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Degradation Study of new solvents for CO₂ capture in post-combustion.

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Abstract

Post-combustion CO₂ capture in flue gas with solvent is currently the most advanced technology. A major problem associated with chemical absorption of CO₂ using the benchmark ethanolamine (MEA) is solvent degradation through irreversible side reactions with CO₂ and O₂. So, new amines development with higher chemical stability becomes essential. This work is based on chemical stability study of 17 different molecules: alkanolamines, diamines, and triamines without alcohol function. Effects of temperature, CO₂, and O₂ on degradation have been studied. Knowledge of degradation products and main reactions allows a better understanding of amines chemical stability for CO₂ capture application.

© 2009 Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).Keywords: CO₂ post-combustion capture; amine degradation; mechanisms; structure-properties relationships.

1. Introduction

Carbon dioxide removal from flue gas is important to reduce greenhouse effect. CO₂ absorption with reversible chemical reaction using aqueous alkanolamines solution is currently the most appropriate method for low pressure CO₂ sources. Among all known solvents, MEA is the benchmark molecule because of its properties towards CO₂ capture (low price, high water solubility, high absorption capacity and fast kinetic). However, a major problem associated with chemical absorption using MEA is degradation through irreversible side reactions with CO₂ and O₂ which leads to numerous problems with the process: solvent loss, foaming, fouling, increased viscosity and corrosion. So, developing new amines with higher chemical stability is essential. Polyamines could be good candidates: a second amine function could indeed favourably replace alcohol function.

Alkanolamines degradation has been described in literature for a while: *N*-methyldiethanolamine (MDEA) and diethanolamine (DEA) are well-known solvents for their application in gas treatment and MEA is proposed for post-combustion process. Thermal degradation was only reported by Chakma and Meisen [1] who have established the

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relative stability of MDEA with temperature. Many articles concerning degradation of MEA [2-11], MDEA [1, 12-15] and DEA [16-22] in presence of CO₂ and/or O₂ were published. Main degradation products were identified but few reaction mechanisms were proposed to explain their formation.

In opposite, polyamines studies have not yet been published. This approach is based on stability comparison between alkanolamines and polyamines in order to identify the impact of replacement of one alcohol function by a second amine function. MEA is the benchmark molecule. Effects of amine function (primary, secondary, tertiary), role of alkyl chain length between two amine functions (2, 3, 4, 5 or 7 atoms) and steric hindrance (2-amino-2-methylpropan-1-ol (AMP)) have been assessed. One example of cyclic compound has been also introduced (*N,N'*-dimethylpiperazine (DMP)). The studied amines are summarized in figure 1.

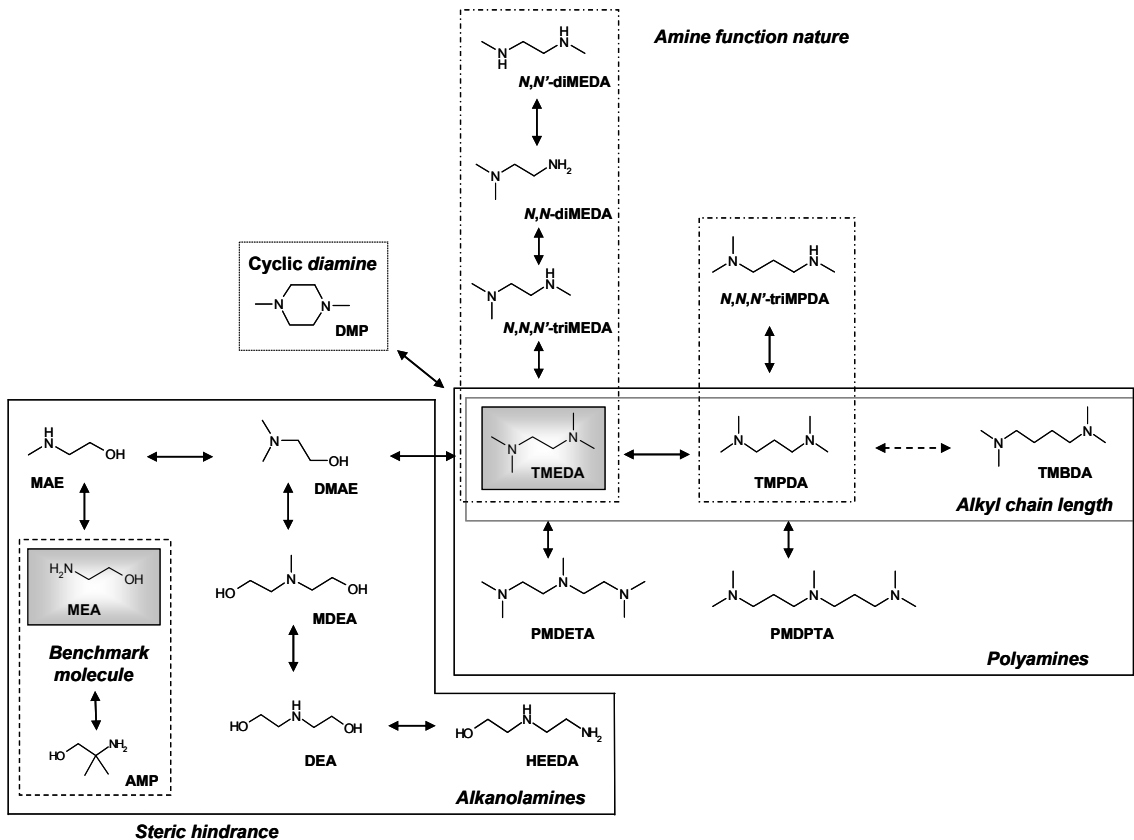


Figure 1. Summary of studied amines.

Thermal, CO₂ and O₂ degradations have been studied to identify effect of temperature and gas presence on chemical stability in the experimental conditions described below.

2. Experimental section

2.1. Degradation conditions

Experiments are conducted in 100 mL stainless steel batch reactors. The operating conditions are summarized in Table 1.

Table 1. Operating Conditions

Amine concentration	4 mol.kg ⁻¹
Temperature	140°C
Gas pressure	Pp (CO ₂) = 2 MPa Pp (Air) = 2 MPa (i. e. Pp (O ₂) = 0.42 MPa)
Time experiment	15 days

All the aqueous amine solutions are degassed before degradation. For a typical run, 40 mL of solvent are loaded into the reactor, stirred magnetically at 250 rpm and heated to the desired temperature. Air or CO₂ are then fed into the vessel up to the desired reactor pressure. After 15 days, the liquid phase is analyzed: gas chromatography (GC), mass spectrometry (MS), ionic chromatography (IC) and nuclear magnetic resonance (NMR).

2.2. Analysis section

Amine and degradation compounds are quantified by gas chromatography. Use of two different methods (one apolar and one polar column) is necessary to optimize separation. Quantification of remaining amine and its degradation products is carried out with an internal standard added to the sample. Identification of degradation products is performed with a coupling gas chromatography-mass spectrometry with electronic impact (EI) and chemical ionization (CI). In some cases, synthesis of molecules is necessary to confirm structure of degradation products. The highest molecular weight compounds are identified with a high resolution mass spectrometry technique (FT-ICR/MS) with electrospray ionization (ESI). In some cases, NMR analyses (¹H and ¹³C) are useful to determine compound structure. Formic, glycolic, acetic and oxalic acids, nitrite and nitrate are quantified by ionic chromatography.

3. Results and Discussion

3.1. Thermal Degradation at 140°C for 15 days

Temperature influence on degradation is important to determine the mechanisms in which CO₂ and O₂ do not occur. Thermal degradation is negligible for 10 amines (degradation rate < 3 %) because their rates are inferior to GC quantification uncertainty and is not significant for 7 amines in comparison with the degradation rates obtained in presence of CO₂. On the other hand, the thermal degradation rate is not always negligible in comparison with O₂ degradation rate, but same products are observed in both cases due to radical mechanisms.

3.2. CO₂ Degradation at 140°C for 15 days (Pp CO₂ = 2 MPa)

As seen in figure 2, large discrepancies of degradation rates appear among amines from the most stable DMP (4.3 %) to the least stable HEEDA (99 %). So, identification and quantification of degradation products are essential for a better understanding of degradation mechanisms.

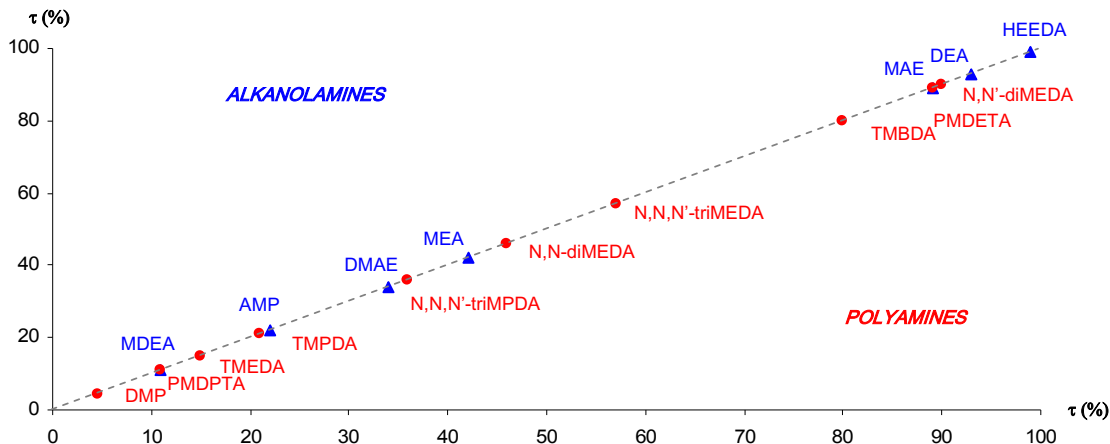


Figure 2. Degradation rates with CO₂ (15 days, 4 mol.kg⁻¹, 140°C, 2 MPa)

3.2.1. Alkanolamines

Figure 3 presents for each ethanolamine the proportion of the degradation products due to different reactions.

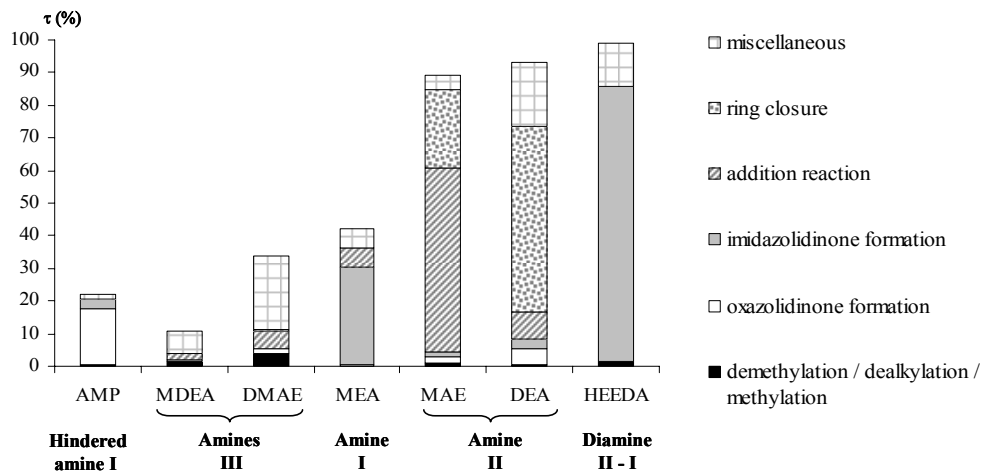


Figure 3. Effect of CO₂ on ethanolamines stability (15 days, 4 mol.kg⁻¹, 140°C, 2 MPa)

Secondary amines are the least stable: they mainly do addition reactions and cyclic compound formation. MEA and HEEDA, which have a primary amine function, form mostly an imidazolidinone. Tertiary and the hindered primary (AMP) amines show a better chemical stability.

Figure 4 presents the general pathway between the different alkanolamines and their degradation products.

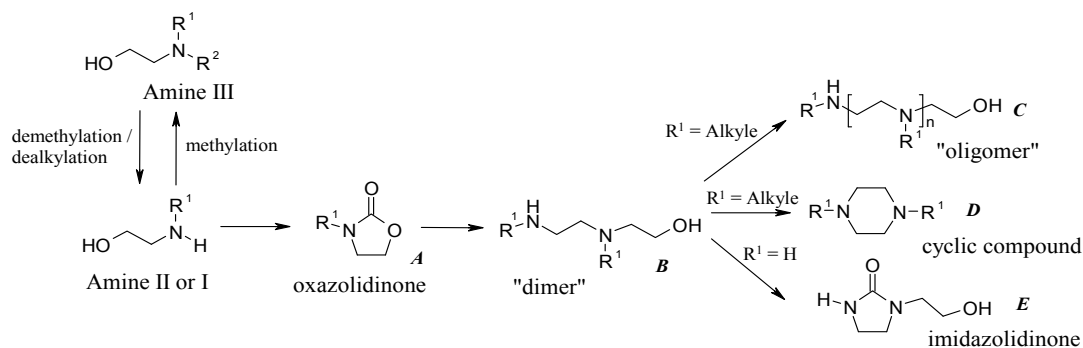


Figure 4. General pathway for ethanolamines degradation with CO₂

The first step of primary and secondary amines degradation is oxazolidinone formation **A** due to carbamate ring closure. Oxazolidinones are very sensitive to nucleophilic reactions and react easily with another amine to give addition products **B** also called dimers. Secondary amines are less stable because they are usually more nucleophilic than primary and tertiary amines. The addition product **B** can be degraded into three different kinds of compounds regarding to the nature of R¹: if R¹ is an alkyl group (secondary amine case), imidazolidinones **E** are not favourable unlike polymers **C** (new addition reactions) or piperazines **D**. Differences noticed between MAE (*N*-methylethanolamine) and DEA are due to R¹ nature: if it is an hydroxyethyl group (DEA), ring closure reaction will be easier than addition reaction. If R¹ is an hydrogen atom (MEA or HEEDA), the main degradation product is an imidazolidinone which is a cyclic urea, very stable product. HEEDA, which is also the addition product of MEA, has NH-CH₂-CH₂-NH structure very favourable to lead to imidazolidinone. This is the reason why it is the less stable alkanolamine of the selection.

Tertiary amines are more stable because of a preliminary demethylation or dealkylation step which is necessary to initiate significant degradation.

Concerning AMP, steric hindrance of amine function prevents the oxazolidinone ring-opening into an addition product. This explains the lower degradation rate of AMP compared to MEA and the accumulation of oxazolidinone: AMP forms a stable hindered oxazolidinone.

3.2.2. Polyamines

Figure 5 presents for each diamine the proportion of the degradation products due to different reactions.

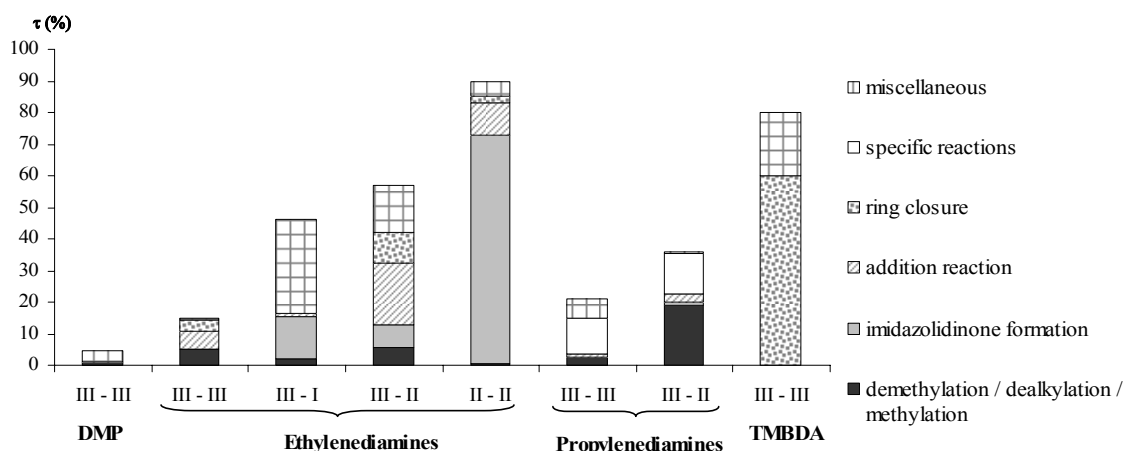


Figure 5. Effect of CO₂ on diamines stability (15 days, 4 mol.kg⁻¹, 140°C, 2 MPa)

In the case of ethylenediamines, main degradation reactions are the same as for ethanolamines. Figure 6 presents the general pathway between the different ethylenediamines and their by-products.

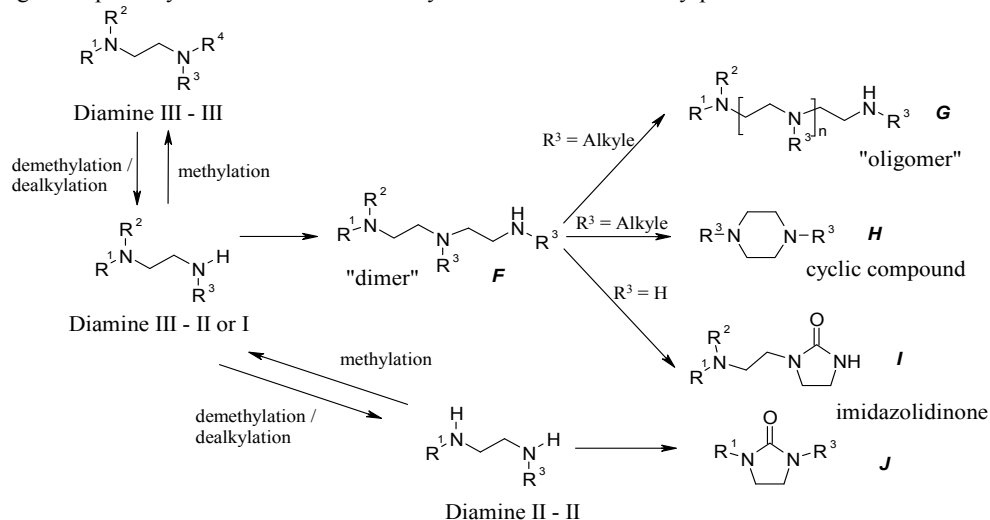


Figure 6. General pathway for ethylenediamines degradation with CO₂

Ethylenediamines III-II react as secondary ethanolamines and form mostly addition products **G** and cyclic products **H**. Ethylenediamines III-I lead to imidazolidinones (**I** and **J**) for the same reason as MEA, i.e. due to the formation of an intermediate product with NH-CH₂-CH₂-NH structure. By the way, ethylenediamines II-II which present also the same structure have a higher degradation rate into imidazolidinones. If molecules have only tertiary amine functions, demethylation or dealkylation is necessary to promote further degradations, so they are more stable than the others as for ethanolamines. Comparison of DMP with its homologous linear molecule, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), shows an increased stability due to the cyclic structure: demethylation is the only degradation reaction.

Concerning propylenediamines, degradation reactions are similar to the previous ones: demethylation, dealkylation and methylation are quite favourable contrary to ring closures, addition reactions and cyclic ureas formation (*N,N'*-dimethyltetrahydropyrimidinone) which do not occur significantly. In fact, these last reactions are in competition with specific ones, for example Hofmann elimination due to the labile proton on β position of nitrogen atom as mentioned in figure 7.

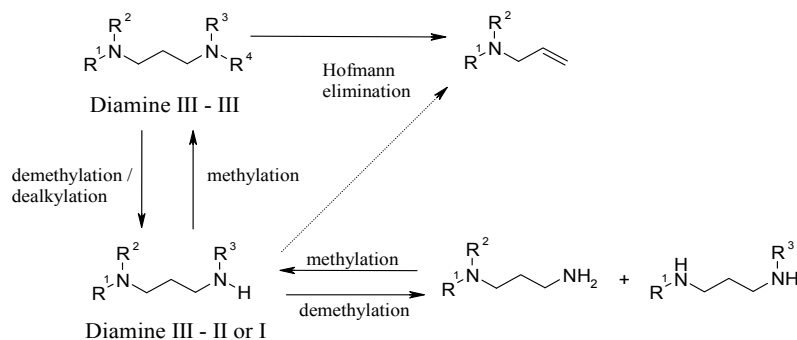


Figure 7. General pathway for propylenediamines degradation with CO₂

Unlike tertiary amines seem to be more stable, TMBDA behaviour is quite particular: this amine degrades significantly into cyclic compounds although it is a diamine III-III. *N*-methylpyrrolidine and a salt of dimethylpyrrolidinium are the main degradation compounds identified by NMR analysis. This result can be explained by influence of the alkyl chain length between the two amine functions: thus, if the two amino groups are separated by 4 or 5 atoms, it allows very favourable five- or six-membered rings formation. It is the same explanation for the high degradation rate of *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) which gives a large amount of DMP.

So, the most stable structures in presence of CO₂ are cyclic amines, hindered primary amines and tertiary amines except polyamines whose amine functions are separated by 4 or 5 atoms. On the other hand, secondary amines are less stable like molecules which have or can form NH-CH₂-CH₂-NH structure. When a compound has a good leaving group and a nucleophilic function, polymers and cyclic compounds are obtained in large amounts. If a labile proton is located on β position of the nitrogen atom, specific reactions may occur, for example Hofmann elimination which gives allylamines.

3.3. Oxidative Degradation at 140°C for 15 days (Pp air = 2 MPa).

Degradation study under air pressure is important for two reasons: firstly, O₂ is not a negligible component of flue gas (approximately 5 %) and secondly, it was assumed that ethanolamines reactivity was due to alcohol function. Degradation rates are reported in Figure 8.

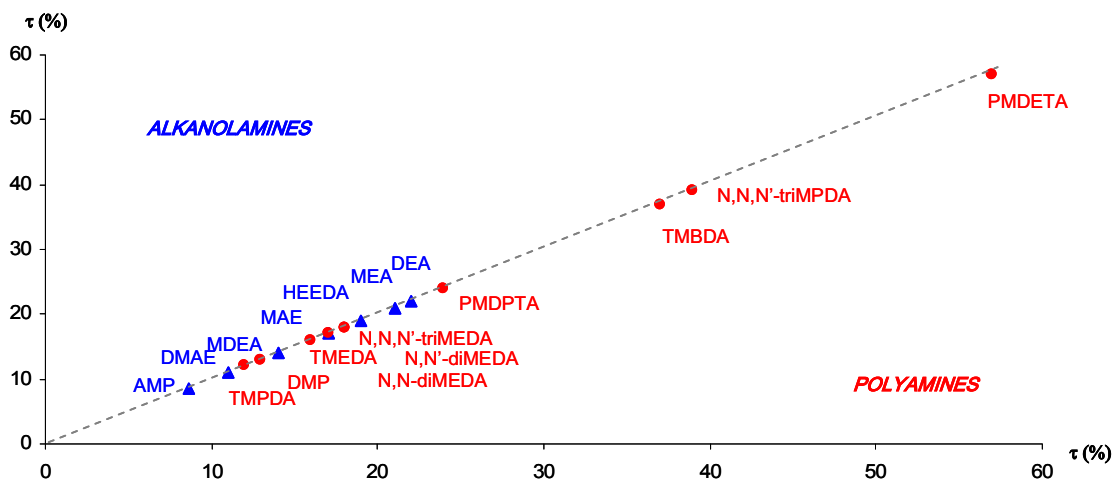


Figure 8. Degradation rates with air (15 days, 4 mol.kg⁻¹, 140°C, 2 MPa)

In these conditions, most of degradation rates are between 8.5 and 24 % that is lower than in presence of CO₂. Three molecules (PMDETA, TMBDA and *N,N,N'*-triMPDA) are significantly more sensitive to O₂. All amines of this study do mainly demethylation, methylation (except for MEA) and dealkylation reactions and carboxylic acids formation with much lower rates. Some specific reactions take place. Oxidation of ethanolamines into amino acids is observed but in a small amount. Ethylenediamines always give piperazinones and propylenediamines degrade into allylamines due to Hofmann or Cope elimination. Replacement of alcohol function by a second amine function does not occur upon degradation, as it could be assumed. Relating to amine function nature, tertiary amines are slightly more stable than primary amines and secondary amines. Steric hindrance (AMP) has also decreased degradation by avoiding highly volatile compounds formation. Surprisingly, contrary to CO₂ degradation, cyclic structure does not contribute in the same manner: DMP degrades at 13 % whereas its homologous linear molecule (TMEDA) degrades at 16 %. Concerning *N,N,N'*-triMPDA, demethylation, dealkylation and Hofmann or Cope elimination are observed but, contrary to the diamine III-III (TMPDA), other reactions occur significantly (for example methylation) which

explains its higher degradation rate. Finally, the high degradation levels obtained with PMDETA and TMBDA are due to alkyl chain length which allows very favourable five- or six-membered rings formation.

4. Conclusion

Analogies and differences have been noticed between ethanolamines and polyamines. Main degradation reactions have been identified, either similar (demethylation, addition reactions and ring closures) or specific to structure (oxidation of alcohol function for ethanolamines and Hofmann or Cope elimination for propylenediamines). Relationships between amine structure and stability have been proposed to predict chemical stability for other amines.

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5. Appendices: Amines abbreviations

AMP = 2-amino-2-methylpropan-1-ol
 DEA = diethanolamine
 DMAE = *N,N*-dimethylaminoethanol
 DMP = *N,N'*-dimethylpiperazine
 HEEDA = *N*-(2-hydroxyethyl)ethylenediamine
 MAE = *N*-methylaminoethanol
 MDEA = *N*-methyldiethanolamine
 MEA = ethanolamine
 PMDETA = *N,N,N',N',N''*-pentamethyldiethylenetriamine
 PMDPTA = *N,N,N',N',N''*-pentamethyldipropylenetriamine
 TMBDA = *N,N,N',N'*-tetramethylbutanediamine
 TMEDA = *N,N,N',N'*-tetramethylethylenediamine
N,N-diMEDA = *N,N*-dimethylethylenediamine
N,N'-diMEDA = *N,N'*-dimethylethylenediamine
N,N,N'-triMEDA = *N,N,N'*-trimethylethylenediamine
 TMPDA = *N,N,N',N'*-tetramethylpropylenediamine
N,N,N',N'-triMPDA = *N,N,N',N'*-trimethylpropylenediamine