CHAPTER II
BACKGROUND OF ALKANOLAMINE DEGRADATION

This chapter reviews the background of alkanolamine degradation in the CO_2 removal process. The first section provides detailed information on analytical techniques used to detect and quantify alkanolamines and their degradation products. Gas chromatography (GC), liquid chromatography (LC), capillary electrophoresis (CE), and less the investigated infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) techniques are also discussed and compared. Section 2 deals with the kinetics and mechanism of oxidative alkanolamine degradation followed by degradation inhibitors used to prevent oxidative degradation of alkanolamines during the CO_2 absorption process in the third section. The concluding section reviews sulfur induced degradation of alkanolamines.

2.1 Analytical Techniques for Determination of Alkanolamines and Their Degradation Products

2.1.1 Gas Chromatography (GC)

The gas chromatography technique (GC) using conventional detectors such as thermal conductivity (TCD) and flame ionization (FID) was one of the earliest methods utilized for analysis of alkanolamines and their degradation products. Its early development was limited to separation of alkanolamines such as MEA, DEA and TEA using different packed columns. In this period, derivatization of alkanolamines prior to analysis, a tedious and time-consuming process, was required to circumvent the problems encountered with the high polarity effect of alkanolamine molecules on GC separation.

According to Brydia and Persinger (1967), prior to the analysis, MEA, DEA and TEA were first converted to trifluoroacetyl derivatives using trifluoroacetic anhydride (TFA). The derivatization served to reduce excessive peak tailing of high polar alkanolamines. The alkanolamine derivatives mixtures were then subjected to the GC technique using a column of 5% neopentylglycol succinate on Chromosorb-

G. The result showed a clear separation of these alkanolamines in which MEA eluted first followed by DEA and then TEA. Piekos et al. (1975) also used an alternative derivatizing agent of N, O-bis(trimethylsilyl) (BSA) to convert alkanolamines to less polar compounds in order to obtain a complete GC elution and reduction of peak tailing. The analysis was done on a GC column of 3% OV-1 coated on diatomite CQ stationary phase. A good separation of MEA, DEA, and TEA were also obtained. However, these techniques using derivatizing agents still suffered from a drawback in that it could not tolerate high water content in the alkanolamine solution which usually ranges from 50 to 90%.

A more favorable approach of direct GC analysis was introduced in 1977 employing a Tenax GC column of a porous polymer based on 2, 6-diphenyl-p-phenylene oxide coupled with temperature programming technique to separate completely MEA, DEA, and TEA within 8 minutes (Saha et al., 1977). Separation of alkanolamine extracted from the direct GC technique was improved in terms of peak shape and symmetry, thus, enhancing quantitative analysis.

The application of the direct GC technique was later expanded to alkanolamine degradation by Kennard and Meisen (1983). Tenax GC was used to separate MEA, DEA and TEA. In addition, it separated some degradation products of CO_2-partially degraded DEA solution. The technique was also applied to DEA plant samples, thus, confirming its industrial application.

GC capillary columns later replaced those of packed columns for degradation analysis due to their superior performances. Dawodu and Meisen (1993) investigated and compared various GC packed and capillary columns for analysis of fresh and degraded alkanolamine solutions. These columns included the following: a packed column-Tenax-TA (a porous polymer based on 2,6-diphenyl-p-phenylene oxide), which they claimed could offer better tolerance to impurities than Tenax-GC; HP-17; 50% phenyl methyl-polysiloxane based, cross-linked capillary column; DB-Wax and Supelcowax 10, which are both based on a polyethylene glycol, fused silica, cross-linked, bonded phase capillary column. A supelcowax 10 capillary column performed better than conventional packed columns in terms of analysis time, peak shape and sample size for degradation analysis.

Capillary column based GC has therefore become a powerful tool in alkanolamine degradation study. With a more advanced detector such as mass spectrometer (MS), structural identification of degradation products of alkanolamines typically encountered in a CO_2 absorption process is possible. This enables the study of degradation mechanisms. GC-MS found use in a 1991 study in which products identification of carbonyl sulphide (COS)-induced DEA degradation was attempted (Dawodu and Meisen, 1991). A mixture of COS and N_2 was used to degrade 10-40 wt% DEA solution in a stirred stainless steel autoclave. In addition to elemental and infrared analysis, GC-MS could mostly identify the major degradation products.

GC-MS was later applied to the oxidative degradation of MEA for kinetic studies (Supap et al., 2001). To improve separation of MEA and its oxidative degradation products, degraded MEA samples were diluted using deionized water with a ratio of 1 to 5 prior to the analysis. A capillary column of HP-Innowax containing cross-linked polyethylene glycol was used to separate the compounds in the temperature programmed GC oven. The MS was used as a detector generating mass fragmentation pattern for each component which was then matched with the database for identification.

A more recent study has utilized GC with multi-detectors for identification of degradation products in MEA plant samples (Strazisar et al., 2003). The detectors consisted of MS, fourier transform infrared spectrophotometer (FTIR), and atomic emission detectors (AED). A combination of 2 GC capillary columns consisting of 14 %-(cyanopropyl-phenyl)-methylpolysiloxane coated DB-1701 and nitroterephtahlic acid-modified poly(ethylene glycol) coated Nukol was used to completely characterize MEA degradation products. Multiple uses of GC detectors in this study assisted in proposing formation pathways of some degradation products.

Later studies have been focused on degradation mechanism of alkanolamines because its knowledge can assist in formulating a degradation prevention strategy. The GC-MS technique has been useful for degradation product identification. A comprehensive study of the pathways of formation of products of MEA oxidative degradation using a single GC-MS analytical tool has been reported

(Bello and Idem, 2005). Slightly modified GC-MS conditions from a previous work by Supap et al. (2001) was used for the analysis of MEA oxidative degradation products in the reported study. The MS identified a number of products by matching their mass spectra with the compound database. This information was then used to formulate oxidative degradation pathway of MEA under various conditions (i.e. with/without CO_2). In addition, a similar GC-MS technique was used by the same research group to also study role of MDEA in preventing oxidative degradation in a blended MEA/MDEA system (Lawal et al., 2005). Pathways of the oxidative degradation of mixed MEA/MDEA were proposed based on the GC-MS-identified product information.

2.1.2 Liquid Chromatography (LC)

Since GC application can be limited to those molecular compounds of high volatility, ionic species and high molecular weight products often encountered in degraded alkanolamine can be potentially left undetected. LC can overcome this limitation although it requires more steps of sample and mobile phase preparation for analysis than is encountered in the GC.

Dating back to 1982, ion exclusion technique was used to separate acid mixture degradation products in MEA, DEA and MDEA degraded liquid samples. The technique was capable of detecting carboxylic acids such as formic, oxalic and acetic acids in air-bubbled MEA, DEA and MDEA samples (Blanc et al., 1982).

The separation of various inorganic and organic anions generated by degradation reactions in rich and lean MDEA plant samples using anion exchange columns of Ionpac AS9-SC and Ionpac AS10 has been reported (Kadnar and Rieder, 1995). Three methods were developed respectively for separation of fluoride, acetate, propionate, butyrate, and formate using Ionpac AS10 with $Na_2B_4O_7$ mobile phase, determination of nitrate, phosphate, sulfate, oxalate, thiocyanate, and thiosulfate using Ionpac AS9-SC with $Na_2CO_3/NaHCO_3$ mobile phase, and detection of chloride when it could not be detected by method 2 due to the presence of carbonate. Method 3 used Ionpac AS10 with mobile phase of NaOH. The techniques

performed well in terms of compound separation and sensitivity. However, these LC techniques required a costly ion suppression system which needed to be continuously regenerated, thereby increasing the operating cost.

Rooney et al. (1998) also applied LC using anion exchange technique to the analysis of various laboratory air-degraded alkanolamines including MEA, DEA and MDEA. The study was specifically aimed at measuring heat stable salts (e.g. carboxylate ions) generated by oxidative degradation during CO_2 capture process. The technique showed its capability in detecting in ppm level, formate acetate and glycolate which were the major products found in most of the degraded solutions.

The cation exchange mode of the LC with Ionpac CS10 and CS12 A was also used to separate alkanolamines such as MEA, DEA, TEA and MDEA as well as cations in water samples, piperazine in MDEA solution, and corrosion inhibitors (Kadnar, 1999). The best separation for alkanolamines and cations in water sample was obtained with gradient step runs using Ionpac CS10 and 15-20 mM sulfuric acid mobile phase (H_2SO_4). The analysis time was also improved when the concentration of H_2SO_4 was raised to 40 mM. On the other hand, piperazine in MDEA solution could be successfully determined with Ionpac CS12A using 20-25 mM H_2SO_4 mobile phase eluent. This technique was also reported to be applicable for detecting a corrosion inhibitor in water samples also using a CS12A with 16.5 mM H_2SO_4 solution cation column.

Since the conductivity mode of the detector was used for the LC techniques described in the previous sections, additional ion suppression systems also served to lower the detector response to the eluents in order to enhance the signal from eluted compounds, thus increasing the cost of analysis. This disadvantage was later overcome by using a direct ion chromatographic technique as shown in the work of Kaminski et al. (2002). This study used a high performance liquid chromatograph (HPLC) with a Nucleosil SA column packed with a strong cationic exchange of sulphonic acid to analyze MEA, DEA and MDEA plant samples and their inorganic cations, as well as some degradation products. The conductivity detector was replaced by a less complex refractive index detector (RID)

in order to complete the analysis without a complicated ion suppression system. Mobile phases containing various ratios of potassium nitrate (KNO_3), sodium dihydrogen phosphate (NaH_2PO_4), potassium dihydrogen phosphate (KH_2PO_4), 85% phosphoric acid (H_3PO_4) and water were tested for the optimum composition. About 0.088 kmol/m^3 aqueous solution of KH_2PO_4 acidified with 85% H_3PO_4 to pH 2.6 was found to give the best separation of the alkanolamines and their basic degradation products. However, this approach was only tested in desulphurization and wastewater treatment processes. Analysis of amines and their degradation products in the CO_2 capture process using this technique has not yet been reported, to our knowledge.

A more recent study reported by Strazisar et al. (2003) also utilized ion chromatographic technique using the conductivity detector to determine inorganic species in MEA plant samples. An Ionpac CS14 cationic exchanger column was used in combination with Na_2CO_3/$NaHCO_3$ mobile phase buffer solution. This technique was able to capture sodium, potassium, calcium, iron, copper, zinc, aluminum, selenium, and arsenic cationic species in lean MEA solutions and reclaimer bottoms.

2.1.3 Capillary Electrophoresis (CE)

Up to the present time, the capillary electrophoresis (CE) technique has not been directly applied for the analysis of alkanolamines and their degradation analysis. However, its features are attractive due to reduction in costs as well as effort needed for method development as compared to the GC and LC techniques. CE also consumes almost zero liquid mobile phase and samples during analysis. The column is also simpler and lower in cost as compared to those of GC and HPLC that are both more complex and costly. However, the downside of CE is that it requires heavy dilution for high concentration applications. This might limit its use to alkanolamine analysis since the applicable concentration, using MEA as an example, is in the range of 3 - 7 kmol/m^3. But if only the degradation products which are typically present in low concentration are of interest, it can become the method of choice.

Altria et al. (1995) confirmed the benefits of CE compared to HPLC technique. This study used the CE technique to determine compounds of basic drugs including imidazole which was later detected in the current study as one of the oxidative degradation products. A basic capillary was used having the length of only 35 mm. The electrolyte was 25 mM NaH_2PO_4 adjusted to the pH 2.3 using H_3PO_4 solution. The UV detector was used throughout the analysis. Acidic drugs were also successfully analyzed later with CE using $Na_2B_4O_7.10H_2O$ as the electrolyte (Altria et al, 1997). Therefore, the CE technique shows great potential, perhaps, for the determination of basic and acidic degradation products being formed during the oxidative degradation process.

Recently, CE has been demonstrated for its use in the determination of alkanolamines in water/ethanol extracts of wrapping materials containing volatile corrosion inhibitors (Pereira and Tavares, 2004). Although, this work only aimed at using CE to analyze volatile corrosion inhibitors including MEA, DEA and TEA in plastic, paper and foam, its use could absolutely be applied to alkanolamine analysis in the CO_2 capture process. This work used a simple fused silica capillary with only 45 mm effective length. A diode array detector was used to capture the UV absorbing species in the samples. The optimal electrolyte solution consisted of imidazole, hydroxyisobutyric acid (HIBA), and 18-crown-6 ether each having the concentration of 0.01 kmol/m^3. MEA, DEA and TEA in extracted samples could be successfully separated from each other.

2.1.4 Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance Spectroscopy (NMR)

The most recent use of IR technique was also applied to the analysis of MEA oxidative degradation systems (Chi and Rochelle, 2002; Goff and Rochelle, 2004). It was used to measure the gas production rate of gaseous ammonia (NH_3) evolved from the reaction of MEA and oxygen. The measurement was done online by directing the gas outlet from the reaction chamber to the IR device. Although IR shows good potential in gas phase analysis of degradation systems, the technique does not separate degradation compounds. If used alone, it could complicate degradation product information resulting in difficult interpretation.

Nuclear Magnetic Resonance (NMR) is another powerful technique especially for structural elucidation. Without a separation attempt, MEA plant samples were directly analyzed for structural information of impurities and degradation products resulting from reaction of CO_2, COS and CS_2 with MEA (Talzi, 2004; Talzi and Ignashin, 2002). Despite the fact that complicated NMR patterns were obtained as a result of analyzing a complex mixture of degradation products, their reaction pathways were proposed. This has indicated a drawback of the NMR similar to that of the IR when a stand-alone unit of these techniques is used. Spectrum of non-separated degraded alkanolamine samples resulting from NMR reading would be highly complex. It would also contain mixed information of products, thus, hindering easy interpretation. A solution to this is to respectively combine a separation device, GC or HPLC, before the IR and/or NMR. These technique combinations, therefore, first separate alkanolamines and their degradation products before sending each component to be analyzed separately by IR and NMR, thus, enabling precise interpretation.

2.2 Kinetics and Mechanism of Oxidative Degradation of Alkanolamines

In the early stage of the oxidative degradation studies, the research was only focused on detection of the existence of the oxidation and qualitative analysis of the oxidation products. As early as 1937, a set of experiment was conducted to rank oxidation resistance of MEA, TEA and diaminoisopropanol by passing O_2 through a glass tube containing those alkanolamines for 160 hours (Gregory and Shcarmann, 1937). The resistance was found to be in the order of MEA > TEA > diaminoisopropanol. There was no information on kinetic and mechanism given from this study. Due to a limitation of the analytical technique, individual acid product of MEA oxidation in MEA alone or in glycol solution could not be identified but later detected as a steam-distillable acid mixtures (Lloyd and Taylor, 1954). MEA oxidative degradation products such as ammonia, water, carboxylic acids and amides were later identified thus confirming their existences (Hofmeyer et al., 1965).

One of the first oxidation mechanisms of MEA used for CO_2 capture was proposed in the 60's. As reviewed by Rooney et al., (1998), the mechanism attributed to Jefferson Chemical is shown in Figure 2.1. The pathway for MEA oxidation was triggered by the reaction of MEA with O_2 initially producing α-amine acetaldehyde. The acetaldehyde was further oxidized to glycine and to glycolic acid. The acid reacted with O_2 giving glyoxalic acid which was finally oxidized to oxalic acid. Although, the mechanism was useful, it only proposed oxalic acid as a final product. Not only did this mechanistic not include other degradation products, kinetic data was not provided to support the mechanism.

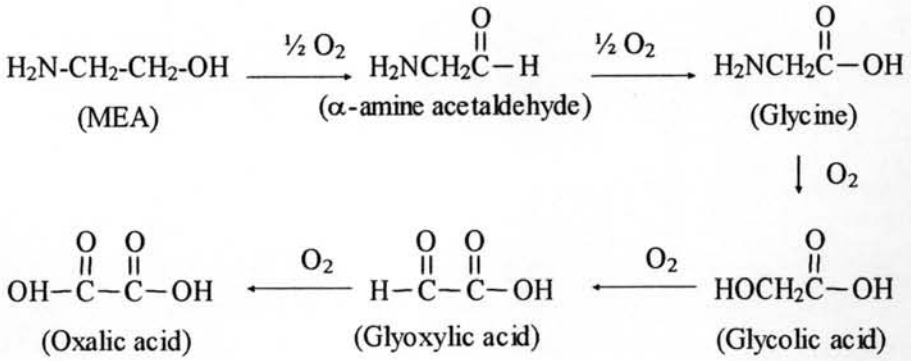

Figure 2.1 One of the first oxidation mechanisms of MEA.

In 1998, a study was able to compare oxidation resistance of various alkanolamines including their mixtures (Rooney et al., 1998). The experiments were conducted by bubbling O_2 into alkanolamine solutions with and without the presence of CO_2. In the absence of CO_2, oxidation resistance increased in the order of 30% DEA > 50% MDEA > 30% MDEA > 50% diglycolamine (DGA) > 20% MEA whereas the resistance order changed to 30% DEA > 50% DGA > 20% MEA > 50% MDEA > 30% MDEA when CO_2 was present. Various acidic degradation products were detected including formic and acetic acids. A mechanism accounting for formation of formic and acetic acids was proposed by adding their pathways into the previous mechanism shown in Figure 2.1. Acetic acid was thought to form by decomposition of MEA giving NH_3 and vinyl alcohol. They then reacted to give

acetaldehyde which finally converted to acetic acid. Formic acid was generated from fragmentation of α-amino acetaldehyde, an intermediate proposed from the previous mechanism. The modified mechanism by Rooney, Dupart, and Bacon is shown in Figure 2.2

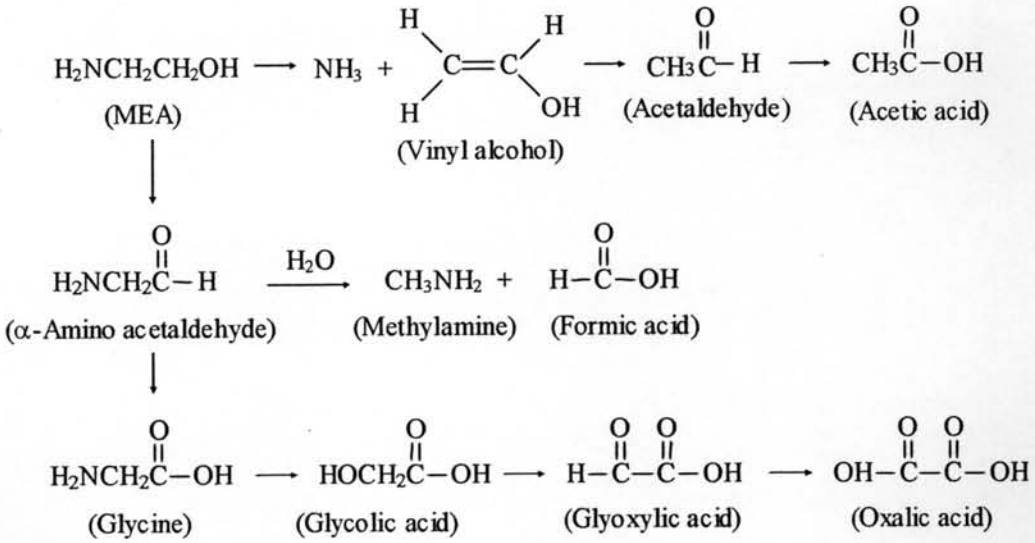

Figure 2.2 Oxidative degradation of MEA with formation pathways of formic and acetic acid (Rooney et al., 1998).

Once again, the mechanism did not account for all degradation products detected in the study. As well, the role of CO_2 was not included in the mechanism which could be a vital step in the degradation process. Although, the percent amine lost was given, it still did not show any rate information of the oxidation reactions.

In 2001, a kinetic rate expression was developed in an attemp to represent the oxidative degradation of MEA in a flue gas treating unit (Supap et al., 2001). The kinetic formulation was based on a power law analysis using the initial rate of MEA oxidation at various MEA concentrations, oxygen pressures, and temperatures. Not only did the kinetic rate model and its analysis show the complexity of the MEA oxidative degradation, the severe effect of O_2 was also confirmed by its order of reaction. The degradation rate was also found to be sensitive to an increase in temperature and the concentrations of O_2 and MEA. Although this study presented a useful kinetic model for prediction of MEA oxidative degradation, the model was not

developed based on any mechanism. As a result, the model still suffered from not being capable of describing mechanistically the role of MEA and O_2 in the degradation system.

A mechanism of the oxidative degradation of di-isopropanol amine (DIPA) has been proposed by Smit et al. (2002). The mechanism was based on formation of the hydroxyl radical ($OH^{\cdot}$) which was proposed to be generated from O_2 under a high temperature condition. $OH^{\cdot}$ abstracts an α-hydrogen next to nitrogen atom to give another radical. This radical then reacts with O_2 to produce a peroxy radical which takes up one more hydrogen from another DIPA molecule. The compound splits at either N-C or C-C bond respectively forming amine/lactic acid mixture and amine/formic acid/acetic acid mixture. This mechanism is shown in Figure 2.3.

Another investigation on MEA oxidation was conducted by studying the rate of degradation by measuring the rate of evolution of NH_3 in the gas phase (Chi and Rochelle, 2002). The experiments used air to degrade MEA solution in a reactor with/without CO_2 at 328 K absorption temperature. Metal additives (Fe), oxidation catalysts, and potential oxidation inhibitors were also added in some experiments to evaluate their effects. In terms of rate measurement, FT-IR was used to measure NH_3, a degradation product, generated during the degradation process. The MEA degradation rate expression was proposed based on the rate of evolution of NH_3 in the presence of either dissolved or ferrous iron.

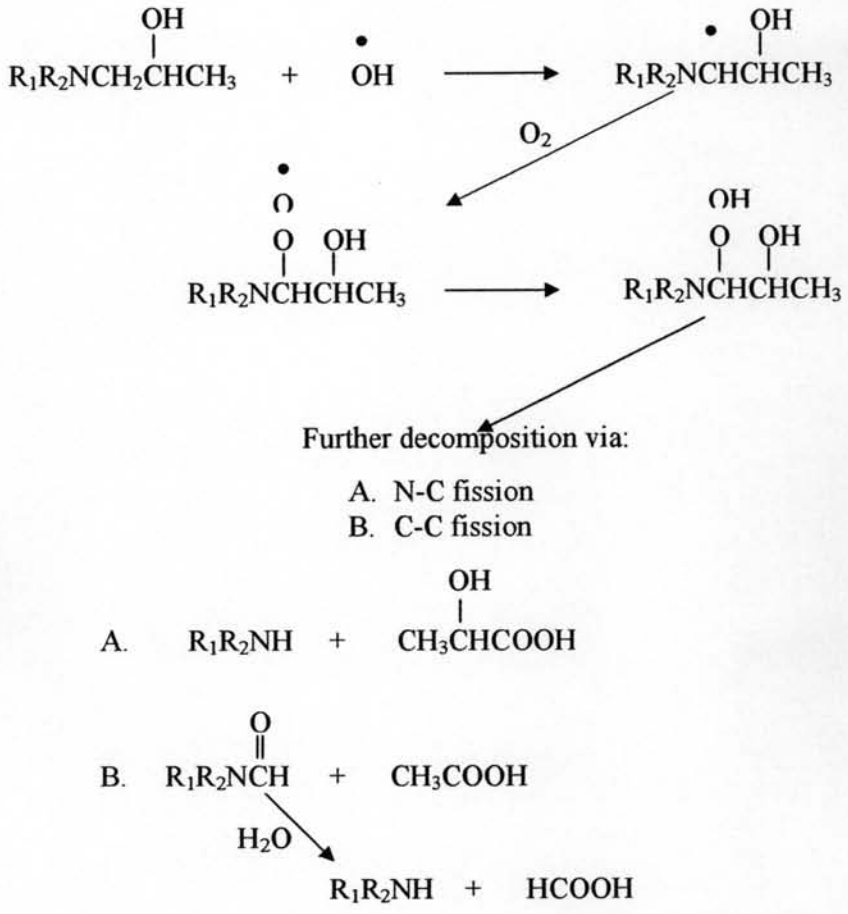

Figure 2.3 DIPA oxidation mechanism

(Smit, Van Heeringen, and Van Grinsven, 2002).

Not only was the MEA concentration term absent, but also, the most degradation rate-influencing parameter, O_2, was also missing in the proposed rate equation. In addition, they did not include most degradation products and their detection techniques, which have been reported and developed for aqueous liquid phase amine systems (Blanc et al., 1982; Kadnar and Rieder, 1995; Kaminski et al., 2002; Rooney et al., 1998; Strazisar et al., 2003). These factors could limit the application of their kinetic equation.

In addition to the kinetic model, Chi and Rochelle (2002) also proposed MEA degradation mechanism shown in Figure 2.4, by inserting the role of O_2 into some previously proposed mechanisms such as those of chlorine dioxide-induced triethylamine oxidative fragmentation (Hull et al., 1969) and potassium hexacyanoferrate (III)-induced trialkylamines oxidation (Audeh and Smith, 1970). Unfortunately, neither chlorine dioxide nor potassium hexacyanoferrate (III) was a usual compound encountered in the alkanolamine systems. These could lead to a less accurate characterization of their oxidation mechanism.

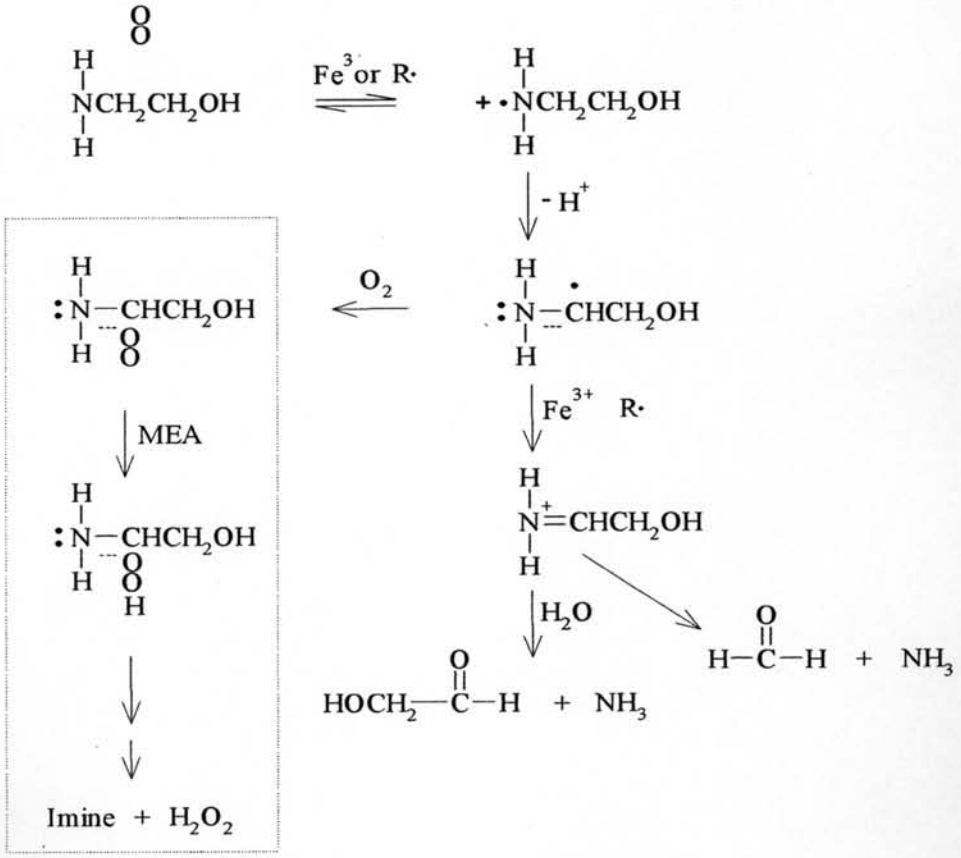

Figure 2.4 MEA oxidation mechanism (Chi and Rochelle, 2002).

Strazisar et al. (2003) employed various analytical techniques to identify the MEA degradation products in plant samples in which pathways of some of those products were proposed including 2-oxazolidone, N-acetlyethanolamine, and 1-hydroxyethyl-2-piperazinone. It must be noted that there was the addition of sodium carbonate to the reclaimer in order to liberate MEA from its heat-stable salts. This process, therefore, could alter the oxidation mechanisms by generating more products. As a result, the proposed pathways might not solely account for the MEA oxidative degradation system.

The kinetics and mechanism of MEA oxidative degradation has recently been investigated (Goff and Rochelle, 2004). The MEA degradation mechanism was reported to be unclear but was thought primarily to involve two different mechanisms of electron abstraction and hydrogen abstraction. Electron abstraction mechanism was set off by free radical Fe^{3+} removing electron from the MEA

nitrogen atom to form an amine radical. The amine radical then reacted further to finally give aldehyde and NH_3. The latter mechanism was triggered by a radiation-induced radical which removed a hydrogen for the nitrogen, the α-carbon, or the β-carbon of MEA molecule. The kinetics of MEA degradation was indirectly analyzed by measuring the rate of evolution of NH_3. The rate of NH_3 formation was concluded to be dependent of agitation speed, thus, controlled by O_2 mass transfer. The degradation rate of MEA in actual CO_2 capture unit was also thought to be mass transfer limited.

A more recent study proposed detailed pathways of 2 degradation systems consisting of MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 under various conditions (Bello and Idem, 2005). The effects of O_2 pressure, presence of CO_2, MEA concentration, and degradation temperature were all taken into account upon building the degradation mechanisms. A change in temperature or the addition of CO_2 to the degradation system were both found to alter the MEA degradation mechanisms. The extent of degradation was found to decrease in the order of MEA-H_2O-O_2 followed by MEA-H_2O-O_2-CO_2 and MEA-H_2O-CO_2. A comprehensive study of the kinetics of MEA oxidative degradation was later proposed (Bello and Idem, 2006). General mechanisms were first proposed for the systems with/without CO_2. The kinetic equations were then derived based on those mechanisms so that it could analyze the oxidation of MEA in various environments including with/without a corrosion inhibitor (e.g. sodium metavanadate).

Lawal et al., (2005) studied the mechanistic role of MDEA in preventing the degradation of MEA in blended MEA-MDEA systems. The presence of MEA in the blended system was found to change the degradation mechanism of the MEA alone system. In addition, at temperature higher than 393 K, MDEA was found to be more prone to oxidation than MEA, thus preferentially degrading to protect MEA during CO_2 absorption process. The kinetics of the blended system was studied later in 2006 (Lawal and Idem, 2006). The kinetic rate model was not actually presented in this work. However, the degradation rate of blended system with/without CO_2 was analyzed as a function various variables including total amine concentration, temperature and MEA/MDEA ratios. An increase in total amine concentration was

found to increase the degradation rate, while an increase of CO_2 concentration (CO_2 loading) gave the opposite effect. A change in the ratio of MEA/MDEA concentration was found to affect the rate of degradation of both alkanolamines in a complex manner.

Uyanga and Idem (2007) demonstrated the first attempt in investigating the kinetics of MEA degradation in the presence of both O_2 and SO_2. The kinetic experiments were carried out in a stirred batch reactor using varied MEA concentrations, O_2 and SO_2 concentrations in the simulated gas mixture and temperature. A corrosion inhibitor, $NaVO_3$, was also evaluated and found to increase the rate of MEA degradation. Two kinetic models were proposed. The first model was formulated based on power law approach. The second kinetic expression was a modified version of the first equation to allow the model to be usable in systems with or without SO_2. Although the kinetics predicted rate of MEA degradation with good accuracy, they were unable to describe the degradation mechanistically. Thus, the roles of MEA, O_2, SO_2 and CO_2 could not be demonstrated.

2.3 Degradation Inhibitors

Complete removal of O_2 or SO_2 from gas streams to prevent degradation of alkanolamine seems to be highly complicated and practically difficult. Especially, the detection and removal of O_2 is known to be time consuming and also labor-intensive (McKnight, 1988). This has made the addition of an effective degradation inhibitor a more attractive method of choice. To the present knowledge, information of degradation inhibitors used in CO_2 absorption unit is still very limited in the open literature.

Rooney et al. (1998) and Rooney and Dupart (2000) studied the oxidative degradation of various alkanolamines including MEA, DEA and MDEA. The study also provided a useful recommendation in applying O_2 scavengers normally used in boiler water feed such as sulfites, hydroxylamines, and hydrazine to reduce O_2 to ppm level in alkanolamine systems. However, addition of these scavengers was only

recommended as a short-term solution for low levels of oxygen contamination. To locate the source of O_2 was seen as a more appropriate long-term solution.

Useful guidelines for selection of appropriate inhibitors have been made available in a literature. According to Veldman (2000), O_2 concentration in alkanolamine unit was normally low, thus only allowing the reaction to proceed as a partial oxidation reaction to produce carboxylic acids rather than full oxidation of the alkanolamine to CO_2 plus NO_2. Their DEA degradation experiments showed that partial oxidation of DEA to carboxylic acids proceeded at temperatures of less than 323 K with dissolved O_2 of less than 1 ppm in the solution. Based on this finding, they concluded that for inhibitors to work effectively, they must scavenge O_2 at ambient temperature and should have more favourable kinetics than the partial oxidation reactions involved in degradation.

The use of a commercial corrosion inhibitor which also acted as O_2 scavenger was reported to control bicine (bis(2-hydroxyethyl) glycine) level, an oxidative degradation product in a commercial MDEA-based gas treating unit (Howard, 2001). Two solutions to control O_2 from degraded MDEA to bicine were compared; 1) injection of an O_2 scavenger into the inlet gas before it entered into the alkanoalmine treating unit, 2) scavenging O_2 in the liquid alkanolamine solution. The second solution which comes with a lower chemical usage was selected due to a low concentration of O_2 in alkanolamine solution to treat (lower than in the inlet gas). For 4-month use of the inhibitor/scavenger, the rate of bicine build-up in MDEA solution was reduced from 60 ppm/day to 6 ppm/day. Unfortunately, the inhibitor/O_2 scavenger information was not disclosed in the literature.

Chi and Rochelle, (2002) investigated additives as potential degradation inhibitors in iron catalyzed MEA oxidative degradation system with and without CO_2. The additives consisted of ethylenediaminetetraacetic acid (EDTA), bicine, glycine, and diethylethanolamine (DEMEA). Only EDTA and bicine were reported to be effective in reducing the degradation rate of MEA. EDTA was found to decrease the rate of oxidation of MEA when CO_2 was present. However, it had no effect when CO_2 was absent from the oxidation system. Interestingly, bicine, a degradation product itself (Howard, 2001), was also found to be effective in reducing

the MEA oxidative degradation rate. It decreased the degradation in systems with and without CO_2. It must be noted that a contradictory result was reported by this study in terms of CO_2 loading effect in MEA degradation system. An increase in CO_2 loading was found to increase the degradation rate. This result was opposite to those investigated by other works (Roony et al., 1998; Bello and Idem, 2005; Lawal et al., 2005).

The most recent study on degradation inhibitors of copper and iron catalyzed oxidative degradation of MEA was published in 2006 (Goff and Rochelle, 2006). Various compounds including undisclosed inorganic Inhibitor A, sodium sulfite (Na_2SO_3), formaldehyde were evaluated in copper and iron catalyzed oxidative degradation of monoethanolamine (MEA). The experiments were all carried out using conditions corresponding to the top and bottom of the absorber with 7 kmol/m^3 MEA, air containing 21% O_2, lean/rich CO_2 loading, and 328 K. Inhibitor A was found to successfully reduce the MEA oxidation rate in both copper and iron catalyzed systems. It could also inhibit the degradation in systems with lean and rich CO_2. Inhibitor A was also found to inhibit the MEA degradation more easily in Cu catalyzed system and rich CO_2 loading than in Fe catalyzed and lean CO_2 loading environments, respectively. Na_2SO_3 also decreased MEA degradation rate in both copper and iron catalyzed systems. For copper-catalyzed MEA degradation, Na_2SO_3 decreased the degradation rate until its concentration reached 100 ppm. The degradation rate was found to increase if a higher concentration was used. Formaldehyde also reduced the degradation rate but it was not as effective as Inhibitor A. Both Na_2SO_3 and formaldehyde were more effective inhibitors for copper than iron catalyzed degradation. It was also concluded that Na_2SO_3 and formaldehyde were also decomposed during the MEA degradation while Inhibitor A was not. Unlike Na_2SO_3 and formaldehyde, Inhibitor A therefore, did not need to be further added or replaced later in the process.

2.4 Sulfur Induced-Degradation of Alkanolamines

The concern of alkanolamine degradation induced by sulfur species in CO_2 capture from flue gas streams arises from the existence of SO_2 formed by the process of coal combustion. The formation of SO_2 is a result of the reaction of elemental sulfur within the coal matrix and air-derived O_2. SO_2 can be further oxidized to give SO_3. These reactions are stoichiometrically shown as follows;

$$S_{coal} + O_2 \rightarrow SO_2 \tag{2.1}$$

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{2.2}$$

The concentrations of SO_2 and SO_3 are dependent on the quantity of sulfur contained in the original coal and the conditions of the combustion process. Prior to CO_2 removal, SO_2 is usually removed in flue gas desulfurization units known as FGD units using a number of existing techniques. According to Speight (1994), FGD may be divided into wet and dry process. In wet scrubbing, for example, slurries of limestone ($CaCO_3$) or lime ($Ca(OH)_2$) (Speight, 1994) is brought into contact with flue gas, thus, respectively removing SO_2 as a wet sludge of $CaSO_3/CaSO_4$ or $CaSO_3$. On the other hand, dry limestone known as dolomite ($CaCO_3.MgCO_3$), in a dry process, is used within the combustor removing SO_2 as calcined products along with sulfite and sulfate salts. Even after subjecting to one of these FGD processes, a flue gas stream often contains SO_2 and is carried over to contact with the alkanolamine in CO_2 removal unit. This induces alkanolamine degradation. At the present time, very few studies on SO_2-related degradation of alkanolmines have been reported. On the other hand, alkanolamine decomposition by other sulfur species such as carbonyl sulfide (COS) and carbon disulfide (CS_2) usually present in natural gas is available, although limited. This is as a result of more research focus previously given to the natural gas processing. Therefore, COS and CS_2 degradation are more reviewed since the information are worthwhile and may be applicable to SO_2-induced degradation of alkanolamines.

An Investigation on COS-induced degradation of MEA and DEA was reported (Pearce et al., 1961). MEA was found to be more susceptible to COS than DEA producing products of diethanol urea, oxazolidone, and N-(2-hydroxyethyl) ethylenediamine (HEED). Degradation pathway of MEA and COS was suggested to be analogue to those of CO_2-induced degradation, with the exception that COS degraded MEA more quickly than CO_2 (Berlie et al., 1965). The identification using GC/MS showed fifteen major products from DEA-COS degradation including MEA, acetone, butanone, and a sulfur-containing solid (Dawodu and Meisen, 1991). Mechanism and kinetics were elucidated 3 years later in which COS was found to initially proceed through a faster solubility and hydrolysis followed by a slower reaction with DEA and side reactions (Dawodu and Meisen, 1994).

Kohl and Reisenfeld (1985) summarized CS_2-induced degradation of primary and secondary alkanolamines by first forming substituted dithiocarbamates followed by thiocarbamates. A more comprehensive laboratory test for CS_2 degradation of DEA was conducted showing that the mechanism consisted of formation of DEA dithiocarbamate acid salts which reacted further to form a solid, followed by a slower set of reactions initiated by CS_2 hydrolysis (Dawodu and Meisen, 1996).

Rooney and Dupart (2000) discussed effect of H_2S and SO_2 in alkanolamine treating unit in corrosion aspect. It stated that O_2 could oxidize H_2S present in the gas streams to form elemental sulfur (S^0), sulfite (SO_3^-), thiosulfate ($S_2O_3^-$) and sulfate (SO_4^{2-}) along with dithionites ($S_2O_4^-$) and polythionates ($S_nO_6^-$). Some of these species form heat-stable salts with alkanolamines giving rise to corrosion in the capture unit. It also summarized that SO_2 would all convert to sulfate. Accumulation of this species would eventually force the alkanolamine solution to be disposed of leading to increase of operating cost.

Smit et al., (2002) investigated alkanolamine degradation in the presence of H_2S and O_2. They suggested a range of reactions leading to formation of thiosulfate, sulfur, polysulphides and sulfate;

$$2H_2S + O_2 \leftrightarrow 2S^0 + 2H_2O \quad (2.3)$$

$$2S^0 + 2O_2 \leftrightarrow 2SO_2 \quad (2.4)$$

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad (2.5)$$

$$2R_1R_2NH + nS + H_2S \leftrightarrow (R_1R_2NH)_2H_2S_{n+1} \quad (2.6)$$

$$2R_1R_2NH^+HS^- \leftrightarrow R_1R_2NH_2^+HS_2^- + R_1R_2NH_2 + 2H^+ + 2e \quad (2.7)$$

$$2HS^- + 3H_2O \leftrightarrow S_2O_3^{2-} + 8H^+ + 8e \quad (2.8)$$

$$HS^- + 4H_2O \leftrightarrow SO_4^{2-} + 9H^+ + 8e \quad (2.9)$$

The studies also compared the degradation of DIPA and DEA in the presence of both O_2 and H_2S. It was found that the rate of organic acids formation was slightly lower for DIPA, whereas the rate increased dramatically in the DEA system. The product distribution was also further analyzed with the conclusion that the presence of H_2S produced acetic acid as a major product while in the absence of H_2S, glycolic and formic acids were the main products detected.