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The Chemical Fixation of Carbon Dioxide by Tetramethylguanidine and Triazabicyclo dec-5-ene Bases

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ABSTRACT

The fixation of CO_2 using guanidine bases; 1,1,3,3-tetramethylguanidine (TMG) and 5,7-triazabicyclo[4.4.0] dec-5-ene (TBD) has been investigated. Solution Nuclear magnetic resonance (NMR) studies were carried out for the reaction between CO_2 and the guanidine bases at normal temperature and pressure, i.e Ca. 30 °C and 1 atm. Analysis of results obtained using 1- dimentional ^{13}C NMR and 2-dimentional ^{15}N (HMBC) both indicated successful reaction between CO_2 and TBD and also CO_2 with TMG. Both products were observed to be stable at room temperature and pressure. Based on the results obtained, it was concluded that, the CO_2 can be fixed with TMG and TBD at normal conditions of temperature and pressure. Finally it was also proposed that, the method used could be useful for the uptake and release of atmospheric CO_2.

Keywords: Carbon dioxide, Chemical fixation, Heteronuclear Multiple-Bond Correlation Tetramethylguanidine, Triazabicyclo decene

INTRODUCTION

Many organic super bases are known (Ishikawa, 2009), such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,1,3,3-tetramethylguanidine (TMG) etc. Among these, TBD and TMG are the most common super bases widely used in organic synthesis. This is because of their high pKa value (Ishikawa, 2009). Examples of TBD and TMG catalysed reactions include, nitroaldol (Henry) reactions (Simoni, *et al*., 2000), Michael-addition reactions (Kalita and Kumar, 2011; Ye, *et al*., 2005; Ma, and Cheng, 2009), Aldol and Knoevenagel condensation reactions (Takahashi, *et al*., 2006).

Generally, amines are well known to form carbamate salts on reaction with carbon dioxide, and this forms the basis of many processes for the capture of carbon dioxide (North and Pasquale, 2009) The carbamate salts can be considered as activated forms of carbon dioxide. The formation of a carbamic (zwitterionic) complex formed by the reaction of CO_2 with 1,8-diazabicycloundecene (DBU) was investigated by Perez *et al*., (2002). The catalyst was efficient for the activation of CO_2 due to the presence of π electrons on the imine nitrogen, which attack the electrophilic carbon centre of the CO_2.

CO_2 is an inexpensive and environmentally benign reagent, which has found several applications in the industry. The development of suitable methods at laboratory scale in the preparation of interesting CO_2 containing compounds such as organic carbonates is an important alternative to avoid the use of toxic reagents such as phosgene and its derivatives. Cyclic carbonates are useful as polar aprotic solvents, and as precursors for polycarbonate materials.

Guanidines have been used as heterogeneous catalysts in several base catalyzed organic reactions, such as Michael addition (Ye, *et al*., 2005; Ma and Cheng, 1999), transesterification of vegetable oils (Serchelli, *et al*., 1999), aldol and knoevenagel condensation reactions (Takahashi, *et al*., 2006) esterification of glycerol (Serchelli, *et al*., 1997) and in cyclo addition of carbon dioxide to cyclic carbonate (Jerome, *et al*., 2004; Adam and Batagarawa, 2013; Appaturi and Adam, 2013; Babarini, *et al*., 2003).

Several homogeneous guanidines have been reported as catalysts in the conversion of carbon dioxide to cyclic carbonates. For instance, Heldebrant *et al.* (2005), studied the effect of water on the reaction of DBU with CO_2. The white solid product formed was suspected to be due to the presence of $(DBUH^+)$ (HCO_3^-) complex. However, no visible reaction was observed in the absence of water.

Pereira *et al.* (2008) also studied the chemical fixation of CO_2 with guanidines. They speculated that, both carbamic and bicarbonate products were formed during the reaction. Characterisation of the products indicated that, the CO_2 fixation is a kinetically reversible process.

The solubility of several gases including CO_2 in tetramethyl guanidinium lactate was studied by Yuan *et al.* (2006). Among the gases studied, CO_2 was the most soluble.

Similarly, the detailed mechanism of Michael reactions catalysed by bicyclic guanidines have been discussed by Fu and Tan (2011). The process described several modes of hydrogen bonding which occur between the guanidine conjugate acid and the reaction substrates.

The functional groups containing nitrogen atoms such as $–NH_2$, -NH- and tertiary amines have been utilised as effective catalysts for the uptake and release of CO_2 (Zhang *et al.,* 2011).

The aim of the present investigation was to carry out a simple reaction between CO_2 and 2-superbases (Guanidines) at ordinary condition of temperature and pressure and further study the products obtained using 1- and 2- dimensional Nuclear Magnetic Resonance technique.

MATERIALS AND METHODS

The CO_2-fixation experiment was carried out using analaR TMG (99 % BDH) and TBD (98 % BDH) without further purification supplied by BDH chemicals. The reaction of CO_2 with TBD was carried out in the presence of acetonitrile as a solvent, and in the absence of any organic solvent for TMG. Both experiments were conducted based on literature report (Pereira, *et al.,* 2008).

Reaction of CO_2 with Tetramethylguanidine

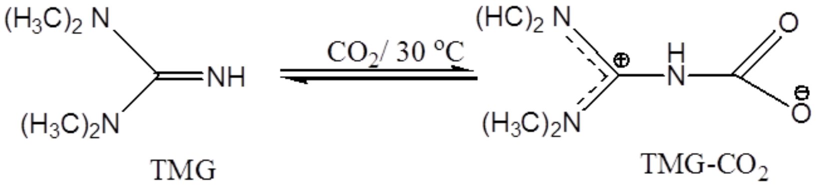
The reaction of CO_2 with Tetramethylguanidine was easily carried by transferring 5 mL (40 mmol) of tetramethylguanidine solution in to two-neck round bottom flask, and then CO_2 from a balloon was bubbled at room temperature (Ca. 30 °C) while stirring at 250 rpm for 2 h. A white solid precipitate was formed. The product was transferred in to a test tube, sealed and kept under refrigeration for further analysis.

Reaction of CO_2 with Triazabicyclodecene

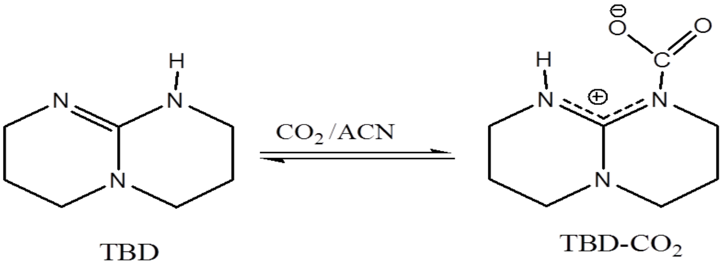
The reaction of CO_2 with TBD was carried out in the presence of fresh solution of acetonitrile. 5,7-triazabicyclo[4.4.0] dec-5-ene, 0.1 g (0.72 mmol) was placed in a two-neck round bottom flask and by 5 mL acetonitrile solution was added slowly to form a homogeneous mixture. CO_2 was bubbled from a balloon at room temperature (Ca. 30 °C) into the mixture while stirring at 250 rpm for 2 h. A white solid product was also formed. It was carefully transferred in to a test tube, sealed and kept under refrigeration for further analysis.

RESULTS AND DISCUSSION

Schemes 1 & 2 show the proposed equations for the reaction of CO_2 with the homogeneous bases, namely: 1,1,3,3-tetramethylguanidine and 1,5,7-triazabicyclo[4.4.0]dec-5-ene.



Scheme 1: Equation showing TMG activated with CO_2 as activating agent under ambient conditions.



Scheme 2: Equation showing TBD activated with CO_2 as activating agent in acetonitrile solvent.

Figure 1 shows the ^{13}C NMR for the TMG. Two characteristic chemical shifts could be seen. The first one at 40 ppm, correspond to the four equivalent methylene carbons of the $N(CH_3)_4$ group, while the second chemical shift at 169 ppm, corresponds to the imine carbon (C=N) present in the guanidine structure.

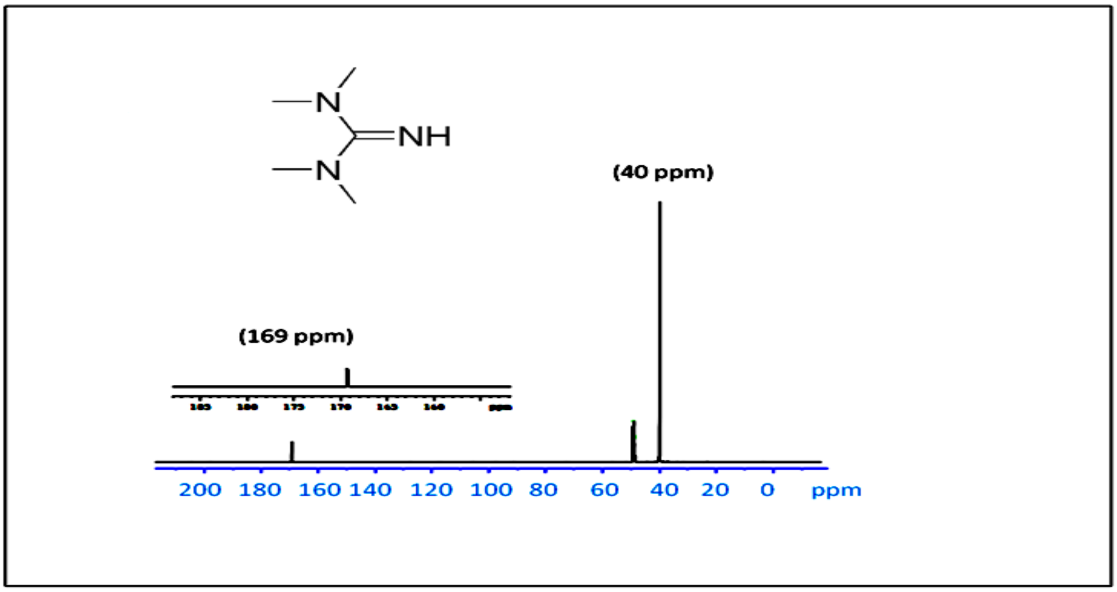


Fig. 1: The ^{13}C NMR spectra of tetramethylguanidine.

Fig. 2 shows the 13C NMR spectrum of TDB activated with CO_2 in acetonitrile solvent. it is interesting to note that, the chemical shift of the imine carbon (C=N) has moved from 169 ppm to 165 ppm, while the additional peak at 160 ppm could be ascribed to the presence of the carbonyl carbon from the activated CO_2. The chemical shift at 49 ppm could be due to the acetonitrile solvent.

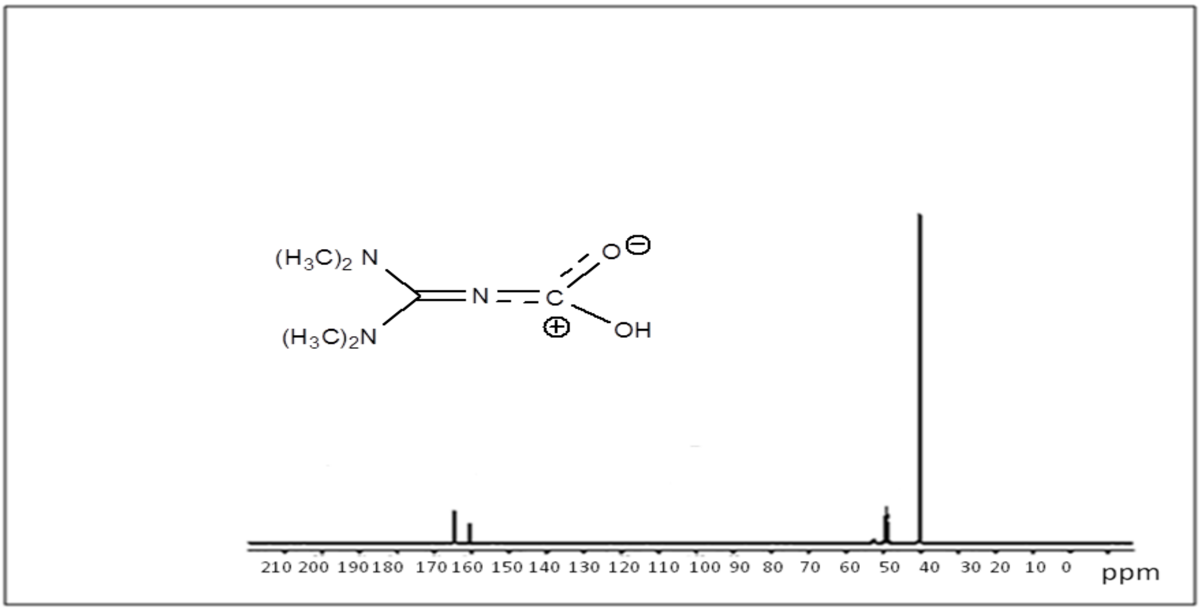


Fig. 2: The ^{13}C MAS NMR spectra of TMG-CO_2 product at 30 °C.

Figure 3 shows a series of ^{13}C NMR chemical shifts for the TMG-CO_2 adduct at various low temperature. The spectral analysis at 0, -15, -25, and -30 °C did not show any significant change in their chemical shifts. This indicated the relative stability of the TMG-CO_2 over a range of low temperature conditions. However, comparing the relative intensity of the peaks at 160 and 165 ppm, it can be observed that, as the temperature increases from -35 °C to 0 °C, the intensity of the peak at 160 ppm decreases, this could be due to release of adsorbed CO_2 from the TMG.

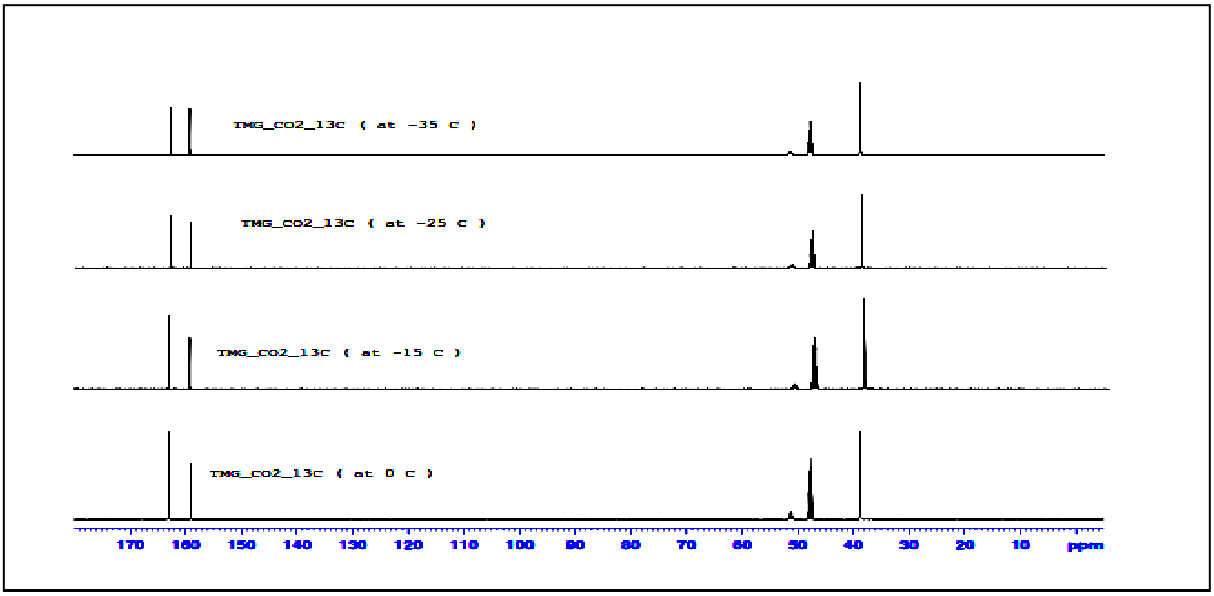


Fig. 3: The ^{13}C NMR spectra of TMG-CO_2 over a range of low temperature conditions.

Fig. 4 shows the ^{13}C solution NMR spectra of TBD. In addition to the three non-equivalent CH_2 peaks at 20, 37 and 46 ppm, and the chloroform (solvent) peak at 77 ppm, the imine carbon peak also appeared at 151 ppm.

The chemical shifts of TBD-CO_2 adduct, is shown in Fig. 5. The three non-equivalent CH_2 peaks appeared at 19, 35 and 44 ppm. The additional peaks at 149 and 162 ppm could be ascribed to the presence of some charge separated specie and a carbonyl carbon which are thought to be among the reaction products respectively (Pereira, *et al.*, 2008) .

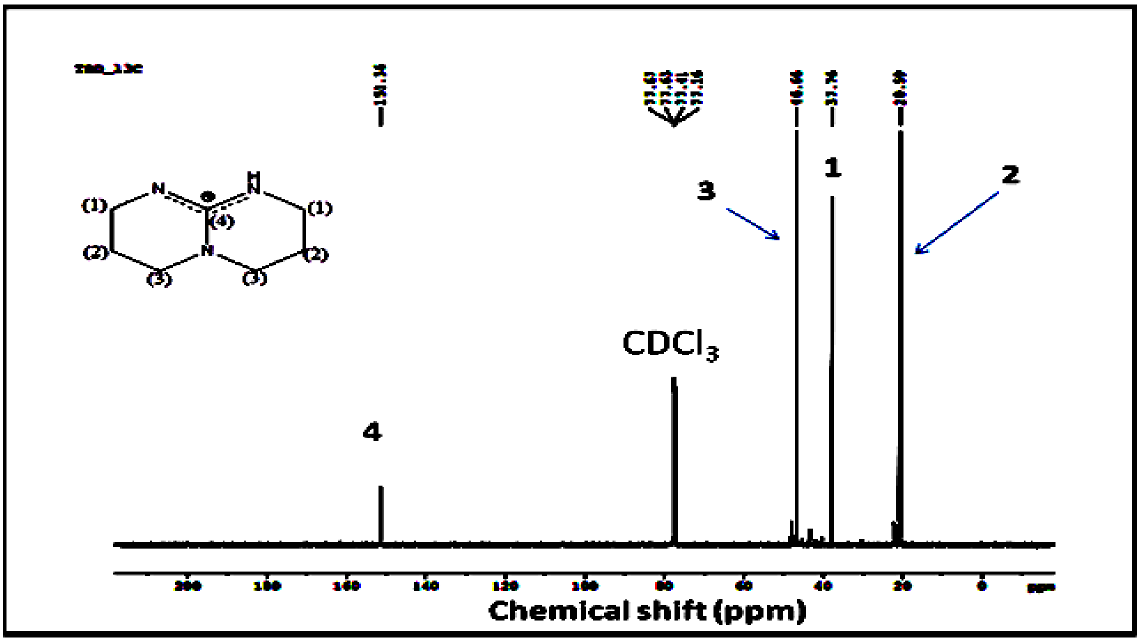


Fig 4: The ^{13}C NMR spectrum of TBD in $CDCl_3$ solvent.

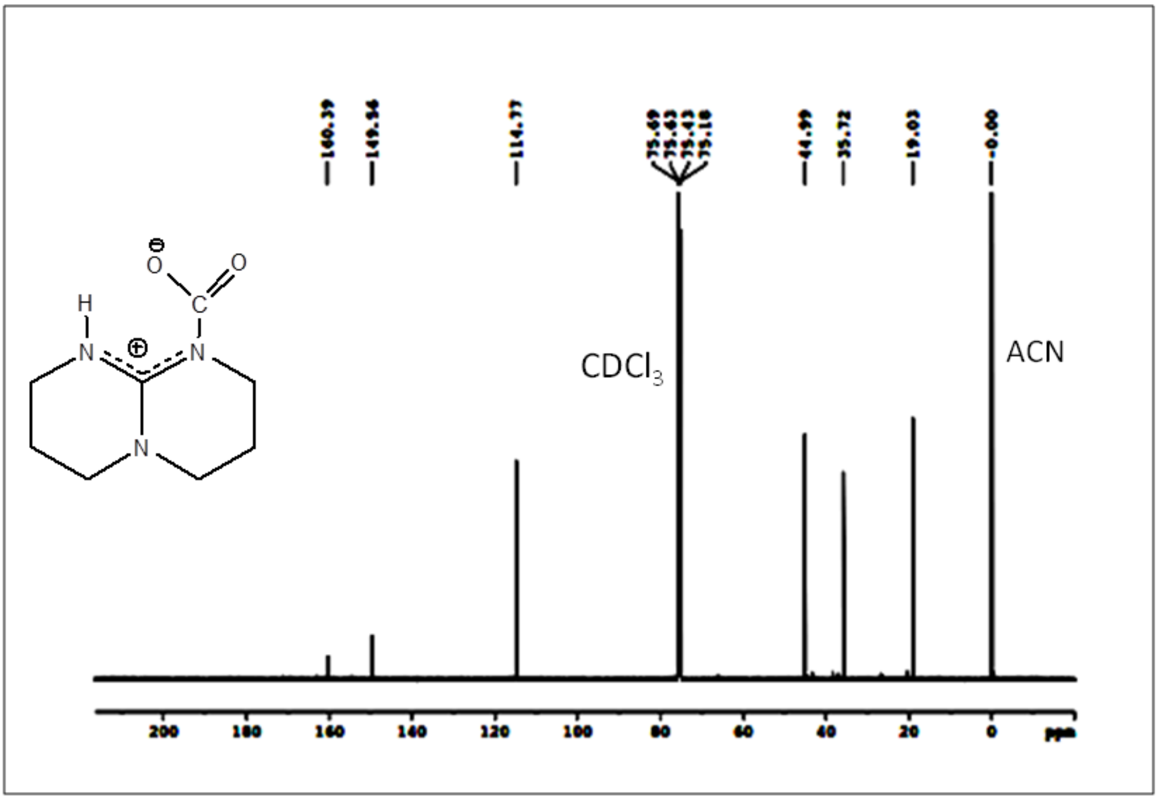


Fig. 5: The ^{13}C NMR for the TBD-CO_2 adduct in $CDCl_3$ solvent.

^{15}N Heteronuclear Multiple-Bond Correlation (HMBC) experiment

Due to inherent difficulties to obtain clear result for the ^{13}C NMR of the TBD-CO_2 adduct, ^{15}N(HMBC) experiment was also performed. HMBC is a 2-Dimentional (2D) experiment that identifies the correlation between the proton nuclei and other nuclei such as ^{13}C and ^{15}N. Because of the low relative abundance of Nitrogen in samples, it is often difficult or impossible to generate ^{15}N spectra. Fig. 6 shows the ^{15}N spectrum for the HMBC correlation experiment. Two peaks were observed at ca. 72 ppm (labelled as N_1) and 78 ppm (labelled as N_2). This indicated that, two out of the three nitrogen atoms present on the structure are equivalent, while the third one is different. This could be associated with resonance, which was partly responsible for the symmetry of the molecule. Similarly, the ^{1}H NMR spectra showed three characteristic peaks at 2.0 ppm (labelled as H_2), 3.3 ppm (labelled as H_3) and 3.4 ppm (labelled as H_1). It should be noted that, these protons are labelled according to their carbon atoms. Thus from the spectrum shown in Fig. 6.7, the following correlations can be made. The proton at the chemical shift of 2.0 ppm is a multiplet and showed intense correlation with both nitrogens (N_1 and N_2), these are labelled as H_2-N_1 and H_2-N_2 correlations. The proton line at about 3.3 ppm is a triplet and correlated with the nitrogen at 72 ppm (N_1), this proton is separated from the nitrogen by a single bond. This correlation is also labelled as H_3-N_1. The proton line at 3.4 ppm is also a triplet and shows correlation with the two nitrogens. The proton showed strong correlation with the nitrogen at 78 ppm, and this is labelled as H_1-N_2 correlation, and the same proton line at 3.4 ppm also showed three bond correlations with the nitrogen at 72 ppm, this is labelled as H_1-N_1. However, this correlation is clearly weaker, which suggested that, it occurs through the resonance nitrogen (N_1). From the foregoing discussion it can be speculated that, the compound consisted of resonance structure with the presence of carbamate ion from the CO_2 activation.

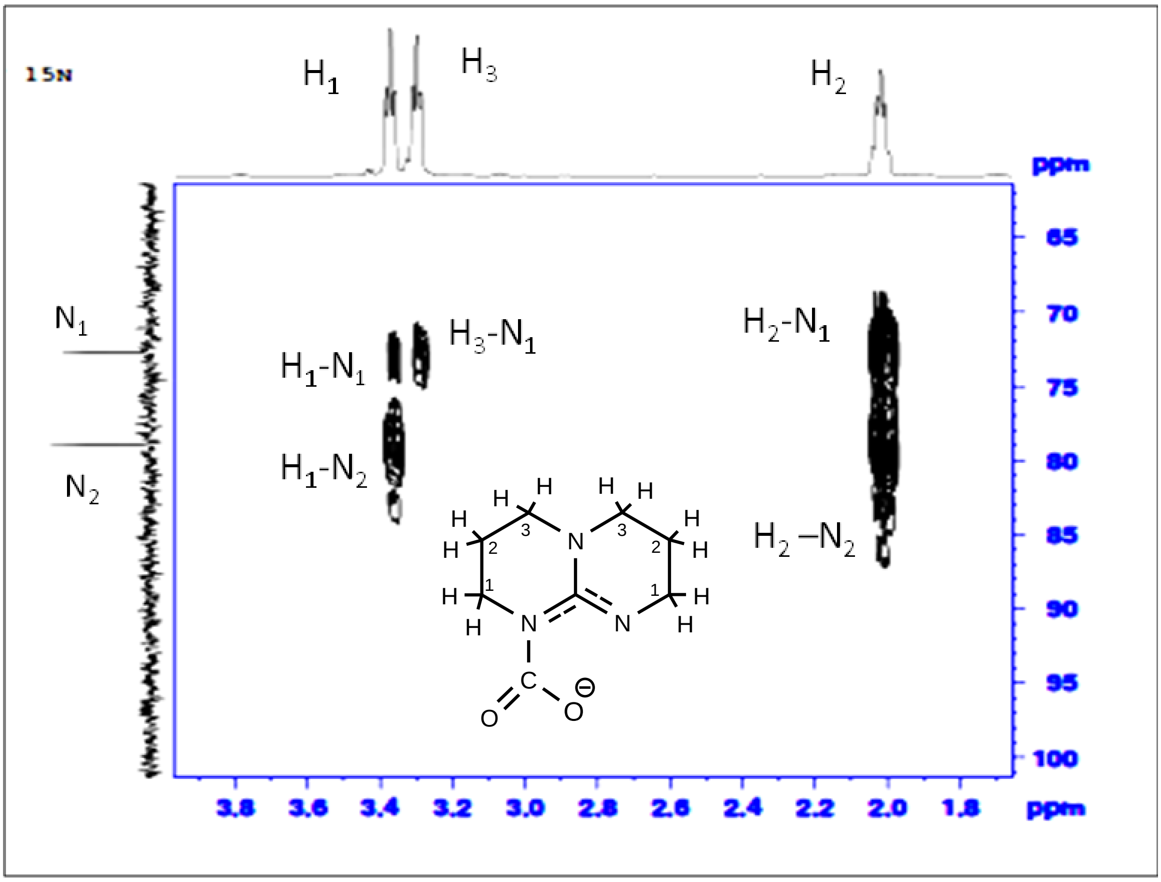


Fig. 6: The HMBC ^{15}N NMR spectra for TBD-CO_2 adduct

CONCLUSION

The reaction of CO_2 with homogeneous bases is essential for CO_2 to further participate in chemical processes (Srivastava, 2005). In this study, both TMG and TBD proved to be important compounds for the capture and activation of CO_2. The activation was thought to be through nucleophilic interaction between the conjugate acid of the guanidine base and the electrophilic centre from the carbon dioxide. Characterisation of the reaction products indicated positive interaction between the CO_2 and the guanidines. Based on the results it can be concluded that CO_2 can be activated by the nitrogen-base compounds such as guanidines. And for the first time, ^{15}N NMR HMBC experiment was used to confirm the structure of the adducts.

REFERENCES

Adam, F., & Batagarawa, M. S. (2013). Tetramethylguanidine–silica nanoparticles as an efficient and reusable catalyst for the synthesis of cyclic propylene carbonate from carbon dioxide and propylene oxide. *Applied Catalysis A: General*, *454*, 164-171.

Appaturi, J. N., & Adam, F. (2013). A facile and efficient synthesis of styrene carbonate via cycloaddition of CO 2 to styrene oxide over ordered mesoporous MCM-41-Imi/Br catalyst. *Applied Catalysis B: Environmental*, *136*, 150-159.

Barbarini, A., Maggi, R., Mazzacani, A., Mori, G., Sartori, G., & Sartorio, R. (2003). Cycloaddition of CO_2 to epoxides over both homogeneous and silica-supported guanidine catalysts. *Tetrahedron letters*, *44*(14), 2931-2934.

Fu, X., & Tan, C. H. (2011). Mechanistic considerations of guanidine-catalyzed reactions. *Chemical Communications*, *47*(29), 8210-8222.

Heldebrant, D. J., Jessop, P. G., Thomas, C. A., Eckert, C. A., & Liotta, C. L. (2005). The reaction of 1, 8-diazabicyclo [5.4. 0] undec-7-ene (DBU) with carbon dioxide. *The Journal of organic chemistry*, *70*(13), 5335-5338.

Ishikawa, T. (2009). *Super bases for organic synthesis: guanidines, amidines and phosphazenes and related organocatalysts* (pp. 251-271). New York: wiley.

Jérôme, F., Kharchafi, G., Adam, I., & Barrault, J. (2004). “One pot” and selective synthesis of monoglycerides over homogeneous and heterogeneous guanidine catalysts. *Green Chemistry*, *6*(2), 72-74

Kalita, P., & Kumar, R. (2011). Immobilization of 1, 5, 7-triazabicyclo [4.4. 0] dec-5-ene over mesoporous materials: an efficient catalyst for Michael-addition reactions under solvent-free condition. *Applied Catalysis A: General*, *397*(1), 250-258.

Ma, D., & Cheng, K. (1999). Enantioselective synthesis of functionalized α-amino acids via a chiral guanidine catalyzed Michael addition reaction. *Tetrahedron: Asymmetry*, *10*(4), 713-719.

North, M., & Pasquale, R. (2009). Mechanism of cyclic carbonate synthesis from epoxides and CO2. *Angewandte Chemie*, *121*(16), 2990-2992

Pereira, F. S., Ribeiro deAzevedo, E., da Silva, E. F., Bonagamba, T. J., da Silva Agostíni, D. L., Magalhaes, A., ... & Gonzalez, E. R. P. (2008). Study of the carbon dioxide chemical fixation—activation by guanidines. *Tetrahedron*, *64*(43), 10097-10106.

Pérez, E. R., da Silva, M. O., Costa, V. C., Rodrigues-Filho, U. P., & Franco, D. W. (2002). Efficient and clean synthesis of N-alkyl carbamates by transcarboxylation and O-alkylation coupled reactions using a DBU–CO_2 zwitterionic carbamic complex in aprotic polar media. *Tetrahedron letters*, *43*(22), 4091-4093.

Sercheli, R., Vargas, R. M., & Schuchardt, U. (1999). Alkylguanidine-catalyzed heterogeneous transesterification of soybean oil. *Journal of the American Oil Chemists’ Society*, *76*(10), 1207-1210.

Sercheli, R., Ferreira, A. L., Guerreiro, M. C., Vargas, R. M., Sheldon, R. A., & Schuchardt, U. (1997). Encapsulation of N, N′, N ″-tricyclohexylguanidine in hydrophobic zeolite Y: Synthesis and catalytic activity. *Tetrahedron letters*, *38*(8), 1325-1328.

Simoni, D., Rossi, M., Rondanin, R., Mazzali, A., Baruchello, R., Malagutti, C., ... & Invidiata, F. P. (2000). Strong bicyclic guanidine base-promoted Wittig and Horner-Wadsworth-Emmons reactions. *Organic letters*, *2*(24), 3765-3768.

Srivastava, R., Srinivas, D., & Ratnasamy, P. (2005). CO 2 activation and synthesis of cyclic carbonates and alkyl/aryl carbamates over adenine-modified Ti-SBA-15 solid catalysts. *Journal of Catalysis*, *233*(1), 1-15

Takahashi, T., Watahiki, T., Kitazume, S., Yasuda, H., & Sakakura, T. (2006). Synergistic hybrid catalyst for cyclic carbonate synthesis: Remarkable acceleration caused by immobilization of homogeneous catalyst on silica. *Chemical communications*, (15), 1664-1666

Ye, W., Xu, J., Tan, C. T., & Tan, C. H. (2005). 1, 5, 7-Triazabicyclo [4.4. 0] dec-5-ene (TBD) catalyzed Michael reactions. *Tetrahedron letters*, *46*(40), 6875-6878.

Yuan, X., Zhang, S., Chen, Y., Lu, X., Dai, W., & Mori, R. (2006). Solubilities of gases in 1, 1, 3, 3-tetramethylguanidium lactate at elevated pressures. *Journal of Chemical & Engineering Data*, *51*(2), 645-647.

F. Xiao and T. Choon-Hung, *Chem. commun., 47 (2011) 8210-8222.*

Zhang, J., Sun, J., Zhang, X., Zhao, Y., & Zhang, S. (2011). The recent development of CO_2 fixation and conversion by ionic liquid. *Greenhouse Gases: Science and Technology*, *1*(2), 142-159.