aliphatic Amino Acids and Comparison with the Rates of Racemization. *International Journal of Chemical Kinetics*, 35, 602-610.
- Lindley, C.R.C.; Calvert, J.R.; Shaw, J.H. **1979**. Rate studies of the reactions of the (CH<sub>3</sub>)<sub>2</sub>N Radical with O<sub>2</sub>, NO, and NO<sub>2</sub>. *Chemical Physical Letters*. 67, 57-62.
- Loeppky, R.N.; Gnewuch, C.T.; Hazlitt, L.G.; McKinley, W.A. **1979**. N-nitrosamine fragmentation and N-nitrosamine transformation. In Anselme, J.P., ed. N-nitrosamines. Washington, D.C. Am. Chem. Soc. Symposium Series 1979, 101, 109-123.
- Loeppky R.N.; Singh, S.P.; Elomari, S.; Hastings, R.; Theiss, T.E. **1998**. Evidence for Radical Cations in Linked Mechanisms of N,N-dialkyl Aromatic Amine Nitration and Nitrosative Dealkylation. *Journal of the American Chemical Society*, 120, 5193-5202.
- Mack, J.; Bolton, J.R. **1999**. Photochemistry of Nitrite and Nitrate in Aqueous Solution: A review. *J. Photochem. Photobio.* 128, 1-13.

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
Dr. William Mitch, Yale University

- Malloy, Q.G.J., Qi, L., Warren, B., Cocker, D.R., Erupe, M.E., Silva, P.J. **2009**. Secondary organic aerosol formation from primary aliphatic amines with NO<sub>3</sub> radical. *Atmos. Chem. Phys.* 9, 2051-2060.
- Masuda, M.; Mower, H.F.; Pignatelli, B.; Celan, I.; Friesen, M.D.; Nishino, H.; Ohshima, H. **2000**. Formation of N-nitrosamines and N-nitramines by the Reaction of Secondary Amines with Peroxynitrite and other Reactive Nitrogen Species: Comparison with Nitrotyrosine Formation. *Chemical Research in Toxicology*, 13, 301-308.
- Mirvish, S.S. **1975**. Formation Of N-Nitroso Compounds: Chemistry, Kinetics, and in Vivo Occurrence. *Toxicology and Applied Pharmacology*, 31, 325-35.1
- NILU, **2009**. Final report on a theoretical study on the atmospheric degradation of selected amines. Braten, H.B.; Bunkan, A.J.; Bache-Andreassen, L.; Solimannejad, M.; Nielsen, C.J. ISBN 978-82-425-2080-7.
- Obiedzinski, M.W.; Wishnok, J.S.; Tannenbaum, S.R. **1980**. N-Nitroso Compounds from Reactions of Nitrite with Methylamine. *Food And Cosmetics Toxicology*, 18, 585-589
- O'Driscoll, P.; Lang, K.; Minogue, N.; Sodeau, J. **2006**. Freezing halide ion solutions and the release of interhalogens to the atmosphere. *J. Phys. Chem. A*, 110, 4615-4618.
- Pellizzari, E. D.; Bunch, J. E.; Bursey, J. T.; Berkley, R. E.; Sawicki, E.; Krost, K. **1976**. Estimation of N-nitrosodimethylamine levels in ambient air by capillary gas-liquid chromatography mass spectrometry. *Anal. Lett.*, 9, 579-594.
- Pires, M.; Rossi, M.J.; Ross, D.S. **1994**. Kinetic and Mechanistic Aspects of the NO Oxidation by O<sub>2</sub> In Aqueous Phase. *International Journal of Chemical Kinetics*, 26, 1207-1227.
- Pitts, J.N.; Grosjean, D.; Vancauwenberghe, K.; Schmid, J.P.; Fitz, D.R. **1978**. Photo-oxidation of aliphatic-amines under simulated atmospheric conditions- formation of nitrosamines, nitramines, amides, and photo-chemical oxidant. *Environ. Sci. Technol.* 12 (8), 946-953.
- Plumlee, M.H.; Reinhard, M. **2007**. Photochemical attenuation of N-nitrosodimethylamine (NDMA) and other nitrosamines in surface water. *Environ. Sci. Technol.* 41, 6170-6176.
- Ridd J.H. **1961**. Nitrosation, Diazotisation, and Deamination. *Quarterly Reviews*, 15, 418-441.
- Riordan, E.; Minogue, N.; Healy, D.; O'Driscoll, P.; Sodeau, J. R. **2005**. Spectroscopic and optimization modeling study of nitrous acid in aqueous solution. *J. Phys. Chem. A*, 109, 779-786.
- Saavedra, J.E. **1981**. Deamination of Primary Aminoalkanols. Formation of Substituted N-Nitroso-1,3-Oxazolidines and N-Nitroso-1,3-Tetrahydrooxazines. *Journal of Organic Chemistry*, 46, 2610-2614.
- Seinfeld, J.H.; Pandis, S.N. Atmospheric Chemistry and Physics. John Wiley & Sons, Inc., New York, **1998**.
- Sharpless, C.M.; Linden, K.G. **2001**. UV photolysis of nitrate: effects of natural organic matter and dissolved inorganic carbon and implications for UV water disinfection. *Environ. Sci. Tech.* 35, 2949-2955.
- Silva, P.J., Erupe, M.E., Price, D., Elias, J. **2008**. Trimethylamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere, *Environ. Sci. Technol.* 42, 4689-4696.

Singer, S.S. **1978**. Kinetics and Mechanism of Aliphatic Transnitrosation. *Journal of Organic Chemistry*, 43, 4612-4616.

Smith, P.A.S.; Loeppky, R.N. **1967**. Nitrosative Cleavage of Tertiary Amines. *Journal of the American Chemical Society*, 89, 1147-1157.

Stefan, M.I.; Bolton, J.R. **2002**. UV direct photolysis of N-Nitrosodimethylamine (NDMA): kinetic and product study. *Helvetica Chimica Acta*. 85, 1416-1426.

Strazisar, B.R.; Anderson, R.R.; White, C.M. **2003**. Degradation Pathways for Monoethanolamine in a CO<sub>2</sub> Capture Facility. *Energy & Fuels*, 17, 1034-1039.

Tricker, A.R.; Preussmann, R. **1992**. Volatile N-Nitrosamines in Mainstream Cigarette Smoke: Occurrence and Formation. *Clinical Investigator*, 70, 283-289.

Tuazon, E.C.; Carter, W.P.L.; Atkinson, R.; Winer, A.M.; Pitts, J.N. **1984**. Atmospheric reactions of N-nitrosodimethylamine and dimethylnitramine. *Environ. Sci. Technol.* 18, 49-54.

Vione, D.; Belmonto, S.; Carnino, L. **2004**. A kinetic study of phenol nitration and nitrosation with nitrous acid in the dark. *Environ. Chem. Lett.* 2 (3), 135-139.

Warthesen, J.J.; Scanlan, R.A.; Bills, D.D.; Libbey, L.M. **1975**. Formation of Heterocyclic N-Nitrosamines from Reaction of Nitrite and Selected Primary Diamines And Amino-Acids. *Journal Of Agricultural And Food Chemistry*, 23, 898-902.

Zhu, C.; Xiang, B.; Chu, L.T.; Zhu, L. **2010**. 308 nm photolysis of nitric acid in the gas phase, on aluminum surfaces, and on ice films. *J. Phys Chem. A*. 114, 2561-2568.

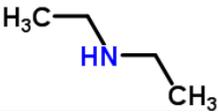
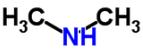
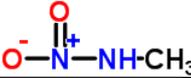
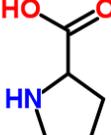
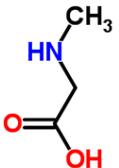
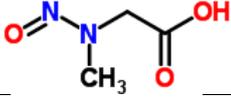
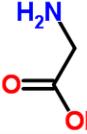
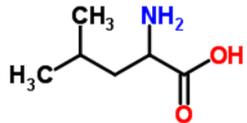
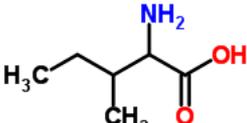
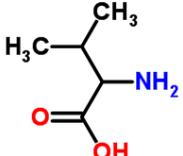
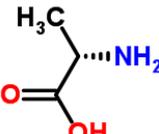
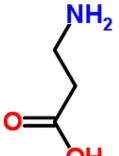
**List of Compounds**

Name	Abbreviation	Formula	CAS	Structure
Monoethanolamine	MEA	$C_2H_7NO$	141-43-5	
Methyldiethanolamine	MDEA	$C_5H_{13}NO_2$	105-59-9	
Diethanolamine	DEA	$C_4H_{11}NO_2$	11-42-2	
N-nitrosodiethanolamine	NDELA	$C_4H_{10}N_2O_3$	1116-54-7	
N-nitrodimethylamine	$NO_2^-$ -DMA	$C_2H_6N_2O_2$	4164-28-7	
N-nitrosodimethylamine	NDMA	$C_2H_6N_2O$	571-61-9	
N-nitrosomorpholine	NMOR	$C_4H_8N_2O_2$	59-89-2	
N-nitromorpholine	$NO_2^-$ -MOR	$C_4H_8N_2O_3$	4164-32-3	
N-nitrosopiperidine	NPIP	$C_5H_{10}N_2O$	100-75-4	
N-nitrosodibutylamine	NDBA	$C_8H_{18}N_2O$	924-16-3	
N-nitrodiethanolamine	$NO_2^-$ -DELA	$C_4H_{10}N_2O_4$	Not available	
N-nitromonoethanolamine	$NO_2^-$ -MEA	$C_2H_6N_2O_3$	Not available	

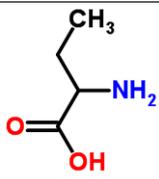
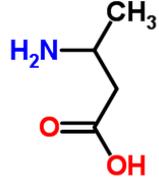
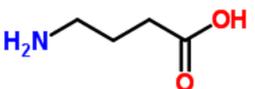
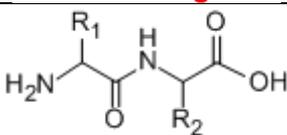
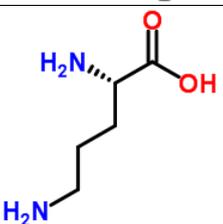
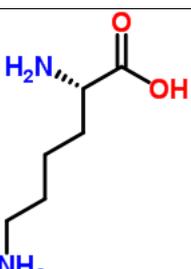
Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
 Dr. William Mitch, Yale University

N-nitrosomethylethanolamine	NO-MELA	$C_3H_8N_2O_2$	Not available	
N-nitromethylethanolamine	NO <sub>2</sub> -MELA	$C_3H_8N_2O_3$	Not available	
Piperazine		$C_4H_{10}N_2$	110-85-0	
2-amino-2-methyl-1-propanol	AMP	$C_4H_{11}NO$	124-68-5	
N-nitrosopyrrolidine	NPYR	$C_4H_8N_2O$	930-55-2	
N-nitrosodiethylamine		$C_4H_{10}N_2O$	55-18-5	
oxazolidinone		$C_3H_5NO_2$	51667-26-6	
N-nitroso-4-methylpiperazine		$C_5H_{11}N_3O$	16339-07-4	
N-nitropiperidine		$C_5H_{10}N_2O_2$	7119-94-0	
Dimethylnitramine (or N-nitrodimethylamine)	DMNA	$C_2H_6N_2O_2$	4164-28-7	
Diethylnitramine (or N-nitrodiethylamine)		$C_4H_{10}N_2O_2$	7119-92-8	
N-nitrosodiethylamine (or Diethylnitrosamine)	NDEA	$C_4H_{10}N_2O$	55-18-5	
Triethylamine		$C_6H_{15}N$	121-44-8	

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
 Dr. William Mitch, Yale University

Diethylamine		$C_4H_{11}N$	109-89-7	
Dimethylamine		$C_2H_7N$	124-40-3	
Methylnitramine		$CH_4N_2O_2$	598-57-2	
L-Proline	Pro	$C_5H_9NO_2$	147-85-3	
N-nitrosoproline	NPro	$C_5H_8N_2O_3$	7519-36-0	
Sarcosine	Sar	$C_3H_7NO_2$	107-97-1	
N-nitrososarcosine	NSar	$C_3H_6N_2O_3$	13256-22-9	
Glycine	Gly	$C_2H_5NO_2$	56-40-6	
Leucine	Leu	$C_6H_{13}NO_2$	328-39-2 61-90-5	
Isoleucine	Ile	$C_6H_{13}NO_2$	443-79-8 73-32-5	
Valine	Val	$C_5H_{11}NO_2$	516-06-3 72-18-4	
Alanine	Ala	$C_3H_7NO_2$	302-72-7 56-41-7	
$\beta$ -Alanine	$\beta$ -Ala	$C_3H_7NO_2$	107-95-9	

Tasks 1 and 3 Report: Critical Literature Review of Nitrosation/Nitration Pathways  
 Dr. William Mitch, Yale University

$\alpha$ -Aminobutyric acid	$\alpha$ -Aib	$C_4H_9NO_2$	2835-81-6	
$\beta$ -Aminobutyric acid	$\beta$ -Aib	$C_4H_9NO_2$	541-48-0	
$\gamma$ -Aminobutyric acid	$\gamma$ -Aib	$C_4H_9NO_2$	56-12-2	
Diazaopeptide				
Ornithine		$C_5H_{12}N_2O_2$	616-07-9 70-26-8	
Lysine	Lys	$C_6H_{14}N_2O_2$	70-54-2 56-87-1	
N-nitrosopipericolic acid		$C_6H_{10}N_2O_3$	4515-18-8	
Piperazine	PZ	$C_4H_{10}N_2$	110-85-0	