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1.0 Predicted nitrosamine and nitramine products of solvent decay

Approach: A total of 13 model solvents suggested by CCM were considered. These solvents represent a mixture of primary, secondary and tertiary amine structures. Predicted nitrosamine and nitramine byproducts were based upon the structures of the solvent amine and its expected decay products when exposed to carbon dioxide, oxygen and NOx. For many of the solvent amines, no experimental data were available. Additionally, little experimental data were available for degradation in the presence of NOx.

Several studies were considered to predict important amine degradation products that could serve as substrates for nitrosation or nitration by NOx. Studies by LePaumier et al. (2009a and b) evaluated degradation products for some amines in the presence of either carbon dioxide or oxygen at 140 °C. In both cases, thermal degradation was much less important than the degradation promoted by these reagents. Carbon dioxide by itself promoted more degradation than did oxygen. Additionally, extrapolation of a study of oxidative degradation of monoethanolamine (MEA) by Sexton and Rochelle (2011) at 55 °C was employed. Lastly, the potential for primary amines to form a secondary amine in the presence of NOx was considered (Obiedzinski et al., 1980). The relative importance of the degradation products was estimated qualitatively. In the material that follows, the most likely precursors are enclosed in black boxes, those of moderate importance are enclosed in red boxes and the likely least important precursors are enclosed in green boxes.

Based upon the summary of nitrosation and nitration chemistry provided in the Tasks 1 and 3 reports of Call-Off 1, potential nitrosamine and nitramine byproducts were predicted, and their estimated relative importance was indicated using the same colored box scheme. The discussion was organized roughly in order of decreasing importance of nitrosamine and nitramine formation (secondary amines > tertiary amines > primary amines). The associated narrative suggests analytical methods that would likely be applicable each group of byproducts.

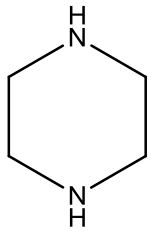
1.1 Secondary Amines

Piperazine (PZ)

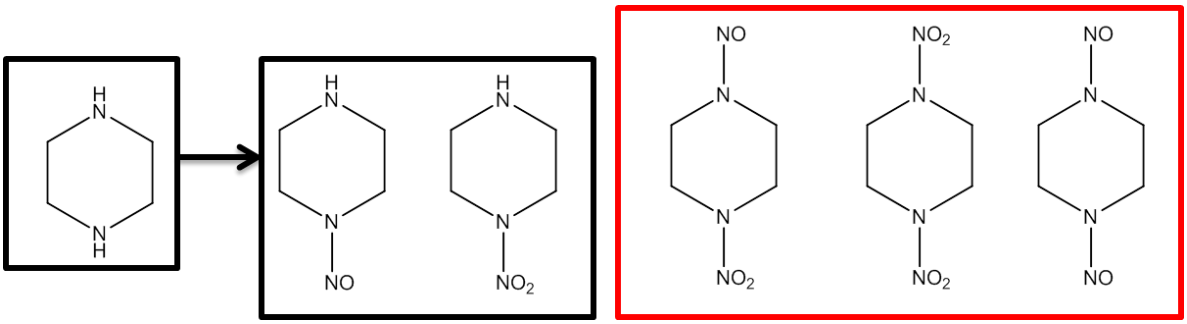
CAS: 110-85-0

Category: secondary diamine

Structure



Product Predictions: Although experimental evidence is limited, piperazine is likely to be a relatively stable secondary amine. In line with this expectation, our experiments in Call-Off 1 indicated that the nitrosated products described below constituted the majority of the total nitrosamine signal. Both amine functional groups are secondary amines, and so are prone to forming stable nitrosated and nitrated byproducts. Our experiments conducted as part of Call-Off 1 suggested that monosubstituted products are more prevalent than the di-substituted products. The monosubstituted products would likely be amenable to LC/MS analysis. The di-substituted products are amenable to GC/MS analysis.

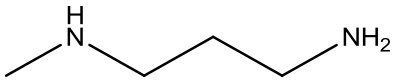


3-amino-1-methylaminopropane (MAPA)

CAS: 6291-84-5

Category: primary amine and secondary amine

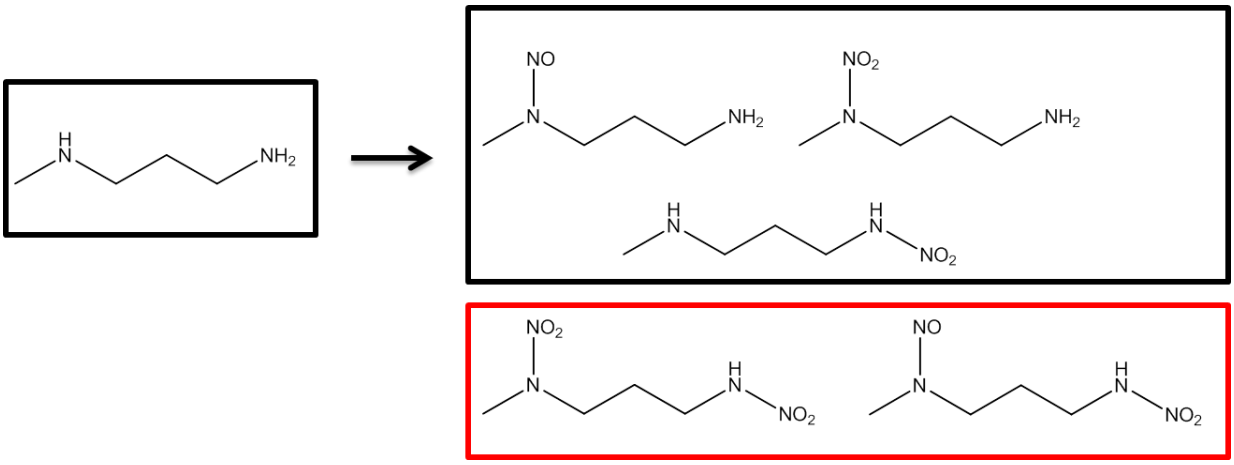
Structure



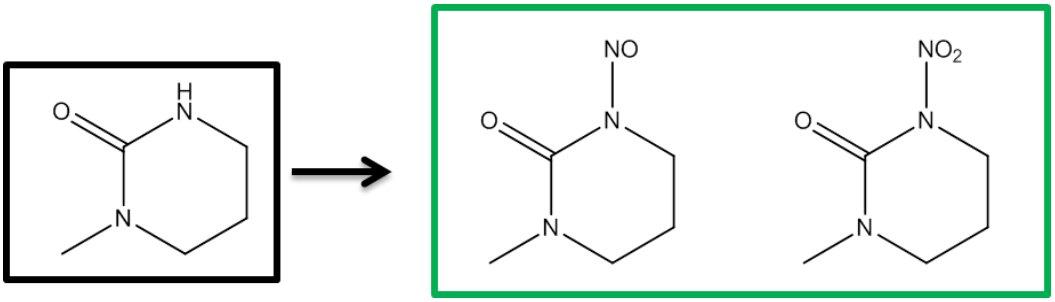
Task 1 Report
Predicted products of solvent decay and experimental plan
Dr. William Mitch

Product Predictions:

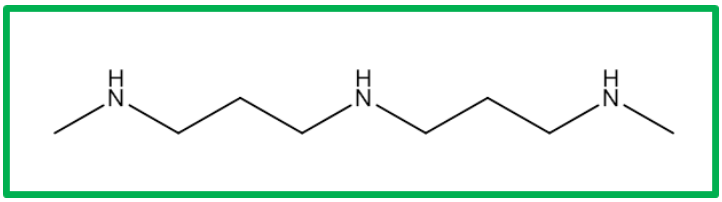
The secondary amine should form stable nitrosamine and nitramine byproducts, while the primary amine should form a stable nitramine. These should be the major nitrosamine and nitramine byproducts. As a diamine, the analytical methods will be similar to piperazine. The mono-substituted products should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine, while the di-substituted products should be amenable to analysis by GC/MS.



The work of LePaumier et al. (2009a) indicates that diamines in the presence of carbon dioxide are prone to forming condensation products with formaldehyde. However, the nitrosated and nitrated products would be unstable nitrosamides or nitramides. These products should be amenable to analysis by GC/MS.



Lastly, reactions with NOx might promote the formation of the relevant secondary amine by a dimerization reaction (Obiedzinski et al., 1980). This product would have three secondary amines capable of forming the full range of nitrosated or nitrated byproducts. However, all of these were rated of minor importance. As part of Call-Off 1, we had found that N-nitrosodiethanolamine was a minor nitrosated byproduct of monoethanolamine. Nitrosation of diethanolamine is likely facile. These findings suggest that diethanolamine formation from monoethanolamine is a relatively minor pathway. The analytical methods would be comparable to those discussed above, or for piperazine.

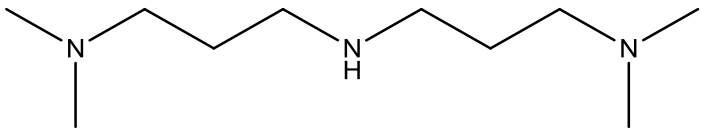


N'-[3(dimethylamino)propyl]-N,N-dimethyl-1,3-propanediamine (TMBPA)

CAS: 6711-48-4

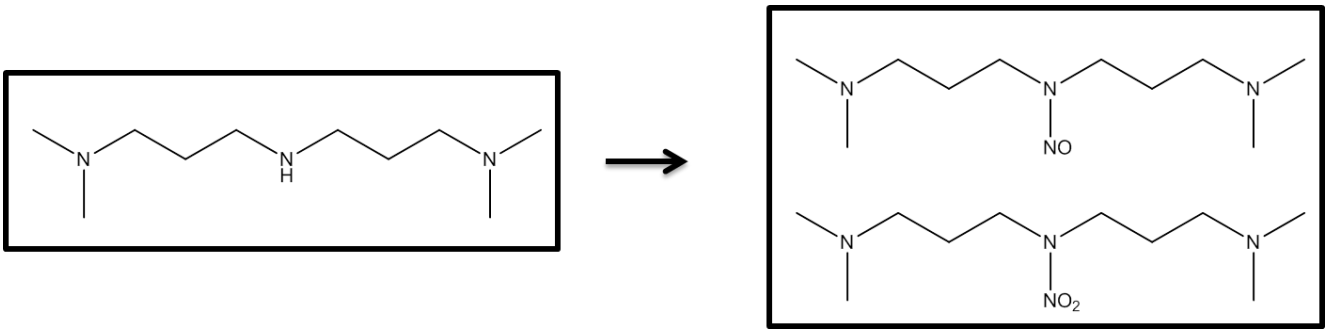
Category: secondary amine and tertiary diamine

Structure

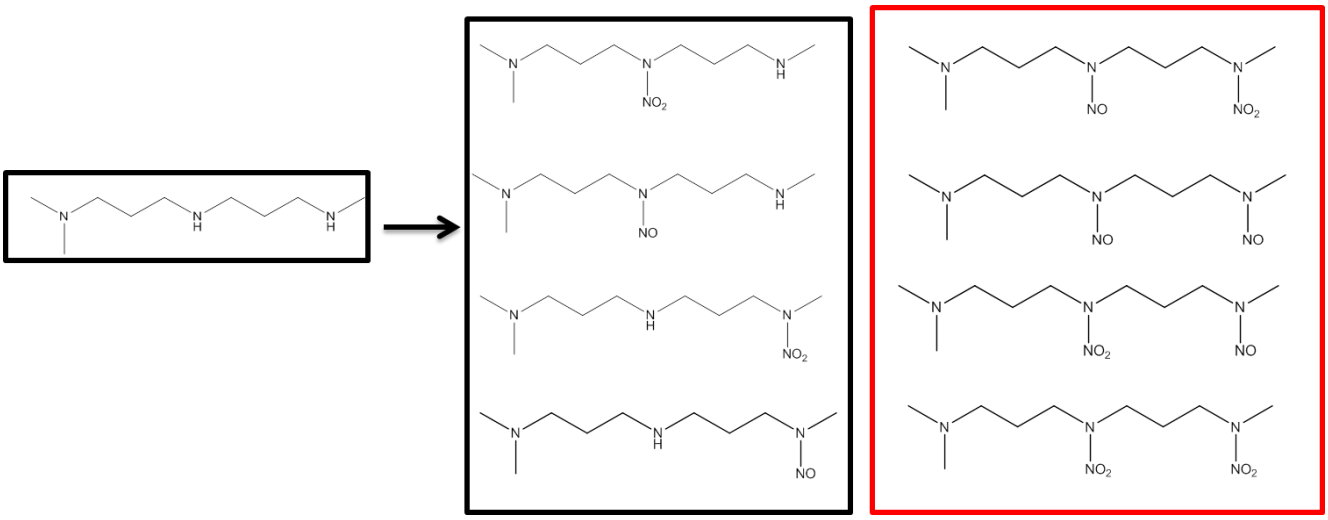


Product Predictions:

The secondary amine is prone to the formation of a stable nitrosamine and nitramine. These are likely to be the major nitrosamine and nitramine byproducts. They should be amenable to analysis by GC/MS.



Based upon the work of LePaumier et al. (2009a,b), dealkylation is likely to yield a secondary diamine product that is prone to the formation of a range of stable nitrosamines and nitramines. Our results with piperazine from Call-Off 1 indicated that monosubstituted products were more prevalent than disubstituted products. The products should be amenable to analysis by GC/MS.



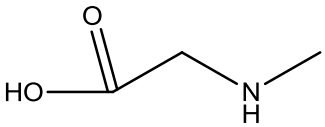
Additional polymerization products are likely to be formed, but these products would be less likely to form stable nitrosamines and nitramines.

Potassium Sarcosine (N-methylglycine)

CAS: 56935-86-5

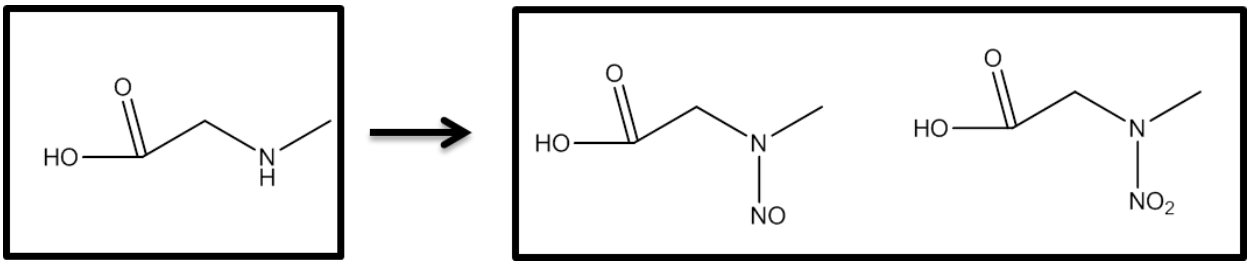
Category: secondary amine

Structure



Product Predictions:

As a secondary amine, sarcosine should form stable nitrosamine and nitramine byproducts. These should be the major nitrosamine and nitramine byproducts of sarcosine. They should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



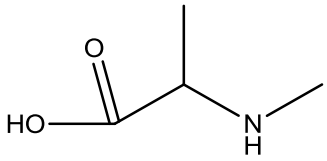
Although formamide and carbamate products are possible, they would preclude formation of stable nitrosamine and nitramine byproducts by converting the amine into a tertiary amine.

N-methylalanine (Alkazid-M)

CAS: 3913-67-6

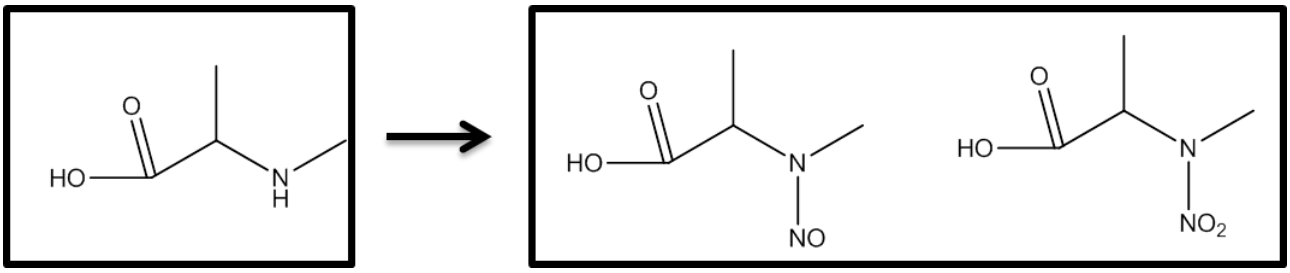
Category: secondary amine

Structure



Product Predictions:

As a secondary amine, N-methylalanine should form stable nitrosamine and nitramine byproducts. These should be the major nitrosamine and nitramine byproducts of N-methylalanine. They should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



Although formamide and carbamate products are possible, they would preclude formation of stable nitrosamine and nitramine byproducts by converting the amine into a tertiary amine.

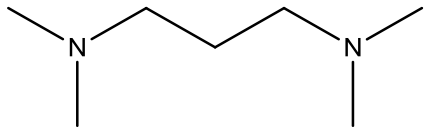
1.2 Tertiary Amines

N,N,N',N'-Tetramethyl-1,3-propanediamine (TMPDA)

CAS: 110-95-2

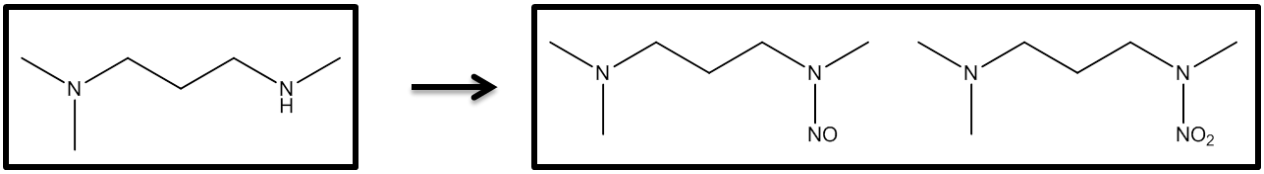
Category: tertiary diamine

Structure



Product Predictions:

Based upon the work of LePaumier et al. (2009a,b), dealkylation is likely to yield a secondary amine product (N,N,N'-trimethyl-1,3-propanediamine) that is prone to the formation of a stable nitrosamine and nitramine. These are likely to be the major nitrosamine and nitramine products for TMDPA. The products should be amenable to analysis by GC/MS.



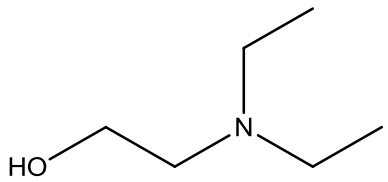
Additional polymerization products are likely to be formed, but these products would be less likely to form stable nitrosamines and nitramines.

Diethylaminoethanol (DEEA)

CAS: 100-37-8

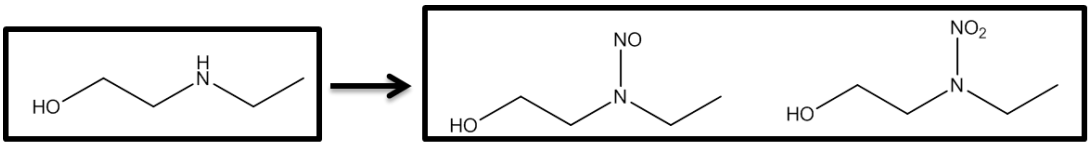
Category: tertiary amine

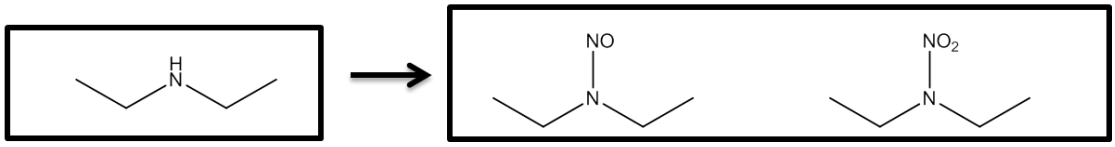
Structure



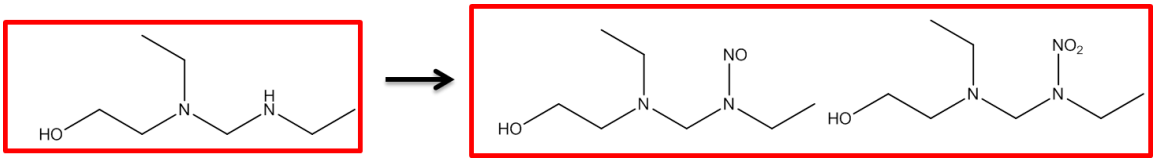
Product Predictions:

Based upon the work of LePaumier et al. (2009a,b), dealkylation is likely to yield secondary amine products (N-ethylethanolamine and diethylamine) that are prone to the formation of stable nitrosamines and nitramines. The products of N-ethylethanolamine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine. The products of diethylamine are amenable to analysis by GC/MS.

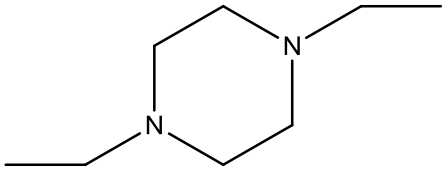




The works of LePaumier et al. (2009a,b) also suggest that polymerization products of N-ethylethanolamine forms a secondary amine that can form stable nitrosated and nitrated products. These products should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



Lastly, works of LePaumier et al. (2009a,b) suggest that piperazines are major degradation products of N-ethylethanolamine. However, the piperazines that form tend to have tertiary nitrogens that would resist facile nitrosation or nitration.

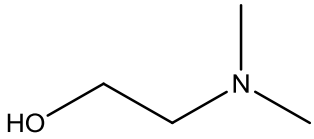


N,N-dimethylethanolamine (DMMEA)

CAS: 108-01-0

Category: tertiary amine

Structure



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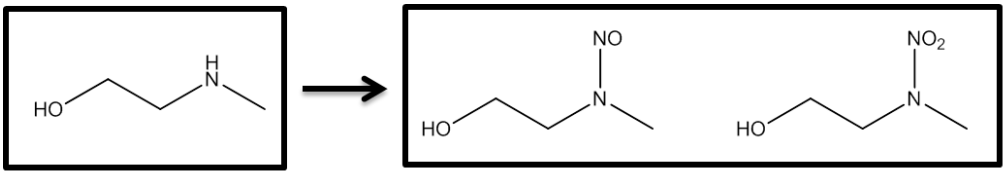
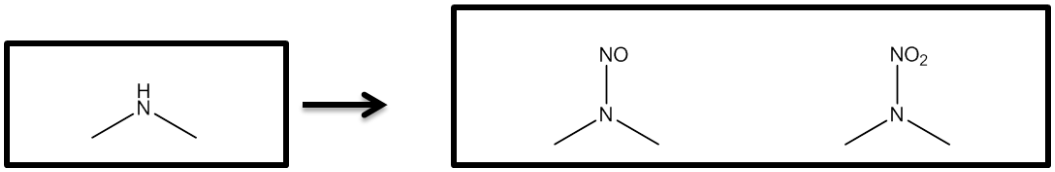
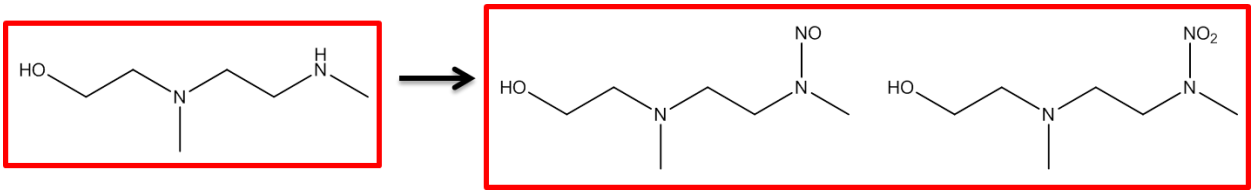
Product Predictions:

Based upon the work of LePaumier et al. (2009a,b), dealkylation is likely to yield secondary amine products (N-methylethanolamine and dimethylamine) that are prone to the formation of stable nitrosamines and nitramines. The products of N-methylethanolamine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine. The products of dimethylamine are amenable to analysis by GC/MS.

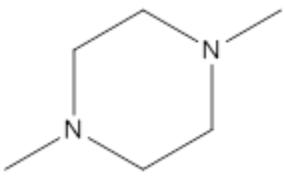




The works of LePaumier et al. (2009a,b) also indicate that polymerization products of N-methylethanolamine forms a secondary amine that can form stable nitrosated and nitrated products. These products should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



Lastly, works of LePaumier et al. (2009a,b) suggest that piperazines are major degradation products of N-methylethanolamine. However, the piperazines that form tend to have tertiary nitrogens that would resist facile nitrosation or nitration.

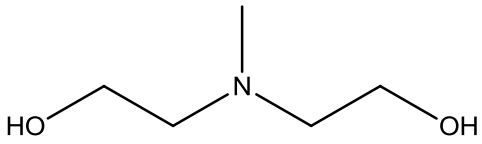


N-methyldiethanolamine (MDEA)

CAS: 105-59-9

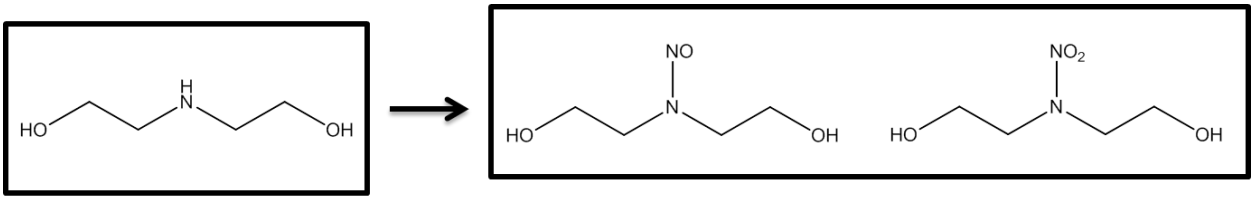
Category: tertiary amine

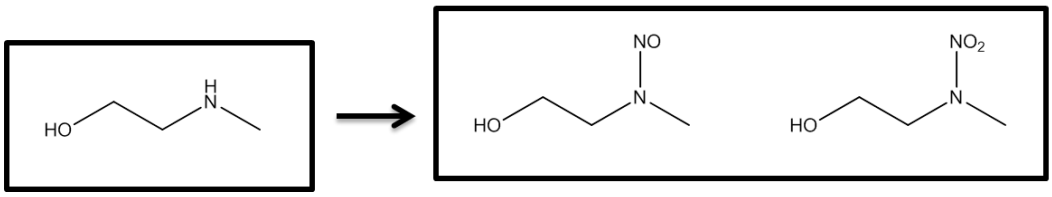
Structure



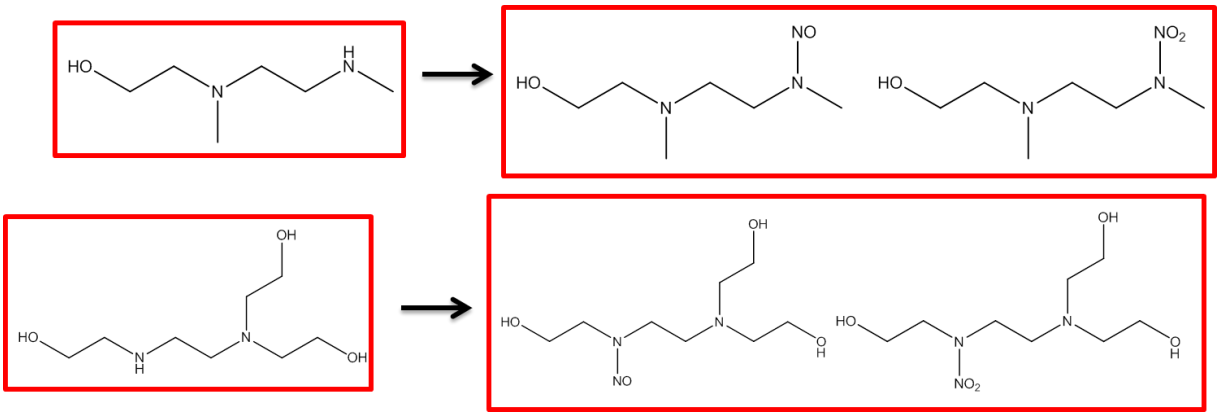
Product Predictions:

Based upon the work of LePaumier et al. (2009a,b), dealkylation is likely to yield secondary amine products (diethanolamine and N-methylethanolamine) that are prone to the formation of stable nitrosamines and nitramines. These products should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.

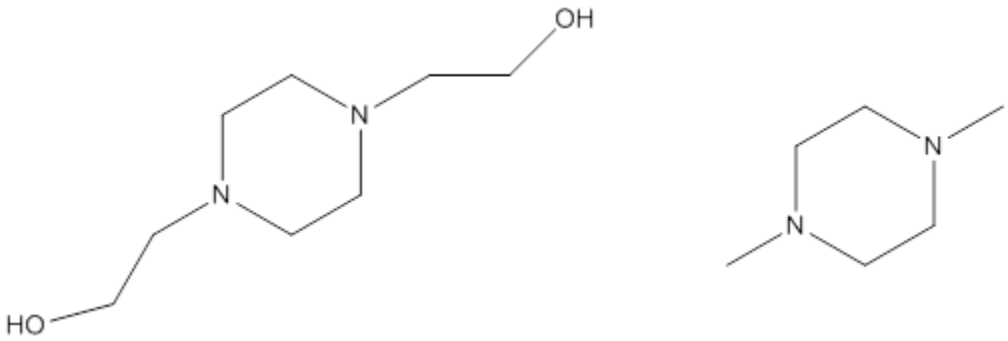




The works of LePaumier et al. (2009a,b) also indicate that polymerization products of these initial dealkylation reactions form secondary amines that can form stable nitrosated and nitrated products. These products should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



Lastly, works of LePaumier et al. (2009a,b) suggest that piperazines are major degradation products of diethanolamine or N-methylethanolamine. However, the piperazines that form tend to have tertiary nitrogens that would resist facile nitrosation or nitration.



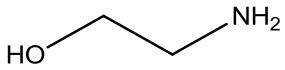
1.3 Primary Amines

2-ethanolamine (MEA)

CAS: 141-43-5

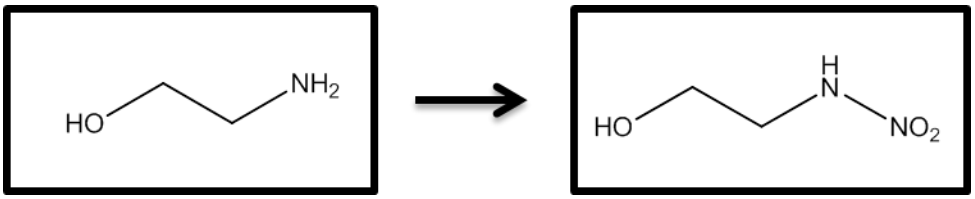
Category: primary amine

Structure

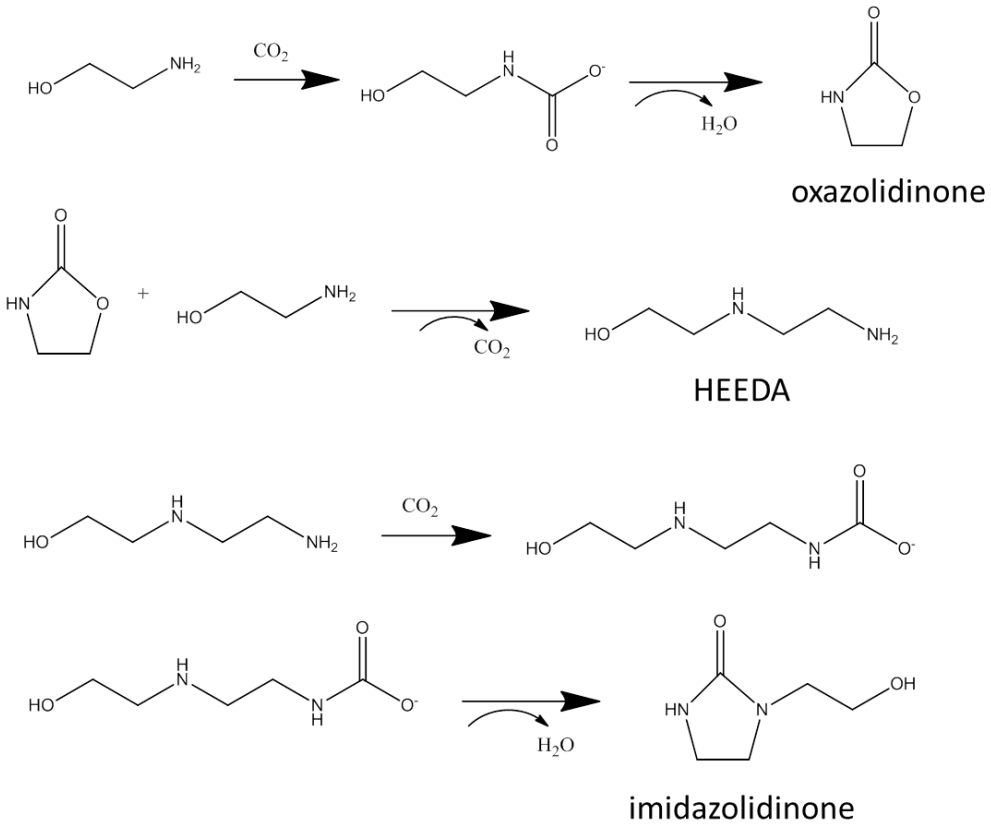


Product Predictions:

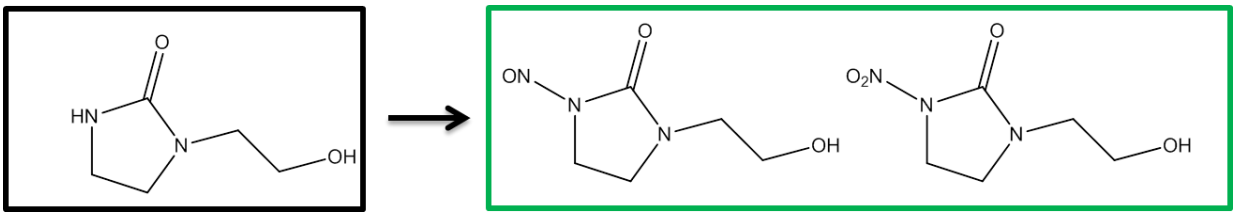
As a primary amine, MEA itself is prone to forming its associated N-nitramine. This nitramine is likely a major product. As an alcohol, this nitramine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



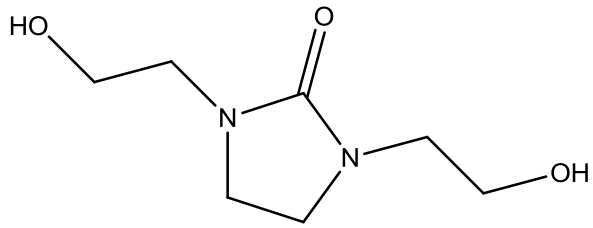
The work of LePaumier et al. (2009a) indicates that, unlike for AMP, oxazolidones are unstable products of MEA in the presence of CO2. Instead, the degradation continues to produce more stable intermediates including HEEDA and imidazolidinones as depicted below. Continued decay produces other, similar products of increasing size.



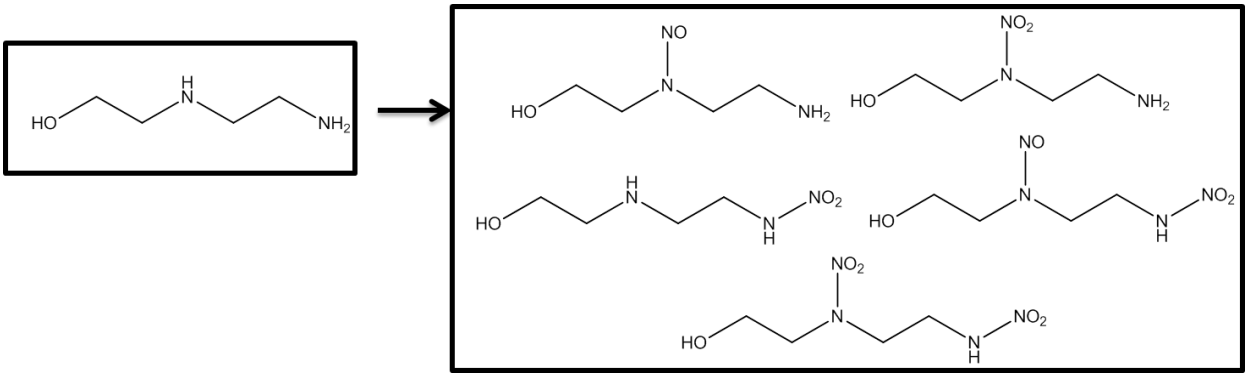
The results of the LePaumier et al. (2009a) study indicated that the imidazolidone depicted below would be the major product. Nitrosation and nitration is most likely at the secondary nitrogen, rather than the tertiary nitrogen, but the products would be a nitrosamide or nitramide that are unstable towards hydrolysis.



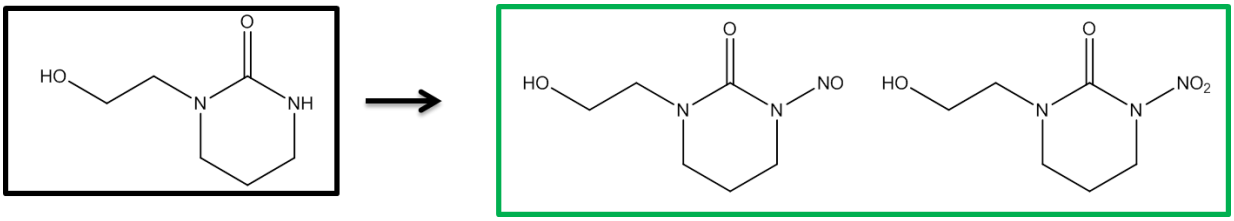
The next most prevalent product was the imidazolidone depicted below. With two tertiary nitrogens in amide functional groups, production of stable nitrosated or nitrated products is even less likely.



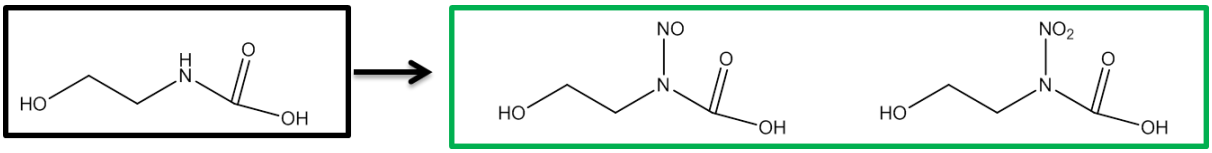
The third most prevalent degradation product associated with carbon dioxide exposure was reported to be HEEDA. HEEDA features one secondary amine and one primary amine. The secondary amine can form a stable nitrosamine and nitramine. The primary amine can form a stable nitramine. Lastly, stable nitroso-nitro and dinitro products are possible as depicted below. All of these products would be amenable to analysis by LC/MS.



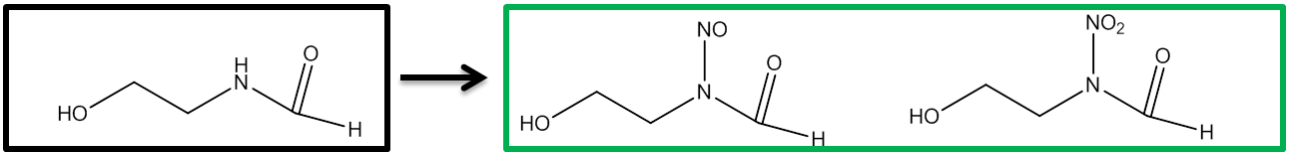
LePaumier et al. (2009b) indicates that oxidative byproduct formation is less important. However, HEEDA-like products form along with a piperazin-2-one as depicted below. Nitrosation or nitration of the secondary amine is possible, but would form an unstable nitrosamide or nitramide. All of these products would be amenable to analysis by LC/MS.



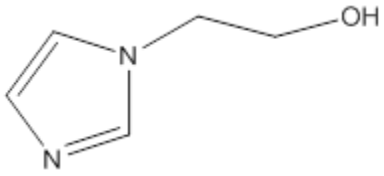
The carbamate is a major product during carbon capture. However, the associated nitrosamides and nitramides are unstable to hydrolysis and so are likely minor products. Both would be amenable to analysis by LC/MS.



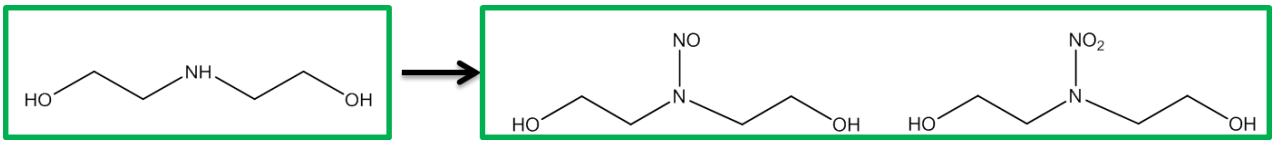
Similar, the study of Sexton and Rochelle (2008) suggests the potential for the formation of a formamide as a major precursor (see below). Although nitrosated and nitrated products are possible, they are unlikely to be stable, as both are amides. Both would be amenable to analysis by LC/MS.



The Sexton and Rochelle (2008) also identified 1-(2-hydroxyethyl)imidazole as a major product of MEA oxidative degradation. Nitrosation or nitration of either nitrogen is not anticipated to form stable nitrosamine or nitramine byproducts.



Lastly, reactions with NOx might promote the formation of the relevant secondary amine (Obiedzinski et al., 1980). This secondary amine could form a stable nitrosamine or nitramine. However, all of these were rated of minor importance. As part of Call-Off 1, we had found that N-nitrosodiethanolamine was a minor nitrosated byproduct of monoethanolamine. Nitrosation of diethanolamine is likely facile. These findings suggest that diethanolamine formation from monoethanolamine is a relatively minor pathway.



2-amino-2-methyl-1-propanol (AMP)

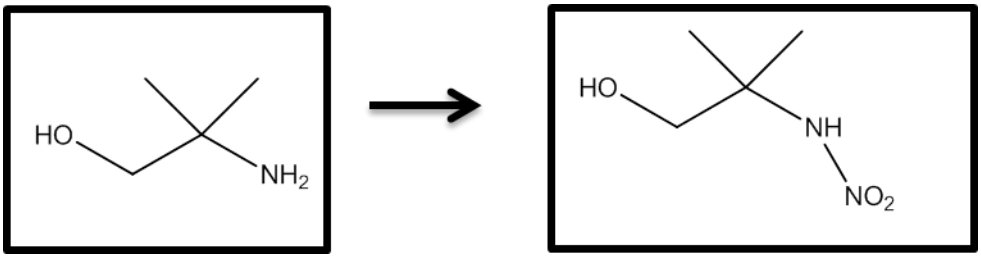
CAS: 124-68-5

Category: Hindered primary amine

Structure

Product Predictions:

As a primary amine, AMP itself is prone to forming its associated N-nitramine. This nitramine is likely a major product. As an alcohol, this nitramine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



The work of LePaumier et al. (2009a) indicates that oxazolidones are two of the major products of AMP in the presence of CO2. Unlike for MEA, these products are relatively stable. The main precursors and potential nitrosamine and nitramine byproducts are similar for both precursors (see below). These byproducts are actually amides. They are coded as moderately important byproducts because the nitroso and nitro substituents promotes their hydrolysis, so they are likely unstable. These byproducts should be amenable to GC/MS analysis.

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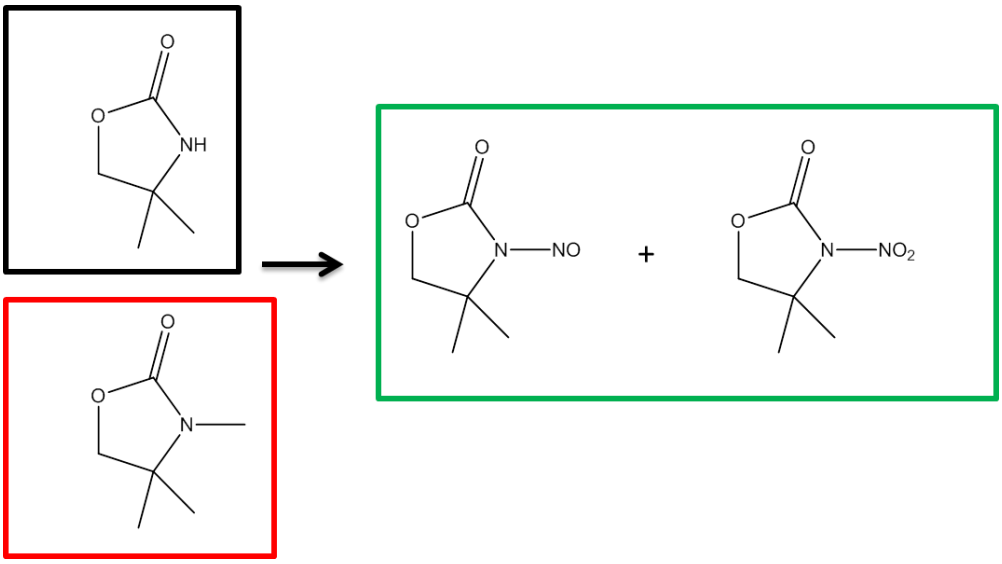
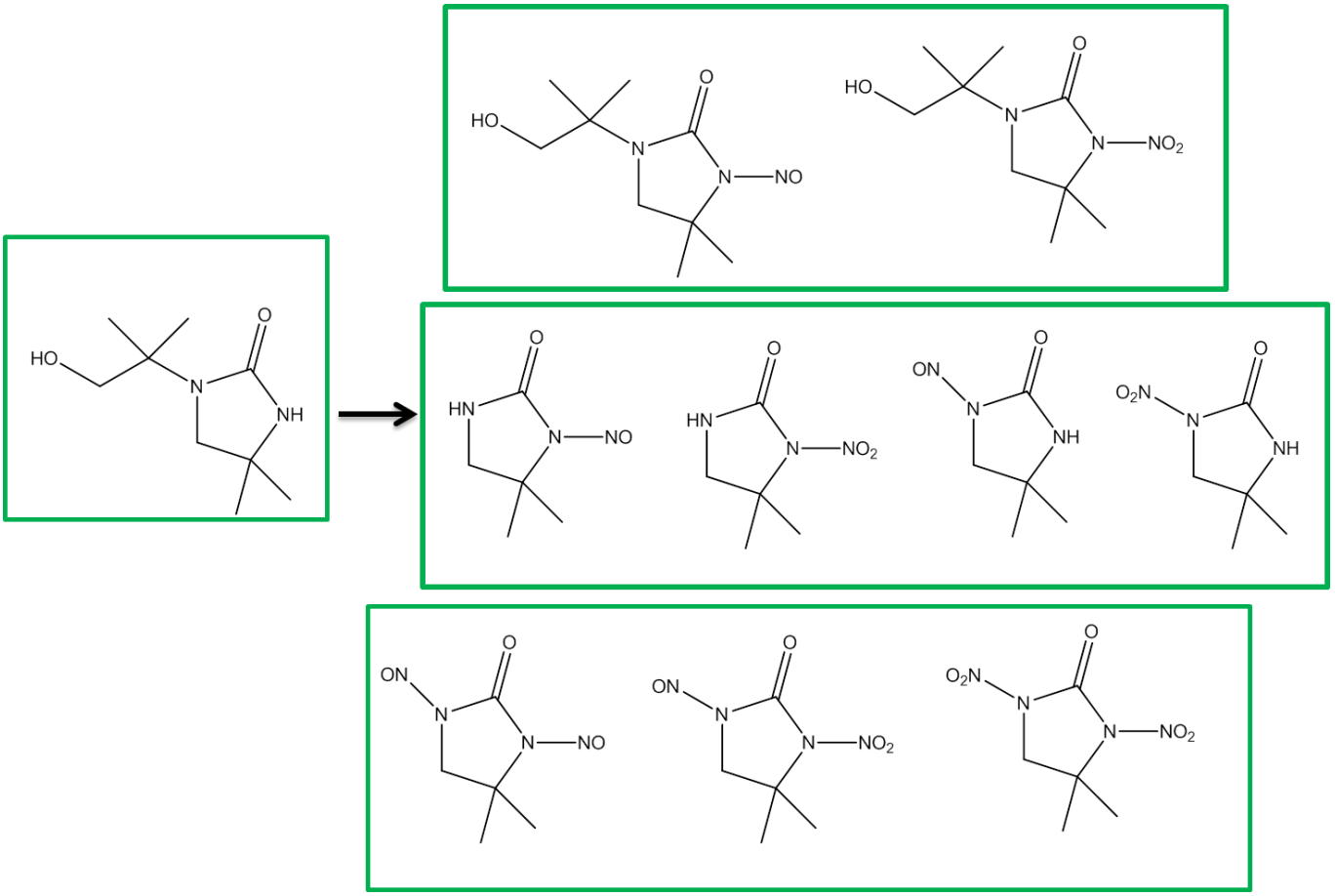
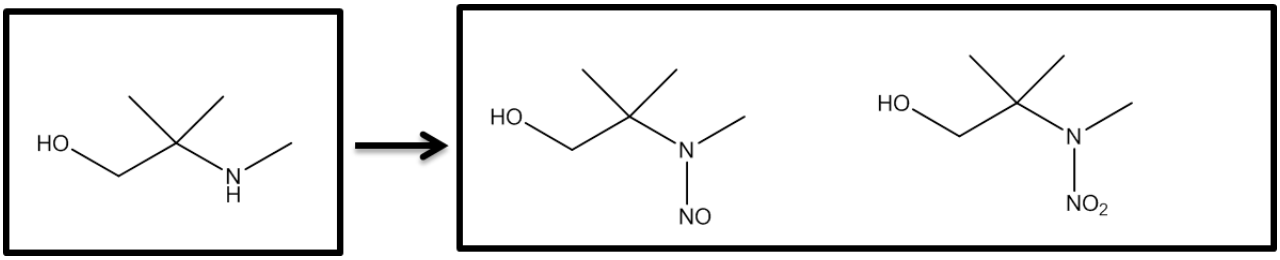
Predicted products of solvent decay and experimental plan
Dr. William Mitch



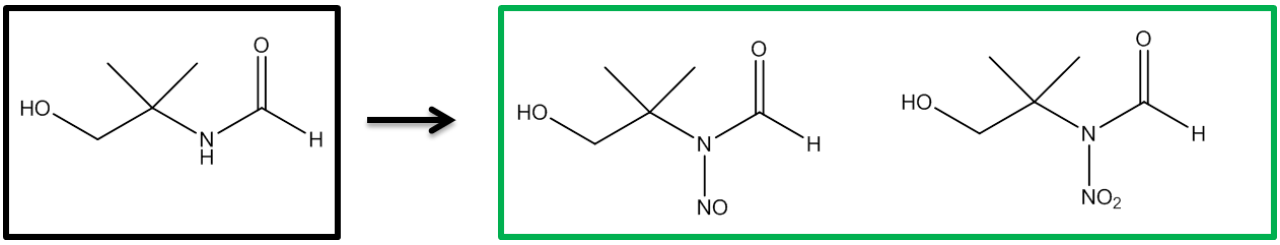
LePaumier et al. (2009a) indicate that the imidazolidone below is a minor product of degradation in the presence of CO2. Accordingly, all of the potential nitrosated and nitrated byproducts are rated as minor. All are nitrosated or nitrated amides and so are likely unstable. Of these, those at the top are most likely to form and would be amenable to LC/MS analysis. The others require a further dealkylation of the precursor, and so are less likely. However, all of these might be amenable to GC/MS analysis.



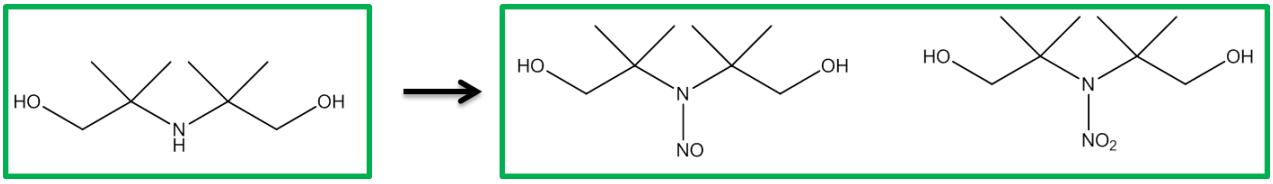
In the presence of oxygen, LePaumier et al. (2009b) indicated that a secondary amine is a major product (see below). This secondary amine could form stable nitrosamines and nitramines as significant, stable byproducts amenable to analysis by LC/MS.



The study of Sexton and Rochelle (2008) suggests the potential for the formation of a formamide as a major precursor (see below). Although nitrosated and nitrated products are possible, they are unlikely to be stable, as both are amides. Both would be amenable to analysis by LC/MS.



Lastly, reactions with NOx might promote the formation of the relevant secondary amine (Obiedzinski et al., 1980). This secondary amine could form a stable nitrosamine or nitramine. However, all of these were rated of minor importance. As part of Call-Off 1, we had found that N-nitrosodiethanolamine was a minor nitrosated byproduct of monoethanolamine. Nitrosation of diethanolamine is likely facile. These findings suggest that diethanolamine formation from monoethanolamine is a relatively minor pathway.



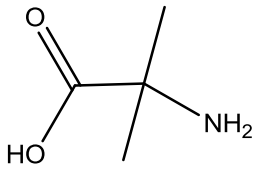
Summary: The nitramine of AMP is anticipated to be a significant byproduct for AMP. As a primary amine, the nitrosamine of AMP would be unstable. Accordingly, AMP is anticipated to post a lower overall risk regarding nitrosamine formation. The secondary amine formed by oxidative decay is likely to be the second most significant precursor for stable nitrosamine and nitramine formation. Although a plethora of other amine precursors are likely to form, many of the associated nitrosamide and nitramide byproducts are unstable towards hydrolysis. Although some of the hydrolysis decay products may preserve the nitroso or nitro substituents, others likely decay to non-nitrosated or nitrated byproducts, further reducing the importance of nitrosamine or nitramine formation from this amine.

2-methylalanine (Alkazid-N)

CAS: 62-57-7

Category: Hindered primary amine

Structure



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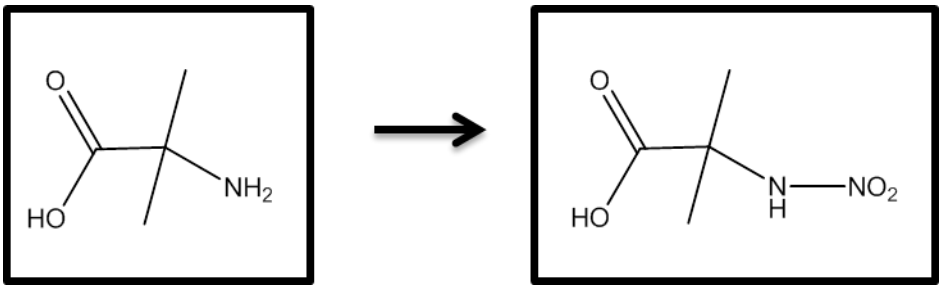
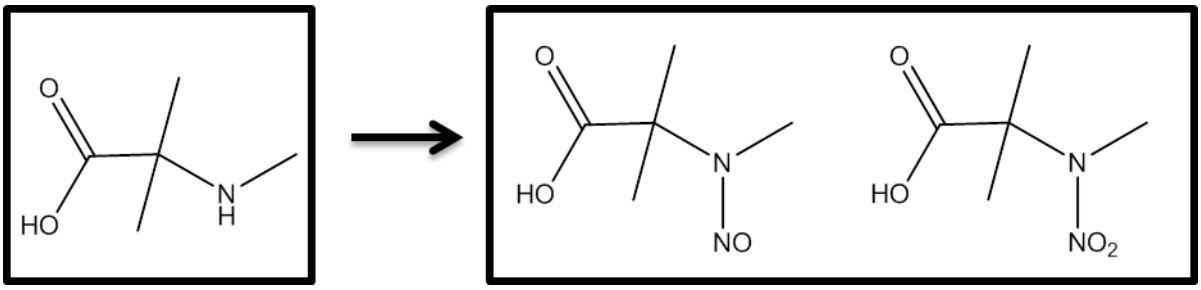
Dr. William Mitch

Product Predictions:

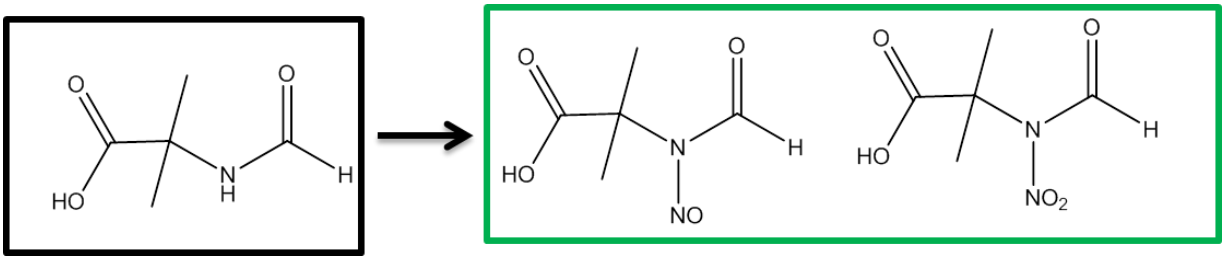
As a primary amine, 2-methylalanine itself is prone to forming its associated N-nitramine. This nitramine is likely a major product. As a carboxylic acid, this nitramine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



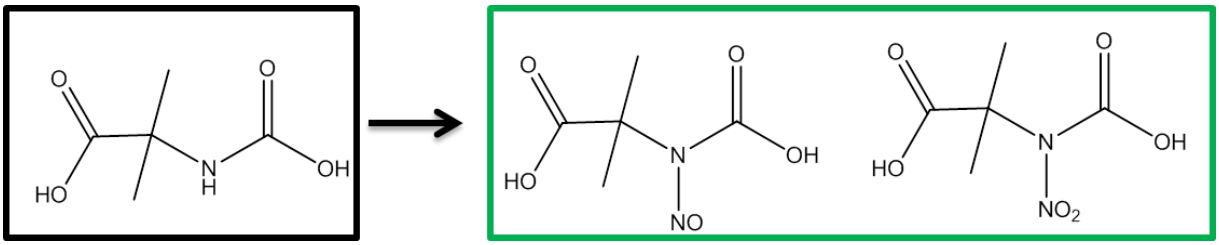
In the presence of oxygen, LePaumier et al. (2009b) indicated that a secondary amine is a major product (see below). This secondary amine could form stable nitrosamines and nitramines as significant, stable byproducts amenable to analysis by LC/MS.



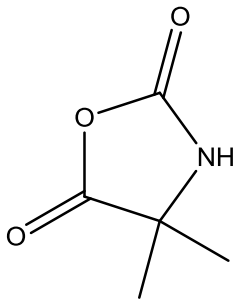
The study of Sexton and Rochelle (2008) suggests the potential for the formation of a formamide as a major precursor (see below). Although nitrosated and nitrated products are possible, they are unlikely to be stable, as both are amides. Both would be amenable to analysis by LC/MS.



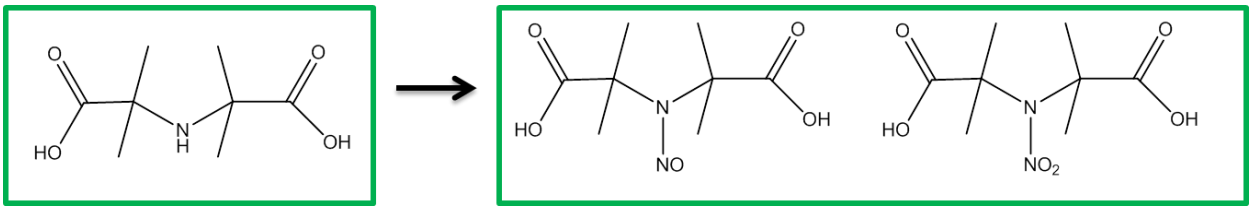
In a similar fashion, the carbamate will form during CO2 capture. It could generate similarly unstable nitrosamides and nitramides:



Cyclization of the formamide or carbamate to form a 5-membered ring comparable to the oxazolidones formed with AMP would form a carboxylic anhydride that would be highly unstable, reverting to the carbamate by hydrolysis. It would likely not even be an observable product.



Lastly, reactions with NOx might promote the formation of the relevant secondary amine (Obiedzinski et al., 1980). This secondary amine could form a stable nitrosamine or nitramine. However, all of these were rated of minor importance. As part of Call-Off 1, we had found that N-nitrosodiethanolamine was a minor nitrosated byproduct of monoethanolamine. Nitrosation of diethanolamine is likely facile. These findings suggest that diethanolamine formation from monoethanolamine is a relatively minor pathway.



2-amino-2-(hydroxymethyl)-1,3-propanediol (TRIS)

CAS: 77-86-1

Category: primary amine

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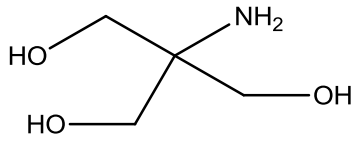
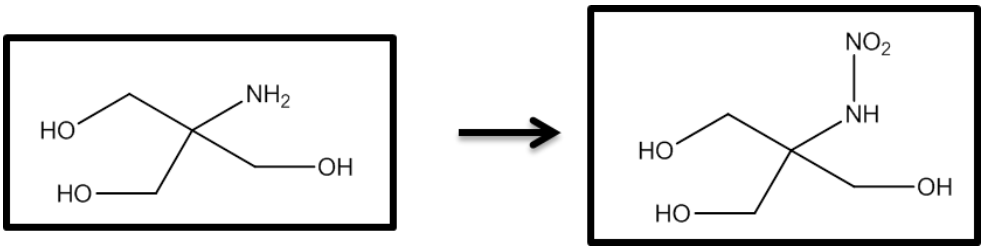
Predicted products of solvent decay and experimental plan
Dr. William Mitch

Structure

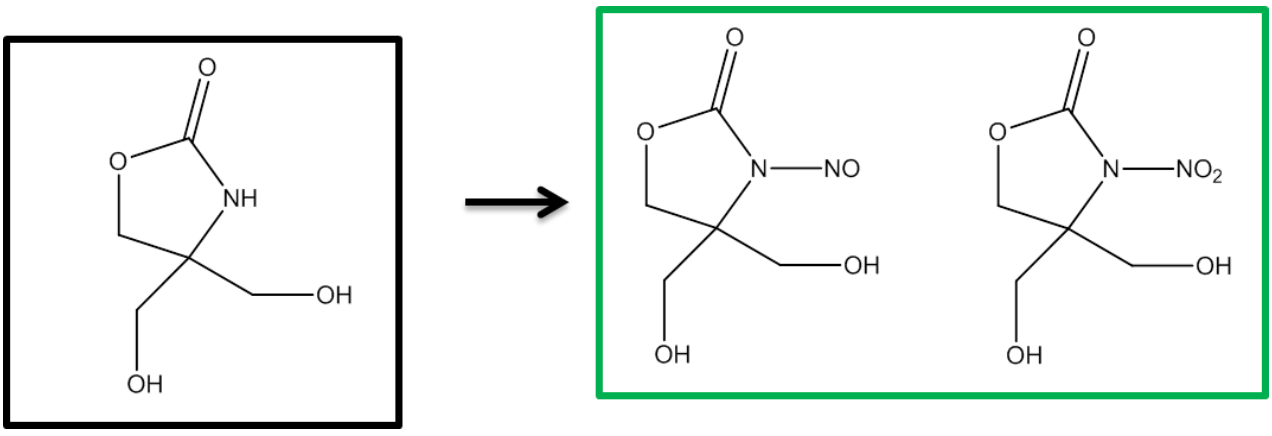


Product Predictions:

As a primary amine, TRIS itself is prone to forming its associated N-nitramine. This nitramine is likely a major product. As an alcohol, this nitramine should be amenable to analysis by the LC/MS method developed for N-nitrosodiethanolamine.



TRIS is structurally similar to AMP. The work of LePaumier et al. (2009a) indicates that oxazolidones are two of the major products of AMP in the presence of CO2. Unlike for MEA, these products are relatively stable. The main precursor and potential nitrosamine and nitramine byproducts for TRIS are depicted b below. These byproducts are actually amides. They are coded as of low importance because the nitroso and nitro substituents promotes their hydrolysis, so they are likely unstable. These byproducts should be amenable to LC/MS analysis.



In the presence of oxygen, LePaumier et al. (2009b) indicated that a secondary amine is a major product of AMP (see below). The analogous secondary amine for TRIS could form stable nitrosamines and nitramines as significant, stable byproducts amenable to analysis by LC/MS.

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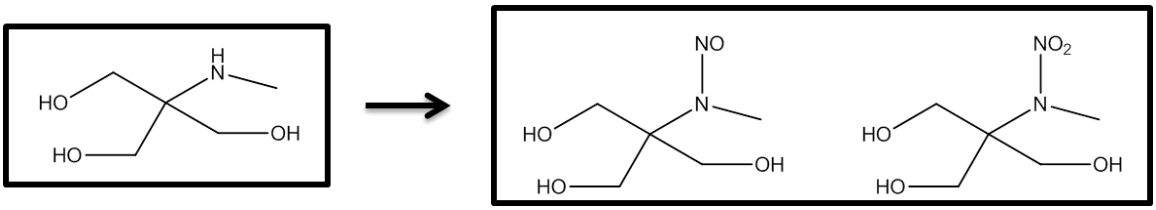
Predicted products of solvent decay and experimental plan
Dr. William Mitch



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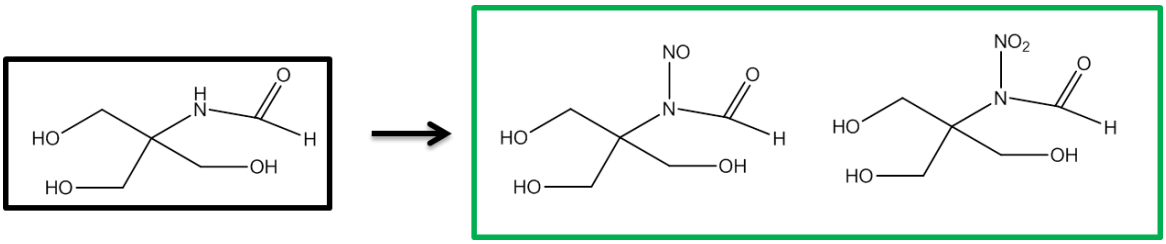
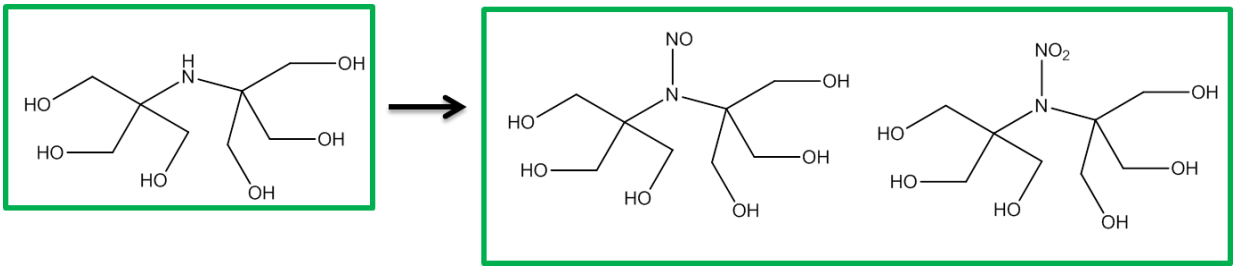


Lastly, reactions with NOx might promote the formation of the relevant secondary amine (Obiedzinski et al., 1980). This secondary amine could form a stable nitrosamine or nitramine. However, all of these were rated of minor importance. As part of Call-Off 1, we had found that N-nitrosodiethanolamine was a minor nitrosated byproduct of monoethanolamine. Nitrosation of diethanolamine is likely facile. These findings suggest that diethanolamine formation from monoethanolamine is a relatively minor pathway.

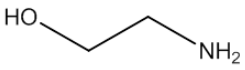


2.0 Experimental Plan

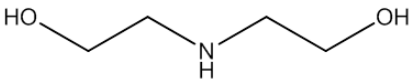
A small-scale Aminox-like pilot reactor will be employed to compare total nitrosamine formation from a range of model amine-based solvent structures. The specific reactor operating conditions (e.g., temperature, CO2 concentration, NO and NO2 concentrations, etc.) will be determined in consultation with CCM. Model amine solvents were selected based upon two criteria: 1) systematic variation in structures and 2) including solvents from the list of 13 likely candidates provided by CCM. A total of 17 solvent amines were selected. Their specific comparison cohorts are described below. Note that some of these solvents are used for different comparisons. However, each would only be tested once to reduce the experimental load. Only total nitrosamine content would be evaluated due to the lack of specific standards for the nitrosamines and nitramines relevant to each amine.

2.1 Primary vs. secondary vs. tertiary amine

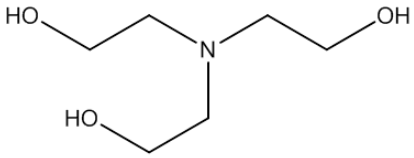
The influence of amine order would be examined via comparison of:



Monoethanolamine
(MEA)



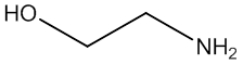
Diethanolamine



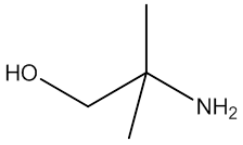
Triethanolamine

2.2 Steric Hindrance

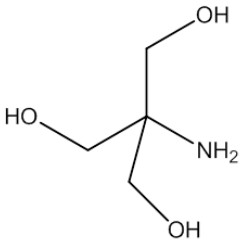
The hindrance to nitrosation posed by adjacent bulky functional groups would be evaluated via comparison of:



Monoethanolamine
(MEA)



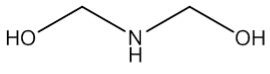
2-amino-2-methyl-1-propanol
(AMP)



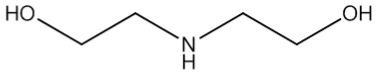
2-amino-2-(hydroxymethyl)-1,3-propanediol
(TRIS)

2.3 Chain length

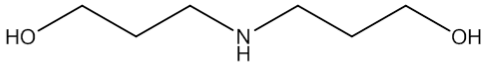
The influence of chain length would be evaluated for primary alkanolamines by comparing:



Dimethanolamine



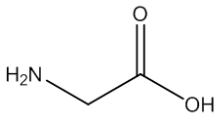
Diethanolamine



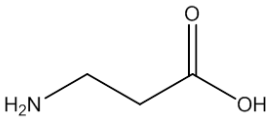
Dipropanolamine

2.4 Distance between carboxylic acid and amine in amino acids

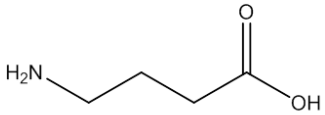
The impact of the distance between the carboxylic acid and amine in amino acids would be tested by comparing:



Glycine



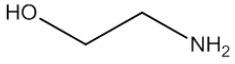
β-Alanine



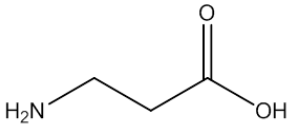
γ-Aminobutyric acid

2.5 Impact of other functional groups on substituted ethanamine derivatives

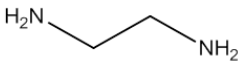
The impact of alcohol, carboxylic acid or amine structures for the second functional group on substituted ethanamines would be evaluated via the following structures:



Monoethanolamine (MEA)



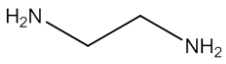
β-Alanine



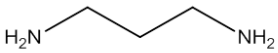
Ethylene diamine

2.6 Primary diamine chain length

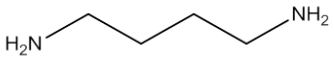
Primary diamines are prone to cyclization reactions. For example, ethylene diamine can form piperazines, with secondary amine components promoting the formation of stable nitrosamines. Five and six-membered rings tend to be the most stable. Accordingly, one might expect that ethylene diamines which can form a six-membered ring (piperazine), would be more prone to forming nitrosamines than diamines with more carbons between the amines. For example, propylene diamine may form an eight-membered ring likely to be less stable than piperazine. This effect would be evaluated by comparison of:



Ethylene diamine



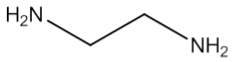
Propylene diamine



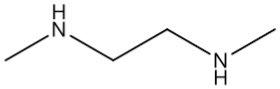
Butylene diamine

2.7 Amine order in diamines

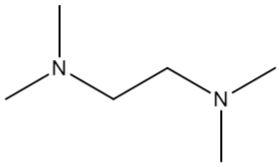
The order of the amines in ethylene diamines would be explored by comparison of:



Ethylene diamine



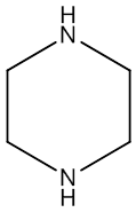
N,N'-dimethyl ethylene diamine



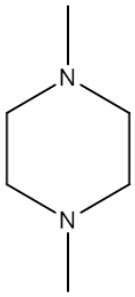
N,N,N',N'-tetramethyl ethylene diamine

2.8 Amine order in piperazines

The effect of amine order in piperazines would be evaluated by comparison of:



Piperazine



1,4-Dimethyl piperazine