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# Catalysts and Inhibitors for MEA Oxidation

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#### Abstract

Aqueous monoethanolamine (MEA) was subjected to oxidation by  $O_2/CO_2$  at  $55\,^{\circ}C$ . Hydroxyethyl-formamide (HEF) and hydroxyethylimidazole (HEI) are the major oxidation products of MEA. Dissolved metals catalyze oxidation in the order copper > chromium/nickel > iron > vanadium. Inhibitors A, B and ethylenediaminetetracetic acid (EDTA) are effective degradation inhibitors. The addition of the expected inhibitors formaldehyde, formate or sodium sulfite had unintended effects on MEA losses. Total carbon and nitrogen analysis shows a greater than 90%closure of the material balance.

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## 1. Introduction

Aqueous monoethanolamine (MEA) is the solvent of choice for CO  $_2$  capture from flue gas because of its high capacity for CO  $_2$  absorption and fast reaction kinetics [1]. In a typical aqueous absorption/stripping process, 7 m MEA is contacted with fluegas containing 1 to 10% CO  $_2$  and 3 to 15% O  $_2$  at 40 to 70% C to get a CO  $_2$  loading of 0.45 to 0.5 mol/mol MEA. The CO  $_2$  is stripped at 100-120% C to provide a lean loading of 0.2 to 0.4 mol CO  $_2$ /mol MEA. Solvent contaminated by degradation products is reclaimed from a slipstream.

Degradation of the solvent occurs by oxidation at absorber conditions and carbamate polym erization in the stripper [2]. Since most gas treating processes using alkanolamines have been operated in the absence of oxygen, oxidative degradation has not been quantified. Oxidative degradation is important because it can impact the environment and process economics and decrease equipment life due to corrosion.

# 1.1. Prior Work

Studies for the U.S. Navy [3-5] measured oxidation of amine solvents in the presence of 25 to 60 ppm dissolved iron. Chi and Rochelle [6] foundthat 0.0001 to 3.2mM dissolved iron produced 0.12 to 1.10mM/hrNH  $_3$  from 7 m

MEA. Sexton [7] observed hydroxyethyl-formamide (HEF) and hydroxyethylimidazole (HEI) as important products of MEA o xidation with Fe cat alyst.

 $V^{+5}$  and  $Cu^{+2}$  are corrosion inhibitors that can be used with aqueous MEA [8]. Blachly and Ravner [9] determined that  $Cu^{+2}$  at 10 ppm was even more effective than dissolve diron as an oxidation catalyst; 40 ppm Ni<sup>+2</sup> was also effective. Goff [10] concluded that  $Cu^{+2}$  had a greater catalytic effect than  $Fe^{+2}$ ; he also showed that the rate of  $NH_3$  evolution is controlled by the rate of  $O_2$  absorption into the amine when catalyzed by  $Cu^{+2}$  or  $Fe^{+2}$ .

Ethylenediaminetetra cetic acid (EDTA) has been identified as an excellent chelator for copper and iron catalysts [11-13]. Fe is a known catalyst for EDTA oxidation [14]. Iminodiacetic acid (diglycine), glyoxylic acid and cyanate have all been identified as anionic degradation products of EDTA in the presence of UV and H<sub>2</sub>O<sub>2</sub> [15].

Inhibitor A has proven to be effective with both iron and copper in aqueous MEA [1 0]. Na<sub>2</sub>SO<sub>3</sub> is a known oxygen scavenger that is used in a range of applications varying from boiler feedwater treating to food packaging [16-18]. The kinetics of sulfite oxidation in aqueous solutions are known to be very fast, and the rate of oxidation is controlled by the rate of oxygen absorption.

Formaldehyde is an expected intermediate in the oxidative degradation of MEA[10,11]. Formate is an observed degradation product from the oxidation of formaldehyde. Since both of these products may compete with MEA for oxygen, they are suitable compounds to screen as degradation inhibitors. Although formaldehyde itself is considered toxic under the Clean Air Act [19], the presence of oxygen should oxidize the formaldehyde to formate, or it may react with MEA and oxygen to form hydroxyethyl-formamide.

Previous work by Sexton [7, 20] established that hydroxyethyl-formamide (HEF), 1-2-(hydroxyethyl)imidazole (HEI), formate, and ammonia are the major products of MEA degradation with catalysis by Fe<sup>+2</sup>.

This goal of this study is to compare and contrast key liquid - and gas -phase oxidation products of MEA in the presence of these degradation catalysts and inhibitors. An oxygen consumption rate is calculated from product rates and their respective stoichiometries in order to determine whether degradation is kinetics controlled or mass transfer controlled by oxygen mass transfer. Additional details of this work and results for the oxidation of other amines are given by Sexton [20].

# 1.2. Experimental Apparatus

With low gas flow, oxygen mass transfer was achieved by vortex entrainment of 100 m l/min of  $98\% O_2/2\% CO_2$  into 350 mL of agitated amine solution controlled at  $55^{\circ}\text{C}$ . With high gas flow, 7.5 l/min of  $air/N_2/2\%$   $CO_2$  was sparged through 400 mL of agitated aqueous amine controlled at  $55^{\circ}\text{C}$ . In both cases, the gas was presaturated with water at  $55^{\circ}\text{C}$ . Additional details on the apparatus are given by Sexton [7, 20].

## 1.3. Analytical Methods

Anionic degradation products were quantified using a Dionex IonPac AS15 Analytical Column and AG15 Guard Column. The mobile phase was KOH: 2mM from 0 to 17 minutes, ramping to 45mM, and held from 26 to 40 minutes. Water used for diluting the concentrated KOH was 18.2 M $\Omega$ \*cm. MEA and cationic degradation products were quantified using two IonPac CS17 columns in series with a CSRS 4-mm suppressor. The mobile phase was 5mM methanesulfonic acid (MSA) from 0 to 7 minutes, 11mM at 7 minutes, then increased from 11mM to 39mM from 12 to 17 minutes, and held at 39mM until 20 minutes.

Nonionic degradation products were determined by HPLC with a Waters T3 C18 column using an evaporative light scattering detector (PL-ELS 2100). The nebulizer and evaporator were both set at  $50^{\circ}$ C with a  $N_2$  flowrate of 1.6 SLM and a light source intensity of 85%. The method started with 1ml/min of 98%  $H_2O/2\%$  acetonitrile (ACN) from 0-3 minutes, ramped to 80%  $H_2O/20\%$  ACN from 3-15 minutes, and held until 20 minutes.

Total amide was determined by treating samples with NaOH and determining additional released organic acids by anion chromatography. However, this method gives systematically lower hydroxyethyl-formamide than direct HPLC analysis. Therefore it is only used for formamide when HPLC analysis is unavailable.

Volatile MEA and degradation products with high gas flow were determined by a gas-phase FTIR, a Temet Gasmet<sup>TM</sup> Dx-4000 held at 180 °C. Amine solutions were loaded by sparging pure CO<sub>2</sub> with continuous weighing on a scale. Additional details on the analytical methods are given by Sexton [7, 20].

## 2. Results

Table 2 gives results at low gas flow rates. The total MEA loss is calculated from initial and final MEA as determined by cation IC; MEA loss rates less than 0.4mM/hr are too small to detect using this method. The total C and N in products was calculated without including formamide by IC or unknowns by HPLC. Total oxygen consumption from products was calculated by multiplying each product rate by its oxygen stoichiometry, shown in Table 1.

Table 1. Oxygen Stoichiometry for Important Liquid and Gas-Phase Oxidative Degradatio
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Product	Stoichiometry (n)
NH <sub>3</sub>	0.0
Formaldehy de	0.25
Formic Acid	0.75
HEI	0.625
HEF	0.75
NO	1.25
$CO_2$	1.25
HNO <sub>2</sub>	1.5
$N_2O$	2.0
Oxalic Acid	2.0

Table 2. Oxidative Degradation Product Rates (mM/hr), Low Gas Flow (7 m MEA, 55°C, 100cc/min 98%O<sub>2</sub>/2%CO<sub>2</sub>, 0.4 moles CO<sub>2</sub>/mole MEA, 1400 RPM), 10-14 days

	Catalyst Effect				Successful Inhibitors					Unsuccessful Inhibitors			
Catalyst (mM)							•					-	
Fe	1			0.1		1	1	1	1	1		1	1
V		1											
Cr/Ni			0.6/0.1		0.6/0.1								
Cu				5						İ	5		
Inhibitor (mM)													
Inhibitor A					100								
Inhibitor B						7.5							
EDTA							2	10	100				
CH₂O										500	500		
Na <sub>2</sub> SO <sub>3</sub>												100	
$CH_2O_2$													500
Results (mM/hr)													
MEA Loss	3.8	2.1	8.0	10.3	1.0	1.2	8.6	1.5	0.1	5.1	8.0	5.1	4.5
Cin Products	6.3	1.6	5.3	20.0	0.0	0.1	3.8	0.7	0.0	5.8	14.6	5.4	4.5
N in Products	2.5	0.6	2.1	7.1	0.0	0.0	1.4	0.2	0.0	2.3	5.3	2.0	2.0
O <sub>2</sub> Consumpt ion	1.9	0.7	1.8	5.6	0.0	0.2	0.9	0.2	0.0	1.7	3.6	1.6	1.6
HPLC (mM/hr)													
HEI	0.66	0.11	0.59	1.70	0.00	0.00	0.37	0.06	0.00	0.64	1.28	0.59	0.55
HEF	0.77	0.10	0.00	3.25	0.00	0.00	0.50	0.09	0.01	0.00	2.27	0.00	0.00
Total unknowns	2.28	0.49	2.91	1.49	0.00	0.00	0.53	0.10	0.06	2.64	0.96	2.87	2.40
Anion IC (mM/ hr)													
Formate	0.29	0.06	0.29	0.73	0.00	0.04	0.05	0.06	0.01	0.22	0.36	0.08	0.14
Formami de	0.35	0.12	0.43	2.35	0.00	0.10	0.21	0.10	0.00	0.68	0.76	0.35	0.42
Oxami de	0.09	0.15	0.19	0.42	0.00	0.03	0.09	0.02	0.00	0.06	0.21	0.31	0.09
Nitrite	0.21	0.05	0.23	0.29	0.00	0.00	0.02	0.00	0.00	0.25	0.17	0.13	0.30
Derived Results													
N in solution (M)			4.14		4.77	4.77			4.91	4.52			4.24
C in solution (M)		10.00	9.82	8.73	5.00	5.00			9.47	9.44	9.54		9.53
N Imbalance (mM/hr)			3.31		0.00	0.09			0.00	1.26			0.19
C Imbalance (mM/hr)		2.88	10.15	0.00	1.91	2.15			0.00	2.79	1.1		2.65

Product rates (mM/hr) are calculated from the final sample analysis and the total reaction time. Amides were determined by both HPLC (HEF only) and anion IC (all general amides). However, the HPLC gives consistently

greater concentration for formamide and is believed to be more reliable. Therefore it has been used in all material balances. Concentrations for unknown peaks from HPLC were estimated assuming the calibration curve for HEI.

Nitrogen in solution was determined using Kjeldahl analysis; total organic carbon in solution was calculated using a Shimadzu TOC analyzer. The nitrogen imbalance is nitrogen unaccounted for after MEA nitrogen and product nitrogen concentrations are subtract ed from total nitrogen in solution; the carbon imbalance is calculated in a similar manner.

Table 3 gives both liquid-phase and gas-phase product rates at high gas flow. For each volatile component, the continuous production rate is integrated over the entire experiment time and reported as an average rate (mM/hr). The overall MEA loss was calculated using cation chromatography and volatile MEA loss was calculated using FTIR. The difference between these two rates gave an MEA degradation loss rate. In 7 m MEA at low gas, the catalyst activity is in the order Fe/Cu > Cr/Ni > Fe > V. With Cu, the oxygen consumption rate is considerably higher than other catalyst systems, suggesting that oxygen mass transfer may be enhanced by reaction in the boundary layer. On the other hand, vanadium catalyzed systems exhibit lower degradation and oxygen consumption rates.

Table 3. Oxidative Degradation Product Rates (mM/hr), High Gas Flow (7 m MEA, 7.5 L/min 15%O  $_2/2\%$ CO  $_2$ ,  $\alpha = 0.40$ , 1400 RPM), 7-10 days

Catalyst (mM)	1	Fe	0.1 Fe / 5 Cu		
Date	7/08	4/08	11/08	5/08	
Results (mM/hr)					
MEA Loss	5.8	3.8	3.5	5.3	
C in Products	1.5	1.1	4.8	5.0	
N in Products	2.0	2.0	3.5	4.0	
O <sub>2</sub> Consumpt ion	0.9	1.1	1.9	1.8	
HPLC (mM/ hr)					
HEF	0.00	0.00	0.87	0.91	
HEI	0.00	0.00	0.23	0.29	
Unknown Peaks	0.54	0.50	0.60	0.45	
Anion IC (mM/hr)					
Formate	0.10	0.18	0.53	0.22	
Formami de	0.16	0.49	0.92	1.05	
Oxami de	0.01	0.10	0.05	0.11	
FTIR (mM/hr)					
NH <sub>3</sub>	1.83	1.69	1.69	1.97	
CO	0.30	0.00	0.00	0.00	
$N_2O$	0.00	0.16	0.16	0.14	
NO	0.12	0.12	0.12	0.06	
$C_2H_4$	0.24	0.00	0.00	0.00	
Formaldehyde	0.09	0.02	0.02	0.01	
Acetaldehyde	0.16	0.06	0.06	0.02	
<b>MEA Volatile Loss</b>	2.5	3.2	3.2	1.9	
Derived Results					
N in solution (M)		4.33		4.39	
C in solution (M)		9.52		9.78	
N Imbalance (mM/hr)		0.46		1.66	
C Imbalance (mM/hr)		3.94		8.90	

Hydroxyethylimidazole, hydroxyethyl-formamide and formate are the most abundant degradation products at low gas. The production rate of HEF is almost an order of magnitude higher with Fe and Cu than with Fe; the production of HEI increases by a factor of three. This results in a carbon formation rate that is approximately three times greater, and an MEA loss rate that is more than double than when copper is absent from solution.

The major difference between the iron catalyzed experiment and the combined iron and copper catalyzed experiment at high gas is the increase in formate and HEF production. HEF production increases by factor of two when copper is added in the high gas apparatus. HEI is only detected at high gas in the presence of iron and copper.

Because ammonia is stripped at high gas rate, it is not available to produce HEI, which is present in much lower concentration than at low gas in the presence of Fe and Cu.

All other major degradation product formation rates, including ammonia, are similar between the two systems. This differs from the results by Goff [10] which indicate greater ammonia rates with copper.

Carbon and nitrogen formation rates in the experiment catalyzed by both chromium and nickel are approximately 15% lower than in the iron catalyzed experiment; most of this is accounted for by the reduced production of HEI. There is once again a noticeable shift from formate (and formamide) to oxalate production. However, measured MEA losses are 53% greater.

With the exception of the experiment performed in the presence of chromium and nickel, the carbon material balance ranges from 87% to 104%. Similarly, the nitrogen material balance ranges from 92% to 101% in these selected experiments.

The gap in the overall carbon and nitrogen material balances is attributed to peaks that still have not been identified using HPLC with ELSD. While HEF and HEI have been positively identified, some combination of five unknown peaks consistently shows up when degraded MEA samples are analyzed using HPLC-ELSD. Most degraded samples containing Fe only have at least 90% of raw peak area unidentified. On the other hand, only 18% to 52% of peak area remains unidentified for degradation experiments conducted in the presence of copper catalyst.

Estimating the unknown peaks as HEI reinforces prior data. Formation rates for the unknown HP LC peaks (using the HEI calibration curve) are greater in the presence of Fe or Cr/Ni than when Fe/Cu is present. Vanadium catal yzed systems exhibit the lowest HPLC production rate. This suggests that the formation of HEF and HEI is favored when Cu is present.

At high gas flow, 48% to 68% of the degraded MEA carbons have been accounted for by measured degradation products; 75% to 100% of the nitrogen loss has been accounted for in degradation products. Although the material balance is not closed, the gap is smaller for the experiments conducted in the presence of iron and copper. The carbon to nitrogen ratio ranges from 1.25:1 to 1.38:1 for this set of experiments.

Inhibitor A is an extremely effective oxidative degradation inhibitor for MEA systems in the presence of chromium and nickel (over a 99% reduction in the formation of all detectable products). Moreover, MEA loss rate was reduced by a factor of eight and is approaching the detection limits of the cation chromatography system.

Experimental results also show Inhibitor B to be extremely effective at inhibiting degradation in the presence of iron catalyst. Carbon and ni trogen-containing products are reduced by 97%, while MEA loss rates were reported in the range of the inhibited Cr/Ni system – only 25% the MEA loss rate of an uninhibited system catalyzed by iron.

Table 2 also details the effect of EDTA concentration on MEA oxidation catalyzed by iron. Both degradation product formation and MEA loss decrease as EDTA concentration is increased. This suggests that in high enough concentrations, EDTA is effective at chelating Fe and inhibiting the formation of observable oxidative degradation products.

Sodium sulfite, formaldehyde and formate were all ineffective as degradation inhibitors for the observed MEA systems. While observed products went down by approximately 15% to 20%, the MEA loss rate increased by about 30% over an iron catalyzed solution in the absence of sodium sulfite. Results from Table 2 also show the addition of formaldehyde had little impact on reducing product rates, and increased the MEA loss rate by about 30%.

The copper-catalyzed MEA system containing 500mM formaldehyde behaved quite similarly to the iron-catalyzed formaldehyde experiment. Hydroxyethyl-formamide is present at a 4:1 ratio with formate. Formate performs slightly better than formaldehyde in the presence of iron, but worse than a system in the absence of formate. Observed carbon and nitrogen products are 20 to 30% lower, but MEA losses are 20% higher.

Oxygen consumption rates range from 0.7 to 5.6mM/hr for low gas experiments performed in the absence of effective oxidative degradation inhibitors; mass transfer of oxygen into the interfacial layer of liquid determines the degradation rate for these low gas experiments. The presence of copper enhances mass transfer such that reaction is taking place in the boundary layer. Experiments performed in the presence of iron as well as a combination of chromium and nickel gave similar  $O_2$  rates.

The low oxygen rate in the presence of vanadium suggests MEA degradation may not be completely mass transfer controlled in the presence of vanadium catalyst, as it approaches rates observed at inhibited conditions. Rates for experiments performed under inhibited conditions ranged from 0.0 to 0.9mM/hr; the degradation rate in these types of experiments is expected to be limited by reaction kinetics. At high gas, o xygen consumption ranged from 0.9 to 1.9 mM/hr. Rates increased by approximately 85% in the presence of copper and iron versus iron only.

## 3. Conclusions

When both iron and copper are present in solution, HEF, HEI and MEA losses increase by a factor of 3 compared to a system absent of iron. High gas experiments supported these observations. In terms of oxidative degradation potential: copper > chromium/nickel > iron > vanadium.

Experiments with low gas flow reveal that HEF and HEI are the major oxidation products of MEA. MEA systems catalyzed by 1mM vanadium produce much less formate (as well as formamide) and HEI, but more oxamide than systems catalyzed by iron. Overall, carbon and nitrogen formation rates were lower, as well as MEA losses.

Chromium and nickel, two metals present in stainless steel alloys, also catalyze the oxidative degradation of MEA. Observed carbon and nitrogen product rates are 20% lower than in an iron catalyzed system, while MEA losses are 55% greater. This suggests that chromium and nickel combined have a greater catalytic effect than iron by itself.

Data from experiments with high gas flow show that a combination of copper and iron creates more HEF (the major carbon-containing degradation product) and HEI than iron by itself. The presence of copper in aqueous MEA solution enhances the production of both formate and HEF, which experiments show is created from either the reaction of formaldehyde or a metal-formate complex with MEA.

Ammonia is the dominant nitrogen-containing degradation product at high gas. At high gas rate,  $NO_x$  is produced and stripped from the solution. On the other hand, at low gas rate where gas is not stripped from solution,  $NO_x$  is retained in the solution and oxidized to nitrite and nitrate. High gas flow experiments show that average ammonia production is independent of metal catalyst, which disagrees with Goff's findings.

Inhibitor A reduces the formation of known products by over 99% and cuts MEA losses by a factor of eight in Cr/Ni catalyzed systems; Sexton [21] previously showed the presence of 100mM Inhibitor A reduces the formation of known degradation products by 90% in an MEA system catalyzed by both iron and copper. In the presence of iron, Inhibitor B reduces product rates by 97% and MEA losses by 75%. Low gas experiments show that a 100:1 ratio of EDTA to Fe is necessary to sufficiently inhibit the oxidation of MEA. At this ratio, no observable MEA losses or oxidative degradation products are detected.

The addition of formaldehyde, formate or sodium sulfite had an unintended effect on MEA losses. They actually increased the rate at which MEA degraded. While observed products decreased, MEA losses increased by 20% to 30% in the presence of these potential inhibitors; the greater concentration of unidentified products offsets the decrease in observed products.

Under assumed mass transfer conditions in the low gas apparatus, calculated oxygen consumption ranges from 1.6 to 1.9mM/hr in all experiments performed in the presence of Fe and Cr/Ni, 3.6 to 5.6mM/hr for experiments performed in the presence of Cu, and 0.7mM/hr in the presence of V. Oxygen consumption rates were 0.2mM/hr or less under assumed inhibited conditions. The experiment performed at 2mM EDTA is in the region controlled by both kinetics and mass transfer.

Total carbon and nitrogen analysis shows that, with the exception of the low gas experiment performed in the presence of Cr and Ni catalyst, there is over a 90% material balance on all selected low and high gas flow experiments.

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