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The Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) with Carbon Dioxide

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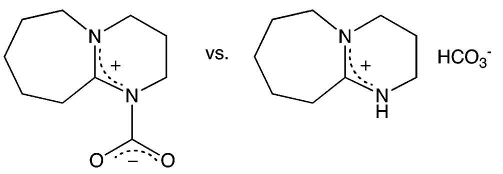
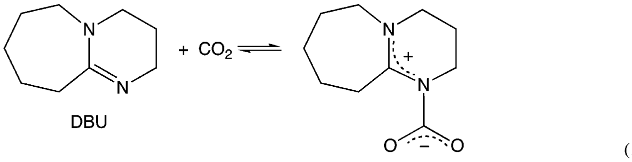


Amidines have been reported to react with CO_2 to form a stable and isolable zwitterionic adduct but previous studies were performed in the presence of at least some water. However, spectroscopy of the reaction between DBU and CO_2 detects the rapid formation of the bicarbonate salt of DBU when wet DBU is exposed to CO_2 and does not indicate that an isolable zwitterionic adduct between DBU and CO_2 forms either in the presence or the absence of water.

Carbon dioxide has the potential to become an important feedstock and reagent for organic chemistry because of the large amounts of CO_2 that are to be collected from emissions of power plants. However, much research is needed to increase the range of syntheses that can be efficiently performed with CO_2. While much attention has been paid to the development of metal-containing catalysts, there have been many examples of reactions of CO_2 that are promoted by bases. Among the many organic bases known to have some promoting ability, the peralkylated[1] amidines and guanidines are superior.[2-7] These bases are effective in promoting various reactions including the hydrogenation of CO_2 to formic acid, the carboxylation of activated methylene compounds with CO_2, and various coupling reactions of CO_2. The most commonly used amidine is 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Although the reason for the effectiveness of these bases for promoting CO_2 fixation is unknown, it has been stated in the literature[8-12] that a zwitterionic adduct forms between the amidine or guanidine and CO_2 (e.g., eq 1 for DBU). Because saturated amine bases are not known to form a stable adduct of this type with CO_2, the adduct has often been cited as an explanation for the promotion effect of amidines.[13-16] For this reason, we endeavored to confirm the existence of this type of adduct.



(1)

The zwitterionic adduct was first reported, so far as we have been able to determine, by Iwatani et al.,[8] who reported that exposing liquid DBU to CO_2 gas gave a white solid, which was identified only by IR and elemental analysis as a DBU·CO_2 adduct. Pérez et al.[9,11] more recently have further characterized the isolated DBU: CO_2 adduct, which they isolated by exposing an acetonitrile solution of DBU to CO_2 gas, but an attempt at obtaining a structure by X-ray crystallography gave instead the structure of the bicarbonate salt due to the presence of adventitious water. Endo et al. reported similar results with a different amidine.[10] Ogawa et al. reported the O=C=S adduct of DBU without characterization.[17,18] However, none of these groups mention using thoroughly dried amidine, although the literature yields of the zwitterionic adduct appear to be lower for those authors who made greater efforts to exclude water. It is therefore uncertain whether the presence of water is necessary for the formation of the adduct or indeed if the formulation of the isolated product as a zwitterionic adduct is correct.

We now report spectroscopic studies of the reaction between DBU and CO_2 in the presence and absence of water, with the aim of clarifying the role of water and the nature of the isolated product. The results support the formation of the bicarbonate salt of DBU when wet

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(1) "Peralkylated" in this context means having alkyl groups rather than protons attached to the N atoms.

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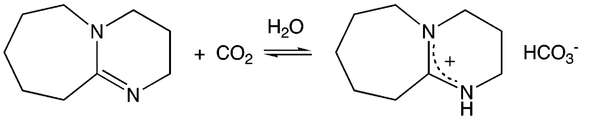
DBU is exposed to CO_2 (eq 2). However, the results do not support the notion that a stable zwitterionic adduct between DBU and CO_2 forms either in the presence or the absence of water.



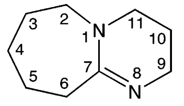
(2)

Results and Discussion: DBU Exposed to CO_2 in the Presence of Water. The formation of a white precipitate from the reaction of CO_2 with wet DBU (H_2O = 700 ppm) was confirmed by bubbling CO_2 through the liquid DBU for 10 min. The initial clear nonviscous liquid instantly turned into a white sludge with large amounts of a white solid precipitating out of solution. The same experiment was repeated with a small amount of Reichardt's solvatochromic dye "$E_T(30)$" dissolved in the DBU. The solution was green, as is normal for this dye when dissolved in a fairly nonpolar liquid such as DBU. Upon exposure to CO_2 (1 bar), the green solution turned red immediately, while the white precipitate formed. The red color indicates that the local polarity of the solution around the solvatochromic dye molecule has greatly increased, consistent with the formation of a polar or ionic species or a strongly hydrogen-bonding species. Repeating this experiment in undried acetonitrile gave a color change from turquoise through purple and finally pink. Turquoise is the normal color for Reichardt's dye in a relatively polar solvent such as acetonitrile. The color change to purple and then pink indicates an increase in polarity, again consistent with the formation of polar or ionic species.

The solid precipitate (species **1**) was prepared synthetically by bubbling CO_2 through a wet solution of DBU (700 ppm water) in acetonitrile (191 ppm water). The IR of the solid sample in KBr showed a peak at 1644 cm^{-1}, similar to Iwatani's report of a new band at 1640 for the "adduct", but we interpret this as evidence of the presence of protonated DBU rather than as evidence of a DBU:CO_2 adduct; [DBUH]Cl for example has a ν(C═N) at 1645 cm^{-1} in KBr. Thus, the new IR band at 1644 cm^{-1} cannot be used as evidence of the formation of a CO_2 adduct. There is also a new band at 836 cm^{-1} that appears in the spectrum of **1** but not in those of DBU or [DBUH]Cl. This band is consistent with the CO_2 out-of-plane vibration of bicarbonate anion, which appears at 835 cm^{-1} for $KHCO_3$.[19]

The ^1H NMR spectrum of **1** was measured in undried $CDCl_3$ rather than in D_2O (as in the literature) so that protons from water would be detectable. This spectrum showed a broad singlet at 5.5 ppm suggesting that the DBU cation was protonated at the amidine nitrogen. The same peak is observed in a 1:1 salt of DBU and Cl_3CCO_2H. The ^{13}C NMR spectrum of **1** in $CDCl_3$ showed that the bridgehead carbon (C(7) using the numbering shown in Chart 1) appears at 162.6 ppm (compared to 161.5 for unreacted DBU). The same carbon in the 1:1 salt of DBU and Cl_3CCO_2H appears at 162.8 in $CDCl_3$. Thus the ^1H and ^{13}C NMR data are entirely consistent with the DBU portion of **1** being simply protonated DBU. The ^{13}C NMR spectrum of **1** also contains a new peak at 161.1 ppm. While this new peak has in the literature been ascribed to DBU·CO_2 zwitterionic adduct (literature value 160.7 ppm in D_2O[11]), we suggest rather that the new peak is consistent with bicarbonate anion. $KHCO_3$ in D_2O appears at 160.4 ppm and $[PMePh_3][O_2COH]$ appears at 160.3 ppm[20] in CD_2Cl_2. The ^{13}C NMR data are summarized in Table 1.

CHART 1. DBU



Note that the ^1H and ^{13}C NMR chemical shifts of DBU in $CDCl_3$ are unaffected by the presence of small amounts of water, as long as there is no CO_2 present. In the presence of 0.5 equiv of water, there is a −0.68 ppm shift in the positions of all of the peaks in the ^{13}C NMR spectrum of DBU, but this is likely a general solvent effect rather than a proton-transfer reaction between water and DBU.

Experiments with ^{13}C enriched CO_2 bubbled through partly dried neat liquid DBU (100 ppm water) showed results confirming small amounts of the DBU bicarbonate (**1**). The ^1H and ^{13}C NMR spectra of the DBU after the exposure to $^{13}CO_2$ showed no evidence of shifting of the DBU peaks or change in coupling due to binding of CO_2. In the ^{13}C NMR spectrum a large peak at 159.0 ppm represents the DBU bridgehead carbon. A small new peak at 157.8 ppm we attribute to $H^{13}CO_3^-$. Note that the chemical shifts in neat DBU differ slightly from those in $CDCl_3$. No free carbon dioxide was seen in the spectrum at its expected shift of ~125 ppm indicating either complete consumption of free carbon dioxide or poor relaxation of the C nucleus. An HMBC experiment showed no evidence of coupling between the new peak (157.8 ppm) and any of the protons on DBU, a result that is consistent with [DBUH][HCO_3] and not consistent with a DBU:CO_2 zwitterionic adduct.

Conductivity measurements on neat DBU or DBU in acetonitrile were performed to detect the formation of ionic species upon exposure of DBU to CO_2. Table 2 presents the conductivity measurements of the DBU solutions. As mentioned previously, wet DBU immediately forms a solid precipitate upon CO_2 bubbling. The sample turned into a thick white sludge that prevented an accurate measurement of the conductivity, although an increase in conductivity was observed, suggesting that some small amount of ionic material (the bicarbonate salt) remained dissolved in the DBU.

When anhydrous DBU (0.75 mL, 7 ppm water) was tested in anhydrous acetonitrile (5 mL), the sample showed a small increase in conductivity upon exposure to CO_2, which is attributed to the formation of the bicarbonate salt of DBU from the residual water in the solution. Increasing the amount of water in the acetonitrile/DBU/CO_2 mixture increased the conductivity, in addition to causing a precipitate to form.

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TABLE 1. $^{13}C\{^1H\}$ NMR Chemical Shifts of Relevant Species in $CDCl_3$[a]

sample	C7	C2	C11	C9	C6	C3	C5	C4	C10	$HOCO_2^-$
DBU	161.5	52.8	48.3	44.1	37.3	29.8	28.5	25.9	22.4	
1	162.6	53.2	48.5	43.1	36.4	29.7	28.3	25.7	22.0	161.1
DBU + Cl_3CCO_2H	162.8	53.3	48.6	42.8	36.1	29.7	28.3	25.7	21.9	
DBU + H_2SO_4	166.3	54.7	48.6	38.7	33.5	28.8	26.2	23.8	19.2	
$[PMePh_3][O_2COH]$[b]										160.4

[a] Chemical shifts referenced to $CDCl_3$ at 77.20 ppm. All mixtures in equimolar ratios. [b] In CD_2Cl_2.[20]

TABLE 2. Conductance Measurements of Solutions of DBU

solution	H_2O content (ppm)	no CO_2 (1/μohm)	with CO_2 (1/μohm)
neat DBU (wet)	700	0	45 (sludge)
neat DBU (dry)	6	0	0
DBU in acetonitrile (wet)	191	75	880
DBU in acetonitrile (dry)	7	4.2	29

The conductivity rises in the presence of both water and CO_2 are attributed to the formation of $[DBUH^+][HCO_3^-]$. The zwitterionic adduct, if present, would not add to the conductivity because it does not consist of free ions. The lack of high conductivity in the dry solutions here suggests that neither the bicarbonate nor any other ionic species are formed in large quantities in the absence of water.

DBU Exposed to CO_2 in the Absence of Water. There is no visual evidence for a reaction between CO_2 and DBU in the absence of water. Dried DBU (2 mL, H_2O content 13 ppm) and a stir bar were charged into a dried stainless steel vessel with viewing windows and pressurized to 10 bar with dry CO_2 (H_2O content <0.5 ppm) at room temperature. The solution remained clear and colorless with no indication of precipitate formation within 4 h of stirring. The same experiment but with Reichardt's dye dissolved in the DBU showed that the solution was nonpolar (i.e. green) both before and after exposure to CO_2 and even after 1 week under 20 bar of CO_2 with constant agitation.

Anhydrous DBU (6 ppm) has no conductivity either before or after exposure to CO_2 (Table 2), indicating no free ions such as bicarbonate salt were formed.

Although the literature states that DBU and CO_2 react in anhydrous acetonitrile to form a precipitate,[11] we found that there is no precipitate if *both* the acetonitrile and the DBU are dry. Dry DBU (2 mL, water content 6 ppm), Reichardt's dye, dry acetonitrile (water content 7 ppm), and a stir bar were charged into a dried stainless steel vessel with viewing windows and pressurized to 17 bar of CO_2 (water content <0.5 ppm) at room temperature. The initial solution was a light turquoise (indicating that acetonitrile is relatively polar) prior to pressurization. At pressure, the solution remained a turquoise liquid and there was no precipitate. Therefore we conclude that the formation of the precipitate, whatever its structure, requires the presence of water, and that in the absence of water, either the product fails to form or it forms in quantities below its solubility limit and in quantities insufficient to change the polarity of either neat DBU or a DBU solution in acetonitrile.

An NMR spectroscopic study was performed with dried DBU without solvent. DBU (<5 ppm water) was charged into a flame-dried NMR tube sealed with a Teflon screw cap. Carbon dioxide was then bubbled through the NMR tube septum from a balloon in an inert atmosphere for 10 min. No precipitate formed. The ^1H and ^{13}C NMR spectra of the solution showed no change in chemical shifts compared to those of DBU before exposure to CO_2.

High-pressure NMR experiments were performed to detect the form in which the CO_2 exists when dissolved in DBU; it could be bound to DBU or it could be simply dissolved. DBU (neat, dried by distillation from CaH_2 to activated molecular sieves) was pressurized with 57 bar of CO_2 and left to equilibrate for 10 h at room temperature. The ^{13}C NMR spectrum shows that the bridgehead DBU carbon (C(9)) does not shift. Dissolved CO_2 was observed at 125 ppm, consistent with a literature report[21] of CO_2 dissolved in a nonpolar liquid. No carboxylate peak was seen in the spectrum and there was no evidence of protonated or carboxylated DBU. This experiment shows that there is no evidence of a stable adduct between CO_2 and DBU in the absence of water at this temperature.

It is still possible that a DBU:CO_2 adduct may form in solution phase, even though we have been unable to detect such a species. Low-temperature spectroscopy or the use of more sensitive techniques, such as IR spectroscopy of nearly equimolar ratios of amine and CO_2 in liquid alkane, may be more successful in the search for the elusive adduct. According to a literature report,[22] this IR technique was able to detect a weak acid−base adduct between pyridine and CO_2. An effort to detect and quantify such interactions between CO_2 and amidines by this method is underway.

In conclusion, all of the spectroscopic data for the reaction between DBU and CO_2 are consistent with the formation of $[DBUH^+][HCO_3^-]$ in the presence of water and no reaction in the absence of water. The white stable solid that forms when DBU is exposed to CO_2 is $[DBUH^+][HCO_3^-]$ and not a DBU:CO_2 zwitterionic adduct. While the zwitterionic adduct may still be theoretically possible, there is no unambiguous evidence yet to demonstrate its existence.

The reason for the efficacy of DBU and other amidines for the promotion of CO_2 fixation may more likely be related to the ability of DBU to stabilize and solubilize bicarbonate anion in organic solvents.

Experimental Section

DBU was purchased from Aldrich and either used "wet" (as received) or "dried" (distilled under vacuum over CaH_2 and then dried with 5 Å molecular sieve). Acetonitrile was purchased from

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Fisher Scientific and was distilled and dried with 4 Å molecular sieve. Supercritical grade CO_2 (Praxair, SFE grade, 99.999%, H_2O <0.5 ppm) and $^{13}CO_2$ (Aldrich, 99% ^{13}C) were used as received.

Conductivity measurements were performed with a multiprobe solution cell. All NMR spectra were aquired on a 400-MHz NMR spectrometer, except for the long-range coupling investigation (performed on a 600-MHz NMR spectrometer) and the high-pressure NMR experiments (performed on a 400-MHz instrument with a 10-mm broadband probe). ^{13}C NMR spectra of samples in $CDCl_3$ were internally referenced to $CDCl_3$ at 77.20 ppm. ^{13}C NMR chemical shifts for the high-pressure experiment were externally referenced to C_6H_6 at 128 ppm. The high-pressure NMR tubes were constructed from PEEK using a modification of the design of Wallen et al.[23] The water content of 100-μL samples of DBU and solvents was measured under nitrogen atmosphere in an inert-atmosphere glovebox with use of a Karl-Fisher titrator.

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