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Thermal degradation pathways of aqueous diamine CO₂ capture solvents

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Abstract

Diamines have shown promise as CO₂ capture solvents, yet very little is known about their pathway for thermal degradation. In this study, diamine thermal degradation was quantitatively monitored in lab-scale experiments on four aqueous diamine solvents; ethylenediamine (EDA) 1,2-propanediamine (1,2-DAP), 1,3-diaminopropane (1,3-DAP) and N-methyl-1,2-ethanediamine (N-MEDA), to gain a more comprehensive understanding of their degradation pathway(s). The major degradation products were identified by high resolution time-of-flight mass spectrometry (TOF-MS). Degradation pathways were proposed showing that the primary thermal degradation route for this class of amine are through carbamate formation followed by intermolecular cyclization to form an imidazolidinone or nucleophilic attack by a free amine to form a diamine urea.

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Keywords: CO₂ capture; thermal degradation; ethylenediamine; degradation pathways

1. Main text

Among current options for post-combustion CO₂ separation in power plants, aqueous amine absorption is considered the most matured technology due primarily to its ability for retrofitting, its long history in acid gas scrubbing and competitive cost compared to other technologies. The most widely studied amine is monoethanolamine (MEA), which has fast CO₂ absorption kinetics and is commercially available. However, the MEA-based

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absorption/stripping technology requires intensive energy and the overall carbon capture process was estimated to increase the cost of electricity by more than 80% for a unit with MEA-based carbon capture compared to without a capture unit, with around 60% of the energy consumption stemming from the solvent regeneration.

Solvent regeneration greatly depends on reboiler temperature and could be a potential mean to reduce the operation energy requirement of a CO₂ capture system, while higher operating pressures in stripper reduce the energy required for the subsequent CO₂ compression. Increasing regeneration temperature is one option to take advantage of the energy saving from increased thermal compression. Given this, it is paramount to better understand the regeneration process in order to lower the overall CO₂ capture cost. Given this a better understanding of the thermal degradation of amine at high temperatures is needed.

Thermal degradation of amines generally occurs at high temperature locations such as the reboiler, bottom of the stripper or in lean-rich heat exchanger. This process generally produces higher molecular weight polyamines including amine dimers, amine trimers and cyclic amines through condensation mechanisms [1]. Degradation has been an important source of the operational cost in CO₂ capture. It not only consumes amine resulting in higher solvent makeup rate but also introduces operational difficulties into the CO₂ absorption/regeneration processes, such as raising foaming tendency and contributing to corrosion [2].

Diamines have shown promise as CO₂ capture solvents, yet very little is known about their pathway for thermal degradation [3-5]. This study focuses on identify the main the thermal degradation pathway(s) of aqueous diamine solvents by studying a set of diamines with structural differences. The conventional thermal degradation pathway for primary amines, such as MEA, is carbamate polymerization. In this mechanism, the MEA carbamate will be dehydrated and cyclize to form oxazolidone (OZD). This compound is a reactive intermediate that continues downstream in the degradation pathway to form additional products such as N-(2-hydroxyethyl)-ethylenediamine (HEEDA), hydroxyethyl-imidazolidinone (HEIA) and other MEA oligomers [6]. These products contain various amine functional groups (primary, secondary and tertiary amines), which could have different reactivities due to their different nucleophilicity and basicity.

Diamines may thermally degrade through similar pathways, but detailed analysis of the diamine degradation pathways has yet to be undertaken. By quantitatively monitoring the formation of diamine thermal degradation products, a more comprehensive understanding to diamine thermal degradation can be gained. In this study, lab-scale diamine solvent degradation was conducted on four aqueous diamine solvents; ethylenediamine (EDA) 1,2-propanediamine (1,2-DAP), 1,3-diaminopropane (1,3-DAP) and N-methyl-1,2-ethanediamine (N-MEDA). The major degradation products were identified by high resolution time-of-flight mass spectrometry (TOF-MS). Degradation pathways and mechanism(s) are proposed and supported with experimental data.

2. Experimental Methods

2.1. Laboratory thermal degradation

Thermal degradation experiments were carried out in cylinders constructed of 1/2-inch OD, 6 inch long 316 stainless steel tubing (10 mL internal volume) [7,8]. The cylinders were welded shut on one end while the other end was capped by a Swagelok end cap. Ethylenediamine (EDA; 99.5%), 1,2-propanediamine (1,2-DAP; 99%), 1,3-diaminopropane (1,3-DAP; 99%) and N-methyl-1,2-ethanediamine (N-MEDA; 95%) were purchased from Sigma-Aldrich. The bulk 2.5 mol/kg solutions were prepared gravimetrically and was pre-loaded with CO₂ to a carbon loading of 0.4 mole CO₂ per mole amine (C/N) with CO₂ gas (Scott Gross, Lexington, KY) prior to filling each cylinder with 5 mL of the loaded amine solution. Nitrogen was sparged through each sample prior to closure to remove any residual oxygen in the sample and cylinder headspace. The sample cylinders were then capped and stored in a thermal degradation ovens maintained at the the experimental temperatures of 125, 135 and 145 °C (± 1.5 °C). The internal temperature of the oven was monitored regularly to ensure a constant temperature during the course of the

experiment. Cylinders were not re-closed and returned to the ovens for further heating after being removed from the oven. To check for leakage, each sample cylinder was weighed before and after incubation. Samples having more than 1.0% weight change were considered as leaking samples and therefore excluded from the final data set. Duplicate sample cylinders were removed from the oven after 50, 100 and 200 hours.

2.2. Time-of-flight mass spectrometry

An Agilent 1260 Infinity HPLC coupled with 6224 Time of Flight (TOF) Mass Spectrometer (LC-TOF-MS) was utilized to identify and quantify the remaining MEA thermal degradation products. The analytical column used was a Pinnacle DB AQ C18, 50 x 3 mm, 3 μ m (Restek Bellefonte, PA). The eluent was water (90%) with formic acid 0.01% and methanol (10%). Injection volume was 5 μ L and the flow rate was 0.3 mL/min for total run time of 6 min. Column temperature was 20 °C. Dual electrospray ionization (ESI) in positive mode with mass range of 40-500 m/z was used. Complete system control and data acquisition were carried out using the Agilent Mass Hunter workstation software version B.05.00. A reference mass solution of purine (121.050873 m/z) and hexakis(1H,1H,3H-tetrafluoropropoxy)phosphazine (922.009798 m/z) was used in the dual ESI configuration to maintain the mass accuracy of the TOF-MS detector. Samples were prepared with MS grade water (Fisher Scientific) to a 100 times dilution factor. Extracted ion chromatograms (EIC) were used for product quantification.

3. Results and Discussion

3.1. Ethylenediamine thermal degradation

In this study, the identification of the diamine thermal degradation products was performed by examining both the initial amine solutions and the most heavily thermally degraded samples, in this study that would be the samples collected after 200 hours at 145 °C. First, the starting loaded diamine solutions were analyzed to determine all of the molecular masses from the starting materials, including any trace contaminants in the amines or in the water used to prepare these solutions. Next the most heavily degradation samples, were analyzed in the same manner showing the molecular masses of the original compounds and any newly produced thermal degradation compounds. Third, a mass spectral subtraction was performed of the thermally degraded sample from the initial solutions. At this point any major remaining mass spectral peaks will correspond to the newly formed thermal degradation compounds. An example of this is shown in Fig. 1 for EDA. The top mass spectra is from the initial loaded 2.5M EDA solution, the middle mass spectra is from the thermally degradation sample (200 hr at 145 °C) and the bottom mass spectra is the result of subtracting the top from the middle. A total of four large peaks were identified; 61.11330 m/z (belonging to unreacted EDA), 87.05592 m/z, 147.12404 m/z and 173.13975 m/z. From these protonated mass-to-charge ratios, molecular formulas can be generated for each of the compounds. Given the relatively small molecular weight of these compounds and the accuracy from the high resolution mass spectra, and by limiting the number elements in these structures to only those that are reasonable from the controlled experiments, the number of possible molecular formulas from these mass-to-charge ratios is very small. In this example for EDA, only one molecular formula matched well with each observed mass-to-charge ratio. Table 1 summarizes the chemical name, measured protonated molecular mass, generated molecular formula, and the calculated protonated molecular mass from the 3 major peaks identified in the thermal degradation samples for EDA.

Table 1. EDA thermal degradation products identified through mass spectral subtraction.

Degradation Product	Measured mass [M+H] ⁺	Generated molecular formula	Calculated mass [M+H] ⁺
2-Imidazolidinone (IZD)	87.05593	C ₃ H ₆ N ₂ O	87.05529
<i>N,N'</i> -bis(2-aminoethyl)-urea (Urea)	147.12404	C ₃ H ₁₄ N ₄ O	147.12404
Cyclic Diurea	173.13975	C ₆ H ₁₂ N ₄ O ₂	173.10330

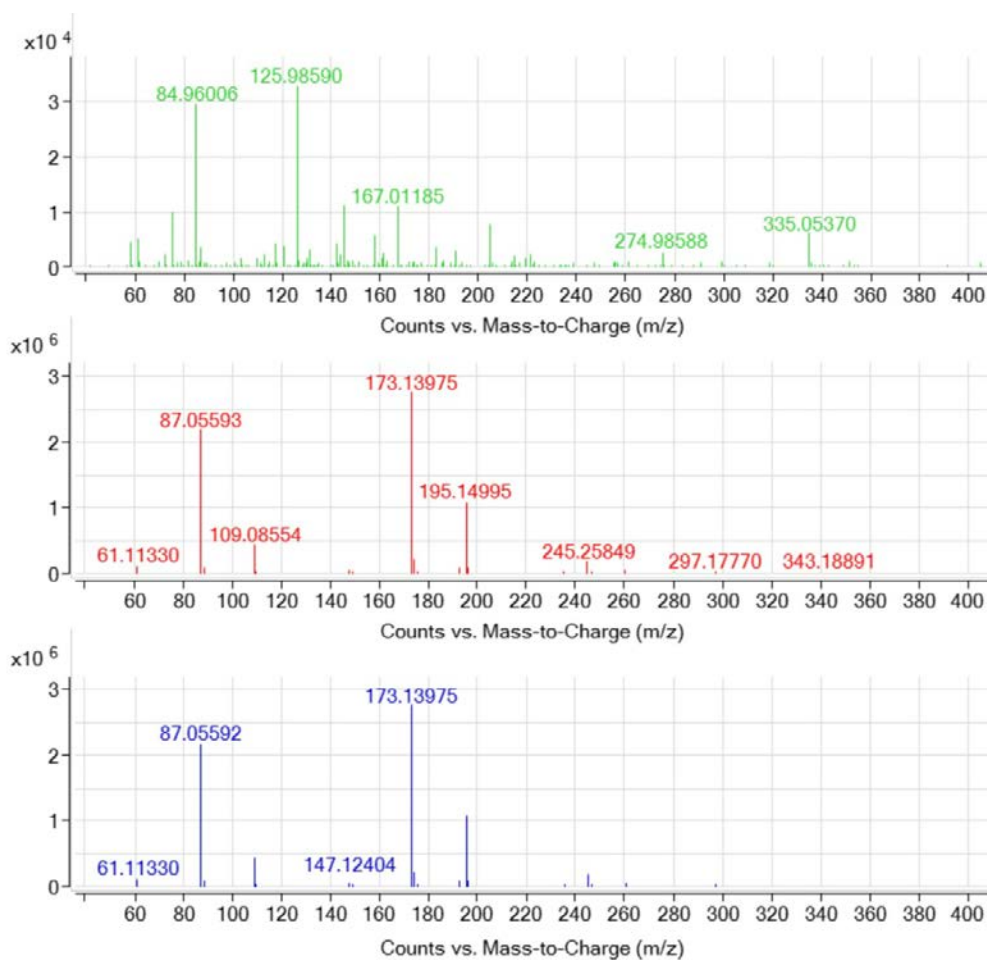


Fig. 1. Mass spectrum of the initial 2.5M EDA solution (top), after thermal degradation at 145 °C and 200 h (middle), and the subtracted mass spectrum (bottom) highlighting the thermal degradation products formed from EDA (the peak at 61.11330 m/z is from unreacted EDA).

Finally, to confirm that the identified compounds were actually from thermal degradation, the mass-to-charge ratios were extracted from all the other thermal degradation samples (50, 100, 200 hours at 125, 135 145 °C). Confirmation of these compounds being produced as the result of thermal degradation can be assumed if each compound increases with time (from 50 - 200 hours) and at elevated temperatures (125 - 145 °C). Fig. 2-4 show the extraction ion chromatograms of the three primary thermal degradation compounds identified; IZD, *N,N'*-bis(2-aminoethyl)-urea, and the cyclic diurea. In each case the response, and subsequently the concentration in each sample, increases from 50 to 200 hours and at each temperature from 125 to 145 °C.

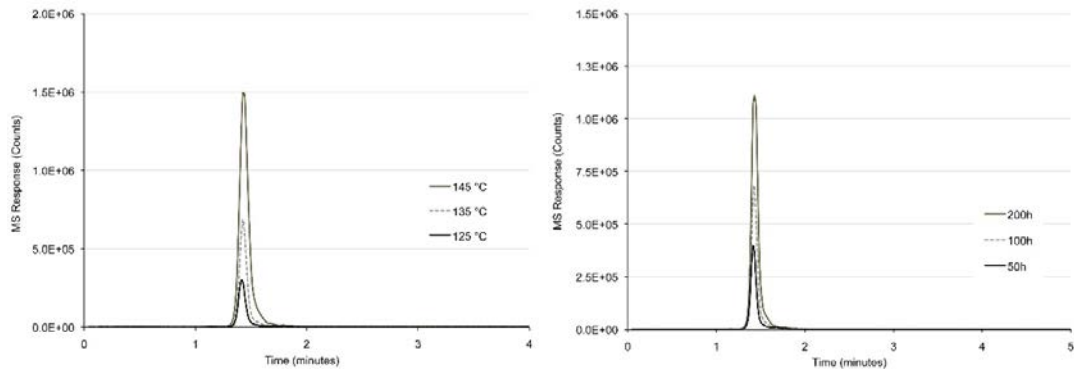


Fig. 2. Representative formation of 2-imidazolidinone (IZD) from EDA at different temperatures (left) and time periods (right).

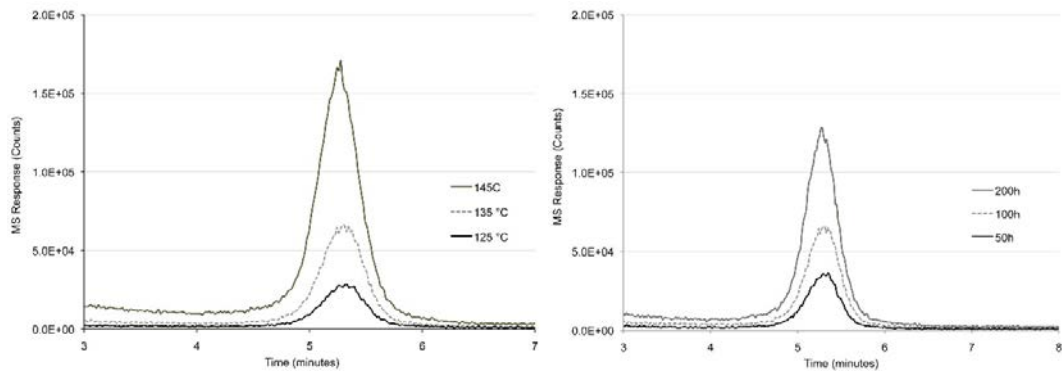


Fig. 3. Representative formation of *N,N'*-(2-aminoethyl)urea from EDA at different temperatures (left) and time periods (right).

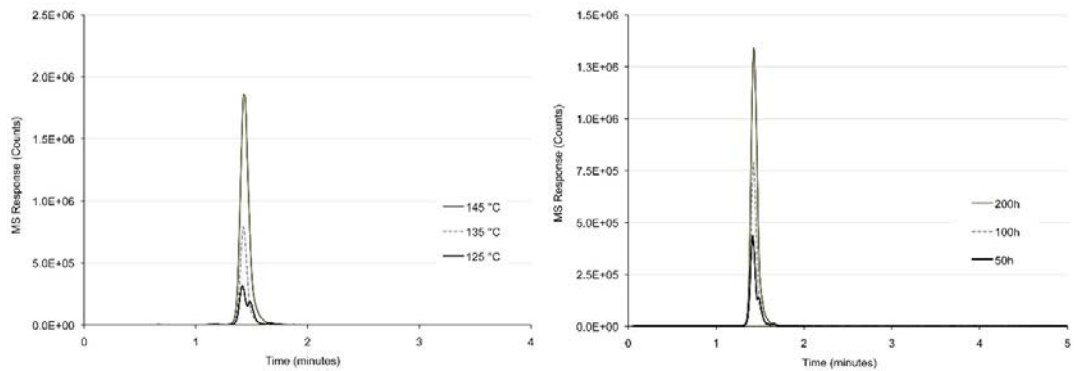


Fig. 4. Representative formation of the cyclic urea from EDA at different temperatures (left) and time periods (right).

Identification of the EDA thermal degradation compounds was accomplished by first looking at published reports, then by applying commonly reported thermal degradation pathways to these diamines. Work by Zhou et al and Hatchell et al. suggested that linear diamines, including EDA, will first form the amine carbamate followed by thermal decomposition through an intermolecular cyclization and dehydration reaction to form an imidazolidinone [3,4]. The 2-imidazolidinone was found in the EDA samples and one of the three major thermal degradation products. Zhou further hypothesized that the imidazolidinone can undergo nucleophilic attack by an additional EDA molecule to form a diethylenediamine urea compound, also known by the IUPAC name of *N,N'*-bis(2-aminoethyl)-urea [3]. This compound was also identified in the EDA samples.

The last major thermal degradation product found in the EDA samples had a protonated molecular weight of 173.13975 m/z, yielding a molecular formula of $C_6H_{12}N_4O_2$. This molecular formula did not fit into any general thermal degradation pathway, but was preliminary identified when it was considered that the diethylenediamine urea can also form a carbamate, then undergoes an intermolecular nucleophilic attack from the amine group at the other end of the molecule. This is actually similar to the reaction that forms imidazolidinone, where one amine group forms a carbamate while the other amine acts as a nucleophile to attack a carbonyl carbon. This compound has not yet been reported in the literature and was not listed in the Chemical Abstracts database, therefore its identification is still considered to be preliminary until it can be confirmed through other methods just as C^{13} -NMR.

The overall thermal degradation pathway for EDA is shown in Fig. 5. The first reaction is EDA carbamate formation, followed by either an intermolecular cyclization to form 2-imidazolidinone or by nucleophilic attack of a free EDA on the carbamate carbonyl to form *N,N'*-bis(2-aminoethyl)-urea. The other thermal degradation product identified is formed when the diethylenediamine urea forms a carbamate, then undergoes a nucleophilic attack.

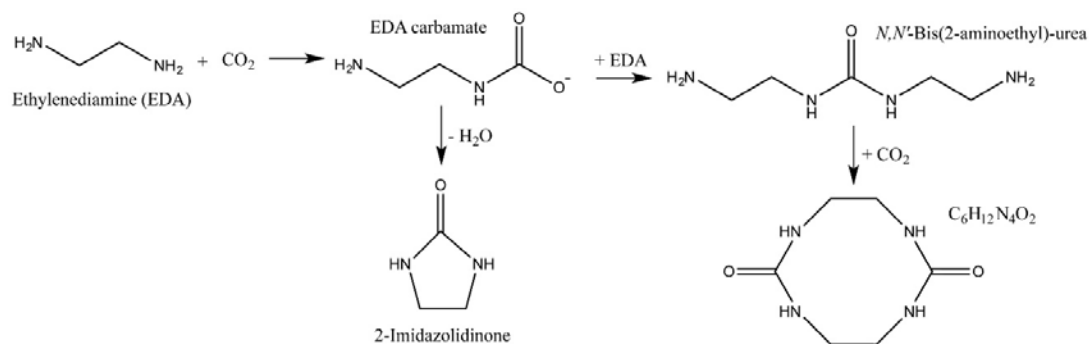


Fig. 5. Proposed thermal degradation pathway of ethylenediamine (EDA).

3.2. Diamine thermal degradation pathways

Three major peaks were also found in the thermal degradation samples for 1,2-propanediamine (1,2-DAP), 1,3-diaminopropane (1,3-DAP) and *N*-methyl-1,2-ethanediamine (*N*-MEDA). The same identification procedure was repeated for these diamine solutions and the same increase with heating time and heating temperatures was observed. Likewise, the same general thermal degradation that was observed with EDA was also seen with these similar diamine compounds under the same degradation conditions.

The proposed thermal degradation pathways for 1,2-diaminopropane (1,2-DAP) is shown in Fig. 6. First is the 1,2-DAP carbamate formation, followed by either an intermolecular cyclization to form an imidazolidinone, in this case 4-methyl-2-imidazolidinone, or by nucleophilic attack of a free diamine on the carbamate carbonyl to form a urea compound. The last thermal degradation product identified is formed when the diamine urea forms a carbamate, then undergoes a nucleophilic attack to yield the large cyclic diurea structure. In this case, both the urea and the cyclic diurea were not listed in the Chemical Abstracts database, therefore their identification is still consider to be preliminary.

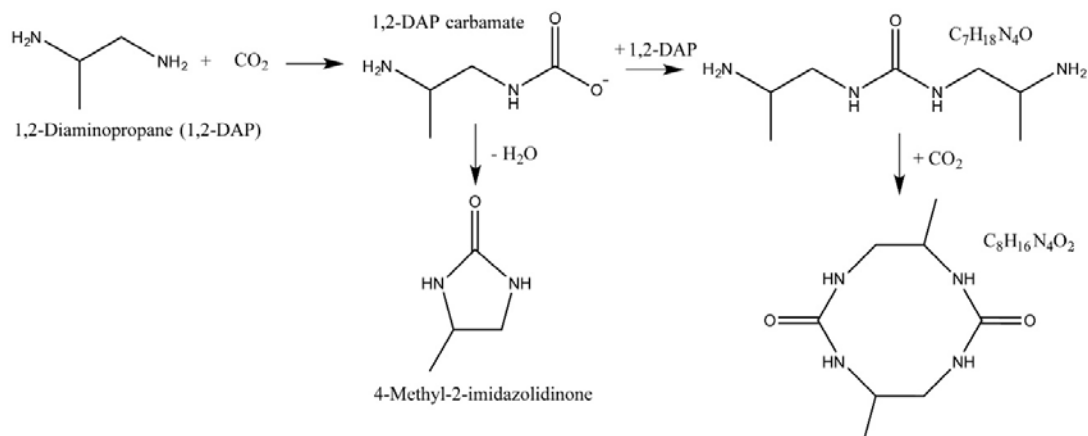


Fig. 6. Proposed thermal degradation pathway of 1,2-Diaminopropane (1,2-DAP).

The proposed thermal degradation pathways for 1,3-diaminopropane (1,3-DAP) is shown in Fig. 7. First we see the 1,3-DAP carbamate formation, followed by either an intermolecular cyclization to form an imidazolidinone, in this case the six-membered tetrahydro-2(1H)-pyrimidione, or by nucleophilic attack of a free diamine on the carbamate carbonyl to form a urea compound, *N,N'*-bis(3-aminopropyl)-urea. The last thermal degradation product identified is formed when the diamine urea forms a carbamate, then undergoes a nucleophilic attack to yield the large cyclic diurea structure. In this case for 1,3-DAP, the cyclic diurea were not listed in the Chemical Abstracts database, therefore its identification is still consider to be preliminary.

The proposed thermal degradation pathways for *N*-methyl-1,2-ethanediamine (*N*-MEDA) is shown in Fig. 8. First the *N*-MEDA forms a carbamate, followed by either an intermolecular cyclization to form an imidazolidinone, in this case the five-membered 1-methyl-2-imidazolidinone, or by nucleophilic attack of a free diamine on the carbamate carbonyl to form a urea compound. The last thermal degradation product identified is formed when the diamine urea forms a carbamate, then undergoes a nucleophilic attack to yield the large cyclic diurea structure. Again, in this case both the urea and the cyclic diurea were not listed in the Chemical Abstracts database, therefore their identification is consider to be preliminary.

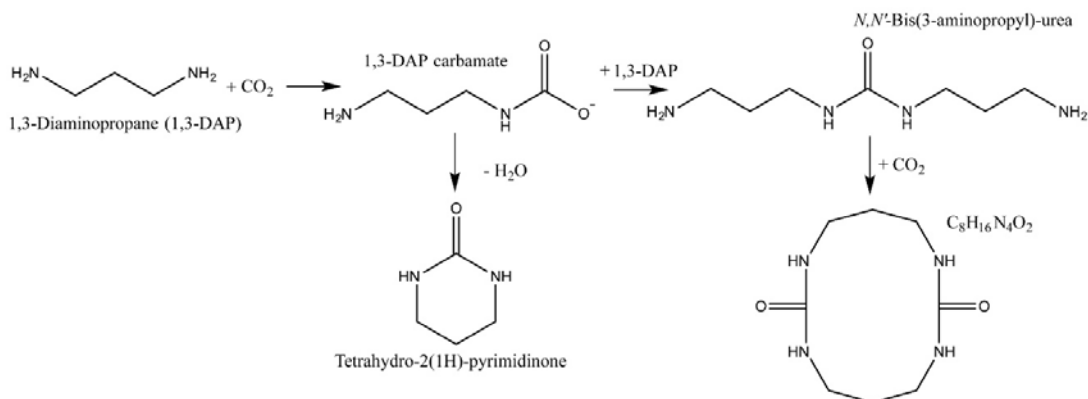


Fig. 7. Proposed thermal degradation pathway of 1,3-Diaminopropane (1,3-DAP).

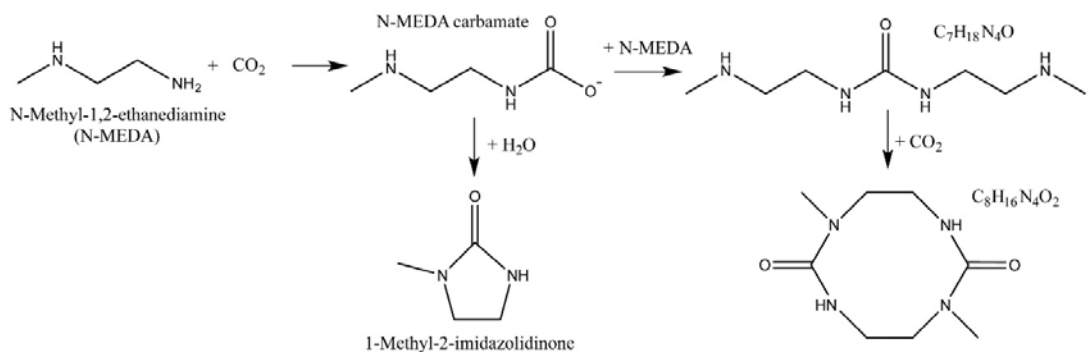


Fig. 8. Proposed thermal degradation pathway of N-Methyl-1,2-ethanediamine (N-MEDA).

4. Conclusions

Diamines have shown promise as CO₂ capture solvents, yet very little is known about their pathway for thermal degradation. In this study, diamine thermal degradation was quantitatively monitored in lab-scale experiments on four aqueous diamine solvents; ethylenediamine (EDA) 1,2-propanediamine (1,2-DAP), 1,3-diaminopropane (1,3-DAP) and N-methyl-1,2-ethanediamine (N-MEDA), to gain a more comprehensive understanding of their degradation pathway(s). The major degradation products were identified by high resolution time-of-flight mass spectrometry (TOF-MS). Degradation pathways were proposed showing that the primary routes are through carbamate formation followed by intermolecular cyclization to yield an imidazolidinone, or nucleophilic attack by a free amine to form a urea.

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