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Oxidative degradation of aqueous amine solutions of MEA, AMP, MDEA, Pz: A review

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Abstract

Alkanolamine based post-combustion capture processes (PCC) are currently the most attractive technologies for CO₂ capture. Solvents are degraded in this service by flue gas components, for example oxygen. Solvent degradation can be classified into two reaction types: 1) amine oxidative degradation through a) autoxidation pathways, b) oxidation in the presence of metal ions and 2) thermal degradation including reactions in the presence of CO₂. This study represents a literature survey of oxidative degradation (reaction type 1a) of 2-Amino-1-ethanol (MEA), 2-Amino-2-methyl-1-propanol (AMP), N,N-Bis(2-hydroxyethyl)methyl-amine (MDEA), and Piperazine (Pz). Thermal degradation products (reaction type 2) are included where appropriate in order to contribute to a more complete degradation overview of these compounds.

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Keywords: CO₂ capture; oxidative degradation; 2-Amino-1-ethanol; 2-Amino-2-methyl-1-propanol; N,N-Bis(2-hydroxyethyl)methylamine; Piperazine

1. Introduction

Among several technologies proposed for CO₂ capture from flue gas streams, alkanolamine based post-combustion capture processes (PCC) are currently the most attractive technologies [1]. These processes are in particular focus for power plant application due to the low CO₂ partial pressure present in the flue gas. Alkanolamine absorbent solvents are degraded in this service by several flue gas components, for example oxygen [2]. It has been estimated that solvent degradation contributes to around 10% of the total cost of CO₂ capture [3]. Degradation prevention requires insight into this process.

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Solvent degradation can be systematized into two main reaction types: 1) amine oxidative degradation through a) autoxidation pathways, b) oxidation in the presence of metal ions and 2) thermal degradation including reactions in the presence of CO₂. The products observed in reaction type 1a) vs. 1b) appear to belong to the same product classes.

This study represents a literature survey of oxidative degradation (reaction type 1a) of 2-Amino-1-ethanol (MEA), 2-Amino-2-methyl-1-propanol (AMP), N,N-Bis(2-hydroxyethyl)methyl-amine (MDEA), and Piperazine (Pz). Thermal degradation products (reaction type 2) are included where appropriate in order to contribute to a more complete degradation overview of these compounds.

The literature up to August 2012 has been evaluated. Amine degradation has been reviewed for sour gas treatment [4], CO₂ capture [5] and as part of a study [6] highlighting the need for MEA PCC solvent management guidelines. Part of the current review has been published inside a specific work package developing a set of methods and procedures for evaluating health and environmental impact of amine solvents for use in CO₂ capture [7].

Degradation studies have been conducted under varying experimental conditions (i.e., amino alcohol concentration: 13-50 wt%; reaction temperature: 20-170°C; oxygen pressure: 0,1 kPa-0,4 MPa; in the presence/without CO₂) also using a variety of analytical techniques (i.e. HPLC, LC-MS, cation-, anion IC, FT-IR, GC-MS). Some products have been indirectly identified. This review is restricted to reporting compounds that have been analyzed and identified. Inside the scope of a contribution to the GHGT-11 conference, the purpose of this review is to provide an overview to the field of oxidative degradation of MEA, AMP, Pz and MDEA solvents.

2. General degradation chemistry

The oxidative degradation of PCC amino alcohol solvents may be classified to be of the autoxidation type proceeding through peroxy intermediates [8-10]. Concentration of thermal vibration energy onto one bond or reaction with oxygen could be the reaction initiating event followed by reaction with oxygen at a rate close to the rate of a diffusion controlled process [11].

The initial step of amine oxidation by a one electron oxidant may be either through electron- or hydrogen abstraction, the former yielding an aminium radical and the latter yielding a α -C or N centered radical. Very fast proton transfer will transform the aminium radical cation into the same α -C or N centered radical [12].

The **electron abstraction mechanism** is based on a series of studies that focused mainly on tertiary amines using chlorine dioxide as a single electron oxidant [13]. These studies indicated that the rate limiting step is electron abstraction from the nitrogen atom to produce an aminium radical which 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 α -C alkylsubstituted amines) together with NH₃.

The electron abstraction mechanism was adopted by Chi [14] who suggested that metal ions like Fe³⁺ could initiate this oxidation reaction. At the same time the reaction scheme was extended by introduction of oxygen leading to formation of a peroxide radical. Reaction of the peroxide radical with another molecule of MEA was thought to produce an amino-peroxide radical and another aminium radical. Decomposition of the amino peroxide would result in an imine and hydrogen peroxide (Figure 1).

Another study puts focus on the **hydrogen abstraction** mechanism [15]. In these studies aqueous solutions of amines were degraded using ionization radiation to create initiating radicals like OH, H \cdot , e $^{-}$ (aq). The proposed reaction scheme is based on formation of cyclic 5-membered ring structures containing O \cdot H or N \cdot H bonds. Three reaction alternatives are proposed for α,β -aminoalcohols: i) hydrogen abstraction from the β -carbon leading to N-C cleavage and formation of aldehyde and NH $_3$; ii) hydrogen abstraction from the α -carbon leading to an imine which is hydrolysed to aldehyde and NH $_3$; iii) electron abstraction from the N atom resulting in N-C and C-C bond scission accompanied by formation of two moles of formaldehyde and ammonia in the case of MEA.

The hydrogen abstraction mechanism is favored by Goff [16] and is supported by molecular simulation studies [17]. The hydrogen- and electron mechanisms provide insight into the first radical forming step. Figure 1 and 2 show proposals for the subsequent reaction with O $_2$. In contrast to MEA, a C-C bond scission step is proposed for AMP.

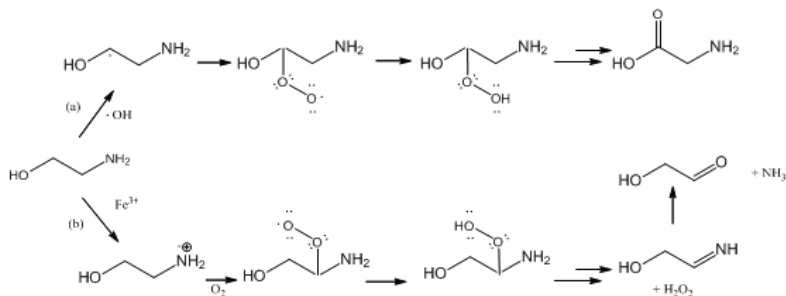


Figure 1: Proposed primary oxidation pathways for MEA. Adopted from Chi [14] and Bedell [10].

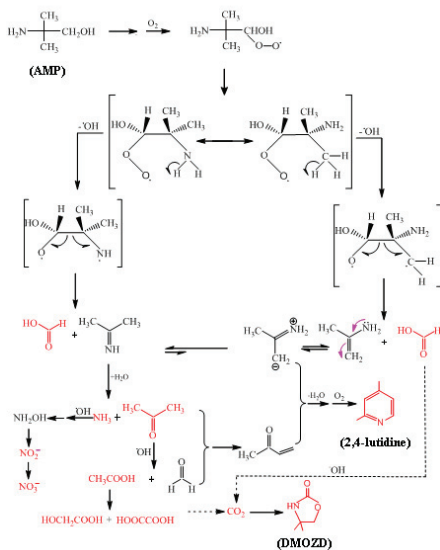


Figure 2: Proposed oxidation pathway for AMP. Reaction products are shown in red [28].

3. 2-Amino-1-ethanol (MEA)

The observed compound classes for oxidative degradation of MEA are shown in Table 1. Observed products are ammonia, organic acids and aldehydes. All of these products may be assumed to be formed by an autoxidation type degradation chain starting with MEA and are thus classified as primary products [2]. In a second step these acids will form 'Heat-Stable Salts' removing CO₂ absorption capacity from the solvent by reaction with MEA. The amides are proposed formed in a secondary step by reaction of acids and the amine function of MEA or other secondary formed amines together with water elimination [18] or

Table 1: identified oxidative degradation compounds of MEA.

compound		reference
org. acids	HCOO ⁻ , CH ₃ COO ⁻ , HOCH ₂ COO ⁻ , (C ₂ O ₄) ²⁻	[2,19,16,20,21,22,26]
inorg. compds.	NH ₃ , NO ₂ ⁻ , NO ₃ ⁻ ,	[23,19,16,14,8,20,21,22]
aldehydes	CH ₂ O, CH ₃ CHO, HOCH ₂ CHO	[16,23,20,22]
amides	HEF, formamides, oxamides,	[16,20,21,22]
amines	methylamines, MAE, BHEEDA, HEEDA, MEA-urea	[2,24,21,22,25,26,19]
cyclic compds.	HEPO-3, HEPO-2, HEI, HEIA, HEP, DMPz	[2,24,25,21,22,26,19]
pilot plant samples		
org. acids	HCOO ⁻ , CH ₃ COO ⁻ , (C ₂ O ₄) ²⁻	[27,18]
amides	HEF, HEA, HHEA, BHEOX, HEHEAA	[18]
cyclic compds.	HEI, OZD, HEPO, HEIA	[27,18]

alternatively by reaction of the amine function with formaldehyde in the presence of oxygen [20]. The cyclic- and the linear mono/polyamine compounds are formed in a thermal degradation reaction sequence [25] of MEA with CO₂ leading to OZD followed by ring opening with MEA and subsequent reaction with another molecule of MEA or OZD (Figure 3). Interestingly, reported reaction conditions allow oxidative fragmentation of MEA to give methylamines and MAE [19].

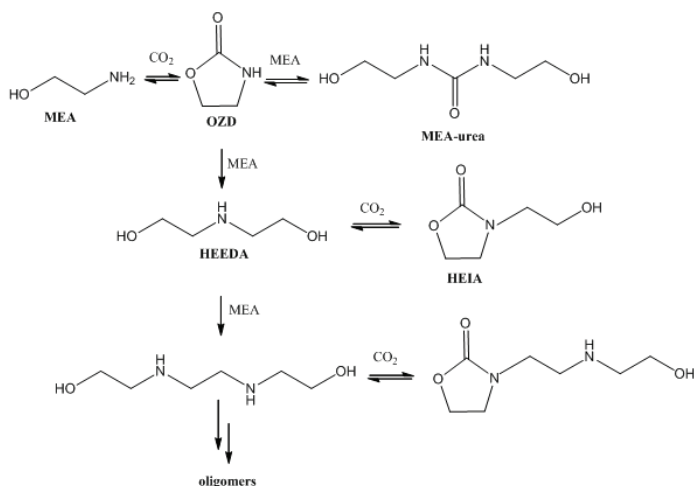


Figure 3: Proposed MEA thermal degradation pathways. Adopted from Davies [25] and Closmann [34].

MEA laboratory degradation results have been compared with a sample of degraded MEA solvent from the Esbjerg pilot plant [18]. This sample was dominated by oxidative degradation rather than thermal degradation products. Furthermore, a significant amount of amides was also observed. This trend has been confirmed by the Niederaussem pilot plant although at lower total degradation level [27].

4. 2-Amino-2-methyl-1-propanol (AMP)

The structure of AMP is related to MEA, however the α -C atom (relative to N) does not contain C-H bonds. The observed oxidation products are shown in Table 2. Ammonia, acetone and formic acid have been proposed as primary oxidation products [28], nitrite, nitrate being secondary oxidation products originating from NH_3 while acidic-, glycolic- and oxalic acid are thought to be the secondary oxidation products of acetone. 2,4-lutidine is proposed to be formed by reaction of acetone, formaldehyde and dimethyl imine, the latter two molecules suggested to be transient intermediate products. 4,4-dimethyl-oxazolidone is expected formed by reaction of the total oxidation product CO_2 with AMP. In a related

Table 2: identified oxidative degradation compounds of AMP.

compound		reference
org. acids	HCOO^- , CH_3COO^- , $\text{HOCH}_2\text{COO}^-$, $(\text{C}_2\text{O}_4)^{2-}$	[19, 28]
inorg. compds.	NH_3 , NO_2^- , NO_3^- , CO_2	[28]
ketone	$\text{CH}_3(\text{CO})\text{CH}_3$	[28]
amines	N-methyl-AMP	[19]
cyclic compds.	DMOZD, N-methyl-DMOZD, 2,4-Lutidine	[19,28]

study [19] products probably formed by oxidative fragmentation (N-methyl-AMP, N-methyl-4,4-dimethyl-oxazolidone) have also been observed.

5. N,N-Bis(2-hydroxyethyl)methylamine (MDEA)

The observed compound classes for oxidative degradation of MDEA are shown in Table 3. Similar to the other amines, organic acids and glycine may be assumed formed by a chain of oxidation reactions starting with the parent alkanol amine. As secondary product unspecified formylamides are observed. Formation of DEA may occur concurrently with a methyl group transfer from MDEA (see below) or by direct oxidation of MDEA. MEA is thought to be a direct oxidation product derived from DEA [29]. Bicine is speculated formed by reaction of DEA with hydroxyacetaldehyde (a compound concurrently formed in degradation of DEA to MEA) followed by oxidation of the aldehyde function [29]. Oxidation of hydroxyacetaldehyde could also lead to formation of glycolic acid.

Table 3: identified oxidative degradation compounds of MDEA.

compound		reference
org. acids	HCOO^- , CH_3COO^- , $\text{HOCH}_2\text{COO}^-$, $(\text{C}_2\text{O}_4)^{2-}$, HES, Bicine, Glycine	[34,2,19,29,35]
amides	formylamides	[19,29,35]
amines	MEA, DEA, MAE, DMAE, HEOD, Pz derivatives	[34,2,19]

The observed methylated primary and secondary amines may be formed by disproportionation of amine and quaternary ammonium ions [30,31]. This reaction can be considered a thermal degradation pathway. This transalkylation reaction is favorable for ammonium ions carrying a methyl, benzyl- or allyl substi-

tuent [32]; hence formation of HES may be assumed not to proceed by this degradation pathway; direct oxidation of MDEA has instead been suggested [29]. HEOD and Pz derivatives have been identified as thermal degradation products of DEA [33].

6. Piperazine (Pz)

In contrast to MEA, AMP and MDEA, Pz is a cyclic amine which may absorb two moles of CO₂ per mole of piperazine. The reported oxidation products are shown in Table 4.

Table 4: identified oxidative degradation compounds of piperazine.

compound		reference
org. acids	HCOO ⁻ , CH ₃ COO ⁻ , HOCH ₂ COO ⁻ , (C ₂ O ₄) ²⁻	[29,20,37,38]
inorg. compds.	NO ₂ ⁻ , NO ₃ ⁻	[20]
amides	formamides*, oxalylamide	[36,20,37,38]
amines	EDA	[36,20,38]

* Different amides are presumed formed but only indirectly estimated.

Conclusion

Reported results may be rationalized by assuming peroxy radical formation as the initial step. Thereafter deamination leads to ammonia, aldehydes/ketones and carboxylic acids as primary products. This first “mix” of products will be oxidized further and/or participate in secondary reactions. The effect of CO₂ on oxidative degradation and in-process formation of small alkyl amines are still open issues needing more investigation. The latter potential degradation route has some bearing on possible in-process formation of volatile nitrosamines which may effect the environmental footprint of this technology.

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Appendix. List of organic substance acronyms

Acronym	Chemical name
AMP	2-Amino-2-methyl-1-propanol
BHEEDA	N,N'-Bis-(2-hydroxyethyl)ethylenediamine
BHEOX	N,N'-Bis-(2-hydroxyethyl)oxamide
Bicine	N,N-Bis(2-hydroxyethyl)glycine
DEA	Diethanolamine
DMAE	Dimethylaminoethanol
DMOZD	4,4-Dimethyloxazolidinone
DMPz	N,N'-Dimethylpiperazine
EDA	Ethylenediamine
Glycine	Aminoethanoic acid
HEA	N-(2-Hydroxyethyl)acetamide
HEEDA	N-(2-Hydroxyethyl)ethylenediamine
HEOD	3-Hydroxyethyl-2-oxazolidinone
HEF	N-(2-Hydroxyethyl)formamide
HEHEAA	N-(2-Hydroxyethyl)-2-(2-hydroxyethylamino)acetamide
HEI	N-(2-Hydroxyethyl)imidazol
HEIA	N-(2-Hydroxyethyl)imidazolidinone
HEIA	N,N'-(2-Hydroxyethyl)imidazolidinone
HEP	N-(2-Hydroxyethyl)piperazine
HEPO-2	(2-Hydroxyethyl)piperazin-2-one
HEPO-3	(2-Hydroxyethyl)piperazin-3-one
HES	Hydroxyethylsarcosine
HHEA	2-Hydroxy-N-(2-hydroxyethyl)acetamide
MAE	N-Methylaminoethanol
MDEA	N,N-Bis(2-hydroxyethyl)methylamine
MEA	Monoethanolamine
MEA-urea	N,N'-Bis-(2-hydroxyethyl)urea
N-methyl-AMP	N-Methyl-2-amino-2-methyl-1-propanol
N-methyl-DMOZD	N-Methyl-4,4-dimethyloxazolidinone
OZD	Oxazolidinone
Pz	Piperazine