



RESEARCH ARTICLE

Tandem Mass Spectrometry Measurement of the Collision Products of Carbamate Anions Derived from CO₂ Capture Sorbents: Paving the Way for Accurate Quantitation

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Abstract

The reaction between CO₂ and aqueous amines to produce a charged carbamate product plays a crucial role in post-combustion capture chemistry when primary and secondary amines are used. In this paper, we report the low energy negative-ion CID results for several anionic carbamates derived from primary and secondary amines commonly used as post-combustion capture solvents. The study was performed using the modern equivalent of a triple quadrupole instrument equipped with a T-wave collision cell. Deuterium labeling of 2-aminoethanol (1,1,2,2-d₄-2-aminoethanol) and computations at the M06-2X/6-311++G(d,p) level were used to confirm the identity of the fragmentation products for 2-hydroxyethylcarbamate (derived from 2-aminoethanol), in particular the ions CN[−], NCO[−] and facile neutral losses of CO₂ and water; there is precedent for the latter in condensed phase isocyanate chemistry. The fragmentations of 2-hydroxyethylcarbamate were generalized for carbamate anions derived from other capture amines, including ethylenediamine, diethanolamine, and piperazine. We also report unequivocal evidence for the existence of carbamate anions derived from sterically hindered amines (*Tris*(2-hydroxymethyl)aminomethane and 2-methyl-2-aminopropanol). For the suite of carbamates investigated, diagnostic losses include the decarboxylation product (−CO₂, 44 mass units), loss of 46 mass units and the fragments NCO[−] (*m/z* 42) and CN[−] (*m/z* 26). We also report low energy CID results for the dicarbamate dianion (O₂CNHC₂H₄NHCO₂[−]) commonly encountered in CO₂ capture solution utilizing ethylenediamine. Finally, we demonstrate a promising ion chromatography-MS based procedure for the separation and quantitation of aqueous anionic carbamates, which is based on the reported CID findings. The availability of accurate quantitation methods for ionic CO₂ capture products could lead to dynamic operational tuning of CO₂ capture-plants and, thus, cost-savings via real-time manipulation of solvent regeneration energies.

Key words: Post-combustion capture, Amines, Carbamate anion

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Introduction

Research into the chemical capture of CO₂ (either via aqueous amine solutions [1–11], ionic liquids [12–17], or metal-organic frameworks [18–27]) has intensified in recent years as a result of the rate at which atmospheric CO₂ levels are rising. At present, the chemisorption route to CO₂

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capture using organic amines at large point sources (e.g., coal-fired power stations) appears to be the most promising immediate technology for the reduction of anthropogenic CO₂ emissions [28].

Our understanding of the process chemistry between aqueous amines and CO₂ is sufficient for small-scale industrial applications, but improvements are still needed before the scale-up and rollout for post-combustion capture purposes. Several groups have proposed reaction equilibria [29–32] (see Scheme 1), which describe the entire process at any level. On the other hand, the molecular properties that confer excellent capture characteristics for certain amines are not well understood, and novel amine discovery/development is an active area of research. Aside from the base catalysis route (Reactions (1) and (2) in Scheme 1, the only viable pathway for tertiary amines to sequester CO₂, [29]), primary (1°) and secondary (2°) amine molecules can react at slightly elevated temperatures (40–60 °C) in an alkaline aqueous environment to form a carbamate derivative R₁R₂NCO₂⁻, which in turn may undergo hydrolysis to yield HCO₃⁻ and water (Reactions 3 and 4 in Scheme 1).

Note that both significant forms of aqueous ‘sequestered’ CO₂ are anionic. In principle, all reactions in Scheme 1 are reversible by acidification of the reaction mixture or by heating. Typical process regeneration temperatures range from 100 to 150 °C. The Lewis base ‘B’ in Scheme 1 is either a molecule of water or amine.

A number of mechanisms based on aqueous kinetic data for the initial endoergic activation reaction by 1°, 2° amines have been proposed over the years [5, 29–31, 33]. Arguably the most controversial is the zwitterion mechanism of Danckwerts [33, 34], which postulates the formation of an ion pair intermediate R₁R₂NH⁺CO₂⁻. To date, there is no evidence supporting the existence of such a species. It should also be stated that the solvent medium cannot be considered passive during the CO₂ capture process, and the mechanism of CO₂ capture by aqueous amines may be catalyzed by localized solvation structure.

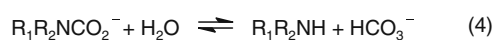
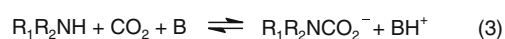
The group of 1°-amines which possess no hydrogen atoms at the alpha position (C_α) to the reactive nitrogen have very desirable aqueous CO₂ capture properties from a regeneration perspective. In industry parlance, this class of CO₂ sorbent is referred to collectively as “sterically hindered” [29, 31]. A unique aspect of the capture chemistry of these species is that either (1) their carbamate derivatives are inherently susceptible to hydrolysis, or (2) there is a

kinetic constraint along the pathway to carbamate formation. Unstable or hydrolysis-prone carbamates are economically desirable, as it is more cost-effective to strip aqueous CO₂ from capture liquors when it is in the form of HCO₃⁻. The performance of sterically-hindered amines has led to speculation that their reactions with CO₂ only generate bicarbonate via reactions 1 and 2 (Scheme 1), much the same as for 3°-amines.

The most commonly used methods for examining the dynamic speciation of aqueous CO₂ capture liquors have been ATR-FTIR and NMR spectroscopies [35–38]. While these techniques afford the simultaneous detection of neutral and ionic species, the sensitivity of these methods is poor relative to mass spectrometry (MS). MS analysis of degraded capture liquors has recently become popular [39, 40], although there is still no report of the detection of a gas-phase carbamate ion derived from an alkanolamine sorbent using this approach. As both forms of sequestered CO₂ in the capture liquors of 1°, 2°-amines are anionic, MS appears to be a natural choice for the quantitation of this process variable. Real-time knowledge of the bicarbonate/carbamate speciation within PCC liquors will enable the determination of accurate heat requirements for solution regeneration, which will afford plant operators the opportunity to dynamically tune regeneration to reduce energy demands and achieve cost savings.

In this paper, we report on the collision-induced dissociation (CID) behavior of carbamate anions derived from functionalized amines; with a few exceptions, these are most commonly alkanolamines. Aside from carbamino protein adducts (proteins with a carboxylated N-terminus) [41] and a recent pre-dissociative vibrational study of piperidine-1-carboxylate [42], there is little information pertaining to hydrolyzed or anionic carbamates in the open literature. The carbamate anions discussed in this work should not be confused with esterified carbamates (NHR-C(=O)OR'), which find widespread application as pesticides and for which there are well-developed techniques for their analysis and quantitation using both GC- and LC-MS [43, 44].

We begin this paper with a detailed examination of the gas-phase chemistry of the carbamate derived from 2-aminoethanol (MEA); both computational and deuterium-labeling CID experiments are used to confirm MS structural assignments. We then proceed to identify similarities between condensed- and gas-phase chemistries, and generalize the 2-hydroxyethylcarbamate results for carbamates derived from more complex alkanolamines. In this context, dissociations common to the carbamate (anion) suite are utilized for the development of a dynamic quantitation method. The method entails separation via ion chromatography (IC) and MS detection using multiple reaction monitoring (MRM). We are particularly interested in developing this method for carbamates derived from sterically-hindered amines, which are typically present at low concentrations and evade detection using NMR and ATR-FTIR. Although sterically-hindered amines are rarely used for CO₂ capture as a sole sorbent, they



Scheme 1. Key equilibria describing aqueous chemistry between amines and CO₂

play a role in synergistic amine blends when the rate of absorption by a mixture of amines is greater than the rate of any of the individual components in isolation. Potential limitations of IC-MRM for carbamate quantitation are also discussed.

Experimental

Reagents and Carbamate Synthesis

The carbamate derivatives of capture amines were generated by mixing equimolar amounts (1–2 mmol) of the respective amine and NaHCO_3 (Sigma, Sydney, Australia, 99.9%) in 15 mL charcoal-filtered water ($R > 18 \text{ M}\Omega$). The amines investigated and their structures are presented in Figure 1. Reagent purity: MEA (Sigma, Sydney, Australia, > 99%), EN (Sigma, Sydney, Australia, 99%), PZ (Sigma, Sydney, Australia, 99 %), AMP (Fluka, Sydney, Australia, 99%), DEA (Aldrich, Sydney, Australia, >99.5%), *Tris* (Sigma, Sydney, Australia, > 99%). The mixtures were then heated to 60 °C in a water bath for 2 h. The solutions were diluted appropriately before direct infusion into the mass spectrometer for CID experiments. 1,1,2,2- d_4 -2-Aminoethanol was purchased from CDN Isotopes (Sydney, Australia).

MS Conditions

All mass spectrometry (MS) experiments were performed using a Waters Acquity HPLC-MS/MS (Sydney, Australia) equipped with an electrospray ionization (ESI) source and a T-wave collision cell (Q_1TQ_2). Typical experimental conditions include: capillary voltage=1.9–2.3 kV; cone voltage=10–30 V; desolvation gas flow=400–800 L/h; curtain gas flow=0–10 L/h; collision cell bias=1–50 V (MS/MS); infusion flow rate=30–50 $\mu\text{L}/\text{min}$. CID experiments were performed at unit mass resolution. The collision gas employed was argon (99.999% purity, BOC, Tighes Hill, Australia). The analyzer background pressure was $< 1.2 \times 10^{-5}$ mbar, which rose to $1.2\text{--}2.3 \times 10^{-3}$ mbar upon admission of the collision gas. Spectra

were averaged over many scans (in some cases >100), particularly the CID spectra for ions of low abundance.

Theory

Gas-phase density functional theory (DFT) calculations were performed for 2-hydroxyethylcarbamate and various proton shift isomers, plus certain reactions of relevance to the CID process. We have used the Minnesota 2006 meta-density functional [45] with an augmented triple-zeta basis set [M06-2X/6-311++G(d,p)]. It has been demonstrated that the M06 meta-functional outperforms B3LYP across the board, and performs as well as CCSD(T) calculations with similar-sized basis sets for reaction energies and barrier heights [46]. All calculations were performed with the GAMESS rev. 1 software package [47]. The MacMolPlt 7.0 program [48] was used for visualization.

Geometry optimizations were performed using a Newton-Raphson steepest descent algorithm until a stationary point was located, characterized by a gradient less than 0.0001. We have used the recommended density of grid points to reduce integration errors in the DFT exchange-correlation quadrature to less than 1 microhartree per atom, namely NRAD=96, NTHE=36 and NPHI=72, producing 248832 grid points per atom. Vibrational analysis was performed for all stationary points. All transition structures exhibit a single imaginary vibrational frequency (NIMAG =1).

Molar heat capacities (C_p , C_v), entropies, enthalpies and free energies at specified temperatures for both molecules and ions were provided by the GAMESS program. All gas phase reaction free energies were calculated according to standard thermochemical conventions [49].

IC-MS/MS

The IC-MS/MS experiments were performed with the Waters Acquity system described above. The modifications

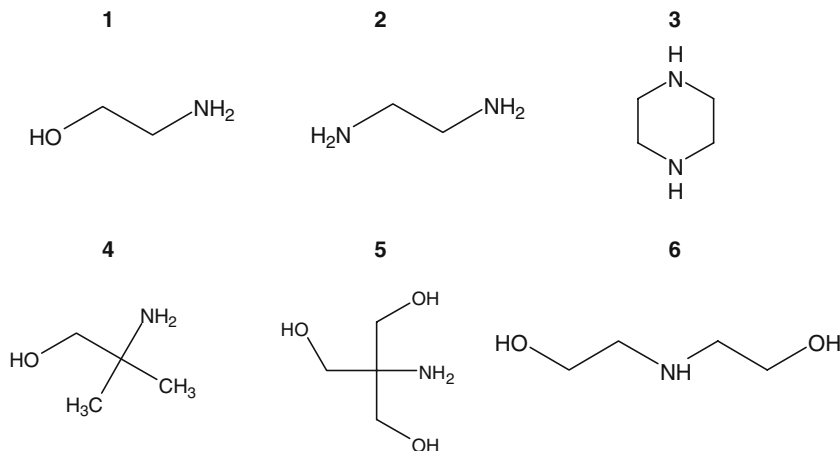


Figure 1. CO_2 capture amines for which chemistry with bicarbonate (specifically carbamate formation) was investigated. 1=2-aminoethanol (ethanolamine, MEA); 2=1,2-diaminoethane (ethylenediamine, EN); 3=piperazine (PZ); 4=2-amino-2-methyl-1-propanol (AMP); 5=2-amino-2-(hydroxymethyl)propane-1,3-diol (*Tris*); 6=2,2'-iminodiethanol (diethanolamine, DEA)

necessary to perform IC separations include: mobile phase A: MeOH, mobile phase B: 10 mM KOH; solvent flow rate 0.3 mL/min; column=Dionex IonPac AS4, 4 mm×250 mm (Lane Cove, Australia); mobile phase gradient: 95.0:5.0 (A: B), t=0 min to 50.0:50.0, t=10 min, to 1.0:99.0 at t=16 min; isocratic to t=26 min; to 95.0:5.0 at t=27 min; isocratic for 3 min. MS settings: ion mode=negative; detection mode=MRM; dwell time=100 ms; interscan delay=20 ms, transitions 103.0→59.0; 104.0→60.0; 129.0→85.0. The manufacturer's setting controlling the resolving power of Q₂ was relaxed for the MRM experiments (from 15 to 13.5).

Results and Discussion

Carbamate Derivative of 2-Aminoethanol

Most mass spectrometers in commercial analytical laboratories rarely operate in negative-ion mode, so our investigations were initially concerned with a method of quantifying protonated carbamic acids in positive-ion mode (carbamates are the conjugate bases of carbamic acids). The low energy positive-ion CID spectrum of putative protonated 2-hydroxyethylcarbamic acid (*m/z* 106, [HOCH₂CH₂CHCO₂H+H]⁺) is presented in the Supplementary Information (Figure S1). Peaks due to consecutive water loss are evident (*m/z* 88, 70), together with a peak which may/may not correspond to protonated formic acid (*m/z* 47). The peak at *m/z* 23 is due to a sodium adduct with the same mass-to-charge ratio as the ion of interest. Without labeling studies, it is impossible to conclude that the mass-selected ion packet is representative of protonated 2-hydroxyethylcarbamic acid. Further confounding positive identification of this ion is the occurrence of *bis-N,N*-(2-hydroxyethyl)amine (DEA) at low concentrations in the MEA stock solution (confirmed separately using ion chromatography, result not shown). Protonated DEA, [(HOC₂H₄)₂NH+H]⁺, has the same mass-to-charge ratio as the protonated carbamic acid derivative of interest. This anomaly could be resolved with elemental composition measurement (accurate mass), but standard triple quadrupole instruments do not possess this capability. For the reasons outlined, quantitation of acid derivatives in positive-ion mode was not pursued further.

The low energy negative-ion CID spectrum of putative 2-hydroxyethylcarbamate (HOC₂H₄NHCO₂⁻) is presented in Figure 2A. The corresponding spectrum for its isoelectronic analogue, the putative carbamate derivative of 1,2-diaminoethane (H₂NC₂H₄NHCO₂⁻, *m/z* 103) is presented in Figure 2B. It is clear from Figure 2B that substitution of the hydroxyl group in MEA for an amine group in EN has only a minor effect on the carbamate fragmentation chemistry, which manifests as a smaller water loss peak for 2-hydroxyethylcarbamate. Common neutral losses and fragment ions, and their relative abundances, are presented in Table 1.

Overall, the excellent correspondence between the CID spectra in Figure 2A and 2B leaves little doubt that

carbamate ions are being sampled, in particular the common losses of 18, 44, and 46 mass units, and the common fragments *m/z* 26, 42. To further dispel any doubt as to the structural identity of *m/z* 104 (Figure 2A) and enable us to conclude we are sampling only carbamate derivatives in the gas phase, putative 1,1,2,2-d₄-2-hydroxyethylcarbamate (*m/z* 108) was synthesized from 1,1,2,2-d₄-ethanolamine and NaHCO₃ and subjected to CID (see Supplementary Information Figure S2). The dominant peak in the spectrum corresponds to loss of 44 mass units (*m/z* 64), which can only be due to CO₂ expulsion and confirms the diagnostic nature of this loss for carbamate species. *M/z* 26 and 42 are also present, and can only correspond to CN⁻ and NCO⁻. Loss of H₂O from the parent ion is also observed (*m/z* 90), but there is no evidence of HDO or D₂O loss, confirming that reactive amino- and hydroxyl-group hydrogens are incorporated in the water molecule lost from the unlabelled congener. A follow-up loss from *m/z* 90 ([C₂D₄N₂O₂]⁻) cannot contribute to the product ion measured at *m/z* 61. This ion could be due to (1) formation of HCO₃⁻ (loss of neutral d₄-ethanimine), (2) loss of HDO after hydrogen scrambling, which in turn facilitates CO loss from a metastable product ion, (3) loss of HD from either d₄-aminoethanolate or d₄-(2-hydroxyethyl)azanide, or (4) loss of d₃-acetaldehyde to form d₁-carbamate, NHD-CO₂⁻. To help resolve the origin of *m/z* 61, *m/z* 64 ([C₂D₄H₂O₂N]⁻ was generated in-source and subjected to MS/MS (quasi-MS³). Fragments at *m/z* 61 and *m/z* 58 were detected (see Supplementary Information Figure S3), however this result simply identifies '(iii)' as a potential pathway to formation of this ion packet. Neighboring substituent effects in the gas phase chemistry of functionalized radical amine cations, as identified by Schwarz and Levsen [50], leads to activation of C–H bonds proximal to ionized heteroatoms, and explains the incorporation of deuterium in the neutral losses giving rise to *m/z* 61, 60, and 58. As these ions are not integral to our identity assignment, no further comment is necessary.

The negative-ion MS/MS spectra presented in Figure 2 establish that carbamates can be readily synthesized and identified using tandem mass spectrometry. Theoretical studies described in the next section shed light on the energetics of carbamate dissociations. 2-Hydroxyethylcarbamate is chosen as a model system due to its small size (56 electrons, computationally tractable), and because it is the carbamate derivative of MEA, the most studied and widely-used amine for CO₂ scrubbing.

2-Hydroxyethylcarbamate Dissociations: M06-2X/6-311++G(d,p)

It is reasonably well established that the lowest energy gas phase conformer for 2-hydroxyethylcarbamate (HOC₂H₄NHCO₂⁻, Structure 1 in Figure 3) is hydrogen-bonded between the carbamate CO₂ moiety and the hydroxyethyl OH group [51, 52]. Other isomeric forms, which are possible intermediates in pre-dissociative rearrangements,

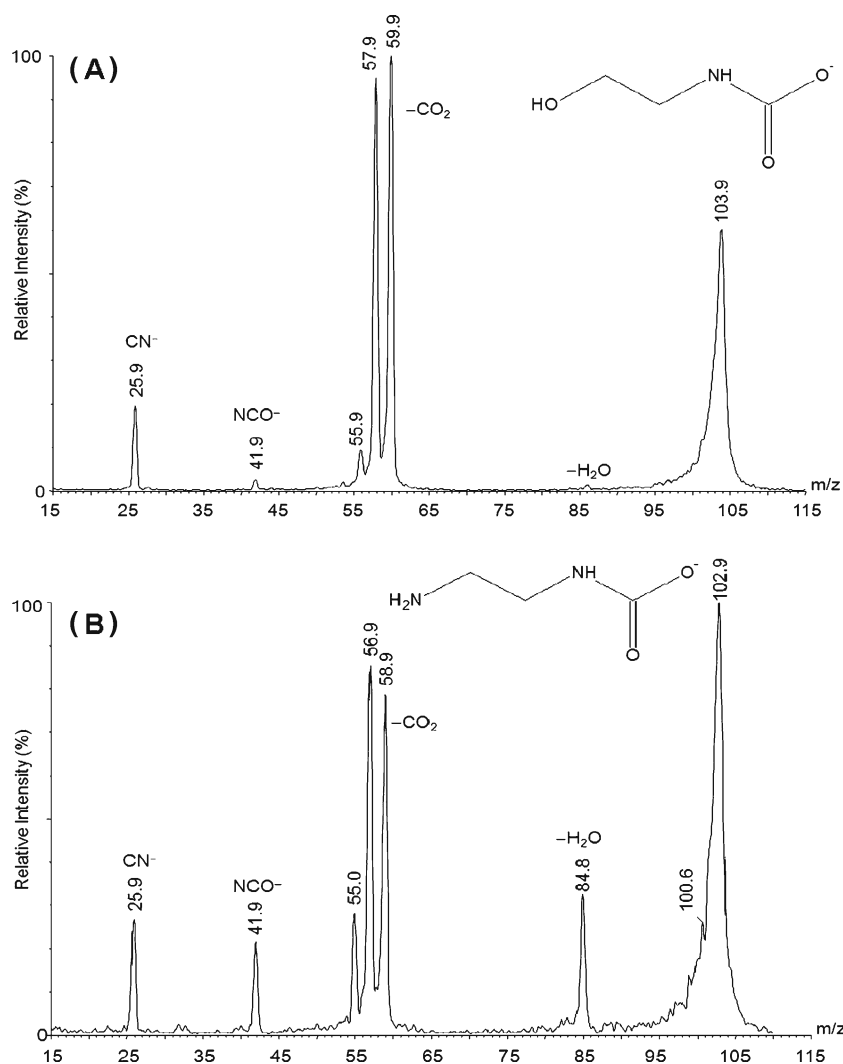


Figure 2. (A) Negative-ion low energy CID spectrum of 2-hydroxyethylcarbamate, $\text{HOC}_2\text{H}_4\text{NHCO}_2^-$; (B) negative-ion low energy CID spectrum of 2-aminoethylcarbamate, $\text{H}_2\text{NC}_2\text{H}_4\text{NHCO}_2^-$

include carboxy(2-hydroxyethyl)azanide (*syn*- $\text{HOC}_2\text{H}_4\text{NCO}_2\text{H}^-$, Structure 2 in Figure 3; *anti*- $\text{HOC}_2\text{H}_4\text{NCO}_2\text{H}^-$, Structure 3 in Figure 3), and 2-(carboxyamino)ethanolate (*syn*- $\text{O-C}_2\text{H}_4\text{NHCO}_2\text{H}$, Structure 4 in Figure 3; *anti*- $\text{O-C}_2\text{H}_4\text{NHCO}_2\text{H}$, Structure 5 in Figure 3). The lowest energy

conformers of these species were found to be +61.3 kJ and +108.7 kJ less stable than Structure 1, respectively, and will not play a significant role in condensed phase chemistry. In addition, the relative energies of several 2-aminoethylcarbonate conformers were determined ($\text{O}_2\text{CO-C}_2\text{H}_4\text{-NH}_2$, structures

Table 1. Normalized CID Neutral Loss/Product Ion Abundances for the Carbamate Derivatives of CO_2 Capture Amines Investigated in this Work. T-cell bias=12 V. Dissociation Products Specific to a Particular Carbamate are not Presented

Parent amine (see Figure 1)	Normalized carbamate CID product abundance (%), T-cell bias=12 V						
	R-carbamate, R =	2-hydroxyethyl	2-aminoethyl	Bis(2-hydroxyethyl)	Piperazine-1 ^a	(1-hydroxypropan-2-yl)	1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl <i>Tris</i>
Neutral loss/product ion:							
$-\text{H}_2\text{O}$	1.3	32.0	4.7	-	-	-	18.9
$-2\times\text{H}_2\text{O}$	-	-	0.6	-	-	-	2.0
$-\text{CO}_2$	76.1	40.8	72.0	84.4	89.1	54.9	54.9
-46	19.2	20.0	12.3	13.7	10.9	-	2.4
-48	2.3	2.9	-	-	-	-	-
NCO^-	0.1	3.2	<0.1	-	-	-	-
CN^-	1.0	1.2	-	-	-	-	-

^aPiperazine-1-carboxylate

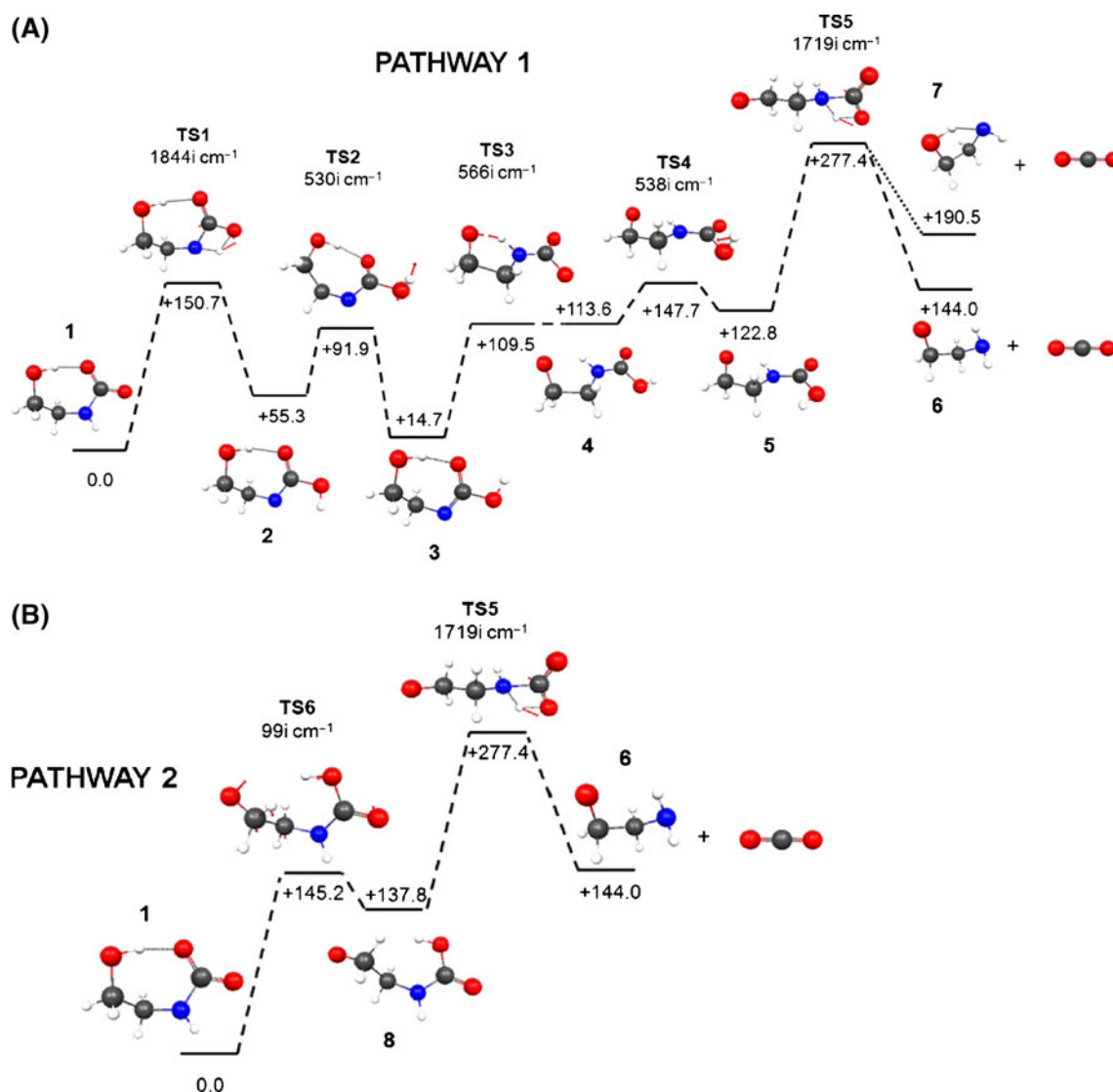


Figure 3. M06-2X/6-311++G(d,p) potential energy surfaces for CO₂ loss from 2-hydroxyethylcarbamate (Pathways 1 and 2). All energies are in kJ relative to the most stable conformer of 2-hydroxyethylcarbamate (1, 0.0 kJ). TS=transition structure; carbon=black, hydrogen=white, oxygen=red, nitrogen=blue. Vectors describing reactive atomic motions in TS's are in red

not shown); the most stable conformer was found to be +19.0 kJ/mol higher in energy than Structure 1. We conclude that only 2-hydroxyethylcarbamate is being sampled from aqueous amine solutions and studied in the mass spectrometer.

One important aspect of CO₂ loss from 1 is the form of the product ion [C₂H₆O₂N]⁻; direct loss will presumably lead to 2-hydroxyethylazanide (Structure 7 in Figure 3), whereas intramolecular proton migration from the hydroxyl group to the nitrogen atom (either accompanying or immediately following CO₂ loss) will lead to 2-aminoethanolate (Structure 6 in Figure 3). The density functional results suggest that the 2-aminoethanolate form is far more stable (by +46.5 kJ/mol) than the 2-hydroxyethylazanide form. To determine whether the migration accompanies or follows carbamate decarboxylation, the 2-hydroxyethylazanide to 2-aminoethanolate proton transfer transition structure (TS) was located. The relative free energy of this TS represents the proton migration activation

energy, and was found to have an energy of +41.6 kJ/mol relative to 2-aminoethanolate (confirmed by intrinsic reaction coordinate (IRC) calculations). DFT occasionally performs poorly for barrier heights [53], so coupled cluster calculations with perturbative triples corrections and an augmented correlation-consistent triple- ζ basis set [CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(d,p)] were used to determine the single point energies for the three participating structures, i.e., the two minima and the connecting TS. The relative free energies at the two levels of theory are presented in Table 2 for comparison.

Both sets of calculations agree that intramolecular proton transfer is barrierless, and 2-hydroxyethylazanide is inherently unstable. This conclusion is qualified on the basis that the M06-2X/6-311++G(d,p) geometries accurately represent the CCSD(T) geometries at the corresponding potential energy surface points.

Table 2. Relative Energies of 2-Aminoethanolate, 2-Hydroxyazanide, and the Connecting Transition Structure

Structure	SCF energies (hartree)		Relative free energies (298 K, kJ/mol)		Relative energies (0 K, kJ/mol)	
	M06-2X/ 6-311++G(d,p)	CCSD(T)/ aug-cc-pVTZ	M06-2X/ 6-311++G(d,p)	CCSD(T)/ aug-cc-pVTZ	M06-2X/ 6-311++G(d,p)	CCSD(T)/ aug-cc-pVTZ
2-Aminoethanolate	-209.7663371	-209.4752307	00.0	00.0	00.0	00.0
TS	-209.7465832	-209.4559034	41.7	40.5	41.3	40.2
2-Hydroxyethylazanide	-209.7468252	-209.4567026	46.5	43.9	41.3	44.0

Decarboxylation Pathways for 2-Hydroxyethylcarbamate

According to the calculations, the decarboxylation of 1 to produce CO₂ and 2-aminoethanolate anion is endoergic by +144.0 kJ/mol. With reference to Figure 3, several hydrogen transfer reactions have a similar energy demand. Two pathways which were identified as resulting in decarboxylation involve migration of the hydroxyethyl group proton to (1) an azanide-imidoate nitrogen, Pathway 1 TS 3 and Structure 4, and (2) an aminocarboxyl oxygen, Pathway 2 TS6 and Structure 8. Pathway 1 begins with an intramolecular proton migration (TS1 and Structure 2) to form 2-hydroxyethylazanide (Structures 2 and 3) before isomerization to an ethanolate form (Structures 4, 5, and TS 4) and then decarboxylation; Pathway 2 results in direct formation of *anti*-2-(carboxyamino)ethanolate, Structure 8. Decarboxylation proceeds exclusively via TS5 and has an energy demand of +277.4 kJ/mol (+66.3 kcal/mol). IRC calculations confirm that intramolecular proton migration with the carboxyamino group leads to breaking of the N-CO₂ bond, generating 2-aminoethanolate (Structure 6) and carbon dioxide.

Attempts were made to locate a TS corresponding to concerted proton-transfer/CO₂⁻ loss; this path corresponds to the shift of the hydroxyethyl proton to the amino nitrogen with concerted N-CO₂ bond-breaking. A TS was located, but it did not lead to direct dissociation [TS8, see Supplementary Information (S4)]; instead, reaction path following in both directions confirmed that TS8 leads only to hydrogen exchange between the OH and NH groups via a quasi 4-coordinate ammonium structure (N-C bond length = 1.601 Å). In any case, the relative energy of TS8 (+134.2 kJ/mol) lies below the energy of dissociated CO₂ and 2-aminoethanolate (+144.0 kJ/mol). All searches for stable ammonium structures (PES minima) were unsuccessful. We conclude that gas-phase decarboxylation is a multi-step process, and proceeds through a carbamic acid intermediate.

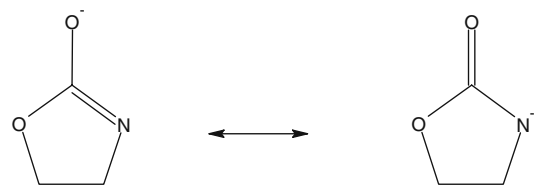
Stepwise Loss of H₂O and CO Via an Isocyanate Intermediate; Carbamate (NH₂-CO₂⁻) Formation from 2-Hydroxyethylcarbamate

All TSs referred to in the following discourse are presented in Supplementary Information (S5). A TS for water loss which is consistent with the results from the isotopologue

studies of 2-hydroxyethylcarbamate was also located. That is, the water molecule eliminated possesses the hydrogen atoms originally attached to (1) the amino nitrogen and (2) the oxygen of the hydroxyethyl group. The free energy of activation was found to be +137.5 kJ/mol, and leads to formation of 2-isocyanatoethanolate (⁻O-C₂H₄-N=C=O). The calculations also reveal that the extended isocyanatoethanolate structure cyclises with a negligible activation energy to form either an oxazolate or an oxazolidinide (Scheme 2).

The low intensity of the isocyanatoethanolate product ion in the CID spectrum of 2-hydroxyethylcarbamate (*m/z* 86, Figure 2A) suggests further decomposition of the dehydration product might be facile. Indeed, the computations indicate that loss of NCO⁻ (isocyanate anion) from the dehydration product requires a free energy of activation of +269.4 kJ/mol, and explains the origin of the peak at *m/z* 42 in Figure 2A. In contrast, the loss of CO requires an activation energy of +500.8 kJ/mol (almost 5.2 eV). With reference to the CID spectrum of 1,1,2,2-d₄-2-hydroxyethylcarbamate (HO-C₂D₄-NH-CO₂⁻, see Supplementary Information) the absence of a peak at *m/z* 62 suggests CO loss from the isocyanatoethanolate anion is not operative at the collision energies employed.

One final TS is worth mentioning. Carbamate, or NH₂CO₂⁻, is the simplest ion with a carboxy group attached to an amino centre and is readily derived from ammonia and bicarbonate solutions. Decomposition of 2-hydroxyethylcarbamate via fission of the N-C_α bond (with an associated hydrogen migration) could conceivably give rise to carbamate ion. A TS was found which leads to formation of carbamate, accompanied by an C_α-N hydrogen shift, with a relative energy of +319.1 kJ/mol with respect to Structure 1. The energy required for this decomposition is only slightly larger than the decarboxylation activation energy, so it is likely that *m/z* 61 in the CID spectrum of 1,1,2,2-d₄-2-hydrox-



4,5-dihydro-1,3-oxazol-2-olate

2-oxo-1,3-oxazolidin-3-ide

Scheme 2. 2-Hydroxyethylcarbamate dehydration products

yethylcarbamate (Supplementary Information, Figure S2) has contributions from NHD-CO_2^- .

2-Hydroxyethylcarbamate Dissociations In Vacuo: Correspondence with the Condensed-Phase

Amine degradation will be a significant cost factor for large-scale post-combustion CO_2 capture operations. The CID experiments reported in this paper are low energy in nature and ion fragmentation results from gentle heat transfer to the ions during several collisional encounters with a neutral target gas (Ar). While there are clear disparities between the environment of an ion in the dilute vacuum and one forming multiple hydrogen bonds within a dielectric protic solution, some correspondence between the decomposition chemistry in the two phases cannot be excluded. Several relevant aspects have been identified in this study, and are discussed below.

A clear parallel can be found in the facile loss of CO_2 from carbamate ions in the gas- and condensed phases. One of the many reasons post-combustion CO_2 capture using aqueous amines is considered an attractive greenhouse gas abatement option is the low thermal energy of solvent regeneration. Temperatures less than $150\text{ }^\circ\text{C}$ are usually sufficient to decompose carbamates. It is doubtful though, that the decomposition proceeds via the same mechanism in vacuo as in the condensed phase (in the presence of a protic solvent).

Dehydration of gas-phase carbamate ions leads to formation of isocyanates. Isocyanates are important polymer intermediates (e.g., polyurethanes) and must be prepared in the laboratory under anhydrous conditions in order to avoid the unwanted generation of carbamates. It is likely that the MEA degradation product 2-oxazolidinone, encountered in degraded capture solutions [54], is not the result of amine oxidation, but rather decomposition of the carbamate during solvent regeneration at elevated temperatures. It appears that a small percentage of MEA degradation via this pathway will be unavoidable during normal CO_2 capture plant operations.

Ammonia and organic acids (oxalic, glycolic, acetic and formic) are usually monitored during CO_2 capture operations as a metric of solvent performance [54]. Aqueous metal ions or metal surfaces (in which the metal is in a low-oxidation state) are known to contribute to capture amine degradation and, particularly, to the abundance of ammonia as a degradation product. Relative to amine regeneration, a small additional activation energy (41.7 kJ/mol in excess of the decarboxylation energy) is sufficient to induce acetaldehyde loss from 2-hydroxyethylcarbamate. This suggests NH_2CO_2^- could be formed from $\text{HO-C}_2\text{H}_4\text{-NH-CO}_2^-$ (2-hydroxyethylcarbamate), particularly during solvent regeneration. Acetaldehyde is believed to be a primary solvent degradation product of MEA, and well established oxidation chemistry will produce the C_2 -acids (given above) from this inter-

mediate. Carbamate should also decompose to NH_3 and CO_2 under the conditions employed to regenerate loaded or CO_2 -rich MEA solutions. The computational results indicate that ammonia should also be considered as a carbamate- or thermal-degradation product, and not simply as an oxidative degradation product.

We now turn our attention to the CID spectra of more complex alkanolamines, which are used in post-combustion capture solvents.

CID Spectra of bis(2-Hydroxyethyl)Carbamate and Piperazine-1-Carboxylate

Both bis(2-hydroxyethyl)carbamate (m/z 148) and piperazine-1-carboxylate (m/z 129) are carbamates derived from secondary functionalized amines. They are, respectively, the CO_2 capture products of DEA (6, Figure 1) and PZ (3, Figure 1), both of which are promising candidates for post-combustion capture application. The CID spectra of both carbamates exhibit strong CO_2 -loss peaks [appearing at m/z 104 and 85, respectively, see Supplementary Information (S6)], as well as losses of 46 mass units. Beyond this, there are few spectral similarities. There is a small water loss peak in the spectrum of bis(2-hydroxyethyl)carbamate, however there is no evidence of water loss in the spectrum of piperazine-1-carboxylate; both water and CO_2 are lost sequentially from bis(2-hydroxyethyl)carbamate. Instead of a water loss peak at m/z 111, a very small peak at m/z 112 indicates piperazine-1-carboxylate might lose ammonia. Overall, the distinctive peaks corresponding to the losses of 44, 46 mass units leave little doubt that the ions sampled are carbamates. We refrain from further peak assignments as labeling and theoretical studies have not been undertaken.

We now apply the knowledge gained from the study of relatively “stable” carbamates to the putative carbamates of classical “sterically hindered” primary amines and answer the vexing question: Do sterically hindered amines form carbamates? Both the sterically-hindered amines (2-amino-2-methyl-1-propanol (AMP, 4 in Figure 1) and Tris(hydroxymethyl)aminomethane (Tris, 5 in Figure 1) find application in post-combustion capture solvents: the former in promoted amine mixtures, and the latter as a vapor pressure inhibitor for volatile ammonia capture solutions.

Sterically-Hindered Amines Also form Carbamates: Dissociation Spectra of (1-Hydroxypropan-2-yl)Carbamate and [1,3-Dihydroxy-2-(Hydroxymethyl) Propan-2-yl]Carbamate

To date, there have been no reports relating to the detection of carbamates derived from sterically hindered functionalized amines. The CID spectrum of the putative carbamate derivative of Tris(hydroxymethyl)aminomethane is presented in Figure 4. The spectrum presented was averaged over many scans, and the cone voltage and gas were kept

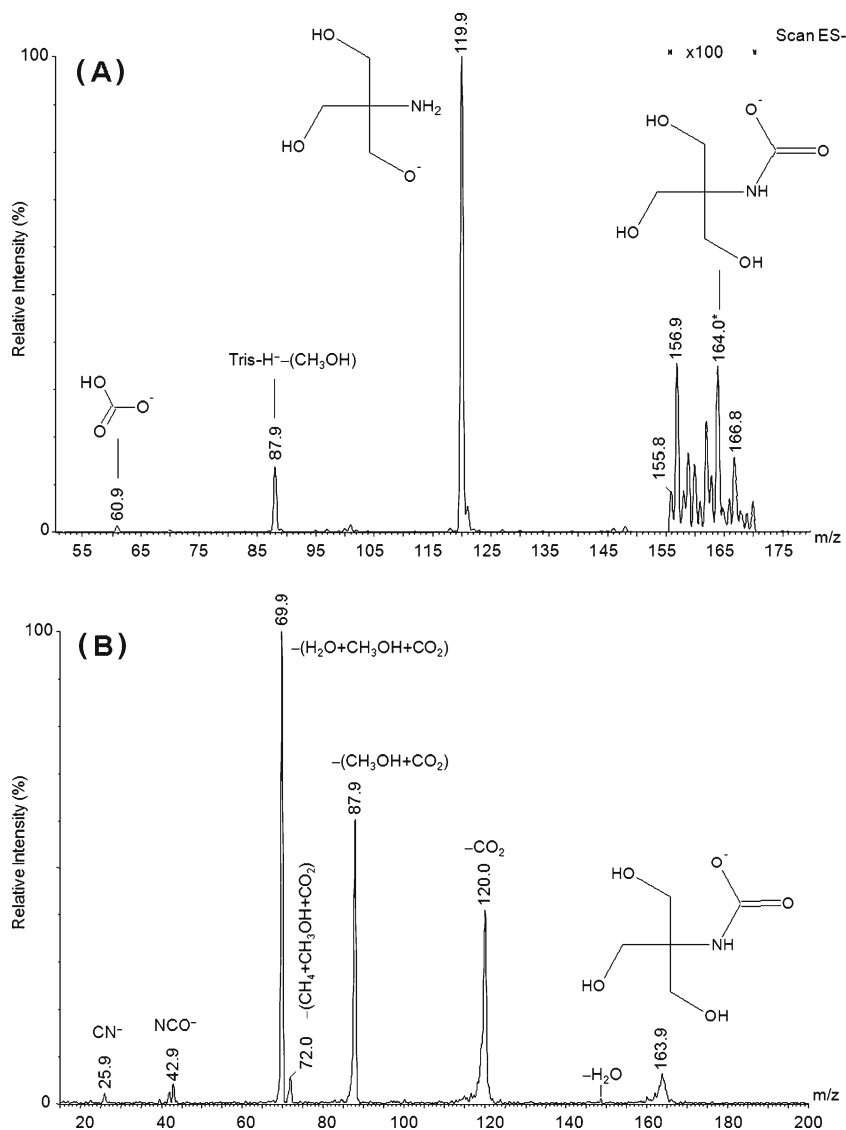
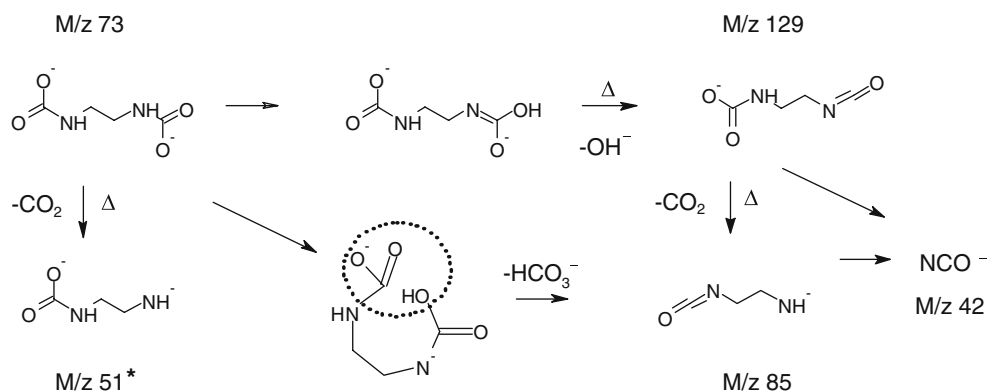


Figure 4. (A) The broad scan negative-ion spectrum of the aqueous reaction mixture from which [1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]carbamate was sampled using ESI-MS; (B) low energy negative-ion CID spectrum of [1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]carbamate

low (10–20 V and 0–50 L/min) in order to facilitate carbamate observation and detection. Also shown in this figure, is the broad scan ESI-negative ion spectrum of the aqueous reaction mixture from which the carbamate ion was sampled. It is evident that the peak subsequently mass-selected for interrogation at m/z 164 ([1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]carbamate, the carbamate derivative of *Tris*) is quite weak; this could be a consequence of the propensity of the carbamate species to hydrolyze, or to a particular kinetic constraint to its formation. The behavior of sterically-hindered amines in CO_2 capture solutions was believed to parallel that of tertiary amines, i.e., this class of amine was assumed to act purely in a base-catalytic role, not interacting directly with either aqueous CO_2 or bicarbonate. The CID spectra of (1-hydroxypropan-2-yl)carbamate [see Supplementary Informa-

tion (S7)] and [1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]carbamate demonstrate the existence of carbamates for these species. Diagnostic fragments and ions of *Tris*-carbamate include peaks at m/z 26 (CN^-), m/z 42 (NCO^-), and direct loss of 44 mass units (CO_2) together with methanol and water loss peaks. The major dissociation pathway for (1-hydroxypropan-2-yl)carbamate is loss of CO_2 , with smaller peaks corresponding to loss of CO_2 followed by (1) H_2 , (2) H_2O , and (3) NH_3 . A small peak due to CN^- at m/z 26 is barely discernable, but nevertheless present. These findings concur with theoretical results, which support the stability of the carbamates for these species [55, 56], and dispels the notion of specific base-catalysis for this class of capture amines.

As there are several capture amines, which are functionalized diamines, the dicarbamate (dianion) derivative of



Scheme 3. Dissociations observed for m/z 73 derived from an aqueous mixture of NaHCO_3 and ethylenediamine. The asterisk denotes a fragmentation that was not observed

ethylenediamine has also been investigated, and the results discussed below.

CID Behavior of a Dicarbamate: Ethane-1,2-Diyldicarbamate

A small peak at m/z 73 observed in the broad scan ESI-negative ion spectrum of the ethylenediamine/ NaHCO_3 mixture was mass-selected and subjected to CID experiments. The resulting spectrum is presented in the Supplementary Information (S8). Peaks at m/z 129, 102, and 85 indicate the parent ion is doubly-charged. The various fragmentations are rationalized according to Scheme 3.

All fragmentation pathways of ethane-1,2-diyldicarbamate lead to charge-separation; most result from multiple dissociation processes following the initial loss of OH^- .

Carbamate Separation Using Ion-Chromatography

A method capable of separating and quantifying the carbamates which form during CO_2 capture could offer unprecedented insight into the synergistic capture performance of amine blends. Blends or mixtures of more than two amines can exhibit CO_2 capture rates, which are greater than the sum of the rates of the individual constituents under identical conditions. Such a method would also offer the benefits described earlier concerning regeneration energy cost-savings.

The total ion chromatogram for a mixture of three carbamate derivatives is presented in Figure 5; the ion chromatograms for each of the MRM transitions monitored (one for each carbamate) are presented in the Supplementary Information (S9). The solution analyzed consisted of a

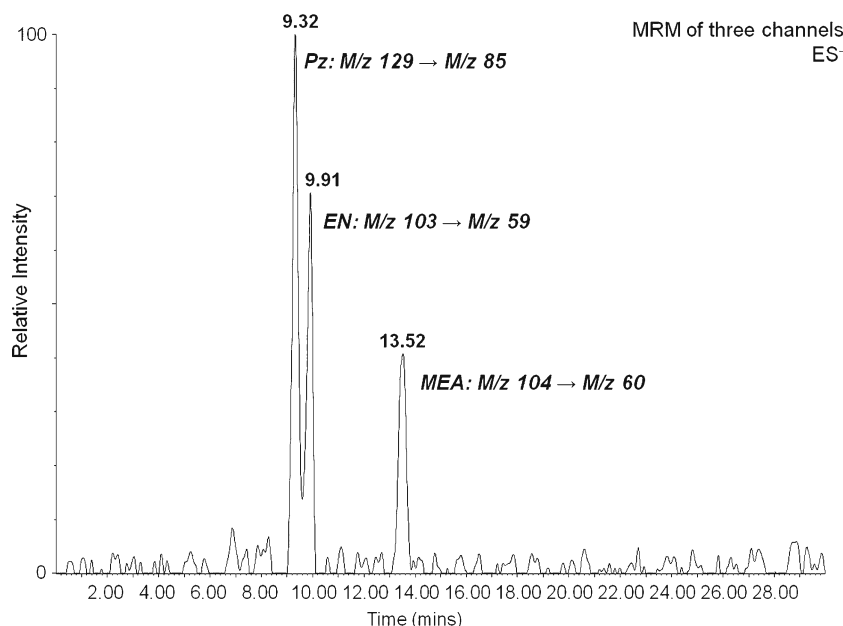


Figure 5. Negative IC-MS/MS (MRM) total ion chromatogram of a 1:1:1:3 molar mixture of 2-aminoethanol, 1,2-diaminoethane, piperazine, and NaHCO_3 . MRM transitions give rise to decarboxylation peaks (loss of CO_2) for each carbamate derivative

1:1:1:3 mixture of MEA:PZ:EN:HCO₃⁻. Although the IC-method effectively separates the carbamates, which should enable determination of the response of the MS detector with varying carbamate concentration, quantifying each component will require synthesized standards which are currently unavailable. Overall, the effect of the electrospray process on the abundance of the carbamate ions is not yet clear, as the total ion counts for each carbamate are relatively low (<500 counts for each component). Unlike positive-ion mode, the low mass region (*m/z* 20–200) in negative-ion ES is not as crowded with solvent ions, so good detection limits can be achieved, even with low analyte ion counts. The high selectivity of MRM further enhances analyte sensitivity.

Conclusions

The carbamate derivatives of CO₂-capture sorbents are readily synthesized via the addition of 1°, 2°-amines to aqueous solutions containing NaHCO₃, followed by gentle heating. Carbamate ions prepared in this way can be transferred directly from the solution phase to the gas phase using electrospray ionization, and subjected to MS/MS experimentation. With the exception of 3°-amines, the results demonstrate both the existence and gas-phase stability of carbamate species for all amines, including those classed as “sterically hindered.” The high abundance of the decarboxylation dissociation product is consistent with condensed-phase amine scrubbing chemistry, as exemplified by the widespread application of this technology for reversible CO₂ capture. Although the mechanism of N–CO₂⁻ bond cleavage in aqueous solutions is likely to involve base molecules acting as proton shuttles, the low temperatures required for process solvent regeneration (100–150 °C for alkanolamines) suggests the carbamate group is easily activated. Other aspects of the gas-phase chemistry of carbamates i.e., carbamate dehydration leading to isocyanate formation, and C_α–N bond cleavage generating NH₂–CO₂⁻ from more complex alkanolamine-carbamates, were also identified, and appear relevant to condensed-phase process chemistry.

It is inevitable that “sterically-hindered” amines will form carbamates during solvent-based CO₂ capture from gas streams, as bicarbonate ions are generated via the reaction of OH_(aq)⁻ and CO_{2(aq)} in alkaline solutions, regardless of the choice of amine sorbent. This finding indicates that mechanistically, CO₂ activation in aqueous solutions is feasible via both the carbamate and base-catalyzed routes for all 1°, 2°-amines. It does not explain why equilibrium 4 in Scheme 1 apparently lies far to the right for sterically hindered amines, or if these amines react directly with solvated CO₂. We put forward the following proposition: The hydrolysis or conversion of carbamates to bicarbonate can be observed for aqueous sorbents such as MEA and DEA on a timescale of minutes to hours [57]. This process must be rapid for sterically-hindered functionalized amines, so we contend that these amines disrupt the local solution

structure to the extent that loss of order at the solute-solvent interface facilitates the hydrolyzing solvent molecule achieving the critical/reactive configuration. The result is almost instantaneous bicarbonate formation. On the other hand, this desirable trait also inhibits amine–CO₂ interactions, since the rates of CO₂ capture by sterically-hindered amines are usually less than those of unhindered 1°, 2°-amines, but greater than 3°-amines.

The results presented in this work demonstrate that the separation and sensitive detection of carbamates in CO₂ capture process liquors is achievable using IC-MRM. Method development for the quantitation of carbamate derivatives—which were not investigated as part of this work—will need to consider carbamate dissociations on a case-by-case basis. Work investigating the MS detector response to carbamates with variation of the CO₂ loading is ongoing.

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