Stable Carbonium Ions. XLIV.[1] The Cleavage of Protonated Aliphatic Carboxylic Acids to Alkyloxocarbonium Ions

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Abstract: A series of protonated aliphatic carboxylic acids has been studied in $HSO_3F–SbF_5–SO_2$ solution. O-Protonation was observed at −60° by nmr spectroscopy with negligible exchange rates. At higher temperatures, cleavage to oxocarbonium ions takes place. The kinetics of cleavage were measured for primary, secondary, and tertiary acids.

Earlier papers in this series have reported the nmr observation of protonated alcohols,[3] ethers,[4] thiols, and sulfides,[5] and their cleavage to carbonium ions in the strong acid system, $FSO_3H–SbF_5$. We now wish to report the observation of protonated aliphatic carboxylic acids in the same acid system and a study of the kinetics of their cleavage to oxocarbonium ions.

The nmr spectra of protonated acetic, propionic, and benzoic acids in $FSO_3H–SbF_5$ have been reported.[6] The equilibrium protonation of a number of carboxylic acids in sulfuric acid–oleum media, as well as the second ionization to form the acyl cation, has been studied.[7] In the latter study, the half-ionization acidity for protonation and cleavage was determined by observation of the downfield shifts in the nmr band positions of the acids.

Table I. Chemical Shifts (in ppm)[a] of Protonated Acids and Their Corresponding Oxocarbonium Ions

	Protonated acid, (*J*, cps)[b]				Oxocarbonium ion, (*J*, cps)[b]		
	OH	CH_3	CH_2	CH	CH_3	CH_2	CH
HCO_2H II	13.40, d (3.5)			9.70, t (3.5)			
III	13.57, d (3.5)			9.30, d of d			
	13.02, d (15.0)			(15.0 and 3.5)			
CH_3CO_2H	13.03						
	12.33	3.18			4.35		
$CH_3CH_2CO_2H$	12.73	1.95, t (7.0)	3.67, q (7.0)		2.42, t (7.0)	4.58, q (7.0)	
	12.43						
$CH_3(CH_2)_2CO_2H$	12.75						
	12.42	1.30, t (7.0)	2.15, sx (7.0)		1.60, t (7.0)	2.75, sx (7.0)	
			3.32, t (7.0)			4.45, t (7.0)	
$CH_3(CH_2)_3CO_2H$	12.98					2.27, m	
	12.65	1.5–2.7, m	3.58, t (6.5)		1.62, t (6.5)	2.90, p (6.5)	
						4.58, t (6.5)	
$(CH_3)_2CHCO_2H$	12.67						
	12.40	1.75, d (7.0)		3.52, sp (7.0)	2.22, d (7.0)		4.55, sp (7.0)
$(CH_3)_2CHCH_2CO_2H$	13.13	1.67, d (6.0)	3.45, d (6.0)	2.83, m	1.92, d (6.0)	4.52, d (6.0)	2.90, m
	12.75						
$(CH_3)_3CCO_2H$	12.60						
	12.42	2.11			2.58		

[a] Referred to external TMS. [b] Multiplicity: d, doublet; t, triplet; q, quartet; m, multiplet; p, pentuplet; sx, sextet; sp, septet.

In the strong acid system $FSO_3H–SbF_5$, all the aliphatic carboxylic acids studied were completely protonated and we were able to study their cleavage to the corresponding alkyloxocarbonium ions under nonequilibrium conditions.

$$RCO_2H \xrightarrow[-60°]{FSO_3H–SbF_5–SO_2} RCO_2H_2^+ \xrightarrow[\Delta,\ -H_2O]{FSO_3H–SbF_5–SO_2} RCO^+$$

Results and Discussion

The following aliphatic carboxylic acids were protonated in $FSO_3H–SbF_5–SO_2$ solution at −60°: formic, acetic, propionic, pivalic, *n*-butyric, isobutyric, valeric, and isovaleric acids.[7a]

The protonated acids give well-resolved nmr spectra in $FSO_3H–SbF_5$ diluted with SO_2, showing slow exchange rates at −60°. Figures 1–8 show these nmr spectra at −60°. Assignments of the nmr chemical shifts and coupling constants are summarized in Table I.

The protons on oxygen occur at lower field than in protonated alcohols[3] and ethers[4] but are more shielded than those in protonated aliphatic ketones and alde-

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[1] Part XLIII: G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586 (1967).

[2] National Institute of Health Postdoctoral Research Investigator, 1966–1967.

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

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

[5] G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *ibid.*, **89**, 2996 (1967).

[6] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

[7] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

[7a] Note Added in Proof. We recently succeeded in isolating methylcarboxonium hexafluoroantimonate, $CH_3CO_2H_2^+SbF_6^-$, as a crystalline salt from solutions of acetic acid in 1:1 molar $HF–SbF_5$ solution.

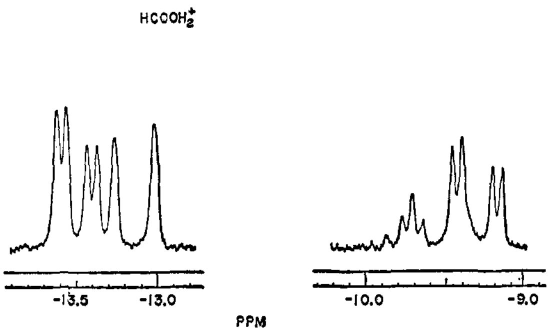


Figure 1.

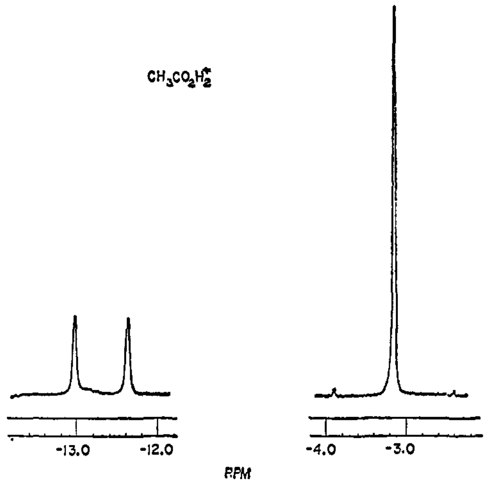
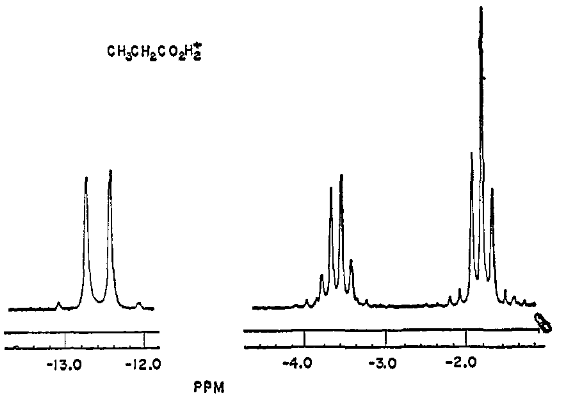


Figure 2.



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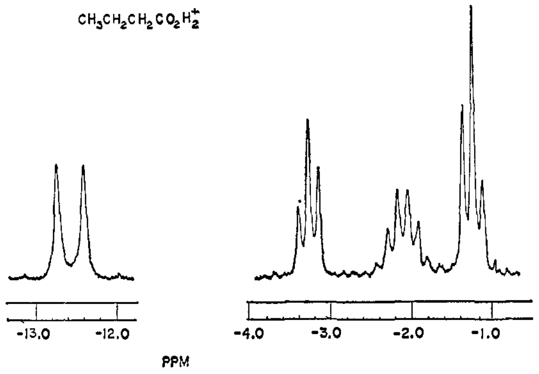

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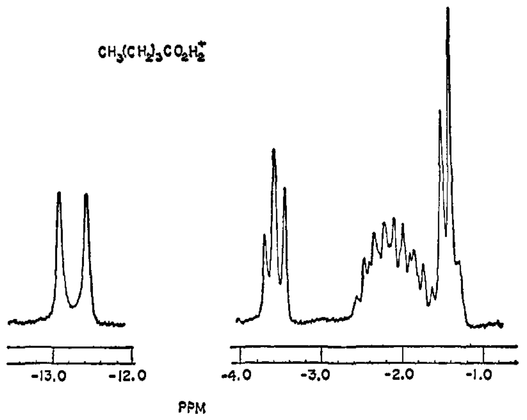
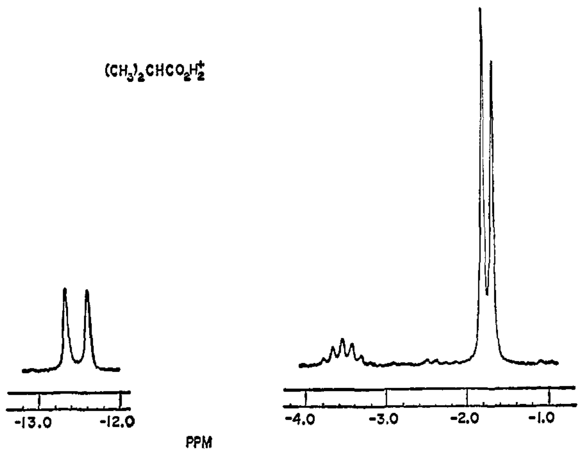


Figure 5.



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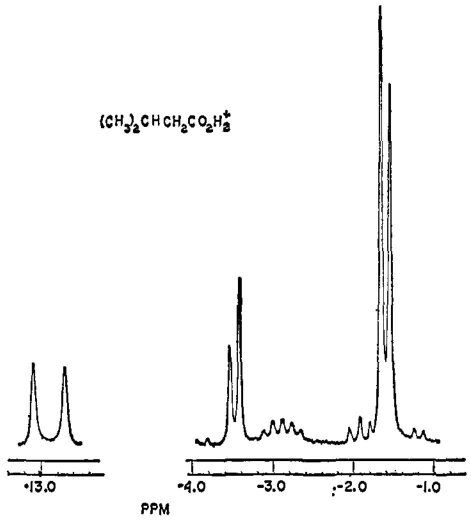
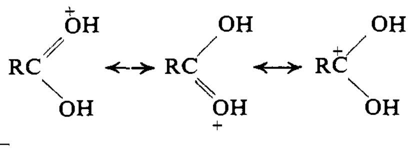


Figure 7.

hydes.[8] This is consistent with the partial double-bond character in the protonated acids.



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[8] See ref 1; G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582 (1967).

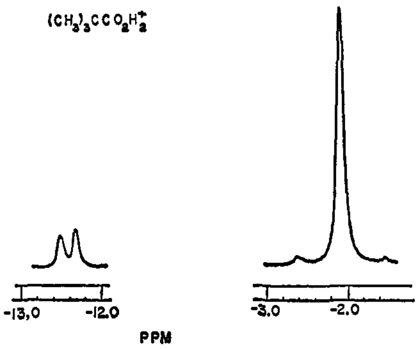
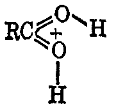


Figure 8.

With the exception of formic acid, all the acids studied had two peaks of equal area in the hydroxyl region at −60°. At higher temperature (*ca.* −30°) the two peaks collapse to a single resonance line with an average chemical shift, and at still higher temperature (*ca.* 0°) proton exchange with the solvent is sufficiently rapid to cause merging of the low-field signal with the solvent peak.

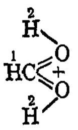
The nonequivalence of the hydroxyl protons at low temperature is interpreted as a result of the protonated acids having the structure I, as was suggested by Gillespie.[6]



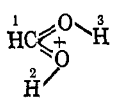
I

Since no coupling was observable in acetic acid and higher homologs the two nonequivalent hydroxyl protons could not be assigned. To help in elucidating this problem, we investigated the protonation of formic acid.[9]

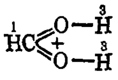
Two forms of protonated formic acid were observed corresponding to structures II and III.



II



III



IV

The cisoid structure II rather than the corresponding transoid structure IV is assigned on the basis of the coupling constant $J_{1,2}$ and comparison with the coupling constant in protonated aldehydes.[8] In structure III, the difference in the cisoid and transoid couplings $J_{1,2}$ and $J_{1,3}$ enables H_2 to be unambiguously assigned to the lowest field resonance (see Table I).

We find that structure III for the protonated formic acid predominates over structure II by a factor of about 2:1. Since this is the ratio required of a statistical distribution of the two forms, this result indicates that the two forms are of similar stability.[9a]

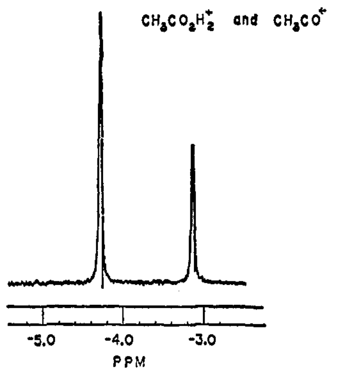


Figure 9.

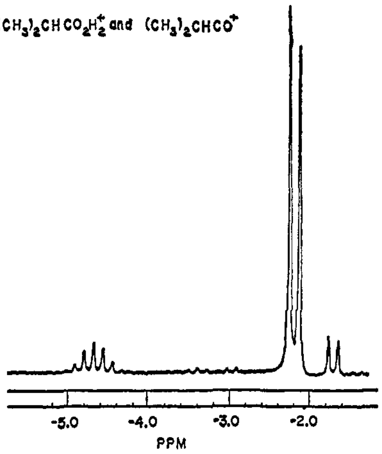


Figure 10.

When solutions of protonated aliphatic carboxylic acids were allowed to warm up to between −30 and 0°, the nmr spectra indicated cleavage to the corresponding oxocarbonium ions.[10] Figures 9–11 illustrate this in the case of acetic, isobutyric, and valeric acids. In all cases, the spectra for the oxocarbonium ion generated agreed well with those reported in an earlier paper in this series,[11a] although a medium effect causing a downfield shift was noted.

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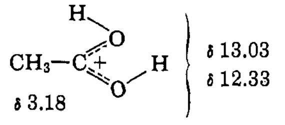
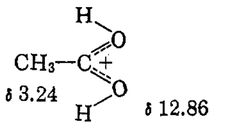
(9) After the conclusion of our investigation, the nmr spectrum of formic acid in HF-BF_3 was reported by H. Hogoveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean [*Chem. Commun.*, 898 (1966)], although in the solvent system used, part of the spectrum was obscured by the solvent peak.

(9a) Note Added in Proof. In a communication just published (M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967), two isomeric forms of protonated acetic acid were reported with identical methyl chemical shifts, based on the observation of a small (3% of the total O–H integration) second C–OH^+ singlet peak. The observation clearly was based on analogy with protonated formic acid. As seen from Figure 2, a shoulder at 12.86 ppm is present which, on reinvestigation (with Dr. M. Calin) and repeat time averaging in FSO_3H–SbF_5 (1:1) diluted with SO_2 at −80°, indeed can be substantiated to be a real resonance absorption of the siomeric ion V. It must be noted that



IV



V

the corresponding methyl resonance of ion V can also be observed at 3;27 ppm, thus 5.4 Hz deshielded from the methyl resonance in ion IV. Integration of the peak areas clearly indicates that we are indeed observing ion V, in which both the OH and CH_3 resonances are different from those in ion IV.

(10) The peak of variable intensity due to water is observed at 10.2 ppm. However, it has not yet been definitely established whether this resonance is due exclusively to H_3O^+ or to an intermediate hydrolysis product of the acid system FSO_3H–SbF_5. For simplicity, this peak as well as the main acid peak at 10.7 ppm were deleted from the spectra.

(11) (a) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, **85**, 1328 (1963); (b) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

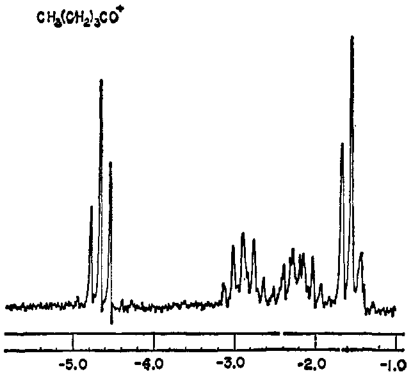


Figure 11.

The cleavage of a protonated acid to give an oxocarbonium ion is formally analogous to the rate-determining step in the $A_{Ac}1$ mechanism for the acid hydrolysis of esters.[11b] A particularly pertinent example is the hydrolysis of methyl benzoate in concentrated sulfuric acid which has been shown to be independent of the water concentration, in regions where it is known that the ester is completely protonated.[12] We thus expect, and indeed find, that the cleavage of protonated acids in $FSO_3H–SbF_5$ shows simple first-order kinetics. The rate of disappearance of the protonated acid and appearance of the oxocarbonium ion was followed by integration of appropriate peaks in the nmr spectrum.

$$RCO_2H_2^+ \xrightarrow[k_1]{FSO_3H-SbF_5} R\overset{+}{C}{=}O + H_3O^+$$

The rate constants evaluated for this reaction are compared in Table II and the Arrhenius parameters given in Table III. The entropy of activation for this process has been discussed,[13] and it was concluded that a small positive entropy of activation should be observed. Experimentally for the hydrolysis of esters, by this mechanism, this is indeed found, although a trend for the entropy change to decrease with increasing acidity is well known.[14] We consider the entropies of activation found for the cleavage of protonated acids are consistent in view of the strongly acidic solvent. The negative entropy changes may be interpreted as indicating a greater difference in solvation than in the weaker acid systems.

Table II. Relative Rates of Conversion of Protonated Acids to Oxocarbonium Ions[a]

$CH_3CO_2H_2^+$	1.00
$CH_3CH_2CO_2H_2^+$	1.46 ± 0.05
$(CH_3)_2CHCO_2H_2^+$	1.23 ± 0.06
$(CH_3)_3CCO_2H_2^+$	0.56 ± 0.02
$(CH_3)_2CHCH_2CO_2H_2^+$	1.15 ± 0.06

[a] Rates at −24° referred to acetic acid, errors determined by the method of least squares.

Table III. Activation Parameters Calculated at 0°

	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	No. of pts on plot
$CH_3CO_2H_2^+$	16.3 ± 1.5	−13.1 ± 5	5
$CH_3CH_2CO_2H_2^+$	14.8 ± 0.5	−18.6 ± 3	6
$(CH_3)_2CHCO_2H_2^+$	14.7 ± 0.3	−19.0 ± 3	6
$(CH_3)_3CCO_2H_2^+$	15.9 ± 0.5	−15.5 ± 3	6

[a] $\Delta H^{\ddagger} = E_a - RT$, units in kcal/mole. [b] $\Delta S^{\ddagger} = 4.576 \log A/T - 49.203$, time in seconds and entropy in standard units (eu).

The differences in the rate constants for primary, secondary, and tertiary carboxylic acid cleavage is small (Table II) and contrasts both in magnitude and reactivity sequence with the cleavage of ethers and alcohols in the same acid system. Deno's results[7] on the equilibrium protonation and ionization of carboxylic acids suggest that a secondary acyl cation (oxocarbonium ion) is more stable than a primary one and that a similar, although smaller, difference exists between the corresponding protonated acids. If this is still true in the acid system $FSO_3H–SbF_5–SO_2$, our results require that the relative stabilities be inverted in the transition state for the cleavage reaction.

Experimental Section

Materials. All acids were reagent grade commercial chemicals and used without further purification.

Nmr Spectra. A Varian A56-60A nmr spectrometer with variable-temperature probe was used for all spectra. The spectra of the protonated carboxylic acids were recorded using a 1:1 molar solution of $HSO_3F–SbF_5$ which had been saturated with SO_2 at 20°. Chemical shifts quoted in Table I are referred to external TMS. Temperature measurements were made by means of a thermometer constructed so as to fit the nmr tube used and checked by determining the chemical shift difference between the OH quartet and the methyl doublet of methanol. The rate of disappearance of the protonated acid and appearance of the acyl cation was followed by integration of appropriate peaks in the nmr spectrum. The ratio of the integral of the disappearing peak to the sum of the integrals of the two peaks measured was used in calculation of rate constants. This method allows for any variation in instrumental factors during the run. In no case did the sum of the two integrals show any significant trend with time, indicating that no decomposition was taking place. The disappearance of protonated acid was found to be first order. At least 20 integrals were used to evaluate the first-order rate constant. This rate constant was found to be reproducible and to be independent of the initial concentration of the carboxylic acid (Table IV).

Table IV. Effect of Concentration on First-Order Rate Constants

	$k_1 \times 10^2$, min^{-1} [a]	
	20:1[b]	10:1
$CH_3CH_2CO_2H_2^+$	1.77	2.10
$(CH_3)_2CHCO_2H_2^+$	1.55	1.47
$(CH_3)_3CCO_2H_2^+$	0.89	0.79

[a] Temperature −8.5°. [b] Molar concentration ratio of 1:1 $FSO_3H–SbF_5$ to acid.

Acknowledgment. Support of this work by a grant of the National Institutes of Health (GM 14082-01) is gratefully acknowledged.

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(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 771.

(13) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

(14) M. L. Bender, H. Ladenheim, and M. C. Chen, *J. Am. Chem. Soc.*, **83**, 123 (1961).