

Oxidative Degradation of Monoethanolamine

Susan Chi

Gary T. Rochelle* (gtr@che.utexas.edu, 512-471-7230)

The University of Texas at Austin

Department of Chemical Engineering

Austin, Texas 78712

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Abstract

Oxidative degradation of monoethanolamine (MEA) was studied under typical absorber condition of 55°C. The rate of evolution of NH₃, which was indicative of the overall rate of degradation, was measured continuously in a batch system sparged with air. Dissolved iron from 0.0001 mM to 1 mM yields oxidation rates from 0.37 to 2 mM/hr in MEA solutions loaded with 0.4 mole CO₂/mole MEA. Ethylenediaminetetraacetic acid (EDTA) and N,N-bis(2-hydroxyethyl)glycine effectively decrease the rate of oxidation in the presence of iron by 40 to 50%. Ferrous ion caused oxidation in unloaded MEA with stoichiometry from 0.1 to 0.33 mol NH₃/mol Fe⁺². Fe⁺² from 0.0001 to 3.2 mM yielded rates from 0.12 to 1.1 mM/hr. Ferric did not appear to catalyze oxidation in unloaded MEA

Introduction

Aqueous monoethanolamine (MEA) is used extensively to remove CO₂ from flue gas. MEA degrades in the presence of oxygen and CO₂ resulting in extensive amine loss and equipment corrosion as well as generating environmental impacts.

In a flue gas stream, which contains 5-10% O₂ and 10% CO₂, three types of degradation can occur. Carbamate polymerization requires high temperatures and carbon dioxide, produces high molecular weight degradation products, and is expected to occur at the higher temperature of the stripper. Oxidative degradation requires oxygen and is catalyzed by iron, produces oxidized fragments of the solvent such as organic acids and NH₃, and is expected to occur in the presence of dissolved O₂ in the liquid holdup at the bottom of the absorber. Lastly, thermal degradation is encountered at temperatures higher than 205°C; therefore, it is the least common. This work focuses on the oxidative degradation of MEA.

A number of researchers have measured MEA oxidation rates in the past with prolonged oxidation experiments and often under forced oxidation conditions. Kindrick et al. (1950) measured oxidation of 2.5 N MEA with 0.5 atm O₂ and 0.5 atm CO₂ at 80°C for 7 days by titrating the effluent for NH₃ at the end of the experiment. Blachly and Ravner (1964) sparged 4N MEA with air at 55°C, and both NH₃ and peroxide production rates were measured by titration every day for about a week. Rooney et al (1998) sparged 20 wt % MEA with air at 80°C for 28 days, and anions such as acetate, formate and glycolate were measured every 7 days.

In this study the generation of NH₃ was measured in a continuous, real-time mode using a Fourier Transform Infrared analyzer. Additives such as iron and chelating agents were introduced into the solution without any disturbance to the system. Any changes in the production of NH₃ were quickly detected and easily compared to the baseline rate with no

additives. The initial degradation rate at each condition was measured in less than two hours. Employing this technique, the effect of iron, CO₂ loading, and potential inhibitors and catalysts on the oxidative degradation rates of MEA were determined at 55°C.

Expected Mechanisms and Results

Fundamental Studies

Studies at Edgewood Arsenal have quantified the oxidation of amines by chlorine dioxide and other single electron oxidants (Rosenblatt et al., 1963, 1967a, 1968; Dennis et al., 1967, Davis et al., 1968; Hull et al., 1967, 1969a, 1969b, 1969c). A number of papers by Lindsay Smith et al. (Audeh and Lindsay Smith, 1970, Lindsay Smith and Mead, 1973, 1967) have quantified the oxidation of tertiary amines by hexacyanoferrate (Fe(CN)₆⁻³). Since Fe⁺³ is most likely the catalyst/reactant in our system, these results with single electron oxidants are highly relevant. The mechanism for MEA oxidation according to the general scheme proposed by these researchers is shown in Figure 1 (Hull et al., 1969a). The boxed mechanism is proposed by this study to introduce the role of oxygen. Oxygen reacts with the imine radical to form the peroxide radical which leads to the production of imine and hydrogen peroxide. Ammonia and hydroxyacetaldehyde are hydrolysis products of the imine molecule whereas formaldehyde and ammonia are formed when imine undergoes the mechanism of oxidative fragmentation (Dennis et al., 1967).

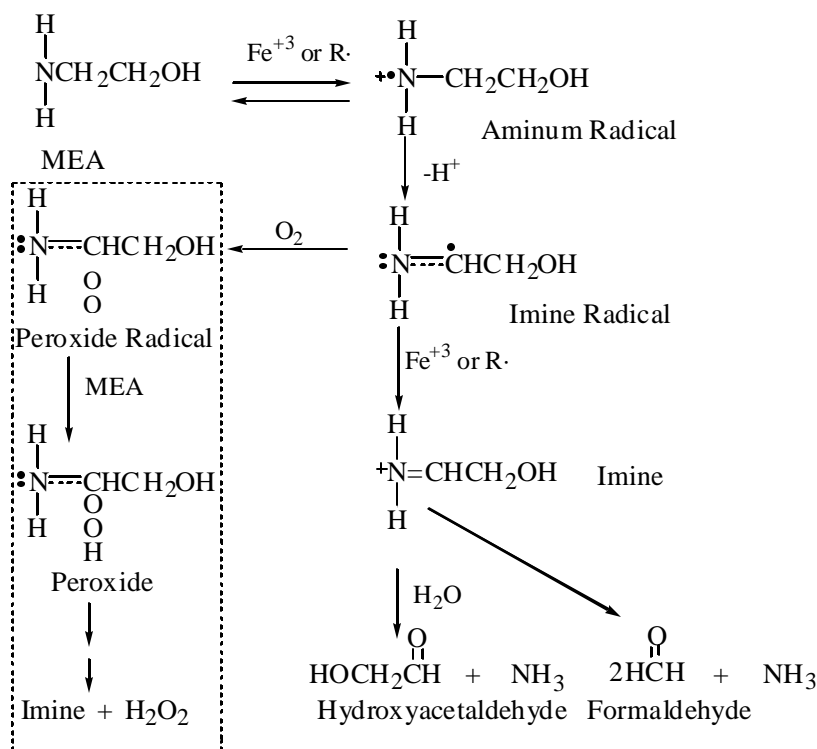


Figure 1 Degradation of MEA by Single Electron Oxidation

Aldehydes formed in MEA oxidation can undergo further reactions. For instance, formaldehyde and hydroxyacetaldehyde can readily react with MEA (Sander and Jencks, 1968). At high pH, formaldehyde is oxidized to formate by Fe(CN)₆⁻³ (Singh et al., 1969) and other similar single

electron oxidants. Hydroxyacetaldehyde can react at room temperature with oxygen to produce the corresponding organic acid (Denisov et al., 1977; Sajus and Seree De Roch, 1980).

The catalytic role of ferrous ion in sulfite oxidation has been studied (Ulrich, 1983; Lee and Rochelle, 1988; Russell, 1960). Reactions of ferrous with O_2 produce free radicals such as $O_2^{\bullet-}$ and OH^{\bullet} and H_2O_2 (Stumm and Lee, 1961) that may react directly with the amine. The Fe^{+3} / Fe^{+2} couple could also react reversibly with amines/aminium radicals to make the corresponding imine (Ferris et al., 1967, 1968) that is subject to oxidation.

Studies at Industrial Conditions

Oxygen is known to be present in streams such as flue gas or in CO_2 contaminated air in submarines. The efforts of the U.S. Navy to clean up CO_2 contaminated air in nuclear powered submarines drove the earliest work on oxidative degradation of alkanolamines. Kindrick et al. (1950a) subjected 39 amines including MEA and eleven mixtures of amines to prolonged oxidation at $80^\circ C$ for 7 days and measured amine loss and production of NH_3 .

Blachly and Ravner (1964) performed aeration experiments on MEA at $55^\circ C$ and measured the production of NH_3 and peroxides. They arrived at three important conclusions: 1) CO_2 was required for the production of NH_3 and peroxide; no degradation occurred in its absence, 2) N,N-diethanolglycine at 1.5 wt% was effective in reducing degradation caused by Fe^{+2} , Fe^{+3} , Cr, and Ni^{+2} , but not Cu^{+2} , 3) EDTA was effective in inhibiting oxidation with Cu^{+2} only.

Rooney et al. (1998) quantified the rate of oxidation of various alkanolamines including MEA in the presence of O_2 with and without CO_2 present by analyzing for heat stable salts such as acetates, formates, glycolates, and oxalates. They observed that oxidation rates were lower in all amines with 0.25 mole CO_2 /mole amine than in the unloaded amine solutions.

Experimental Methods

Figure 2 shows the overall flow diagram and the experimental setup.

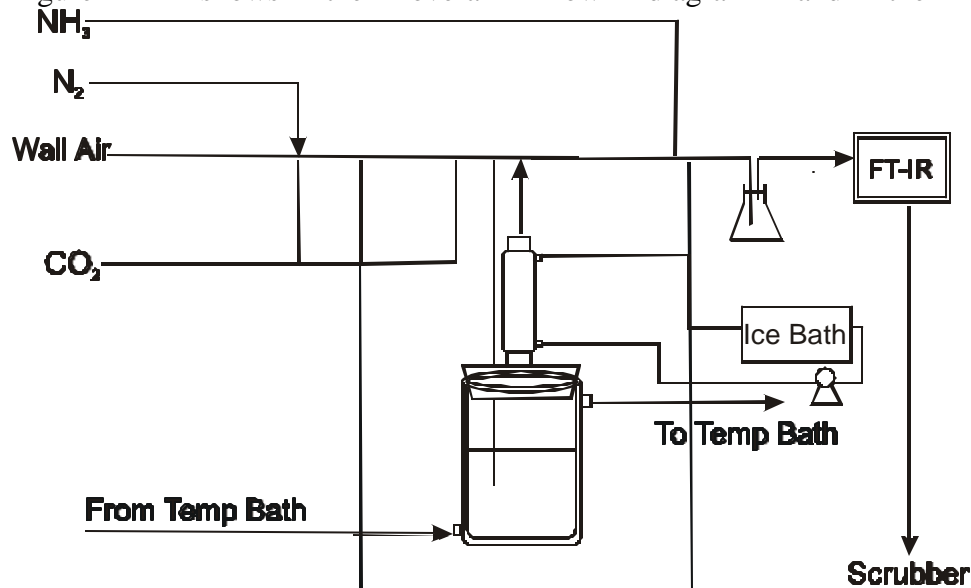


Figure 2 Experimental Flow Diagram for MEA Oxidation.

The flow system was capable of sparging N₂, air, air with 2% CO₂, and pure CO₂ into a jacketed reactor depending on the conditions of the experiment. The system operated in a batch mode for the liquid phase. The exit gas from the reactor was diluted with either air or N₂ to eliminate water condensation in the tubing leading to a Perkin Elmer FT-IR spectrometer. This system also allowed for convenient ammonia calibration via bypassing the reactor and delivering a known concentration of NH₃ directly to the analyzer. All gases were sent to a knockout flask before reaching the FT-IR, after which they were sent to the scrubber.

All of the experiments were performed with 5L/min of air or nitrogen sparged into 500 ml of MEA solution at 55°C. The LCI (Low Chloride Iron) grade monoethanolamine used in all of the experiments was produced by a commercial supplier. Analysis indicated that this batch of MEA contained 0.02 ppm of iron, less than 0.5 ppm of chloride, and 1 ppm of sulfate. The original stock solution was refrigerated at 4°C. Concentrations of MEA solutions were conveniently expressed in units of molality (mol MEA / kg water).

Results

Data Reduction

An example of raw data generated with the FT-IR is shown in Figure 3. The figure plots the integrated area underneath the peak centered at 970 cm⁻¹ against time in minutes.

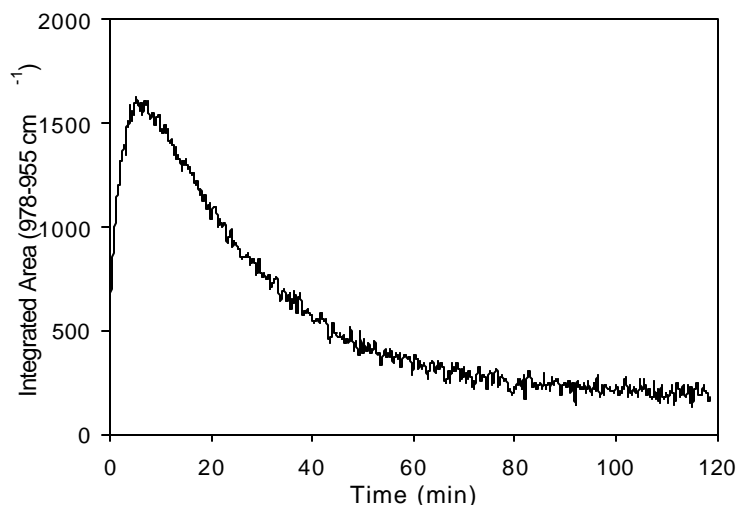


Figure 3 FT-IR Raw Data for Oxidation of 5 m Unloaded MEA with Air

The NH₃ calibration equation is used to convert integrated areas into concentrations in ppm. The concentration units can be converted into the instantaneous rate with units of mM/hr simply by multiplying by the gas rate and dividing by the volume to obtain the unsteady state rate or instantaneous rate of NH₃. All the manipulated raw data will plot this instantaneous rate of NH₃ production against time (in hours). Refer to Figure 4 as an example.

An unsteady state model of exponential decay can be used to predict the initial stripping behavior of dissolved NH₃ in solution (Chi, 2000) (Figure 4). In the first hour, air stripped out the dissolved NH₃ in the MEA solution until the rate became constant. The time constant in the

model depends on the gas rate, the liquid volume, and the equilibrium partition coefficient for NH_3 in the reactor and the condenser. Typical values of this time constant are around one hour. The steady state rate of NH_3 production reached in this experiment was 0.12 mM/hr.

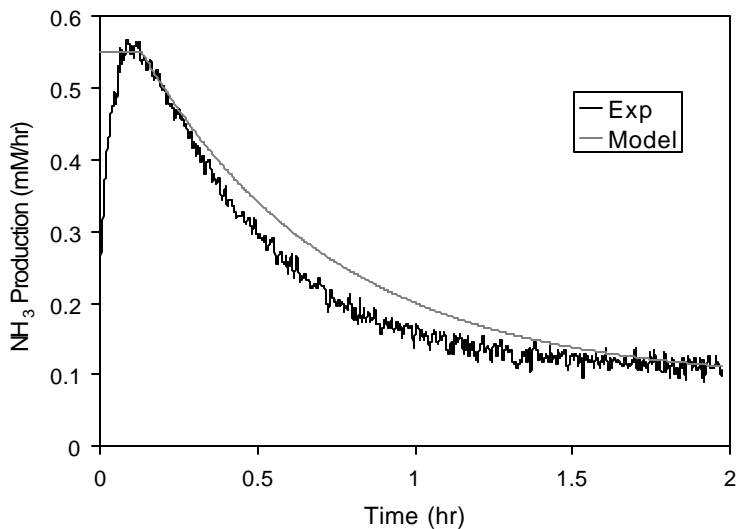


Figure 4 Experimental Data for Oxidation of Unloaded 5 m MEA with Air

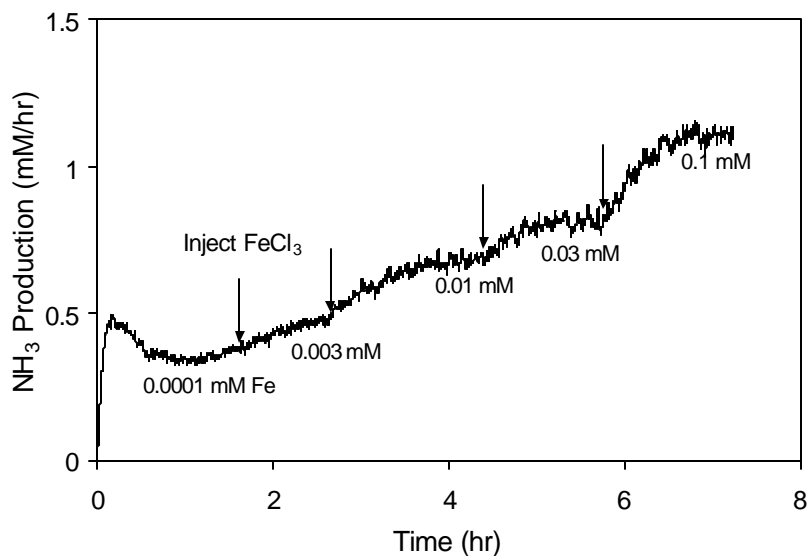


Figure 5 Multiple Steady States with Increasing Ferric Concentrations in 7 m MEA with 0.4 mole CO_2 /mole MEA

Typically, one experimental series provided information on several rates measured under different experimental conditions. Figure 5 illustrates an experiment where several steady-state rates can be extrapolated. Ferric chloride was injected into the reactor in increasing concentrations after the previous reaction reached steady state. Arrows indicate the exact points of injection. Each steady-state rate is labeled with its cumulative ferric chloride concentration in solution.

Table I Multiple Steady-state Rates with 0.4 mole CO₂/mole MEA

Total (mM)	FeCl ₃	Rate (mM/hr)
0.0001		0.35
0.003		0.48
0.010		0.68
0.030		0.81
0.100		1.11

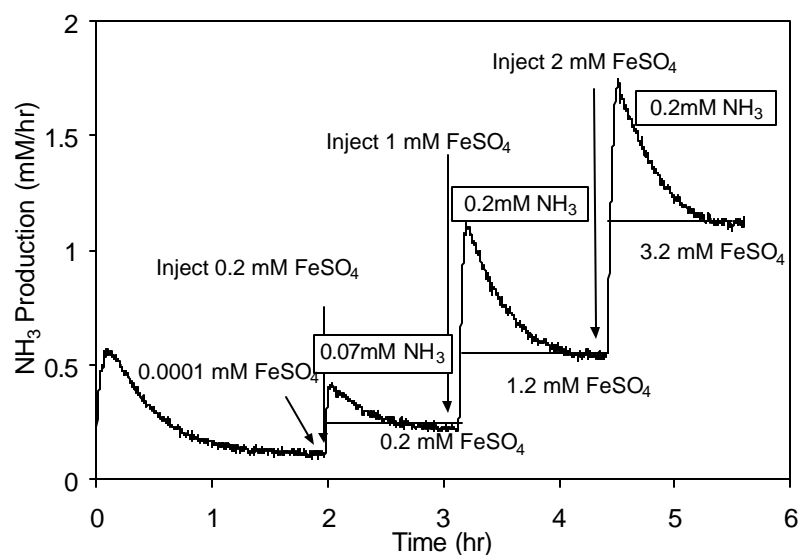


Figure 6 Multiple Steady States with Increasing Ferrous Concentrations in 7 m Unloaded MEA.

Under different experimental conditions, the instantaneous rate behavior of the reaction may differ; however, the steady state rates are obtained in the same manner. Figure 6 shows the unusual oxidation phenomenon with ferrous ion in unloaded MEA solution oxidized with air. Upon injection of ferrous sulfate, NH₃ was produced instantaneously in solution and was stripped out in a period of one hour. A higher steady state was reached with each successive addition of iron, and each is labeled with the total iron concentration responsible in establishing it. These steady state rates are tabulated in Table II.

Table II Multiple Steady-state Rates in Unloaded 7m MEA

Total Fe (mM)	Rate (mM/hr)
0.0001	0.11
0.20	0.22
1.2	0.54
3.2	1.11

The reaction of MEA with ferrous ion as presented by the data in Figure 6 exhibits a stoichiometric effect that can be quantified. Each triangle is integrated to obtain the total concentration of NH_3 upon injection of a specific ferrous sulfate concentration, and the concentration of NH_3 produced are boxed in Figure 6. The reaction stoichiometry corresponding to the injected iron concentration can be determined.

Experimental Conditions

Table III is a comprehensive list of experimental conditions studied in this work. All experiments were conducted at 55°C to represent absorber conditions. MEA concentrations were varied from 2.5 m to 12 m (13 to 42 wt %). ABB typically uses 15-20 wt % MEA, and Fluor Daniel uses 30 wt % with corrosion inhibitors added.

Table III Experimental Conditions

MEA (m)	2.5 - 12 (13 - 42 wt%)
O_2 (mole fraction)	0, 0.21
CO_2 Loading/ pH _(25C)	0/12.7, 0/10.3, 0.4/10
Fe^{+3} (mM)	0.0001 - 4
Fe^{+2} (mM)	0.0001 - 3.2
EDTA (mM)	0 - 13
Bicine (mM)	0 - 100
Glycine (mM)	0, 75
Formaldehyde(mM)	0, 2
H_2O_2 (mM)	0, 1
Diethylethanolamine (mM)	0,100
KMnO_4 (mM)	0, 1

Most experiments were carried out with air; a few experiments were performed in nitrogen. Three MEA solution conditions were examined: zero CO_2 loading which gives a solution pH of 12.7, zero CO_2 loading with HCl added to achieve pH 10.3, and 0.4 mol CO_2 /mol MEA which gives a pH of 10. In the first solution, most of the MEA is present as free MEA, whereas the second contains a mixture of free MEA as well as MEA^{H^+} . With 0.4 mol CO_2 /mol MEA, MEA carbamate, MEA^{H^+} , and free MEA are all present. Data collected at 0.4 CO_2 loading were most

representative of the actual degradation rates encountered in the absorber. The first two conditions of loading/pH were examined to understand the mechanisms of oxidation. Metals (Fe), oxidation catalysts (Fe, KMnO_4 , H_2O_2), potential oxidation inhibitors (EDTA, bicine, glycine, DMMEA), and degradation products (formaldehyde) were added.

Rate Data

A detailed description of all the experiments, their conditions, the steady-state rate and stoichiometry associated with each condition is shown in Table IV. Each experiment is identified by its date and defined by its conditions of MEA concentration, O_2 , CO_2 loading, and final solution pH measured at 25°C .

The additives and their *cumulative* concentrations in solution are tabulated along with their corresponding rates. Since the original MEA reagent contained 0.02 ppm of dissolved iron, the first steady state is actually the rate at 0.02 ppm iron. The actual sequence of additions is shown from top to bottom in the *Additives* column. Since chemicals were added sequentially, any steady-state rate represents the rate at the *solution* condition at that point and not necessarily the condition that is listed in the preceding column. For instance, in experiment 071300 a rate of 0.13 mM/hr was obtained from oxidation of unloaded 5 m MEA (originally containing 8.39×10^{-5} mM Fe) with air. 1 mM of Fe^{+3} was injected to this solution, and the rate of 0.13 mM/hr persisted. 1 mM of Fe^{+2} was added to the solution at this point, 6 mM EDTA was then injected into this solution shortly after, and the system was given time to reach steady state. A production rate of 0.33 mM/hr was obtained. This rate represents the rate of NH_3 production in a MEA solution containing 1 mM Fe^{+2} , 1 mM Fe^{+3} , and 6 mM EDTA. See Figure 7. Arrows point to the exact point of chemical injection while the steady states are labeled by the species present in solution that were responsible in establishing those rates.

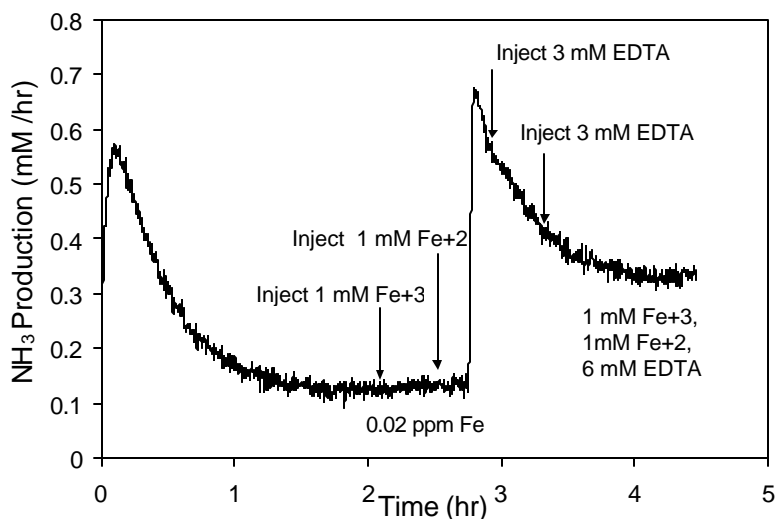


Figure 7 Oxidation of Unloaded 5 m MEA

Table IV Rate of evolution of NH₃ from MEA solution sparged at 55°C

Date	MEA (m)	O ₂	CO ₂ Loading mol CO ₂ /mol MEA	Final pH _{25°C}	Additives (mM)	Rate (mM/hr)
62700	2.5	Y	0	12.7	Fe _{initial} 4.7E-05	0.10
62700	10	Y	0	12.7	Fe _{initial} 1.4E-04	0.20
70700	5	N	0	12.7	Fe _{initial} 8.4E-05 Ferric 1 Ferrous 1 KMnO ₄ 2 EDTA 10	0 0 0 stoich = 0.97 0.27
71300	5	Y	0	12.7	Fe _{initial} 8.4E-05 Ferric 1 Ferrous 1 EDTA 6	0.13 0.13 - 0.33
71700	5	Y	0	12.7	Fe _{initial} 8.4E-05 EDTA 5 Ferrous 0.20 Ferrous 1.2 Ferrous 3.2	0.11 - 0.22 0.54 1.11
71800	5	N	0	12.7	Fe _{initial} 8.4E-05 EDTA 5 Ferric 4 Ferrous 1	0 - 0 0
72000	5	Y	0	12.7	Fe _{initial} 8.4E-05 (NH ₄) ₂ SO ₄ 1	0.12 stoich = 1.87
72600	5	Y	0	12.7	Fe _{initial} 8.4E-05 EDTA 5 Ferric 1	0.12 - 0.20
81500	7	Y	0.4	9.5	Fe _{initial} 1.1E-04 Ferrous 1	0.37 2.06
81600	12	Y	0	13	Fe _{initial} 1.5E-04 Ferrous 1	0.21 0.39
90800	7	Y	0	12.7	Fe _{initial} 1.1E-04 formaldehyde 2	0.16 0.16
90900	7	N	0	12.7	Fe _{initial} 1.1E-04 H ₂ O ₂ 1	0.00 2.06; stoich = 1
91000	7	Y	0.4	9.96	Fe _{initial} 1.1E-04 Ferric 1	0.37 2.32
91300	7	Y	0.4	9.93	Fe _{initial} 1.1E-04 Ferric 0.20 EDTA 4.45	0.40 1.77 1.06
91400	7	Y	0	11.57	Fe _{initial} 1.1E-04 glycine 75 Ferric 1	0.16 0.23 0.30

Date	MEA (m)	O ₂	CO ₂ Loading mol CO ₂ /mole MEA	Final pH _{25°C}	Additives (mM)	Rate (mM/hr)
91600	7	Y	0.4	10.05	Fe _{initial} 1.1E-04	0.35
					Ferric 0.003	0.48
					Ferric 0.010	0.68
					Ferric 0.030	0.81
					Ferric 0.1001	1.11
					EDTA 13	0.86
92000	7	Y	0	10.27	Fe _{initial} 1.1E-04	0.18
					Ferric 0.1	0.39
					Ferric 1	0.75
					Bicine 86	0.33
92200	7	Y	0.4	10.05	Fe _{initial} 1.1E-04	0.36
					Ferrous 0.01	0.94
					Ferrous 1.0	1.70
					Bicine 1	1.64
					Bicine 10	1.29
					Bicine 100	0.80
100200	7	N	0.4	10	Fe _{initial} 1.1E-04	0
					Ferric 1	0
100300	7	Y	0.4	10	Fe _{initial} 1.1E-04	0.37
					Ferric 1	1.77
					DEMEA 100	1.65

For experiments where chemicals were added in series of increasing concentrations, the table also provides the sequence of conditions. Experiment 92200 is an example of such an experiment. Figure 8 illustrates the times of chemical injection (arrows) and the steady-state rates (boxed) along with the concentration of responsible species. Experiment 92200 began with 7 m MEA solution with 0.4 mole CO₂/mole MEA oxidized with air to yield a steady state rate of 0.36 mM/hr. 0.01 mM of Fe⁺² was added, and a rate of 0.94 mM/hr was reached. The concentration of Fe⁺² in the MEA was increased to a total solution concentration of 1 mM by injecting 0.99 mM Fe⁺² into the reaction, and a rate of 1.7 mM was obtained. 1 mM bicine was added to this MEA solution containing 1 mM Fe⁺², resulting in a slightly decreased rate of 1.64 mM/hr. With a solution concentration of 10 mM bicine and 1 mM Fe⁺², the steady state rate fell to 1.29 mM/hr. And lastly, a rate of 0.8 mM/hr was obtained with a solution bicine concentration of 100 mM and Fe⁺² concentration of 1 mM.

Discussion

Effect of Iron

The experimental data strongly support the conclusion that iron is an important catalyst in MEA oxidation. All of the iron data are summarized in Figure 9 where the rate of NH₃ production is plotted as a function of iron concentration.

With 0.4 mol CO₂ /mol MEA, the rate of oxidation increased a factor of five with the addition of 1 mM iron. The rate increased with ferrous or ferric concentration in the same manner. This behavior is consistent with the expectation that ferrous oxidizes rapidly to ferric in the presence of oxygen with rates around 100-200 mM/hr (Brown, 1987). Essentially all iron was present as

ferric under these experimental conditions. The NH_3 production steady state rate behavior as a function of iron concentration can be described as:

$$\text{Rate (mM/hr)} = 0.36 \left(\frac{[\text{Fe}^{+3/+2}]}{0.0001 \text{mM}} \right)^{0.2}$$

It is clear from this data that as little as 1 ppm (0.01 mM) of iron in solution can cause the rate to increase a factor of three to 1 mM/hr.

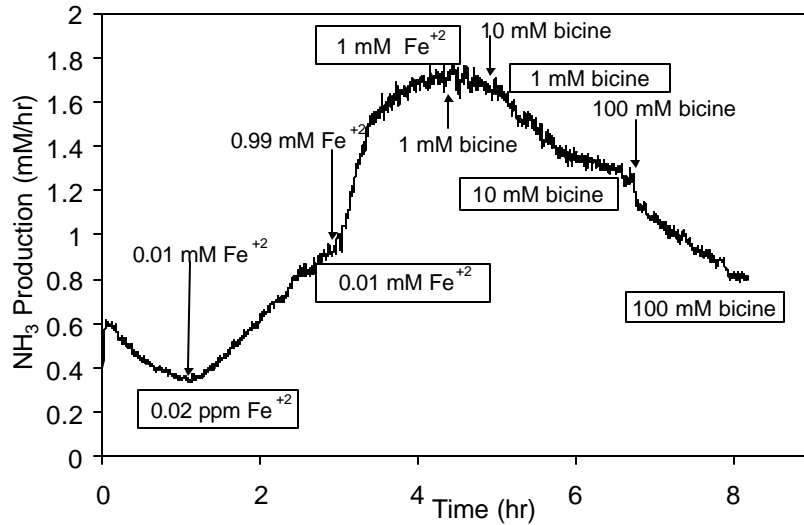


Figure 8 Injection Times and Steady States for Experiment 092200: Oxidation of 7 m MEA with 0.4 mole CO_2 /mole MEA with Air

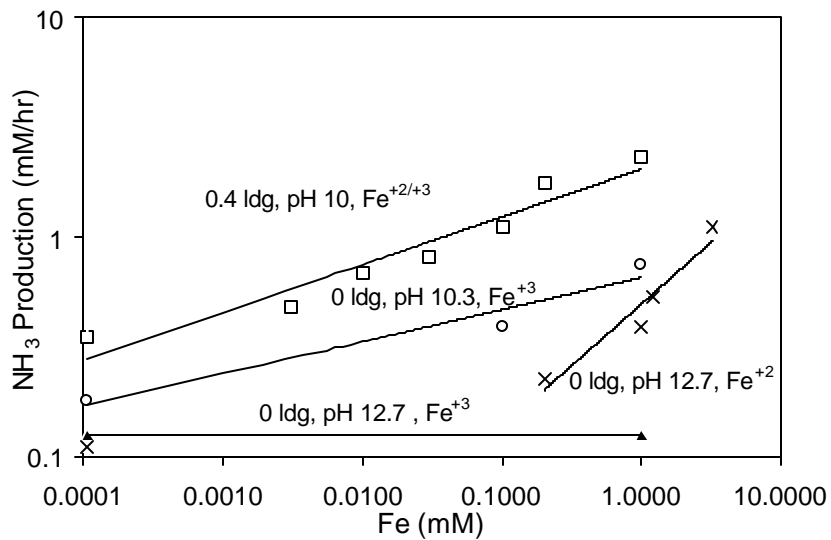


Figure 9 Effect of Iron in 7 m MEA at 55 °C. (\square Fe^{+2} and \blacklozenge Fe^{+3})

When the pH of the unloaded MEA solution was decreased from 12 to 10.3 with the addition of 0.3 mole HCl/mole MEA, a similar rate behavior was observed with ferric. The only amine species present in this particular solution were free MEA and MEA^{H^+} . The steady-state rate initially was lower than the rate in loaded solutions. The oxidation rates observed in unloaded MEA (pH 10.3) were three times slower than the rates obtained with 0.4 mole CO_2 /mole MEA. Although these rate data were collected with ferric, it is reasonable to expect that data with ferrous would follow the same trend.

In unloaded MEA (pH 12), the rate corresponding to each ferrous concentration is labeled in Figure 6. The rates can be linearly correlated with ferrous concentrations (Figure 10). When ferric was used to oxidize MEA at zero loading, the rate remained at the same steady state with the addition of ferric concentration over four orders of magnitude. A possible explanation is that ferric hydroxide ($\text{Fe}(\text{OH})_3$) precipitates at pH 12.7 seriously limiting the concentration of ferric ions in solution.

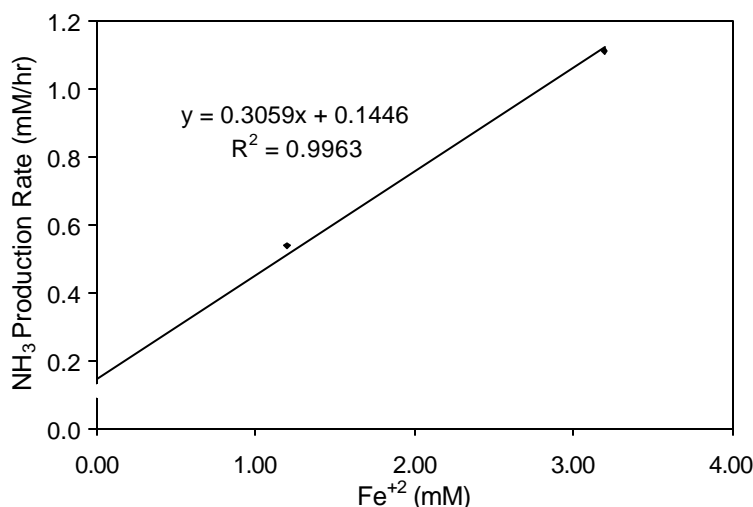


Figure 10 Rate Dependence on Total Ferrous Concentration in Unloaded MEA

The ferrous reaction stoichiometry can be derived from the data in Figure 6, where the integrated areas are shown.

Figure 11 shows the resulting stoichiometry as a function of the ferrous *added* (not total ferrous). The stoichiometry (mol NH_3 produced/mol Fe^{+2} added) varied from 0.1 to 0.33. This is consistent with the expected mechanism of iron oxidation (Stumm and Lee, 1961). Ferrous oxidizes to ferric in the presence of oxygen to produce the oxygen radical O_2^{\bullet} and the hydroxide radical OH^{\bullet} . O_2^{\bullet} is generated only when oxygen is present, but OH^{\bullet} can be generated when ferrous reacts with hydrogen peroxide (H_2O_2). If OH^{\bullet} is responsible for the oxidation of MEA, then 3 moles of ferrous produce 1 mole of OH^{\bullet} which can attack a mole of MEA to yield 1 mole of NH_3 . The stoichiometry consistent with this mechanism would range from 1/3 to smaller ratios depending on the efficiency of the reaction. It is intuitive that not all the OH^{\bullet} would react with MEA; it can react with more ferrous as suggested by the mechanism. The moles of NH_3 produced per mole of ferrous decreased from 0.3 to 0.1 with each successive addition of ferrous suggesting that the reaction of ferrous with MEA was not always 100% efficient.

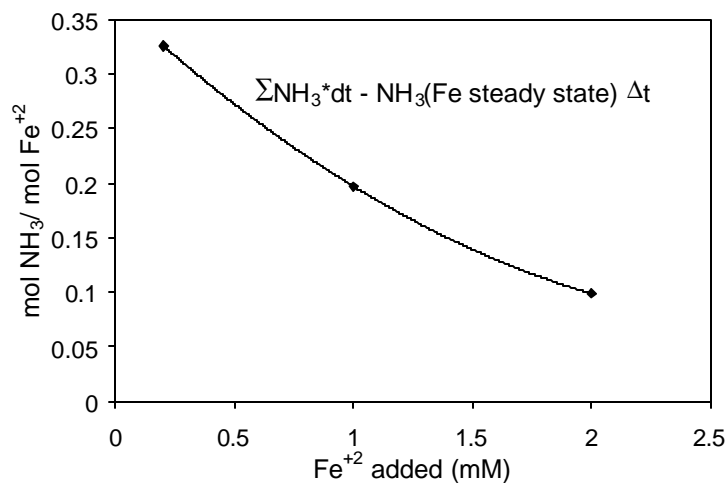


Figure 11 Ferrous Stoichiometry in Unloaded MEA

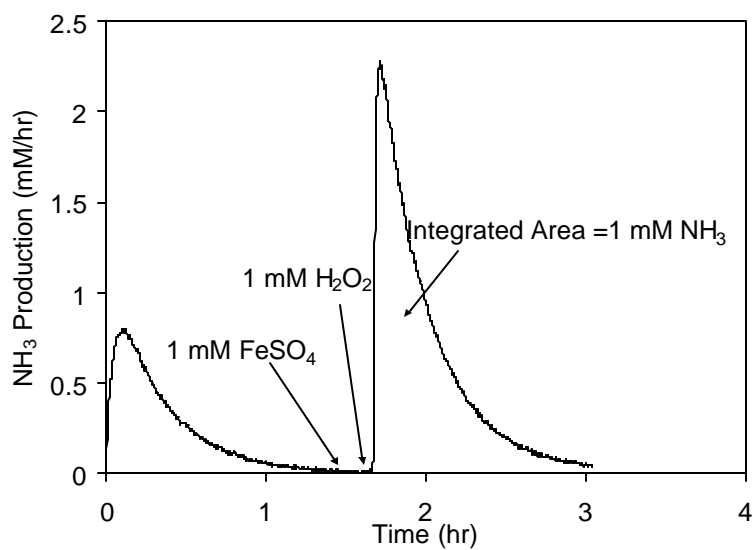


Figure 12 Oxidation of 7 m Unloaded MEA by H₂O₂ in N₂

To test the hypothesis of oxidation by OH[•], an experiment was performed in N₂, thus precluding the presence of any O₂[•]. The oxidation rate of MEA with iron in the absence of oxygen was zero as seen in Exp 70700. As expected, the addition of ferrous into a solution of MEA in the absence of oxygen resulted in no NH₃ being produced. When 1 mM hydrogen peroxide was introduced into this solution, 1 mM of NH₃ was produced.

Refer to Figure 12 for times of chemical injection as well as area under the peak integrated for total NH₃ produced per 1mM H₂O₂. The only radical present in this solution was the hydroxide radical and it reacted in a one-to-one ratio with MEA to produce NH₃; therefore, it is reasonable

to conclude that OH^\bullet was directly involved in the attack of a MEA molecule. The addition of KMnO_4 (exp. 70700) produced 0.97 mol NH_3 /mol KmnO_4^- .

Effect of CO_2 Loading

A dramatic increase in NH_3 production rate was observed in loaded compared to unloaded MEA solutions. This effect can be seen in the iron data. The steady-state rate in unloaded 7 m MEA solutions was consistently 0.16 mM/hr whereas the rate with 0.4 mol CO_2 /mol MEA was 0.36 mM/hr. These rates are highly reproducible as seen in Table IV.

Effect of CO_2 loading on degradation suggests that the MEA carbamate species is more susceptible to oxidation than free MEA. An alternative explanation is that the low pH of the solution allows more iron to stay in solution and catalyze oxidation.

Blachly and Ravner (1964) studied MEA oxidation by measuring NH_3 and peroxide production. The first important conclusion of this study was that in the absence of CO_2 , no degradation was observed. The addition of 1% CO_2 to the air stream simulating submarine atmospheric conditions resulted in almost instantaneous degradation characterized by the production of ammonia and peroxides.

CO_2 loading was observed to have an opposite effect on MEA oxidation, as well as oxidation of other amines, in the studies by Rooney et al. (1998). They concluded that CO_2 decreased the oxidation of amines, since the total anions (acetate, formate, glycolate) measured were less for all the amines they tested when CO_2 was present compared to when CO_2 was not present in solution.

Oxidation rates have been quantified using different degradation products. Ammonia production increased in the presence of CO_2 , whereas anion production decreased. Rooney et al. (1998) proposed that anions such as acetate and formate, are further oxidation products of their aldehyde precursors. Since these aldehydes (Figure 1) are stable species, the anions were detected much later and only in small quantities (Rooney, 1998). In loaded solutions, formaldehyde may be more readily stripped from solution because there is less free MEA present to react with it. In unloaded solutions the aldehyde may be retained by interaction with the amine; therefore, there is more opportunity for the formation of formate.

Effect of EDTA

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that binds strongly and rapidly to metal ions. EDTA was examined by Blachly and Ravner (1964) and determined to be an effective inhibitor of Cu^{+2} catalyzed oxidation of MEA. EDTA was not effective with ferrous and ferric.

Experiments with EDTA were performed in both loaded and unloaded MEA to determine its effectiveness in inhibiting oxidation. Figure 13 shows the effect of EDTA in 7 m MEA solutions with 0.4 CO_2 loading. The solid curve consists of rates measured in the absence of EDTA as a function of ferric concentrations. When 4.5 mM EDTA was injected into this solution containing 0.2 mM Fe^{+3} , the steady state rate decreased 40% from 1.77 mM/hr to 1.06 mM/hr (See Exp 91300). When 13 mM EDTA was injected into a solution with 0.1 mM Fe^{+3} , the steady state rate also decreased 40% from 1.11 to 0.86 mM/hr (See Exp 91600). Thus upon the addition of more EDTA, no further effect was observed.

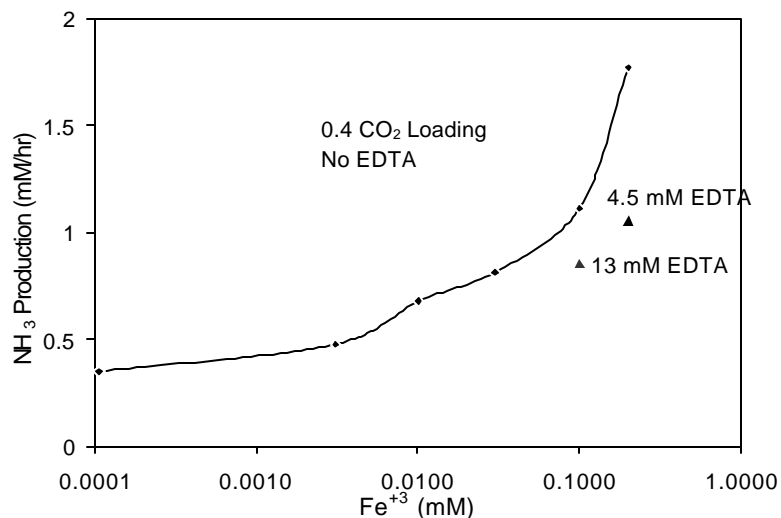


Figure 13 Effect of EDTA in 7 m MEA with 0.4 mole CO₂/mole MEA

In unloaded MEA solutions, EDTA had a negligible effect on the oxidation rate. Comparing experiments 71300 (without EDTA) to 71700 and 72600 (with 5 mM EDTA), the rates with no additional ferrous were ~0.12 mM/hr in all three cases (Table V).

Table V Effect of EDTA in Unloaded 5 m MEA with No Additional Iron

Experiment	[EDTA] (mM)	Rate (mM/hr)
71300	0	0.13
71700	5	0.11
72600	5	0.12

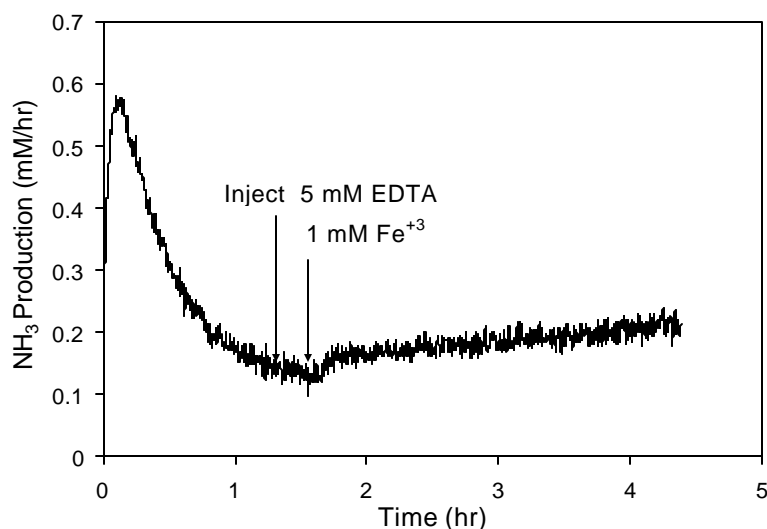
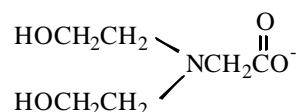


Figure 14 Effect of EDTA in Unloaded MEA with 1 mM Fe⁺³

As a matter of fact, not only was EDTA ineffective in unloaded MEA solutions, it was observed to even increase the rate of oxidation with ferric in unloaded solutions. Recall that in the unloaded MEA, ferric did not catalyze oxidation as illustrated on the bottom curve on Figure 9. However, if EDTA is added to the solution prior to the ferric, the rate was observed to increase from 0.12 to 0.2 mM/hr as shown in Figure 14.

Effect of Bicine

Bicine is a common name for the chemical compound N,N-Bis (2-hydroxyethyl)glycine. Bicine is a tertiary amine or just glycine with two ethanol groups attached to the nitrogen. At high pH, it is present in its anion form:



Bicine is a standard additive used by the U.S. Navy to minimize MEA degradation in submarines at a level of 1.5 wt% in 25 wt% MEA (Blachly and Ravner, 1964). Blachly and Ravner (1964) concluded in their study that bicine acted as a peroxide scavenger and greatly reduced oxidation of MEA by both ferrous and ferric.

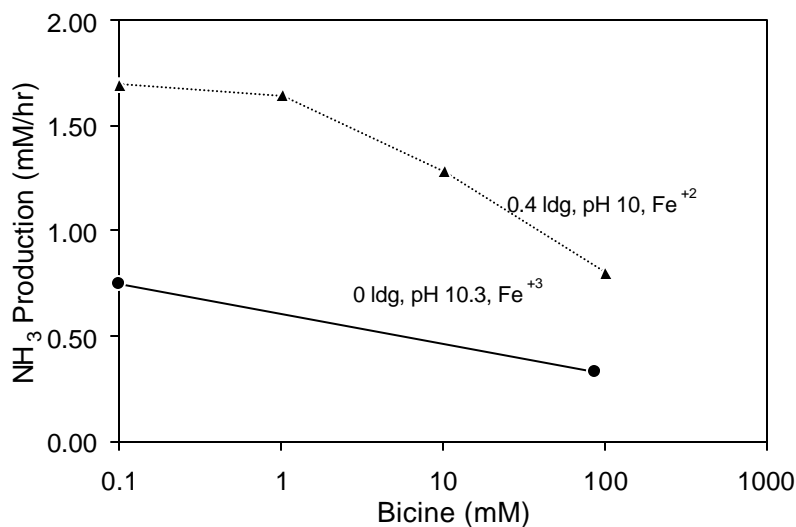


Figure 15 Effect of Bicine in 7 m MEA with 1 mM Fe^{+2/+3}

Figure 15 shows the effectiveness of bicine with 7 m MEA containing 1 mM ferrous or ferric. In both solutions (0.4 loading and pH 10.3/ 0 loading), a bicine concentration of 100 mM decreased the rate by a factor of two.

Comparison with Other Studies

Rates of MEA degradation from this study can be compared to the rates obtained in past studies. The experimental conditions and the rates for MEA direct studies are summarized in Table IV.

Table VI Comparison of Degradation Rates with Previous Studies

Study	[MEA] (m)	T °C	CO ₂ l/dg / % CO ₂	Products Detected	Analytical Method	[Fe] (mM)	Rate (mM/hr)
This Work	7	55	0.4	NH ₃	FT-IR	0.0001	0.36
This Work	7	55	1% (air)	NH ₃	FT-IR	0.0001	0.16
This Work	7	55	1%	NH ₃	FT-IR	1	0.45
This Work	7	55	0.4	NH ₃	FT-IR	1	1.7
Blachly (1964)	5	55	1%	NH ₃	Titration	< 0.0001	0.14
Girdler (1950)	3	80	50%	NH ₃	Titration	0.5-1.0	0.3
Rooney (1998)	4	80	0.25	Anions	IC	*	1.1

* Produced by Dow and used without further purification

As illustrated in Table VI, the MEA oxidation rates obtained in this study are comparable to the rates obtained in other studies. The main differences may result from variations in experimental conditions and experimental methods employed in each study. Blachly and Ravner studied oxidation in 1% CO₂, which is equivalent to the air oxidation experiments conducted in this study. Their MEA iron concentration was not reported; however, the report did specify that all MEA used was redistilled and stored at 40°F in evacuated sealed vials until needed. Therefore, their iron content should be comparable to the iron content of the low metal grade MEA used in this study. The air oxidation rate with unloaded MEA in this study was 0.16 mM/hr which compared well with the Blachly and Ravner rate of 0.14 mM/hr.

The rate of 1.7 mM/hr obtained in 7 m MEA with 0.4 mole CO₂/mole MEA with 1 mM Fe in this study was comparable to the rate of 1.1 mM/hr in 4 m MEA with 0.25 mole CO₂/mole MEA obtained by Rooney. The differences should be greater due to the iron content of the MEA used in these studies. Since the two studies were detecting different degradation products, the results cannot be directly compared.

The rate of 1.7 mM/hr obtained in this study using 7 m MEA with 0.4 mole CO₂/mole MEA with 1 mM Fe was significantly greater than the rate obtained in the Girdler study with 50% CO₂ and 0.5-1.0 mM Fe.

This work verified the inhibiting role of bicine on MEA degradation in the presence of iron (Blachly and Ravner, 1964). Figure 2.7 shows negligible degradation in MEA containing 1.5 wt% bicine and 0.5 mM iron. The effect of bicine was easily detected in this work where the rate dropped a factor of two shortly after its injection.

Blachly and Ravner (1964) concluded that EDTA (~ 40 mM) was less effective with 30 ppm (0.5 mM) of Fe⁺². The oxidation rate was as high as 0.26 mM/hr for the first two days, and dropped to 0.08 mM/hr and persisted from day three until day six. In this work, a rate of 0.3 mM/hr was observed with 5 mM EDTA and 0.5 mM Fe⁺² in 5 m MEA oxidized by air.

Conclusions

(A) Effect of CO₂ Loading

Oxidation rates with 0.4 mole CO₂/mole MEA were two times faster than rates in unloaded solutions with no additional iron. This confirms the results of Blachly and Ravner (1964) who also measured production of NH₃. It disagrees with the results of Rooney et al. (1998) who measured the production of organic acids. The rate dependence on loading as well as the rate with a typical lean loading of 0.2 are left to be determined in the future.

(B) Role of Iron

Iron is an important catalyst in oxidation of MEA to NH₃. As little as 1 mM iron can increase the rate by a factor of five with 0.4 mole CO₂/mole MEA. The rate dependence on dissolved iron from 0.0001 to 1 mM is given by:

$$\text{Rate(mM/hr)} = 0.36 \times \left(\frac{[\text{Fe}^{+3/+2}]}{0.0001\text{mM}} \right)^{0.2}$$

In loaded solution, the rate depends on the total concentration of iron in solution, regardless of its oxidation state. In order to minimize oxidation of MEA, it would be necessary to decrease the iron content below 0.01 mM.

Without CO₂, only ferrous ion catalyzes oxidation. Ferric does not appear to increase NH₃ production in unloaded solutions, possibly due to its solubility limit at high pH. The steady-state rate of NH₃ production depends linearly on ferrous ion:

$$\text{Rate (mM/hr)} = 0.306 [\text{Fe}^{+2}] + 0.145$$

In unloaded MEA solutions, the reaction stoichiometry ranges from 0.1 to 0.3 moles NH₃/mole Fe⁺² added. Hydrogen peroxide reacts with MEA in the absence of O₂ to produce 1 mole NH₃/mole H₂O₂. It can be concluded from these results that the hydroxide radical was responsible in the degradation of MEA to NH₃.

(C) Oxidants Other than Oxygen

Neither Fe⁺² or Fe⁺³ cause degradation to NH₃ without O₂ in loaded and unloaded MEA. The reaction of H₂O₂ or KMnO₄ with MEA rapidly produced NH₃, and the reaction stoichiometry was determined to be 1 mole NH₃/mole H₂O₂ or KMnO₄.

(D) Oxidation Inhibitors

Both bicine and EDTA are moderate oxidation inhibitors in loaded solutions. Bicine reduced the rate a factor of two in MEA containing 1 mM iron. EDTA reduced oxidation rate 20 to 40% in loaded MEA with ~0.2 mM iron. Commercial use of these chelators should consider potential adverse effects on corrosion.

(D) Application to Acid Gas Treating

Typical makeup rate in acid gas treating with 15-20 wt % MEA is 0.1 lb MEA/ton CO₂. With 30 wt % MEA, the typical makeup rate is 1.5 lb MEA/ton CO₂. The rich loading is 0.45, and the lean loading is 0.2. Assuming a liquid holdup of five minutes, the typical degradation rate is 7.4 mM/hr for 30 wt % MEA and 0.33 mM/hr for 15-20 wt% MEA.

The rate of oxidative degradation was 1.8 mM/hr with 0.4 loading in 30 wt % MEA containing 1 mM of iron at 60 °C. The higher makeup rate in commercial use of 30 wt% MEA may result from higher temperature carbamate polymerization.

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