



Oxidative stability of structurally varied amines for post-combustion CO₂ capture

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ABSTRACT

Amine degradation is one of the key issues that hampers the implementation of amine-based post combustion carbon capture technology. In this work, the oxidative degradation of fourteen structurally varied amines were experimentally studied by measuring the amine loss, alkalinity change, ammonia yield, and degradation product. There is a linear relationship between amine loss against alkalinity change and ammonia yield, indicating that the degradation product either loss reactivity for CO₂ absorption or emit out as the small molecule. The results have shown that amine stability generally increased with amine order and stronger steric hindrance effect. Most primary and secondary amines showed more than 40 % amine loss after 336 h degradation experiment, while most of tertiary amines showed less than 10 % amine loss. This may be due to the exposed amine groups of primary and secondary amines. The oxidative degradation mechanism was studied based on density functional theory (DFT) calculations.

1. Introduction

Carbon dioxide (CO₂) is one of the greenhouse gases emitted by human activities and deemed as the main cause of climate change. According to the latest data from the International Energy Agency (IEA, 2023), global CO₂ emissions from energy consumption and industrial processes in 2022 reached a new high over 36.8 Gt, with growing by 0.9 % or 321 Mt compared to 2021. Net-zero carbon emission has been a world-wide consensus. Carbon capture, utilization, and storage (CCUS) is an important and effective way to achieve this goal (Jung et al., 2024; Teixeira et al., 2024).

Research on the use of absorbent to capture CO₂ has been carrying on for nearly a century and the technology has good opportunity to be scaled up for post-combustion CO₂ capture (Rochelle, 2009). In the 1930 s, a patent was granted to use aqueous ammonia solution to absorb CO₂ from flue gas or combustion gas (Bottoms, 1930). In this process, ammonia in packed absorber chemically binds CO₂ at low temperature to generate ammonium carbamate. The absorbent is then sent to stripper for regeneration at high temperature. CO₂ is then released simultaneously. However, the application of ammonia leads to a severe

absorbent loss during the CO₂ capture process and an environmental pollution concern (Darde et al., 2009). Moreover, the salt precipitation during the reaction between ammonia and CO₂ can affect the mass transfer and the transportation issues (Dave et al., 2009). Currently, post-combustion CO₂ capture process with alkanolamine is one of the most mature technologies (Zheng et al., 2024; Zheng et al., 2022), which can effectively decarbonize flue gas with low CO₂ partial pressure. The benchmark solvent, monoethanolamine (MEA) has characteristics of fast absorption rate, low viscosity, low price, and has been tested in pilot plants (Artanto et al., 2012; Khakharia et al., 2015; Notz et al., 2012; Moser et al., 2011).

However, degradation is one of the main drawbacks in amine-based post-combustion CO₂ capture technology. This issue leads to solvent loss, performance deterioration, and equipment corrosion. Amine degradation can be categorized as thermal degradation and oxidative degradation. Thermal degradation occurs in the stripper where the temperature is usually above 120°C. Researchers have shown that CO₂ loading is of great significance for thermal degradation (Lepaumier et al., 2009a; Lucas Braakhuis et al., 2022). Oxidative degradation mainly takes place in absorber due to 5 %-10 % oxygen contained in flue

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gas (Vevelstad et al., 2013; Jorgensen et al., 2022). The amine loss caused by oxidative degradation is accounting for 70 % of the total degradation loss. Although some researches have studied the oxidative degradation of MEA (Parks et al., 2020; Chi & Rochelle, 2002; Silva et al., 2012; Fredriksen & Jens, 2013) and other amines (Parks et al., 2021; Vevelstad et al., 2023), more works are required to further understand the complex oxidative degradation (Rieder et al., 2017). It has been reported that oxidative degradation can be catalyzed by certain transition metals, which come from equipment corrosion (such as Fe^{2+} and Fe^{3+}) (Gao et al., 2012; Nainar & Veawab, 2009), fly ash (such as Cr^{2+} and Zn^{2+}) (Chandan et al., 2014), or corrosion inhibitors (such as CuCO_3 and NaVO_3). The initial step of oxidative degradation could be explained by hydrogen abstraction mechanism (Rosenblatt et al., 1967; Smith & Mann, 1969) or electron abstraction mechanism (Goff & Rochelle, 2004). Oxidative degradation products are of large quantity and can be divided into two categories: general products and solvent-specific products (Vevelstad et al., 2023). The oxidative degradation of all alkanolamines gives general degradation products, which include ammonia, organic acids, aldehydes, and smaller alkylamines (Fredriksen & Jens, 2013). Solvent-specific degradation products are related to amine molecular structure and include larger amines (such as diamines), amines with cyclic structures (such as imidazole, piperazinone, and imidazolidone), amino acids, amides, nitrosamines, nitramines, and etc. (Vevelstad et al., 2023). Amine stability is a key aspect to be considered before conducting large-scale testing or implementing new amines. Therefore, oxidation stability and thermal stability should be considered in the early stages of solvent development.

This work studied the oxidative degradation of fourteen amines. Amine oxidation experiments were carried out under harsh conditions, including higher concentrations of O_2 and dissolved iron to accelerate the degradation process. The oxidative degradation experiments of structurally varied amines were carried out under the same experimental conditions. The amine loss, alkalinity loss and ammonia emission were measured to evaluate amine oxidative stability. The effects of amine structure on the oxidative stability were assessed, including amine order and steric hindrance. Ionizable degradation products including formate, nitrate, nitrite, and oxalate were analyzed. Density functional theory (DFT) calculations were used to deepen the understanding of the oxidative degradation mechanism of the studied amine.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using deionized water produced by ultra-pure water purification system, which was purchased from Dongguan Taoshi Water Treatment Equipment Co., Ltd. Carbon dioxide (CO_2 , 99.99 %) and Oxygen (O_2 , 99.99 %) gas were provided by Changsha Mind Gases Co., Ltd. Methanol (CH_3OH , ≥ 99.7 %), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, ≥ 99.8 %), sodium nitrate (NaNO_3 , ≥ 99.0 %), sodium nitrite (NaNO_2 , ≥ 99.0 %), formaldehyde aqueous solution (CH_2O , 37 ~ 40 %), sulfuric acid (H_2SO_4 , 95 %~98 %), and sodium hydroxide (NaOH , 99.5 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ferrous sulfate (FeSO_4 , 98 %), sodium formate (HCOONa , 99.5 %), and 1,2-Propanediol ($\text{C}_3\text{H}_8\text{O}_2$, 99.5 %) were purchased from Macklin. Benzyl alcohol ($\text{C}_7\text{H}_8\text{O}$, 99 %) was acquired from Aladdin. Mass flow controllers were provided by Beijing Sevenstar Flow Co., Ltd. All chemicals were used without further purification.

2.2. Oxidative degradation experiments

2.2.1. Preparation of amine solution

The concentrations of primary and secondary amines were 5 $\text{mol}\cdot\text{L}^{-1}$, while the concentration of tertiary amine was 4 $\text{mol}\cdot\text{L}^{-1}$. To avoid the AMP sedimentation after CO_2 absorption, the concentration of AMP was set to 4 $\text{mol}\cdot\text{L}^{-1}$. The amine solution was preloaded to 0.4 mol

CO_2 per mol amine.

2.2.2. Experimental process of oxidative degradation

As shown in Fig. 1, oxidative degradation experiments were carried out at simulated absorber conditions in 250 mL three-necked flask with magnetic stirrer and condenser. The temperature was controlled using a water bath. Two mass flow controllers (MFCs) were calibrated and used to regulate gas composition. After the gas mixing, a water saturator was employed to pre-saturate the gas mixture with water. The gas mixture then entered six three-necked flasks through gas dispersion tube with 30 ~ 50 μm of pore size. Rotameters were adopted to distribute gas flow to each three-necked flask, which contained aqueous amine solution and FeSO_4 . The water bath-cooled Graham condensers were set above the flasks to mitigate solvent loss. In addition, quantitative water makeup was applied. Ammonia (NH_3) generated during the oxidative degradation experiment was absorbed by 1 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 solution. All the oxidative degradation experiments were performed for two weeks, with samples taken out at 12, 24, 36, 48, 168, and 336 h, respectively.

2.2.3. Reaction conditions

The initial gas composition was designed for the oxidative degradation of primary and secondary amines to maintain the loading at 0.4 mol $\text{CO}_2\cdot\text{mol amine}^{-1}$. For this, the gas composition of 98 % O_2 and 2 % CO_2 was adopted. However, this CO_2 pressure was not enough to maintain the loading of tertiary amine (Buvik et al., 2021). Therefore, the oxidative degradation experiments of tertiary amines were carried out with a total of 20 $\text{mL}\cdot\text{min}^{-1}$ gas mixture containing 83.5 % O_2 and 16.5 % CO_2 . The total gas flow of 20 $\text{mL}\cdot\text{min}^{-1}$ was applied to each three-necked flask. Each flask contained 200 mL aqueous amine solution and 0.5 $\text{mmol}\cdot\text{L}^{-1}$ FeSO_4 . The reaction temperature was maintained at 60°C. The solubility of FeSO_4 in both 3AP and MEA solutions were tested before conducting oxidative degradation experiment. The solution was under ultrasonic for 2 h, and then stand overnight. Sulfate concentration was analyzed by anion chromatography to calculate FeSO_4 solubility.

2.3. Analytical methods

2.3.1. Gas chromatography analysis

Gas chromatography (GC) was used for analysis of amine concentrations, which were calculated using the internal standard method. For MEA and MDEA, 1,2-propanediol ($\text{C}_3\text{H}_8\text{O}_2$) was adopted as an internal standard, while for other amines, benzyl alcohol ($\text{C}_7\text{H}_8\text{O}$) was employed as an internal standard. The degraded solvent (0.5 mL), methanol (2 mL), and internal standard reagents (0.1 g) were placed in a 5 mL borosilicate glass vial and the mixed solutions were injected into gas chromatography through 1 μL microliter syringes. Analyses were complete using FULI 9790II gas chromatograph equipped with FID detector. A SE-54 capillary column (25 m \times 0.32 mm \times 0.5 μm) with nitrogen carrier gas was adopted for the separation of degradation products with an initial column temperature of 140°C for 2 min. The column temperature was then increased to 240°C with heating rate of 30°C $\cdot\text{min}^{-1}$ and held for another 2 min. All samples were tested in replicates 3 to 5 times, and the average value was taken to calculate the amine concentration. Amine loss was calculated by equation (1):

$$C_{\text{loss}} (\%) = \frac{C_{\text{initial}} - C_{\text{end}}}{C_{\text{initial}}} \times 100\% \quad (1)$$

Where C_{loss} – amine loss; C_{initial} – initial amine concentration, $\text{mol}\cdot\text{L}^{-1}$; C_{end} – amine concentration after oxidative degradation experiment, $\text{mol}\cdot\text{L}^{-1}$.

2.3.2. Alkalinity analysis

The alkalinity loss was measured by 916 Ti-Touch Potentiometric Titrator purchased from Metrohm. Amine solution (0.3 g) and deionized water (20 mL) were placed in a beaker and titrated with standard hydrochloric acid (HCl) solution. The consumption of HCl solution was

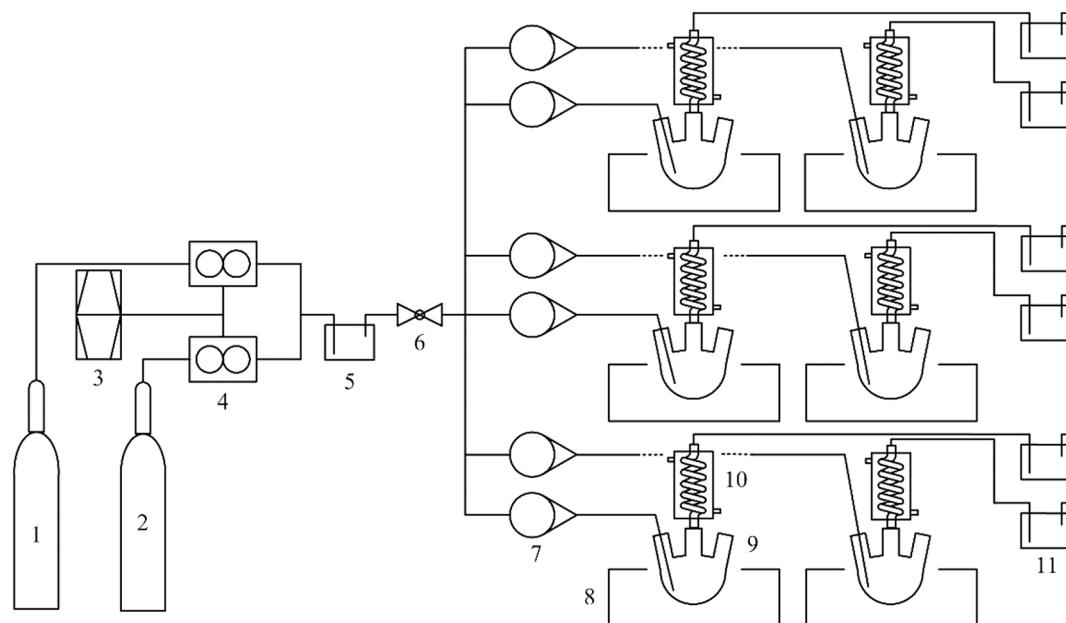


Fig. 1. Schematic of the oxidative degradation setup. 1-O₂ cylinder; 2-CO₂ cylinder; 3-Mass flow controllers; 4-Mass flow meters; 5-Water saturator; 6-Gas distributor; 7-Rotameters; 8-Magnetic stirring water bath; 9-Three-necked flask; 10-Graham condensers; 11-NH₃ absorption bottles.

recorded when the titration endpoint was reached. The alkalinity was calculated by equation (2):

$$\text{Alkalinity (mol} \cdot \text{kg}^{-1}) = \frac{C_{\text{HCl}} \cdot V_{\text{HCl}}}{m_{\text{amine}}} \quad (2)$$

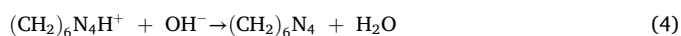
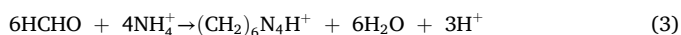
Where C_{HCl} –concentration of HCl solution, mol·L⁻¹; V_{HCl} –consumption of HCl solution, mL; m_{amine} – amine solution quantity, kg.

2.3.3. Viscosity measurement

The viscosity was measured by ViscoQC 300-L rotational viscometer provided by Anton Paar. A 7.5 mL of amine solution was used, and the viscometer was calibrated before each viscosity test.

2.3.4. Volatile compound analysis

The NH₃ generated during oxidative degradation was absorbed by H₂SO₄ to form NH₄⁺. The method for determining the concentration of NH₄⁺ in H₂SO₄ solution was as follow: Firstly, a few drops of phenolphthalein, 0.5 mL of H₂SO₄ solution and 10 mL of deionized water and were placed in a conical flask and titrated with standard NaOH solution. The consumption volume of NaOH was denoted as V_1 . Then, another 0.5 mL H₂SO₄ solution, 2 mL formaldehyde aqueous solution (CH₂O), 10 mL deionized water, and a few drops of phenolphthalein were placed in a conical flask. The flask was under magnetic stirring for 5 min to convert NH₄⁺ into hexamethylene tetraammonium cations ((CH₂)₆N₄H⁺) and H⁺. The reaction equations are shown in equations (3), (4), and (5). The mixed solution was then titrated with standard NaOH solution and the consumption of NaOH solution was recorded as V_2 . The value of ($V_2 - V_1$) was the volume of NaOH consumed by NH₄⁺.



2.3.5. Ion chromatography analysis

Formate, nitrate, nitrite, oxalate, and sulfate were quantified by ion chromatography (IC) using a Shine CIC-D100 system equipped with a SH-AP-1 analytical column (4 × 250 mm), SH-GP-2 guard column (4 × 50 mm), conductivity detection, and SHY-A-7 suppressor operated at

35°C. The concentration of NaOH eluent was 14 mmol·L⁻¹. Anion standards were prepared using HCOONa, NaNO₃, NaNO₂, Na₂C₂O₄, and Na₂SO₄ in the concentration range from 1 to 50 mg·L⁻¹. The degraded amine samples were diluted between 1:10 and 1:200 with deionized water, depending on the degree of loss of amine concentration.

2.3.6. CO₂ loading measurement

The CO₂ loading of amine solution was determined by the device shown in the Fig. S1. The flask contained amine solution, deionized water, and methyl orange solution. The liquid level was recorded as V_1 in measuring burette before titrating. The amine solution was titrated with standard HCl solution, and an excess HCl solution was used to ensure complete CO₂ release. The liquid level was recorded as V_2 in measuring burette after titrating. The CO₂ loading of amine solution was calculated by equation (6):

$$\alpha (\text{mol} \cdot \text{mol}^{-1}) = \frac{V_2 - V_1 - V_{\text{HCl}}}{22.4 \times V_{\text{amine}} \times C_{\text{amine}}} \times \frac{273.15}{T} \quad (6)$$

Where α – CO₂ loading of amine solution, mol·mol⁻¹; V_2 – final liquid level in measuring burette, mL; V_1 – initial liquid level in measuring burette, mL; V_{HCl} – consumption of HCl solution, mL; V_{amine} – volume of amine solution, mL; C_{amine} – concentration of amine solution, mol·L⁻¹; T – ambient temperature, K.

2.3.7. ¹³C nuclear magnetic resonance (NMR) spectroscopy analysis

The ¹³C NMR spectroscopy was obtained by AVANCE III Bruker 400 MHz NMR spectrometer. The amine solution was dissolved in deuterium oxide, and the number of scans was set as 100.

2.4. Computational methods

All calculations in this paper were performed based on DFT using the procedure established in our previous work (Ouyang et al., 2024). The Gaussian 09 was used for at the level of theory of B3LYP/6-311++G (d, p) under 25°C. The optimized structure was confirmed by calculating local minima in the absence of imaginary frequencies in the vibrational spectra. The enthalpies (ΔH) and free energies (ΔG) of all species were calculated using Solvation Model based on Density (SMD) implicit solvent model. The energy difference between the transition state (TS) and

both reactants at infinite separation was used to calculate the reaction energy barrier.

3. Results and discussion

3.1. Oxidative degradation

The oxidative degradation leads to amine loss, alkalinity loss, and NH_3 emission. In addition, physical property (such as viscosity) is affected by the change of solvent composition. The normalized concentration of all the studied amines throughout 336 h of oxidative experiments is shown in Fig. 2 and Table S1. As can be seen from Figs. 2, 3AP and AMP show significant less amine loss and NH_3 yield among the primary and secondary amine, respectively. The concentration of other four primary amines, MEA, 1AP, 2AP, and AMB, decreased rapidly and found to have over 45 % amine losses after 336 h of oxidative degradation experiment. The total NH_3 concentrations in their products were higher than $55 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine, initial}}$. Additionally, two secondary amines, MAE and EAE, showed amine losses of greater than 40 %, which is similar to that of the four primary amines mentioned above. However, the total NH_3 concentrations in their degradation products were less than $30 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine, initial}}$. It was shown that the volatile products of secondary and tertiary amines oxidative degradation consist of methylamine and dimethylamine, in addition to NH_3 (Lepaumier et al., 2009b). As shown in Fig. 2 (b), all tertiary amines except 1DMA2P kept a slow degradation rate and had less than 10 % amine loss after 336 h of oxidative degradation experiment. The total NH_3 concentrations in their

products were less than $8 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine, initial}}$, showing the excellent stability on oxidative degradation of the tertiary amines. A comprehensive comparison of amine stability related to its molecule structure will be discussed in the following section.

Alkalinity is an indicating parameter of the ability of amine solution to neutralize protons. The higher alkalinity indicates a better capability to absorb more CO_2 . Viscosity is also an important parameter of amine solution. It affects the mass and heat transfer in the CO_2 capture system. As a result, alkalinity, CO_2 loading, and viscosity of the amine solution before and after oxidative degradation experiment were studied in this work. The alkalinities and CO_2 loadings of all the studied amines after 336 h of oxidative degradation experiment are summarized in Table S2. Most of the studied amines can maintain the CO_2 loading greater than $0.3 \text{ mol } \text{CO}_2 \cdot \text{mol}^{-1}_{\text{amine}}$. Fig. 3 (a) shows a comparison of amine loss and alkalinity loss of all the studied amines. It was observed that the level of amine losses was close to that of alkalinity losses, suggesting that there are few alkaline substances in their liquid oxidative degradation products. Among the studied primary and secondary amines, only 3AP and AMP had less than 10 % alkalinity loss, while the others showed alkalinity loss over 35 %. This observation is consistent with the amine loss data presented in Fig. 2 (a). Interestingly, all the studied tertiary amines (excepting 1DMA2P) had less than 10 % alkalinity loss. Fig. 3 (b) shows a linear relationship between amine loss and NH_3 yield. The results indicated that the degradation product either loss reactivity for CO_2 absorption or emit out as the small molecule, such as NH_3 .

The viscosity of amine solvent affects the interphase mass transfer and diffusion process of CO_2 in the liquid phase, thereby affecting the

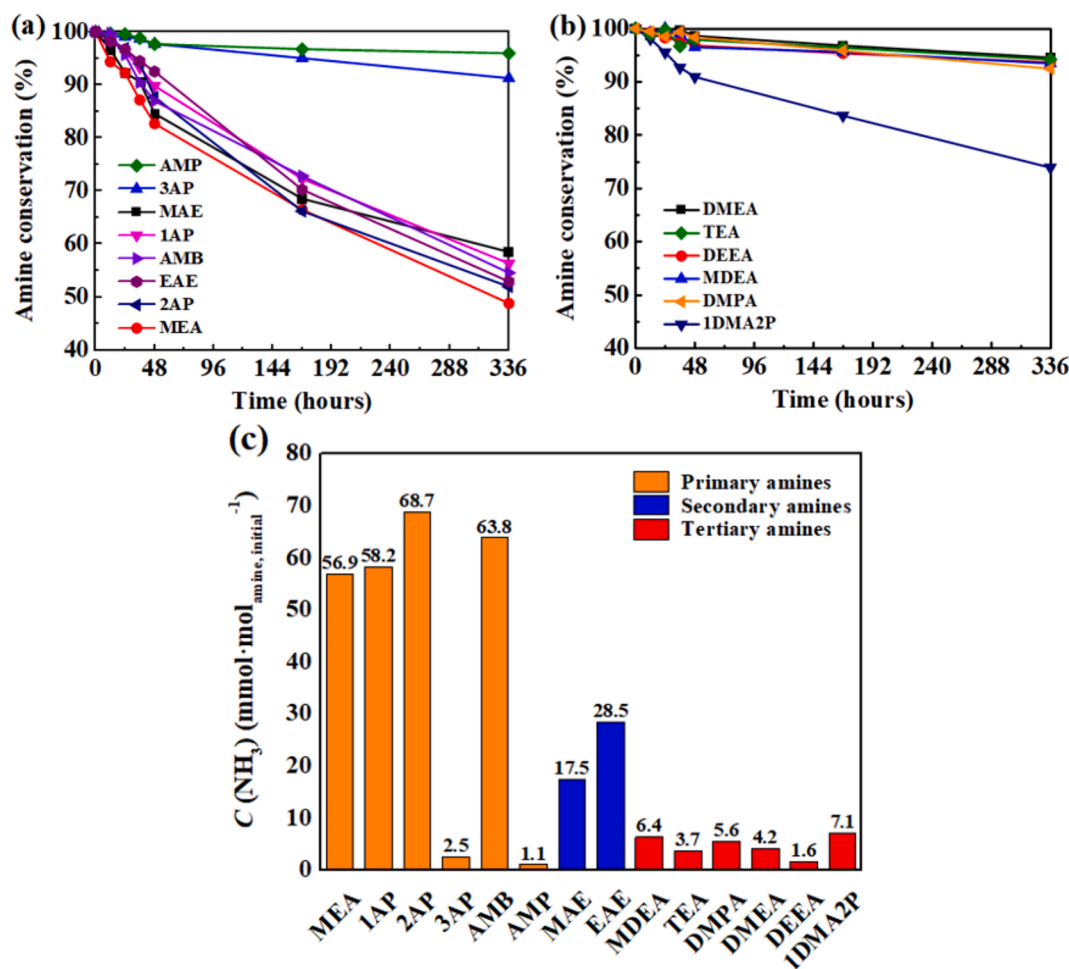


Fig. 2. Normalized amine concentrations of primary and secondary amines (a), normalized amine concentrations of tertiary amines (b), and total NH_3 concentrations in the products (c) throughout 336 h of oxidative degradation experiment (Quantification made by GC and corrected for sampling loss).

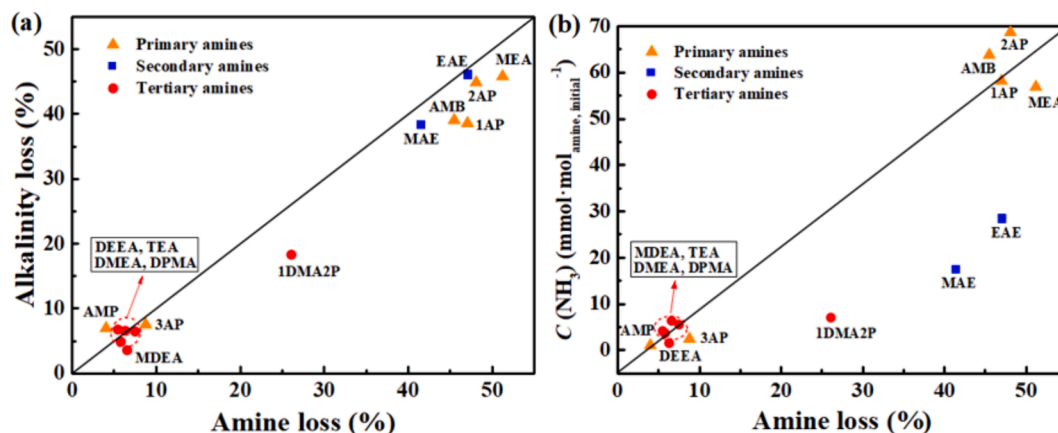


Fig. 3. Comparison of amine loss and alkalinity loss (a), total NH_3 concentrations (b) of all the studied amines after 336 h of oxidative experiments.

capture efficiency of CO_2 . Table S3 shows the viscosity of amine solvent after 336 h of oxidative degradation experiments. It can be seen that all amine solutions showed a decrease in viscosity. This result indicates the change of solvent composition. The 3AP solution showed a less viscosity drop compared with the primary and secondary amines, owing to the lower amine loss and the higher CO_2 loading of 3AP solution after the degradation experiment. Although most of the tertiary amine shows a strong resistance to the oxidative degradation, it shows an apparent drop of solution viscosity due to the decrease of CO_2 loading. In an actual continuous cyclical operation, the solution viscosity can be elevated by amine make-up and accumulation of the amine degraded products. In the practical application, the viscosity will increase when solvent make-up is applied, and by-products accumulate in the degraded solvent.

3.2. The influence of amine structure on the oxidative degradation

The influence of amine structure variation (such as steric hindrance, amine order, chain length, and hydroxyethyl substitution) on the oxidative degradation is studied by comparing MEA and the other thirteen alkanolamines. Amine losses of all the studied amines are shown in Fig. 4.

The effect of amine order on the oxidative degradation is summarized in Fig. 5. The benchmark MEA with 51.2 % amine loss was used as a baseline for the comparison. As can be seen from Table 1, the

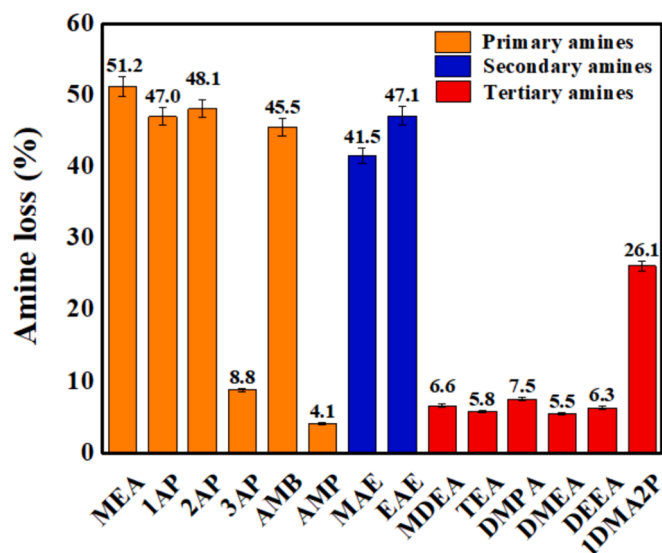


Fig. 4. Amine losses of all the studied amines after 336 h of oxidative degradation experiments.

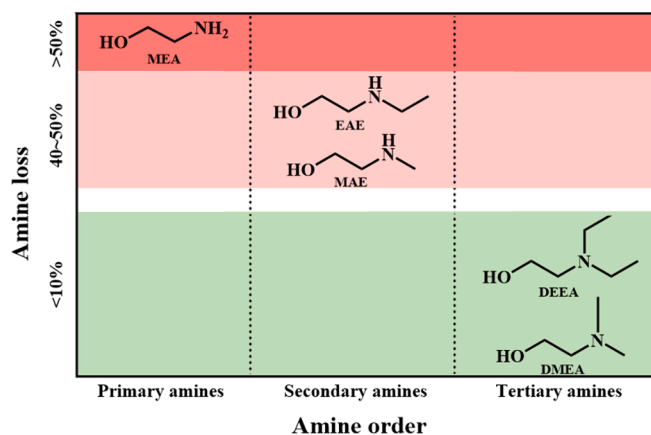


Fig. 5. The effect of amine order on the oxidative degradation.

structures of MAE (secondary amine) and DMEA (tertiary amine) are similar to that of MEA. One difference is MAE and DMEA have one and two additional methyl groups attached to the nitrogen atom. From the experiment, amine loss of DMEA (5.5 %) was lower than that of MAE (41.5 %) and MEA (51.2 %), respectively (see Fig. 4). A similar behavior can be observed in the case of MEA, EAE, and DEEA (in which EAE and DEEA have one and two ethyl groups attached to the nitrogen atom, as presented in Table 1). These observations indicate that the amine stability increase with the number of alkyl group attached to the nitrogen atom. Additionally, it was found that most of the primary amines are more prone to oxidative degradation than highly substituting amines, possibly because of the exposed amine groups (Buvik et al., 2021). For the secondary amine, an extension of methyl group in MAE to ethyl group in EAE resulted in the increase of amine loss from 41.5 % to 47.1 %, as given in Fig. 4. Lepaumier et al. (2010) showed that a preliminary demethylation reaction is required for tertiary amines to cause significant degradation, which increases the chemical stability of tertiary amines. In this work, most of the tertiary amine solution (including, MDEA, TEA, DMPA, DMEA, and DEEA) exhibited amine loss less than 10 %. Interestingly, there was no significant difference in amine loss among the studied tertiary amine solutions regarding the hydroxyethyl substitution.

In addition to an amine order, a steric hindrance also affects the amine stability against oxidative degradation. Fig. S2–S17 show the ^{13}C NMR spectroscopy of all the studied amine solutions, which is used to obtain the structure information of their functional groups and substituents. A comparison is made based on the steric hindrance effect of different amines, as shown in Fig. 6. Compared to MEA, 2AP has an

Table 1
Summary of structures and purities of the studied amines.

Compound	Abbreviation	Structure	CAS number	Purity	Manufacturer
Monoethanolamine	MEA	<chem>HOCH2CH2NH2</chem>	141-43-5	99 %	Aladdin
DL-1-Amino-2-propanol	1AP	<chem>CC(O)C(N)</chem>	78-6-6	99 %	Rhawn
DL-Alaninol	2AP	<chem>CC(N)C(O)</chem>	6168-72-5	98 %	Macklin
3-Amino-1-propanol	3AP	<chem>HOCH2CH2CH2NH2</chem>	156-87-6	99 %	Aladdin
2-Amino-2-methyl-1-propanol	AMP	<chem>CC(C)(N)CO</chem>	124-68-5	≥95 %	Meryer
2-Amino-1-butano	AMB	<chem>CCC(N)CO</chem>	96-20-8	97 %	Aladdin
2-(Methylamino)ethanol	MAE	<chem>CCNCCO</chem>	109-83-1	99 %	Aladdin
2-(Ethylamino)ethanol	EAE	<chem>CCNCCO</chem>	110-73-6	98 %	Aladdin
2-Dimethylaminoethano	DMEA	<chem>CN(C)CCO</chem>	108-01-0	99 %	Aladdin
2-(Diethylamino)ethanol	DEEA	<chem>CCN(CC)CCO</chem>	100-37-8	99 %	Macklin
3-Dimethylamino-1-propanol	DMPA	<chem>CN(C)CCCO</chem>	3179-63-3	99 %	Aladdin
N-Methyldiethanolamine	MDEA	<chem>CN(CCO)CCO</chem>	105-59-9	99 %	Meryer
Triethanolamine	TEA	<chem>CCN(CCO)CCO</chem>	102-71-6	98 %	Rhawn
1-Dimethylamino-2-propanol	1DMA2P	<chem>CC(C)(N)CO</chem>	108-16-7	98 %	Meryer

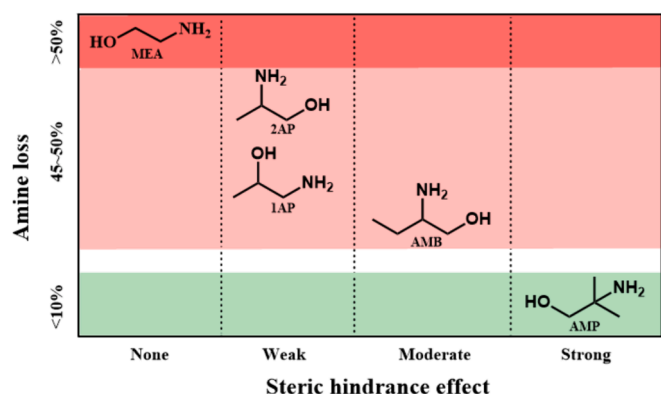


Fig. 6. The effect of steric hindrance on oxidative degradation.

additional methyl group on the α -carbon, while 1AP has an additional methyl group on the β -carbon (see Table 1). From 51.2 % amine loss of MEA, the amine loss of 2AP and 1AP reduced to 48.1 % and 47.0 %, respectively. This indicates that the presence of an additional methyl group on the α -carbon or β -carbon slightly increases the amine stability. The amine groups of 1AP and 2AP are shielded by steric hindrance effect, which protect molecules from free radical attack and reduce the chain propagation reaction. This is beneficial for the termination of free radical reactions.

In the case of AMB, the amine molecule has an additional ethyl group on α -carbon respecting MEA (Table 1). The steric hindrance effect of AMB is then stronger than that of 2AP and 1AP (which have one methyl group on the α -carbon or β -carbon in the structure). This can further lead to a decline of amine loss of AMB (45.5 %) respecting that of MEA (51.2 %). In the case of AMP, the two additional methyl groups on the α -carbon provided a strong steric hindrance effect that destabilized the carbamate and shifted the reaction products from carbamate to bicarbonate and carbonate (Ciftja et al., 2014). Owing to the significant difference in a form of reaction product, AMP solution exhibited an excellent stability with only 4.1 % amine loss. This is comparable with tertiary amine, which can only generate protonated amine, bicarbonate, and carbonate upon CO_2 absorption. The excellent stability of AMP and tertiary amines under oxidative conditions indicates that oxidative degradation take place through carbamates, rather than the direct reaction of amines with oxidant. In addition, the steric hindrance of AMP makes it difficult to form free radical on α -carbon, preventing the cleavage of C-N bonds (Lepaumier et al., 2009b). To conclude, the additional alkyl group on the main chain of primary and secondary amine molecule provides stronger steric hindrance effect and leads to stronger stability against oxidative degradation.

In conclusion, primary amines are more prone to oxidative degradation than highly substituting tertiary amines, possibly because of the exposed amine groups. Steric hindrance plays a vital role in the stability of oxidative degradation. The presence of an additional substituent group, methyl or ethyl group, on the α -carbon or β -carbon relative to the amine group increases oxidative stability. The amine groups of sterically

hindered amine are shielded by steric hindrance effect, which protect molecules from free radical attack and reduce the chain propagation reaction.

There are two outliers that need to be specifically mentioned. 1DMA2P, which had 26.1 % amine loss, presented itself as an outlier compared with DMEA. If the hydroxyl group in tertiary amine has a relatively suitable distance from the amine group, usually spacing two or three carbon atoms, an intramolecular hydrogen bond will be formed between a nitrogen atom and a hydrogen atom. This is a more stable molecular configuration (Cacela et al., 2001; Puxty et al., 2009). As shown in Fig. 7, intramolecular hydrogen bond is formed within 1DMA2P molecule. However, the steric hindrance introduced by the additional methyl group on β -carbon reduces the stability of hydrogen bond, resulting the cleavage of chemical bond and the formation of acetone and dimethylamine (Buvik et al., 2021). Therefore, steric hindrance reduces the oxidative stability of tertiary amines that form intramolecular hydrogen bonds. In addition, 3AP, which is a linear primary amine without steric hindrance effect, showed significant lower amine loss that is comparable with tertiary amine or primary amine with strong steric hindrance effect (shown in Fig. 4). To understand such behavior, more discussion will be provided in the following section accompanied with degradation products identification and DFT calculation.

3.3. Oxidative degradation products

Anion IC analysis was used to quantify amine degradation products (i.e., formate, nitrate, nitrite, and oxalate). The information of other anions (e.g., acetate and glycolate) was not available as they cannot be distinguished with each other in IC spectrum. Fig. 8 and Table S4 show that the total concentrations of formate, nitrate, nitrite, and oxalate are less than $2 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$ for AMP, 3AP, and tertiary amines. This is consistent with the amine loss results (shown in Fig. 2). The concentration is normalized based on the initial amine concentration. The rest of the amine solvents generated over $15 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$ anionic compounds. Formate is one of the most common primary products of amine oxidation degradation. It is found in all amine solvents and accounted for more than 30 % of all measured anionic compounds. Formic acid is mainly formed through the oxidation of aldehydes or oxalic acid (Lepaumier et al., 2009b). Oxalate concentration is much lower than formate concentration, partially because oxalic acid can be oxidized to form formic acid. Nitrate and nitrite are mainly present in the oxidative degradation products of amines with relatively high NH_3 yield (e.g., MEA, EAE, AMB, 1AP, and 2AP) because nitrate and nitrite are formed through the oxidation of NH_3 at gas–liquid interface.

Fig. 9 and Table S5 show the concentration of formate, nitrite, nitrate, and oxalate in the products of MEA and 3AP as a function of time. Formate is the main ionizable product of the oxidative degradation of MEA and 3AP. For MEA, the initial formate formation rate was slow, and the formate concentration at 48 h was only $1.3 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$. There are few numbers of free radicals at the initial stage of oxidative degradation reaction, resulting in a slow reaction rate. Formate concentrations then increased to $11.7 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$ and $32.2 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$ at 168 and 336 h, respectively, showing a significant increase in formation rate. The formation rates of nitrate and nitrite were relatively stable because of the limitation of the NH_3 concentration at the gas–liquid interface. For 3AP, the concentration of nitrate and

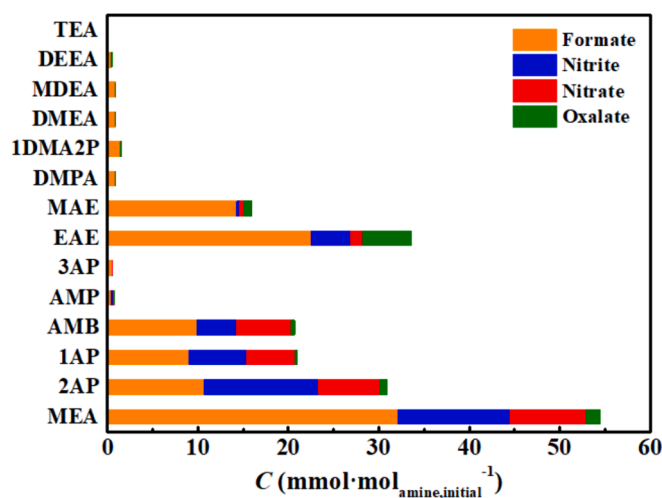


Fig. 8. Concentrations of formate, nitrate, nitrite, and oxalate quantified in end samples of oxidative degradation experiments.

nitrite in the oxidation degradation products were less than $0.02 \text{ mmol} \cdot \text{mol}^{-1}_{\text{amine,initial}}$ during the whole experiments, while formate concentration increased slowly.

3.4. DFT calculation

It is generally accepted that amine oxidative degradation is triggered by O_2 radicals directly or a free radical initiated by O_2 in flue gas (Vevelstad et al., 2023). There are two types of mechanisms of oxidative degradation where primary amine with heteroatoms degrades via hydrogen abstraction from α -carbon (Goff & Rochelle, 2004) and tertiary amine go through electron abstraction mechanism (Chi & Rochelle, 2002; Goff & Rochelle, 2004). Fig. 10 shows the hydrogen abstraction mechanism for the oxidative degradation of MEA and 3AP. The reaction mechanism of 3AP is adapted from that of MEA. The initiation reaction in the hydrogen abstraction mechanism is the ionization of alkanolamines in aqueous solutions (Lepaumier et al., 2009b). MEA can form a cyclic structure by hydrogen bonding between $\text{HN} \cdots \text{O}$ or $\text{OH} \cdots \text{N}$. Free radicals can abstract a proton from N atoms or C atoms to form amine radicals. The newly formed amine radical can transfer the radical through the cyclic structure, eventually leading to the cleavage of N–C bonds, resulting in degradation products such as ammonia and acetaldehyde radicals. Acetaldehyde radicals can abstract protons from other amine molecules to produce amine radicals and acetaldehyde. In terms of mechanism verification, some molecular simulation studies have verified the correctness of the transition state of the cyclic structure formed by MEA (Alejandro et al., 2000).

DFT modeling the formation of distinct radicals from MEA and 3AP was carried out according to the above reaction mechanism. Ethyl radical (Et^\bullet) and peroxy radical (O_2^\bullet) were used as the free radicals that react with amine (Parks et al., 2021). Tables S6 and S7 show the free energies for the formation of distinct radicals from MEA and 3AP, respectively. The free energy for the reaction of MEA and Et^\bullet is smaller than that for the reaction of MEA and O_2^\bullet , showing a greater predisposition to this reaction. As can be seen from Figs. 11 and 12, the free energy for the formation of amine radical on α -C after reaction with Et^\bullet

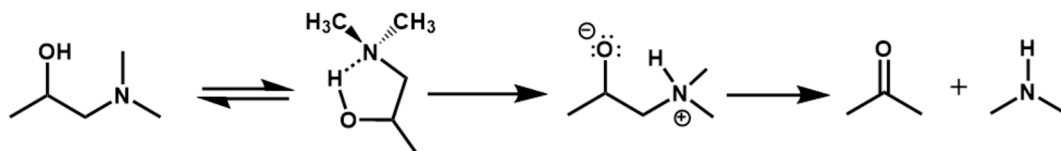


Fig. 7. Suggested mechanism for the formation of acetone and dimethylamine during 1DMA2P degradation.

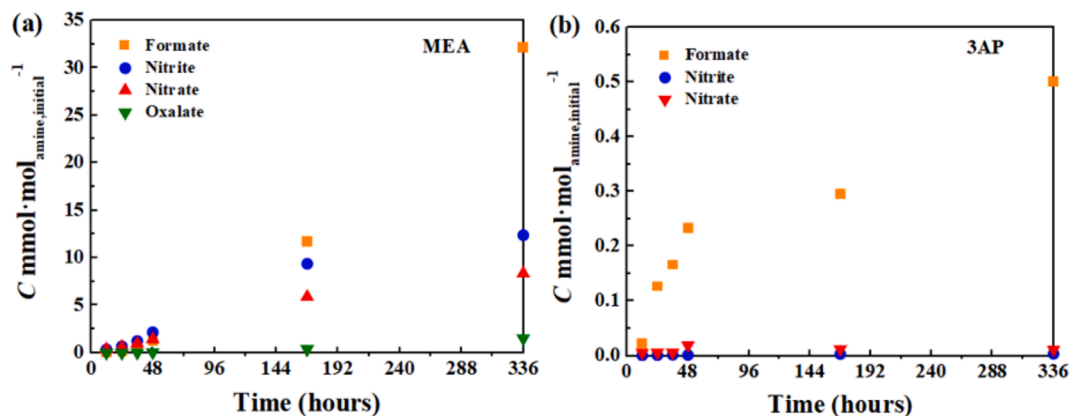


Fig. 9. Concentrations of formate, nitrate, nitrite, and oxalate as a function of time: MEA (a), and 3AP (b).

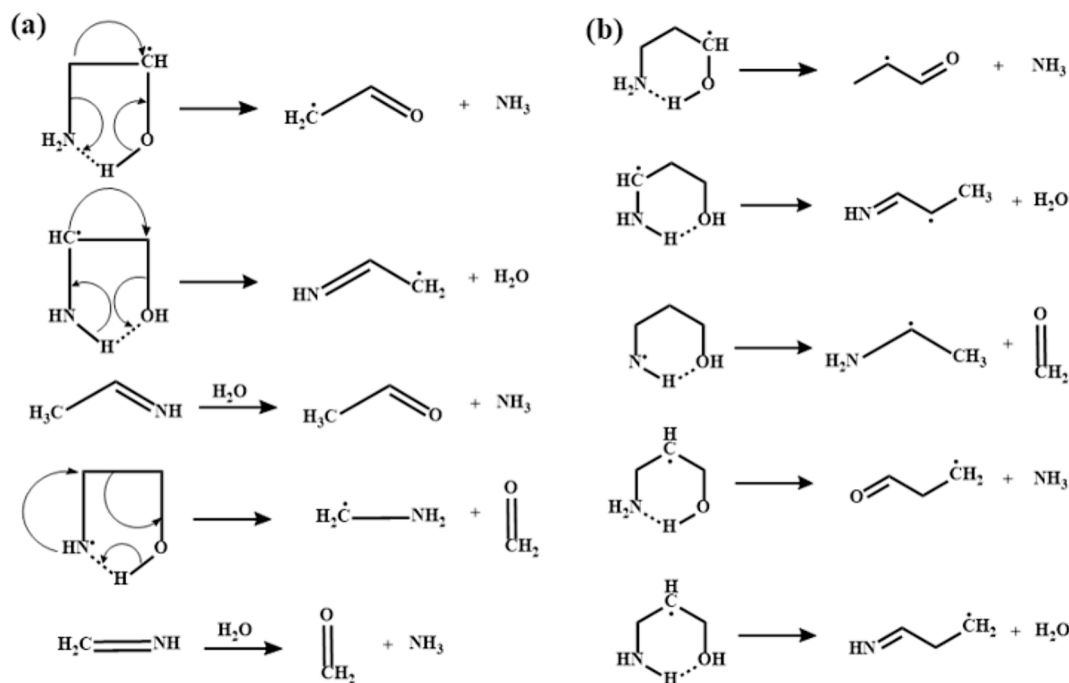


Fig. 10. Hydrogen abstraction mechanism for the oxidative degradation of MEA (a) and 3AP (b).

is the lowest for both MEA and 3AP, which has more thermodynamic advantages. The reaction energy barriers for the formation of 3AP radicals at all sites are higher than those for the formation of MEA radicals. In addition, the free energies of the formed MEA radicals are generally lower than those of the formed 3AP radicals. Therefore, the formation of MEA radicals is more advantageous in terms of kinetics and thermodynamics.

Tables 2 and 3 show the results of ΔH and ΔG for the chain propagation reaction of both MEA radicals and 3AP radicals according to hydrogen abstraction mechanism. It can be seen that ΔH and ΔG of the amine radical reactions on all the sites except for on N site are negative, showing an exothermic and spontaneous reaction. Smaller ΔH and ΔG are observed for the chain propagation reactions of 3AP radicals than those of MEA radicals, suggesting that 3AP reaction products is thermodynamically more stable.

The studies suggest that the excellent oxidative stability of 3AP might be attributed to the fact that metals did not catalyze oxidative degradation for their insolubility in 3AP solution (Liu et al., 2014). In order to determine whether the metal ions solubility affects 3AP oxidation degradation, the solubility of FeSO_4 in both MEA and 3AP

solutions was tested, respectively. The FeSO_4 solubility in $5 \text{ mol} \cdot \text{L}^{-1}$ MEA and 3AP solutions at 25°C are 44.3 and $44.7 \text{ mg} \cdot \text{L}^{-1}$, respectively. This suggests that the excellent stability of 3AP is independent of metal ions solubility.

In conclusion, since 3AP is more stable than MEA against oxidative degradation, the formation of distinct radicals may dominate the amine degradation instead of the chain propagation reaction.

4. Conclusion

This work focused on the influence of different amine structural characteristics on amine oxidative stability. Fourteen amines varying in amine order, steric hindrance, chain length, and the number of hydroxyethyl groups were studied under harsh oxidative conditions. Amine oxidative stability generally increases with increasing order from primary, secondary and tertiary amines, respectively. AMP with steric hindrance in molecular structure exhibits excellent stability with only 4.1 % amine loss, which is comparable with tertiary amines. The excellent stability of AMP and tertiary amines under oxidative conditions indicates that oxidative degradation may take place through

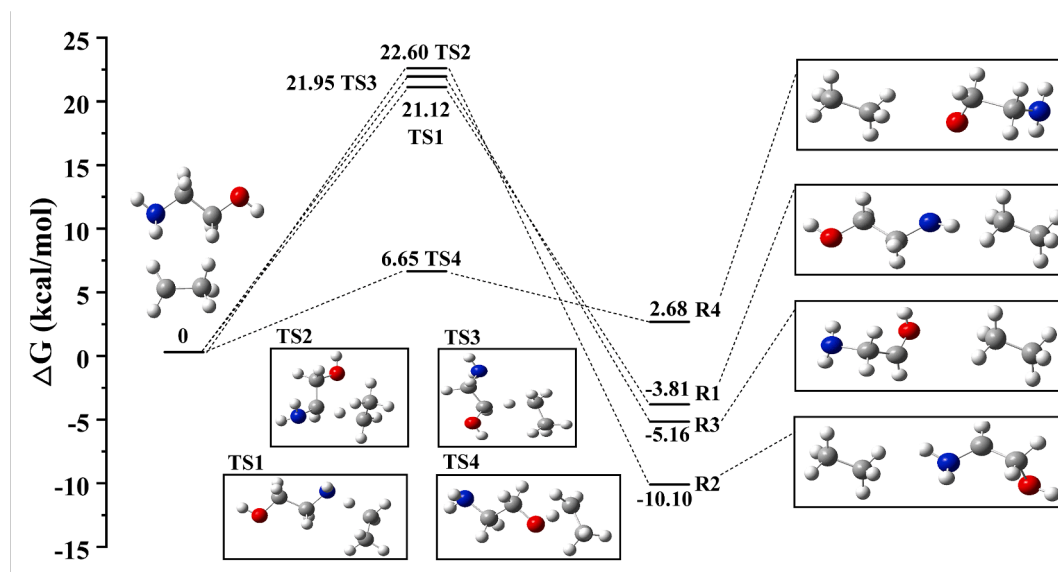


Fig. 11. DFT-calculated ΔG for the hydrogen radical abstraction from four sites on MEA by an ethyl radical. The site of MEA radical formation: R1 – N; R2 – α -C; R3 – β -C; R4 – O.

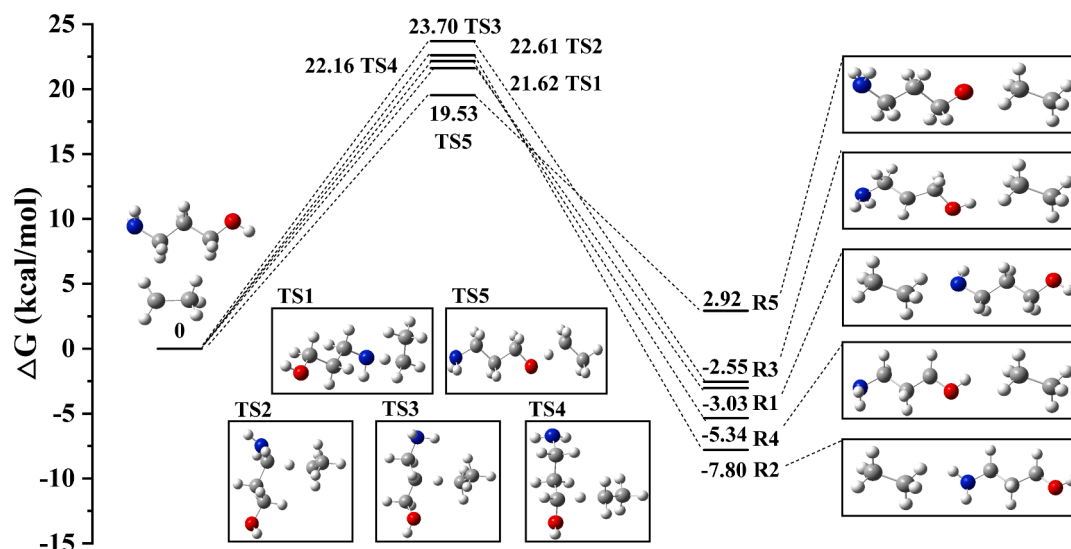


Fig. 12. DFT-calculated ΔG for the hydrogen radical abstraction from five sites on 3AP by an ethyl radical. The site of 3AP radical formation: R1 – N; R2 – α -C; R3 – β -C; R4 – γ -C; R5 – O.

carbamates. Formic acid is mainly formed through the oxidation of aldehydes or oxalic acid. Oxalate was mainly present in the oxidative degradation products of amines with relatively high amine loss. Nitrate and nitrite originating from NH_3 were mainly present in the oxidative degradation products of amines with relatively high NH_3 yield.

DFT modeling the reaction process of free radicals from MEA and 3AP were carried out according to hydrogen abstraction mechanism. The calculation results show that the formation of MEA radicals is more advantageous in terms of kinetics and thermodynamics than the formation of 3AP radicals, while 3AP reaction products is thermodynamically more stable. The calculation results combined with experimental conclusions indicate that the formation of distinct radicals may dominate the amine degradation instead of the chain propagation reaction.

Amine stability is a key aspect to be considered before conducting large-scale testing or implementing new amines. This work helps to identify features of amine structure that can resist degradation under oxidative conditions and provides theoretical guidelines for the solvent

development and consequential technology scale up.

CRediT authorship contribution statement

Qi Liu: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Tong Luo:** Software, Formal analysis. **Yiyan Yin:** Software, Formal analysis. **Yan Ouyang:** Software, Formal analysis. **Min Xiao:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Hongxia Gao:** Resources, Funding acquisition. **Teerawat Sema:** Writing – review & editing. **Zhiwu Liang:** Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Table 2

Free energies and enthalpies for the chain propagation reactions of MEA radicals.

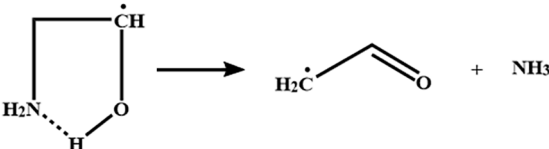
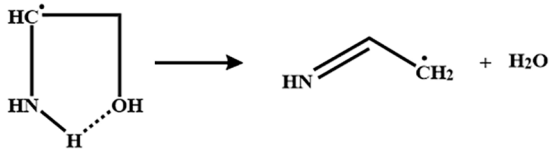
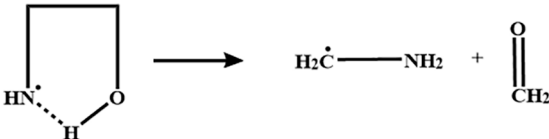
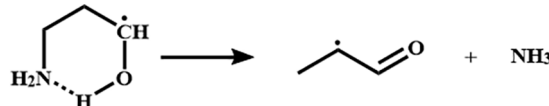
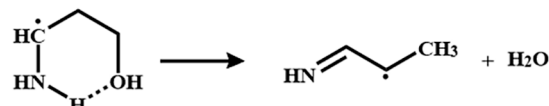
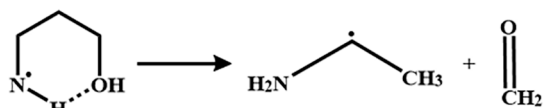
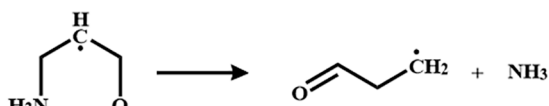

Hydrogen abstraction mechanism for MEA	ΔH (kcal·mol ⁻¹)	ΔG (kcal·mol ⁻¹)
	-5.97	-16.98
	-4.59	-13.90
	12.42	0.75

Table 3

Free energies and solvation enthalpies for the chain propagation reaction of 3AP radicals.

Hydrogen abstraction mechanism for 3AP	ΔH (kcal·mol ⁻¹)	ΔG (kcal·mol ⁻¹)
	-12.48	-24.04
	-12.36	-22.23
	8.31	-3.38
	-1.30	-12.03
	-0.58	-10.73

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2024.120458>.

References

- Alejandre, J., Rivera, J.L., Mora, M.A., Garza, V., 2000. Force field of monoethanolamine. *J. Phys. Chem. b* 104 (6), 1332–1337.
- Artanto, Y., Jansen, J., Pearson, P., Do, T., Cottrell, A., Meuleman, E., Feron, P., 2012. Performance of MEA and amine-blends in the CSIRO PCC pilot plant at Loy Yang Power in Australia. *Fuel* 101, 264–275.
- Bottoms, R.R., 1930. Process for separating acidic gases. United States Patent 1783901.
- Buvik, V., Vevelstad, S.J., Brakstad, O.G., Knuutila, H.K., 2021. Stability of structurally varied aqueous amines for CO₂ capture. *Ind. Eng. Chem. Res.* 60, 5627–5638.
- Cacela, C., Fausto, R., Duarte, M.L., 2001. A combined matrix-isolation infrared spectroscopy and MO study of 1-amino-2-propanol. *Vib. Spectrosc.* 26 (1), 113–131.
- Chandan, P., Richburg, L., Bhatnagar, S., Remias, J.E., Liu, K., 2014. Impact of fly ash on monoethanolamine degradation during CO₂ capture. *Int. J. Greenh. Gas Control* 25, 102–108.
- Chi, S., Rochelle, G.T., 2002. Oxidative degradation of monoethanolamine. *Ind. Eng. Chem. Res.* 41, 4178–4186.
- Ciftja, A.F., Hartono, A., Svendsen, H.F., 2014. Experimental study on carbamate formation in the AMP-CO₂-H₂O system at different temperatures. *Chem. Eng. Sci.* 107, 317–327.
- Darde, V., Thomsen, K., van Well, W.J.M., Stenby, E.H., 2009. Chilled ammonia process for CO₂ capture. *Energy Procedia* 1 (1), 1035–1042.
- Dave, N., Do, T., Puxty, G., Rowland, R., Feron, P.H.M., Attalla, M.I., 2009. CO₂ capture by aqueous amines and aqueous ammonia-A comparison. *Energy Procedia* 1 (1), 949–954.
- Fredriksen, S.B., Jens, K.J., 2013. Oxidative degradation of aqueous amine solutions of MEA, AMP, MDEA, Pz: A review. *Energy Procedia* 37, 1770–1777.
- Gao, J., Wang, S., Sun, C., Zhao, B., Chen, C., 2012. Corrosion behavior of carbon steel at typical positions of an amine-based CO₂ capture pilot plant. *Ind. Eng. Chem. Res.* 51 (19), 6714–6721.
- Goff, G.S., Rochelle, G.T., 2004. Monoethanolamine degradation: O₂ mass transfer effects under CO₂ capture conditions. *Ind. Eng. Chem. Res.* 43, 6400–6408.
- Iea, 2023. In: CO₂ Emissions in 2022, p. 4.0.
- Jorgensen, T.B., Abad, K., Sarma, M., Guzman, M.I., Thompson, J.G., Liu, K., 2022. Research on oxygen solubility in aqueous amine solvents with common additives used for CO₂ chemical absorption. *Int. J. Greenh. Gas Control* 116, 103646.
- Jung, J.Y., Seo, Y., Wood, C.D., 2024. Application of amine infused hydrogels (AIHs) for selective capture of CO₂ from H₂/CO₂ and N₂/CO₂ gas mixture. *Chem. Eng. Sci.* 288, 119799.
- Khakharia, P., Mertens, J., Huizinga, A., Vroey, S.D., Fernandez, E.S., Srinivasan, S., Vlugt, T., Goetheer, E., 2015. Online corrosion monitoring in a postcombustion CO₂ capture pilot plant and its relation to solvent degradation and ammonia emissions. *Ind. Eng. Chem. Res.* 54 (19), 5336–5344.
- Lepaumier, H., Picq, D., Carrette, P.L., 2009a. New amines for CO₂ capture. I. Mechanisms of amine degradation in the presence of CO₂. *Ind. Eng. Chem. Res.* 48, 9061–9067.
- Lepaumier, H., Dominique Picq, D., Carrette, P.L., 2009b. New amines for CO₂ capture. II. Oxidative degradation mechanisms. *Ind. Eng. Chem. Res.* 48, 9068–9075.
- Lepaumier, H., Martin, S., Picq, D., Delfort, B., Carrette, P.L., 2010. New amines for CO₂ capture. III. Effect of alkyl chain length between amine functions on polyamines degradation. *Ind. Eng. Chem. Res.* 49, 4553–4560.
- Liu, H., Namjoshi, O.A., Rochelle, G.T., 2014. Oxidative degradation of amine solvents for CO₂ capture. *Energy Procedia* 63, 1546–1557.
- Lucas Braakhuis, L., Høisæter, K.K., Knuutila, H.K., 2022. Modeling the formation of degradation compounds during thermal degradation of MEA. *Ind. Eng. Chem. Res.* 61, 2867–2881.
- Moser, P., Schmidt, S., Uerlings, R., Sieder, G., Titz, J.T., Hahn, A., Stoffregen, T., 2011. Material testing for future commercial post-combustion capture plants-results of the testing programme conducted at the Niederaussem pilot plant. *Energy Procedia* 4, 1317–1322.
- Nainar, M., Veawab, A., 2009. Corrosion in CO₂ capture process using blended monoethanolamine and piperazine. *Ind. Eng. Chem. Res.* 48 (20), 9299–9306.
- Notz, R., Mangalapally, H.P., Hasse, H., 2012. Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA. *Int. J. Greenh. Gas Control* 6, 84–112.
- Ouyang, Y., Liu, Q., Luo, T., Luo, Q.L., Xiao, M., Gao, H.X., Liang, Z.W., 2024. Experimental and computational study of the thermal degradation of primary amines used in CO₂ capture. *Chem. Eng. Sci.* 288, 119786.
- Parks, C., Alborzi, E., Akram, M., Pourkashanian, M., 2020. DFT studies on thermal and oxidative degradation of monoethanolamine. *Ind. Eng. Chem. Res.* 59, 15214–15225.
- Parks, C.M., Hughes, K.J., Pourkashanian, M., 2021. Modeling AMP degradation product formation. *Ind. Eng. Chem. Res.* 60, 18337–18360.
- Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns, R., Maeder, M., Attalla, M., 2009. Carbon dioxide postcombustion capture: A novel screening study of the carbon dioxide absorption performance of 76 amines. *Environ. Sci. Technol.* 43 (16), 6427–6433.
- Rieder, A., Dhingra, S., Khakharia, P., Zangrilli, L., Schallert, B., Irons, R., Unterberger, S., van Os, P., Goetheer, E., 2017. Understanding solvent degradation: A study from three different pilot plants within the OCTAVIUS project. *Energy Procedia* 114, 1195–1209.
- Rochelle, G.T., 2009. Amine scrubbing for CO₂ capture. *Science* 325, 1652–1654.
- Rosenblatt, D., Hull, L., De Luca, D., Davis, G., Weglein, R., Williams, H., 1967. Oxidations of amines. II. Substituent effects in chlorine dioxide oxidations. *J. Am. Chem. Soc.* 89, 1158–1163.
- Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K., 2012. Understanding 2-ethanolamine degradation in postcombustion CO₂ capture. *Ind. Eng. Chem. Res.* 51, 13329–13338.
- Smith, P.J., Mann, C.K., 1969. Electrochemical dealkylation of aliphatic amines. *J. Org. Chem.* 34 (6), 1821–1826.
- Teixeira, P., Correia, P., Pinheiro, C.I.C., 2024. CO₂ capture by CaCO₃-MgO and CeO₂-MgO sorbents promoted by ternary alkali metal salts in a fixed bed reactor. *Chem. Eng. Sci.* 289, 119856.
- Vevelstad, S.J., Grimstvedt, A., Elnan, J., Silva, E.F., Svendsen, H.F., 2013. Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. *Int. J. Greenh. Gas Control* 18, 88–100.
- Vevelstad, S.J., Grimstvedt, A., François, M., Knuutila, H.K., Haugen, G., Wiig, M., Vernstad, K., 2023. Chemical stability and characterization of degradation products of blends of 1-(2-hydroxyethyl)pyrrolidine and 3-amino-1-propanol. *Ind. Eng. Chem. Res.* 62, 610–626.
- Zheng, L.Y., Guo, Z.Y., Liu, H., Guo, K., Liu, C.J., 2024. Experimental study on single CO₂ bubbles freely rising in MEA/DEEA blended solutions: Bubble behavior and mass transfer. *Chem. Eng. Sci.* 287, 119751.
- Zheng, W.C., Luo, Q.L., Liu, S., Wang, N., Luo, X., Gao, H.X., Liang, Z.W., 2022. New method of kinetic modeling for CO₂ absorption into blended amine systems: A case of MEA/EAE/3DEA1P trisolvant blends. *AIChE J.* 68, e17628.