Stable Carbonium Ions. CVII. Diprotonated Hydroxycarboxylic Acids and Their Cleavage in Fluorosulfuric Acid–Antimony Pentafluoride Solution[1]

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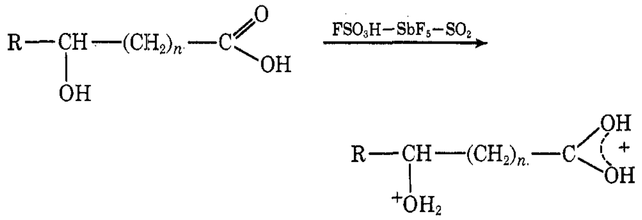
A series of hydroxycarboxylic acids were protonated in fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution at low temperature. Oxygen diprotonation was observed for all the hydroxy acids studied. At higher temperature, α-hydroxycarboxylic acids undergo dehydration to give the corresponding lactides. Protonated 3-hydroxybutyric acid undergoes dehydration to give protonated crotonic acid at 0°. Lactone formation was observed for protonated 4-hydroxybutyric acid at room temperature.

We have previously reported the observation of protonated aldehydes,[3] ketones,[4] alcohols,[5,6] carboxylic acids,[7] thiocarboxylic acids,[8] and ketocarboxylic acids[9] in superacid solutions by nmr spectroscopy. In continuation of our studies we wish now to report the protonation of hydroxycarboxylic acids and their cleavage reactions in fluorosulfuric acid–antimony pentafluoride solution.

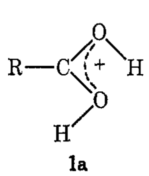
In FSO_3H–SbF_5–SO_2 solution, all the aliphatic hydroxycarboxylic acids studied were completely diprotonated. Studying the temperature dependence of these systems we were able to observe, depending on the relative position of the OH and CO_2H group, dehydration of protonated α-, β-, and γ-hydroxycarboxylic acid to form the corresponding lactide, α,β-unsaturated carboxylic acid and lactone, respectively.



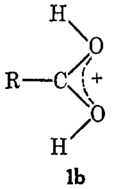
$n = 0, 1, 2$

The following aliphatic hydroxycarboxylic acids were examined in FSO_3H–SbF_5–SO_2 solution: **glycolic, lactic, 3-hydroxypropionic, 3-hydroxybutyric** and **4-hydroxybutyric acid.** The derived pmr parameters of protonated hydroxycarboxylic acids are summarized in Table I.

It has been shown that two isomeric species (**1a** and **1b**) are found for protonated formic and acetic acid in superacid systems.[7,10,11] Isomer **1a** is the predominant species for both protonated formic and acetic acid, and in the protonation of higher homologs isomer **1b** is not observed. The two OH protons of the predominant species, **1a**, are in different environment and hence give different chemical shifts at low temperature. The same observations were made for protonated thiocarboxylic acids[8] and dithiocarboxylic acids.[12] The OH protons of protonated glycolic, lactic, 3-hydroxypropionic and 3-hydroxybutyric acid, however, could not be resolved even at a temperature as low as −80°. This observation is in accord with that of protonated ketocarboxylic acids[9] and dicarboxylic acids[13] in which, when the two functional groups are too close together, only a singlet absorption was observed for the $-CO_2H_2^+$ protons. As the two functional groups are separated further, such as in the case of protonated 4-hydroxybutyric acid, the two OH protons of the $CO_2H_2^+$ group at low temperature gave two singlets.

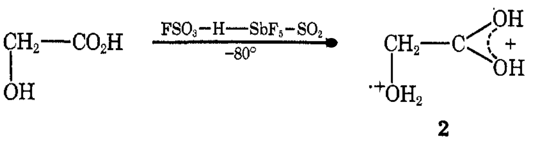


1a



1b

The nmr spectrum of **protonated glycolic acid** (2) in FSO_3H–SbF_5–SO_2 solution at −80° showed two low field singlets in the OH region at δ 14.2 (broad) and 13.5 (sharp) and another two singlets for the methylene protons at δ 6.10 and 5.96. The relative area ratio of the resonance at δ 6.10 and 5.96 is dependent on the acid concentration in SO_2. When the superacid concentration was increased in the sample, absorptions at lower field were increased at the expense of the higher field resonance. Furthermore, the OH protons at δ 14.2 are much more deshielded than those of protonated acetic acid. Hence we assign the absorptions at δ 14.2 and 6.10 to the protons on carboxylic oxygen and the methylene protons of the diprotonated species **2.**



2

The $^+OH_2$ protons of the diprotonated species are not observed and are probably covered by the acid solvent peak at δ 10.9 to 12.0, or exchanging. By studying further hydroxycarboxylic acids, such as **lactic acid** and **2-hydroxy-2-methylbutyric acid** (see Discussion), it is indicated that the absorptions at δ 13.5 and 5.90 are due

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[1] Part CVI: G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3908 (1970).

[2] National Institutes of Health Predoctoral Research Investigator, 1970.

[3] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967).

[4] G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

[5] G. A. Olah and E. Namanworth, *ibid.*, **88**, 5327 (1966).

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[7] G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

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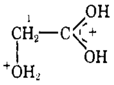
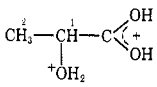
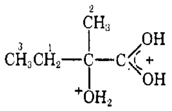
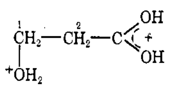
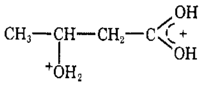
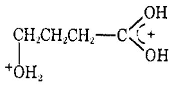
[12] G. A. Olah and A. Ku, *J. Org. Chem.*, **35**, 331 (1970).

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

TABLE I

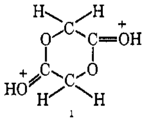
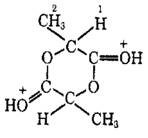
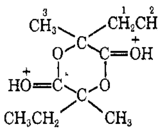
PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF HYDROXYCARBOXYLIC ACIDS IN FSO_3H-SbF_5 SOLUTION DILUTED WITH SO_2

Compd	Registry no.	°C	$\overset{+}{CO_2H_2}$	$\overset{+}{OH_2}$	H_1	H_2	H_3
	25951-46-6	−80	14.2[c]		6.10		
	25951-47-7	−60	14.1[d]		6.06	2.23 (d, 7.5)[e]	
	25951-48-8	−60	14.5[f]		2.55 (q, 7.5)	2.25	1.30 (t, 7.5)
	25951-49-9	−80	13.5		5.43	4.10	
		−30	13.4	10.8 (t, 4.0)	5.46 (m)	4.10 (t, 5.0)	
	25951-50-2	−60	13.1	10.4 (d, 3.8)	5.66 (m)	3.78 (d, 4.7) 3.80 (d, 6.5)	1.88 (d, 6.5)
	25951-51-3	−60	12.7	9.93 (t, 3.5)	5.03 (m)	3.48 (t, 7.0)	2.66 (qi, 7.0)

[a] In parts per million referred to external TMS. [b] In hertz as indicated following the multiplicity in the parenthesis. [c] Observed only below −70°. [d] Observed below −90°. [e] Multiplicity: d, doublet; t, triplet; q, quartet; qi, quintet; m, multiplet. [f] Observed only below −80°.

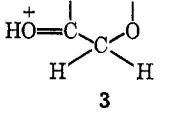
TABLE II

PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF PROTONATED LACTIDES FORMED FROM THE CORRESPONDING PROTONATED α-HYDROXYCARBOXYLIC ACIDS IN FSO_3H-SbF_5-SO_2ClF SOLUTIONS

Compd	Registry no.	°C	OH	H_1	H_2	H_3
	25966-55-6	−70	13.5	5.90		
	26039-36-1	−60	13.3	6.06 (m)	2.06 (d, 7.2)[c]	
	25966-56-7	−30	13.3	2.50 (q, 7.0)	1.21 (t, 7.0)	2.20 (s)

[a] In parts per million referred to external TMS. [b] In hertz as indicated following multiplicity in the parenthesis. [c] Observed only below −70°.

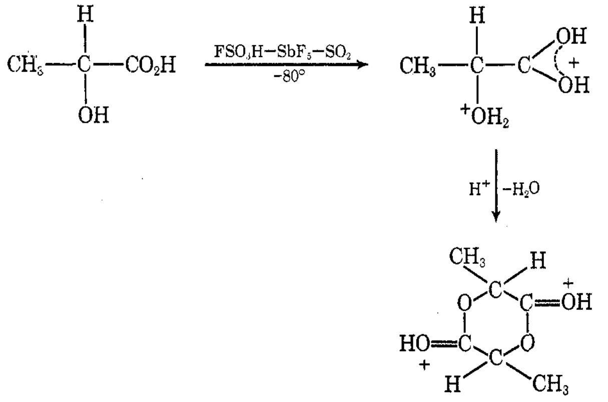
to the protons on oxygen and methylene protons of protonated 2,5-dioxo-1,4-dioxane (**3**) at −70°. Isolation



3

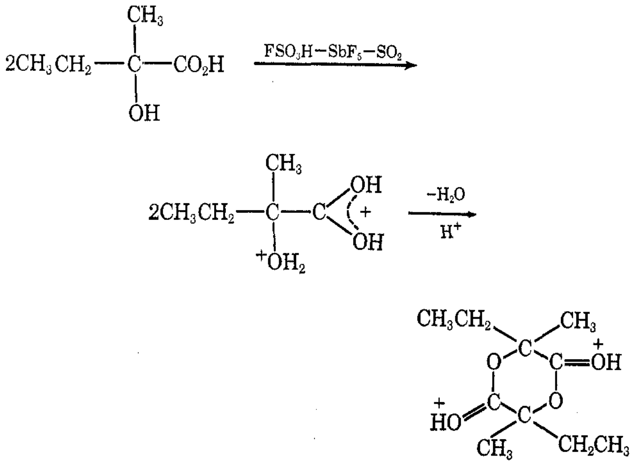
of lactides from the superacid solutions is difficult because they cannot be treated with water or hydroxylic solvents without solvolysis. The identity of the protonated lactides was, however, confirmed when authentic lactides were dissolved in FSO_3H-SbF_5-SO_2 solution −70° and gave identical pmr spectra (nmr data of protonated lactides are summarized in Table II).

Protonated lactic acid (added as the lithium salt) in FSO_3H-SbF_5 solution diluted with SO_2 at −80°, gave an nmr spectrum having the methyl doublet at δ 2.33, methine multiplet at δ 6.20 and a low field peak at δ 14.1. The resonance at δ 14.1 is assigned to the $-CO_2H_2^+$ protons and is much more deshielded than that of the OH protons of protonated propionic acid (δ 12.73)[7] indicating that lactic acid is diprotonated. The $^+OH_2$ protons again are not observed and are possibly overlapped by, or exchanging with, the acid solvent peak. As the temperature of the solution was increased to −60°, new peaks at higher field of each absorption appeared, which we believed to be due to the formation of protonated lactide **4**. The nmr spectrum at −60° showed the $C{=}\overset{+}{O}H$ singlet, methyl doublets, and the methine multiplets of protonated lactide **4** at δ 13.3, 2.06, and 6.06, respectively. At −30°, the rate of the formation of the protonated lactide is increased and readily goes to completion.



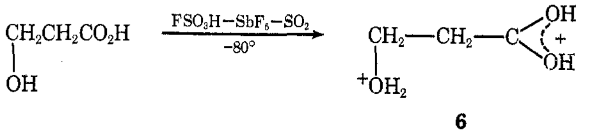
4

2-Hydroxy-2-methylbutyric acid in 1:1 $FSO_3H-SbF_5-SO_2$ solution is also diprotonated. At −80° the nmr spectrum showed a broad low field peak at δ 14.5 which is assigned to the $CO_2H_2^+$ protons. The $^+OH_2$ absorptions could be overlapped by or exchanging with the acid solvent peak at δ 11.4∼12.3 is not observed. The methyl triplet appeared at δ 1.30, ethyl quartet at δ 2.55, and the methyl singlet at δ 2.25. As the temperature of the solution increased to −30°, a new methyl triplet at δ 1.31, ethyl quartet at δ 2.50, and methyl singlet at δ 2.20 appeared, and all appeared at a higher field than those of protonated 2-hydroxy-2-methylbutyric acid. In addition, the nmr spectrum also showed a sharp singlet at δ 13.3, indicating that protonated 2-hydroxy-2-methylbutyric acid at −30° undergoes dehydration to give the 2,5-ethyl-2,5-methyl-3,6-oxo-1,4-dioxane (**5**). Conversion of protonated 2-hydroxy-2-methylbutyric acid to **5** goes to completion when the sample is kept at −30°.



5

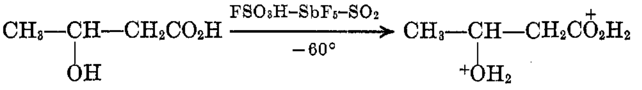
3-Hydroxypropionic acid (**6**) is diprotonated in FSO_3H-SbF_5 solution diluted with SO_2 at −80°. The $-CO_2H_2^+$ protons appear as a singlet at δ 13.5. The resonance of $^+OH_2$ is overlapping with the acid solvent peak at δ 10.7–11.2 at −80°. At −30°, as the acid solvent peak shifted to δ 11.0–11.3, the $^+OH_2$ absorption appeared as a triplet with a coupling constant of 4.0 Hz at δ 10.8. The chemical shifts and coupling constants of the methylene protons are summarized in Table I. Diprotonated 3-hydroxypropionic acid in $FSO_3H-SbF_5-SO_2$ solution is stable. The nmr spectrum showed no significant change from −80° to room temperature.



$$\underset{OH}{CH_2}CH_2CO_2H \xrightarrow[-80°]{FSO_3H-SbF_5-SO_2} \underset{^+OH_2}{CH_2}-CH_2-C\overset{OH}{\underset{OH}{\langle +}}$$

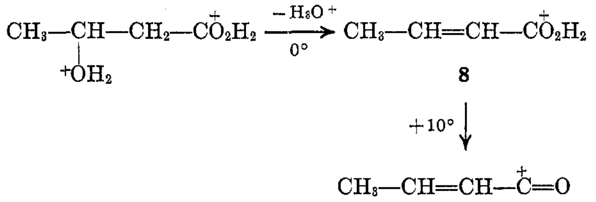
6

3-Hydroxybutyric acid in FSO_3H-SbF_5 solution with SO_2 as diluent, is also diprotonated (**7**). The $\overset{+}{C}O_2H_2$ protons appear as a singlet at δ 13.3 which could not be resolved even at a temperature as low as −100°. The $^+OH_2$ protons appear as a doublet with a coupling constant of 3.8 Hz at δ 10.5. The methine proton appeared as a multiplet at δ 5.9 and the two methylene protons appeared at δ 3.96 (doublet, J = 5.0 Hz) and δ 4.0 (doublet, J = 6.5 Hz). The methyl protons appeared as a doublet at δ 2.1. Protonated 3-hydroxybutyric acid is stable up to 0°. At higher temperature dehydration occurred (indicated by the strong intense H_3O^+ absorption at δ 10.25) to form protonated crotonic acid **8** which at +10° undergoes further dehydration to give the corresponding α,β-unsaturated oxocarbonium ion **9**.



$$CH_3-\underset{OH}{CH}-CH_2CO_2H \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} CH_3-\underset{^+OH_2}{CH}-CH_2\overset{+}{C}O_2H_2$$

7

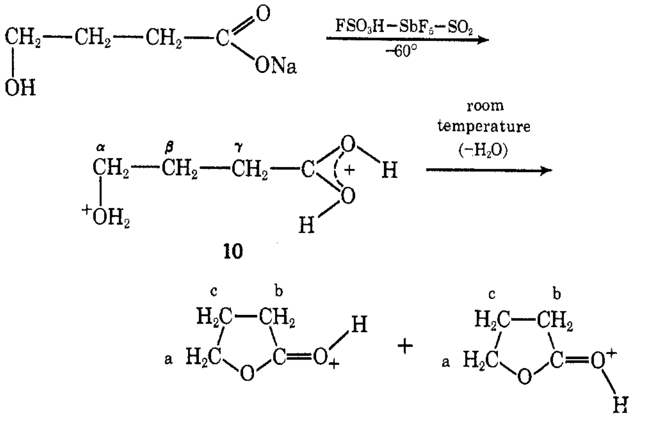


$$CH_3-\underset{^+OH_2}{CH}-CH_2-\overset{+}{C}O_2H_2 \xrightarrow[0°]{-H_3O^+} CH_3-CH{=}CH-\overset{+}{C}O_2H_2 \xrightarrow{+10°} CH_3-CH{=}CH-\overset{+}{C}{=}O$$

8

9

In "magic acid," **4-hydroxybutyric acid** (added as sodium salt) also undergoes diprotonation to give ion **10**. The nmr spectrum of **10** recorded at −60° showed the $-CO_2H_2^+$ and $^+OH_2$ protons at δ 2.17 and 9.93, respectively. The latter is a triplet with a coupling constant of 3.5 Hz, the former is resolved to two singlets at −70° indicating, as in the case of protonated simple carboxylic acids, that the two protons of $^+CO_2H_2$ are



10

11

magnetically nonequivalent. The α-methylene protons appeared as multiplet at δ 5.03, the γ-methylene protons as a triplet at δ 3.48, and the β-methylene protons centered at δ 2.66.

At room temperature, protonated 4-hydroxybutyric acid rearranged slowly to the corresponding protonated γ-butyrolactone **11**. The nmr spectrum of this solution cooled back to −80° showed the $\text{C}{=}\overset{+}{\text{O}}\text{H}$ proton at δ 12.25 and 12.03 with a relative area ratio of 75:25%, indicating that two isomeric species of protonated lactone **11** are formed. The three methylene groups a, b, and c of the protonated lactone appeared as triplets and quintet at δ 5.45 3.53, and 2.75, respectively. It is noted that the nmr spectrum showed no $-\overset{+}{\text{O}}\text{H}_2$ absorptions and of course the coupling between $-\overset{+}{\text{O}}\text{H}_2$ and the methylene protons is absent. The nmr spectrum is identical with that of the protonated authentical γ-butyrolactone.

Experimental Section

Materials.—All hydroxycarboxylic acids used in this study were commercially available materials.

Nmr Spectra.—Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra.

Preparation of Protonated Hydroxycarboxylic. Acids.—The procedure used for the preparation of solutions of protonated hydroxycarboxylic acids was identical with that described previously.[14]

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[14] G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).

Stable Carbonium Ions. CVIII. Protonated Lactones and Their Cleavage Reactions in Fluorosulfuric Acid–Antimony Pentafluoride Solution[1]

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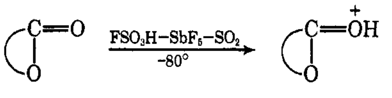
A series of lactones were protonated in fluorosulfuric acid–antimony pentafluoride solution at low temperature. With the exception of protonated δ-valerolactone, α-acetyl-γ-butyrolactone, coumarin, dihydrocoumarin, and 4-hydroxycoumarin, two isomeric species were found for all the protonated lactones studied. Structure assignments for these two isomers are proposed. Protonated lactones in $\text{FSO}_3\text{H–SbF}_5\text{–SO}_2$ solution are stable except protonated β-butyrolactone which undergoes alkyl–oxygen cleavage and deprotonation to give protonated crotonic acid at −40°. Protonated α-angelicalactone at −60° undergoes acyl-oxygen cleavage to give the corresponding protonated ketooxocarbonium ion.

In continuation of our preceding study of the protonation of hydroxycarboxylic acids,[1] we felt it of interest to study the protonation and cleavage reactions of lactones in $\text{FSO}_3\text{H–SbF}_5\text{–SO}_2$ solution.

Extensive kinetic studies were carried out on the hydrolysis of β-lactones.[3] With the exception of Hogeveen's recent report[4] of the behavior of α,α-dimethyl-β-propiolactone in hydrogen fluoride–boron trifluoride solution, no study of lactones in superacid media has been reported. We wish now to report such a systematic study of the protonation and cleavage reactions of lactones in superacid media.

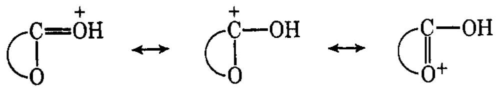
Results and Discussion

In $\text{FSO}_3\text{H–SbF}_5$ solution diluted with SO_2 generally at −80°, all the lactones studied, *e.g.*, β-propiolactone, β-butyrolactone, γ-butyrolactone, γ-valerolactone, α-bromo-γ-butyrolactone, α-bromo-γ-valerolactone, α-acetyl-γ-butyrolactone, δ-valerolactone, α-angelicalactone, coumarin, dihydrocoumarin, and 4-hydroxycoumarin, were protonated on the carbonyl oxygen atom.



The protonated lactones give well resolved pmr spectra. Assignments of the pmr chemical shifts and coupling constants of the parent and protonated lactones are summarized in Table I.

The proton on oxygen of protonated lactones occurs at lower field than those in protonated alcohols[5,6] and ethers[7] but are more shielded than those in protonated aliphatic ketones[8] and aldehydes,[9] similar to those in protonated alkylcarboxylic acids[10] and esters.[11] This is consistent with the partial double bond character in the protonated lactones.



With the exception of protonated δ-valerolactone, α-acetyl-γ-butyrolactone, coumarin, dihydrocoumarin, and 4-hydroxycoumarin, all the lactones studied gave two low field peaks in the $\text{C}{=}\overset{+}{\text{O}}\text{H}$ region at low temperature. This indicates the existence of hindered rotation about the C—O bond. In all cases no coupling was

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[3] For references, see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1965, Chapter 12.

[4] H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1303 (1968).

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[6] G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

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

[8] G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

[9] G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967).

[10] G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

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