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Article

Stability of Structurally Varied Aqueous Amines for CO_2 Capture

Vanja Buvik, Solrun J. Vevelstad, Odd G. Brakstad, and Hanna K. Knuutila*

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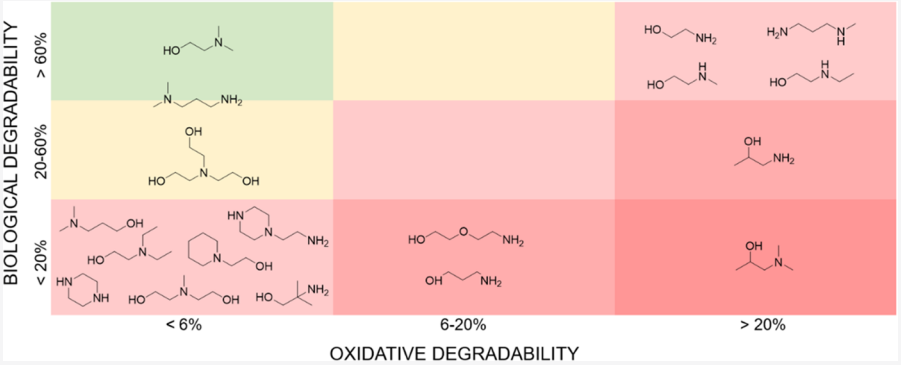

ABSTRACT: Eighteen structurally varied amines were subjected to harsh oxidative conditions, and their stability was assessed and seen in the context of biological and thermal stability. Steric effects play a large role in the stabilization of amines under oxidative conditions, and the presence of carbon dioxide plays a vital role in the degradation pathway of ethanolamine (MEA). Tertiary amines are generally very stable, and are known not to form carbamates to any large extent. Many steric effects play a vital role in stabilization, such as chain length, substituents located both close to and farther from the nitrogen atom, and bond strain. A correlation is seen between biodegradability and oxidative degradability, giving similar degradability in both cases. There are, however, promising exceptions to this, such as 3-(dimethylamino)-1-propylamine (DMAPA) and 2-dimethylaminoethanol (DMMEA), which are stable under oxidative conditions, but also biodegradable. Direct correlations between oxidative stability and ecotoxicity or thermal stability are not seen.

1. INTRODUCTION

Increasing concentrations of atmospheric carbon dioxide (CO_2) due to anthropogenic industrial emissions are leading to dramatic and irreversible changes in the global climate. Capture of CO_2 from large emission points, such as cement and steel production, waste incineration, or energy production, on the way to a global society relying on renewable energy, should be implemented immediately. Already in 2014, the Intergovernmental Panel on Climate Change (IPCC) stated that any climate change mitigation strategy not containing carbon capture and storage (CCS) would be more expensive than the one where it is included.[1] According to more recent reports and studies, carbon capture, utilization, and storage (CCUS) are needed to avoid the global average temperatures from rising more than 2 °C before 2050[2,3] and to achieve zero emissions.[4]

CO_2 capture using liquid amine solvents has been performed for nearly a century and is already considered a mature technology as well as a viable and attractive option for large-scale CO_2 removal from large flue gas emission sources.[2,5] Amines chemically bind CO_2 at low temperature or increased pressure, mainly forming carbamates, bicarbonate or carbonate, in a reaction that can be reversed either by increasing the temperature or decreasing the pressure. One of the main reasons why the implementation is still limited is the cost of operation, both because of the energy intensity of the regeneration step and because of degradation issues, leading to unpredictable replacement costs and potential interruption of operation. Despite this, amine scrubbing is still the least expensive means of large-scale postcombustion CO_2 capture.[6] Development of novel amine solvents or solvent blends aims to combat these challenges. Although amine degradation has been thoroughly studied over the last decades, many aspects of the complex degradation processes are yet to be explained.[7,8]

Flue gas contains a range of components that impact the stability and degradability of the amines. First, CO_2 plays a major role in thermal degradation, where studies show a huge significance of CO_2 loading of the amines.[9] Second, the presence of oxygen gives rise to oxidative degradation.

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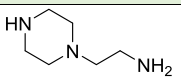
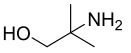
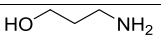
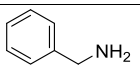
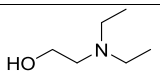
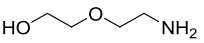
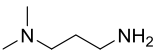
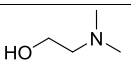
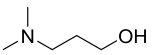
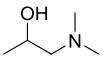
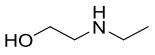
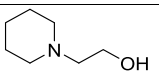
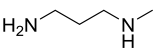
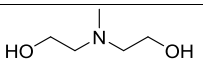
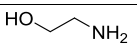
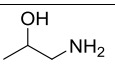
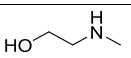
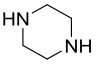
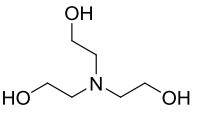
Table 1. List of the Amines Studied, Their Structure, as Well as Their Purity

Compound	Abbreviation	Structure	CAS-number	Purity
1-(2-Aminoethyl)piperazine [a]	AEP		140-31-8	99%
2-Amino-2-methyl-1-propanol [b]	AMP		124-68-5	99%
3-Aminopropanol [a]	AP		156-87-6	99%
Benzylamine [a]	BzA		100-46-9	99%
2-(Diethylamino)-ethanol [a]	DEEA		100-37-8	≥ 99.5%
2-(2-Aminoethoxy)ethanol (Diglycolamine®) [b]	DGA		929-06-6	98%
3-(Dimethylamino)-1-propylamine [b]	DMAPA		109-55-7	99%
2-(Dimethylamino)-ethanol [a]	DMMEA		108-01-0	≥ 99.5%
3-(Dimethylamino)-1-propanol [b]	DMPA		3179-63-3	99%
1-(Dimethylamino)-2-propanol [a]	1DMA2P		108-16-7	≥ 99%
2-(Ethylamino)ethanol [a]	EAE		110-73-6	≥ 98%
1-(2-Hydroxyethyl) piperidine [a]	1-(2HE)PP		3040-44-6	99%
3-(Methylamino) propylamine [a]	MAPA		6291-84-5	≥ 97.0%
N-Methyldiethanolamine [a]	MDEA		105-59-9	≥ 99%
Ethanolamine [a]	MEA		141-43-5	≥ 99.0%
(±)-1-Amino-2-propanol [b]	MIPA		78-96-6	≥ 99%
N-(Methylamino)-ethanol [a]	MMEA		109-83-1	≥ 98%
Piperazine [a]	PZ		110-85-0	99%
Triethanolamine [a]	TEA		102-71-6	> 99%

[a]Purchased from Sigma-Aldrich Norway AS/Merck Life Sciences. [b]Purchased from ACROS Organics.

Furthermore, the presence of inorganic species originating from flue gas or construction materials also impacts both the degree and pathways of solvent degradation.[10−13] Degradation patterns and the type of compounds formed during oxidative

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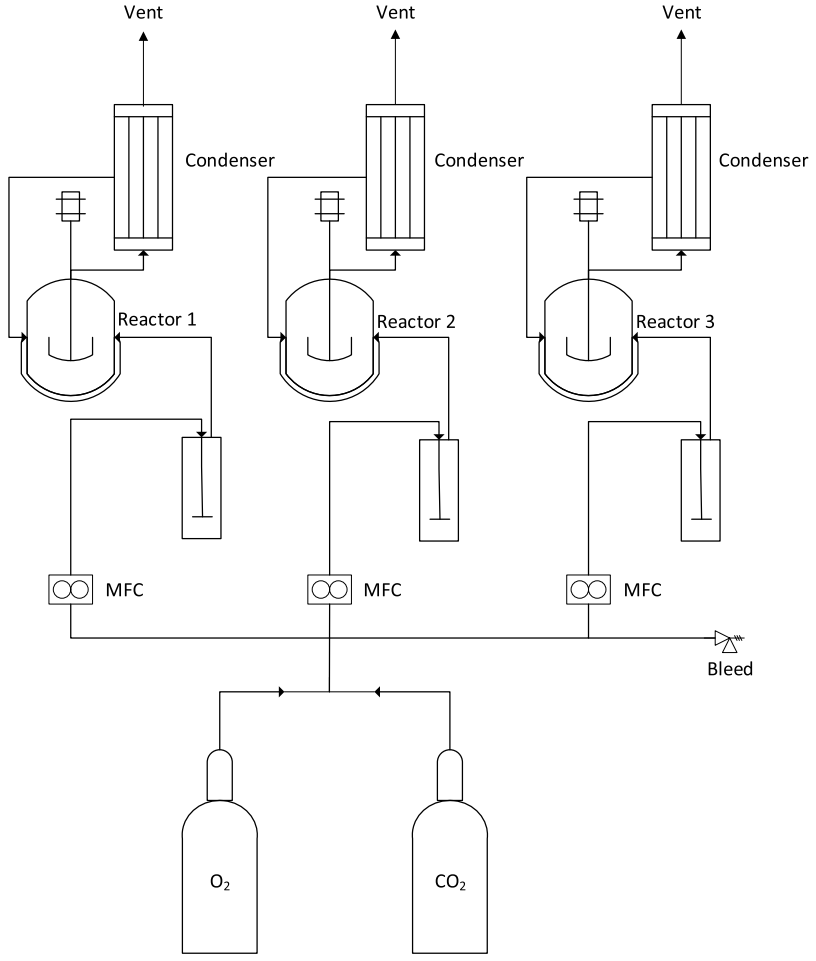

Figure 1. Schematic of the oxidative degradation setup.

degradation vary a lot from one amine to another, and depend on the overall process conditions. A number of studies on degradation are available for compounds formed during ethanolamine (MEA) degradation[14−16] as well as for some other amines.[17,18] Oxidative degradation reactions typically produce among other formic, acetic, and oxalic acids in the initial degradation steps, which are attributed to the rise of corrosion and fouling in the capture plants.[19,20] The initiation step of the oxidative degradation pathways is not fully understood, but most studies point toward an electron abstraction mechanism,[21,22] although hydrogen abstraction and the less commonly assumed reaction between amine radicals (aminium) and water are also described as possible pathways. Following these, primary degradation compounds are a range of secondary products, formed by the reaction between these and the amines.[17,23−26] Thermal degradation pathways also occur due to the increased temperatures in the desorber column. These pathways seem to be better understood than oxidative degradation pathways.[27−30]

This work does not attempt to fully understand the degradation mechanisms of every single amine compound studied, but rather aims to identify features that can allow a fast assessment of amine stability under oxidative conditions. Despite the harsh degradation conditions in these experiments, including higher concentrations of oxygen and dissolved iron than can be expected in reality, an overall picture of degradability can still be formed. Stability of the amine is a critical aspect to be considered before moving toward large-scale testing or implementation of a novel amine. It is also potentially a showstopper for upscaling, and, therefore, oxidative and thermal stability should be considered in an early stage of solvent development.

When upscaling amine-based CO_2 removal to the industrial level, potential environmental impacts must, also, be considered. Environmental persistence of emitted compounds may result in potential long-term effects and accumulation in the biota. Thus, ensuring that organic solvents enzymatically decompose by microbial digestion (often called biodegradation) is essential.

This study is divided into three main parts:

- First, the oxidative degradability at absorber conditions of a series of structurally different amines is measured under identical conditions. Also, the influence of the presence of CO_2 on oxidative stability is assessed in ethanolamine (MEA).
- Second, the biodegradability of some new amines is studied and compared to the literature data for amine biodegradation in seawater.[31]
- Finally, the oxidative degradation results are compared to the literature data for biological and thermal stability to discuss whether oxidative degradability can be used to assess these key properties of the amines and vice versa.

Titration, ion chromatography (IC), total nitrogen (TN), and total inorganic carbon (TIC) analyses as well as liquid chromatography coupled with mass spectrometry have been

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used as means of detection and quantification of the degraded amines.

Mechanisms and pathways of oxidative degradation have been studied for many years but are yet to be completely understood. This work contributes to the existing knowledge base about the oxidative degradation reactions of amines but does not contain mechanistic studies to conclude on the pathways of the reactions. The results do, however, point out reasons for considering the carbamate route to have a higher significance in these reactions than earlier assumed.

2. MATERIALS AND METHODS

2.1. Chemicals. All solutions were prepared gravimetrically using deionized water from an in-house purification system at NTNU unless otherwise specified. Oxygen (O_2) and carbon dioxide (CO_2) gas were purchased from AGA in N5.0 purity. Millipore water for analytical use was obtained from a Dionex ICW-3000 water purification system from Merck Millipore, and methanesulfonic acid (MSA, CAS: 75-75-2, ≥99.0%) for cation ion chromatography (IC) was purchased from Merck Life Science/Sigma-Aldrich Norway. Supplier and purity information of the tested amines is given in Table 1. Analytical standards for the anion IC analyses were prepared from sodium formate (CHO_2Na, ≥99.0%, CAS: 141-53-7) and sodium oxalate ($C_2O_4Na_2$, ≥99.5%, CAS: 62-76-0) obtained from Sigma-Aldrich, and sodium acetate ($C_2H_3O_2Na$, ≥99.0%, CAS: 127-09-3) was obtained from Merck. Potassium hydroxide (EGC III KOH, CAS: 1310-58-3) was purchased from Thermo Scientific in eluent generator cartridges.

2.2. Oxidative Degradation Experiments. Oxidative degradation experiments were performed at simulated absorber conditions in custom-made open, water bath-heated, double-jacketed glass reactors with magnetic stirring (approximately 250 mL), as shown in Figure 1. The reactor temperature was maintained at 60 °C and the water bath-cooled Graham condensers at 5 °C. Each reactor was filled with 200 mL of the gravimetrically prepared 30 wt % (*aq.*) amine solvent mixture, which was preloaded to 0.4 mol of CO_2 per mol amine and contained 0.5 mM iron sulfate ($FeSO_4{\cdot}7H_2O$). A mixture of O_2 and CO_2 gas was sparged through the solutions from Alicat mass flow controllers (MFC) and through Pyrex glass gas distribution tubes of porosity grade 1, under constant magnetic stirring for the total experimental time of three weeks. Empty gas wash bottles were used as safety solvent traps between the mass flow controllers and the gas distribution tubes in case of power outage. Sampling from the liquid phase was performed regularly through a septum on top of each reactor. Each experiment was performed in two or three parallels, and the data presented in this work are given as the average values, with the standard deviation of the sample average given as the uncertainty. Uncertainty within each analytical method is given in the description of each method and is additional to the standard deviation of the sample average.

The initial experimental procedure was designed for maintaining the loading of the primary amines at 0.4 mol CO_2 per mol amine. For this, a total of 60 mL min^{-1} of gas was used, containing 2% CO_2 and 98% O_2. This CO_2 pressure was not high enough to maintain the loading of 0.4 of the tertiary amines; as a result, the first experiments conducted with tertiary amines had a lower CO_2 loading. Some experiments were, therefore, run with a total of 60 mL min^{-1} gas flow containing 16.5% CO_2 and 83.5% O_2 to keep the loading constant. Finally, the oxidative degradation of tertiary amines was performed using a higher total flow of gas. In these experiments, the same O_2 flow as for primary and secondary amines (58.8 mL min^{-1}) was used, but the CO_2 flow was increased to achieve the required CO_2 partial pressure to maintain a loading of 0.4 mol CO_2 per mol amine, resulting in a higher flow. No significant difference in degradation could be seen in the tertiary amines tested under different conditions, so some of these experiments were not repeated.

2.3. Marine Biodegradability Tests. Closed bottle biodegradation tests of amines were performed by SINTEF Ocean, according to the OECD guideline 306 "Biodegradability in seawater".[32] Natural seawater was collected from a local Norwegian fjord (Trondheimsfjorden; 63°26′N, 10°24′E). The seawater was transported to the laboratory of SINTEF Ocean through a polyethylene pipeline system from a depth of 80 m, well below the thermocline, and securing stable temperatures the year around. The seawater had a salinity of 34‰, and the water source was considered to be nonpolluted. The seawater was filtered (50 μm), acclimated (20 °C) for 5 days, aerated for 20 min (bubbling of sterile-filtered air), and amended with inorganic nutrients (N, P, Ca, Mg, and Fe sources) (OECD).[32] Biological oxygen demand (BOD) bottles (275 mL) were completely filled (no headspace) with acclimated, filtered, and nutrient-amended seawater with 2 mg L^{-1} test substances, aniline (positive control), or nutrient-amended seawater without test- or control substance (seawater blank). Biocide test solutions (50 mg L^{-1} $HgCl_2$) were included to determine potential abiotic degradation. The solutions were incubated at 20 °C for up to 28 days, and bottles were sacrificed for dissolved oxygen (DO) analyses on days 0, 7, 14, and 28 (duplicate samples except on day 0). The BOD of each substrate was determined by calculating the differences between DO concentrations in blank and test solutions. The ultimate biodegradability of each substance was determined as the percentage of its theoretical oxygen demand (ThOD). ThOD was calculated assuming complete mineralization to CO_2 of the test substance and release of nitrogen in the form of ammonia (NH_3) or nitrogen dioxide (NO_2).[32] NO_2 is formed in the further reaction of NH_3 with oxygen, resulting in ThOD of NH_3 being lower than that of NO_2.

2.4. Analytical Methods. The concentration of amine in the solutions was determined by titration with sulfuric acid (H_2SO_4, 0.2 N) according to Ma'mun et al.,[33] a procedure with an uncertainty of ≤2%. For all of the samples, the concentration of amine was back-calculated to the solution without CO_2 and corrected for evaporation of water and degradation products, assuming a linear loss throughout the experiment, as the total mass of the solution is only known for the start and end solutions.

The total concentration of heat-stable salts (HSS) was determined according to a method described by Reynolds et al.[34] by adding approximately 2 g of the sample to 40 mL of activated Dowex 50W-X8 ion-exchange resin (Merck, CAS: 69011-20-7) and 40 mL of deionized water. The mixture was partly covered and heated to 70 °C under magnetic stirring for an hour and then left to cool to room temperature and settle. The supernatant was carefully transferred to another container through a frit, and the ion-exchange resin was extracted repeatedly by the addition of 40 mL of water, stirring for 1 min, leaving the resin to settle, and combining the resulting supernatant by filtering, until the supernatant attained the pH of the deionized water. The combined supernatants were titrated with 0.05 M sodium hydroxide (NaOH, CAS: 1310-

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73-2) to determine the molar concentration of cationic species. Analysis of 30 wt % (*aq.*) MEA with known concentrations of oxalic, formic, and acetic acids showed deviations of ±0.007 mol kg^{-1} (max 7%).

Quantification of amine concentrations by ion chromatography (IC) was performed on a Thermo Scientific Dionex ICS-5000 system, using a Thermo Scientific Dionex IonPac CS19 analytical column (2 × 250 mm), with a CG19 guard column (2 × 50 mm) and an eluent consisting of 15 mM methanesulfonic acid (MSA) in ultrapure water from an ICW-3000 Millipore purification system. Calibration was performed with each compound for every analysis, and all data were processed using the chromatography processing software Chromeleon 7. The method used for cation chromatography was based on that developed and used by Fytianos et al.[35] Standard solutions of concentrations between 10 and 100 ppm of the compound (amine) to be quantified were prepared and analyzed along with the diluted samples. The standards were used to construct a calibration curve for each individual amine and each individual analytical procedure, and their conductivity signals (peak areas) were used to calculate the concentration of the original samples.

Acetate, formate, and oxalate were quantified using a Thermo Scientific Dionex ICS-5000 system located at USN Porsgrunn, with a Dionex AG11-HC RFIC analytical (4 × 250 mm) and guard column (2 × 50 mm) and conductivity detection. The column compartment was kept at 35 °C and the cell temperature at 30 °C. A gradient of potassium hydroxide (KOH), generated by an eluent generation (EG) system, was used as the eluent, with the program given in Table 2. Standards of the organic acids were prepared in the concentration range from 1 to 30 ppm, and the degraded amine samples were diluted between 1:100 and 1:350 with deionized water, depending on their known total content of heat-stable salts (HSS). All standards and samples were filtered from any remaining particulate matter before analysis.

Table 2. KOH Eluent Gradient Used for Anion Separation in IC

Time (min)	$c_{KOH\ start}$ [mM]	$c_{KOH\ stop}$ [mM]
0−30	3	3
30−32	3	30
32−52	30	30
52−54	30	60
54−64	60	60
64−66	60	3
66−74	3	3

Quantification of the concentrations of some alkanolamines was performed by liquid chromatography coupled with mass spectrometry (LC-MS), performed by SINTEF Industry on a UHPLC Agilent 1290 Infinity System with an Agilent 6490 Triple Quadrupole detector. An Ascentis Express Phenyl-Hexyl, 2.7 μm HPLC Column and a Discovery HS F5 HPLC Column, both from Sigma-Aldrich Co. LLC, were used for analyte separation. MEA and *N*-methylaminoethanol (MMEA) were quantified using an isotope-labeled internal standard, and the results exhibited a typical uncertainty of 3%. Quantification of 3-(methylamino)propylamine (MAPA) and diisopropylmethyl amine (DMPA) in samples analyzed without isotope-labeled standards exhibited an uncertainty of 5%.

A Shimadzu TOC-L_{CPH} analyzer equipped with a TN unit and an auto sample injector (ASI) was used for the quantification of CO_2 loading as total inorganic carbon (TIC) and total nitrogen (TN). The instrument was calibrated with sodium bicarbonate ($NaHCO_3$) for the CO_2 analysis and potassium nitrate (KNO_3) for the nitrogen analysis. The uncertainty of the CO_2 quantification was ≤2%, when used in the range of 10−500 ppm carbon. The TN analysis was only used to compare the nitrogen content in the start and end samples, as matrix effects have proven to impact the ability of the method to quantify different amines with a universal calibration. Both the TIC and TN analyses were performed in the range of <500 ppm N to avoid saturating the detector signal. The principle of quantification of inorganic carbon in the sample is based on acidification with phosphoric acid (H_3PO_4, 25 wt %), releasing the inorganic carbon, including that bound as carbamate, as CO_2. The detection is then made with a nondispersive infrared detector (NDIR), selectively measuring at the wavelength of bond vibrations in the CO_2 molecule. Nitrogen can be combusted over a platinum catalyst at 720 °C and fully converted to NO_2, which is detected and quantified by a chemiluminescence detector.

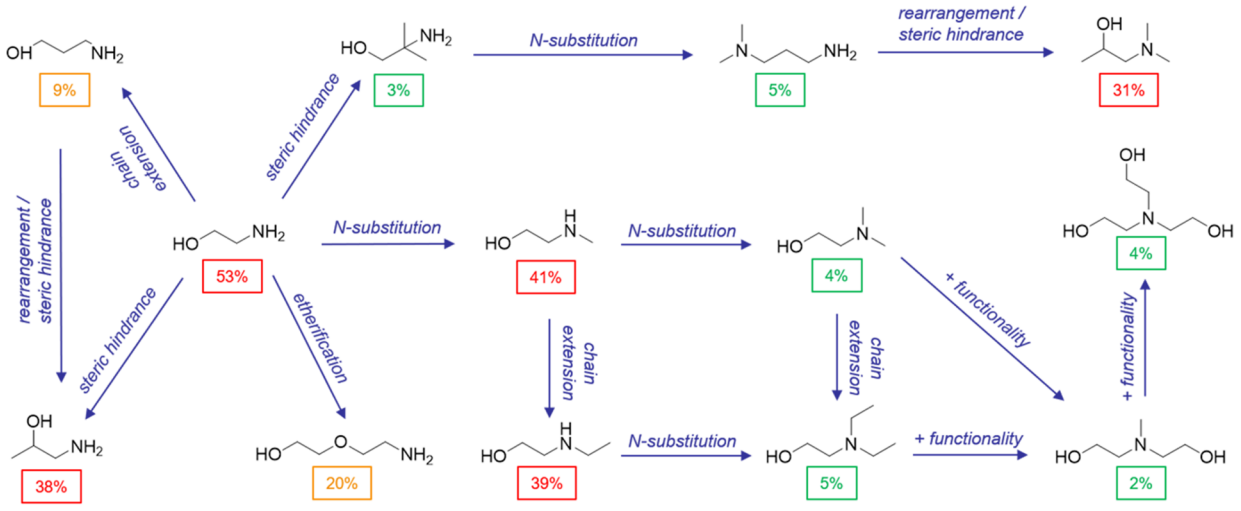

Figure 2. Amine loss after 21 days under oxidative conditions in relation to their structural characteristics for noncyclic alkanol monoamines.

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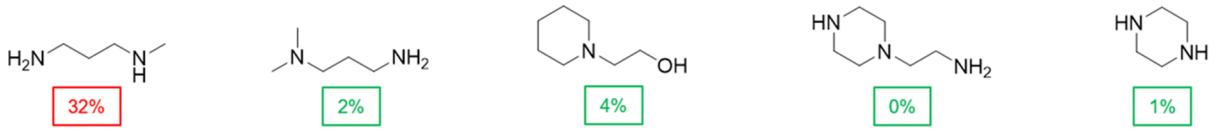

Figure 3. Amine loss after 21 days under oxidative conditions in relation to their structural characteristics for diamines, cyclic amines, and a triamine.

3. RESULTS AND DISCUSSION

3.1. Oxidative Degradation. Oxidative degradation of amines was primarily quantified as the loss of alkalinity throughout the experiments, as this reflects the CO_2 capture efficiency of the solvent. TN analysis, IC, and LC-MS were used both for validation and for supporting information about the degradation patterns of the amines. The effect of the amine structure on oxidative stability is shown in Figures 2 and 3. Overall, the trend shows that all tertiary amines are generally stable under oxidative conditions, secondary and primary amines less so, in agreement with the studies of Lepaumier et al.,[17] Voice and Rochelle,[36] and Voice et al.[37] This is, however, only true if no additional steric hindrance is present in the proximity of the nitrogen group(s), such as Lepaumier[17] postulated for 2-amino-2-methyl-1-propanol (AMP). If the oxidative degradation mechanisms mainly take place via carbamates and not pure amines reacting with the oxidant, this pattern can partly be explained by the lack of carbamate formation from tertiary amines. The most stable primary amine studied in this work, the sterically hindered AMP, is also known for forming bicarbonate over carbamate in aqueous solutions.[38] Next, a more detailed discussion is given.

As mentioned earlier (Section 2.2), the experimental conditions needed adjustment to the vapor−liquid equilibrium properties of the tertiary amines, and several tests with five different amines hardly gave significant differences in degradability regardless of CO_2 or O_2 concentrations and end loading of CO_2. A comparison of the different tested experimental conditions can be seen in Table 3, where each given amine was subjected to the oxidative degradation conditions for three weeks, with two different compositions of the gas phase or different total gas flows. The table shows the total loss of amine (alkalinity) at the end of the experiment. All experiments had a loading of 0.4 mol CO_2 per mol amine at the start of the experiment. As shown in Table 3, all tertiary amines tested, except for 1DMA2P, had losses of <5% alkalinity during three weeks under highly oxidizing conditions.

If the compounds studied have comparable structures, apart from a small substituent on the nitrogen atom, increasing the order of the amine, a general increase of stability can be seen with increasing order. This can be seen for the three amines in the center of Figure 2, MEA, MMEA, and 2-dimethylaminoethanol (DMMEA). The only structural feature differing is the substitution of hydrogen by methyl groups on the nitrogen atom, which increases the stability from 53% amine loss (MEA), through 41% (MMEA) to only 4% (DMMEA). A similar trend can be observed when comparing 2-(ethylamino)ethanol (EAE) and *N*,*N*-diethylethanolamine (DEEA). A combination of the carbamate formation reaction of tertiary amines and an exposed amine group can make the primary amines more prone to degrade oxidatively than amines of higher substitution. Moreover, other structural features also increase oxidative stability. Figure 4 shows the degradation of a selection of primary amines over time and shows that all amines with more complexity degrade slower than MEA. Addition of steric hindrance in β-position relative to the amine group, such as in amino-2-propanol (MIPA), increases oxidative stability. Increasing steric hindrance by addition on the α-position, such as in AMP, increases the oxidative stability of a primary amine to the range of tertiary amines in this study. Even just extending the chain length relative to MEA, looking at the primary amine 3-aminopropanol (AP) and 2-(2-aminoethoxy)ethanol (DGA), increases the stability significantly. The results of this study suggest that the carbamate of the amine may play a more significant role in the oxidative degradation pathways than previously assumed. This assumption is further supported by an oxidative degradation experiment with MEA, identical with the other experiments, but without the addition of CO_2. In this case, the amine loss is

Table 3. Influence of CO_2 and O_2 Concentrations on End Loading and Degradability of Tertiary Amines Given in Total Amine Loss after Three Weeks

Amine	% CO_2	F_{total} [mL min^{-1}]	α_{end} [mol$_{CO_2}$ mol^{-1}]	Amine loss (%)
DEEA	16.5	60	0.7	1 ± 2[a]
	3.5	60	0.4	4 ± 0.4
DMMEA	16.5	70.4	0.7	3 ± 1
	2.0	60	0.2	4 ± 0.4
DMPA	16.5	60	0.5	3[b]
	3.5	60	0.2	5 ± 1
MDEA	16.5	70.4	0.5	2 ± 1
	2.0	60	0.1	3 ± 0.2
TEA	16.5	60	0.3	3 ± 1
	3.5	60	0.04	3 ± 0.2

[a]This experiment was run with two different solutions/concentrations of *N*,*N*-diethylethanolamine (DEEA), so the uncertainty is given here as the deviation from the average of the two, not the standard error of the parallels. [b]Only one parallel was studied, hence, no uncertainty apart from that of the analytical methods can be given.

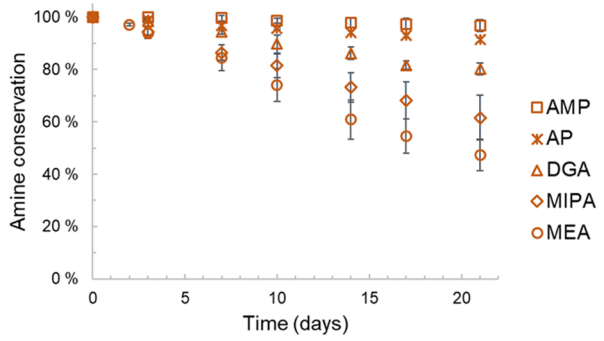

Figure 4. Normalized amine concentration of primary amines throughout the 21-day oxidative degradation experiments. Quantification made by amine titration and corrected to CO_2-free solution and corrected for water loss.

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only 3 ± 1%, as can be seen in Figure 5. At the same time, carbamate-forming AP[39] is more stable than MEA. Thus, the

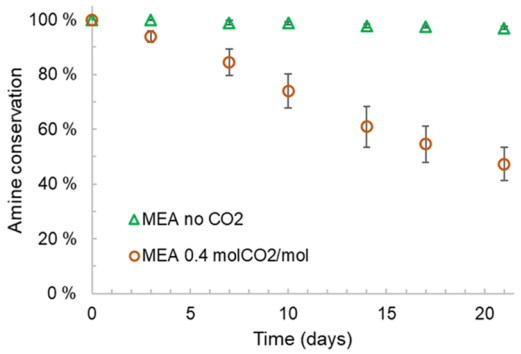

Figure 5. Oxidative degradation of MEA in the absence and the presence of CO_2.

results are not conclusive, and more mechanistic studies are needed to fully understand the role carbamate may play in the degradation mechanisms of amines.

Figure 6 shows that secondary amines can also be relatively unstable under oxidative conditions; both MMEA and EAE as

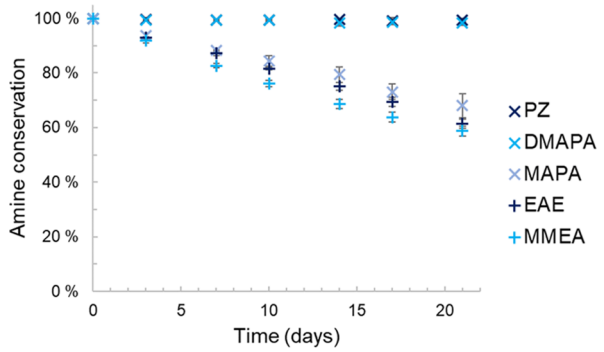

Figure 6. Normalized amine concentration of secondary (+) and diamines (×) throughout the 21-day oxidative degradation experiments. Quantification made by amine titration and corrected to CO_2-free solution and corrected for water loss.

well as MAPA, a diamine with one secondary and one primary amine group, gave a high relative amine loss after 21 days under oxidative conditions. However, the diamine piperazine (PZ) containing two secondary amine groups is very stable throughout the whole experiment. With its cyclic form, the lower flexibility of the C−N bond compared to MMEA, EAE, and MAPA can explain this stabilizing effect. The step in a radical reaction where electron transfer can take place requires the reactants to arrange the position of its atoms to the configuration of the products since this reaction is very fast.[40] This means that certain flexibility within the bonds of molecules being oxidized is required for the oxidation to occur. The rigidity of the C−N bonds in PZ may be less likely to enter a configuration where the radical oxidation reaction can take place. The high oxidative stability observed for PZ in this work is in agreement with that of Voice and Rochelle.[36]

As discussed earlier, most of the studied tertiary amines showed amine losses <5% after three weeks under oxidative conditions. Even the diamine 3-(dimethylamino)-1-propylamine (DMAPA), which contains a primary amine functionality, and the cyclic 1-(2-aminoethyl)piperazine (AEP), containing both a primary and a secondary amine function. In the case of AEP, the secondary amine group is incorporated in the cyclic structure, like PZ, so this group is protected by the rigidity of the ring structure. The primary groups of DMAPA and AEP are likely shielded by steric effects that protect the molecules from attack or constructing a lower compatibility with the radical donor, potentially favoring termination rather than propagation. A sterically hindered molecule has less bond flexibility and less possibility to exist in many configurations, such as resonance forms and rotational isomerism. 1DMA2P presented itself as an outlier among the tertiary amines, with a total amine loss of 31% after 21 days under oxidative conditions. Despite being tertiary, this amine behaves more like the structurally similar, although primary, MIPA. It can be speculated whether a hydroxy substituent in the β-position to the nitrogen on a secondary carbon may be unfavorable for stability, allowing for the mechanism shown in Figure 7 to take place. In this suggested mechanism, both amines form acetone, and additionally, 1DMA2P forms dimethylamine and MIPA ammonia, all volatile degradation compounds. This may be the predominant degradation mechanism for 1DMA2P, but in MIPA, the content of nonalkaline nitrogen, as seen in Figure 8, indicates that other pathways may be more or as dominant.

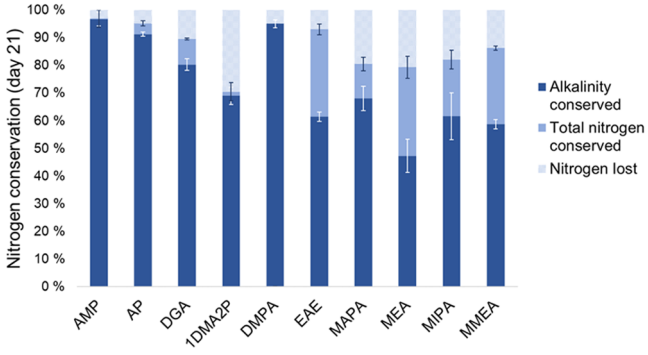

Figure 8. Loss of alkalinity and total nitrogen after 21 days under oxidative conditions for primary, secondary, and diamines. Analyzed by amine titration, TIC, and TN.

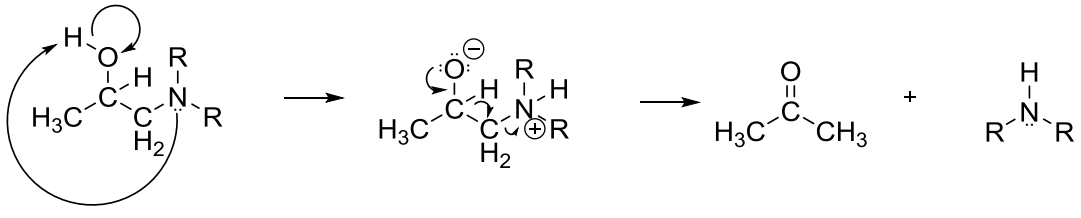

Figure 7. Suggested mechanism for the formation of acetone and dimethylamine/ammonia during 1DMA2P (R = CH_3) and MIPA (R = H) degradation.

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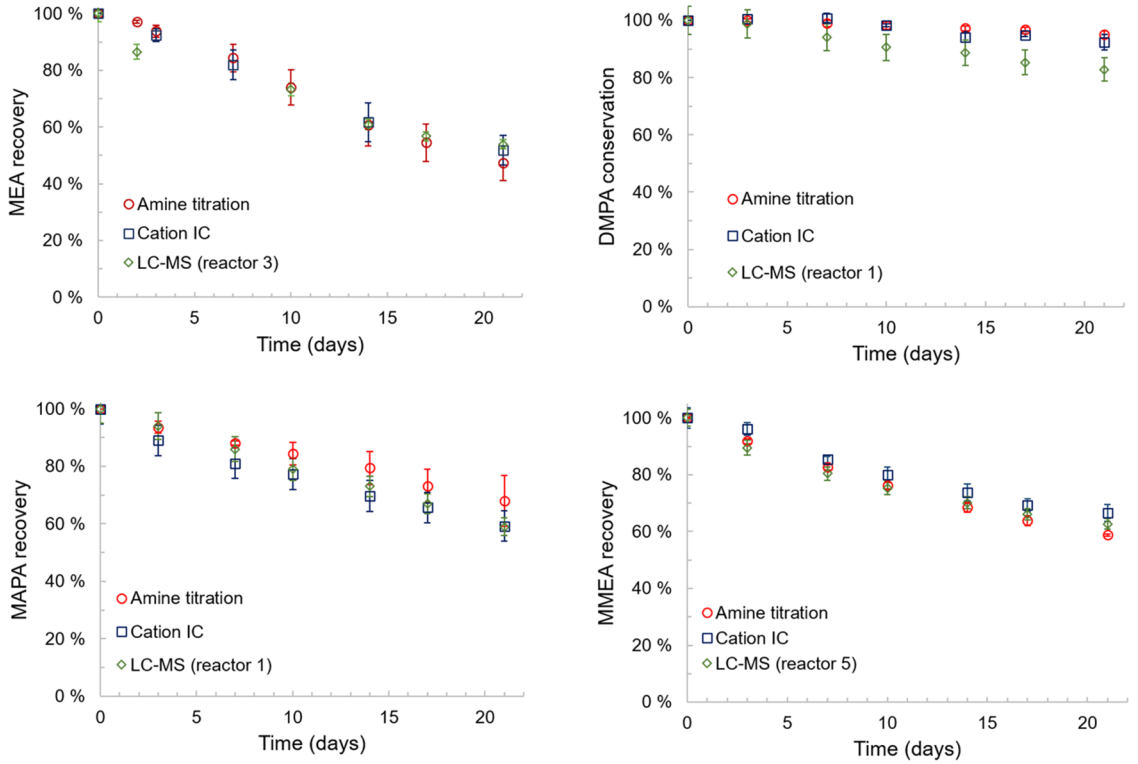

Figure 9. Normalized amine concentration measured by amine titration and cation chromatography from the same samples and experiments. Error bars for titration and IC represent the standard error between the parallel reactors and the data points the average value of the 2 or 3 parallels, and for LC-MS, they represent the uncertainty of the method. MMEA recovery given from experiment with 17 °C condenser temperature.

To introduce further structural variance to the study, we wanted to see the effect of adding an aromatic functionality to the amine. Therefore, we attempted to study the aromatic amine benzylamine (BzA) under oxidative conditions, both in 30 and 15 wt % (*aq.*) concentrations. In both cases, phase separation occurred before a week had passed. A thick, viscous, and dark organic phase with a higher density than water was formed, and no alkalinity could be detected in the aqueous phase anymore. At 60 °C, the benzylamine carbamate was soluble in water, although it precipitated at room temperature, as reported in Richner et al.[41] Therefore, the attempt to study BzA, an aromatic amine, under these conditions was abandoned.

The analysis of total nitrogen content after three weeks of oxidative degradation, compared to the start, as well as comparing it to the remaining alkalinity of the solutions, gives an impression of the type of degradation compounds formed, as shown in Figure 8. It is evident that volatile nitrogen-containing degradation compounds, such as ammonia (NH_3), have been formed where the nitrogen content of the initial solution has not been conserved throughout the experiment. This approach does not identify the volatile, nor the less-volatile, degradation compounds, but it allows an assessment of the amount of emissions that can be expected from a given amine. The primary amines form a more or less equal amount of volatile and less-volatile nitrogen-containing degradation products. This is probably due to the cleavage of the C−N bond forming NH_3 that escapes the liquid phase. Secondary amines like MMEA and EAE are known to form volatile alkylamines,[42] so at least for these, we can assume that a significant part of the nitrogen lost is not in the form of NH_3. For the secondary amines, more of the nitrogen is contained in the liquid phase in the form of nonalkaline degradation products. No correlation between nitrogen loss and amine volatility could be found when looking at the respective boiling points. This can be seen illustrated in the Supporting Information, in Figure S1. The high loss of nitrogen from MAPA correlates with what was observed by Vevelstad et al.[43] when using a similar open-batch oxidative degradation setup.

3.2. Comparison of Different Methods of Amine Analysis. For control and comparison, the concentration of amine was measured by cation ion chromatography (IC) in addition to amine titration to validate the results obtained by the titration by an independent method. IC separates ionic components based on their charge density and affinity to the mobile and stationary phases of the chromatographic system. The signal obtained from each component in the form of a peak, which can be integrated and quantified by comparison to a calibration curve, is characteristic for the amine but can also overlap with other compounds of similar charge densities. Other compounds can also falsify the titration results, as all alkaline components will give the same signal. Comparing the results from the two methods increases the certainty of the measured concentrations originating from the desired compound.

For four amines, a time series was also sent for LC-MS analysis at an external laboratory, for further validation and comparison. A visual representation of the results from the three different analytical methods is shown in Figure 9. The different methods show some deviations from one another, but overall, the same trends. Throughout the experimental period, the remaining alkalinity measured by titration in MAPA is higher than the amount of MAPA quantified by cation IC and LC-MS, although the standard error of the average of the two

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parallel experiments overlap. MAPA with its two amine functionalities is likely to degrade on just one of them and remain active or alkaline despite being degraded. A deviation between titration and IC/LC-MS is, therefore, expected in this case. The relatively large deviation between LC-MS and IC/titration for DMPA may be due to the lack of an internal deuterated standard of DMPA, also yielding a higher uncertainty for this amine and MAPA, than for MEA and MMEA, where internal standards were used for quantification.

3.3. Heat-Stable Salts (HSS). Anion IC analyses were performed on the end samples after 21 days of oxidative degradation of the amines. Formate, acetate, and oxalate were measured in diluted samples of all amines, and Figure 10 shows the concentrations of these in the amines where a quantifiable amount of at least one of the acids was found.

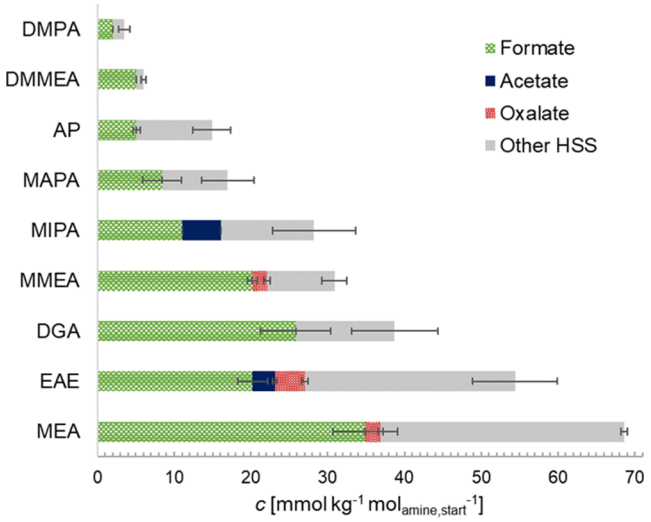

Figure 10. Concentrations of HSS quantified in end samples of oxidative degradation experiments. Error bars represent the standard deviation of the average of parallels.

Formate could be quantified in all of the amine samples that degraded significantly during the three-week experiments and in DMMEA and DMPA, both of which had low relative amine losses. Since most of the amines that are unstable under oxidative conditions also are carbamate-forming amines, it seems likely that carbamate plays a more significant role than it had in the earlier suggested degradation mechanisms. The possibility of formate originating from the carbonyl group of the amine carbamate, as illustrated in Figure 11, should therefore be considered.

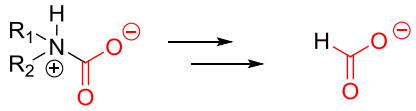

Figure 11. Formate may be formed through a direct redox reaction on carbamate.

Acetate was only found in concentrations above the quantification limit in two of the degraded solutions, EAE and MIPA, and oxalate in three, EAE, MEA, and MMEA. Acetate and formate have both been observed to be formed in other oxidation studies of MIPA.[44] EAE or similar structures have not been seen to be particularly prone to form acetate under oxidative conditions, but we suggest that the reaction may take place as depicted in Figure 12, where the positively charged nitrogen in EAE allows for an attack by an oxygen radical or a superoxide ion formed in the solution. Following an analogous mechanism, DMPA, MAPA, and MMEA would form formate.

The total heat-stable salt analysis shows that there are other ionizable degradation products present than the three, which were quantified by ion chromatography, some of which could also be observed in the anion chromatograms, although not identified. The ion chromatogram of the degraded MEA can be found in the Supporting Information, as depicted in Figure S2.

3.4. Biodegradation. Since alkanolamines may not evaporate in the environment and have poor affinities for soil,[45] these compounds may end up in aquatic systems and eventually in seawater. Since biodegradation of several alkanolamines was faster in fresh water than in seawater,[31,46−48] biodegradability in seawater may also be used as a good representation of biodegradability limitations of amines in this work.

Five amines were tested for ultimate biodegradation in seawater, and the results are presented in Table 4, where the amines are also classified as natural or synthetic. The results show that 1-(2HE)PP, 1DMA2P, and AEP have low marine biodegradability, below 20%, whereas DMMEA and DMAPA are highly biodegradable. As expected, and also observed in previous studies, the naturally occurring amines have a higher biodegradability than synthetic amines. In addition to the results given here, abiotic tests were performed for all amines, all showing that they do not degrade in the absence of microbes under the given conditions (results given in Table S8).

Piperazine and piperidine (AEP and 1-(2HE)PP) showed poor degradabilities, as previously seen with some other cyclic amines.[31] The two degradable amines (DMMEA and DMAPA) were associated with terminal alcohol or amine groups, typically subjected to enzymatic attack during amine biodegradation.[50,51]

3.5. Comparison of Oxidative, Thermal, and Biodegradation. Since one of the most common pathways of biological amine degradation reactions occurs through catalysis by the monoamine oxidase enzymes,[52] it is not unexpected to find a correlation between oxidative and aerobic biological degradability (Figure 13). Most of the amines that were unstable under oxidative conditions in the experiments performed in this work also showed a high biodegradability when compared to the results of marine biodegradability studied both in this work and in previous studies.[31] There are, however, some amines that are stable under oxidative conditions and still have a high biodegradability, properties that are favorable from a combined industrial and environmental perspective. Another observed trend in Figure 13 is that most of the highly degradable amines are of natural origin and the ones showing low degradability are of synthetic origin. In the case of biodegradability, this makes sense, as there is a compatibility between natural compounds and enzymes, but it can interestingly also be seen as a trend for oxidative degradability in the absence of microorganisms. Ideally, for industrial use, one would want an amine that would be stable under oxidative conditions but biologically unstable so that it can degrade in nature in case of a spill. This is the case for two of the tested amines, DMMEA (94% of ThOD) and DMAPA (55% of ThOD). DMMEA was pointed out as a promising

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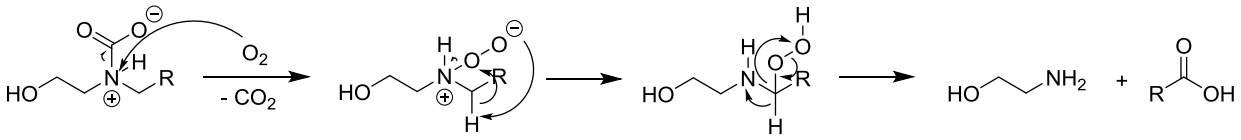

Figure 12. Suggested mechanism for the degradation of MMEA- (R = H) or EAE-carbamate (R = CH_3) to MEA and formic (R = H) or acetic acid (R = CH_3).

Table 4. Biodegradability Measured According to the OECD Guideline 306 under the Assumption That Nitrogen Digestion forms Ammonia (NH_3) or Nitrogen Dioxide (NO_2) after 28 Days of Incubation[a]

Amine	Biodegradability (% of ThOD-NH_3)	Biodegradability (% of ThOD-NO_2)	Natural product
AEP	12.5 ± 0.2	7.8 ± 0.2	no
DMMEA	98.7 ± 1.3	77.6 ± 1.0	yes
DMAPA	96.7 ± 0.0	67.7 ± 0.0	yes
1DMA2P	5.2 ± 1.7	4.3 ± 1.4	no
1-(2HE)PP	3.4 ± 2.8	2.9 ± 2.4	no
aniline (reference)	100.8 ± 2.0	83.0 ± 1.7	yes

[a]The amines are also characterized as natural products or not.[49]

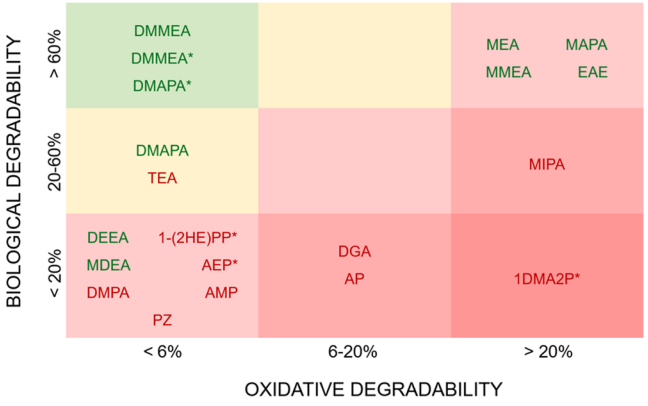

Figure 13. Marine biodegradability (% of ThOD-NH_3) of amines from Eide-Haugmo et al.[31] and this work (*) categorized according to their biological and oxidative degradability. Oxidative degradability given as alkalinity lost after 3 weeks under oxidative conditions. Natural (green) amines are generally more biodegradable than non-natural amines (red).

solvent by Eide-Haugmo[53] because it has relatively high thermal stability and biodegradability, which can be seen in Figure 13. All compounds with a biodegradability above 60% of ThOD are considered readily biodegradable.

The knowledge of biological degradability is insufficient for assessing the total impact of an amine in case of a spill in nature. Ecotoxicity tests provide additional information that allows assessing the amines potential effect on the local environment if leaked. Eide-Haugmo et al.[31] also studied this in a marine environment and the ecotoxicity was tested according to the ISO/DIS guideline 10253, with the marine diatom *Skeletonema costatum*.[54] There is no visible correlation between biological degradability and ecotoxicity in this case. None of the amines from this study were deemed acutely toxic to marine life, but many of them fall into the category of "slightly toxic."

In addition to the conditions with high oxygen availability and relatively low temperatures, as simulated in these oxidative degradation experiments, thermally aggravating conditions are met in the desorber and reboiler of a CO_2 capture plant. To assess the overall stability of the amines tested, a comparison with thermal degradation data from Davis et al.[28] and Eide-Haugmo[53] is given in this section. Because the experiments were performed under slightly different conditions, the degradability is normalized in regard to the amine with the highest amine loss at the end of the experiment as shown in Figure 14, which was MEA in the study of Davis et al.[28] and

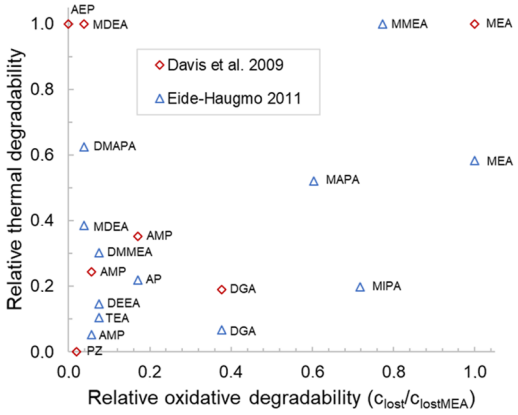

Figure 14. Comparison of the relative oxidative and thermal degradability of 14 of the studied amines. Davis et al.[28] studied degradability with 0.4 mol CO_2 per mol amine and amine concentration of 3.5−8.4 mol kg^{-1} (40 wt %) for 4 weeks and Eide-Haugmo[53] with 0.5 mol CO_2 per mol amine and amine concentration 2.1−4.6 mol L^{-1} (30 wt %) for 5 weeks, both in stainless steel cylinders at 135 °C.

MMEA in Eide-Haugmo,[53] since small differences in experimental conditions make a direct comparison and visualization difficult. The oxidative degradability has also been normalized in relation to the amine loss of MEA. Exact amine losses can be found in Table S5. The comparison shows that oxidative stability not necessarily means thermal stability, as AEP, MDEA, and DMAPA all seem very promising after studying their stability under oxidative conditions but have proven to have a low relative thermal stability.

4. CONCLUSIONS

After nearly 3 decades of studies focusing on mechanistic understanding of oxidative degradation of amines, there are still many unknowns when it comes to its reaction pathways. This work contributes to the existing knowledge with some new insights from laboratory-scale degradation experiments.

Ethanolamine (MEA) has a high oxidative stability in the absence of CO_2, indicating that MEA carbamate partakes in the initiation step of the oxidative degradation reaction. In contrast, 2-amino-2-methyl-1-propanol (AMP), which is a similar but sterically hindered primary amine known to form bicarbonate over carbamate in reaction with CO_2, hardly degrades under oxidative conditions. This does, however, not

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explain the full extent of degradability of amines, as some typical carbamate-forming amines, such as 3-aminopropanol (AP), have higher stability than MEA. Further mechanistic studies are recommended to determine the role of carbamate in the degradation mechanisms of amines.

Eight of the nine studied tertiary amines show high oxidative stability under experimental conditions and had losses of alkalinity ≤5% after three weeks subjected to 98% O_2, CO_2-loading, iron, and 60 °C.

Steric hindrance and high substitution can give oxidative stability to amines, regardless of the number of substituents on the nitrogen atom. In addition to AMP, other primary amines such as 3-aminopropanol (AP), amino-2-propanol (MIPA), and 2-(2-aminoethoxy)ethanol (DGA) have a higher oxidative stability than MEA, likely due to steric effects.

Secondary amines, such as *N*-methylaminoethanol (MMEA) and 2-(ethylamino)ethanol (EAE), are generally unstable, but even here, steric constraint around the nitrogen atom, such as in the ring structure of piperazine (PZ) and 1-(2-aminoethyl)-piperazine (AEP), drastically increases the oxidative stability.

There seems to be a correlation between oxidative and biological degradability. Oxidative degradation tests can, to a large extent, be used to predict biological degradability, but there is, fortunately, no exclusive relationship between the two properties, meaning that amines with high oxidative stability and ready biodegradability exist.

Oxidative and thermal stability do not correlate, so testing of both these properties seems necessary for solvent stability assessment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c00502.

> Calculations of uncertainty, corrections of measured concentrations, and theoretical oxygen demand (ThOD); and supplementary data for all included graphics (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hanna K. Knuutila − *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway;* orcid.org/0000-0003-2057-1743; Email: hanna.knuutila@ntnu.no

Authors

Vanja Buvik − *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway*

Solrun J. Vevelstad − *SINTEF Industry, NO-7465 Trondheim, Norway*

Odd G. Brakstad − *SINTEF Ocean, NO-7465 Trondheim, Norway*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.1c00502

Notes

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