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Oxidative degradation mechanisms for amines in flue gas capture

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Abstract

The use of amines for CO_2 capture from flue gases involves one distinct difference and challenge from traditional amine acid gas capture: the presence of dioxygen and its role in the oxidative degradation of the amine. Insights on mechanisms of degradation in flue gas CO_2 capture can be obtained from observations of other gas treating processes – primarily trace O_2 contamination in "traditional" gas treating amine units as well as the autoxidation of amino acids during oxidative dehydrosulfurization using iron chelates. Three distinct pathways for degradation initiation will be discussed: thermal, direct metal ion oxidation and dioxygen reduction intermediate reactions (most likely generated from metal ions). Possible mechanisms will be tied together within a framework of varied amine plant process conditions, pointing out where each mechanism may be an important contributor to the overall amine degradation. The ultimate goal of these considerations is to predict and control amine degradation in CO_2 capture systems.

1. Introduction

Regenerable amine systems are often proposed to capture CO_2 from direct fired power plants. Though amines have been used and studied for decades for removal of CO_2 from hydrocarbon streams [1], their use in an oxidizing environment such as a flue gas has been more limited. Amine degradation can produce several negative effects on the operation of a gas treating unit.

1. Operating Cost
    a. The replacement cost of amine for an MEA system was shown by Saxena [2] to be about 4% of the total cost of CO_2 sequestration. It should also be realized that solvents which are more costly than MEA may have lower degradation rates or may reduce other cost factors such as energy or capital.
    b. increased viscosity caused by degradation could increase the costs associated with solvent pumping.
2. Performance
    a. mass transfer limitations can be caused by increased viscosity
    b. modified vapor-liquid equilibria – conversion of the original amine to alternate amines will usually change the solution alkalinity. More basic amines may have higher affinities for CO_2 and exhibit favorable reaction kinetics, but may result in higher regeneration energies. Build up of salts in solution will reduce the equilibrium physical solubility of CO_2.
    c. Formation of acidic degradation products will form non-thermally regenerable salts (heat stable salts) which will reduce the solution's capacity for CO_2. Technologies such as electrodialysis and ion exchange can be used to regenerate heat stable salts.
3. Capital/Material of Construction Issues – acidic degradation products may be more corrosive and some diamines produced may act as chelants to remove protective films from metal surfaces. Such corrosivity could necessitate more expensive materials of construction.

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The influence of O_2 on amine degradation in non-flue gas applications has received limited study [3]. Much of the chemistry that has been reported for flue gas applications is the same [4,5], though the problem becomes more acute with the increase from parts per million O_2 impurity levels to the percentage levels found in flue gas. Additional complications arise from other flue gas impurities such as SO_2, NO_x and fly ash.

It is important to realize that degradation conditions will vary within the gas treating plant. As will be explored in this paper, different mechanisms may be involved in different parts of the plant. For instance, the highest O_2 concentration and the lowest temperature will occur within the absorber while the highest temperature and lowest O_2 content will be found in the reboiler.

Though traditional gas treating applications involve only trace amounts of dioxygen, organic compound degradation has been well studied in the iron chelate hydrodesulfurization processes such as SulFerox[SM] and LOCAT[TM]. In these processes air saturation is often encountered. The chemistry of these processes [6,7] involves the use of ferric complexes to oxidize H_2S to elemental sulfur which precipitates and is filtered from solution. The reduced iron complex is then reoxidized to the ferric state by contact with air. In this type of process, large amounts of the amino acid chelating agent are degraded until makeup ligand must be added to the solution. A large effort by several companies and academic groups was directed toward the understanding and control of this degradation. In this report some learnings from that process will be applied to the degradation occurring during flue gas CO_2 capture.

There are two major types of possible amine degradation mechanisms that will be discussed in this paper:
  A. Thermal degradation (in the absence of CO_2 and O_2)
  B. Autoxidation – degradation in which O_2 participates. These reactions can be important for starting materials, degradation products and CO_2 reaction products.

A third type of degradation involving irreversible reactions between CO_2 and amines will not be discussed in this report. The further reaction of primary and secondary amines to form oxazolidones and diamines has been thoroughly reviewed [8,9]. The diamines formed via these routes can greatly contribute to corrosion. Though this report shall center on the degradation reactions of tertiary amines, primary and secondary amines can also undergo similar reactions of types A and B. It should also be realized that these reactions can transform tertiary amines to primary and secondary amines which can undergo the irreversible reactions with CO_2.

2. Thermal (Anaerobic) Degradation

In a standard amine scrubber configuration, the highest temperature experienced in a reboiler is usually about 130°C. Most industry experience has shown that thermal degradation is not significant under these conditions. More recently there have been discussions of the energy saving advantages of running a stripper at elevated pressure and temperature, especially for CO_2 capture. This could mean temperatures much higher than 130°C.

Shown in Figure 1 are several possible pathways for thermal reactions of amines. Most thermal degradation reactions discussed in the literature (for amino acids [10] and amines such as piperazine [11]) fall into the realm of pyrolysis with temperatures above 500°C. These reactions involve C-C and C-N cleavage as well as elimination of H_2 followed by HCN elimination.
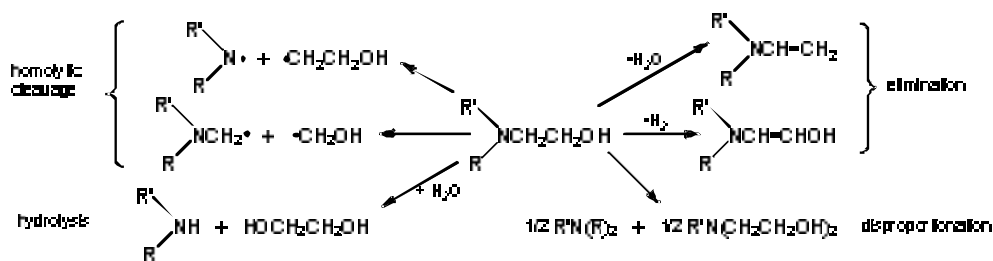

Figure 1. Modes of Thermal Degradation.

Studies of alkanolamine thermal degradation in gas treating applications are very limited. Reza [12] investigated the anaerobic degradation of both DEA and MDEA at 200°C. DEA with CO_2 showed the most degradation (and higher than that of DEA with H_2S). Presumably the DEA/CO_2 system involves some of the reactions of CO_2 with primary and secondary amines which were referred to earlier. In the case of MDEA, the degradation rate increased equally with CO_2 or H_2S loading which strongly implies

that there is a pH effect and not a CO_2 specific reaction. Davis [13] also studied the degradation of several amines at 135°C at various CO_2 loadings and concentrations.

Most homolytic cleavage reactions have been studied at very high temperatures and no data have been reported for elimination reactions of the type shown above under flue gas capture conditions. A close example of hydrolysis of alkanolamines is the hydrolysis of amino acid chelating agents. The following reaction (Figure 2) was studied at 175° and 200°C by Martell [14,15].
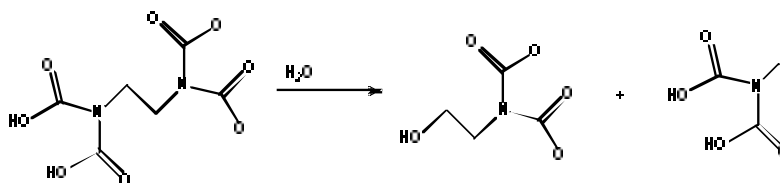

Figure 2. Hydrolysis of Amino Acid Chelating Agents.

From these results, an activation energy of 37 kcal/mol was calculated. These results can be used to calculate the hydrolysis of EDTA at 135°C which predicts a ½-life of about 11 days. The Davis studies at 135°C with 0.4 loading of CO_2 show the following ½-lives: AMP = 637 days, MEA=71 days, MDEA = 57 days, DETA = 8 days. Thus on the basis of relative reaction rates, hydrolysis is a reasonable pathway. Though substantial hydrolysis of cyclohexylamine to cyclohexanol was demonstrated at 260°C in four hours (in the presence of a catalyst) [16], others have suggested unfavorable thermodynamics for hydrolysis of both amines and amino acids [17].

No product analysis was provided in either the Davis or Reza thermal degradation studies and recent work at Dow failed to detect more than trace quantities of ethylene glycol, the expected product of hydrolysis. Two major products identified in the Dow study during the anaerobic degradation of MDEA were TEA and DMEA. That they were formed in equimolar amounts at the early stages of reaction is consistent with the disproportionation (or transethoxylation) reaction in Figure 3.
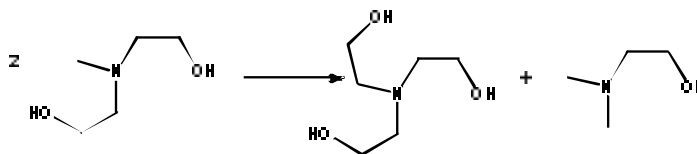

Figure 3. Disproportionation of MDEA.

This alkanolamine "scrambling" chemistry is supported by reactions reported by BASF [18] in which mixtures of TEA and ammonia are heated together with a strong base at 250°C to produce MEA and DEA. The formation of small amounts of bicine, a TEA autoxidation product has been reported to form in non-flue gas applications of MDEA [19].

Another form of oxidation that can occur absent of dioxygen is that of direct oxidation by a metal ion. For example, Martell has shown that Fe(III) will oxidize EDTA to produce CO_2, formaldehyde and decarboxymethylated product ED3A [20]. This reaction was studied at 100-140°C in the absence of dioxygen with a reported activation energy of 29 kcal/mol. The calculated half-life at 135°C is 3.4 hours. Thus the direct reaction of Fe(III) could be two orders of magnitude faster than the metal-free reactions discussed above. Such a reaction could involve the one-electron oxidation by Fe(III) to produce the amino acid radical shown in Figure 4.
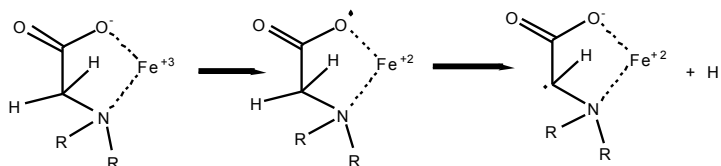

Figure 4. One-electron Oxidation by Metal Ions.

Martell suggested a mechanism in which the radical is further oxidized by another Fe(III) to produce an α-hydroxy compound which decomposes to formaldehyde and CO_2.

Other metal ions with the proper redox potential should be able to participate in a similar intramolecular oxidation. For instance, Kumar [21] reports that Ag(II) will oxidize MEA at (presumably) room temperature with a half life of 1.2 hours. Kumar also detected formaldehyde as a product and proposed that the radical formed (from the one electron oxidation) decomposed to

formaldehyde and a methylamine radical which could recouple or further decompose (with assistance from Ag(I)) to formaldehyde and ammonia.

These direct oxidation studies showed relatively fast reactions utilizing a 1:1 ratio of the substrate to metal ion. In flue gas amine chemistry, this is most likely a trace chemistry (metal ions due to fly ash leaching or corrosion) issue, but one which should occur at substantial rates in the higher temperature regimes of th e process.

Chi [22] studied the effect of metal ion spiking (including both ferrous and ferric) on MEA degradation. Though most experiments were performed in the presence of O_2, a few were performed under N_2 with Fe(III) salt spiking and did not exhibit degradation. There are several possible explanations for why no degradation was seen.

1. Chi monitored ammonia production and not MEA disappearan ce. It is probable that ammonia is not an initial product of Fe(III) attack on MEA.
2. The temperature (55°C) and times employed in the experiments were not sufficient to see direct oxidation by Fe(III). The temperature employed by Chi was more representative o f absorber conditions than that in the reboiler.
3. Soluble iron may not have existed at the conditions of the experiment due to ferric ion hydrolysis and precipitation of $Fe(OH)_3$.

The last point about the solubility of iron in metal ion spiking experiments deserves some consideration. The oxidizable substrate in the chelant degradation studies is of course desig ned to hold metal ions in solution while most gas treating amines are not as effective. Table 1 compares the calculated maximum free Fe^{3+} ($Fe(H_2O)_6^{3+}$) concentration based on an aqueous solubility product const ant along with a "free" Fe^{3+} concentration cal culated from known stability constants for Fe(III) + T EA using concentrations found in typical metal ion spiking experiments. In this case for several pH values (covering varied CO_2 loadings) the calculations show that the "free" Fe^{3+} concentrations gre atly exceed its maximum solubility. Thus in a spiking experiment with this system, one would expect that most of the iron will (at equil ibrium) end up as a solid phase and thus may not serve as a good model for Fe(III) dissolved into the solution from fly ash leaching or corrosion mechanisms.

Table 1. Calculated Fe^{3+} concentrations for 4.9M TEA with 0.001M Fe (III) at 25°C. Ksp = 2.5 x 10^{-39} = $[Fe^{3+}][OH^-]^3$. Speciation based on $TEAH^+$, $[Fe(TEA)]^{n+}$, $Fe(TEAH)^{n+}$ Values from reference 23 and 24.

pH	[OH⁻]	Max Allowable [Fe³⁺]	Calc. [Fe³⁺]
9	10^{-5}	2.5 x 10^{-24}	2.3 x 10^{-11}
10	10^{-4}	2.5 x 10^{-27}	2.1 x 10^{-11}
11	10^{-3}	2.5 x 10^{-30}	2.0 x 10^{-11}
12	10^{-2}	2.5 x 10^{-33}	2.0 x 10^{-11}

In contrast to the Fe^{3+} system, a similar calculation using Cu(II) equilibrium constants s howed that free Cu^{2+} concentrations are orders of magnitude below the solubility limits. Therefore spiking experiments under these conditions can be considered to be homogeneous, though different Cu (II) - amine species may exhibit different reactivities than simple aquo Cu(II).

To summarize about thermal (an aerobic) degradation: under standard and high temperature reboiler conditions, decomposition (via hydrolysis or disproportionation) of amines occurs as a relatively slow process. The introduction of metal ion contaminant s may allow for a much faster oxidation to occur. Both of these processes could be more important when combined with dioxyg en, the subject of the next section.

3. Degradation in the Presence of Dioxygen - Autoxidation

Oxidation of most stable organic compounds is sluggish at room temperature and occurs readily only at high temperature. Obviously the amines in flue gas capture applications experience a higher temperature, but still low relative to pyrolysis conditions. This low kinetic reactivity of dioxygen can be explained by considering spin conservation requirements. The ground state for O_2 is a triplet (a diradical). Most stable organic compounds and the dioxygen reduction products, H_2O and H_2O_2 are singlet molecules. The direct reaction of a triplet molecule with a singlet to give singlet products is a spin -forbidden process. This means that the reaction between dioxygen and substrate should occur at a very low rate, which is determined by the time required for spin in version to occur. This is generally a slow process except at elevated temperatures.

In reported studies of amine autoxidation, combinations of high O_2 partial pressures, higher than ambient lab temperatures, and long reaction times (often several weeks) had to be employed to see substantial degrees of reaction. Metal ion spiking resulted in much faster reactions. As discussed earlier, the metal ions may directly react with amine, but in the presence of dioxygen, they may act as catalysts to activate t he dioxygen. Metal complexes, due to their abilities to act as radicals with varied spin multiplicities can provide spin -allowed pathways for reaction. Thus, reaction of dioxygen and amine is spin-allowed if the number of electrons on a ternary complex (metal ion + amine + O_2) remains constant throughout the reaction.

Dioxygen complex intermediates as oxidants. Amine complexes of Fe(II), Cu(I) and other metal ions have been shown or proposed to form dioxygen complex es, both stable and short-lived [25,26]. Oxidation of amines via dehydrogenation of the C-N bond has been demonstrated via Co(II) dioxygen complexes, though the reaction was limited to amines with aromatic groups that could form conjugated imine products. Aliphatic amines such as tetraeth ylenepentamine did not oxidize in these cobalt systems and the amine ligand/Co(II) system was well known to form stable dioxygen complexes [38]. Other metal complex dehydrogenations of coordinated amines which may proceed via short lived O_2 complex interm ediates include autoxidation of ethylenediamine (dehydrogenation of both C-N bonds) with Ru(II) [39,40] and Os(II) [41], macrocyclic amines with Fe(II) [42] and peptides with Co(II) [43]. Whether or not dioxygen complexes are involved, dehydrogenation rea ctions (imine formation and subsequent imine products) of amines should be considered when in the presence of transition metal ions and dioxygen.

Free radical pathways for autoxidation. In studies of the iron chelate hydrodesulfurization degradation, it was noticed that long (several days) exposure to air sparging at room temperature did not cause degradation. This was consistent with the predicted slow amino acid hydrolysis and oxidation by Fe(III). It was only after introducing the reducing agent H_2S that ligand degradation was detected. Iron chelates, synthesized with Fe(II) and converted to Fe(III) with air, also exhibited degradation. This chemistry can be explained in terms o f dioxygen reduction products such as superoxide, peroxide and hydroxyl radical.

It should be remembered that these reduction intermediates are weak acids and may exist in two protonation states in amine solutions. As shown by the pKa values in Figure 5, superoxide should exist in the anionic form, peroxide in both mono and diprotonated forms and hydroxyl radical can also exist as the oxide radical anion. For example, with pKa values of 11.7 and 11.8 (values at 25°C), both oxide radical anions and hydroxyl may exist in an unloaded (lean) amine solution, while high CO_2 loadings will lower the pH enough so that hydroxyl will predominate. The rate constant for reaction of glycine anion has been reported to be ten times higher for hydroxyl than for the oxide radical ion.
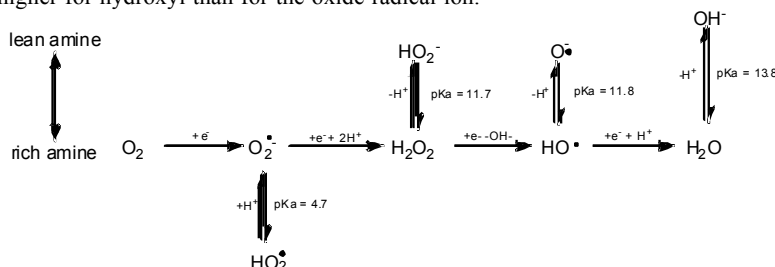

Figure 5. Primary Dio xygen Reduction Species at Amine Process Conditions.

For the amino acid chelants, it was noted that the most reactive species was hydroxyl radical (HO ·). Compilations of reaction rates [27] show that compounds such as E DTA, NTA, HEDTA, and glycine have reaction rate constants of 10^9-10^{10} L-mole^{-1}s^{-1}. Products that were seen to build up in solution had lower reactivities toward hydroxyl. For instance, the rate constant for oxalate (which can build up to problem levels in the process) was only 7.7 x 10^5. It was also shown that additives which had high hydroxyl radical rate constants (such as thiosul fate and sulfite) could act as hydroxyl radical scave ngers [28]. Because the rate constants were close to diffusion limitations and because of the high substrate concentrations, these additives could only act as competitive scavengers and not totally eliminate the degradation.

Data on reactivity of amines w ith dioxygen reduction intermediates are harder to find, but some of the results shown in Table 2 support the highest reactivity for hydroxyl. It should be mentioned that alternatives to hydroxyl radical have been proposed to account for some subtle diffe rences between Fe(II)/H_2O_2/O_2 reactions and reactions of hydroxyl produced via pulse radiolysis [37]. For purposes of this discussion, it is easiest to consider the chemistry in terms of hydroxyl radical.

Schwartz [31] presented the scheme in Figure 6 for the anaerobi c reaction of hydroxyl radical (formed via radiolysis) with TEA. The driving force for reactions with hydroxyl is usually the formation of water with C -H bonds being the ones most often abstracted. Though C -H bond dissociation energies (BDE) are significantly lower than those of O-H, BDE's for N -H are closer to those of C -H, which could allow for N -H abstraction in some cases of primary and secondary amines [46].
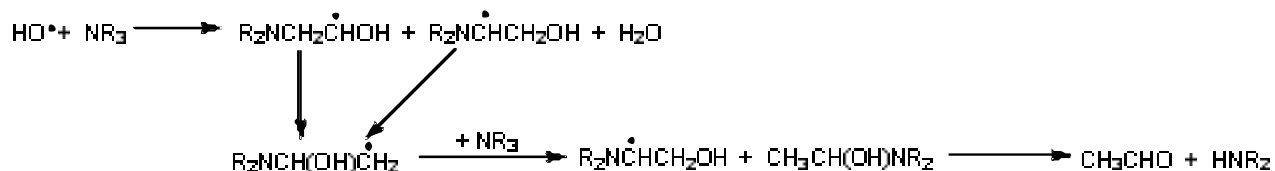
Figure 6. Oxidation of Tertiary Amines by Hydroxyl Radical
Table 2 . Rate Constants for Dioxygen Reduction Intermediates at 25°C.

REACTION	RATE (L -mol^{-1}-s^{-1})	REF
Dioxygen: $RH + O_2 \rightarrow$ products	slow	
n-propylpyrrolidine + O_2	1.1×10^{-3}	29
Superoxide: $RH + O_2^{\cdot} \rightarrow R\cdot + HO_2^{-}$		
$(HOCH_2)_3CNH_2 + O_2^{\cdot}$	<0.42	30
Glycine + $O_2^{\cdot}$	48.6	30
Glycine + $HO_2\cdot$	<0.001	30
Peroxide: $RH + HO_2^{-} \rightarrow R\cdot + HO\cdot + H_2O$	slow	
Hydroxyl: $RH + HO\cdot \rightarrow R\cdot + H_2O$	10^8-10^{11}	
Ethylenediamine + $HO\cdot$	5.5×10^9	27
Ethylamine + $HO\cdot$	5.1×10^9	27
Triethylamine + $HO\cdot$	1×10^{10}	27
TEA + $HO\cdot$	8×10^9	31
$TEAH^{+} + HO\cdot$	2×10^9	31

Once the reaction has been initiated by formation of the carbon based radical, subsequent reaction with dioxygen should be extremely ra pid as shown by representative rat e constants presented in Table 3 . Figure 7 shows the reaction proposed for the dioxygenation of an MEA radical.

Table 3 . Reaction of Dioxygen with Organic Radicals (from reference 32).

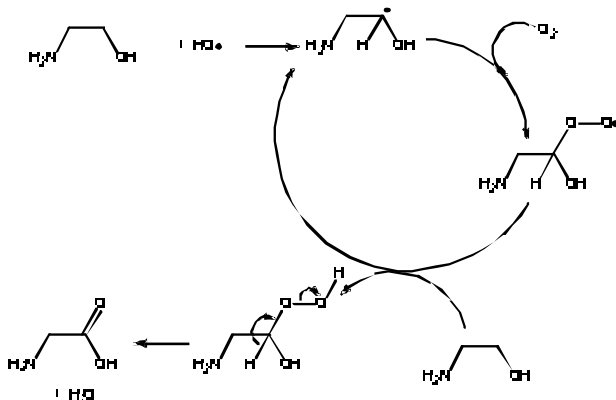| Radical	pH	K (L -mol^{-1}s^{-1})
$H_2NCHCO_2^{-}$ (glycine)	7.9	1×10^9
$^{-}O_2CCH_2NHCHCO_2^{-}$ (IDA)	7	8×10^8
$CHOHCH(NH_2)CO_2^{-}$	7	2.4×10^9
$\cdot CH_2N(CH_3)_2$	10.4	3.5×10^9

Figure 7. Proposed Reaction Pathway for Production of Glycine from MEA.

The further reaction of the organic peroxy radical involves abstraction of a hydrogen atom from another amine molecule in a scheme similar to what is often proposed in hydrocarbon autoxidations. This provides a p ot ential chain step to sustain further oxidation. Tho ugh glycine (the product shown above) has been noted as an MEA oxidation product [3], radical formation on the carbon adjacent to the nitrogen would be expected to yield glycolamid e which has not been reported as a product. It is possible that glycolamide would hydrolyze to form glycolic acid and ammonia, both of which have been noted as MEA oxidation products. In the hydrodesulfurization chelant degradation chemistry, such a keto intermediate was dete cted by mass spectral analysis in freshly degraded solutions, though only oxalate and R RNH (the expected hydrolysis products) were noted after several days as shown in the equation below.
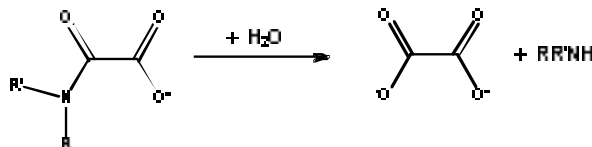
Figure 8.

Figure 9 summari zes the different radical chemistries. There are three potential pathways to form the organic radical;
  A.   the direct one-electron oxidation by a metal ion. As a high temperature reaction, this is most l ikely to occur at reboiler conditions and of course requi res the introduction of an appropriate metal ion by corrosion or fly ash leaching. Reoxidation of the metal ion can result in hydroxyl radical formation. The reoxidation process is expected to be faster than the reduction by reaction with amine. Thus in an oxygen rich environment, metal ion reduction could be a limiting factor. SO_2 derived sulfite ion is known to reduce metal ions such as Fe(III) [33] and Co(III) [34].
  B.   abstraction of hydrogen atoms by hydroxyl radical. T his abstraction as well as the dioxygen reduction which produces it should proceed at low (absorber) temperatures.
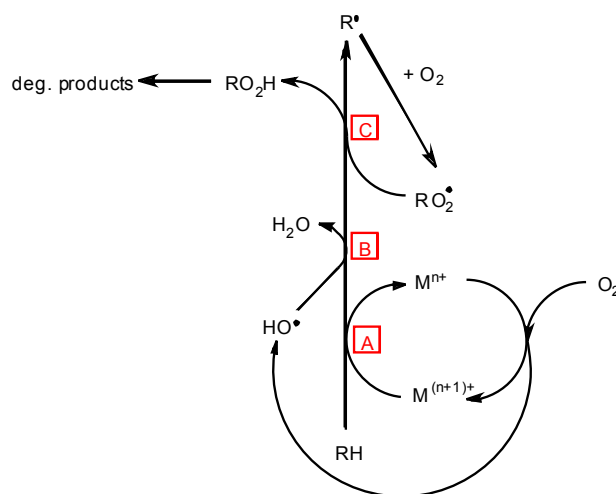 C.   abstraction of hydrogen atoms by the organoperoxy radical.

Figure 9. Amine Autoxidation Routes.

The autoxidation mechanisms shown above all depend on initiation by metal ions. This underscores the need for good flyash removal upstream of an amine scrubber.   Corrosion, the other means for introducing metal ions should be, for the most part, autocatalytic with respect to the formation of corrosive degradation products. Use of thermally stable amines and those amines not susceptible to degradation via CO_2 reactions should greatly reduce the corrosion rate and hence the amine autoxidation rate.

Additives to reduce degradation.   Various types of additives have been proposed to reduce amine degradation.
  1.   Control of metal ions with chelating agents such as EDTA has been proposed to reduce degradation of MEA in a CO_2 capture process [35]. Though some inhibition was noted, the effect was short -lived, possibly due to EDTA degradation. Use of iron chelates in hydrodesulfurization however, showed that the ferrous EDTA chelates were very potent Fenton catalysts (activating intermediate peroxide as well as dioxygen toward hydroxyl radical format ion). Additionally, EDTA would be expected to increase the degree of metal ion solubilization from contaminant fly ash and could also be corrosive toward protective films formed on mild steels.
  2.   Use of potential hydroxyl radical scavengers. A recent patent [36] claims the use of sulfite and thiosulfate to reduce amine consumption, though no examples were give which quantified the effect on amine consumption. As discussed above, there is reason to believe that additives which are capable of reducing hydrox yl radical, may also be able to reduce metal ions and assist in their redox cycling to produce more degradation.

CHEMICAL ABBREVIATIONS: MEA = ethanolamine , DEA = diethanolamine , TEA = triethanolamine, MDEA = N-methyldiethanolamine , DMEA = N,N -dimethylethanolamine AMP = 2-amino-2-methyl-1-propanol, DETA = diethylenetri amine, EDTA = ethylenediaminetetra acetic acid, ED3A = ethylenediamine triacetic acid, HEDTA = N -hydroxyethyl, N, N',N' triacetic acid, NTA = nitrilotriacetic acid

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