

Available online at www.sciencedirect.com**Energy
Procedia**

Energy Procedia 4 (2011) 1608–1615

www.elsevier.com/locate/procedia

GHGT-10

Degradation of MEA; a theoretical study

Solrun Johanne Vevelstad^{a*}, Ingvild Eide-Haugmo^a, Eirik Falck da Silva^b, Hallvard F. Svendsen^a^aNorwegian University of Science and Technology, 7491 Trondheim, Norway
^bSINTEF Materials and Chemistry, 7465 Trondheim, Norway

Abstract

CO₂ capture with alkanolamines has been in use since 1930, where MEA is the most studied absorbent for post-combustion. In order to prevent degradation, it is important to understand the degradation mechanisms, which in turn requires knowledge of both stoichiometry and kinetics of the reactions. The stability of the degradation products is a starting point when exploring possible mechanisms, and can be determined from the Gibbs free energy of the net reaction. In the present work, quantum mechanical calculations and continuum solvation models are used to calculate the reaction energy for different oxidative degradation reactions and to verify the suggested mechanism for thermal degradation of MEA with CO₂. The suggested total reaction mechanisms for thermal degradation with CO₂ were found to be energetically favorable, and oxalic acid, oxalamide and 1-(2-hydroxyethyl)-imidazole (HEI) were found to be of the most probable oxidative degradation products.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).Keywords: Monoethanolamine (MEA); degradation mechanisms; CO₂ capture, theoretical study

1. Introduction

A wide range of technologies exist for separation and capture of CO₂ from gas streams, of which a large number is based on absorption into solvents. Alkanolamines have been used as absorbents for several decades, MEA being the most studied absorbent. In the absorption processes, problems relating to degradation may be significant, causing not only loss of amine but also corrosion, foaming, fouling and plugging of the equipment, in addition to environmental problems [1]. MEA itself is an accepted chemical regarding marine environment, as is supported by ecotoxicity and biodegradation measurements [2]. However mapping of MEA degradation compounds is important to characterize the system and to be able to use existing technology such as water wash to avoid emission of amine or amine degradation compounds.

Degradation may occur thermally with CO₂ present, or through oxidative degradation, depending on the conditions. In order to prevent degradation, it is important to understand the degradation mechanisms, which in turn

* Corresponding author. Tel.: +47-7359-4030; fax: +47-7359-4080.
E-mail address: solrun.vevelstad@chemeng.ntnu.no.

requires knowledge of both the reaction stoichiometry and kinetics. The stability of the degradation products is a starting point when exploring possible mechanisms, and can be determined from the Gibbs free energy of the net reaction.

In the present work quantum mechanical calculations and continuum solvation models are used to calculate the reaction energy for different degradation reactions. Such calculations are widely used to elucidate the mechanisms of chemical reactions. The work presented is, as far as we know, the first theoretical work done on amine degradation.

Thermal degradation has been studied for a long time, but degradation studies for an oxidizing environment, as in flue gas, are more limited. Oxidative degradation of alkanolamines is believed to take place through radical formation, and the process has been found to be catalyzed by iron. The specific mechanisms are still not fully understood and there are primarily two different mechanisms suggested that give the same degradation products [3]. Reaction pathways for some of the most common degradation products have been suggested [4]. For degradation of the alkanolamines with CO₂, 2-oxazolidone is believed to be a key primary degradation product [5-7], as it reacts to form further compounds. A reaction mechanism for the formation of this product has been suggested, though it has not been verified [8].

2. Method

Geometry optimization, frequency and solvation calculations were carried out in the Gaussian 03 software [9]. The molecules were assembled using Spartan version 8 [10]. For the oxidative degradation calculations the B3LYP method was used, while the calculations for degradation with CO₂ were carried out at the Hartree-Fock level of theory. 6-31G(d) and 6-311++G(d,p) basis sets were utilized for the calculations. The total Gibbs free energy of reaction was calculated using a thermal correction for the energies in the gas phase, and adding the Gibbs free energy of solvation. The solvation energy was calculated with IEF-PCM model.

3. Results and Discussion

Suggested reactions for some of the oxidative degradation products of MEA from literature [3, 4, 11, 12], are given below in table 1.

Table 1: Enthalpy and Gibbs free energy for the suggested reactions.

Compound	Net reaction from MEA.	ΔH kcal	ΔG kcal
Formic acid	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 1/2 \text{O}_2 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{H} + \text{NH}_3$	-64	-89
Formaldehyde	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 1/2 \text{O}_2 \longrightarrow 2 \text{H}-\text{C}(=\text{O})-\text{H} + \text{NH}_3$	-25	-54
Formamide	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 0,5\text{O}_2 + \text{NH}_3 \longrightarrow \text{H}_2\text{N}-\text{C}(=\text{O})-\text{H} + \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$	-67	-99
Acetic acid	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 1/2 \text{O}_2 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{CH}_3 + \text{NH}_3$	-72	-94
Vinylalcohol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 \longrightarrow \text{NH}_3 + \text{H}_2\text{C}=\text{CH}-\text{OH}$	19	-6
Acetaldehyde	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 \longrightarrow \text{NH}_3 + \text{H}_2\text{C}=\text{CH}-\text{OH} \rightleftharpoons \text{H}_3\text{C}-\text{C}(=\text{O})-\text{H}$	3	-20
Glycine	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{O}_2 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2 + \text{H}_2\text{O}$	-116	-144
α -amino-acetaldehyde	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 1/2\text{O}_2 \longrightarrow \text{H}_2\text{N}-\text{CH}_2-\text{C}(=\text{O})-\text{H} + \text{H}_2\text{O}$	-48	-75
Glycolic acid	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{O}_2 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{OH} + \text{NH}_3$	-113	-136
Hydroxy-acetaldehyde	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 1/2\text{O}_2 \longrightarrow \text{HO}-\text{CH}_2-\text{C}(=\text{O})-\text{H} + \text{NH}_3$	-44	-65
Glyoxylic acid	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 3/2 \text{O}_2 \longrightarrow \text{HO}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H} + \text{NH}_3 + \text{H}_2\text{O}$	-151	-185

Oxalic acid		-234	-258
Oxalamide		-248	-284
N-(2-hydroxyethyl)-formamide (HEF)		-61	-105
N-(2-hydroxyethyl)-acetamide (HEA)		-68	-108
Nitric acid	$\text{NH}_3 + 2\text{O}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O}$	-144	-146
Nitrous acid	$\text{NH}_3 + 3/2\text{O}_2 \longrightarrow \text{HNO}_2 + \text{H}_2\text{O}$	-113	-119
2-methyl-aminoethanol (MMEA)		-114	-178
2-((2-[2-hydroxyethyl)amino]ethyl)-amino)ethanol (BHEEDA)		10	-28
N-(2-hydroxyethyl) ethylenediamine (HEEDA)		6	-23
1-(2-hydroxyethyl)-imidazole (HEI)		-135	-219
4-(2-hydroxyethyl) piperazine-2-one (4-HEPO)		-113	-174

1-(2-hydroxyethyl) piperazine-2-one (1-HEPO)	$3 \text{ HO-CH}_2\text{-CH}_2\text{-NH}_2 + \text{O}_2 \longrightarrow \text{1-HEPO} + 3\text{H}_2\text{O} + \text{NH}_3$	-112	-174
Oxiran	$\text{HO-CH}_2\text{-CH}_2\text{-NH}_2 \longrightarrow \text{Oxiran} + \text{NH}_3$	31	8

The calculations show that some of the most commonly suggested oxidative degradation products are favorable and that all of the reactions, except for vinylalcohol, acetaldehyde, 2-((2-[2-hydroxyethyl]amino)ethyl)amino)ethanol (BHEEDA), *N*-(2-hydroxyethyl)ethylenediamine (HEEDA) and oxiran are exothermic. It was shown that acetaldehyde is more stable than vinylalcohol which is explained by the keto-enol equilibrium where the keto form is more stable than the enol form [13]. Acetic acid is believed to be formed with vinylalcohol/acetaldehyde as intermediates and the low amount of acetic acid could be explained by the fact that these two products are less favorable than most of the other compounds. The comparison of Gibb free energy for formamide, oxalamide and products from the route suggested by Rooney [4] at 328K from one MEA molecule can be seen in Figure 1.

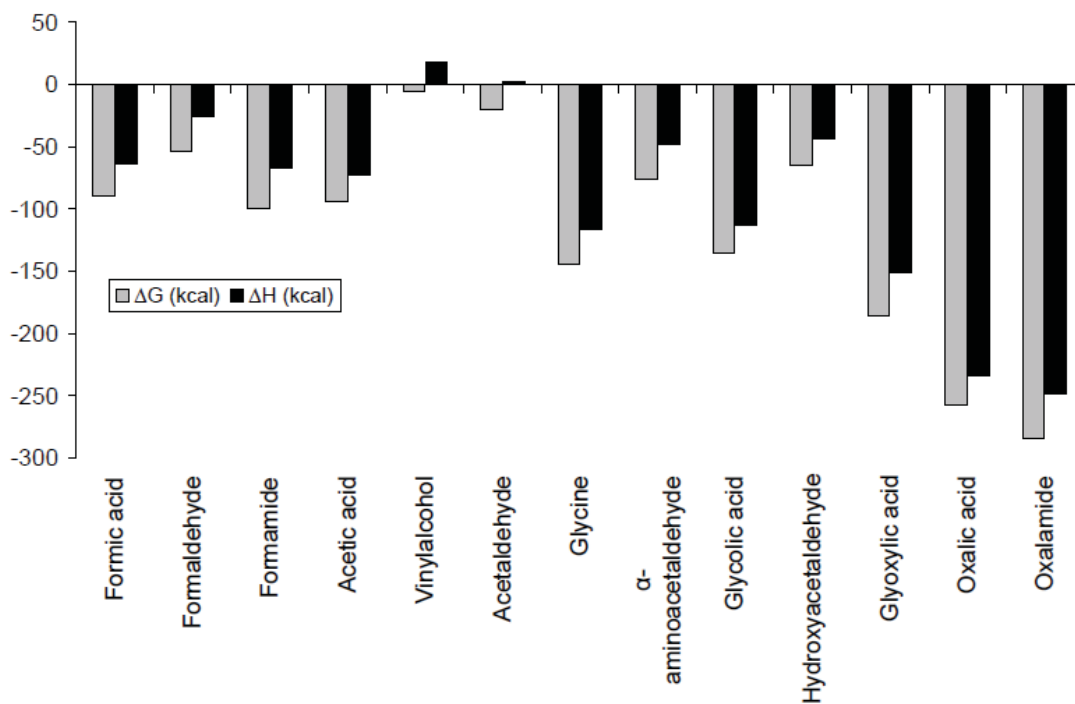


Figure 1: Enthalpy and Gibbs free energy for the compounds.

Figure 1 shows that the amide of the different compounds is more favorable than the acid form of the same compound. Sexton suggested that the total amide content could be verified by treating the degradation samples with sodium hydroxide before analyzing the samples on the Ion chromatograph [12, 14]. The comparison between some of the bigger molecules formed from one MEA molecule can be seen in Figure 2.

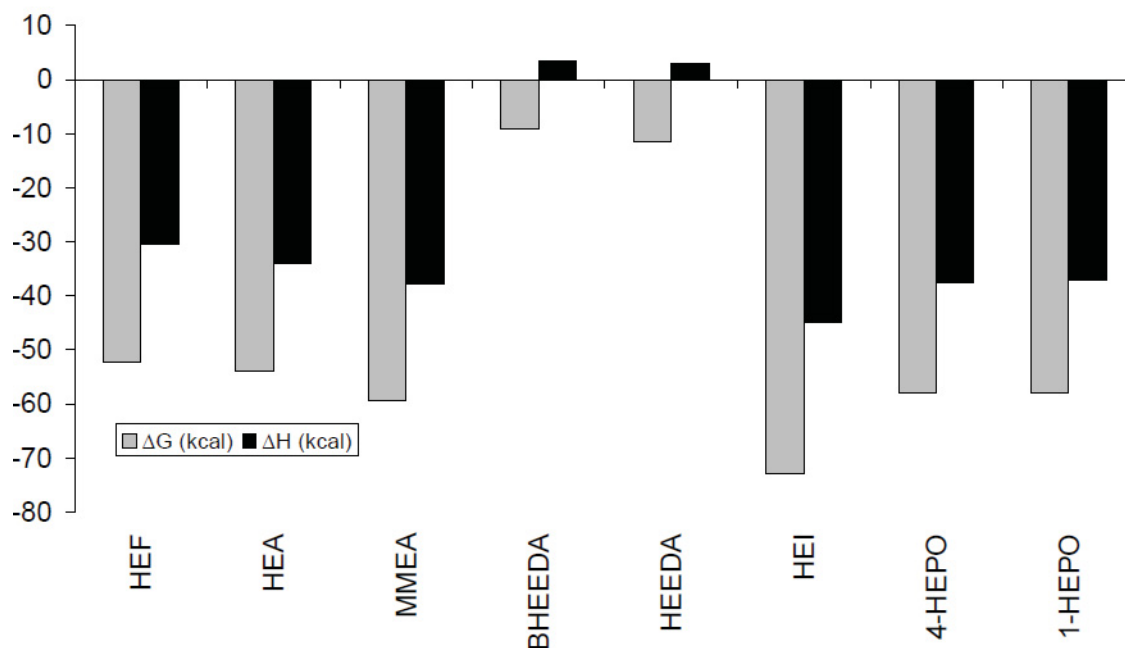


Figure 2: Enthalpy and Gibbs free energy for the larger compounds formed (see table 1).

Sexton et al. found that HEF and HEI were the major degradation compounds in the liquid phase [15]. Lepaumier et al. also suggested that 2-methyl-aminoethanol (by the Clarke-Eshenweiler mechanism) and piperazinone were common degradation compounds [11], and the calculations show that these products are favorable.

All the calculations were done without considering additives, such as iron, and also the neutral form of the compounds were studied even if the acid is deprotonated in the degradation mixture. Several of the compounds are also intermediates and react further, for example glyoxylic acid is believed to be an intermediate for oxalic acid. The Gibbs free energy and the enthalpy were also computed for different temperatures; however the thermal effect was small.

For thermal degradation of MEA with CO_2 , the reaction is believed to proceed through the MEA Carbamate. 2-Oxazolidone is then formed through a cyclization reaction of the carbamate, see Figure 3. It is unlikely that the reaction will proceed without a proton donor, which will react with the hydroxyl group to form water. The most likely proton donor is thought to be the protonated ethanolamine, 2-hydroxyethan ammonium (MEAH^+). This gives a suggestion for the total degradation mechanism in which the carbamate reacts with MEAH^+ to form 2-oxazolidone, MEA and water. The transition state for the suggested reaction was found through a relaxed potential energy scan, see Figure 4, supporting the suggested mechanism. The suggested total reaction for the formation of 2-oxazolidone from the carbamate had a total Gibbs free energy of reaction of -12.74 kcal/mol, and a reaction enthalpy of -124.97 kcal/mol. The results show that the formation of 2-oxazolidone is favorable with this reaction.

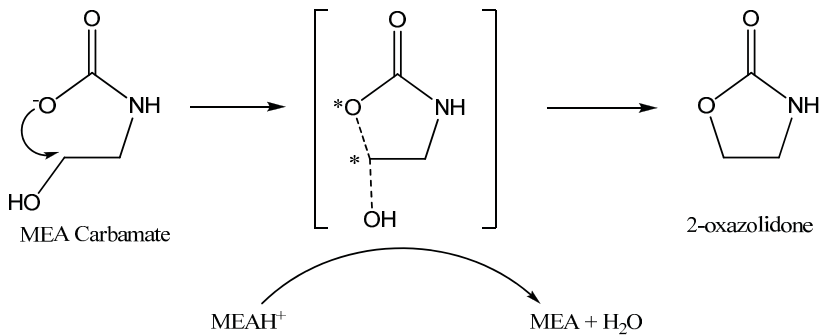


Figure 3: Suggested mechanism and transition state for the degradation of MEA carbamate to 2-oxazolidone.

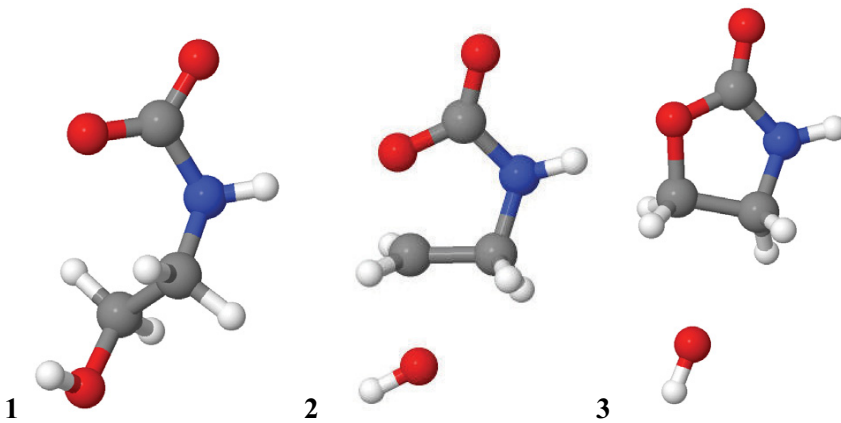


Figure 4: Optimised 1) starting point 2) transition state and 3) end point for the formation of the degradation product 2-oxazolidone from MEA Carbamate.

4. Conclusion

For the oxidative degradation of MEA most of the suggested reactions were energetically favorable, and oxalic acid, oxalamide were shown to be the most favorable degradation products. The formation of HEI was slightly more favorable than formation of the rest of the larger molecules studied. For thermal degradation of MEA with CO₂, a transition state was found for the formation of 2-oxazolidone from carbamate. The total reaction was found to be favorable. However, the Gibbs free energy of the reaction was considerably less for the degradation with CO₂ than for the oxidative degradation reactions.

Acknowledgement

This publication forms a part of the REACT project and the SOLVIt project, performed under the strategic Norwegian research program Petromaks and CLIMIT. The authors acknowledge the partners in REACT: StatoilHydro, Shell and the Research Council of Norway and in SOLVIt: Aker Clean Carbon, Gassnova, EON, Scottish Power, Statkraft and the Research Council of Norway for their support.

References

1. Kohl, A.L. and Nielsen, R.B., *Gas purification*. 1997.
2. Eide-Haugmo, I., Brakstad, O.G., Hoff, K.A., Sørheim, K.R., da Silva, E.F., and Svendsen, H.F. Environmental impact of amines *Energy Procedia* (2009).**1**(1): 1297.
3. Goff, G.S. and Rochelle, G.T. Monoethanolamine Degradation: O₂ Mass Transfer Effects under CO₂ Capture Conditions *Ind. Eng. Chem. Res.* (2004).**43**: 6400
4. Rooney, P.C., Dupart, M.S., and Bacon, T.R. Oxygen's role in alkanolamine degradation *Hydrocarbon Process.* (1998). 109
5. Lepaumier, H., Picq, D., and Carrette, P.L. Degradation study of new solvents for CO₂ capture in post-combustion *Energy Procedia* (2009).**1**(1): 893.
6. Straziar, B.R., Anderson, R.R., and White, C.M. Degradation pathways for monoethanolamine in a CO₂ capture facility *Energy & Fuels* (2003).**17**: 1034.
7. Polderman, L.D., Dillon, C.P., and Steel, A.B. Why monoethanolamine solution breaks down in gas-treating service *Oil & Gas Journal* (1955).**54**: 180.
8. Davis, J.R., Gary Thermal degradation of monoethanolamine at stripper conditions *Energy Procedia* (2009).**1**(1): 327.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, et al., *Gaussian 03, Revision E.01.*, in *Gaussian, Inc.* 2004: Wallingford CT.
10. *Spartan'08* Wavefunction, Inc. Irvine, CA.
11. Lepaumier, H., Picq, D., and Carrette, P.L. New Amines for CO₂ Capture. II. Oxidative Degradation Mechanisms *Ind. Eng. Chem. Res.* (2009).**48**: 9068.
12. Sexton, A.J., *Amine oxidation in CO₂ capture processes*. 2008, The University of Texas: Austin. p. 262.
13. Carey, F.A. and Sundberg, R. *Advanced Organic Chemistry, Part B: Reaction and Synthesis*. 4th ed. 2001: Springer.
14. Sexton, A.J. and Rochelle, G.T. Catalysts and inhibitors for MEA oxidation *Energy Procedia* (2009).**1**: 1179
15. Sexton, A.J. and Rochelle, G.T. Catalysts and inhibitors for oxidative degradation of monoethanolamine *International Journal of Greenhouse Gas Control* (2009).**3**: 704