

**Theoretical evaluation of the probability to form
and emit harmful components from the aqueous
amine solution MEA, MDEA, AMP, PZ
and some of their mixtures**

A literature report

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Executive Summary

The present report represents a systematic survey of amine degradation products from the amines MEA, MDEA, AMP and PZ, reported in the literature before August 1, 2010. Potential degradation products have been reported to be (specific compounds or classes of compounds) one or more of the following: NH_3 , primary amines / alkanolamines, secondary amines / alkanolamines, tertiary amines / alkanolamines, aldehydes (formaldehyde, acetaldehyde), carboxylates, amides, piperazines, piperazinones, oxazolidones, nitrosamine, imidazolidinones, N, N-disubstituted urea, nitramines. The main focus has been on oxidative degradation products as these are expected to cause the most harmful degradation products or precursors for such if emitted.

The degradation products with the highest probability of being present in the vapour phase have been suggested.

Nitrite and nitrate have been reported as MEA degradation products. Secondary amines may form nitrosamines with nitrite in basic conditions in the presence of formaldehyde, and unidentified nitrosamine(s) have been observed in spent flue gas solvent. The possibility for quaternary amines as nitrosamine precursors might be considered. Nitramine formation has to be considered but no report relating to nitramine formation in aqueous MEA solution under flue gas capture conditions was found.

The wide spread of reported reaction conditions and applied analysis methods make direct comparison of results difficult. Relative probabilities and quantitative formation rates for the various reported *inter*- and *intra*-molecular oxidative degradation reactions are not reported. Studies analysing the oxidative degradation rates for MEA or other amines are not comparable with studies analysing the degradation products. Reports describing a complete mass balance were not found, and no study was found that directly links laboratory results to results of a pilot plant. A careful evaluation of the applied analysis methods is needed in the interpretation of the reported results. In conclusion, insufficient data exist for the quantification of formation rates for oxidative degradation products for the individual amines.

No reports were found concerning the product composition comparison (qualitatively or quantitatively) in metal catalyzed alkanol amine oxidation as compared to the catalyst free systems.

The study has uncovered serious gaps in the current knowledge concerning the possibility to form harmful degradation products. There is not consensus in the scientific literature with respect to the types of degradation products formed from the individual amines. The current knowledge and understanding of oxidative degradation of amines rely on extrapolations from earlier studies without validating the underlying chemistry. Updated reaction schemes including supportive information linked to actually formed degradation products remain to be reported. Mechanistic studies of oxidative degradation under relevant conditions are not reported even for the benchmark amine MEA. Contradictory data have been reported regarding the effect of CO_2 loading on amine degradation. Systematic studies with quantitative data have not been found regarding the effect of flue gas composition. The potential formation of nitrosamines under alkaline process conditions is not understood. The report contains research recommendations to fill the identified gaps.

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PART 1 AMINE DEGRADATION

1 Introduction

1.1 Scope of Study

An amine based CO₂ capture plant may cause harmful emissions to the atmosphere. Amines and degradation products from reactions in the process and in the atmosphere are of particular concern but there is limited knowledge about the possibility for various amines to form and emit such compounds.

The scope of this study is to review and summarize the classes and individual degradation products that have been reported in selected literature for the individual amines MEA, MDEA, AMP and PZ (Fig. 1), as well as for the solvents A, B and C (Table 1). The study is, as far as possible, based on a selection of available literature from peer reviewed journals and books. However, also other literature (conference proceedings, presentations, internal reports) has been referred to when deemed necessary.

The report aims at pointing out the most relevant oxidative degradation products from the respective amines. The report further aims at pointing out the most relevant degradation products under anaerobic conditions. In both cases, special focus is on the possibility to form amines, and the concomitant potential of forming nitrosamines (secondary amines) and nitramines. It can not be excluded that components other than those identified in the herein reported literature may be formed or may be speculated to be formed, yet discussions about such compounds are beyond the scope of this report.

The report also aims at evaluate any concomitant products like nitrosamines and nitramines that may be formed from the generic amines and/or their degradation products.

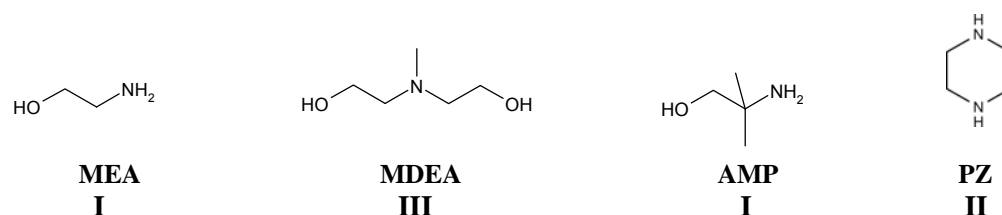


Fig. 1 Chemical structures of primary (I) and tertiary (III) alkanolamines (MEA, MDEA, AMP) and secondary (II) diamine (PZ).

Table 1 Generic amines

Solvent A	Solvent B	Solvent C
MEA (30 wt %)	AMP (25 wt %)	MDEA (25 wt %)
H ₂ O (70 wt %)	PZ (15 wt %)	MEA (5 wt %)
	H ₂ O (60 wt %)	H ₂ O (60 wt %)

The different structural characteristics for the generic amines in Fig. 1 will affect their CO₂ absorption capacity as well as their possibility to form various degradation products. The generic amines encompass variations in properties expected for proprietary solvents.

1.2 The CO₂ Capture Process

The CO₂ capture plant discussed is the standard absorption-desorption plant. The main discussion will assume a process using the standard 30 % wt aqueous MEA solution as absorbent. Other processes will be discussed afterwards as deviations.

1.2.1 Traditional Process

A cursory process description of the traditional CO₂ capture process (Fig. 2) is given in the following.

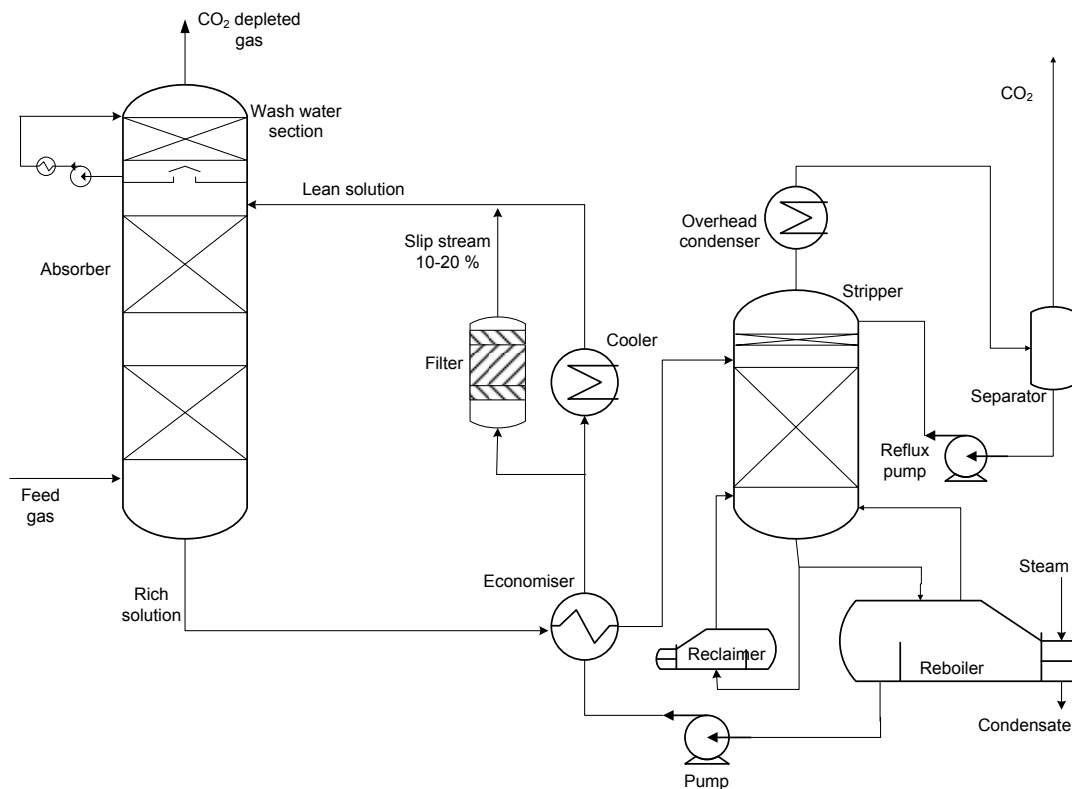


Figure 2. Flowsheet for the standard absorption-desorption process.

After pre-treatment the exhaust gas to be treated is fed to the bottom of the absorber where CO₂ is removed counter-currently with the absorbent. The column is customarily fitted with a water wash section at the top where there is a separate liquid circulation, essentially water, and its function is to remove absorbent vapors from the CO₂ depleted gas. The CO₂ rich absorbent solution is pumped to the desorption section via heat transfer for pre-heating. The CO₂ is stripped by water vapour counter-currently in the stripper. The vapour is generated in situ in the reboiler that is usually heated by steam. The stripper overhead is cooled to condense and recover water vapour. This water is recycled back to the stripper. The CO₂ lean absorbent solution is pumped back to the absorber via heat exchange with the rich absorbent and further cooled.

There are no high pressures involved in the process itself. The CO₂ compression involves high pressures, but is outside the scope of this discussion. The absorber is 1.0 to 1.1 bar abs, and the stripper operates at 1.5 to 2 bar abs. The rest of the pressures are in-between. Enough said about the pressures.

The feed gas from an energy plant is normally quite warm. Its temperature will no doubt vary, but 80 °C upwards to well over 100 °C is common. This gas is usually pre-treated. Cooling to a desired process temperature is part of this pre-treatment. Feed gas temperature to the absorber is usually in the range 40-50 °C, but it could well be higher. It is usually left a little warmer than 40 °C to avoid cooling the gas below its dew point.

The CO₂ absorption process is exothermic. The effect of water mass transfer could be both endothermic and exothermic depending on whether water is absorbed or desorbed, and that would depend on the feed gas dew point and the temperature in the column. The CO₂ lean absorbent solution entering at the top would be expected to be in the range 35-45 °C. Lower or higher temperatures could be used, but this would have a profound effect on the plant's water balance. There is also the question of a suitable cooling agent and its temperature, e.g. cooling water. For a 30 % wt aqueous MEA solution, with the feed temperatures discussed, there could be intermediate temperatures of 70-80 °C in the column. There is maximum somewhere along the column while the ends are cooled by gas and liquid respectively. Where the maximum is, depends on the exact conditions. The maximum could be both above or below the middle. The CO₂ loading in the lean solution entering will be in the range 0.15 – 0.22 mol CO₂ per mol MEA. The rich solution exiting is reported in the range 0.40 to 0.45 mol CO₂ per mol MEA. There has been a trend towards higher lean loadings in recent optimisations of the process.

The temperature in the water wash section in the top is very dependent on available cooling for the wash water loop. It is desirable to keep it as low as possible to maximise the solubility of the MEA and thus aid the prevention of absorbent emission. Given that the gas leaves the CO₂ absorption section in the range 40 – 50 °C, the wash temperature will be no higher than this, and most probably a little lower. The question of the plant's water balance is again a necessary consideration, partly for economic reasons. Since there is still CO₂ left in the gas after the CO₂ absorption section, and the water wash is really a dilute solution of MEA, the absorbed MEA will be loaded with CO₂ to a level allowed by the partial pressure of CO₂ at the wash temperature. The loading level will depend on the amount of CO₂ left. For a gas fired power station (GTCC) with 90 % CO₂ recovery, loadings in the order of 0.40 mol CO₂ per mol MEA could be achieved since the liquid is recycled with only a small bleed.

The desorption column is closer to isothermal condition because the water mass transfer moderates the temperature profile. The top of the column could have 105-115 °C while the bottom could see 115-125 °C. These temperatures are pressure dependent. A higher pressure will give a higher temperature. The CO₂ loading in the absorbent solutions will be as in the absorber, but with the highest loading in the top and the lowest in the bottom. Actually, a substantial amount of CO₂ will flash off in the liquid distributor in the column top due to the pre-heating in the "economiser". The loading after this flash may be reduced to 0.37-0.40 mol/mol.

The conditions in the reboiler is very much like the bottom of the desorption column, but it is really in the reboiler that the absorbent achieves its lowest CO₂ loading. The desorber overhead condenser and cooler will see temperatures of 110 and down to 30 °C. There is little MEA here due to the wash effect of the recycled condensate. The lean-rich heat exchanger is operated with a temperature approach of 10-20 K. This means that the cold end will have temperatures from that of the absorber bottom to 10-20 K above. The hot end will have the reboiler temperature on one side and be 10-20 K colder on the other side. The lean amine cooler will have cooling water or air on one side and lean amine on the other. The lean amine will have temperatures 10-20 K higher than the rich amine at one end and the absorber liquid feed entry temperature at the other.

Liquid hold-ups are very relevant when it comes to evaluating chemical reactions and their extents of conversion. However, this is a value closely associated with apparatus design. As such it is more convenient to discuss this separately.

In general, the important process parameters influencing amine solution degradation are temperature and residence time, for example too high temperature and long residence time in the stripper column reboiler.

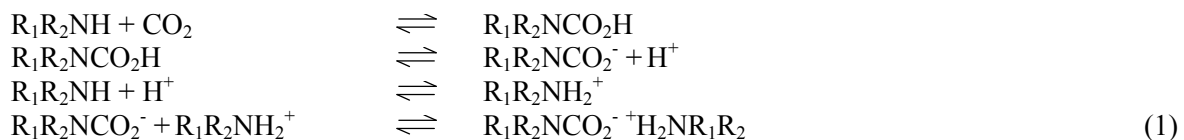
A typical worst case scenario may thus be

- In the absorption column: non-plug-flow conditions, high temperature, long residence time, at column top excessive entrainment of droplets in general and aerosols in particular.
- In the desorber section: hot spots in the reboiler (also reclamer).

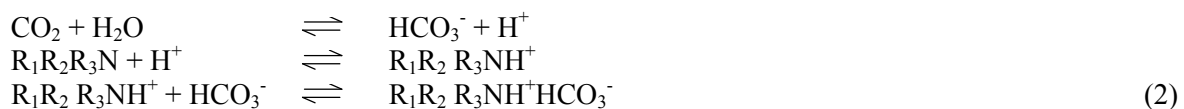
This worst case scenario is difficult to quantify because it assumes design mistakes at the engineering stage.

1.3 CO₂ Absorption by Amines

The capacity of an aqueous amine solution to chemically absorb CO₂ is a function of the pathway by which CO₂ reacts and the basicity of the amine (expressed by its pK_a). Generally, the kinetically and thermodynamically preferred reaction for primary and secondary amines is to react with CO₂ to form carbamic acid with the subsequent formation of a carbamate (Eq. 1), hence the overall stoichiometry of amine: CO₂ is 2:1 (Puxty *et al.* 2009; Versteeg *et al.* 1996).



The alternative pathway is the formation of bicarbonate, where the amine simply acts as a base hence the overall stoichiometry of amine: CO₂ is 1:1 (Eq. 2). This is the only reaction pathway for tertiary amines due to their lack of ability to form stable carbamates (Crooks and Donnellan 1990, Little *et al.* 1990). This pathway may contribute also for some sterically hindered primary and secondary amines (Puxty *et al.* 2009).



1.4 Degradation Reactions

Under the varying conditions of lean/high loading^a, with/without oxygen present, and at low/high temperatures, degradation of aqueous amine solutions are usually classified as follows (Chi *et al.* 2002; Rochelle *et al.* 2001):

- 1) Oxidative degradation: Requires oxygen, results from radical reactions, is catalysed by metal ions (*e. g.* iron), results in oxidised fragments of the solvent (*e. g.* organic acids, NH₃), and is expected to take place in the liquid hold-up in the absorber bottom.
- 2) Carbamate polymerisation: Requires high temperatures and CO₂, produces high molecular weight degradation products (oligomers/polymers, cyclic compounds) and is expected to take place at the higher temperature of the stripper. Relevant for primary and secondary amines but not for tertiary amines. Reaction products are typically – but not necessarily only – higher molecular weight components.
- 3) Thermal degradation: Takes place mainly at temperatures > 200 °C and is less studied.

^a Loading: the molar ratio CO₂:amine, commonly denoted α

2 Oxidative Degradation

2.1 General Degradation Chemistry

MEA is the most extensively studied amine for the use in CO₂ capture, yet the mechanism for the oxidative fragmentation remains uncertain. Two earlier studies are those frequently cited in the literature regarding MEA degradation although the reaction conditions are significantly different from those experienced in the CO₂ capture process. These are described in the following.

2.1.1 Electron Abstraction Mechanism

The electron abstraction mechanism is based on a series of studies in the 1960's that focused mainly on tertiary amines (Dennis *et al.* 1967, Hull *et al.* 1969, Rosenblatt *et al.* 1969; at the Edgewood Arsenal by the US Army Chemical Research and Development Laboratories). As chlorine dioxide (ClO₂), a single electron oxidant, was used, the studies bear relevance to oxygen radical reactions. MEA was included in some of the studies (Dennis *et al.* 1967), and the scheme representing the summary of the findings (Hull *et al.* 1969) is depicted in Fig. 3 for the case of MEA (path i, ia). The degradation of MEA and AMP were reported (Dennis *et al.* 1967).

These studies suggested that for the (mainly tertiary) amines studied, the rate-limiting step (Fig. 3) was electron abstraction from nitrogen to produce an aminium radical. The aminium radical subsequently loses a proton to produce an imine radical. Further loss of an electron by reaction with another radical results in an imine. Hydrolysis of the imine produces an aldehyde (or a ketone for an α -C-alkylsubstituted amine) together with NH₃ (Path ia). Alternatively, fragmentation (N-H and C-C bond scission) produces formaldehyde and NH₃ (path ib). The experimental results from degradation of MEA with ClO₂ showed that formaldehyde and NH₃ were produced (Hull *et al.* 1969). The degradation of AMP was reported to produce NH₃, formaldehyde and acetone also according to Fig. 1 (path i and ib) (Dennis *et al.* 1967). As expected, the dimethyl-substituted α -carbon gives other degradation products from AMP compared to the unsubstituted MEA.

The electron abstraction mechanism was found by this research group to prevail for the tertiary amines studied. A hydrogen abstraction mechanism from the α -carbon was also recognised but was found to dominate only for benzyl amine (Hull *et al.* 1967).

The electron abstraction mechanism was adopted by Chi (Chi and Rochelle 2002) who suggested that other free radicals like Fe³⁺ could initiate the reaction. These authors further extended the reaction scheme and introduced the role of oxygen by formation of peroxide radical (Fig. 1, Path ii). This could react with another molecule of MEA to produce an amino-peroxide radical and another aminium radical. Decomposition of the amino-peroxide would result in an imine and hydrogen peroxide.

Based on this reaction scheme, degradation of MEA was suggested to produce formaldehyde, hydroxyacetaldehyde and NH₃ as primary reaction products (Chi and Rochelle 2002). The authors studied the degradation of MEA in the presence of metal ions but monitored only the formation of NH₃ hence the proposed reaction pathway ii (in Fig. 3) was not fully confirmed.

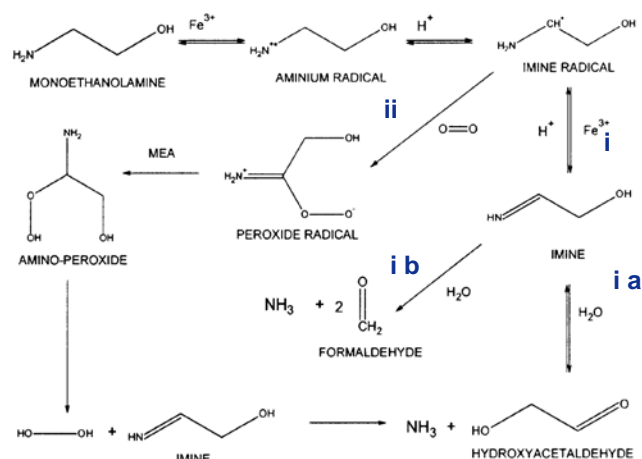


Fig. 3 MEA degradation by electron abstraction (one-electron oxidation): Proposed reaction scheme (Dennis *et al.* 1967, Hull *et al.* 1969, Chi and Rochelle 2002)

2.1.2 Hydrogen Abstraction Mechanism

Another study suggested that MEA would degrade by a hydrogen abstraction mechanism (Petryaev *et al.* 1984). In these studies (also by the US Army Chemical Research and Development Laboratories), aqueous solutions of amine were degraded using ionization radiation to create initiating radicals like OH, H[•], e⁻ (aq).

The proposed reaction scheme for MEA in alkaline solution (pH > 6) (Fig. 4) relies on the formation of cyclic 5-membered ring structures with O⁻...H- or N⁻...H-bonds. Three alternatives for radical formation from α,β -aminoalcohol are envisaged: (i) Abstraction of a hydrogen from the β -carbon results in N-C bond cleavage and yields an aldehyde in addition to NH₃; (ii) abstraction of a hydrogen from the α -carbon yields an imine that is further hydrolysed to an aldehyde, again accompanied by NH₃ formation; (iii) abstraction of an electron from nitrogen resulting in both N-C and C-C bond scission, hence two moles of formaldehyde results per mole MEA in addition to NH₃.

For MEA, the reported decomposition products are NH₃ and acetaldehyde (Petryaev *et al.* 1984), indicating that route i) and/or ii) are prevailing. Petryaev in addition reported the degradation of DMAE (dimethylaminoethanol) to produce acetaldehyde and dimethylamine, pointing to path i) as a preferred route. For other α,β -aminoalcohols, the preferred reaction path will depend on the specific structure of the starting compound.

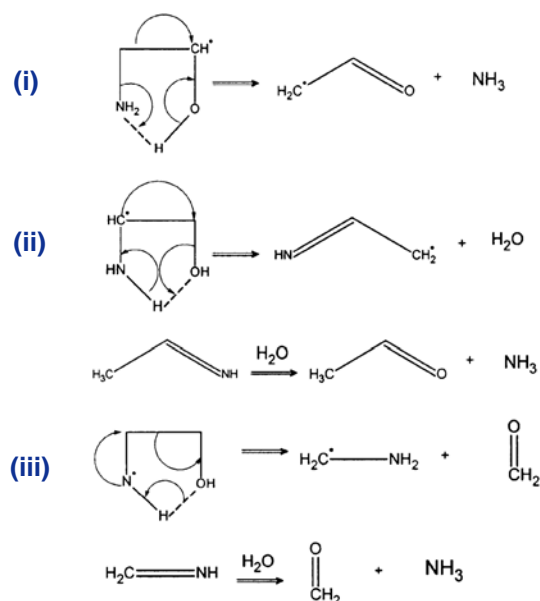


Fig. 4 MEA degradation by hydrogen abstraction: Proposed reaction scheme for α,β -aminoalcohols (Petryaev *et al.* 1984, Goff and Rochelle 2004).

The H-abstraction mechanism via a cyclic intermediate/transition state is supported by molecular simulation studies (Goff and Rochelle 2004; Vorobyov *et al.* 2002). The mechanism is favoured by Goff (Goff and Rochelle 2004) in preference to the earlier electron abstraction mechanism (Fig. 3).

According to the reaction scheme in Fig. 3 as well as the actually analysed products (Dennis *et al.* 1967), degradation of MEA results in formaldehyde and NH_3 . According to the reaction scheme in Fig. 4 (Petryaev *et al.* 1984), the formation of acetaldehyde and NH_3 is suggested and also supported by experimental reports. It further implies that NH_3 is a primary oxidative degradation product.

The two above mentioned reaction schemes qualitatively show potential routes to MEA degradation products. Yet, neither of the schemes directly accounts for the role of oxygen or of any dissolved metals. Further, the mechanisms do not take into account the various MEA species present in a CO_2 loaded solution. Studies of MEA oxidative degradation mechanisms under conditions relevant for the CO_2 capture from flue gas remain to be done.

2.1.3 Reaction schemes

The reaction schemes in according to Hull *et al.* (Fig. 3) and Petryaev (Fig. 4), albeit not of recent date, are still those demonstrating some understanding of a general oxidative degradation mechanism. They serve as a general guide to shed light on how structural variations in the parent amines (primary/secondary/tertiary; steric hindrance, α,β -alkanolamine vs α,β -diamine) may influence conceivable reaction pathways. The schemes have been elaborated for MEA (Appendix 1).

2.1.4 Heat Stable Salts

Aldehydes are highly susceptible to autooxidation in the presence of oxygen, yielding the corresponding carboxylic acids (Fessenden and Fessenden 1994). Heat stable salts (HSS) may be formed from the amine with carboxylic acids. Also acidic species like SO_x , NO_x , HCl and HF (impurities in the flue gas) will lead to the formation of Heat Stable Salts (HSS) in any amine system.

2.2 MEA

Experimental studies that have been reported for the oxidative degradation of MEA are summarised in the following. The studies are performed over a wide range of experimental conditions (gas flow rates, concentrations, presence of accelerating/inhibiting components), as well as with a wide range of direct and indirect analysis methods. Several studies have partly analysed the liquid solution for aqueous, non-volatile degradation products, and some have analysed the volatile degradation components. Yet, no reports have been found that closes the gas and liquid phase material balances for the MEA solution. Few studies relevant for industrial (absorber) conditions are reported. No mechanistic studies for the oxidative degradation of MEA under relevant conditions have been reported.

2.2.1 Studies by the Dow Chemical Co.

Hofmeyer (Hofmeyer *et al.* 1956) quantified the rate of MEA oxidative degradation by measuring the NH_3 evolution from the amine solution and the loss of basicity of the liquid amine solution. No other degradation products were reported.

Rooney (Rooney *et al.* 1998) investigated the degradation of MEA and other amines in loaded and unloaded solutions by bubbling a stream of compressed air at low flow rates (5,5 mL/min) through the amine solutions at 82 °C (conditions relevant for air clean-up in submarines). The reported MEA degradation products in the absence of CO_2 were formate and glycolate. In loaded systems, mainly formate was reported in addition to small amounts of acetate. The reaction scheme proposed to account for the observations (Fig. 5) is a modification of the one proposed by Jefferson Chemical (Scheimann 1962) with paths (i) and (ii) to account for the formation of the additional products not reported in the previous studies. The formation of methylamine by (ii) is not commented nor supported by experimental evidence in the report and only serves the purpose of accounting for the formation of the observed formic acid.

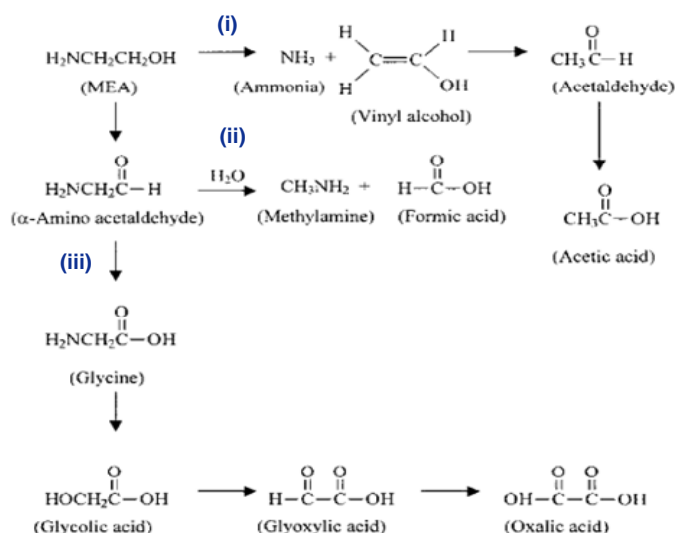


Fig. 5 MEA degradation: The role of oxygen in alkanolamine degradation (Rooney 1998, Jefferson Chemical in Scheimann 1962).

Rooney (Rooney *et al.* 1998) reported that degradation rates were lower in loaded compared to unloaded solutions, as evidenced by the analysis of total anions found after MEA degradation (4 weeks/82 °C) (Table 2). These results are in contrast to reports by others (Chi 2002, Blachly *et al.* 1966, Kindrick *et al.* 1950).

Table 2 Comparison of anion formation (4 weeks/82 °C) for MEA, MDEA and DEA (Rooney *et al.* 1998).

Amine	Loaded*	Rates of formation ($\mu\text{mol}/\text{kg}_{\text{solution}} \text{hr}^{-1}$)				
		Acetate	Formate	Glycolate	Oxalate	Total anions
MEA (20 wt %)	no	1,4	27,3	19,5	0,0	48,2
MEA (20 wt %)	yes	1,5	16,5	0,0	0,0	18,0
MDEA (50 wt %)	no	2,8	7,8	10,2	0,0	20,8
MDEA (50 wt %)	yes	2,3	10,3	8,6	0,0	21,2
MDEA (30 wt %)	no	11,3	7,3	13,2	0,0	31,8
MDEA (30 wt %)	yes	6,7	6,9	10,0	0,0	23,6
DEA (30 wt %)	no	1,5	7,4	1,9	0,0	10,8
DEA (30 wt %)	yes	1,2	1,8	0,2	0,0	3,2

* $\alpha = 0,25$ for loaded solutions

2.2.2 Studies by the US Navy

In the Girdler studies (Kindrick *et al.* 1950a), 39 amines (including MEA) and 11 amine mixtures were studied in accelerated degradation experiments using 50 % CO₂/50 % O₂ (80 °C/7 days), and with 25 – 60 ppm dissolved iron. Based on analysis of amine loss and NH₃ formation, the relative stability of amines to oxidative degradation was found to be: tertiary > primary > secondary.

MEA degradation experiments by Blachly (Blachly and Ravner 1966) were done under a variety of different conditions but mainly at 55 °C with a flow rate of air of 1 cc/ml solution /min (300 ml solution; 3-13 days). Degradation of MEA took place only in the presence of CO₂. The degradation rate was measured by monitoring the rate of NH₃ evolution. In addition, this study the first to show the formation of peroxide during degradation of MEA, although no peroxide structure was identified structure.

The general chemistry of MEA was extensively reviewed by Scheimann (Scheiman 1962).

2.2.3 Studies by the US Department of Energy

Strazisar (Strazisar *et al.* 2003) reported the first liquid analysis of a degraded MEA sample from an industrial application (reclaimer bottom; CO₂ from a coal fired power plant). The liquid phase and the volatile components were analysed by anion chromatography and by GC-MS and FT-IR, respectively. In addition to the known carboxylic acid degradation products, a range of new degradation products like other carboxylic acids, amides and oxazolidone were listed based on a NIST library match (Stein *et al.* 1998). However, all liquid analyses were performed on the rich MEA solution. Thus, it is not possible to determine whether the “new” reaction products are absorber/stripper or in the reclaimer (where MEA is present in high concentration and at high temperatures). The mixture presumably contained oxidative degradation products from the absorber as well as products resulting from carbamate polymerisation, from thermal degradation in the reclaimer, and presumably from cross-reactions between the components present. Unspecified nitrosamines were reported in this work as well as piperazines and piperazinones. The formation of piperazines was supported in another study (Khitrin *et al.* 2002) in which a total amount of 0,39 wt % of secondary amines were determined in the absorber sample. In this study, piperazines were also identified as reaction products.

2.2.4 Studies by the University of Regina

Comprehensive studies on MEA and MDEA/MEA degradation have been reported from the research group at the University of Regina. Supap (Supap *et al.* 2001) attempted to quantify the kinetics of MEA degradation under conditions encountered in a typical flue gas treating process at 20 – 70 °C and at elevated O₂ pressure (241-345 kPa) (no CO₂ present). Kinetics was regressed based on the rate of

MEA loss and the O₂ consumption rate. The latter may be uncertain as the pressure of volatile reaction products (NH₃) was not accounted for. Further, as it is not unlikely that these experiments were done under mass transfer conditions, the degradation kinetics may not be assumed to be accurate (Goff 2005).

Bello (Bello and Idem 2006) studied the degradation of MEA at 55 °C, 100 °C and 120 °C at various O₂ levels and CO₂ loadings. The MEA degradation rate with time was monitored by the change in MEA concentration by HPLC analysis. No degradation products were reported. As expected the MEA degradation increased with increasing temperature, MEA concentration, O₂ pressure and in the presence of vanadium. The proposed rate model suggested that CO₂ acted as a degradation inhibitor, in other words that unloaded solutions degraded faster than loaded solutions.

In another study by Bello (Bello and Idem 2005), degradation experiments of MEA (5 mol/L and 7 mol/L) were performed at 55 °C, 100 °C and 120 °C with O₂ (2,5 bar, 3,5 bar) and with various CO₂ loading ($\alpha = 0-0,44$). A significant number of degradation products (40 – 50) were reported. Some of these were expected products previously reported in literature (NH₃, formate). However, most of the suggested products were rather unexpected and lack support by references to other literature. Several of the reaction schemes proposed to account for their formation seem unjustified. Absent in the list of degradation products formed in the presence of CO₂ are thermal degradation products and carbamate polymerisation products that have previously been identified by others (Polderman *et al.* 1955, Yazvikova *et al.* 1975). It is unexpected that the systematic changes in reaction conditions were not reflected in the corresponding ranges of degradation products (Fig. 6). Increasing the O₂ pressure from 250 to 350 kPa resulted in an abrupt change to give a very different range of degradation products. Increasing the MEA concentration from 5 mol/L to 7 mol/L resulted in a reduction in the number of degradation products from 19 to 2 which was ascribed to a lower O₂ availability in the higher concentration case. Such abrupt change in this concentration range is in contradiction to the work by others (Goff and Rochelle 2005).

Table 3. Summary of the Oxidative Degradation Products Obtained with 5 mol/L MEA

250 kPa of O ₂ at 100 °C, 530 h				350 kPa of O ₂ at 100 °C, 732 h			
S/N	product	molecular formula	area %	S/N	product	molecular formula	area %
Major Products							
1	<i>N</i> -formyl- <i>N</i> -methylformamide	C ₃ H ₅ NO ₂	0.93	1	1,3,4-dehydroproline	C ₅ H ₇ NO ₂	1.08
2	1,2,3,6-tetrahydro-1-nitrosopyridine	C ₅ H ₈ N ₂ O	9.33	2	ethylamine	C ₂ H ₇ N	0.54
3	3-methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	5.16	3	1 <i>H</i> -imidazole-4-carboxylic acid methyl ester	C ₄ H ₆ N ₄ O	1.16
4	3,4-dehydro-DL-proline	C ₅ H ₇ NO ₂	0.54	4	3- <i>cis</i> -5-heptadien-1-ol	C ₇ H ₁₂ O	26.48
5	4-ethylcyclohexene	C ₈ H ₁₄	1.33				
6	1,2-ethanediol	C ₂ H ₆ O ₂	0.76				
7	3- <i>cis</i> -5-heptadien-1-ol	C ₇ H ₁₂ O	1.08				
Minor Products							
8	nitrosomethane	CH ₃ NO	0.11	5	3,3-(1,2-ethanediy)bis(sydnone)	C ₆ H ₆ N ₄ O ₄	0.11
9	ethylamine	C ₂ H ₇ N	0.31	6	1-methyl-1 <i>H</i> -imidazole-2-methanol	C ₅ H ₈ N ₂ O	0.28
10	2,2-dimethyl-3-(2 <i>H</i>)-furanone	C ₆ H ₈ O ₂	0.19	7	2,4-dihydro-4,5(3 <i>H</i>)-pyrazol-3-one	C ₅ H ₈ N ₂ O	0.07
11	uracil	C ₄ H ₄ N ₂ O ₂	0.43	8	6-hydroxy-4(1 <i>H</i>)-pyrimidinone	C ₄ H ₄ N ₂ O ₂	0.03
12	1 <i>H</i> -imidazole-4-carboxylic acid methyl ester	C ₄ H ₆ N ₄ O	0.13				
250 kPa of O ₂ at 55 °C, 341 ^h							
S/N	product	molecular formula	area %				
Major Products							
1	12-crown-4	C ₈ H ₁₆ O ₄	2.10				
2	2-(2-ethoxyethoxy)ethanol	C ₆ H ₁₄ O ₃	1.82				
Minor Products							
3	15-crown-5	C ₁₀ H ₂₀ O ₅	0.18				
4	1,4,7,10,13,16-hexaoxacyclooctadecane	C ₁₂ H ₂₄ O ₆	0.05				

Table 4. Summary of the Oxidative Degradation Products Obtained with 7 mol/L MEA at 120 °C

250 kPa of O ₂ at 135 h				350 kPa of O ₂ at 164 h			
S/N	product	molecular formula	area %	S/N	product	molecular formula	area %
1	3,3-(1,2-ethanediy)bis(sydnone)	C ₆ H ₈ N ₄ O ₄	0.88	Major Products			
				1	6-hydroxy-4-(1H)-pyrimidinone	C ₄ H ₄ N ₂ O ₂	0.59
				2	1H-imidazole-4-carboxylic acid methyl ester	C ₅ H ₆ N ₂ O ₂	0.62
				3	1H-imidazole	C ₃ H ₄ N ₂	0.71
2	methylpyrazine	C ₅ H ₆ N ₂	0.07	4	1,3,5-triazine	C ₃ H ₃ N ₃	13.42
				Minor Products			
				5	methylpyrazine	C ₅ H ₆ N ₂	0.21
				6	2-propanone oxime	C ₃ H ₇ NO	0.14
				7	ethylamine	C ₂ H ₇ N	0.21
				8	N-formyl-N-methylformamide	C ₃ H ₅ NO ₂	0.28
				9	1-amino-2-propanol	C ₃ H ₉ NO	0.03
10	2,4-dihydro-4,5(3H)-pyrazol-3-one	C ₅ H ₈ N ₂ O	0.08				
11	5-(hydrazinocarbonyl)imidazole	C ₄ H ₆ N ₄ O	0.21				

Fig. 6 The effect of operating conditions on postulated MEA degradation products, as identified by GC-MS library match (Bello and Idem 2005).

Degradation products in this study (Bello and Idem 2005) were identified using GC-MS methods developed in this group (Supap *et al.* 2001) with library search to match mass spectra in the NIST database (NIST 1998; Stein *et al.* 1998). The statistical matches for some of the major reaction products were as low as 10 %. In general, it is by no means unlikely that a range of products may form as the result of degradation and concomitant cross-reaction of firstly formed degradation compounds. Still, the accuracy of the analytical method and the assignment of specific structures of the degradation products based on MS library matches may be questioned. These extensive studies on oxidative degradation are only briefly or not at all referred to in more recent work (Lepaumier *et al.* 2009, Sexton and Rochelle 2009).

Excluding questionable analysis methods and interpretations as well as reaction schemes, some general trends regarding MEA degradation rates seem apparent from the aforementioned kinetic data (Supap *et al.* 2001, Bello *et al.* 2006).

Based on a comparative study of different analysis techniques (GC-MS, HPLC-RID, CE-DAD), it was recommended to analyse MEA and degradation products by a combination of several techniques (Supap *et al.* 2006).

2.2.5 Studies at the University of Texas at Austin

The Rochelle group (Chi *et al.* 2002, Goff *et al.* 2004, Sexton *et al.* 2009) reported a series of studies on degradation rates of MEA (and other amines). The effect of added metals and of catalyst inhibitors on degradation rates were extensively studied, mostly at low gas rates and low mass transfer conditions.

These studies assume that NH₃ is a primary degradation product and refer to the reaction scheme depicted in Fig. 3. The instantaneous NH₃ formation was monitored by FT-IR (Chi and Rochelle 2002). Degradation of unloaded / loaded (α = 0,4) MEA (2,5 – 12 mol/L) was done at 55 °C in a system sparged with air and showed that oxidation rates were 2 times faster in loaded compared to unloaded solutions. This is in agreement with the results from Blachly (Blachly and Ravner 1966) but not with Rooney (Rooney *et al.* 1998). No degradation products other than NH₃ were reported.

Goff (Goff and Rochelle 2004, Goff 2005) likewise reported the degradation of MEA at 55 °C by monitoring the evolution of NH₃ under different amine concentration (1,0 – 14 mol/L), O₂ concentration (0 – 17 vol %), CO₂ loading (α=0,15 – 0,40), various metal ions (Fe, Cu; catalysts) and agitation rates (200 – 1500 rpm). The author preferred a reaction scheme according to Petryaev (Petryaev *et al.* 1984) (Fig. 4) but reported no analyses of degradation products other than NH₃. Mass transfer effects were investigated and it was postulated that most of the previous kinetic studies had been performed under conditions that were mass transfer limited.

More recent studies in this group differentiated reaction conditions and monitored not only degradation rates by total MEA loss (cation IC) or NH₃ formation, but also various degradation products under low and high gas flow (Sexton 2008, Sexton and Rochelle 2009). The experimental conditions were 55 °C with 2 % O₂ (low gas) and 15 % O₂ (high gas), respectively, and with 2 % CO₂ ($\alpha = 0,4$). Degradation of MEA was accelerated by the addition of Fe and/or Cu and various degradation inhibitors were added, under conditions that secured kinetically controlled degradation. Solutions were analyzed for degraded products by IC and HPLC and gas phase volatile products were analysed by FT-IR.

Oxidative degradation products (low gas) are listed in Table 3. For all four different catalyst combinations, HEF (hydroxyethylformamide), HEI (hydroxyethylimidazole) and formate were reported the most abundant degradation products. The amides were identified indirectly by analysis of the corresponding carboxylates obtained after hydrolysis, rendering a question mark to the results. HEF and HEI were directly analysed by HPLC. The formation of HEF under these conditions is not clear (Sexton 2008). It is suggested that HEI might be formed from NH₃, formaldehyde, glyoxal and MEA, all of which could be present in the degraded solution (Arduengo 2001). Significant amounts of non-identified degradation products were also present.

Oxidative degradation products (high gas) are listed in Table 4. Noticeable in the high gas study was that small amounts of formaldehyde and acetaldehyde were directly observed by FT-IR analysis. Their oxidation products (carboxylates) were analysed as usual by anion IC. It was suggested that the much lower analysed amount of HEF and HEI was due to the stripping of the volatile aldehydes and NH₃ at high gas.

Table 3 Oxidative degradation products from MEA in the presence of metal catalysts at low gas (Sexton and Rochelle 2009).

Catalyst concentration (mM)	Fe (1)	V (1)	Cr/Ni (0,6/0,1)	Fe/Cu (0,1/5)
Results (mM/h)				
MEA loss	3,8	2,1	8	10,3
Carbon in products	6,3	1,6	5,3	20
Nitrogen in products	2,5	0,6	2,1	7,1
O ₂ consumption	1,9	0,7	0,7	5,6
HPLC (mM/h)				
HEI	0,66	0,11	0,59	1,7
HEF	0,77	0,1	0	3,25
Total unknown	2,28	0,49	2,91	1,49
Anion IC (mM/h)				
Formate	0,29	0,06	0,29	0,73
Formamide	0,35	0,12	0,43	2,35
Oxalate	0,02	0,01	0,02	0,04
Oxamide	0,09	0,15	0,19	0,42
Nitrite	0,21	0,05	0,23	0,29

Table 4 Oxidative degradation products from MEA in the presence of metal catalysts at high gas (Sexton and Rochelle 2009).

Catalyst concentration (mM)	Fe (1)	Fe/Cu (0,1/5)
Results (mM/h)		
MEA loss	5,8	3,5
Carbon in products	1,5	4,8
Nitrogen in products	2	3,5
O ₂ consumption	0,9	1,9
HPLC (mM/h)		
HEI	0	0,87
HEF	0	0,23
Anion IC (mM/h)		
Formate	0,1	0,53
Formamide	0,16	0,92
Oxamide	0,01	0,05
FT-IR (mM/h)		
NH ₃	1,83	1,69
CO	0,3	0
N ₂ O	0	0,16
NO	0,12	0,12
C ₂ H ₄	0,24	0
HCHO	0,09	0,02
CH ₃ CHO	0,16	0,06
MEA volatile loss	2,5	3,2

The addition of formaldehyde (expected inhibitor) had the unintended effect of increasing the MEA oxidative degradation rate (Sexton 2009) and increasing the amount of unidentified products. The formation of NO, N₂O, CO and C₂H₄, in addition to NH₃, was reported by FT-IR.

2.2.6 Studies at the IFP^b

Lepaumier (Lepaumier *et al.* 2009) reported the oxidative degradation of altogether seven alkanolamines, herein MEA, at accelerating conditions (140 °C/ 2 MPa air = 0,42 MPa O₂). It may be noted, from these conditions, that CO₂ seems to be present. It was claimed that the product composition remained the same as for lower oxygen levels and lower temperatures but supporting data were not presented. Formate and glycolate, together with other carboxylates, were reported to be predominant products, in accordance with results from others (Hull *et al.* 1967, Petryaev *et al.* 1984, Rooney *et al.* 1998).

A general summary reaction scheme for products other than carboxylic acids is shown in Fig. 7. GC was used to detect unreacted MEA as well as degradation products in the liquid phase. The degradation products were identified by GC-MS library match. The vapour phase was not analysed.

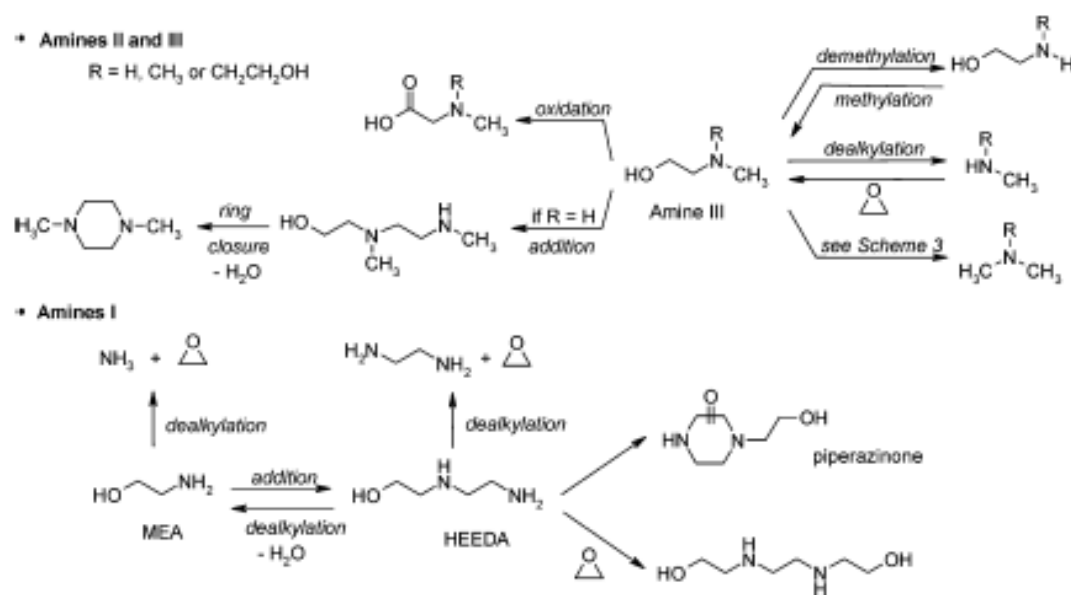


Fig. 7 General summary reaction scheme for the oxidative degradation of MEA and other alkanolamines (Lepaumier *et al.* 2009)

MEA trimers (linear and branched) and cyclic piperazinone derivatives were reported as degradation products from MEA (Fig. 8). In particular, the formation of (small amounts) of MAE was reported albeit not accompanied by a proposed reaction scheme to account for the anticipated methylation of MEA.

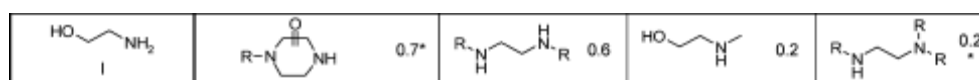


Fig. 8 Oxidative N-containing degradation products from MEA (Lepaumier *et al.* 2009).
(R = CH₂CH₂OH)

Some of the proposed pathways for the degradation of MEA appear less likely and are not supported by experimental evidence or by literature. The proposed reaction scheme for the formation of piperazinones requires the formation of HEEDA (N-(2-hydroxyethyl)ethylenediamine) that was not identified among the MEA oxidative degradation products (but was reported from anaerobic degradation). HEEDA is normally produced via a carbamate reaction route which may in principle be plausible also under these reaction conditions where some CO₂ may be present (see above).

^b IFP, échangeur de Solaize and Université de Savoie

Piperazinones have not hitherto been identified among MEA degradation products except in an industrial reclaimer bottom sample (Strazisar *et al.* 2003). It could be questioned – on a general basis - whether the high temperature in the GC injection chamber (> 275 °C) renders thermal and/or polymerisation degradation not unlikely.

The proposed reaction pathway to produce trimers relies on the formation of ethylene oxide. Supporting experimental data for formation of this cyclic ether is not provided by the authors, but others have suggested the formation of ethylene oxide in the thermal degradation of MDEA (Chakma and Meisen 1997).

The authors claim^c that “for all amines, we think that volatile compounds are formed: ammoniac, methylamine, dimethylamine, and/or trimethylamine, depending on structure of the starting amine”. The nature of the starting amine and the resulting methylamine(s) are not specified and, with respect to MEA, the proposed reaction schemes (Lepaumier *et al.* 2009) do not seem to account for the formation methylamines. However, it could be speculated that further degradation of the methylated degradation product MAE could result in methylamine by analogy to Petryaev (Petryaev *et al.* 1984).

Disregarding the questions concerning product identification by GC-MS and several less likely reaction schemes, some general trends are noted: MEA provides the lowest amount of N-containing degradation products among the 7 alkanolamines (Lepaumier *et al.* 2009), while the formation of carboxylate degradation products from MEA is second highest of the amines investigated. It should be remembered that the oxidative experiments were carried out at a high temperature and probably with CO₂ present.

Transalkylations (dealkylation/alkylation) are well known in industrial processes where various catalysts may be employed to control and optimise the ratio of primary, secondary and tertiary amines at high temperatures (King *et al.* 2010). Formation of transalkylated products during degradation of MDEA has also been reported at medium (Rooney *et al.* 1998) and at elevated temperatures (Chakma and Meisen 1997).

2.2.6 Experiments performed in the presence of catalysts

Several of the reported studies in Table 3 are done in the presence of metal ions. Metal ions (Fe²⁺, Cu²⁺, V³⁺) have catalytic properties for the oxidative degradation of alkanolamines (Chi *et al.* 2002, Goff 2005, Goff *et al.* 2004, Sexton 2008, Sexton *et al.* 2009, Blachly *et al.* 1966) and are frequently used in academic studies to accelerate the reaction, assuming that the degradation products will remain the same (Sexton 2008). However, no study has been reported regarding the effect of metal catalysts on the type and distribution of degradation products.

2.2.7 Summary of knowledge for degradation products from MEA

The main knowledge from literature reports concerning degradation of the MEA is listed in Table 5, comprising reports for oxidative degradation as well as for degradation under anaerobic conditions (Section 3).

^c Confirmed by information from the corresponding author

Table 5 Summary of literature data for degradation of MEA

MEA		Operating conditions										Products reported									
Entry no	Reference	Type of study	Amine [conc]	Temp. [°C]	O ₂ [type/pressure]	CO ₂ [loading/pressure]	Duration [time]	Cat/inhib	Reactor	Process relevance	Analytical methods	NH ₃	Aldehydes	Carboxylates	Amides	Methylamines	Amines	Cyclic	NO _x , nitrites, nitrates, others		
1	Rooney, P. C.; Dupont, M. S.; Bacon, T. R. (1998)	ind	30 - 50 %	80	sparged, 5.5 ml air/min		28 days			absorber	IC (anionic)	NH ₃	CH ₂ O, CH ₃ C ₂ HO	formate, acetate, glycolate, oxalate		MA					
2	Rooney, P. C.; Dupont, M. S.; Bacon, T. R. (1998)	ind	30 - 50 %	80	sparged, 5.5 ml air/min	$\alpha = 0.25$	28 days			absorber	IC (anionic)	NH ₃	CH ₂ O, CH ₃ C ₂ HO	formate, acetate, glycolate, oxalate		MA					
3	Peilyaev, E. P.; Pavlov, A. V.; Shadyro, O. I. (1994)	acad	0.1 M	20		0		irradiation		absorber	chemical	NH ₃	CH ₂ CHO								
4	Dennis, W. H., Jr.; Hull, L. A.; Rosenblatt, D. H. (1967)	acad		20		0	seconds/minutes	ClO ₂		absorber	chemical	NH ₃	CH ₂ O								
5	Lepaumier, H.; Piqué, D.; Carrette, P. L. (2009)	acad	4 mol/kg ⁻¹	140	2 MPa air (0.42 MPa O ₂)	0	15 days		100 ml batch, stainless steel	absorber	GC, FT-ICRMS (high res.)	NH ₃		formate, acetate, glycolate, oxalate	MA, DMA, TMA	MAE, (RNHCH ₂ CH ₂ NHR), (RNHCH ₂ CH ₂ NR ₂)	4 (or 1-), (hydroxyethyl)perazine-2-one	nitrites, nitrates, EO			
6	Chi, S. J.; Rochelle, G. T. (2002)	acad	13-42 wt %	55	air, CO ₂	$\alpha = 0.4$	8 hrs	Fe / EDTA	semibatch	absorber	FT-IR	NH ₃	CH ₂ O, HOCH ₂ CHO						H ₂ O ₂		
7	Goff, G. S.; Rochelle, G. T. (2004)	acad	13-42 wt %	55	air ($\alpha = 0.15$); air/2 % CO ₂ ($\alpha = 0.40$)	$\alpha = 0.15$; 0.4	17 - 33 hrs	Fe, Cu inhibitors	sparged/agitated (mass transfer)	absorber	FT-IR	NH ₃	CH ₂ O, HOCH ₂ CHO	formate, acetate, glycolate, oxalate							
8	Sexton, A. J.; Rochelle, G. T. (2009); Sexton (2008)	acad	7 m	55	air (100 cm ³ /min); b) 15 % O ₂ (7.5 m ³ /min)	$\alpha = 0.4$; 2 %	300 hrs	Fe/Cu inhibitors	high agitation speed	absorber	HPLC, anion IC, FT-IR, NMR	NH ₃	CH ₂ O, CH ₂ CHO	formate, oxalate	HEF, formamide, oxamide		HEI		CO, N ₂ O, NO, C ₂ H ₄		
9	Blachly & Ravner (1966)	ind	4 N	55	air (1 ml/ml soln)	1 %	3 - 13 days			absorber	chemical	NH ₃							peroxides (unidentified)		
10	Kinrick et al (Girdler studies; US Navy) (1950)	ind	3.1 m	80	50 %	50 %	7	Fe		absorber	titration	NH ₃									
11	Bello, A.; Idem, R. O. (2005, 2006)	acad	5 m, 7 m	55-120	2.5 - 3.5 bar	$\alpha = 0 - 0.44$				absorber/stripper	GC-MS (NIST), HPLC, CE	x	x	x	x	x	x	x	x		
13	Lepaumier, H.; Piqué, D.; Carrette, P. L. (2009)	acad	4 mol/kg ⁻¹ (ca 25 wt % MEA)	140		$\alpha = 0 / 0.4$ (0 / 2 MPa)	15 days		100 ml batch, stainless steel	reboiler, stripper	GC, GC-MS, FT-ICRMS				MA, DMA, TMA	HEEDA, RNHCH ₂ CH ₂ NR ₂	HEA, R,R-imidazolidone				
14	Davis, J.; Rochelle, G. (2009)	acad	15 - 40 wt %	100 - 150		$\alpha = 0.2 - 0.5$	8 weeks		10 ml stainless steel	stripper	IC, HPLC						HEEDA	HEA	MEA-urea		
15	Davis, Clesmann (2009; presentation)	acad	7 m	135		$\alpha = 0.4$	60 days			stripper	IC, HPLC						HEEDA	HEA, cyclic urea of trimer	MEA-urea, trimer, tetramer		
16	Stražisar, B. L.; Anderson, R. R.; White, C. M. (2003)	ind	55-200				cont. process			reclaimer sample	GC-MS (high res., library)	x		x						nitrosamines (unspec.)	
17	Supap, T.; Idem, R.; Tonitwachuthikul, P.; Sawan, C. (2006)	acad	5 kmol/m ³	55 - 120	2.5	$\alpha = 0.51$		-	600 ml	absorber/stripper	GC-MS (NIST), HPLC, CE	x	x	x					x		
18	Supap, T.; Idem, R.; Aroonwilas, A.; Tonitwachuthikul, P.; Chakma, A.; Kybett, B. D. (2001)	acad	2 - 11 kmol/m ³	120 - 170	2.41-3.45						no analysis of products										
19	Khitim, S. V.; Fule, S. L.; Devyaterikova, S. V. (2002)	ind								reclaimer sample	GC-MS									N-hydroxyethyl-PZ, dIME-PZ, others	
20	Folderman, Steele (1995)	acad															HEEDA	HEA	HEA		

***Bold:** Analysed and considered relevant; Plain: Analysed, considered less relevant with respect to gas phase composition; *Italic:* Uncertain; indirectly analysed, suggested by generalisation of reaction schemes

2.3 MDEA

2.3.1 MDEA oxidative degradation studies: Experimental reports

MDEA, a tertiary amine, has a theoretical loading capacity of 1,0 mol CO₂/ mol amine (Eq. 2), in contrast to primary and secondary amines that have a theoretical loading capacity of 0,5 mol CO₂/mol amine (Eq. 1). Only a few studies report the oxidative degradation of MDEA, alone or in blends.

2.3.2 Studies by the Dow Chemical Co.

Rooney (Rooney *et al.* 1998) reported the formation of formate, acetate and glycolate in addition to unknown species (oxalate?) for the degradation of MDEA (Table 2). Demethylation was observed. The total amount of carboxylate was 800–1000 ppm, while the formation of DEA was twice as high

2.3.3 Studies at BASF AG

A family of solvent blends of different so-called activator systems with MDEA is known as BASF's aMDEA. One example of such a solution is MDA/PZ. No reports on degradation product studies were found for these blends that have been commercial for two decades.

2.3.4 Studies by the University of Regina

Several reports on kinetics and product distribution from the oxidative degradation of MDEA/MEA blends have been reported by this group (Lawal *et al.* 2005, Lawal and Idem 2005, Lawal and Idem 2006), following the experimental set-up as reported previously for the oxidative degradation of MEA (Supap *et al.* 2001, Supap *et al.* 2006, Bello and Idem 2005, Bello and Idem 2006). The temperature range was typically 55 – 120 °C, the overall amine concentration was 5-9 mol/L, the O₂ pressure was 250 kPa and the CO₂ loading was 0-0,4. The vast amount (80 – 100) of degradation products reported were analysed by GC-MS methods previously described in the group (Supap *et al.* 2001) with identification based on MS library match in the NIST (1998) database. The results do not seem to reflect the systematic variations in reaction conditions, neither are they supported by plausible reaction schemes nor by other literature. The expected DEA (demethylation of MDEA) and MAE are identified for some but not all experiments, and DMAE was not identified. Noticeably absent in the products reported from degradation in the presence of CO₂ are thermal degradation products and carbamate polymerisation products that have previously been identified by others (Polderman *et al.* 1955, Yazvikova *et al.* 1975).

Questions arise to the reported identification of degradation products due to the aforementioned uncertainties (Section 2.2.4). Yet, some general trends may seem apparent from an overall evaluation: i) MDEA is more prone to oxidative degradation than MEA and is preferentially oxidised in the blend; ii) the stability of MDEA/MEA blends to oxidative degradation decreases in the order MDEA/MEA/O₂ > MDEA/MEA/O₂/CO₂ > MDEA/MEA/CO₂.

2.3.5 Studies by the University of Texas at Austin

Closmann (Closmann *et al.* 2009) reported the production of formate and amide (unspecified, indirectly analysed) from the oxidative degradation of MDEA at 55 °C (98 % O₂, 2 % CO₂). It was also found that MDEA degradation was significantly reduced in an MDEA/PZ blend.

2.3.6 Studies by IFP

Lepaumier (Lepaumier *et al.* 2009) reported the oxidative degradation of MDEA at accelerating conditions (140 °C/ 2 MPa air). The presence of CO₂ can not be excluded. The expected NH₃, formate, acetate, glycolate and oxalate reported by others (Rooney *et al.* 1998, Petryaev *et al.* 1984) were reported. The N-containing degradation products (Fig. 9) were small amounts of the demethylated product DEA, the N,N-dimethylated degradation product DMAE and the N-methylated MAE. The high GC injection chamber temperature (> 275 °C) means that reactive conditions during analysis can not be excluded. The degradation products were identified by MS library match (partly with high resolution FT-ICR MS).

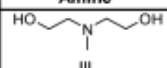
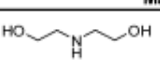
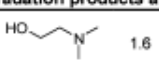
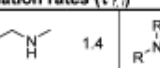

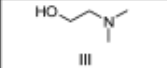
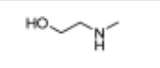
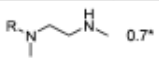

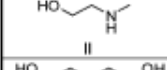
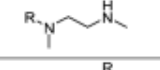
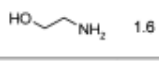


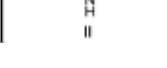
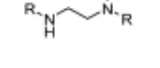
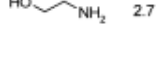
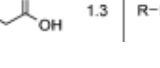
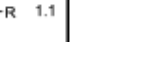
	Amine	Main degradation products and formation rates ($\tau_{r,i}$)				
MDEA		 2.6	 1.6	 1.4	 0.5	
DMAE		 4.6	 0.7*	 0.2*		
MAE		 4.4*	 1.6	 1.1	 0.5	
DEA		 3.5*	 2.7	 1.3	 1.1	

Fig. 9 Oxidative N-containing degradation products from MDEA (DMAE, MEA and DEA) and their further oxidative degradation products (Lepaumier *et al.* 2009). ($R = CH_2CH_2OH$).

The general summary reaction scheme in Fig. 6 was suggested to account for the various N-containing degradation products. Demethylation/dealkylation was suggested to be a main degradation reaction for secondary as well as for tertiary amines in general, thus also of MDEA, and a radical mechanism was proposed to account for the formation of DEA and DMAE (Fig. 9). The formation of ethylene oxide was justified with reference to Chakma (Chakma and Meisen 1997) although the reaction path in the latter case was different and relied on quaternary ammonium ions.

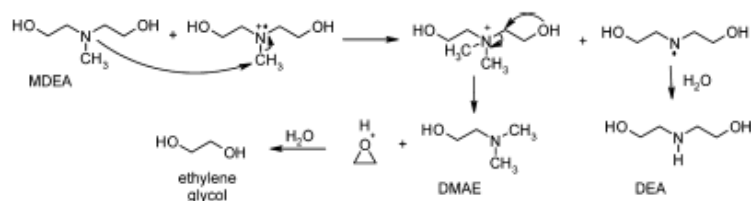


Fig. 10 Proposed radical mechanism for the formation of DMAE from MDEA (Lepaumier *et al.* 2009)

It was claimed that the volatile degradation products di- and trimethylamine were identified in the liquid phase (but not in the vapour phase due to their high volatility). Further supporting experimental data were however not presented. The suggested general reaction schemes (Fig. 10) do not immediately account for the formation of any of these amines as direct oxidation products from MDEA, however their formation may be speculated from *e. g.* the degradation product MDEA according to general reaction schemes (Fig. 3, Fig. 4).

2.3.7 Summary of knowledge for degradation products from MDEA

The main knowledge from literature reports concerning degradation of MDEA is listed in Table 6, comprising reports for oxidative degradation as well as for degradation under anaerobic conditions (Section 3). Also, further degradation of DEA, DMAE and MAE has been included.

Table 6 Summary of literature data for degradation of MDEA. Additionally, data for MAE, DMAE and DEA are included.

MDEA										Products reported															
Entry no	Reference	Type of study	Amine studied	Amine [conc.]	Temp. [°C]	O ₂ [type/pressure]	CO ₂ [loading/pressure]	Duration [time]	Ca/(mole h)	Reactor relevant	Analytical methods	NH ₃	Aldehydes	Carboxylates	Amides	Methylamines	MAE	DMAE	DEA	HEA	HEE	Amines	Cyclic	NO _x , nitrites, nitrates, others	
1	Rooney, P. C.; DuPart, M. S.; Bacon, T. R. (1998)	ind	MDEA	30–50 %	80	5.5 ml air /min	-	28 days	-	absorber	IC (anionic)	NH ₃	CH ₂ O, CH ₃ CHO	formate, acetate, glycolate		MA		DEA							
1	Rooney, P. C.; DuPart, M. S.; Bacon, T. R. (1998)	ind	MDEA	30–50 %	80	sparged 5.5 ml air /min	$\alpha = 0.25$	28 days	-	absorber	IC (anionic)	NH ₃	CH ₂ O, CH ₃ CHO	formate, acetate, glycolate		MA	DEA								
2	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009)	acad	MDEA	4 mol*kg ⁻¹	140	2 MPa air (0.42 MPa O ₂)	0	15 days	-	100 ml, batch, stainless steel	GC, FT-ICR/MS	NH ₃		acetate, glycolate, oxalate, R ₂ NCH ₂ CO ₂ H	MA, DMA, TMA	MAE	DMAE	DEA						nitriles, nitrates	
3	Clesmann, F.; Nguyen, T.; Rochelle, G. T. (2009)	acad	MDEA	7m MDEA	55 (100–135)	2 %	98 % 0.1–0.3	-	Fe	absorber	IC			formate	amides										
1	Rooney, P. C.; DuPart, M. S.; Bacon, T. R. (1998)	ind	DEA	30–50 %	80	sparged 5.5 ml air /min	$\alpha = 0.25$	28 days	-	absorber	IC (anionic)	NH ₃	CH ₂ O, CH ₃ CHO	formate, acetate, glycolate, oxalate											
5	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	DEA	4 mol*kg ⁻¹	140	2 MPa air (0.42 MPa O ₂)	-	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS	NH ₃		acetate, glycolate, oxalate	MA, DMA, TMA	MEA							THEED	aminoacid	
6	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	DMAE	4 mol*kg ⁻¹	140	2 MPa air (0.42 MPa O ₂)	-	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS	NH ₃		acetate, glycolate, oxalate	MA, DMA, TMA	MAE							RNMeCH ₂ CH ₂ NHMe, RNMeCH ₂ CH ₂ NMe ₂		
7	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	MAE	4 mol*kg ⁻¹	140	2 MPa air (0.42 MPa O ₂)	-	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS	NH ₃		acetate, glycolate, oxalate	MA, DMA, TMA	MEA	DMAE						RNMeCH ₂ CH ₂ NHMe	EG	
8	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	MDEA	4 mol*kg ⁻¹	140	-	0 / 0.4 (0 / 2 MPa)	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS							DMAE	DEA			TEA	HEO, HEP, RNEL-PZ	EG	
9	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	DEA	4 mol*kg ⁻¹	140	-	0 / 0.4 (0 / 2 MPa)	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS											THEED	HEO, HEP, RNMeCH ₂ PZ	EG	
10	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	DMAE	4 mol*kg ⁻¹	140	-	0 / 0.4 (0 / 2 MPa)	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS											RNMeCH ₂ CH ₂ NHMe	HEO, HEP, RNEL-PZ	EG	
10	Lepaumier, H.; Ploq, D.; Carrelle, P. L. (2009, 2009)	acad	MAE	4 mol*kg ⁻¹	140	-	0 / 0.4 (0 / 2 MPa)	15 days	-	100 ml, batch, stainless steel	GC, GC-MS, FT-ICR/MS											RNMeCH ₂ CH ₂ NHMe	dlMe-PZ, Me-oxazolidone		
11	Chakma, A.; Meisen, A. (1988, 1997)	acad	MDEA	20–50 wt %	100–200	-	1.4–4.2 MPa	8–55 h	-	600 ml stainless steel	GC-MS		CH ₂ CHO			TMA	MAE	DMAE	DEA			TEA	DMP, HMP (1,12-hydroxyethyl)-4-methylpiperazine, others	EO	
12	Kim and Saitori (1984)	acad	DEA	3.2M	120	-	-	35 days	-	stripper												TEA	HEO, HEP		
13	Petyayev, E. P.; Pavlov, A. V.; Shaabyro, O. I. (1984)	acad	DMAE	0.1 M	20	-	0	-	-	absorber	chemical				DMA										
14	Lawai, A. O.; Idem, R. O. (2005, 2005)	acad	MDEA blends	7–9 mol /l (0.1–0.4)	55–120	2.5	0–0.50	-	-	600 ml stainless steel	GC-MS	x	x			x	x	x	x	x	x	x	x	x	
15	Dawodu, O. F.; Meisen, A. (1998)	acad.	MDEA blends	3.4 M	120–180	-	2.58 MPa	-	-	stripper	GC-MS						MAE	DMAE	DEA			TEA	HEO, HEI, N-disubstituted PZ		

***Bold: Analysed and considered relevant.** Plain: Analysed, considered less relevant with respect to gas phase composition; *Italic: Uncertain; indirectly analysed, suggested by generalisation of reaction schemes*

2.4 AMP

AMP, a sterically hindered primary amine, is postulated to be more resistant to oxidative degradation as it has no α -hydrogen, hence is not able to form an imine which is assumed to be a first step in proposed oxidative degradation mechanism (Fig. 3). AMP is assumed to be less prone to oxazolidone formation due to steric hindrance. Limited information is found in the literature concerning the oxidative degradation of AMP.

2.4.1 Studies by the U.S. Army Edgewood Arsenal

Dennis (Dennis *et al.* 1967) reported the oxidative fragmentation of AMP by chlorine dioxide to produce ammonia, formaldehyde and acetone, in accordance with a general reaction scheme analogous to the one in Fig. 3, *i. e.* a radical fragmentation by N-C α as well as C α -C β bond scissions.

2.4.2 Studies by IFP

Lepaumier (Lepaumier *et al.* 2009) investigated the oxidative degradation of AMP at accelerating conditions (140 °C/ 2 MPa air). In addition to various carboxylates, N-containing degradation products were analysed by GC and identified by MS library match as N-methyl-AMP and 4,4-dimethyloxazolidone (Fig. 11), and were the same under both oxidative and anaerobic conditions. These degradation products seem not accounted for in the general reaction schemes proposed by the authors (Fig. 7).

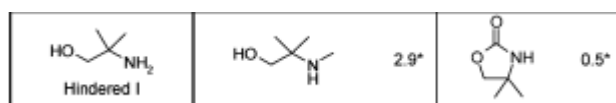


Fig. 11 Oxidative N-containing degradation products from MDEA (DMAE, MEA and DEA) and their further oxidative degradation products (Lepaumier *et al.* 2009). ($R = CH_2CH_2OH$).

It could be speculated that formation of an oxazolidone may be due to the presence of CO₂ as well as the high temperature during the oxidative degradation experiments (see above). This indicates that the steric hindrance in AMP does not prevent oxazolidone formation as earlier anticipated (Rochelle *et al.* 2001). Mono-, di- or trimethylamines are claimed on a general basis from the authors but due to the substitution pattern of AMP, the formation of any of these is difficult to envisage from this generic amine.

2.4.3 Summary of knowledge for degradation products from AMP

The main knowledge from literature reports concerning degradation of the AMP is listed in Table 7, comprising reports for oxidative degradation as well as for degradation under anaerobic conditions (Section 3).

2.5 PZ

Piperazine (PZ), a cyclic diamine, may absorb two moles of CO₂ per mole of piperazine. Prior work on PZ as degradation solvent focused on VLE studies under various conditions. (Bishnoi *et al.* 2002, Hilliard 2008).

2.5.1 Studies at the U. S. Army

Oxidative degradation of PZ by a one-electron mechanism with ClO₂ was reported by Rosenblatt (Rosenblatt *et al.* 1967) to give EDA (ethylene diamine) and formaldehyde although specific experimental data were not reported.

2.5.2 Studies at the University of Texas at Austin

Alawode (Alawode 2005) attempted to quantify the degradation of PZ by analysing piperazine loss by GC analysis from a PZ/K₂CO₃ (1:2) solution at 55 °C (98 % O₂, 2 % CO₂). Acetate was analysed (anion IC) as the main degradation product.

Sexton (Sexton 2008) reported the degradation of PZ in the presence of metal catalysts at 55 °C with low gas (98 % O₂, 2 % CO₂) to produce EDA, formamide and formate as the main degradation products.

Closmann (Closmann *et al.* 2009) reported thermal degradation rates for PZ/MDEA blends and monitored the overall production of formate. Unspecified diamine compounds (after hydrolysis) were monitored but no experiments on PZ alone were reported.

Freeman (Freeman *et al.* 2010) reported, under conditions as above, the formation of EDA, together with formate, oxalate and unspecified formamides (*e. g.* N-formylpiperazine, N-formylethylene diamine) as the primary oxidative degradation products from PZ (Table 8), in the presence of various metal catalysts and inhibitors. The lower degradation of PZ compared to MEA is evident. The claimed formation of formamides was not further accounted for.

Table 8 Oxidative degradation of PZ (Freeman *et al.* 2010).*

Amine	Amine concentration (m)	Additives (mM)	Rate of formation (mM/h)			Amine loss
			Formate	Formamide	EDA	
MEA	7	1,0 Fe	0,29	0,35	-	-3,8
PZ	8	0,6 Fe ²⁺ , 0,25 Cr ³⁺ , 0,25 Ni ²⁺	0,005	0,007	0	-1,1
PZ	8	4,0 Cu ²⁺	0,14	0,24	0,43	-3
PZ	10	0,1 Fe ²⁺ , 0,25 V ⁴⁺	0,006	0,013	0	-0,8
PZ	10	4,0 Cu ²⁺ , 0,1 Fe ²⁺ , 100 Inhib	0,011	0,016	0,009	-1,1

* Different amides were presumed to be formed, but were only indirectly estimated after hydrolysis and lumped as “formamide”.

2.5.3 Summary of knowledge for degradation products from PZ

The main knowledge from literature reports concerning degradation of PZ is listed in Table 9, comprising reports for oxidative degradation as well as for degradation under anaerobic conditions as described in Section 3.

3 Degradation in the Absence of Oxygen

In the stripper, the amines are present as carbamates and/or carbonates of low toxicity. Primary and secondary α,β -alkanolamines degrade anaerobically by carbamate polymerisation. Extensive work has been done on a number of amines, with DEA as the by far most studied. Tertiary amines do not form carbamates with CO_2 but degradation may still take place by transalkylation. In other words, in addition to the high molecular weight polymer degradation products, lower molecular weight amines may be formed also in the stripper at least for some amines. Anaerobic degradation is briefly reviewed in the following for MEA, MDEA, AMP and PZ in order to identify potential volatile amine degradation products.

3.1 MEA

Poldermann (Poldermann and Steel, 1955) suggested a reaction scheme for the thermal degradation of MEA. In this, MEA-carbamate forms, in a reversible reaction, 2-oxazolidone and in a subsequent reaction with another MEA molecule HEIDA (1-(2-hydroxyethyl)-2-imidazolidone) is formed. HEIDA could then hydrolyze to produce HEEDA (N-(2-hydroxyethyl)-ethylenediamine).

Davis (Davis and Rochelle 2009, Closmann 2009) suggested an updated reaction scheme (Fig. 12) where HEEDA is firstly formed from the oxazolidone intermediate. HEIA is subsequently formed by cyclization of HEEDA. According to this scheme, a series of ring closures/openings will give the corresponding cyclic / acyclic dimers, trimers, tetramers *etc.* Any dimeric, trimeric *etc* primary or secondary amine present in the degraded mixture might react with oxazolidone, giving rise to a range of secondary degradation products of higher molecular weights. Such cross-over reactions were reported to take place in blends of MEA with AMP, PZ and other amines (Closmann 2009).

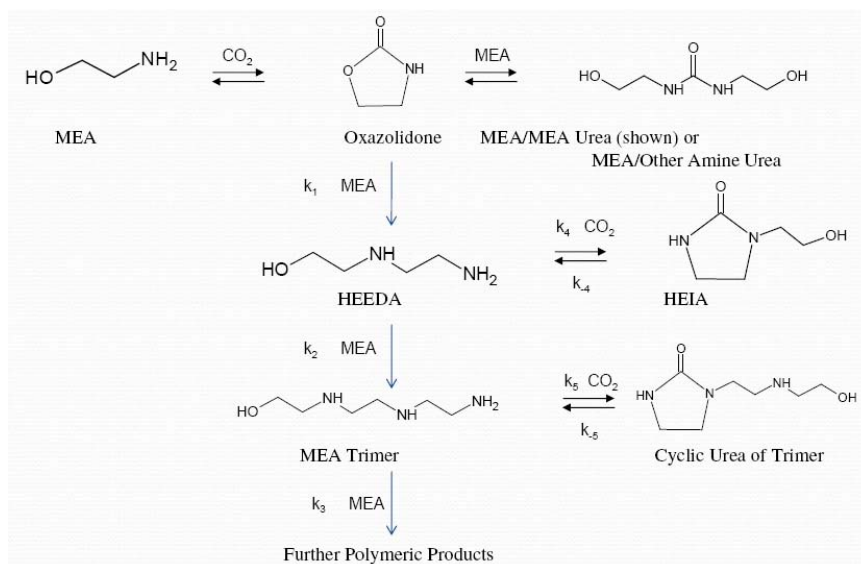


Fig. 12 Proposed pathways for the degradation of MEA via oxazolidone as a central intermediate, resulting in imidazolidinones and oligomers/polymers from MEA. (Davis and Rochelle, 2009; Closmann 2009).

MEA-urea, HEEDA and HEIA were identified as anaerobic degradation products from MEA as depicted in Fig. 13.

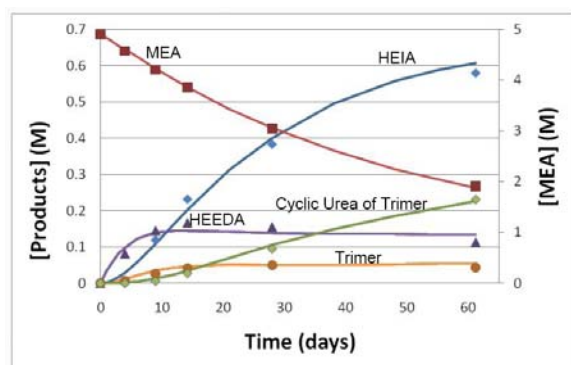
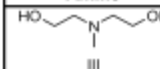
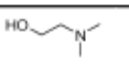
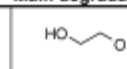
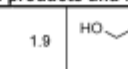
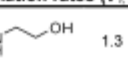
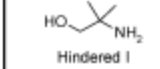
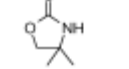
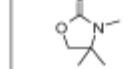
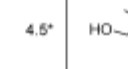
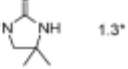

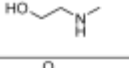
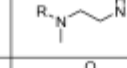
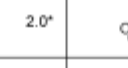

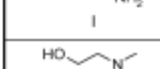
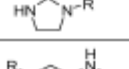
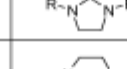
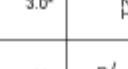
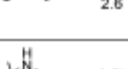
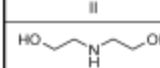
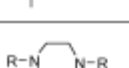
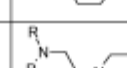
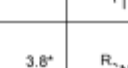
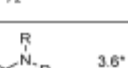
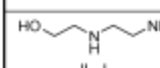
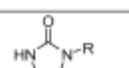
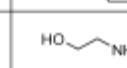
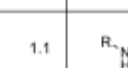
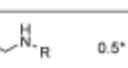







Fig. 13 Carbamate polymerisation of MEA (Closmann 2009).
 HEEDA = hydroxyethylenediamine; HEIA = 1-(2-hydroxyethyl)-2-imidazolidinone.

Lepaumier (Lepaumier et al. 2009) reported the degradation of seven alkanolamines, hereunder MEA, at elevated temperatures (140 °C) in the presence of CO₂ (absence of O₂). Table 10 gives an overview of the reported degradation products for the various amines as identified by GC-MS.

Table 10 Degradation products for various amines at 140 °C (2 MPa CO₂, amine concentration 4 mol/Kg) (Lepaumier et al. 2009).

Amine	Main degradation products and formation rates ($\tau_{1/2}$)				
MDEA 	 4.1	 1.9	 1.3	 1.0	
AMP 	 13*	 4.5*	 1.3*	 0.3*	
DMAE 	 4.0	 2.0*	 1.5	 0.7	
MEA 	 12	 3.0*	 2.6	 0.4*	
MAE 	 15*	 11	 6.5*	 1.9	
DEA 	 19	 3.8*	 3.6*	 2.9*	
HEEDA 	 84	 1.1	 0.5*	 0.5	

MEA was reported to give mainly HEIA (N-(hydroxyethylimidazolidone) together with minor amounts of bis-hydroxyethyl-imidazole, HEEDA (MEA dimer) and N,N,N-tris-(hydroxyethyl)ethylenediamine. The carbamate degradations were in general reported to be significantly higher than the oxidative degradations of the same amines.

Strazisar (Strazisar et al. 2003) reported the liquid analysis of a degraded MEA sample from an industrial application (reclaimer bottom). The composition was analysed by GC-MS and a range of degradation products were proposed based on a NIST (Stein et al., 1998) library match. The mixture contained oxidative degradation products from the absorber as well as products resulting from

carbamate polymerisation, from thermal degradation in the reclaimer, and presumably from cross-reaction between the components present.

3.2 MDEA

3.2.1 MDEA

MDEA, a tertiary amine, forms carbonates with MDEA and does not degrade via the carbamate - oxazolidine pathway (Polderman *et al.* 1955, Chakma and Meisen 1997).

Chakma (Chakma and Meisen 1988, Chakma and Meisen 1997) investigated the degradation of MDEA in the absence of O₂ at elevated temperatures (100 – 200 °C) and pressures (1,4-4,2 MPa CO₂) at concentrations 20 – 50 wt %, and found that MDEA, contrary to the current belief, degraded in the presence of CO₂. The reaction scheme proposes a protonation pathway and relies on the formation of quaternary salts (Fig. 14). Transalkylation of MDEA results in DMAE and DEA as the primary degradation products. An analogous protonation pathway will result in the formation of MAE and TMA from DMAE. DEA and MAE were not directly detected in the degraded reaction mixture but were postulated as intermediate products based on the further degradation products (Fig. 14) and on supplementary GC tests. This study reported formation of small amounts of trimethylamine but not of dimethylamine. In addition, formation of ethylene glycol was reported.

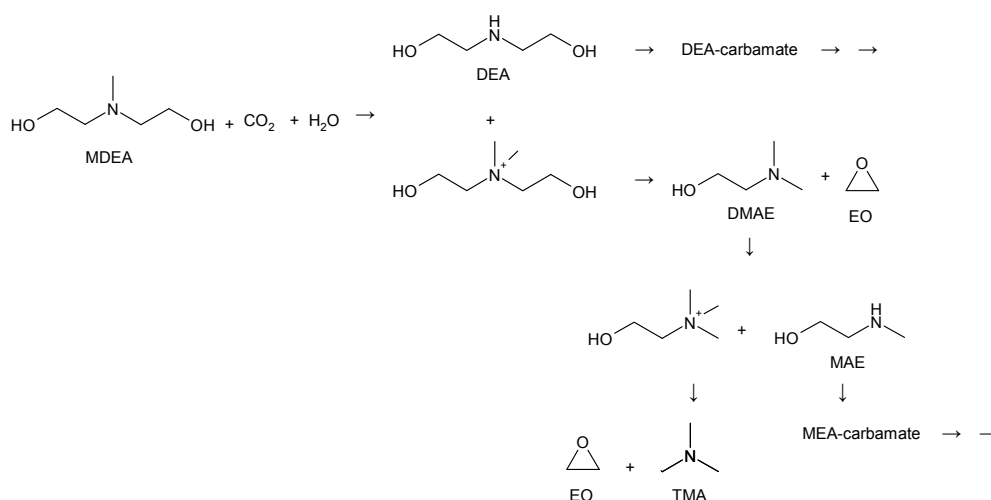


Fig. 14 Proposed reaction scheme for the degradation of MDEA and its firstly formed degradation products (100 – 200 °C/1,4 – 4,2 MPa CO₂) (after Chakma and Meisen 1997).

Chakma (Chakma and Meisen 1997) further identified N-substituted piperazines as MDEA degradation products and suggested that the primary degradation intermediates DEA reacted via its carbamate to form cyclic degradation products. In other words, once a primary or secondary α,β -hydroxylamine is produced as degradation product from MDEA, CO₂ exerts its role and the degradation route via carbamate may be followed. It was reported that the degradation of MDEA increased with temperature and with pressure. It was also documented that the main products were the same at different temperatures (140 °C and 200 °C) hence the use of higher temperatures for accelerating the reaction seemed justified at least in this high temperature range (Fig. 15).

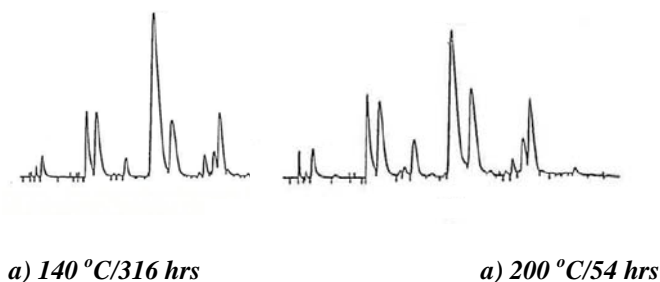


Fig. 15 Gas phase chromatogram of MDEA degraded at 140 °C and 200 °C, (Chakma and Meisen 1997).

Lepaumier reported the degradation of the aforementioned seven α,β -alkanolamines also in the absence of oxygen (Lepaumier et al. 2009). A general reaction summary scheme was presented (Fig. 16) and other detailed reaction schemes were proposed, *e. g.* for the transmethylation/ transalkylation according to a protonation/alkylation pathway. The MDEA degradation products listed in Table 10 shows that DMAE is the main degradation product followed by DEA and TEA (triethanolamine). Under non-oxidative conditions, MDEA was found to be the more stable among the seven alkanolamines that were investigated.

The MDEA degradation products DMAE and DEA may degrade further, *e. g.* according to the general pathway proposed in Fig. 16 and the degradation products for DEA and DMAE shown in Table 10.

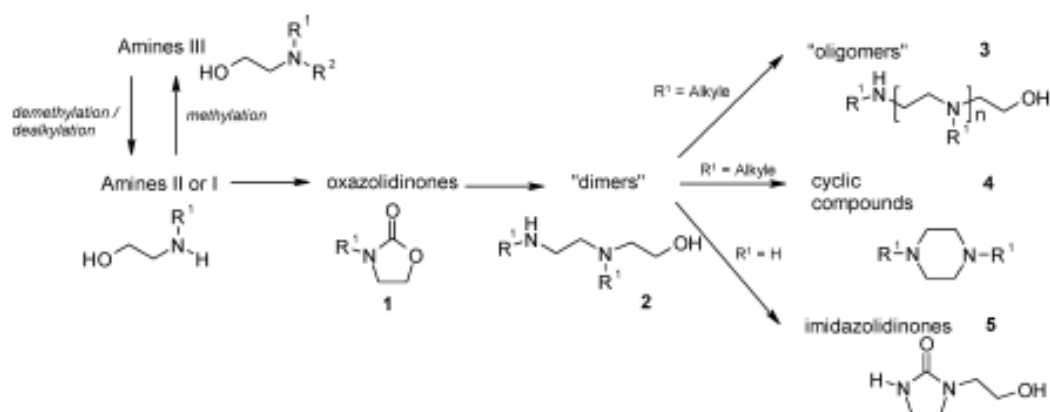


Fig. 16 Proposed general pathway for ethanolamine degradation with CO_2 (Lepaumier et al. 2009).

MDEA apparently forms the same primary degradation products whether oxygen is present or not: DEA is reported from oxidative degradation (Rooney *et al.* 1998, Lepaumier et al. 2009) as well as in the presence of CO_2 (Chakma and Meisen 1997, Lepaumier et al. 2009). Likewise, DMAE is reported both in the presence (Lepaumier and Carrette) and in the absence of oxygen (Chakma and Meisen 1997, Lepaumier et al. 2009). Lastly, MAE is reported as oxidative degradation product (Lepaumier et al. 2009) as well as in the presence of CO_2 (Chakma and Meisen 1997). No oxazolidinones or imidazolidinones are expected to be formed directly from MDEA degradation in the presence of CO_2 at high temperatures as the carbamate degradation route is not an option for the tertiary MDEA. However, degradation products being themselves secondary amines (DEA, MAE) may well degrade by carbamate polymerisation via the respective oxazolidinones.

3.2.2 DEA carbamate polymerisation

Holub (Holub *et al.* 1998) reported substituted ethylene diamine, substituted piperazine and oxazolidone as the main classes of degradation products from DEA.

Kennard and Meisen (Kennard and Meisen, 1985) identified HEP (bis-hydroxyethylpiperazine), HEO (hydroxyethylimidazolidone) and THEED (trishydroxyethylenediamine) as the main reaction products from the carbamate degradation of DEA (90 – 250 °C). The same products were identified by Kim (Kim and Sartori, 1984).

3.2.3 MDEA blends

Dawodu (Dawodu and Meisen 1996, Dawodu and Meisen 1997) investigated blends of MDEA with MEA and DEA, respectively, at various temperatures (120 – 180 °C) and reported disubstituted piperazines, imidazolidones, and various branched compounds as the main degradation products. The rate of degradation was found to be MDEA > MEA < DEA (most degraded).

3.3 AMP

AMP is a sterically hindered amine that is assumed to be less able to form a stable carbamate, hence it is suggested that AMP will be less subject to degradation by the carbamate polymerisation route initiated (Chi and Rochelle 2001, Puxty *et al.* 2009).

Closmann (Closmann 2009) reported the degradation of AMP at 135 °C to be 12 wt % during 8 weeks. It was further reported that AMP was far more stable when in a blend with MEA (3 wt % loss during 8 weeks). The degradation rates were measured by monitoring the change in amine concentration. No analysis of AMP degradation products were reported.

Lepaumier (Lepaumier and Carrette, 2009) reported the formation of the AMP-oxazolidone and its N-methyl analogue, in addition to an imidazole and N-Methyl-AMP when AMP was degraded at 140 °C (Table 10, Fig. 16). Thus, from this study it appears that despite the steric hindrance, AMP is able to form the 5-membered oxazolidone structure normally observed in carbamate polymerisations. However, it also seems that subsequent ring opening reactions to form linear dimer and trimer do not take place. This is in accordance with observations from another sterically hindered amine, namely di-2-propanolamine (Kim, 1988) where the absence of di- and tri-amino degradation products is ascribed to the steric hindrance in this amine.

3.4 PZ

PZ is a diamine and not an α,β -hydroxylamine, hence is not able to form an oxazolidone. As carbamate polymerisation is assumed to pass through such an intermediate, PZ is assumed not to undergo degradation via carbamate polymerisation.

No reports on the degradation of PZ alone in the absence of oxygen were found. Closmann (Closmann 2009) reported the degradation of an MDEA/PZ blend (100 – 150 °C, $\alpha = 0,2 - 0,26$), and proposed a protonation pathway similar to the one by Chakma (Chakma and Meisen) (Fig. 17) to account for the

observed crossover degradation products; the demethylated degradation product DEA from MDEA, and the methylated PZ.

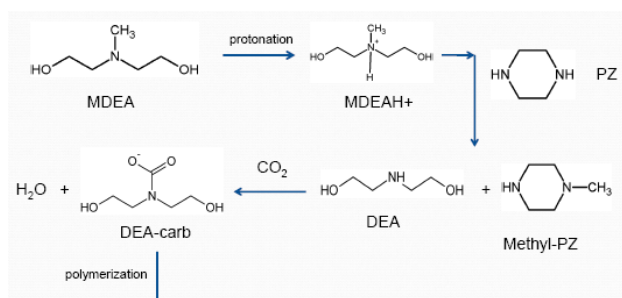


Fig.17 Proposed reaction scheme for the degradation of an MDEA/PZ blend via a protonation pathway. (Closmann 2009).

Freeman (Freeman *et al.* 2010), reported that PZ, in the presence of CO₂ and without O₂, is resistant to degradation at temperatures up to 150 °C but degrades at 175 °C (8 wt % loss per week). The thermal degradation was reported in terms of amine loss. EDA was reported as a degradation product only at > 175 °C.

3.5 Oxidative degradation rates and relative degradation stability

3.5.1 Studies on degradation rates and the effect of process parameters

Some of the main studies on degradation rates are listed in Table 11. Typically, amine degradation rates have been measured by monitoring the evolution of NH₃ and/or the reduction in amine concentration, often under conditions that are not directly relevant compared to the absorber conditions. Some of the reports mainly concern thermal degradation at higher temperatures without oxygen (gas sweetening). Further, different components have been monitored during the degradation and different analysis methods have been applied.

Reports on measured formation rates for degradation products other than those mentioned above are scarce and reports for the formation rates of volatile amines are not found.

Reports on the effect of loading on degradation rates are contradictory. Rooney (Rooney *et al.* 1998) and Bello (Bello and Idem 2005) reported that degradation decreased for loaded compared to unloaded MEA. Blachly (Blachly and Ravner 1966) reported that no degradation of MEA took place in the absence of CO₂. Lepaumier (Lepaumier *et al.* 2009) reported higher degradation in general for loaded systems compared to unloaded. None of these studies were performed under conditions directly applicable in the absorber.

Systematic studies were not found about the effect of flue gas composition, in particular oxygen, NO and N₂O level, on degradation rates and selectivity for the various degradation products, however Sexton (Sexton and Rochelle 2009) (Section 2.5.5) reported the effect of high and low gas on the degradation products from MEA. Studies of degradation rates in this group mainly focused on elucidating the effect of various metal catalysts and inhibitors on the overall degradation rate and this was typically monitored by the NH₃ evolution or the reduction in amine solvent concentration.

Reported information concerning experimental conditions, analysis and degradation rates is summarised in Table 11. As already explained, direct comparison of degradation rates is difficult, and

insufficient data exist to support development of predictive models for the degradation rates under relevant (absorber) process conditions even for the benchmark amine MEA.

Table 11 Studies on degradation rates for MEA, MDEA, AMP and PZ*.

Entry no	Reference	Amine	T	Amine conc.	O ₂	CO ₂	Degrad. cat	Liq. Vol	Space time	Analysis	Analytical method	Rate	Rate
			[°C]	[m]			[mM]	[L]	[min]			[mM/h]	[% amine loss per week]
1a	Rooney <i>et al.</i> (1998)	MEA	82	5,4 (20 wt %)	air (36 ml air/hr)	0	-	1	182	anions	IC	0,03 - 0,07	
1b	Rooney <i>et al.</i> (1998)	MEA	82	5,4 (20 wt %)	air	0,25 M/M	-	1	182	anions	IC	0,03 - 0,07	
1c	Rooney <i>et al.</i> (1998)	MDEA	82	50 wt %	air (36 ml air/hr)	0	-	1	182	anions	IC	0,02 - 0,03	
1d	Rooney <i>et al.</i> (1998)	MDEA	82	50 wt %	air	0,25 M/M	-	1	182	anions	IC	0,02	
2	Blachly and Ravner (1964)	MEA	55	5,4	air	1 %	< 0,0001	0,3	1	NH ₃	titration	0,02 - 0,14	
3	Girdler Studies (1950)	MEA	80	3,1	50 %	50 %	0,5 - 1,0	0,1	1		titration	0,36 - 1,32	
4	Hofmeyer <i>et al.</i> (1956)	MEA	75	5,4	100 %			0,2	0,35			5	
5a	Chi and Rochelle (2002)	MEA	55	7		0,4	< 0,0001 (Fe)	0,4	0,05	NH ₃ (?)	FT-IR	0,36	
5b	Chi and Rochelle (2002)	MEA	55	7	1 % (air)	0	< 0,0001 (Fe)	0,4	0,05	NH ₃ (?)	FT-IR	0,16	
5c	Chi and Rochelle (2002)	MEA	55	7		0,4	1 (Fe)	0,4	0,05	NH ₃ (?)	FT-IR	0,45	
5d	Chi and Rochelle (2002)	MEA	55	7	1 % (air)	0	1 (Fe)	0,4	0,05	NH ₃ (?)	FT-IR	1,7	
6	Goff and Rochelle (2003)	MEA	55	7	air	?		0,3	0,04	NH ₃	FT-IR	0,48 - 5,00	
7a	Goff and Rochelle (2004)	MEA	55	7	air	0 % ($\alpha = 0,15$); 2 % ($\alpha = 0,40$)	0,0002 - 0,2	0,5	0,06	NH ₃	FT-IR	0,25 - 8,25	
7b	Goff and Rochelle (2004)	MEA	55	7	air	0 % ($\alpha = 0,15$); 2 % ($\alpha = 0,40$)	0,0002 - 0,2	0,5	0,06	NH ₃	FT-IR	0,25 - 8,25	
8	Sexton and Rochelle (2009)	MEA	55	7	98 %	2 %	1 (Fe)	0,35		MEA, amide*	IC, FT-IR, HPLC	1 - 8,6	
9a	Freeman <i>et al.</i> (2010)	PZ	55	8 - 10	98 %	2 %	0,1 (Fe), 4,0 (Cu), others	0,375		PZ, amide*	IC, titr.	1,1 - 3,0	
9b	Freeman <i>et al.</i> (2010)	MEA	55	7	98 %	2 %	1,0 (Fe)	0,375		MEA	IC, titr.	3,8	
9c	Freeman <i>et al.</i> (2010)	PZ	135 / 150	10	-	$\alpha = 0,3$	-			PZ	IC, titr.		0,25 / 0,80
9d	Freeman <i>et al.</i> (2010)	MEA	135 / 150	7	-	$\alpha = 0,4$	-			MEA	IC, titr.		5,3 / 11
10a	Closmann <i>et al.</i> (2009)	MDEA	55	7	98 %	2 %	Fe			formate; amide	IC		0,0024; 0,165
10b	Closmann <i>et al.</i> (2009)	PZ/MDEA		7	98 %	2 %	Fe, Cu, others			formate; amide	IC		0,016; 0,016
11	Davis and Rochelle (2009)	MEA	135	15 - 40 wt %		$\alpha = 0,2 - 0,5$	-			MEA, HEIA, HHEDA, MEA-urea	HPLC, IC		2,5-6
12	Supap <i>et al.</i> (2001)	MEA	55 - 100	2-11 kmol/m ³	4 mol/m ³	0	-	0,23		MEA	GC-MS	0,03 - 0,04	
13a	Supap <i>et al.</i> (2006)	MEA	55 - 120	11,4; 17,9 mol %	2,5; 3,5 bar	0	-	0,23		MEA	GC-MS	0,001 - 0,042	
13b	Supap <i>et al.</i> (2006)	MEA	55 - 120	11,4; 17,9 mol %	2,5; 3,5 bar	0,44 M/M	-	0,23		MEA	GC-MS	0,003 - 0,01	
14a	Lepaumier and Carrette (2009) (I)	MEA	140	4 mol/kg (30 wt %)	0	20 bar	-			MEA, degrad. prod.	GC, GC-MS		9
14b	Lepaumier and Carrette (2009) (II)	MEA	140	5 mol/kg (30 wt %)	20 bar air (4,2 bar O ₂)	-	-			MEA, degrad. prod.	GC, GC-MS		10,5
15a	Lepaumier and Carrette (2009) (I)	MDEA	140	4 mol/kg (50 wt %)	0	20 bar	-			MDEA, degrad. prod.	GC, GC-MS		4,1
15b	Lepaumier and Carrette (2009) (II)	MDEA	140	5 mol/kg (50 wt %)	20 bar air (4,2 bar O ₂)	0	-			MDEA, degrad. prod.	GC, GC-MS		7
16a	Lepaumier and Carrette (2009) (I)	AMP	140	4 mol/kg	0	20 bar	-			AMP degrad. prod.	GC, GC-MS		9
16b	Lepaumier and Carrette (2009) (II)	AMP	140	4 mol/kg	20 bar air (4,2 bar O ₂)	0	-			AMP, degrad. prod.	GC, GC-MS		4,3
17	Chakma and Meisen (1997)	MDEA	100 - 200	20 - 50 wt %	-	1,38 - 4,24 Mpa	-	1		MDEA, degrad. prod.	GC, GC-MS	0,024	

* Amides: Indirectly analysed (hydrolysis with subsequent IC analysis)

* K_G' = apparent mass transfer coefficient = rate / PO_2 (Goff *et al.* 2004)

Several of the earlier kinetic studies from the group at the University of Texas at Austin were most likely limited by O₂ mass transfer (Goff 2004). It was suggested that at concentrations > 7,0 m MEA, degradation rates were oxygen mass transfer controlled, while at concentrations < 2,0 m MEA, degradation rates were kinetically controlled, while in solutions of intermediate concentrations effects of both kinetics and oxygen mass transfer were exhibited. Goff (Goff and Rochelle 2004) suggested that industrial oxidative degradation rates are mass transfer limited and estimated the industrial oxidative degradation rates of MEA to be 0,29 – 0,73 kg MEA/mton CO₂. The degradation

stoichiometry was suggested to be in the range of 0,5 – 2,5 mol O₂ per mol of MEA degraded (Goff , Rochelle 2004, Sexton and Rochelle 2009).

3.5.2 Relative degradation stabilities

Relative degradation stabilities as reported in the literature for MEA, MDEA, AMP and PZ are listed in Table 12. The general trend of decreasing stability in the order tertiary > primary > secondary is confirmed for the alkanolamines, albeit with some contradictory results (Rooney et al. 1998, Lawal et al. 2005). Data for PZ and AMP are very limited.

Table 12 Relative degradation stabilities of amines

Reference	Temp. (°C)	O ₂	CO ₂	Relative degradation stability (decreasing stability)
Rooney <i>et al.</i> (1998)	82		20 – 50 wt %	DEA > MDEA > MEA
Rooney <i>et al.</i> (1998)	82	Air (sparged)		DEA > MEA > MDEA
Lepaumier <i>et al.</i> (2009)	140	2 MPa air		AMP > MDEA > HEEDA > MEA > DEA
Lepaumier <i>et al.</i> (2009)	140		2 MPa	MDEA > AMP > MEA >> DEA, HEEDA (general: III > hindered I > I > II)
Sexton <i>et al.</i> (2008)	55	98 %	2 %	PZ > MEA
Closmann <i>et al.</i> (2009)	55	98 % O ₂	2 %	MDEA/PZ > MDEA > PZ
Closmann (2009)	135		$\alpha = 0,4$	PZ >> AMP >> MEA
Freeman <i>et al.</i> (2010)	55	98 %	2 %	PZ > MDEA
Freeman <i>et al.</i> (2010)	55		$\alpha = 0,3; 0,4$	PZ >> MDEA
Lawal <i>et al.</i> (2005)	55-120	250 kPa	$\alpha = 0,1-0,5$	MEA > MDEA
Lawal and Idem (2005)	55-120	250 kPa	$\alpha = 0-0,53$	MDEA/MEA/O ₂ > MDEA/MEA/O ₂ /CO ₂ > MDEA/MEA/CO ₂
Bello and Idem (2005)	55-120	250-350 kPa	$\alpha = 0-0,44$	MEA-O ₂ > MEA-O ₂ -CO ₂ > MEA-CO ₂
Dawodu and Meisen (1996)	120-180		2,58 MPa	MDEA > MEA > DEA
Girdler studies (Kindrick <i>et al.</i> 1950)				relative stability of amines to ox. degrad.: tertiary > primary > secondary

4 Summary of components likely to be present in the gas phase above an oxidised amine solution

4.1 Volatility of amine solvents

Amine volatility is a key screening criterion for amines to be used in CO₂ capture. Although there are several publications on the VLE of the binary MEA-H₂O system, only a few have directly measured volatility, more specifically the vapour mole phase fraction of the benchmark amine MEA. Volatility data have been reported for MDEA (Closmann *et al.* 2009), and in a very recent paper (Nguyen *et al.* 2010) volatility data are reported for the amines MEA, AMP, PZ and MDEA/PZ. At the lean loading conditions (where volatility is of greatest interest), the amines were ranked in the following order of increasing volatility:

$$7 \text{ mMDEA}/2 \text{ m PZ} < 8 \text{ m PZ} < 7 \text{ m MEA} < 5 \text{ m AMP}$$

The MEA partial pressure increased as expected with amine concentration and temperature, and decreased linearly with loading because MEA is converted to MEA carbamate and protonated MEA. According to the stoichiometry of the MEA - CO₂ reaction to produce carbamate, the volatility of the MEA should be around zero at a loading of 0,5. In practice, the loading is typically 0,4.

4.2 Degradation products likely to be present in the vapour phase

In this section, the findings from the previous sections have been aggregated to give table overviews of those degradation products, presumably formed in the absorber or in the stripper, that seem most probable to be formed for the amines MEA, MDEA, AMP and PZ.

A subjective evaluation of the probability of finding these components in the gas phase above an oxidised MEA solution has been indicated. It is obvious that in the case of degradation products belonging to the class of primary, secondary and tertiary amines, amines, their probability of being present in the gas phase above an oxidised amine solution will be modified by the relative concentrations and the temperature, and reduced with increased loading of CO₂. The evaluation in the table does not take such modifications into account, hence may indicate a “worst case” with respect to the probability of finding any amine in the vapour phase above an oxidised amine solution. The main focus has been on oxidative degradation products. However, as volatile degradation products may also be formed in the stripper hence be circulated in the system, such assumed products have been included..

4.2.1 MEA

The various degradation products proposed in literature to be formed in the oxidative degradation of MEA were summarised in Table 5. Based on these literature findings, the compounds most likely to be present in the gas phase above an oxidised MEA solution can be speculated to be the ones listed in Table 13.

Table 13 Degradation products potentially present in the gas phase above an oxidised MEA solution.

Name	CAS no	Acronym	Structure formula	Melting point [°C]	Boiling point [°C]	Density [g/cm ³]	Vapor pressure (at 20 °C)	Boiling point/ volatility	Observed	Probability
2-Aminoethanol Monoethanolamine	141-43-5	MEA	HOCH ₂ CH ₂ NH ₂	10,3	170	1,012	0,458 Torr, 25 Pa (20 °C)	+	+	h
Ammonia		Ammonia	NH ₃					+	+	h
Formaldehyde	50-00-0	Formaldehyde	CH ₂ O		- 21 (pure)			+	-	m
Acetaldehyde	75-07-0	Acetaldehyde	C ₂ H ₄ O		20,2	0,788		+	-	m
2-Methylaminoethanol N-Methylethanolamine	109-83-1	MAE	HOCH ₂ CH ₂ NHCH ₃		159	0,935	0,5 mmHg	-	+	m
Formamide Methanamide		Formamide	CH ₃ NO	2 - 3	210	1,133	0,08 mmHg	-	-	l
2-[(2-aminoethyl)amino]- ethanol N-(2-hydroxyethyl)ethylenediamine	111-14-1	HEEDA	HOCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂		243	1,03	0,01 mmHg	-	+	l
1-Piperazineethanol	103-76-4		PZ-EIOH		243-246	1,061		-	+	l

Formaldehyde and acetaldehyde are generally accepted as oxidative degradation products from MEA yet the direct reports of the aldehydes under industrially relevant oxidizing conditions are scarce (Sexton and Rochelle 2009), indicating that these are transient products and thus it is speculated that the probability of finding these components in the gas phase is on a medium level. Formamide is reported by indirect analysis method (Sexton and Rochelle 2009) and is ascribed low probability. MAE is reported in low amounts (Lepaumier et al. 2009) and has a high boiling point thus is ascribed medium/low probability. HEEDA is suggested to have medium/low probability of being present in the gas phase. Hydroxyethylimidazole (HEI) and hydroxyethylformamide (HEF) are not included due to their high boiling points.

Formation of methylamine has been suggested for the oxidative degradation of MEA (Rooney *et al.* 1998) (Fig. 5), and can be generalised from the reaction scheme of Petryaev (Petryaev *et al.* 1984) (Fig.

4). Formation of mono- di- or trimethylamine is claimed on a general basis by Lepaumier (Lepaumier et al. 2009) from unidentified amines, however the unambiguous identification of formation of any of mono- di- or trimethylamine from MEA remains to be seen.

A substantial number of unexpected degradation products were suggested in some reports using GC-MS library matches for product identification. These have not been further considered with respect to degradation products potentially present in the gas phase above an oxidised solution of MEA.

Inorganic gases (NO, N₂O, CO) are reported and their presence is relevant with respect to reaction with other components (Sexton and Rochelle 2009) however these are not included in the table.

4.2.2 MDEA

The various degradation products proposed in literature to be formed in the degradation of MDEA are summarised in Table 6. Based on these literature findings, the compounds most likely to be present in the gas phase above an oxidised MDEA solution can be speculated to be the ones listed in Table 14.

Dimethylamine has been reported as a degradation product of DMAE (Petryaev *et al.* 1984) which is again reported as a degradation product from MDEA (Lepaumier et al. 2009, Chakma and Meisen 1996). No other unambiguous identification of dimethylamine as degradation product was found in any of the reports, neither from MDEA itself nor from any of the reported MDEA degradation products DEA and MAE.




Table 14 Degradation products potentially present in the gas phase above an oxidised MDEA solution.

Name	CAS no	Acronym	Structure formula	Boiling point	Density	Vapor pressure	Boiling point/ volatility	Observed	Probability
				[°C]	[g/cm ³]	(at 20 °C)			
Bis(2-hydroxyethyl)methylamine Methyl diethanolamine	105-59-9	MDEA	(HOCH ₂ CH ₂) ₂ NCH ₃	247	1,04		+	+	h
Ammonia		Ammonia	NH ₃				+	+	h
Formaldehyde	50-00-0	Formaldehyde	HCHO	- 21 (pure)			+	-	m
Acetaldehyde	75-07-0	Acetaldehyde	CH ₃ CHO	20,2	0,788		+	-	m
Methylamine	74-89-5	Methylamine	CH ₃ NH ₂	-6	0,699 (-10,8 °C)	3970 Torr	+	-	l
Trimethylamine	75-50-3	Trimethylamine	(CH ₃) ₃ N	2,87	0,67		+	-	m
Dimethylamine	124-40-3	Dimethylamine	(CH ₃) ₂ NH	7	0,67		+	-	m
N,N-Dimethyl-2-hydroxyethylamine N, N-dimethyl-2-ethanolamine	108-01-0	DMAE	(HOCH ₂ CH ₂) ₂ NH	133 - 134	0,89	6,12 mmHg (100 mmHg /55 °C)	+	+	h
2-Methylaminoethanol N-Methylethanolamine	109-83-1	MAE	HOCH ₂ CH ₂ NHCH ₃	159	0,935	0,5 mmHg	+	+	h
Ethanol, 2-[methyl(2-(methylamino)ethyl)amino]-	17225-70-6		HOCH ₂ CH ₂ OHNMeCH ₂ C H ₂ NHMe	209 ± 15	0,936	4,56 *10 ⁻³ Torr	+	+	m
diethanolamine (2,2'-iminodiethanol)	111-42-2	DEA	(HOCH ₂ CH ₂) ₂ NH	217	1,09		+	+	h

4.2.3 AMP

The various degradation products proposed in literature to be formed in the oxidative degradation of AMP are summarised in Table 7. Based on these literature findings, the compounds most likely to be present in the gas phase above an oxidised AMP solution can be speculated to be the ones listed in Table 15.


Table 15 Degradation products potentially present in the gas phase above an oxidised AMP solution

Name	CAS no	Acronym	Structure formula	Molecular formula	Melting point [°C]	Boiling point [°C]	Density [g/cm ³]	Vapor pressure (at 20 °C)	Boiling point/ volatility	Observed	Probability
2-amino-2-methyl-1-propanol Aminomethylpropanol	124-68-5	AMP		C ₄ H ₁₁ NO	24 - 28	165	0,934	<1 mmHg (25 °C)	-	+	m
Ammonia		Ammonia	NH ₃	NH ₃					+	+	h
Formaldehyde	50-00-0	Formaldehyde	HCHO	CH ₂ O		- 21 (pure)			+	-	m
Acetaldehyde	75-07-0	Acetaldehyde	CH ₃ CHO	C ₂ H ₄ O		20,2	0,788		+	-	m
Acetone	67-64-1	Acetone	CH ₃ COCH ₃	C ₃ H ₆ O		56,5	0,7925		+	-	m
2-Methyl-2-(methylamino)-1-propanol	27646-80-6	Me-AMP		C ₆ H ₁₃ NO		165	0,93	<1 mmHg	+	-	m
4, 4-Dimethyl-oxazolidone	26654-39-7			C ₅ H ₉ NO ₂		272	1,039		-	+	l

4.2.4 PZ

The various degradation products proposed in literature to be formed in the oxidative degradation of PZ were summarised in Table 9. Based on these literature findings, the compounds most likely to be present in the gas phase above an oxidised PZ solution can be speculated to be the ones listed in Table 16. These comprise direct oxidation products from PZ. A subjective evaluation of the probability of finding the various components in the gas phase above an oxidised PZ solution has been indicated.

Table 16 Degradation products potentially present in the gas phase above an oxidised PZ solution.

Name	CAS no	Acronym	Structure formula	Melting point [°C]	Boiling point [°C]	Density [g/cm ³]	Vapor pressure (at 20 °C)	Boiling point/ volatility	Observed	Probability
Piperazine	110-85-0	PZ		106	146	1,1	21 Pa	+	+	h
Formaldehyde	50-00-0	Formaldehyde	HCHO		- 21 (pure)			+	-	m
Acetaldehyde	75-07-0	Acetaldehyde	CH ₃ CHO		20,2	0,788		+	-	m
ethylenediamine (1,2-diaminoethane)	107-15-3	EDA	H ₂ NCH ₂ CH ₂ NH ₂	9	116	0,899		+	+	m
formamides (unspecified; N-formylpiperazines, N-formylethylenediamine)			HCONHR		> 200			-	-	l/m

4.2.5 Degradation products of the types primary, secondary and tertiary amines

Table 17 is a further particular detailing of the degradation products of various amine types that have been reported. These amines are focused as secondary amines, be it the amine solvent or degradation products therefrom, may form nitrosamines (Section 7).

Table 17 Amine degradation products reported in literature from the generic amines.*

Amine		Type	Bond scission/ alkylation	Amine degradation products	
				Ox. degrad.	Anaerobic degrad.
MEA		I	C-N, C-C methylation	MA? MAE RNMeCH ₂ CH ₂ NHMe	HEEDA, PZ-EtOH
MDEA		III	C-N, C-C, methylation/demeth., alkylation/dealk.	DMA?, TMA? MAE DEA DMAE	MEA MAE DEA DMAE TEA
	MAE	II	C-N, C-C, methylation/demeth., alkylation/dealk.	DMA, TMA? MEA DMAE RNMeCH ₂ CH ₂ NHMe	RNMeCH ₂ CH ₂ NHMe diMe-PZ
	DMAE	III	C-N, C-C, methylation/demeth.	DMA, TMA? MAE RNMeCH ₂ CH ₂ NHMe	MAE RNMeCH ₂ CH ₂ NHMe
	DEA	II	C-N, C-C, dealkylation/alk.	DMA?, TMA? MEA THEED	TEA Mono-N-subst. PZ
AMP		I Steric. hind.	C-N, methylation	Me-AMP	Me-AMP
PZ		II Diamine	C-N, C-C	EDA	EDA

* R = CH₂CH₂OH

MEA (Solvent A)

MAE is reported a possible secondary amine degradation product from oxidative degradation of MEA (Lepaumier et al. 2009). HEEDA is a degradation product from anaerobic degradation of MEA. N-piperazineethanol has been reported from the process. No reports confirmed the formation of mono- or dimethylamine.

MDEA

Carbamate formation can not take place for MDEA. Apparently, transalkylation involving quaternary ammonium species gives rise to various higher/lower amine degradation products from MDEA, under oxidative as well as anaerobic degradation. Several reports support this: The secondary amines DEA and MAE were reported as degradation products from MDEA, and the degradation product DMAE (tertiary amine) was reported to degrade further to MAE and RNMeCH₂CH₂NHMe (Lepaumier et al. 2009). Rooney reported the formation of DEA from MDEA (Rooney et al. 1998). The formation of dimethylamine from the degradation of MDEA was claimed at elevated temperatures (140 °C). One report confirmed dimethylamine as a degradation product from DMAE albeit under different reaction conditions compared to those in the absorber (Petryaev et al. 1984).

AMP

The secondary amine Me-AMP, from N-methylation of AMP, was reported as amine degradation product from AMP, under oxidative as well as anaerobic conditions.

PZ

The primary diamine EDA was reported as amine degradation product from the secondary diamine PZ, under oxidative as well as anaerobic conditions.

4.3 Generic solvents – components in the vapour phase

Reports on amine blends are scarce. The short evaluation of degradation products possibly present in the gas phase above an oxidised solution of the amine blends below is mainly based on additive results reported from the individual amines.

Solvent B: AMP/PZ

No reports were found in literature on any compositions of AMP and PZ. Based on additive results from reports on the individual amines, Me-AMP and EDA are suggested to be the amine degradation products for Solvent B in the gas phase above the absorbant solution.

Solvent C: MDEA/MEA

Based on additive results from the individual amines, the secondary amines MAE, DEA, HEEDA and RNMeCH₂CH₂NHMe (R=CH₂CH₂OH) are potential amine degradation products from MDEA which may be found in the gas phase above the absorbant solution. Dimethylamine can not be ruled out as a degradation product in the gas phase from Solvent C. Reports on MDEA/MEA blends list a range of rather unexpected degradation products (Lawal *et al.* 2005, Lawal and Idem 2005), thus the formation of such degradation products would require additional verification.

Relative ranking

On the basis of the reported relative degradation rates (Table 12), the reported amine degradation products, the overall degradation rates, and the chemical structure of the individual amines (Fig. 1), an attempt to rank qualitatively the generic solvents with respect degradation could be as shown below. However, it should be emphasised that there are limited relevant data for the individual amines and not consensus even for these.

- 1) Solvent A: MEA (oxidises most)
- 2) Solvent C: MEA/MDEA (oxidises medium)
- 3) Solvent B: AMP/PZ (oxidises least)

5 Probability of emission from generic solvents

Vapour phase components emission

The composition of the vapour phase will of course not be representative for the composition of the mixture of emitted compounds but will depend *e. g.* on the efficiency of the water wash.

Droplet emission

Furthermore, it must be assumed that mist may be carried over from the absorber through the ERT. Hence even non-volatile components, ions included, may be present in the atmospheric liquid phase. Tests of atmospheric liquid phase shall include samples representing the absorber liquid. Such droplets will represent a different population with respect to composition compared with rain and condensate.

6 Analysis methods

An in-depth evaluation of the various techniques reported for the analysis of amine degradation products is beyond the scope of this report. However, some general comments are given below.

The combination of different analysis methods is required to allow the simultaneous identification and quantification of the various classes of amine degradation products. Typically, the various degradation studies employ different analysis methods depending on their research focus.

Identification of degradation products in earlier reports typically relied on chemical derivatisation (Dennis *et al.* 1967, Petryaev *et al.* 1984), ion chromatography (Rooney *et al.* 1998) and GC using comparison and/or spiking with references (Chakma and Meisen 1997). More recent work utilises FT-IR not only for monitoring NH₃ but also for the analysis of some degradation products (Sexton and Rochelle 2009) and additionally reports the use of HPLC to complement or verify results from other analysis methods (Sexton and Rochelle 2009, Supap *et al.* 2006).

The results from extensive use of GC-MS where structures of a huge range of degradation products are identified by matching their (quadrupole) mass spectra with commercial mass spectra *e. g.* of the NIST (National Institute of Standards and Technology) database should be evaluated with great care (Bello and Idem 2005, Lawal *et al.* 2005, Bello and Idem 2005). The ability of any such search system to distinguish between different potential compounds is limited, and the “best match” may not at all be the right compound (NIST 08 User’s Guide). Also others rely solely on GC-MS for identification of degradation products, hence several of the proposed degradation products can not be said to be unambiguously identified (Lepaumier *et al.* 2009).

PART 2

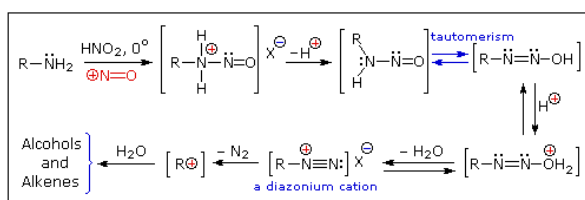
NITROSAMINE FORMATION

7 Nitrosamines

Primary aromatic nitrosamines are formed by reaction with electrophiles such as NO^+ . This reaction is leading to synthesis of the well known diazonium salts (Houben-Weyl).

Primary aliphatic nitrosamines may react by a similar route, however, since the aliphatic diazonium intermediate is not stabilised through mesomery with an aromatic substituent, primary aliphatic nitrosamines are deaminated (Houben-Weyl). Secondary amines stop at the nitrosamine stage due to the lack of a hydrogen atom at the nitrogen (Houben-Weyl). Thus for instance, DEA and PZ will form nitrosamines if nitrosated, while MEA will deaminate as first reaction step (see below).

Primary Amines



Secondary Amines

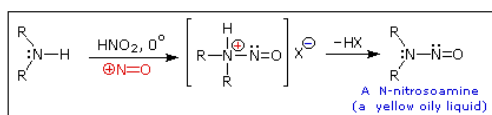


Fig. 18 Reaction mechanism for nitrosation of primary and secondary amines

Nitrosation of MEA is reported to give the deamination product acetaldehyde which reacts further with excess MEA and is ultimately nitrosated to N-nitroso-2-methyl-1,3-oxazolidine (see Fig. 19) (Saveedra 1981). However, upon exposure of MEA to NO_x in a flue gas scrubbing pilot plant, N-nitroso-diethanolamine is formed (Pedersen *et al.* 2010).

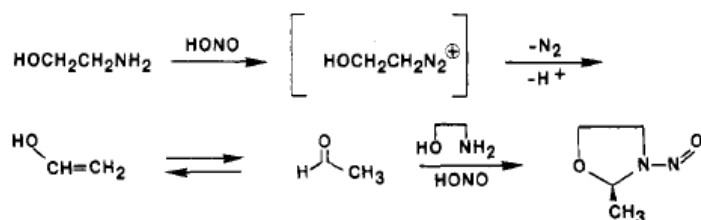
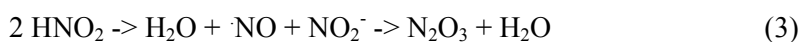
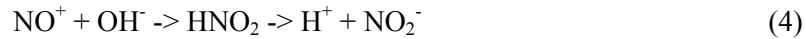


Fig. 19 Reaction scheme for deamination of MEA (Saveedra 1981).

The most common nitrosation agents are derivatives of nitric acid, *i.e.* NO_x ($X = \text{OAlk}, \text{NO}_2, \text{NO}_3,$ halogen or OH_2^+). Typically HNO_2 is produced *in situ* by reaction of NO_2^- with an acid. Through a self protonation reaction of HNO_2 the nitrogen trioxide (N_2O_3) electrophile is formed (Fridmann *et al.* 1971). N_2O_3 is also formed when contacting the NO_x components NO and NO_2 with water (Holleman-Wiberg 1976).



In weakly acidic conditions, or in the presence of a strong nucleophile (*i.e.* OH^-), NO is converted into nitrous acid and further into the nitrite anion. At $\text{pH} > 7$, the equilibrium in (33) is displaced completely to the right (Lewis 1955).



In aq. solution at $\text{pH} > \text{pK}_a$ of HNO_2 the rate of nitrosation drops rapidly with increasing pH because the concentration of active nitrosating species generated in situ decrease. No nitrosation by aq. nitrite has been observed above pH 7.5. When formaldehyde is added to neutral or alkaline solution nitrite can nitrosate secondary amines, but at a slower rate than in acid solution (Keefer and Roller 1973). The proposed mechanism is shown in Fig. 20.

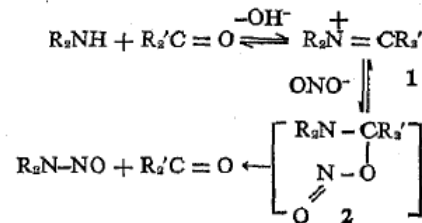


Fig. 20 Formaldehyde catalyses reaction of NO_2^- and R_2NH to nitrosamines at pH 6,4-11 (Keefer and Roller 1973).

Secondary amines react with N_2O_3 and N_2O_4 gas dissolved in aq. alkaline solution (pH 6-14) at a rate greater than acidified nitrite (Challis and Kyrtpoulos 1976).

NO alone is inactive for nitrosation but is oxidized by O_2 to NO_2 and thus the reactive nitrosating agents N_2O_3 and N_2O_4 are formed (Williams 1977). Rapid nitrosation by NO under anaerobic conditions occurs in the presence of iodine, Ag(I), Cu(II), Zn(II), Fe(III) or Cu(II) salts (Challis and Butler 1968).

A recent report (Kemper *et al.* 2010) suggests that quaternary amines may be nitrosamine precursors themselves (and not via their lower order amines). The nitrosamines studied and the reaction conditions are different compared to the amines under absorber conditions, and the reaction pathway is far from understood. Still, this might augur for a hitherto not considered reaction for the formation of nitrosamines in basic conditions.

In conclusion it may be stated that unidentified nitrosamine(s) has been observed in spent flue gas solvent using a nitrosamine functional group specific test (Strazisar 2003). Exposure of MEA to NOx in a pilot plant and in a batch reactor showed formation of N-nitroso-diethanolamine (Pedersen *et al.* 2010). It thus seems that reaction conditions (ionic environment?) control selectivity since oxazolidine derivatives are formed in the case of preparative deamination conditions (Saveedra 1981) and N-nitroso-diethanolamine is formed in the NOx study reported by Pedersen *et al.* The literature showing that nitrosation based on NOx in alkaline conditions is possible is thus confirmed for the MEA/NOx case. Recent research regarding the formation of nitrosamines directly from quaternary amines should be investigated since this compound class is present in the degraded alkanolamine solution (i.e HSS: heat stable salts). Furthermore this report may point to yet another portential nitrosamine formation route which has hithero not been recognized.

Furthermore, primary and tertiary amine solvent degradation reactions may lead to secondary amines. Thus nitrosamine formation in primary and tertiary alkanol amine capture solvents must be an issue of concern and focus. However, it has to be kept in mind that NO_2 and NOx formation from NO is a second order kinetic process and that under actual capture conditions catalyst and substrate (secondary amine) concentrations may be very low. Last not least products and selectivities differ from reaction products generated in acidic or neutral conditions (see Fig. 19).

Since nitrite and nitrate are formed as alkanolamine degradation products (Sexton 2008), nitramine formation has to be considered. Monoethanolamine nitrate (MEAN) is a known explosive (Petersen *et*

al. 1983). However, no report relating to nitramine formation in aq. MEA solution under flue gas capture conditions has been found in the literature.

In conclusion, studies by Pedersen et al. have confirmed that nitrosamines may be formed under alkaline conditions. Furthermore, the secondary amine MAE has been reported formed from the primary amine MEA thus leading to nitrosamine formation from a MEA solution. Obviously use of secondary amines, as for instance PZ, may lead to directly to nitrosamine formation.

PART 3

CORROSION IN ALKALINE AMINE PLANTS

It has not been shown that laboratory corrosion studies can be quantitatively correlated to plant corrosion. Thus the reported laboratory data are to be taken as qualitative information only.

Laboratory electrochemical based corrosion testing of AMP, MEA, DEA and MDEA show corrosion of carbon steel to be dependent on CO₂ loading, amine type, amine concentration and solution temperature (Fig. 22) (Veawab *et al.* 1999). Similar results have been reported on these amines by Dow Chemicals (DuPart *et al.* 1993) and for MEA/PZ blends (Nainar and Veawab 2009). However, the AMP is not confirmed by other results by the same investigators (Veawab *et al.* 1999).

Table 2. CO₂ Loading in Aqueous Amine–CO₂ System at the Testing Condition of 3 kmol/m³, 80 °C, and CO₂ Saturation

amine type	CO ₂ loading (mol/mol)	corrosion rate (mpy)
MEA	0.565	136.4
DEA	0.442	89.1
MDEA	0.243	67.6
AMP	0.554	125.9
mixture of MEA and MDEA	0.435	77.6
mixture of DEA and MDEA	0.365	72.4
mixture of MEA and AMP	0.561	127.3

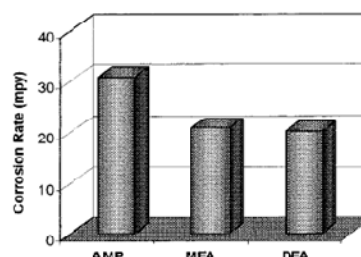


Figure 6. Comparison of corrosion rates among single amine systems under 3 kmol/m³, 80 °C, and 0.2 CO₂ loading.

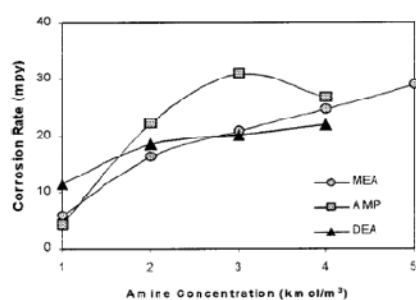


Figure 7. Effect of amine concentration on corrosion rate under 80 °C and 0.2 CO₂ loading.

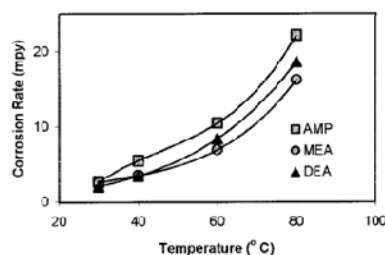


Figure 9. Effect of solution temperature on corrosion rate under 2 kmol/m³ and 0.2 CO₂ loading.

Fig. 23 Laboratory alkanol amine corrosion tests with CO₂ atmosphere and carbon steel (Veawab *et al.* 1999).

Heat stable salts (Chapel *et al.* 1999, Aaron and Tsouris 2005) show an influence on the rate of carbon steel corrosion. Laboratory corrosion test of various acids dissolved in 50 wt% MDEA solution is shown in Fig. 24 (Rooney *et al.* 1996, Rooney *et al.* 1997). It is speculated that the high corrosion rate of oxalic acid is due to the high equilibrium constant for the complexation of the oxalic anion with Fe²⁺ or Fe³⁺. Similar results have been observed for a 30 wt% MEA solution containing various acids. Relative corrosion rates for the different solutions containing 10000 ppm acid are shown in Figure 25 (Tanthapanichakoon and Veawab 2006).

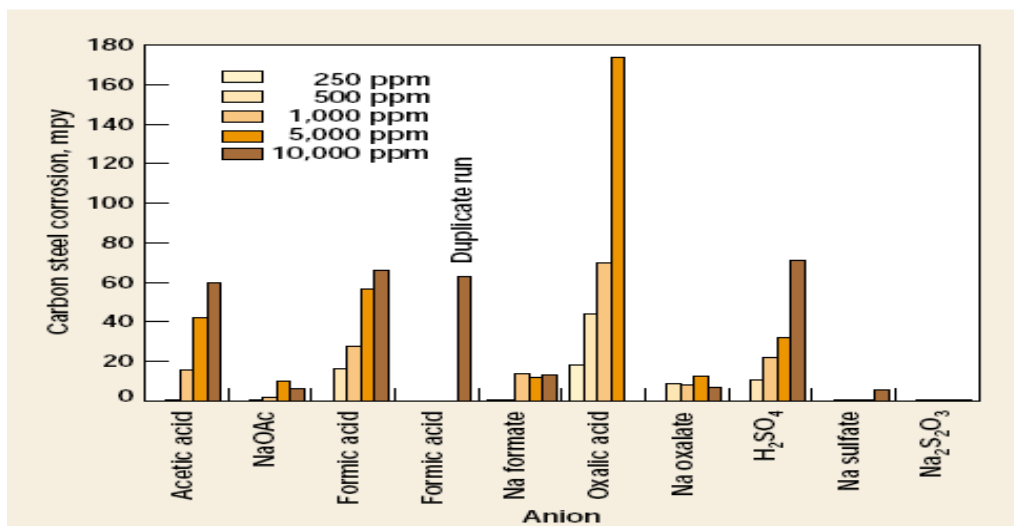


Fig. 24 Corrosion test of acids in 50 wt% MDEA solution; 7-day test at 121 °C (Rooney et al. 1996, Rooney et al. 1997).

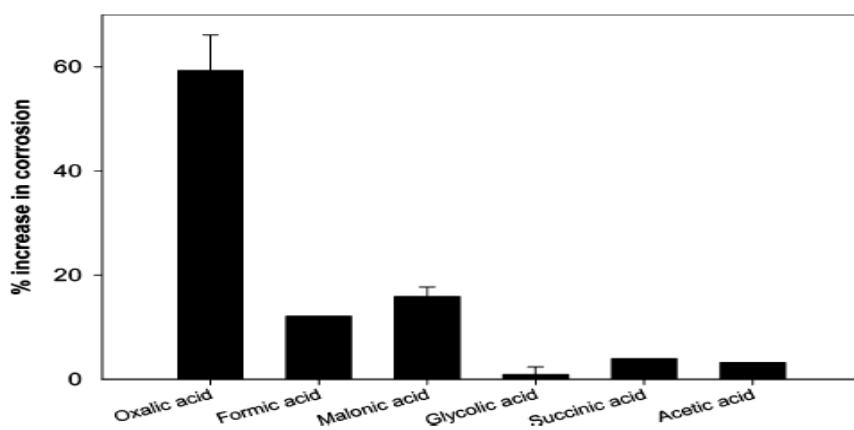


Fig. 25 Percent increase in corrosion rate at 10000 ppm acid concentration (30 wt% MEA solution, 0.2 mol CO₂/mol MEA loading, 80°C, electrochemical corrosion measurement) (Tanthapanichakoon and Veawab 2006).

8.2 Effect of corrosion products on the formation of byproducts

It is well known that Ni, Cu, Fe, V salts speed up oxidative degradation of alkanol amines (Chi 2000, Chi et al. 2002, Goff 2006, Sexton 2008). There is no study to our knowledge on qualitative or quantitative product composition comparison in metal catalyzed aerobic alkanol amine oxidation as compared to the catalyst free systems. It is generally assumed that metal catalysts speeding up the oxidation reaction neither change product composition nor product selectivity.

8.3 Corrosion inhibitors

In general, corrosion inhibitors may suppress reaction (d) and (e) (Fig. 21) by surface coverage of amines or plate out of arsenic and antimony. More success is claimed by 'passivators' which oxidise Fe²⁺ to Fe³⁺ oxide which forms an adherent and corrosion passivating film (Kohl and Nielsen 1997).

PART 4 SUMMARY, CONCLUSIONS AND RESEARCH RECOMMENDATIONS

9 Summary and Conclusions

9.1 Amine degradation products

9.1.1 General

Amines subject to absorber and stripper conditions may undergo a range of oxidative and anaerobic degradation reactions depending on the specific structure of the amine as well as on the specific reaction conditions. The scientific literature concerning the formation of oxidative degradation products for MEA, MDEA, AMP and PZ has been reviewed. Despite high overall activity in the field, the amount of experimental work and the understanding of the degradation chemistry were found to be far less than anticipated in beforehand.

Reaction schemes

Oxidative amine degradation takes place by radical reactions causing C-N and/or C-C bond scission. Reaction schemes, mainly referring to MEA, have been extrapolated from earlier studies (Dennis *et al.* 1967, Petryaev *et al.* 1984, Rooney *et al.* 1998) without validating the chemistry for other generic amines or for the specific experimental conditions in particular in the absorber. More recent reports (Bello and Idem 2005, Lepaumier *et al.* 2009) broaden the range of proposed degradation products but are not always supported by justified chemical reaction schemes. Mechanistic studies of oxidative degradation are not reported even for the benchmark amine MEA. Updated and justified reaction schemes linked to degradation products remain to be reported.

Summary of technical reports

The wide spread of reported reaction conditions and applied analysis methods make direct comparison of results difficult. Studies analysing the oxidative degradation rates for MEA or other amines are not comparable with studies analysing the degradation products. No reports describing a complete mass balance were found. A careful evaluation of the applied analysis methods is needed in the interpretation of the reported results.

Reported experimental reaction conditions frequently differ from the actual process conditions. Transferability of results is most often not verified. No study was found that directly links laboratory results to results of a pilot plant.

There is not consensus in the scientific literature with respect to the types of degradation products formed from the individual amines. Relative probabilities and quantitative formation rates for the various conceivable *inter*- and *intra*-molecular oxidative degradation reactions are not reported in the scientific literature. Hence, insufficient data exist for the quantification of formation rates of the different suggested degradation products.

Analysis methods

The analysis method should also be considered when evaluating the reported degradation products. Typically, the various degradation studies employ different analysis methods depending on their research focus and the compounds to analyse: Chemical derivatization, anion and cation chromatography, GC-MS, NMR, HPLC. The combination of different analysis methods is required, but in practise not often found, to allow the simultaneous identification and quantification of the various classes of amine degradation products.

9.1.2 Amine degradation products from generic solvents

The various groups of degradation products reported in literature for the individual amines MEA, MDEA (including reported degradation products from DEA, DMAE and MAE), AMP and PZ are summarised in Table 18.

Table 18 General groups of degradation products reported from individual amines.

Amine degradation products	Analysis methods	MEA	MDEA	DEA	DMAE	MAE	AMP	PZ
NH ₃	FT-IR, titration	x	x	x	x	x	x	
Primary amines / alkanolamines	IC, GC-MS, HPLC		x	x		x		x
Secondary amines / alkanolamines	IC, GC-MS, HPLC	x	x		x		x	
Tertiary amines / alkanolamines	IC, GC-MS, HPLC		x	x		x		
Aldehydes (formaldehyde, acetaldehyde)	FT-IR, HPLC	x						x
Carboxylates	IC	x	x	x	x	x	x	
Amides	HPLC, indirectly	x	x					x
Piperazines	GC-MS	x	x	x				
Piperazinones	HPLC, GC-MS	x						
Oxazolidones					x	x		
Imidazolidinones	HPLC, GC-MS	x						
N, N-disubst. urea	HPLC	x						
Nitrosamines				x		x		x
Nitramines								

Table 19 summarises, for each individual amines MEA, MDEA, AMP and PZ, the compounds belonging to the above groups that are most likely to be present in the vapour phase above an oxidised solution of the amine. This list was delivered to WP2. In addition, the possibility for in process-formation of nitrosamines from secondary amines (solvents or their degradation products) must be considered (Section 9.2).

Table 19 Compounds most likely to be present in the vapour phase above an oxidised amine solution.*

Amine in solvent	Compound in effluent	Bp	Volatility	Observed	Probability
MEA		[°C]			
	MEA	170	+	+	h
	NH ₃		+	+	h
	HCHO	-21	+	-	m
	CH ₃ CHO	20,2	+	-	m
	MAE	155-156	-	+	m
	HEEDA	-	-	+	m
	H ₂ NCHO	210	-	-	l
MDEA	MDEA	247	+	+	h
	NH ₃		+	+	h
	HCHO	-21	+	-	m
	CH ₃ CHO	20,2	+	-	m
	DMAE	133-134	+	+	h
	MAE	155-156	+	+	h
	DEA	217	+	+	h
	Me ₃ N	3	+	+	h
	Me ₂ NH	7	+	-	m
AMP	AMP	165	-	+	m
	NH ₃		+	+	h
	HCHO	-21	+	-	m
	CH ₃ CHO	20,2	+	-	m
	CH ₃ COCH ₃	56,5	+	-	m
	MeAMP		-	+	m
PZ	PZ	146	+	+	h
	HCHO	-21	+	-	m
	CH ₃ CHO	20,2	+	-	m
	H ₂ NCH ₂ CH ₂ NH ₂	116	- -	+	l
	H ₂ NCHO	210	-	-	l

9.1.3 The effect of process conditions

The effect of process conditions on the formation of harmful compounds is not clear from the literature reports:

- Solvent composition: Reliable data not reported.
- CO₂ loading: Contradictory data reported.
- Amine concentration: Qualitative data reported.
- Flue gas composition, oxygen, NO and NO₂ level: No systematic studies with quantitative data have been found
- *Increasing temperature in general increases the extent of degradation reactions.*

9.1.4 Ranking of generic solvents

There is not consensus regarding relative degradation rates and the specific amine degradation products in reported work for the individual amines, and insufficient or no data exist for Solvent B and Solvent C below. An attempt to propose a qualitative ranking of the generic solvents can at best be based on the chemical structures of the individual amines and the reported relative degradation rates (see e. g. Table 12). In light of this, a proposed ranking could be:

- 1) Solvent A: MEA (oxidises most)
- 2) Solvent C: MEA/MDEA (oxidises medium)
- 3) Solvent B: AMP/PZ (oxidises least)

9.2 Formation of nitrosamines and nitramines

Primary and tertiary amines may give secondary amines as degradation products hence the formation of (unspecified amounts) of nitrosamines in the process can not be excluded. Piperazine, a secondary diamine, is inherently prone to nitrosamine formation.

- 1) Nitrite and nitrate are formed as MEA degradation products (Sexton 2008).
- 2) Secondary amines may form nitrosamines with nitrite in the presence of formaldehyde (Keefer and Roller 1973), and unidentified nitrosamine(s) has been observed in spent flue gas solvent (Strazisar 2003). The possibility for quaternary amines as nitrosamine precursors might be considered.
- 3) Nitramine formation has to be considered but no report relating to nitramine formation in aqueous MEA solution under flue gas capture conditions was found.

9.3 Emission

Vapour phase components may in principle be emitted to air, to an extent will depend on the efficiency of the water-wash emission.




Droplet with the same composition as the oxidised amine solution i. e. including also non-volatile compounds and ions, may be emitted to air.

10 Research Recommendations

The literature report has revealed that deep knowledge and understanding of the fundamental chemistry has not yet been applied to the interpretation of analysis results and the proposal of reaction schemes for the oxidative degradation of alkanolamines. Plausible reaction mechanisms supported by experimental data are missing. Analysis methods have been insufficient in providing unambiguous identification of degradation products other than carboxylates and ammonia. Based on this, the following studies are proposed:

- 1) Validate reaction schemes and elucidate reaction mechanisms for the benchmark amine MEA under oxidative as well as anaerobic conditions,
 - o taking into account also cross-reactions between the various components potentially present in such a degraded reaction mixture
 - o in order to clarify whether or not the claimed secondary amines may be formed
 - o in order to clarify whether or not formamides/other amides are formed
- 2) Map the effect of process parameters on the MEA degradation kinetics and product selectivity
- 3) Initiate experimental work to investigate NO_x reaction products and their rates of formation from MDEA, DEA and PZ under relevant reaction conditions (basic conditions, including the presence of formaldehyde).
- 4) Consider experimental work to investigate potential nitramine formation.
- 5) Initiate work to determine partitioning coefficients for MEA degradation products in order to close the mass balance gap.
- 6) Based on above, initiate work to close the mass balance gap for MEA.

11.2 Appendix 2: List of organic compounds, acronyms and CAS registry numbers

Name (IUPAC)	CAS no	Acronym	Structure formula	Molecular formula	Appearance	Melting point [°C]	Boiling point [°C]	Density [g/cm ³]	Vapor pressure (at 20 °C)
2-Aminoethanol Monoethanolamine	141-43-5	MEA		C ₂ H ₇ NO	viscous colourless liquid with ammonia	10,3	170	1,012	0,458 Torr, 25 Pa (20 °C)
Bis(2-hydroxyethyl)methylamine Methyl diethanolamine	105-59-9	MDEA		CH ₃ N(C ₂ H ₄ OH) ₂	clear, colorless or pale yellow liquid; ammonia	-21	247	1,04	
2-amino-2-methyl-1-propanol Aminomethylpropanol	124-68-5	AMP		C ₄ H ₁₁ NO		24 - 28	165	0,934	<1 mmHg (25 °C)
Piperazine	110-85-0	PZ		C ₄ H ₁₀ N ₂		106	146	1,1	21 Pa
Ammonia	NH ₃	Ammonia			gas				
Formaldehyde	50-00-0	Formaldehyde		CH ₂ O	colourless gas		- 21 (pure)		
Acetaldehyde	75-07-0	Acetaldehyde		C ₂ H ₄ O	colourless liquid with pungent, fruity odor		20,2	0,788	
2-Methylaminoethanol N-Methylethanolamine	109-83-1	MAE		HOCH ₂ CH ₂ NHCH ₃	clear to pale- yellow, viscous liquid		159	0,935	0,5 mmHg
Formamide Methanamide		Formamide		CH ₃ NO	clear liquid, ammonia-like odour	2 - 3	210	1,133	0,08 mmHg
2-((2-aminoethyl)amino)- ethanol N-(2-hydroxyethyl)ethylenediamine	111-14-1	HEEDA		HOCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂			243	1,03	0,01 mmHg
Nitrogen monoxide	10102-43-9	NO		NO	gas				
Nitrogen dioxide	10102-44-0	N₂O		N ₂ O	gas				
Carbon monoxide	630-08-0	CO		CO	gas				
Methylamine	74-89-5	MA		C H ₅ N	Colorless Gas		-6	0,699 (-10,8 °C)	3970 Torr
Dimethylamine	124-40-3	DMA		C ₂ H ₇ N	Colorless gas with pungent		7	0,67	
Trimethylamine	75-50-3	TMA		C ₃ H ₉ N	Colourless gas		2,87	0,67	
Ethanol, 2-[methyl(2-(methylamino)ethyl)amino]-	17225-70-6		HOCH ₂ CH ₂ OHNMeCH ₂ CH ₂ NHMe	C ₆ H ₁₈ N ₂ O			209 ± 15	0,936	4,56 *10 ⁻³ Torr
Formamide, N-(2-hydroxyethyl)- Hydroxyethylformate	693-06-1	HEF		C ₃ H ₇ NO ₂		na	349 +/-25 (calc)/155 (0,3 torr)	1,09	2,83*10 ⁻⁶
1 - (2 - Hydroxyethyl)imidazole (1H-imidazole-1- ethanol) Hydroxyethyl-imidazole	1615-14-1	HEI		C ₆ H ₈ N ₂ O	white to yellow solid	36-40	202-206/0,024 bar	1,15	1,72*10 ⁻⁴
2-Imidazolidinone, 1-(2-hydroxyethyl)- Hydroxyethylimidazolidinone	3699-54-5	HEIA		C ₆ H ₁₀ N ₂ O ₂		84-85	400 ± 24 (calc)/220 - 240 (20 Torr)	1,211	4,57*10 ⁻⁸ (calc)
2-Imidazolidinone, 1,3-bis(2-hydroxyethyl)-	71298-49-2	"B-HEIA"		C ₇ H ₁₄ N ₂ O ₃		na		1,266	1,57*10 ⁻⁷
2-Piperazinone, 4-(2-hydroxyethyl)-	23936-04-1			C ₆ H ₁₂ N ₂ O ₂		59 - 60	450	1,152	3,39 *10 ⁻⁷ Torr
Ethanol, 2,2'-(1,2-ethanediyl)diimino)bis-	4439-20-7		RNHCH ₂ CH ₂ NHR (R = CH ₂ CH ₂ OH)	C ₆ H ₁₆ N ₂ O ₂			305,1 (calc)/196 (10 Torr)	1,056	7,93*10 ⁻⁵ Torr (25 °C)
<i>N, N', N'-tris(-hydroxyethyl)subst. ethylene diamine</i>			RNHCH ₂ CH ₂ NR ₂ (R = CH ₂ CH ₂ OH)	C ₈ H ₂₀ N ₂ O ₃			> 305		
N,N-Dimethyl-2-hydroxyethylamine N, N-dimethyl-2-ethanolamine	108-01-0	DMAE		(CH ₃) ₂ NCH ₂ CH ₂ OH			133 - 134	0,89	6,12 mmHg (100 mmHg /55 °C)
diethanolamine (2,2'-iminodiethanol)	111-42-2	DEA	(HOCH ₂ CH ₂ CH ₂) ₂ NH	C ₆ H ₁₁ NO ₂			217	1,09	
triethanolamine (2-[bis(2- hydroxyethyl)amino]ethanol)	7376-31-0		(HOCH ₂ CH ₂ CH ₂) ₃ N	C ₆ H ₁₅ NO ₃	pale yellow liquid		335,4	1,126	
amides (unspecified)									
acetone	67-64-1		CH ₃ COCH ₃	C ₃ H ₆ O			56,5	0,7925	
4, 4-dimethyl-oxazolidinone	26654-39-7			C ₆ H ₁₁ NO ₂			272	1,039	
3,4,4-trimethyl-2-Oxazolidinone	15833-17-7			C ₆ H ₁₁ NO ₂			243 +/- 9 (calc)	1,027	
1-Propanol, 2-methyl-2-(methylamino)- oxazolidinone	27646-80-6			C ₆ H ₁₃ NO			165	0,93	<1 mmHg
ethylenediamine (1,2-diamine)ethane)	107-15-3	EDA	C ₂ H ₈ N ₂			9	116	0,899	
formamides (unspecified; N-formylpiperazines, N- formylethylenediamine)			CHONHR						
N-methylpiperazine	109-01-3		C ₆ H ₁₂ N ₂				140	0,882	6,86 Torr
N, N-dimethylpiperazine	106-58-1		C ₆ H ₁₄ N ₂				130-133	0,888	7,50 Torr

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