Stable Carbonium Ions. LXIV.[1] Protonated Carbonic Acid (Trihydroxycarbonium Ion) and Protonated Alkyl (Aryl) Carbonates and Hydrogen Carbonates, and Their Cleavage to Protonated Carbonic Acid and Carbonium Ions. The Possible Role of Protonated Carbonic Acid in Biological Carboxylation Processes

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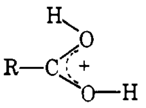
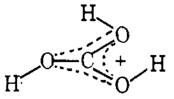
Abstract: Protonated carbonic acid (trihydroxycarbonium ion, $C(OH)_3^+$, III) has been observed in $FSO_3H-SbF_5-SO_2$ solutions of carbonates and bicarbonates at low temperature. It is stable at temperatures up to 0° in the absence of SO_2. Decomposition of the ion in acid media leads to CO_2 and H_3O^+. To confirm the structure, the C^{13} nmr spectrum was obtained and the chemical shift and coupling constant were compared to those found in a series of related compounds including protonated acetone (dimethylhydroxycarbonium ion) and protonated methyl hydrogen carbonate (methyldihydroxycarbonium ion). Also studied was the protonation of alkyl carbonates in the same acid system. Alkyl–oxygen cleavage was observed leading to the formation of carbonium ions and protonated carbonic acid. Protonated carbonic acid was found to be an effective carboxylating agent and it is suggested that it may play an important role in certain biological carboxylation processes.

In the course of our investigations of heteroatom-substituted carbonium ions[3] we have formed mono- and dihydroxycarbonium ions (I and II) in the strong-acid system $FSO_3H-SbF_5-SO_2$. The former were obtained by protonation of ketones[4] and the latter by protonation of carboxylic acids.[5] We wish now to report evidence for the direct observation of the final member of this series, the long-sought-after trihydroxycarbonium ion (protonated carbonic acid, III). Carbonic acid is present to the extent of about 0.4% in water containing dissolved CO_2.[6] The dissociation constant of carbonic acid is very large in comparison with the hydrates of other carbonyl compounds,[7] and this has been taken to reflect the high stability of the unhydrated species, carbon dioxide. The activation energy for the reaction $H_2CO_3 \rightarrow H_2O + CO_2$ has been found from rate studies of the acidification of bicarbonate in a flow system.[8] The value obtained by this method, 16.5 kcal/mol,[8] would suggest that it would be possible to isolate carbonic acid in the pure state. Indeed, a claim of its isolation has appeared,[9] although the authors were unable to obtain spectral evidence for its structure.

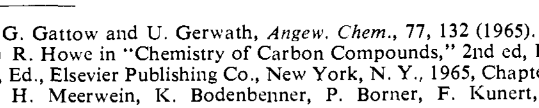

I


II


III

By comparison with carbonic acid, dialkyl carbonates are well known and have high stability.[10] Alkyl hydrogen carbonates are less stable and, at ambient temperature, dissociate into carbon dioxide and the corresponding alcohol.[10] Trialkoxycarbonium ions, derived from dialkyl carbonates by alkylation of the carbonyl group, are also a well-established class of compounds.[11,12] The nmr spectra of these ions (methyl and ethyl) and of protonated dimethyl and diethyl carbonates (in H_2SO_4 solution) have also been reported recently,[13] although in this acid system the OH protons cannot be observed by nmr due to exchange with the solvent.

No observation of protonated carbonic acid (III) in solution has been previously reported, nor has its existence in solution ever, to our knowledge, been postulated or considered. McLafferty,[14] in mass spectroscopic studies of carbonates, called attention to its presence in order to explain some of the double rearrangements observed. Djerassi[15] subsequently, in a detailed mass spectroscopic study of dialkyl carbonates, observed its presence as a significant peak at *m/e* 63.



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(1) Part LXIII: G. A. Olah and J. Sommer, *J. Am. Chem. Soc.*, in press.

(2) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

(3) For a review, see G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

(4) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586 (1967).

(5) G. A. Olah and A, M. White, *ibid.*, **89**, 3591 (1967).

(6) J. T. Edsall and J. Wyman, "Biophysical Chemistry," Academic Press Inc., New York, N. Y., 1958, Chapter 10.

(7) R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 11 (1966).

(8) F. J. W. Roughton, *J. Am. Chem. Soc.*, **63**, 2930 (1941).

(9) G. Gattow and U. Gerwath, *Angew. Chem.*, **77**, 132 (1965).

(10) R. Howe in "Chemistry of Carbon Compounds," 2nd ed, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1965, Chapter 11.

(11) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960).

(12) H. Meerwein, V. Hederick, J. Morschel, and K. Wunderlich, *ibid.*, **635**, 1 (1960).

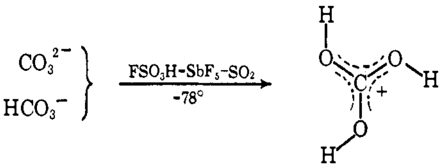
(13) B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966).

(14) F. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963.

(15) P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 2469 (1966).

Results and Discussion

Protonated Carbonic Acid. In the strong acid system 1 : 1 FSO_3H-SbF_5 containing an equal volume of SO_2 as a diluent, and at −78°, sodium, potassium, and barium carbonate as well as sodium hydrogen carbonate were found to dissolve with *no evolution of carbon dioxide*. The nmr spectra at −80° of these solutions consisted, in all cases, besides the two characteristic peaks due to the solvent acid,[5] of a single, sharp resonance at −12.05 ppm (from external TMS). The OH resonance peak is 0.7 ppm more shielded that that in protonated acetic acid[5] and 2.9 ppm more shielded than that in protonated acetone.[4] This shielding sequence is in accordance with that expected for the trihydroxycarbonium ion (III) since the additional charge delocalization in this ion, as compared to the mono- and dihydroxycarbonium ions, would be expected to lead to a relatively shielded OH absorption.



III

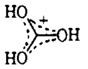
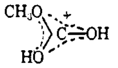
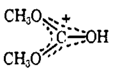
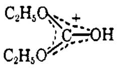
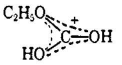
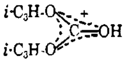
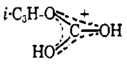
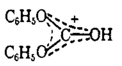
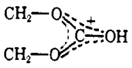
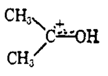
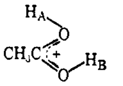
Warming the solution of ion III to −50° resulted in the sudden evolution of CO_2, disappearance of the low-field resonance peak, and an increase in the intensity of the peak at δ 10.20, which is known to be associated with the addition of water to the acid system.[5] It was found possible to keep ion III stable in solution at temperatures up to 0° in the absence of SO_2 in the acid system. It is known from previous work that the acidity of the medium is diminished significantly by the addition of SO_2;[16] thus, clearly the stability of the ion, with respect to dissociation into CO_2 and H_3O^+, must be related to the acidity of the acid system.

Protonated Dialkyl (Aryl) and Alkyl Hydrogen Carbonates. To further substantiate the proposed structure III, the protonation of a series of dialkyl and alkyl hydrogen carbonates was investigated in the acid system together with a study of their mode of cleavage, which was expected to proceed by alkyl-oxygen cleavage to give protonated carbonic acid (III) and carbonium ions.

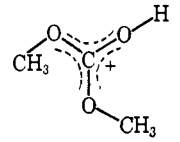
The following dialkyl (aryl) carbonates were protonated in FSO_3H-SbF_5-SO_2 solution at −78°: dimethyl, diethyl, diisopropyl, di-*t*-butyl, and diphenyl carbonate. In addition, methyl hydrogen carbonate (as the sodium salt) and the cyclic esters, ethylene carbonate and vinylene carbonate, were protonated under the same conditions. Assignments of the nmr chemical shifts are summarized in Table I, together with data for some related carbonium ions.

Dimethyl carbonate in 1:1 FSO_3H-SbF_5-SO_2 solution at −80° gave an nmr spectrum consisting of a singlet for the OH proton at δ 11.27 and two peaks at δ 4.52 and 4.40 for the methyl protons. At −43.0° the two methyl signals coalesced, reversibly, to a single peak. The possibility that this magnetic equivalence was related to exchange, with the solvent, of the hydroxyl proton was eliminated by the fact that the OH resonance remained unchanged in both position and intensity up to 10°. This temperature dependence is interpreted as being a consequence of slow rotation about the CH_3O—C= bond, the preferred conformation about the central carbon being that indicated in IV.

Table I. Proton Chemical Shifts of Hydroxycarbonium Ions in HSO_3F–SbF_5–SO_2 Solution

Compound	Temp, °C	δ, ppm[a] OH	CH$_3$	CH$_2$	CH	C$_6$H$_5$
	−80	11.55				
	−80	11.55 11.18	4.47			
	−80	11.27	4.52 4.40			
	−40	11.25	4.46			
	−80	11.02	5.05 4.85	1.56 1.49		
	−30	11.00	4.95	1.52		
	−80	11.23 11.52	5.15	1.65		
	−80	10.75	1.55		5.60	
	−80	10.88 11.33	1.60		5.70	
	−80	12.50				7.68 7.60
	−50	12.37				7.62
	−80	11.77		5.42		
	−65	14.93[b]	3.45			
	−65	13.03 (H_a)[c] 12.33 (H_b)	3.18			

[a] Parts per million from external (capillary) TMS. [b] Reference 4. [c] Reference 5.



IV

It is impossible to decide conclusively whether at low temperatures there is also slow rotation about the C-OH bond as well as the C-OCH_3 bonds since, with both slow and fast rotation (on the nmr time scale), nonequivalence of the methyl groups would be expected.

Comparison between the barriers to rotation in protonated acetic acid and in the methyldimethoxycarbonium ion show that rotation about the C-OH bond should be less hindered than around the C-OCH_3 bonds. Since no further change in the spectrum of protonated dimethyl carbonate was observed from −43.0 to −80° it would seem likely that the rotation about the C-OH bond has not been "frozen out" in the nmr experiment.

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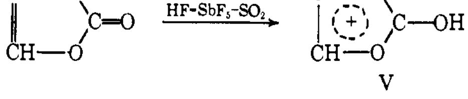
[16] G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, 89, 4752 (1967).

The activation energy for restricted rotation was obtained from the temperature dependence of the spectrum between −54.5 and −43.0°. The value of 8 ± 2 kcal/mol compares favorably with that for the methyldimethoxycarbonium ion (11 ± 4 kcal/mol) in CF_3COOH solution obtained by Ramsey and Taft.[13,17] Although the error in these values of activation energies is large, the trend observed is in the direction expected from the greater charge delocalization and hence the lower C–O bond order in the dimethoxyhydroxycarbonium ion (IV).

At 10° (in the absence of SO_2), the low-field resonance due to the hydroxyl proton coalesced with the solvent-acid peak; however the rest of the spectrum remained unaffected even on prolonged standing of the sample tube at 50°. At 100°, bubbles of gas were evolved and the solution darkened and then solidified.

Nonequivalence of the two alkoxy (aryloxy) groups at low temperatures was also found in protonated diethyl, diisopropyl, and diphenyl carbonates (see Table I). In the latter case, the phenyl groups at −80° gave two broad overlapping peaks of approximately equal area. At −50° these peaks coalesced to a single peak (peak width at half-height 7 Hz). Again this is interpreted as a consequence of hindered rotation about the C_6H_5O–C bond. It is of interest that the OH resonance in protonated diphenyl carbonate shows a significant shift to high field (0.13 ppm) between −80 and −50°. This is not observed in any of the dialkyl carbonates and this is probably attributable to the fact that when the phenyl rings lie in the same plane as the rest of the molecule, the hydroxyl proton would be expected to be deshielded by the ring current effect. Changes in the conformation population as the temperature is raised would be expected to diminish this effect and would account for the observed shift in the resonance position. Protonated ethylene carbonate showed only equivalent methylene protons at −80°.

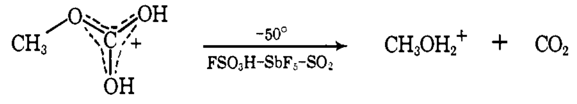
Vinylene carbonate in 1:1 FSO_3H–SbF_5–SO_2 solution was found to be protonated on the carbonyl oxygen. The nmr spectrum at −60° consisted of two peaks, one at δ 8.20 of relative area 2, and one at δ 13.18 of area 1. The OH resonance is thus *ca.* 2 ppm to low field of the OH resonance in the other carbonates studied. In addition, the olefinic protons are deshielded by 1.3 ppm when compared to the neutral molecule in SO_2. This additional deshielding suggests the presence of a significant ring current, the resulting ion being a six-π-electron heteroaromatic system. This is, to our knowledge, the first derivative of a 1,3-dioxolium ion. We have isolated 2-hydroxy-1,3-dioxolium hexafluoroantimonate (V) from an HF–SbF_5–SO_2 solution of vinylene carbonate. This salt is a white crystalline hygroscopic material which darkens when kept at room temperature in the presence of dry air. We are currently investigating its properties, including substitution reactions, and are preparing further examples of this class of compounds.



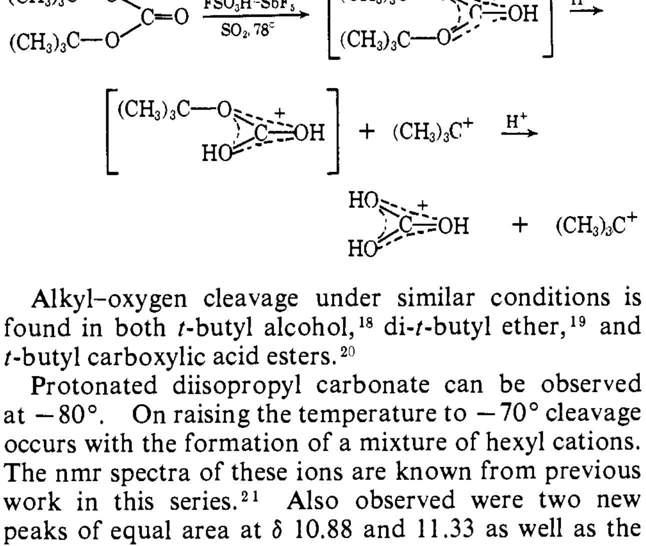
V

The spectrum of protonated methyl hydrogen carbonate between −80 and −50° showed nonequivalence of the hydroxyl protons. As in the case of dimethyl carbonate this is interpreted as indicating that rotation about the CH_3O–C bond is slow on the nmr time scale. Again it is not necessary for rotation about the HO–C bonds to be frozen out, and the available evidence indeed suggests that this is not the case.

At −50° in FSO_3H–SbF_5–SO_2 solution, protonated methyl hydrogen carbonate decomposed with evolution of CO_2 and the resulting spectrum was that of protonated methanol. As in the case of protonated carbonic acid, the temperature at which this occurs is highly solvent dependent.



The mode of cleavage of protonated carbonates in the series di-*t*-butyl, diisopropyl, and diethyl carbonate was studied. On preparation of a solution of di-*t*-butyl carbonate in FSO_3H–SbF_5–SO_2 at −78°, immediate cleavage to the *t*-butyl cation and protonated carbonic acid takes place. Integration of the peaks due to these two species gave the ratio 6:1 required of the cleavage scheme.



Alkyl-oxygen cleavage under similar conditions is found in both *t*-butyl alcohol,[18] di-*t*-butyl ether,[19] and *t*-butyl carboxylic acid esters.[20]

Protonated diisopropyl carbonate can be observed at −80°. On raising the temperature to −70° cleavage occurs with the formation of a mixture of hexyl cations. The nmr spectra of these ions are known from previous work in this series.[21] Also observed were two new peaks of equal area at δ 10.88 and 11.33 as well as the peak due to protonated carbonic acid. In addition, the methyl and methine regions became more complex,[22] although it was impossible to resolve separate resonances. On allowing the reaction to proceed at −70° for an extended period of time, the δ 10.88 and 11.33 peaks in the OH region disappeared and the resulting spectrum contained only the peak due to protonated carbonic acid and peaks due to the mixture of hexyl cations. The new species appearing in the early stages

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[17] Any solvent effect appears to be within the limits of experimental error as evidenced by the fact that we have found the same activation energy for rotation in this ion when generated from trimethyl orthoacetate in 1:1 FSO_3H–SbF_5 solution.

[18] G. A. Olah, J. Sommer, and E. Namanworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967).

[19] G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

[20] G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

[21] G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

[22] Protonated diisopropyl carbonate before cleavage has occurred shows complexity in these regions due, as in the other dialkyl carbonates, to a preferred conformation.

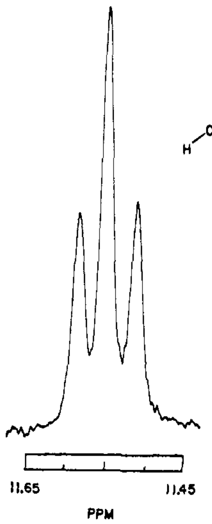
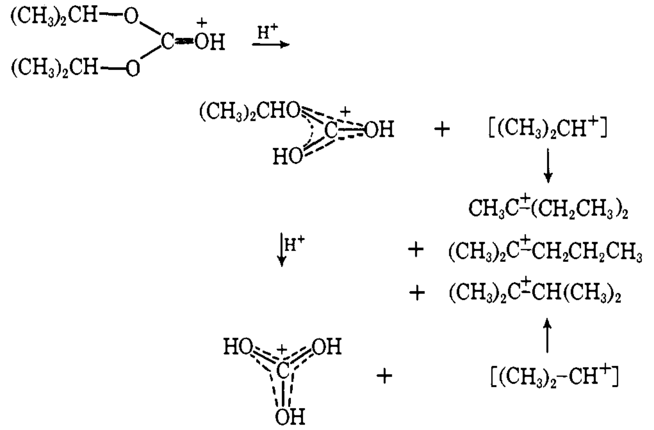
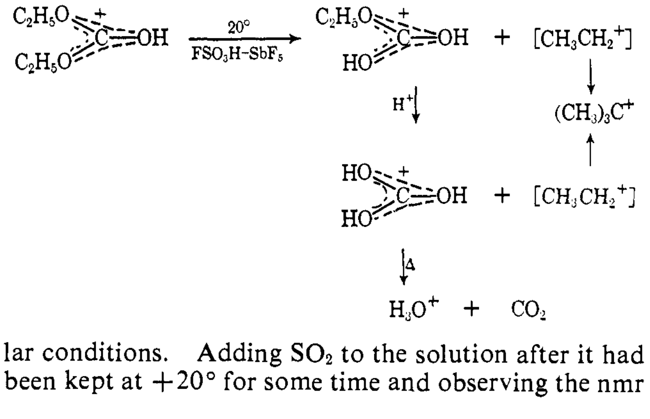


Figure 1. Proton spectrum of 56% C^{13}-enriched protonated carbonic acid (trihydroxycarbonium ion) at 60 MHz.

of cleavage is assigned as protonated isopropyl hydrogen carbonate, which, like methyl hydrogen carbonate, would be expected to show two separate OH resonances. The proposed two-step mechanism for the cleavage is



Protonated diethyl carbonate is more stable than either protonated di-*t*-butyl or diisopropyl carbonates. No cleavage was observed up to +20° in 1:1 FSO_3H-SbF_5 (in the absence of SO_2). At this temperature a signal at δ 4.20 began to develop due to formation of *t*-butyl cation. At this temperature there was also some evolution of CO_2. *t*-Butyl cation is known to be a product of the alkyl-oxygen cleavage of ethyl alcohol,[18,20] diethyl ether,[19] and ethyl acetate[20] under similar conditions. Adding SO_2 to the solution after it had been kept at +20° for some time and observing the nmr



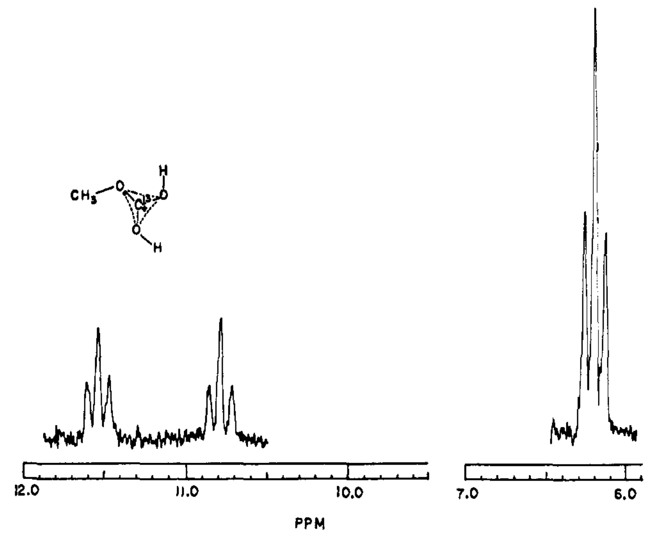


Figure 2. Proton spectrum of 56% C^{13}-enriched methoxydihydroxycarbonium ion at 60 MHz.

spectrum at −80° showed the presence of some protonated ethyl hydrogen carbonate as well as a small amount of protonated carbonic acid. No protonated ethanol was observed as would be formed if cleavage of an ethoxy-carbon bond had occurred. A reaction scheme consistent with these observations is depicted in the following.

C^{13} Magnetic Resonance Spectra

As further evidence for the structure of the trihydroxycarbonium ion (III), the C^{13} magnetic resonance spectrum of the ion was obtained. The proton spectrum of 53% C^{13}-enriched barium carbonate in 1:1 FSO_3H-SbF_5-SO_2 solution at −80° consisted of a singlet due to the C^{12} species centered between a doublet (J_{C-OH} = 4.50 Hz) due to the C^{13}-labeled ions (Figure 1). This value compares with a C^{13}-OH coupling of 6.50 Hz found in protonated acetone and the two J_{C-OH}[23a] coupling constants of 7.50 and 0.5 Hz found in protonated acetic acid.[23] The coupling constants obtained from the proton spectra of C^{13}-labeled ions (Figures 1 and 2) are summarized and compared in Table II.

The C^{13} chemical shifts were obtained by the indor method,[24,25] irradiating the C^{13} sample with a swept 15-MHz frequency source while observing the proton spectrum at 60 MHz. The C^{13} indor spectrum of protonated carbonic acid (Figure 3) consisted of a quartet (J = 4.5 Hz) demonstrating conclusively that the ion has the trihydroxycarbonium ion structure III with three equivalent OH protons. The C^{13} chemical shifts of protonated carbonic acid (III), protonated dimethyl carbonate, protonated methyl hydrogen carbonate, and protonated acetone obtained in this manner are compared, together with the data for other carbonium ions and for the corresponding uncharged precursors in Table III.

As can be seen from Table III, the C^{13} chemical shift for the trihydroxycarbonium ion is in good agreement

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(23) (a) The coupling constants suggest that, on the nmr time scale, there is free rotation about the C-OH bonds analogous to the case of protonated benzoic acid in which $J_{C^{13}OH}$ is 3.50 Hz. (b) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **89**, 7072 (1967).

(24) E. B. Baker, *J. Chem. Phys.*, 37, 911 (1962).

(25) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964).

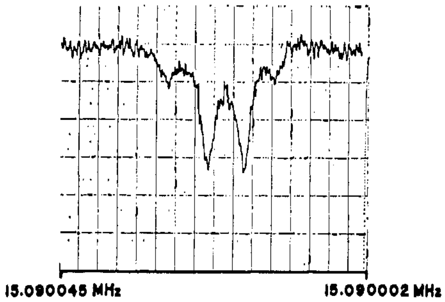
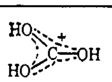
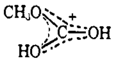
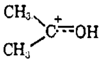
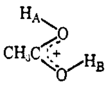
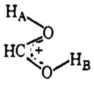
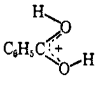


Figure 3. C^{13} indor spectrum of 56% C^{13}-enriched protonated carbonic acid (trihydroxycarbonium ion) observed at 60.002773 MHz.

with the proposed structure. Qualitatively, the effect of increasing delocalization of the charge on the central carbon atom can be seen from the trend to higher field of the C^{13} resonance in the series trimethyl, dimethylhydroxy, methyldihydroxy, and trihydroxycarbonium ion and is also reflected in the decreasing differences in shifts between the charged and the uncharged molecules.

Table II. $J_{C^{13}H}$ Coupling Constants of Hydroxycarbonium Ions in HSO_3F–SbF_5–SO_2 Solution (in Hz)

Ion	Temp, °C	$J_{C^{13}OH}$	$J_{C^{13}OCH_3}$	$J_{C^{13}CH}$
	−80	4.5		
	−80	4.8 5.6	4.8	
	−60	6.5		7.0
	−65	7.5[a] (H_B) 0.5 (H_A)		
	−65	8.2[a] (H_B) 0.5 (H_A)		
	−60	3.5[a]		

[a] Reference 23.

Table III. C^{13} Chemical Shifts of Hydroxycarbonium Ions (in FSO_3H–SbF_5–SO_2 Solution at −78°) and Their Uncharged Precursors[a]

$(CH_3)_3C^{13+}$	−146.5[b]	$(CH_3)_2C^{13}{=}CH_2$	+55[c]
$(CH_3)_2C^{13}OH^+$	− 55.7	$(CH_3)_2C^{13}{=}O$	−12.3[d]
$(CH_3)C^{13}(OH)_2^+$	+1.6[f]	$CH_3C^{13}OOCH_3$	+23[c]
$C^{13}(OH)_3^+$	+28.3	$(CH_3O)_2C^{13}{=}O$	+36[e]
$CH_3OC^{13}(OH)_2^+$	+31.0	$(CH_3O)_2C^{13}{=}O$	+36[e]
$HC^{13}(OH)_2^+$	+17.0[f]	$HC^{13}OOCH_3$	+33[d]

[a] In parts per million from $C^{13}S_2$. The uncharged species have been chosen so that the central carbon atom is approximately sp^2 hybridized and (in the case of the protonated carboxylic acids) to avoid complications due to association of molecules. See footnote *d*. [b] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Baker, *J. Am. Chem. Soc.*, **86**, 1360 (1964). [c] Estimated from the C^{13} shifts in the closely related olefins measured by R. A. Friedel and J. L. Retcofsky, *ibid.*, **85**, 1300 (1963). [d] J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). [e] P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, Chapter 7. [f] Reference 23.

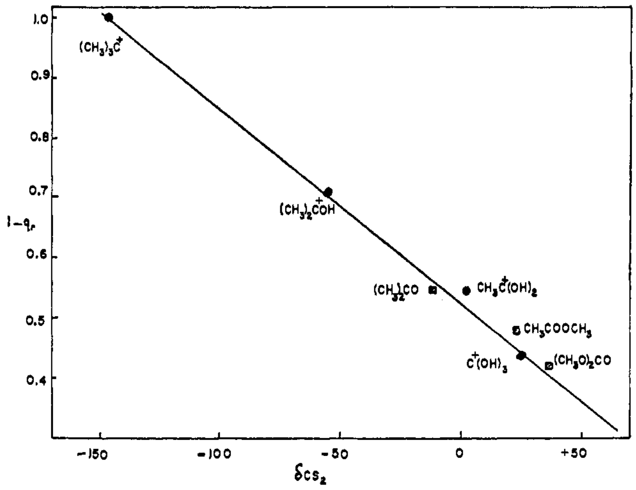


Figure 4. Correlation of π-electron densities (q_r) with C^{13} chemical shifts.

A more quantitative correlation of C^{13} chemical shifts with charge densities was made (with Professor G. Klopman). The π-electron charge densities were calculated using a simple Hückel treatment. For the purposes of this calculation, it was assumed that the π-electron charge in $(CH_3)_3C^+$ is equal to 1. The Hückel parameters used were the recommended ones described by Streitwieser.[26] In addition, the parameters for C=O were taken as the average between the C=O and C—O. The inductive effect of the methyl groups was taken to decrease the value of α of the carbon atom to which it is attached by 0.15β, two methyl groups decreasing it by 0.30β. The complete set of Hückel parameters used is given in the Experimental Section. The result of this treatment was a set of charge densities for the carbonium ions studied which gave a good linear correlation with the C^{13} chemical shifts (Figure 4) (correlation coefficient 0.9925). An empirical equation derived from this plot relating the C^{13} chemical shift with charge density is

$$\delta CS_2 = -306(1 - q_r) + 160 \text{ ppm}$$

This relationship is in poor agreement with a corresponding equation derived for aromatic compounds,[27–29] where the C^{13} shifts were found to be related to the π-electron density by a factor of 160 ppm per electron. This is not, however, an unexpected disagreement since it is clear that a number of other factors must be responsible for determining the chemical shift[30] and comparisons between unrelated series of compounds considering only the π-electron density contribution to the chemical shift must inevitably lead to such discrepancies.

The Possible Role of Protonated Carbonic Acid in Biological Carboxylation Processes

The observation of protonated carbonic acid (III) as a stable chemical entity with substantial resonance stabilization may have major implication in our under-

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(26) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(27) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961); *Tetrahedron Letters*, 274 (1961).

(28) H. Spiesecke and W. G. Schneider, *ibid.*, 468 (1961).

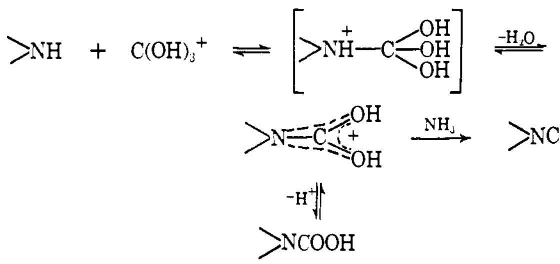
(29) J. B. Stothers, *Quart. Rev.* (London), 144 (1965).

(30) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

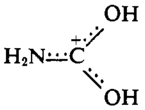
standing of some of the more fundamental biological carboxylation processes. Our present (*in vitro*) observation in specific, highly acidic, solvent systems cannot be simply extrapolated to different environments (*e.g.*, biological systems). However it is possible that on the active receptor sites of enzyme systems (for example, of the carbonic anhydrase type) local hydrogen ion concentration may be very high, as compared with the over-all "biological pH." In addition, on the receptor sites, a very favorable geometry may help to stabilize the active species, a factor which cannot be reproduced *in vitro* model systems.

Carbon-13 magnetic resonance studies of protonated carbonic acid and comparison with data on a series of known carbonium ions indicate that the carbon atom of protonated carbonic acid is fairly electrondeficient and consequently it should be a reactive carboxylating agent. This prediction was substantiated in experiments where III was found to carboxylate ammonia to ammonium carbamate, alkylamines to alkyl carbamates, etc. Our work is continuing in exploring in detail the carboxylating ability of III including biologically important systems like biotin and the possibility of C-carboxylations, and will be reported in detail later.

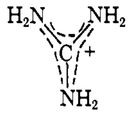
The "reactive form" of carbonic acid in certain systems indeed could be its protonated form III which would account for its high reactivity on active sites.

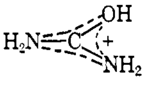


Our previous observation of protonated carbamic acid as a stable species and its carbamylating ability[31] as



well as the stability of mono- (and di-) protonated guanidine and urea[32] seem to support our contention





that protonated carbonic acid like its derivatives is a highly resonance-stabilized intermediate of substantial importance.

Experimental Section

Materials. All compounds used to generate the ions studied were either commercially available materials or were prepared by a standard literature method. C^{13}-enriched barium carbonate (50%), dimethyl carbonate, and acetone were obtained from Merck Sharp and Dohme of Canada, Ltd. Carbon-13 enriched methyl hydrogen carbonate (as the sodium salt) was prepared from sodium methoxide and carbon dioxide, generated from enriched barium carbonate. The method used for the generation of the ions in 1:1 *M* FSO_3H-SbF_5 solution using SO_2 as a diluent has been described in detail in a previous paper.[19]

Nmr Spectra. A Varian Associates HA-60-IL nmr spectrometer with variable-temperature probe was used for all spectra. A TMS capillary was used as the internal lock and all chemical shifts are referred to this standard.

The C^{13} indor spectra were obtained using an NMR Specialties SD-60-B heteronuclear decoupler with the appropriate crystals and probe adaptor. By replacing the audio oscillator frequency stabilizer by a Hewlett-Packard 3300A voltage-to-frequency converter driven by a Hewlett-Packard 3304A voltage-sweep unit, the decoupler frequency can be accurately swept at rates as low as 1 Hz/sec over ranges of 300–1000 Hz. To provide a reliable means of controlling the output of the decoupler, an attenuator from a Varian V4311 RF unit was used.

Frequency measurements were made using a Hewlett-Packard 5245L electronic counter inductively coupled to the final power amplification stage of the decoupler. By resting the recorder arm of the spectrometer on one of the C^{13} satellite peaks in the proton spectrum and monitoring the receiver output using a Sanborn 7700 Series strip chart recorder while simultaneously sweeping the decoupler through the appropriate region, the C^{13} indor spectrum was obtained. The resolution of such spectra, after optimizing the transmitter and decoupler radiofrequency outputs, was of the order of 1.5 Hz (as measured by the peak width at half-height). Chemical shifts were obtained in the usual manner[25] initially from $C^{13}H_3I$ as reference and converted to $C^{13}S_2$ as standard. The accuracy of the chemical shift values is estimated as ±0.2 ppm and was found to be reproducible within these limits. C^{13} shifts obtained by this method and by direct observation of the C^{13} spectra at 15 MHz showed agreement to within 0.5 ppm. Coupling constants determined from the C^{13} indor spectra agreed with those measured from the proton spectra to within 0.3 Hz.

Rotational Barrier in Dimethoxyhydroxycarbonium Ion. Measurements of the separation between the two methyl signals were made at ten different temperatures below coalescence covering a 20° temperature range. The values of the rate constants for restricted $C-OCH_3$ rotation were obtained from the equation[33]

$$k = 1/\tau = \pi\left(\frac{(8.2)^2 - \delta^2}{2}\right)^{1/2}$$

π-Electron Charge Density Calculations. The Hückel parameters used in the calculation of the π-electron charge densities in the series of carbonium ions and carbonyl compounds studied were as follows.

$\alpha_C = \alpha$
$\alpha_O = \alpha + \beta$
$\alpha_{-\ddot{O}-} = \alpha - 2\beta$
$\alpha_{-\dddot{O}-} = \alpha + 1.5\beta$
$\alpha_{\underset{\mid\atop CH_3}{C}} = \alpha - 0.15\beta$

$\beta_{C=C} = \beta$
$\beta_{C=O} = \beta$
$\beta_{C-\ddot{O}} = 0.8$
$\beta_{C\overset{\cdots}{-}O} = 0.9$

In the calculations, no adjustment of these parameters was made to improve the correlation with observed C^{13} chemical shifts.

Acknowledgment. Support of this work by a grant of the National Institutes of Health (GM 140882-02) is gratefully acknowledged. It is a pleasure to acknowledge stimulating discussions with Professors M. Bodanszky, M. F. Utter, and H. G. Wood and the help and interest of Professor G. Klopman in calculation of charge densities.

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(31) G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, 90, 401 (1968).

(32) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, 41, 2642 (1963); G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, in press.

(33) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 222–224.