Carbonic Acid and Its Mono- and Diprotonation: NMR, ab Initio, and IGLO Investigation[1]

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Abstract: The structures and ^{13}C NMR chemical shifts of carbonic acid and its mono- and diprotonated forms were calculated using ab initio and IGLO methods, respectively. The results were compared with the experimentally obtained NMR data under superacidic conditions.

Introduction

Carbonic acid is of special importance in nature. The equilibrium of carbonic acid with carbon dioxide and water and its significance are well recognized and thoroughly studied. Despite

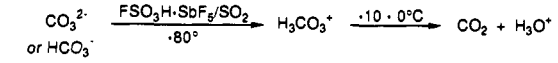
$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

carbonates being the abundant minerals on earth, carbonic acid is difficult to observe spectroscopically in its free form. Carbonic acid is known to be present to the extent of about 0.4% in water containing dissolved CO_2. The dissociation constant of carbonic acid is large in comparison with those of the hydrates of other carbonyl compounds,[2] and this has been taken to reflect the high stability of the unhydrated species, CO_2. However, an activation energy of 16.5 kcal/mol[3] for the dissociation reaction of carbonic acid to water and carbon dioxide suggests that it should be possible to observe carbonic acid in its free state. The theoretically calculated activation barrier for the dissociation reaction is 15.5 kcal/mol at the HF/3-21G level.[4] Indeed, there have been two claims of the preparation of carbonic acid[5,6] as its ether complex, but no spectral evidence was provided.

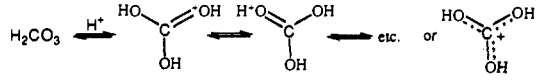
Isolation of the carbonic acid as its ether complex[6] was achieved by the addition of an ethereal solution of anhydrous HCl to a suspension of finely divided sodium bicarbonate in ether at −30 °C. Cooling the solution to −78 °C resulted in the precipitation of crystals of $H_2CO_3{\cdot}Et_2O$. A similar procedure was used by Gattow and Gerwath in their preparation of the dimethyl ether complex of carbonic acid using[5] dimethyl ether and sodium carbonate at −35 °C. They obtained a solid (mp −47 °C) which decomposed violently above 5 °C, yielding water, CO_2, and ether, in the ratio 1:1.02:1.02, respectively. The authors concluded that the solid was $OC(OH)_2{\cdot}O(CH_3)_2$ although NMR and IR spectra were not obtained.

Several calculations on the gas-phase reaction of carbon dioxide with water and with hydroxide ion have been reported,[7] focusing mainly on accurate reaction energies. Liang and Lipscomb[7a] obtained 61 kcal/mol free energy barriers for the former reaction at the MP2/4-31**//4-31G level.

Protonated carbonic acid in superacidic media is remarkably stable, as shown by Olah and White.[8] It can be obtained by simply dissolving carbonates or hydrogen carbonates in FSO_3H–SbF_5 (or other superacids). ^1H and ^{13}C NMR spectroscopy was used to characterize $H_3CO_3^+$. The solutions decompose at about 0 °C to give hydronium ion and carbon dioxide.



The close analogy of protonated carbonic acid with the guanidinium ion best explains its stability. Both are highly resonance stabilized. The observation of stable protonated carbonic acid



has led Olah[8] to suggest that protonated carbonic acid may also play a role in certain biological carboxylation processes.

We wish to report now the extended ^{13}C NMR, ab initio, and IGLO studies on carbonic acid itself, as well as its mono- and diprotonated forms.

Results and Discussion

The solubility of $BaCO_3$ is very low in SO_2ClF, and the addition of HBr gave neither CO_2 nor any detectable carbonates in solution (by ^{13}C NMR using 53% ^{13}C-enriched $BaCO_3$). However, when a few drops of methanol or water were added followed by acids such as HBr or CF_3CO_2H, a carbon resonance at $\sim\delta(^{13}C)$ 163 was observed. With weaker acids such as HCOOH or CH_3CO-OH, only CO_2 (dissolved) could be observed.

Dimethyl carbonate (53% ^{13}C enriched) and di-*tert*-butyl carbonate were also examined. Di-*tert*-butyl carbonate readily protolyses in HBr–SO_2ClF, while dimethyl carbonate does not. We also attempted to study the existence of H_2CO_3–ether complexes in the $BaCO_3$–HCl–ether systems.

From Table I it can be seen that the range of chemical shifts observed is narrow (although conditions were not always strictly identical) and the chemical shifts observed showed no systematic variation with the acids used. The cleavage of di-*tert*-butyl carbonate gives the same species as $BaCO_3$ does, with a similar chemical shift.

Dimethyl ether itself shows no significant chemical shift change ($\sim$0.3 ppm) at −40 °C when excess HCl is added. Since HCl boils at −85 °C, clearly a complex must be formed, but it seems to be very loosely bound or still rapidly proton exchanging (no static $(CH_3)_2OH^+$ is observed). There appears to be no NMR evidence for any H_2CO_3–dimethyl ether complex. However, the addition of $BaCO_3$ to a solution of HCl in CH_3OH gives a peak at $\delta(^{13}C)$ 162.9, which shows very little change upon addition of H_2O. It appears unlikely that a complex such as $H_2CO_3{\cdot}O(Me)_2$ is formed in the presence of the relatively strong acid HCl. The peak at $\delta(^{13}C)$ 162.9 in a solution of $BaCO_3$ in CH_3OH with excess HCl in all probability is due to H_2CO_3. Dimethyl carbonate is not formed under the conditions, but an exchanging system of H_2CO_3 with methyl hydrogen carbonate is plausible.

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Table I. Measured ^{13}C NMR Chemical Shifts[a]

carbonate	temp (°C)	acid	solvent	solubilizer	$\delta(^{13}C)$ (C=O or C=OH$^+$)
$BaCO_3$	−90	FSO_3H–SbF_5 (1:4)	SO_2ClF	–	164.9
$BaCO_3$	−82	HBr	SO_2ClF	CH_3OH	163.1
$BaCO_3$	−80	CF_3COOH	SO_2ClF	–	163.0
$BaCO_3$	−40	HCl	CH_3OH	–	162.9
$BaCO_3$	−40	HCl	CH_3OCH_3	CH_3OH	162.4
$BaCO_3$	−40	HCl	CH_3OCH_3	CH_3OH/H_2O	162.5
$BaCO_3$	−40	HCl	CH_3OH	–	162.9
$(t\text{-}Bu)_2CO_3$	−78	–	SO_2ClF	–	147.5
$(t\text{-}Bu)_2CO_3$	−78	HBr	SO_2ClF	CH_3OH	162.4
$(Me)_2CO_3$	−78	–	SO_2ClF	–	157.1
$(Me)_2CO_3$	−78	HBr	SO_2ClF	–	163.2
$(Me)_2CO_3$	−78	HBr	SO_2ClF	CH_3OH	162.3

[a] Chemical shifts are referenced to external TMS; – means not added.

Table II. Total Energies (in hartrees) and Relative Energies (in kcal/mol Based on MP2/6-31G*//HF/6-31G* + ZPE) of Bicarbonate and Free and Mono- and Diprotonated Carbonic Acids (Zero-Point Vibrational Energy (ZPE) in kcal/mol at the HF/6-31G*//HF/6-31G* Level Given in Parentheses)

structure	HF/6-31G*/ /HF/6-31G*	MP2/6-31G*/ /HF/6-31G*	rel energy (kcal/mol)	MP2/6-31G*/ /MP2/6-31G*
1	−263.078 61 (18.37)	−263.732 57		−163.750 16
H_2CO_3				
2	−263.643 64 (27.07)	−264.291 24	1.9	
3	−263.647 48 (27.27)	−264.294 62	0.0	−264.312 59
4	−263.624 91 (26.05)	−264.273 18	12.3	
5	−263.650 18 (23.26)	−264.304 14	−10.0	
6	−263.648 51 (22.92)[a]	−264.302 48	−9.3	
$H_3CO_3^+$				
7	−263.955 46 (35.15)	−264.593 36	0.0	−264.610 84
8	−263.901 25 (32.98)[a]	−264.552 62	23.4	
9	−263.942 40 (34.85)	−264.580 77	7.6	
$H_4CO_3^{2+}$				
10	−263.913 29 (38.98)	−264.565 92	26.1	
11	−263.961 05 (40.29)	−264.601 91	4.8	
12	−263.940 21 (39.47)[b]	−264.582 50	16.2	
13	−263.970 08 (40.66)	−264.610 27	0.0	−264.628 19
14	−263.952 94 (39.59)	−264.594 96	8.5	
15	−263.937 12 (39.08)[b]	−264.581 39	16.5	

[a] Two imaginary frequencies. [b] One imaginary frequency.

Table III. IGLO Calculated ^{13}C NMR Chemical Shifts

structure	II//MP2/6-31G*	experimental
HCO_3^{-1} (**1**)	159.4	161.2[a]
H_2CO_3 (**3**)	158.5	162.9
$H_3CO_3^+$ (**7**)	169.7	164.9
$H_4CO_3^{2+}$ (**13**)	157.8	

[a] From ref 17.

We also carried out ab initio and IGLO calculations[9,10] on bicarbonate as well as free and mono-, and diprotonated carbonic acids to rationalize the observed experimental results. Initially the possible geometries were optimized at the HF/6-31G* level. The most stable isomers were subsequently determined from relative energies at the MP2/6-31G*//HF/6-31G* level. Finally, the lowest energy structures were further optimized at the MP2/6-31G* level. MP2/6-31G* optimized structures were used to calculate ^{13}C NMR chemical shifts. Optimized structures are depicted in Figure 1, and their calculated energies are summarized in Table II. IGLO calculated ^{13}C NMR chemical shifts are listed in Table III.

Carbonic Acid. The C_{2v} structure **3** is found to be the lowest energy structure. Although structures **5** and **6** are lower in energy than that of **3**, those are in fact molecular complexes between CO_2 and H_2O rather than de facto carbonic acid. Calculations on carbonic acid, although at low levels, have been reported previously. The obtained results[4] match well with those reported here.

Calculated proton affinity of carbonic acid at the MP2/6-31G*//HF/6-31G* level is 177.4 kcal/mol,[11] 10 kcal/mol greater than that of water (Experimental gas phase and calculated (at the MP2/6-31G*//HF/6-31G* level) proton affinities of water are 168.1[11] and 166.5[12] kcal/mol, respectively).

Protonated Carbonic Acid. The symmetrical C_{3h} structure **7** was found to be the global minimum. This structure was suggested for the observed species in superacid solution by Olah et al.[8] on the basis of ^1H and ^{13}C NMR spectroscopy. The ion at −80 °C shows single sharp peaks at $\delta(^1H)$ 12.05 and $\delta(^{13}C)$ 165.4 in the proton and ^{13}C NMR spectra, respectively.

Protonation of carbonic acid on the hydroxyl oxygen atom (**8**) was shown to be unfavorable by 23.4 kcal/mol over protonation on the carbonyl oxygen (**7**). Frequency calculation at the HF/6-31G*//HF/6-31G* level showed that the structure **8** is not a minimum, as it contains two imaginary frequencies.

Diprotonated Carbonic Acid. Structure **13** with C_{2v} symmetry is the lowest energy structure. The structure can be considered as a donor–acceptor complex of H_2O and diprotonated CO_2. As expected, the C—OH_2 bond length (1.367 Å) of diprotonated carbonic acid **13** is slightly greater than the C—OH bond length (1.339 Å) of neutral methanol whereas the C—OH bond length (1.229 Å) of **13** is between the normal C—O and C=O bond lengths, indicating the delocalization of the second charge into two C—OH oxygen atoms.

Theoretical calculations reveal the similarity of diprotonated carbonic acid with the diprotonated guanidinium dication (observed[13] in superacid solutions by NMR). Attempts to observe diprotonated carbonic acid in high-acidity Magic acid (FSO_3H–

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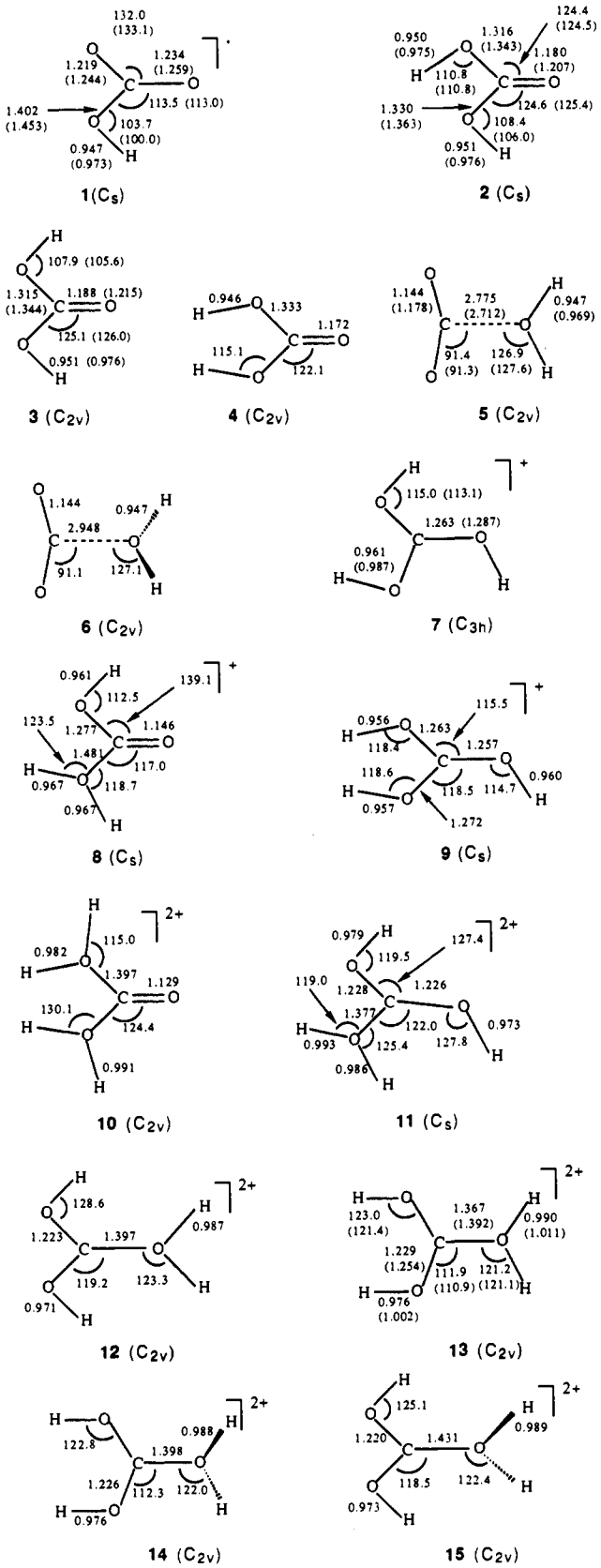
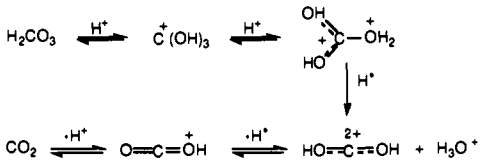


Figure 1. HF/6-31G* optimized structures (MP2/6-31G* optimized).

SbF_5) or fluoroantimonic acid systems were, however, unsuccessful. The ^{13}C NMR chemical shift of protonated carbonic acid hardly changed (±0.5 ppm) with the gradual increase in acidity. Thus any diprotonated carbonic acid formed at these acidities, albeit in low concentrations, would undergo rapid proton exchange under the slow NMR time scale and will not contribute to the observed chemical shift.

The observation that carbonic acid in superacidic media under certain circumstances can act as a carboxylating agent[14] is significant, as it indicates the intermediacy of protonated (or diprotonated) carbon dioxide as the reactive carboxylating agents. Alternatively, protolytic cleavage of carbonic acid which leads to carbon dioxide also suggests involvement of protonated (and diprotonated) CO_2, i.e. $(O{=}C{=}OH)^+$ and $(HO{=}C{=}OH)^{2+}$, respectively.



Using IGLO II basis set and MP2/6-31G* structures, we have calculated ^{13}C NMR chemical shifts for the most stable structures of the parent and mono- and diprotonated carbonic acids as well as bicarbonate ion. The calculated ^{13}C NMR chemical shift of HCO_3^- (1) was found to be $\delta(^{13}C)$ 159.4, in good agreement with the experimental value of $\delta(^{13}C)$ 161.2 (Table III). The calculated chemical shift of protonated carbonic acid 7 is $\delta(^{13}C)$ 169.7, 5 ppm more deshielded than the experimental value of $\delta(^{13}C)$ 165.0. Calculation for carbonic acid 3 gave a value of $\delta(^{13}C)$ 158.5, 1 ppm more shielded than the calculated value of bicarbonate ion. These results seem to indicate that the ^{13}C NMR absorption at $\delta(^{13}C)$ 162.9 in a solution of $BaCO_3$ in CH_3OH with excess HCl is indeed due to H_2CO_3, which may be in equilibrium with protonated carbonic acid. Interestingly, the calculated ^{13}C NMR chemical shift for diprotonated carbonic acid is $\delta(^{13}C)$ 157.8, only 11.9 ppm shielded from the calculated chemical shift of carbonic acid.

Experimental Section

^{13}C NMR spectra were recorded at 20 MHz and were run with either proton decoupling (full NOE) or a gated decoupling mode which gives a fully coupled spectrum with some NOE enhancement. The chemical shifts are referenced with respect to external TMS (The difference between internal and external TMS reference is only +1 ppm in the ^{13}C NMR).

Starting Materials. SO_2 and SO_2ClF were available as described in earlier studies. SbF_5 (Allied-Signal) was doubly distilled and stored in Teflon bottles. All other gases were from Air Products. The ^{13}C-enriched carbonate (53% ^{13}C barium carbonate) was obtained from Merck, Sharp and Dohme. Dialkyl carbonates were from Aldrich and were used as received.

Preparation of Solutions. The carbonate was generally added to the SO_2 or SO_2ClF in a 10-mm NMR tube using ca. 1 mL of solvent. Into this was slowly introduced the requisite acid. In the case of FSO_3H–SbF_5, the carbonate was added to the acid solution. All solutions were made up and kept at −78 °C (using a dry ice–acetone bath).

Method, Basis Set, and Geometry. IGLO calculations were performed according to the reported method.[9,10] Huzinaga[15] Gaussian lobes for the II basis set are as follows: C or O, 9s 5p 1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 5s 1p contracted to [311, 1]; p exponent, 0.65.

Geometries were optimized at HF/6-31G* and MP2/6-31G* levels by using the Gaussian-86[16] series of programs on an Alliant FX/40 computer. The energy minima or the saddle points were confirmed by vibrational frequency calculations at the same level.

Acknowledgment. Support of our work by the National Institute of Health is gratefully acknowledged. We are grateful to professor W. Kutzelnigg and Dr. M. Schindler for providing a copy of their IGLO program.

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