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COMMUNICATION

Observation of Guanidine-Carbon Dioxide Complexation in Solution and Its Role in Reaction of Carbon Dioxide and Propargylamines

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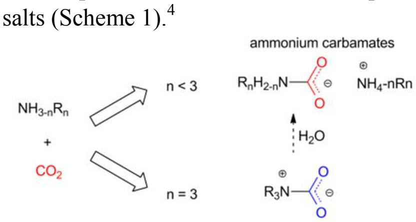
The first observation of guanidine-CO_2 'activation' complexes in solution using ATR-FTIR is reported. While cyclic guanidines TBD and MTBD form stable and detectable complexes with CO_2, other guanidines and tertiary amines do not. Correlation with catalytic activity of these amines/guanidines in reaction between CO_2 and propargylamines indicated that the basicity of the catalyst, rather than its ability to form complexes with CO_2, is the origin of catalytic activity.

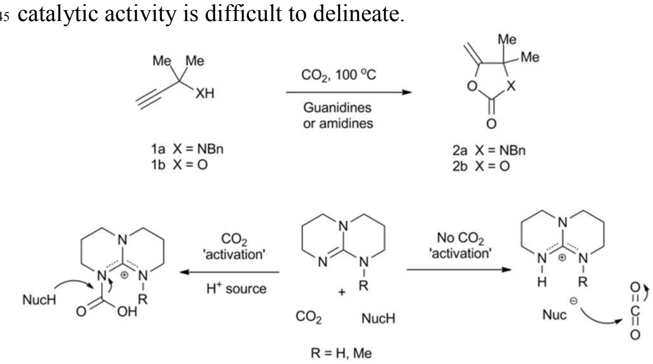
The thermodynamic stability of carbon dioxide (CO_2),[1] is one of the main obstacles in developing practical processes to convert man made CO_2 into useful chemicals. However, facile reactions between organic bases and CO_2 to give carbonate and carbamate salts are well-known and have long been employed in CO_2 scrubbing,[2] and, more recently, switchable polarity solvents.[3] Although these are equilibria, they do not require high energy reactants to effect reactions with CO_2. When trisubstituted amines are employed, the products are zwitterionic complexes instead of carbamate salts (Scheme 1).[4]



Scheme 1 Reactions between CO_2 and N-bases

Villiers and Cantat isolated and characterized the first complexation product of this type between 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and CO_2 in the solid state,[5] and suggested that this could allow activation of CO_2 for catalytic conversion into high value chemicals.[4, 6, 7] Similar complexes have also been proposed by North and co-workers to explain improved catalytic activity in their cyclic carbonate production process in the presence of tributylamine.[8]

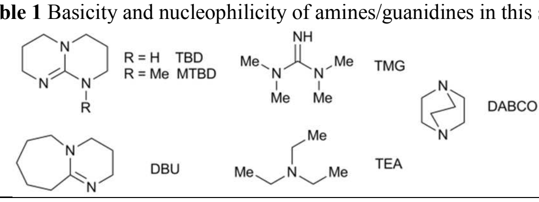
Guanidines, such as 7-methyl-1,5,7-triaza-bicyclo[4.4.0]dec-5-ene (MTBD), have been reported to catalyse reactions between CO_2 and propargylamines (Scheme 2).[9] The proposed mechanism involves deprotonation of the substrate by a superbase, i.e. the guanidine, rather than formation of a guanidine-CO_2 complex. Importantly, guanidines and amidines are both superbases and strong nucleophiles,[10] and the mechanisms outlined in Scheme 2 are equally probable. In addition, *ab initio*, DFT and MD calculations have shown that both nucleophilicity and steric factors modulate complexation between amines and alkanolamines and CO_2.[11] Consequently, the origin of the catalytic activity is difficult to delineate.



Scheme 2 Reaction between CO_2 and propargylamines and possible mechanisms with/without CO_2 'activation'

Understanding 'CO_2 activation', particularly in catalytic context, is fundamental to sustainable CO_2 capture and utilisation processes.[12] Solid state NMR data on DBU.CO_2 and TBD.CO_2 complexes has been previously reported by Franco,[4, 13] Villiers and Cantat.[5] However, attempts to detect and characterise these complexes in solution and to evaluate their relevance to possible catalytic processes using ^{13}C NMR have been unsuccessful.[7d] While equilibrium constants of some amine-CO_2 complexations in pentane have been measured by Johnston et. al.,[14] no such data, even qualitative, is currently available with guanidines. In this communication, we report the first ATR-FTIR study of guanidine-CO_2 complexation in solution and its mechanistic implications in reactions between propargylamines and CO_2.

Table 1 Basicity and nucleophilicity of amines/guanidines in this study



No.	Amine/ Guanidine	pK_a (MeCN)[a]	pK_a (THF)[a]	*N (nucleophilicity in MeCN)*
1	TBD	26.0[10]	21.0[15]	16.2[b],[16]
2	MTBD	25.4[10]	17.9[15]	14.4[b][16]
3	DBU	23.9[10]	16.8[15]	15.3[17]
4	TMG	23.3[10]	15.3[15a]	13.6[b],[16]
5	TEA	18.5[18]	12.5[19]	17.1[20]
6	DABCO	18.3[21]		18.8[22]

[a] pK_a of the conjugated acid; [b] Data measured in dichloromethane.

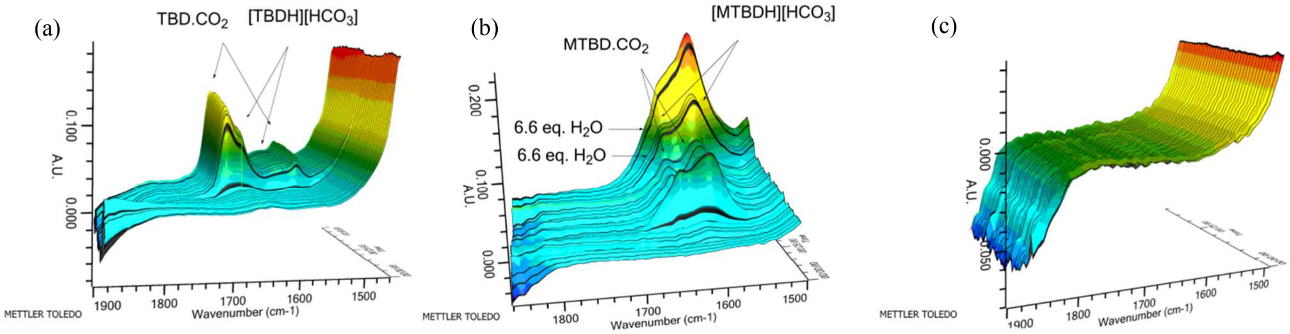


Fig. 1 Time evolution of ATR-FTIR spectra of reaction between CO_2 and THF solution of (a) TBD (7 mM); (b) MTBD (21 mM), followed by addition of water (2 x 6.6 eq.) and (c) TMG (8 mM), TEA (7 mM) or DABCO (9 mM). Data was collected every 30 seconds, at 8 cm^{-1} resolution.

'Activation' of CO_2 with guanidines and amines

ATR-FTIR has been proven as an useful tool in monitoring chemical and physical processes involving CO_2.[23] In the context of monitoring amine/guanidine and CO_2 complexation in solution, it is the ideal technique, exploiting the C=O stretching frequencies of CO_2 (2300 cm^{-1}) and of the zwitterionic complexes (1600-1700 cm^{-1}).

Solutions of TBD, MTBD, TMG, DABCO and TEA (Table 1) in anhydrous THF were treated with CO_2 at 1 atm/25 °C and the reaction progress was monitored by measuring the IR spectra over time. These organic bases were chosen to include active catalysts (TBD, MTBD, TMG) for the reaction in Scheme 2,[9b] and strong nucleophiles which are weaker bases (DABCO, TEA). THF was chosen as solvent due to the poor solubility of the zwitterionic complexes in MeCN, the preferred solvent for catalytic reactions. In all cases, introduction of CO_2 to the system resulted in rapid saturation of CO_2 in solution (within 60 seconds), as observed by the growth of its finger-print frequencies at ~2300 cm^{-1} (stretching) and 660 cm^{-1} (bending).[24]

Formation of two new sets of peaks in the carbonyl region was observed with TBD in THF (Fig. 1a). These are assigned to TBD.CO_2 complex (1683 cm^{-1} (C=O) and 1564 cm^{-1} (C=N)) and [TBDH][HCO_3] (1595 cm^{-1} (C=O) and 1657 cm^{-1} (C=N)). The presence of these two species is consistent with observations of Pérez and Jessop by solid state NMR, given the not-strictly-anhydrous operational conditions of our ATR-FTIR equipment.[7d, 25] The assigned frequencies are also in agreement with solid data, i.e. 1712 and 1605 cm^{-1} for TBD.CO_2 and 1660 and 1600 cm^{-1} for [TBDH][HCO_3].[5] The difference in vibrational frequencies of TBD.CO_2 in the solid state and in THF solution could be attributed to solvation effects, which are significant with zwitterionic structures.[26]

Treatment of MTBD with CO_2 in THF in a similar fashion also resulted in rapid formation of two broad peaks in the carbonyl region (Figure 1b). A small decrease in the intensity of these peaks was observed after 30 seconds, accompanied by formation of a white precipitate. These were attributed to the formation of a saturated solution of MTBD.CO_2, albeit with a small amount of [MTBDH][HCO_3] due to the presence of moisture as with TBD. Portion-wise addition of water to the solution led to complete hydrolysis of the complex MTBD.CO_2 to [MTBDH][HCO_3]. Consequently the frequencies were assigned to MTBD.CO_2 (1648 cm^{-1} (C=O) and 1602 cm^{-1} (C=N)) and [MTBDH][HCO_3] (1598 cm^{-1} (C=O) and 1620 cm^{-1}, 1603 cm^{-1} (C=N)). Two stretching frequencies were observed for $[MTBDH]^+$ due to its lack of symmetry and the assignments were confirmed by comparing with a spectrum of [MTBDH]Cl. The different electronic properties of the guanidines are also reflected in the lower C=O stretching frequency in MTBD.CO_2 compared to that of TBD.CO_2. Bubbling nitrogen through the solution led to the disappearance of the peaks in the carbonyl region. This is the first successful observation of the formation of MTBD.CO_2 complex in solution.

Table 2 Vibrational frequencies of guanidine-CO_2 complexes

Guanidine	Frequency (cm^{-1})	Assignment
TBD	1683	C=O
	1564	C=N
MTBD	1648	C=O
	1602	C=N

Surprisingly, no new peak in the carbonyl region or precipitate was observed when solutions of TMG, TEA and DABCO were treated with CO_2 (Figure 1c). This indicates no detectable complexation between these amines and TMG with CO_2 in THF or acetonitrile. While a low value equilibrium constant (K = 0.046) has been reported for TEA.CO_2,[14] TMG is much more basic and DABCO is much more nucleophilic than TEA (Table 1). Thus, factors other than these are important in this type of complexes. These experimental results are consistently reproduced by our *ab initio* studies. Optimisation of the amine/guanidine-CO_2 complexes in MeCN using the MP2/6-311G(d,p) method was investigated. Only the structures of TBD.CO_2 and MTBD.CO_2 could be successfully optimised to a minimum without breaking the N–CO_2 bond (≤ 1.8 Å). The optimised structures of TBD.CO_2 and MTBD.CO_2 also exhibit significant charge delocalisation on the guanidine, in agreement with computational work by Villiers,[5] which could explain their stability.

Evaluation of catalytic activity

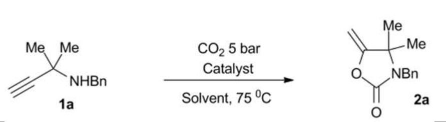
As TMG has been shown to catalyse the addition of CO_2 to propargyl amines,[9] the lack of a TMG.CO_2 complex raised questions about the relevance of these complexes to the catalytic activity of guanidines. Thus, we re-examined the effects of catalyst and solvent in the reaction between propargylamines and CO_2 as reported by Costa (Scheme 2, X = NBn).[9b, 9c] This reaction was reported to work well with TBD, MTBD, TMG and DBU as catalysts at 100-110 ºC, 10 bar CO_2 in acetonitrile, supercritical CO_2 or under neat conditions. Importantly, the reaction also works in water using a bulky guanidine as catalyst and sodium bicarbonate as the source of CO_2. In this study, five solvents of widely different polarity and proton-donating capability (DMSO, MeCN, EtOH, THF and toluene) were examined. Lower pressure of CO_2 (5 bar) and temperature (50–75 ºC) were deliberately chosen to lower the efficiency of the catalysts for better comparison.

Preliminary experiments with the five solvents at 5 bar CO_2, 50 ºC gave little to no catalytic activity for DABCO and DMAP, or for reactions using THF and toluene as solvent, despite the strong complexation between CO_2 and MTBD/TBD in THF described above (supporting information, Table S1). The relevance of guanidine-CO_2 complexes in this type of catalytic reactions is consequently questioned. Subsequent reactions were performed at 75 ºC and 5 bar of high purity CO_2. The solvent and catalyst scopes were narrowed to MeCN/DMSO/EtOH and MTBD/TMG (Table 3). Despite its activity, DBU was not further considered in this study due to our focus on comparison to CO_2 complexation and poor chemical compatibility between DBU and our equipment.

While MTBD showed excellent catalytic activity in MeCN at 10 mol% as reported by Costa et. al.,[9b] only 8% conversion was observed at 1 mol% catalyst loading (Table 3, entries 1 and 5). TMG is a poorer catalyst in MeCN and EtOH (Table S1) but showed equal catalytic performance to MTBD/MeCN in DMSO (Table 3, entries 3 and 7). The lack of evidence for TMG.CO_2 complex in THF and the observed catalytic activity, albeit lower than in DMSO, in a protic solvent such as EtOH suggested that guanidine-CO_2 complexes may not be crucial for the reaction. As demonstrated with ATR-FTIR, addition of EtOH to a solution of MTBD.CO_2 and [MTBDH][HCO_3] in THF led to complete disappearance of IR peaks belonging to MTBD.CO_2 (see supporting information).

The observed catalytic activity can be explained with a basicity-controlled mechanism. TMG is a weaker base than TBD and MTBD in acetonitrile. However, DMSO and EtOH are strongly polar solvents which can effectively stabilize $TMGH^+$. The use of these solvents therefore enables TMG to be a more active catalyst. In order to verify this hypothesis on the origin of catalytic activity in these reactions, catalytic reactions using MTBD/MeCN, TMG/EtOH and TMG/DMSO combinations were performed again in the presence of a small amount of water (0.1 mL of H_2O in 3.0 mL of organic solvent, Table 3, entries 2, 4, 6 and 8).

Table 3 Conversion (%) of **1a** to **2a** using MTBD or TMG as catalyst[a,b]



No.	Catalyst	Loading (mol%)	Solvent		
			MeCN	EtOH	DMSO
1	MTBD	10	100	29	54
2[c]	MTBD	10	99		
3	TMG	10	19	40	100
4[c]	TMG	10		39	100
5	MTBD	1	8		
6[c]	MTBD	1	8		
7	TMG	1		7	6
8[c]	TMG	1		8	61

[a] Reaction were performed using 0.866 mmol of **1a** and catalyst in 3.0 mL of the specified solvent under 5 bar of CO_2 at 75 °C. [b] Conversion was determined using ^{1}H NMR of the crude product.[c] Reaction performed in the presence of 0.1 mL H_2O.

In all cases, no loss of catalytic activity was observed compared to the corresponding reaction under anhydrous conditions, further ruling out guanidine-CO_2 complexes as intermediates. Interestingly, the addition of water resulted in a 10 times increase in product yield using TMG/DMSO conditions at 1 mol% catalyst loading (Table 3, entry 8). This novel catalyst/solvent combination gave a far superior catalytic performance compared to the optimised MTBD/MeCN combination in the literature at 5 bar CO_2, 75 ºC.

Conclusions

The first observation of cyclic guanidine-CO_2 complexes in solution by ATR-FTIR is reported, along with the lack of evidence for observable complexes with TMG and trisubstituted amines. Correlation between these observations and the catalytic activity of these nitrogen bases in reactions between propargylamines and CO_2 did not support activation of CO_2 via this mode of complexation. Instead, the basicity of the catalyst has been shown to be important to the catalytic activity. Consequently, polar solvents (e.g. DMSO), which can stabilize guanidinium cation, are beneficial to the reaction. Similar type of reactivity, i.e. via generation of strong nucleophile rather than direct activation of CO_2, has also been proposed by Leitner and Hölscher in reaction of rhodium-alkyl complexes and CO_2.[27] Finally, a novel catalyst/solvent combination (TMG/DMSO/H_2O) with superior catalytic activity at low catalyst loading has been discovered. This may lead to much more sustainable process from propargylamines to cyclic carbamates using a commercially available and much less expensive catalyst.

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Notes and references

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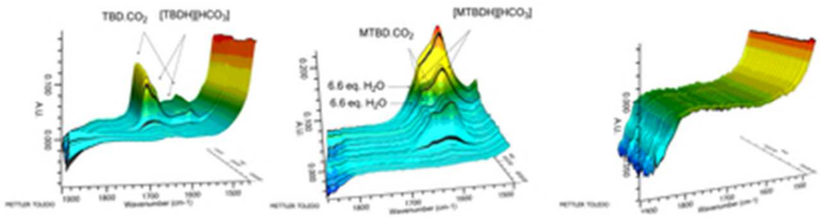

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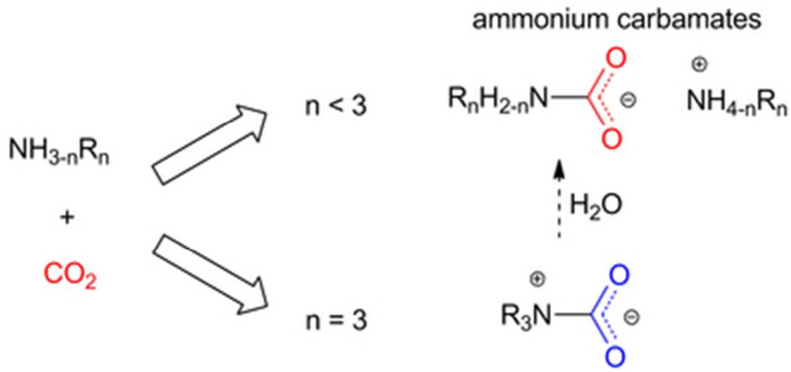

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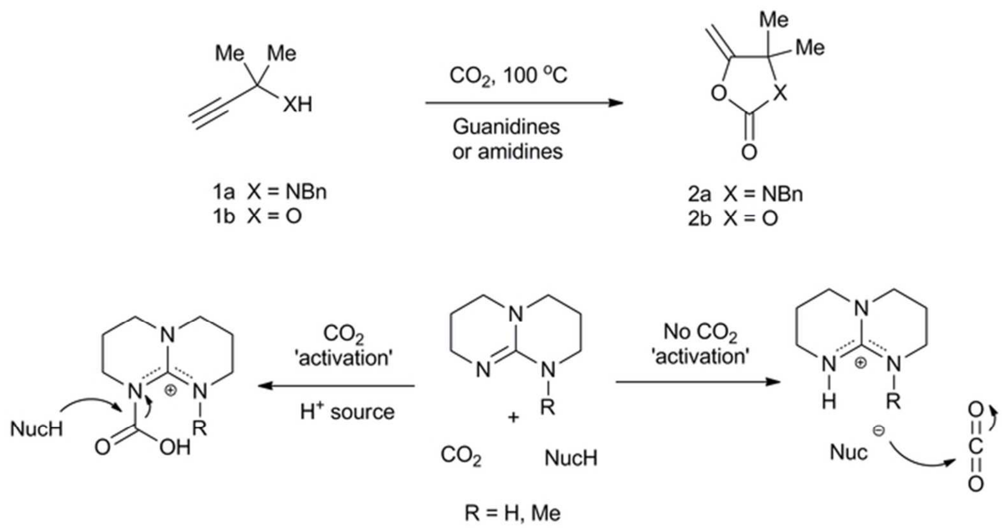

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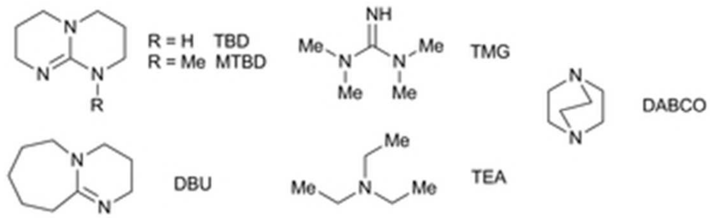

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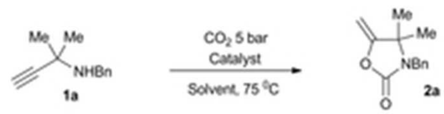

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