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# The Salt-Based Catalytic Enhancement of CO<sub>2</sub> Absorption by a Tertiary Amine Medium

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The rise in atmospheric CO<sub>2</sub> levels due to the effects of human activities poses a serious threat to the world's ecosystems because of global warming and climate change. Efficient methods are needed to limit the elevation of CO<sub>2</sub> level in the atmosphere. Here, we propose an improved CO<sub>2</sub> sequestration method that uses new catalysts, specifically a series of tertiary amine nitrate salts, in an aqueous tertiary amine medium. We synthesized the new catalysts and characterized them by using <sup>1</sup>H and <sup>13</sup>C NMR, single crystal X-ray spectroscopy, and FT-IR spectroscopy. The effects of the catalysts on CO<sub>2</sub> absorption were assessed by using a stopped-flow spectrophotometer, and their heats of absorption and CO<sub>2</sub> absorption capacities were measured with a differential reaction calorimeter (DRC) at high concentrations of the tertiary amine medium. The CO<sub>2</sub> hydration rate constants were determined under basic conditions and the catalysts were found to exhibit higher absorption of CO<sub>2</sub> (a highest value of 430 M<sup>-1</sup>s<sup>-1</sup>) than the tertiary amine medium (133 M<sup>-1</sup>s<sup>-1</sup>). The increased absorption of CO<sub>2</sub> and the low heat absorption energies of the new catalysts suggest that they could be used in post-combustion processes.

### Introduction

Globally, the accumulation of carbon dioxide (CO<sub>2</sub>) in the atmosphere is leading to severe environmental problems.<sup>1-2</sup> To minimize the undesirable effects of climate change and the greenhouse effect, many techniques for controlling CO<sub>2</sub> emissions into the atmosphere have been developed. <sup>3-7</sup> There are four major CO<sub>2</sub> capture technologies available to industry: pre-combustion, post-combustion, oxy-fuel combustion, and electrochemical separation.<sup>8-9</sup> Post-combustion capture is commonly utilized and is considered the most effective industrial CO<sub>2</sub> capture process.<sup>10-13</sup> Aqueous alkanolamine solutions are widely used for the removal of CO<sub>2</sub> in post-combustion processes. The overall process is based on the reversible chemical absorption of CO<sub>2</sub> via an acid–base reaction. Primary, secondary, and tertiary amines are solvents that are frequently used in post-combustion processes. The primary amines are more effective in the absorption of CO<sub>2</sub> than secondary and tertiary amines because of the formation of the stable carbamate species.<sup>14-15</sup> However, the regeneration processes of primary and secondary amines require more energy than that of tertiary amines. Hence, the tertiary amine methyldiethanolamine (MDEA) is commonly employed in CO<sub>2</sub> absorption processes; it has two further advantages: a lower level of solvent degradation, and less energy must be supplied to the stripper to regenerate the absorbent.<sup>16-18</sup>Very recently, CO<sub>2</sub> absorption through the use of the carbonic anhydrase (CA) enzyme<sup>19-20</sup> and its model complexes<sup>21-23</sup> in tertiary amine solution has been demonstrated, and found to exhibit enhanced absorption of CO<sub>2</sub> hydration. However, the use of CA model complexes in highly concentrated tertiary amine medium results in anion coordination with the metal center, which inhibits the fourth catalytic cycle in the generation of bicarbonate, and the CA enzyme is expensive and unstable under industrial conditions.<sup>24</sup> Our approach to this problem is to attempt to improve the efficiency of CO<sub>2</sub> absorption and thus develop a better carbon dioxide capture system. Enhancing the CO<sub>2</sub> absorption capacity of the tertiary amine by adding a suitable absorbent could also possibly reduce the overall cost of the system.

To this end, we synthesized three catalysts that each contains three tertiary amine nitrogens and a nitrate salt, which were found to exhibit enhanced  $CO_2$  hydration activity for the generation of bicarbonate in a tertiary amine medium. This paper discusses the development of these new amine salt based catalysts for the absorption of  $CO_2$  in basic solution, and our DRC experimental results confirm their potential in post-combustion processes.

### Experimental

**Material and methods:** All chemicals purchased were of analytical grade and used without further purification unless otherwise stated. FT-IR spectra were recorded with a KBr disk or the ATR method by using a Varian 640-IR FT-IR spectrometer. UV-Vis spectra were recorded on an OPTIZEN 2120UV spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian 500 MHz and Varian 125 MHz instruments respectively.

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X-ray single crystal structural analysis: A single crystal was mounted at room temperature on the tips of quartz fibers, coated with Paratone-N oil, and cooled under a stream of cold nitrogen. Intensity data were collected on a Bruker CCD area diffractometer running the SMART software package with Mo K $\alpha$  radiation ( $\lambda$ = 0.71073). The structure was determined with direct methods and refined on  $F^2$  by using the SHELXTL software package. The multiscan absorption correction was applied with SADABS, which is part of the SHELXTL program package, and the structure was checked for higher symmetry by using the program PLATON. All non-hydrogen atoms were refined anisotropically. In general, hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to 1.2 times the thermal parameter of the carbon atom to which they were attached. Data collection and experimental details for catalyst 2 (CCDC - 1454963) are summarized in Table S1, and the bond angles and distances are summarized in Table S2.

Stopped-Flow Kinetics Spectrophotometry: The experimental rate constants for the CO<sub>2</sub> hydration reactions catalyzed by the amine nitrate salts were determined with stopped-flow spectrophotometry by using methods similar to those previously described. Prior to each experiment, a solution of CO<sub>2</sub> saturated water was prepared by purging deionized water with 99.99% CO<sub>2</sub> gas at 25°C for at least 60 min. By using Henry's constant, this solution was calculated to contain 33.8 mM CO<sub>2</sub>. The reaction rates were obtained by rapidly mixing the dissolved CO<sub>2</sub> solution and the MDEA solution (1:1, v/v) in the stopped-flow spectrophotometer while recording the time dependent absorbance at  $\lambda$  = 596 nm. The  $k_{cat}$  and  $K_{m}$  kinetic parameters were calculated by using the Michaelis-Menten and Lineweaver-Burk equations. The CO<sub>2</sub> solution and a solution of MDEA+TB (blank), MDEA+bCA+TB or (catalyst+MDEA+TB) were injected into two separate syringe ports in the thermostatic unit and were maintained at 25°C. Each reaction was repeated three times, and the averages of the results were obtained and fitted by using the software Pro-Data Viewer.

Differential Reaction Calorimeter: The CO2 absorption heats and the absorption capacities of MDEA and the amine nitrate salts (1-4) were determined from DRC data (the DRC was manufactured by Setaram). The DRC apparatus consisted of two mechanically agitated glass reactors (250 cm<sup>3</sup>). The reaction temperature was maintained by circulating water from a temperature-controlled bath through the reactor and the jacket. The reactor contained a Joule effect calibration probe and a thermocouple (±0.01°C) for measuring the reaction temperature ( $\Delta T$ ). The reactor was filled with 150 g of each of the amine solvents (10 wt %) containing the amine nitrate salts (2 mM). To enhance the contact between the amine nitrate salts and CO<sub>2</sub>, the 30% CO<sub>2</sub> gas mixture (the balance of which was  $N_2$ ) was supplied in a purge form at 100 mL/min with stirring at 250 rpm. The CO2 absorption rate and reaction completion were evaluated by analyzing the discharge gas with a TCD detector consisting of a Porapak-Q (2 m, Supelco) column (7890N model GC from Agilent). The experimental temperature was maintained at 40°C.

### **Results and Discussion**





Scheme 1: Synthesis of catalyst 2. Reagents: a. 3-nitrobenzaldehyde, EtOH, NaBH<sub>4</sub>, MeOH b. HCHO, NaBH<sub>4</sub>, CH<sub>3</sub>CN/AcOH c. Pd/C, Hydrazine hydrate d. 0.1 M HNO<sub>3</sub>

Synthesis of the catalysts and characterization: To enhance the absorbance of CO<sub>2</sub> by the tertiary amine medium, three amine ammonium nitrate salt catalysts were designed and a simple synthetic method was employed to obtain them in good yield. N1-(2-aminoethyl)-N1-methylethane-1,2-diamine Initially. was treated with various nitro benzaldehydes to obtain the corresponding imines. The resulting imines were subjected to reduction using NaBH<sub>4</sub> to produce the amine intermediates. The amine intermediates were then methylated with formaldehyde and NaBH<sub>4</sub>. The nitro groups were hydrogenated with Pd/C and hydrazine hydrate to obtain the corresponding amines<sup>25</sup>, which were finally treated with diluted HNO<sub>3</sub> to prepare the desired nitrate salts in excellent yields. The synthetic scheme is shown in Scheme 1 and the synthesized amine salts 1-3 are presented in Chart 1. Pentamethyldiethylenetriamine (4) is a commercially available tertiary amine that was tested to assess the effects of CO<sub>2</sub> absorption in the absence of a primary amine nitrate salt. The synthesized amine salts were characterized by performing proton and carbon nuclear magnetic resonance spectroscopy, FT-IR, and mass spectrometry.



Chart 1. Structure of the catalysts 1-4

**Description of the crystal structure:** Suitable off-white crystals of catalyst **2** were obtained from the acetonitrile and diethyl ether diffusion system over four days. The structure of **2** is shown in Fig. 1, and its crystal data as well as selected bond distances and bond

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angles are given in Table 1 and Table S1 respectively. This amine salt forms orthorhombic crystals with Pna2(1) space group. The weak hydrogen bond interaction between the primary amine and



Fig. 1. Single crystal X-ray structure of **2**. ORTEP view showing the 50% probability thermal ellipsoids

the nitrate anion (Fig. S1) suggests that bicarbonate, which is isoelectronic with the nitrate anion<sup>26-28</sup>, may also weakly interact with the primary amine via hydrogen bonding when  $CO_2$  is introduced into a tertiary amine medium containing the amine nitrate salts. The FT-IR spectra confirm the presence of a primary amine salt stretching band in the region 3200-3500 cm<sup>-1</sup>. Further the –NH stretches of amine salt broad peaks in FT-IR show the possible weak hydrogen bonds between the amine group with nitrate anion in 1 (Fig. S2).

Determination of the CO<sub>2</sub> hydration rate constants with stoppedflow kinetics experiments: Highly concentrated amine solutions have successfully been used in post-combustion processes as absorbents. Such absorbents are chosen based on their CO<sub>2</sub> absorption capacities. Primary<sup>29</sup> and secondary amines exhibit higher CO<sub>2</sub> absorption than tertiary amines. However, the regeneration of primary and secondary amine absorbents requires more energy than that of tertiary amines. Furthermore, the use of primary and secondary amines in aqueous solution in postcombustion processes generates a mixture of carbamate and carbonate products (equations 1 & 2), whereas aqueous tertiary amine solutions generate bicarbonate rather than carbamate and carbonate (equation 3).<sup>30</sup> The absence of protons in tertiary amines means that bicarbonate is the sole product of the aqueous amine CO<sub>2</sub> hydration reaction. The following reactions occur simultaneously when CO<sub>2</sub> is absorbed into aqueous amine solutions.31

Primary amine	$CO_2 + 2 RNH_2$		RNH <sub>3</sub> RNHCO <sub>2</sub>	 (1)
Secondary amine	$CO_2 + R_2NH$		$R_2$ NHCO <sub>2</sub>	 (2)
			carbamate	
Tertiary amine	$\mathrm{CO}_2 + \mathrm{R}_3\mathrm{N} + \mathrm{H}_2\mathrm{O}$	$\longrightarrow$	$HCO_3^- + R_3NH^+$	 (3)
			bicarbonate	
	$CO_2 + OH^2$		HCO <sub>3</sub> <sup>-</sup>	 (4)
	$\rm CO_2 + 2H_2O$		$HCO_3^- + H_3O^+$	 (5)

Hence, aqueous tertiary alkanolamine MDEA was used as a reaction medium for the amine salts, which results in the selective production of bicarbonate (HCO<sub>3</sub><sup>-</sup>). The hydration of CO<sub>2</sub> was determined by rapidly mixing dissolved CO<sub>2</sub> solutions (5 mM, 10mM, or 15 mM) and a tertiary amine solution of bovine carbonic anhydrase (bCA) or one of catalysts **1-4** (1:1, v/v) in a stopped-flow spectrophotometer. The time dependent absorbance was recorded at  $\lambda = 596$  nm for thymol blue (TB), a pH indicator.<sup>32,33</sup> The formation of HCO<sub>3</sub><sup>-</sup> during CO<sub>2</sub> absorption or hydration is directly proportional to the decay of the indicator absorbance intensity<sup>17</sup>. The rate constants for the CO<sub>2</sub> hydration reactions were calculated by using the Michaelis–Menten and Lineweaver–Burk equations.

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Fig. 2. Top) Hydration of  $CO_2$  by the aqueous MDEA- $CO_2$  system: black (5 mM), red(10 mM), blue(15 mM). Bottom) the corresponding Lineweaver–Burk plots, where thymol blue(12.5  $\mu$ M) and MDEA(15 mM).

Initially, the experiments were performed in the MDEA reaction medium to establish a base level of CO<sub>2</sub> consumption; the CO<sub>2</sub> hydration rate constant was found to be 133  $M^{-1}s^{-1}$ . Next, the use of the enzyme bCA was found to provide an excellent rate of CO<sub>2</sub> conversion, as expected, with a rate constant of 10.6 ×10<sup>3</sup>  $M^{-1}s^{-1}$  under our experimental conditions. Under similar conditions, when catalyst **1** was used, it was found to produce an enhanced rate of reaction (430  $M^{-1}s^{-1}$ ), which indicates that CO<sub>2</sub> absorption is increased by using a tridentate amine based salt in a basic medium.

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The initial rate constants for the catalysts, bCA, and MDEA are given in Table 1; this table shows that different  $CO_2$  absorption rate constants for the catalysts suggest that adding the same concentration of catalyst varies in the  $CO_2$  absorption behaviour. By using the amine nitrate salts we achieved  $CO_2$  hydration rate constants ranging from 242  $M^{-1}s^{-1}$  to 430  $M^{-1}s^{-1}$ , which suggests that it may be possible to tune the amine nitrate salts so as to provide efficient  $CO_2$  sequestration.



Fig. 3. Top) Hydration of CO<sub>2</sub> by **1** (0.25 mM) in the aqueous MDEA-CO<sub>2</sub> system: black (5 mM), red(10 mM), blue(15 mM). Bottom) the corresponding Lineweaver–Burk plots, where thymol blue(12.5  $\mu$ M) and MDEA(15 mM).

The change in absorbance with respect to hydration of  $CO_2$  by MDEA in tertiary amine solution over a period of 30 seconds was measured for various concentrations of  $CO_2$  [Fig. 2 (left)] and the corresponding Lineweaver–Burk plot is shown in Fig. 2 (right) and also for **1** in Fig. 3. The  $CO_2$  absorption rate constant for the

commercially available amine **4** is less than those of the amine nitrate salts **1**, **2**, and **3** (Table 1). This result confirms that the presence of amine nitrate salts in absorbents **1-3** further enhances their absorption of  $CO_2$ . The low  $CO_2$  absorption is one of the limitations of tertiary amine based  $CO_2$  fixation, such a constraint can be partially overcome by incorporating the catalysts **1-3** into the tertiary amine medium.

Entry	Catalyst	CO <sub>2</sub> loading	Q	ΔΗ
	···· <b>/</b> ··	(mol/mol	(-kJ)	(-kJ /mol of
		solute)	. ,	CO <sub>2</sub> )
1	MDEA	0.64	5.052	61.860
2	1	0.79	4.854	54.496
3	2	0.73	4.492	53.975
4	3	0.67	5.076	61.510
5	4	0.61	6.550	85.899

Table 2. DRC measurement of  $CO_2$  absorption capacities and heats of absorption at 40°C. Q - quantity of heat released,  $\Delta H$  – heat of absorption per mole of  $CO_2$ 

DRC results for the heats of absorption and CO<sub>2</sub> absorption capacities: We tested the CO<sub>2</sub> absorption capacities of the amine nitrate salts in highly concentrated tertiary amine solutions to assess the possible use of the amine nitrate salts in post-combustion processes by performing DRC experiments. It is well established that when CO<sub>2</sub> is exposed to tertiary amines bicarbonate is formed.<sup>36-38</sup> Bicarbonate formation was confirmed in the presence of the amine nitrate salts with <sup>13</sup>C NMR spectra. The <sup>13</sup>C NMR spectra of the mixtures of aqueous amine, a tertiary amine salt, and CO<sub>2</sub> contain peaks at 161 ppm for bicarbonate as a single product. Importantly, the addition of the tertiary amine salts into the tertiary amine solutions was found to enhance the formation of bicarbonate (Fig. S3).



Fig. 4. DRC result: the  $CO_2$  absorption rate for absorbents 1-4 by gas chromatography

The CO<sub>2</sub> absorption heats and the absorption capacities of the tertiary amines and amine nitrate salts (1-3) were determined by using DRC. Carbon capture and storage technologies are based upon gas-liquid absorption systems in which heat is exchanged. The corresponding thermal data for the generated heat can provide critical information about the amount of absorbed CO<sub>2</sub> at a given temperature and gas pressure. Further, such data also provide information about the kinetics of the CO<sub>2</sub> and amine absorbent reactions.<sup>39-40</sup> The DRC apparatus consisted of two mechanically agitated glass reactors (250 cm<sup>3</sup>). Here the reaction temperature was maintained by using a temperature-controlled bath that circulates water through the reactor and the jacket. The DRC

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experimental values of MDEA were compared with previously reported values.<sup>40</sup> Initially, the CO<sub>2</sub> absorption capacity and the heat of absorption of the MDEA (10%) solution were measured. The obtained absorption capacity and heat of absorption at 40°C are given in Table 1. For MDEA, the CO<sub>2</sub> absorption mol/mol absorbent and the heat of absorption are 0.64 and -64.928 kJ respectively. The heats of absorption and absorption capacities of the primary and secondary amines are higher than those of MDEA.<sup>40</sup> Next, under similar conditions absorbent 1 was tested and found to exhibit a higher CO<sub>2</sub> absorption capacity (Table 2, entry 2). Interestingly, the heat of absorption for 1, -54.496 kJ, is less than that of MDEA (Table 2, entries 1&2) which suggest that addition of 1 in highly concentrated amine medium could only increase the absorption of CO2. The heats of absorption for absorbents 2 and 3 are -53.975 and -61.510 kJ, respectively. However, the heat of absorption for 4 is higher than catalysts 1-3 because the direct reaction of 4 with CO<sub>2</sub> in tertiary amine medium. The absorption rates determined from the DRC experiments are shown in Fig. 4. The CO<sub>2</sub> absorption rates of 1-3 are higher than that of MDEA. This result clearly confirms that the addition of the absorbents enhances the absorption of CO<sub>2</sub> by tertiary amine solutions. The highest CO<sub>2</sub> absorption rate was obtained for 1 (Table 2). These results confirm that even in high concentrations of the amine medium the absorbents 1-3 exhibit improved CO<sub>2</sub> absorption.

Based on the stopped-flow kinetic and DRC experiments we conclude that the addition of the synthesized absorbents **1-3** was enhanced the absorption rate of  $CO_2$  by the tertiary amine solutions. More importantly, the heats of absorption for **1-3** are lower than that of the absorbent **4**, which indicates that by adding the appropriate absorbent we could increase the  $CO_2$  absorption rate in tertiary amine medium. Besides, the catalysts **1-3** are more promising because of their high absorption efficiency, whereas the CA model complexes were less tolerant in basic medium for the generated anion from  $CO_2$  and amine.<sup>24</sup>

### Conclusions

In conclusion, we have demonstrated that the addition of the synthesized catalysts increases the absorption of  $CO_2$  by aqueous tertiary amine solutions. The rate constants calculated from stopped-flow kinetics experiments for the catalysts exhibit that the addition of the amine nitrate salts increases the rate of hydration of  $CO_2$ . The DRC experiment results show that the addition of the catalysts to a tertiary amine medium increases the  $CO_2$  mol/mol absorption and also increases the rate of absorption of  $CO_2$ . Overall, our study demonstrates that the incorporation of substituted tertiary amine salts enhances  $CO_2$  absorption and lowers the heat of reaction. Further, these results suggest the tertiary amine based catalysts has an important role in postcombustion capture technology.

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**‡** Experimental procedure, analytical data and crystallographic information of **2** are available in supporting information.

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