International Journal of Greenhouse Gas Control 76 (2018) 142–149

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Both carbamates and monoalkyl carbonates are involved in carbon dioxide capture by alkanolamines

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ARTICLE INFO

Keywords:
Monoalkyl carbonates
Hemiesters of carbonic acid
^{13}C NMR
Alkanolamines
CO_2 capture
Carbamates

ABSTRACT

Among the amines that have been systematically applied for CO_2 capture, several alkanolamines have been proved to be very effective. Although the formation of carbamates – the reaction product of CO_2 and the amine group – is recognized as the most important process, the behavior of a tertiary alkanolamine cannot be explained, because a carbamate cannot be formed. In such a case, the formation of a monoalkyl carbonate (MAC) – a hemiester of carbonic acid and the alcohol group of the alkanolamine – is the most important process. In the present study, we demonstrate that the MAC is formed not only for tertiary alkanolamines, but also for the simpler ones, and that this reaction takes place even in aqueous medium. The species were detected by ^{13}C NMR, which allowed the estimation of the formation constant of MACs for choline, triethanolamine, diethanolamine, and monoethanolamine as 0.44, 2.6, 0.72, and 0.66, respectively. These values are similar to those ones for MACs of aliphatic alcohols and sugars. Although the formation constants are much higher for carbamates, MAC formation becomes a more significant process as the pH is lowered during CO_2 capture. A brief review of previous works demonstrated that MACs could be detected in other experiments whether the authors would aware of this class of compounds.

1. Introduction

Carbon capture and storage (CCS) is one of the current strategies to reduce the concentration of carbon dioxide in the atmosphere. One basic approach is to promote the physical or the chemical sorption of CO_2 on a specific liquid or solid, which is then transported to a convenient place. Changes of either pressure or temperature are used to increase the sorption process during the capture and to reverse the process to release CO_2 allowing the reuse of the sorbent. The energy involved in these two steps must be low allowing the commercial viability of the whole process. This is the reason why NaOH is not appropriate, because the resulting Na_2CO_3 or $NaHCO_3$ demand too much energy to release the captured CO_2. Fortunately, there are suitable basic substances that can be used instead. Different amines have been studied for this purpose. Besides the obvious basic behavior of these amines that favors the formation of HCO_3^-, the formation of carbamate (R_2N-COO^-) is a key point in the process.

Carbamate is the main form of fixed CO_2 when concentrated solutions or pure amines are used. It turns out that this species can be formed for ammonia as well as for primary and secondary amines, but tertiary amines are not able to form carbamates, because of the absence of a leaving hydrogen atom. Even so, some tertiary amines have been successfully applied in CCS, namely alkanolamines. This behavior has intrigued several researchers, but recently Behrens et al. shed some light on the matter by detecting, using nuclear magnetic resonance (NMR), the formation of methyldiethanolamine carbonate – a monoalkyl carbonate (MAC) – in aqueous medium during CO_2 capture (Behrens et al., 2017).

The MACs may be formed by reacting alcohols and CO_2 or HCO_3^-. Although the initial studies about this class date back more than a hundred years (Hempel and Seidel, 1898; Siegfried and Howwjanz, 1909), the presence of this kind of species in aqueous environments has been missed due to the evanescent nature of these compounds. However, modern analytical techniques have been used to detect MACs – or, in a more generic way, the hemiesters of carbonic acid (HECAs). Capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C^{4}D) allowed the determination of physical-chemical properties and equilibrium constants of MACs formed by the reaction of simple alcohols and HCO_3^- in aqueous media (do Lago et al., 2012; Vidal et al., 2011). The same technique was used to quantify monoethyl carbonate in beers and carbonated drinks (Rossi et al., 2012). These species were also detected by electrospray

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https://doi.org/10.1016/j.ijggc.2018.07.005
Received 13 March 2018; Received in revised form 29 June 2018; Accepted 4 July 2018
1750-5836/ © 2018 Published by Elsevier Ltd.

ionization-mass spectrometry (ESI-MS) (do Lago et al., 2014; Vidal et al., 2013). Recently, the isomers of glucose carbonate and other sugar carbonates were detected by ^{13}C NMR (dos Santos et al., 2016). In all these cases, the medium was mainly aqueous, i.e., the concentration of water – a competing nucleophile to the alcohol – is similar or higher than the alcohol. The aim of the present study is to demonstrate that nitrogenated species containing an alcohol group also form HECAs in conditions similar to those ones used for CCS.

2. Experimental section

Choline chloride (purity ≥ 98%), choline hydroxide solution (20% w/w), triethanolamine (TEA) (purity ≥ 97%), diethanolamine (DEA) (purity ≥ 98%), D_2O with 0.75% (w/w) sodium 3-(trimethylsilyl)propionate-2,2,3,3-d$_4$ (TMSP) and $NaH^{13}CO_3$ (purity ≥ 99%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Monoethanolamine (MEA) was obtained from Vetec (purity ≥ 99%) (Duque de Caxias, RJ, Brazil). Hydrochloric acid was acquired from Merck (37%, P.A.) (Darmstadt, Germany). All the solutions were prepared in deionized water (18 MΩ cm) obtained from a Millipore Milli-Q water purification system (Molsheim, France).

The choline solution pH 8.3 was prepared by adding 0.7000 g of choline chloride to 150 μL of D_2O with TMSP, 17 mg of $NaH^{13}CO_3$, and deionized water to a final volume of 1.0 mL. The choline solutions pH 9.2, 11.6, and 12.0 were prepared in a similar way, but adding, respectively, 10.6, 160, and 211 μL of choline hydroxide before completing with deionized water. The final choline concentration was 4.9 mol L^{-1} for all the solutions.

The TEA solution pH 7.4 was prepared by adding 0.7108 g of TEA, 345 μL of D_2O with TMSP, and 328 μL of 37% (v/v) HCl, and deionized water to 2.3 mL. An aliquot of 1.0 mL of this solution was added to 17 mg of $NaH^{13}CO_3$. The final TEA concentration was 2.0 mol L^{-1}.

The DEA solution pH 7.9 was prepared by adding 0.8657 g of DEA, 300 μL of D_2O with TMSP, and 657 μL of 37% (v/v) HCl, and deionized water to 2.0 mL. An aliquot of 1.0 mL of this solution was added to 17 mg of $NaH^{13}CO_3$. The final DEA concentration was 4.0 mol L^{-1}.

The MEA solution pH 11.8 was prepared by adding 1.53 mL of MEA to 750 μL of D_2O with TMSP, 85 mg of $NaH^{13}CO_3$, and deionized water to a final volume of 5.0 mL. The MEA solutions pH 8.5 and 10.0 were prepared in a similar way, but adding, respectively, 2.0 and 0.25 mL of 37% (v/v) HCl before completing with deionized water. The final MEA concentration in these solutions was 5.0 mol L^{-1}.

To 5 mL of 37% (v/v) HCl, 3 mL of MEA/water 1:1 (v/v) were slowly added under stirring and cooling. After that, the solution was heated to eliminate the excess of HCl. Then, the temperature was continuously increased up to 120 °C to evaporate the residual water. After cooling, the crystals of monoethanolamine hydrochloride were formed. The MEA solution pH 6.5 was prepared by adding 0.4880 g of the salt to 165 μL of D_2O with TMSP, 19 mg of $NaH^{13}CO_3$, and deionized water to a final volume of 1.1 mL. The final MEA concentration was 4.3 mol L^{-1}.

The final pH measurement and the ^{13}C NMR spectra were obtained after at least one hour upon the solution preparation. The pH was measured using a HI 8424 pH meter (Hanna Instruments, Woonsocket, RI). The 75.43 MHz 1D 13C-[1H] spectra were acquired at ambient temperature using pulse sequence with 1H decoupling on a Varian Inova YH 300 spectrometer (Palo Alto, CA) equipped with a 5 mm Dual Probe. Typical conditions for the ^{13}C spectra were 1000 transients, spectral width of 19.5 kHz, and 32k data points giving an acquisition time of 1.67 s and FID resolution of 0.6 Hz/point.

3. Results and discussion

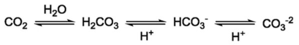
The usual approach that has been used to study CCS by NMR consists in adding CO_2 to the solution under consideration and taking NMR spectra during the process. The problem here is that the total carbon dioxide ($CO_2/HCO_3^-/CO_3^{2-}$) level and pH are changing at the same time, which impairs a precise understanding of the several phenomena taking place. In the present work, the concentration of total carbon dioxide and pH were individually controlled. The idea was to use a fixed amount of $NaHCO_3$ and to adjust the pH of the medium as needed. One problem with this approach is the solubility of the salts, and the solution was to use a relatively small concentration of $NaH^{13}CO_3$. Therefore, despite of using 0.2 mol/L of $NaH^{13}CO_3$, which corresponds to a CO_2 loading of 0.05 to 0.1 mol/mol of alkanolamine, the products are easily detected by ^{13}C NMR.

Another important point is that NMR spectra will show peaks for the individual species or just one peak at a chemical shift value in between the values of the species in equilibrium depending on how fast are the reactions. Typically, the acid/base reactions are so fast – compared to the time scale of NMR phenomena – that independent peaks for the protonated and non-protonated forms are not observed. Therefore, carbonated aqueous solutions will render only one peak for $H_2CO_3/HCO_3^-/CO_3^{2-}$ and the chemical shift will depend on the pH of the solution. Therefore, the notation H_xCO_3 will be used to refer to this set of species. The acid dissociation of a carbamic acid is also a fast process, and just one peak will be detected for the pair carbamate/carbamic acid. In addition, another peak is observed for CO_2, because its hydration is slow enough to make it observable by ^{13}C NMR as an independent peak in solutions of carbamic or carbonic acid.

The pK_a values for carbonic acid are 3.6 and 10.3. The acidity of alkyl carbonic acids is still under investigation, but initial studies suggest that the pK_a values are below 4.0 (Vidal et al., 2011). Different carbamic acids have different pK_a values. However, thanks to the oxygen atom between the carboxyl group and the rest of the molecule, the influence of the backbone is not so important. As a result, a pK_a value of 4.0 can be used as a first approximate value. These values suggest that, for slightly acid to alkaline solutions, H_xCO_3 is mainly HCO_3^-/CO_3^{2-}, while MACs and carbamates are essentially in their anionic monocharged forms.

3.1. Chemical shift for carbonate/bicarbonate/carbonic acid

Before the discussion about MACs and carbamates, the behavior of the ubiquitous H_xCO_3 peak in ^{13}C NMR spectra should be investigated. In aqueous medium, carbon dioxide is involved in a set of well-known equilibria:



$$CO_2 \xrightleftharpoons{H_2O} H_2CO_3 \xrightleftharpoons[H^+]{} HCO_3^- \xrightleftharpoons[H^+]{} CO_3^{-2} \quad (1)$$

The first step is the relatively slow hydration process, while the following steps are fast proton dissociation processes. Therefore, one should expect two peaks in a ^{13}C NMR spectrum: one for CO_2 and another for H_xCO_3. The chemical shift for CO_2 peak is 127 ppm. However, the chemical shift for H_xCO_3 ($\delta_{H_xCO_3}$) depends on the relative amounts of the species according to:

$$\delta_{H_xCO_3} = \alpha_{H_2CO_3}\delta_{H_2CO_3} + \alpha_{HCO_3}\delta_{HCO_3} + \alpha_{CO_3}\delta_{CO_3} \quad (1)$$

where α is the molar fraction of the species in the equilibrium. Taking into account that the first pK_a of carbonic acid is 3.6 and that experiments discussed in this work were carried out at more than 2 pH units above this value, the first term of the summation may be disregarded, and Eq. (1) can be expressed as

$$\delta_{H_xCO_3} = \frac{\delta_{HCO_3}10^{(pK_2-pH)} + \delta_{CO_3}}{10^{(pK_2-pH)} + 1} \quad (2)$$

where pK_2 is acid dissociation constant for HCO_3^{2-}. Although Eq. (2) can be used to predict the chemical shift and identify the peak for H_xCO_3 in a ^{13}C NMR spectrum, there are some problems:

1 Carbon dioxide capture experiments are usually carried out using

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