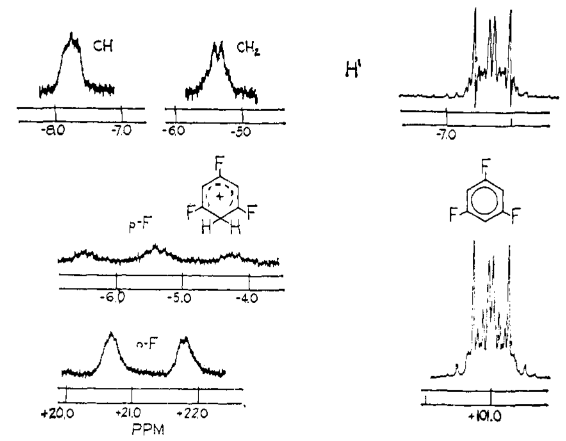
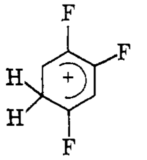
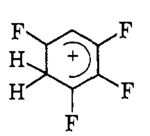


Figure 3. Proton and fluorine nmr spectra of 1,3,5-trifluorobenzene and its benzenonium ion.



VI



VII

We feel that the data obtained concerning nmr chemical shifts and coupling constants yield useful information about the charge distribution in benzenonium ions and about the nature of fluorine proton coupling. Copla, MacLean, and Mackor[11] have calculated the charge distribution in alkylbenzenonium ions based on the chemical shifts of methyl groups in various ring positions. Due to the large difference in chemical shifts of fluorine nuclei in the different ring positions in fluorobenzenonium ions, some similar calculation might lead to interesting conclusions about the ability of fluorine to polarize the π-electron system in reaction intermediates involving fluorinated rings. At the present time we are extending this investigation to include alkylfluorobenzenes, which, it is hoped, will yield useful information about the relative effects of fluorine and alkyl groups on such ions.

Experimental Section

Materials. Fluorobenzene, *m*-, *p*-, and *o*-difluorobenzene, 1,2,3,4- and 1,2,3,5-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene were commercially available materials and were used without further purification. Samples of 1,2,4- and 1,3,5-trifluorobenzene and 1,2,4,5-tetrafluorobenzene were generously made available by Dr. G. Finger, and we are grateful for his help.

Antimony pentafluoride (Allied Chemical Co.) was refluxed overnight while passing a stream of dry nitrogen over it. The material was then twice distilled (bp 150°). Fluorosulfonic acid (Allied Chemical Co.) was distilled (bp 160–164°) before use. The purified acids were stored in Teflon bottles.

Preparation of the Ions. Samples of the protonated fluorobenzenes for nmr studies were prepared by adding 2 ml of the HSO_3F-SbF_5 solution (the ratio of HSO_3F to SF_5 varied between 1:1 and 6:1) which had been cooled to −78° to 0.1–0.2 g of the fluorobenzene which had also been cooled to −78°. Upon warming, while shaking, a clear solution was obtained.

A Varian Associates Model A-56–60A nmr spectrometer equipped with a variable-temperature probe was used for all spectra.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

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[11] C. P. Copla, C. MacLean, and E. L. Mackor, *Tetrahedron*, **19**, *Suppl.*, **2**, 65 (1963).

Stable Carbonium Ions. LII.[1] Protonated Esters and Their Cleavage in Fluorosulfonic Acid–Antimony Pentafluoride Solution

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Received June 5, 1967

Abstract: A series of protonated esters was studied in $HSO_3F-SbF_5-SO_2$ solution. Carbonyl oxygen protonation was observed by nmr spectroscopy with negligible exchange rates. Spectral evidence was found for the existence of isomers of protonated formates. Kinetics of cleavage of a series of protonated methyl esters was studied. Both acyl oxygen and alkyl oxygen cleavage was observed for esters of primary aliphatic alcohols.

We have previously reported the observation of protonated aldehydes,[3] ketones,[4] and acids[5] by nmr spectroscopy. The protonation of esters and their cleavage under acidic conditions has been extensively investigated.[6] Birchall and Gillespie reported the nmr observation of protonated ethyl acetate in HSO_3F-SbF_5 solution at −75° and concluded that only carbonyl oxygen protonation takes place.[7]

We wish now to report the nmr observation of a series of protonated esters in the strongly acidic medium

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[1] Part LI: G. A. Olah and T. Kiovsky, *J. Am. Chem. Soc.*, **89**, 5692 (1967).

[2] (a) National Science Foundation Postdoctoral Research Investigator, 1966–1967. (b) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

[3] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. 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 A. M. White, *ibid.*, **89**, 3591 (1967).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, Chapter 14.

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

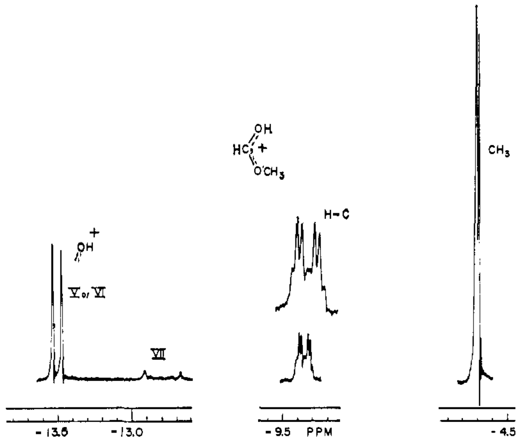


Figure 1.

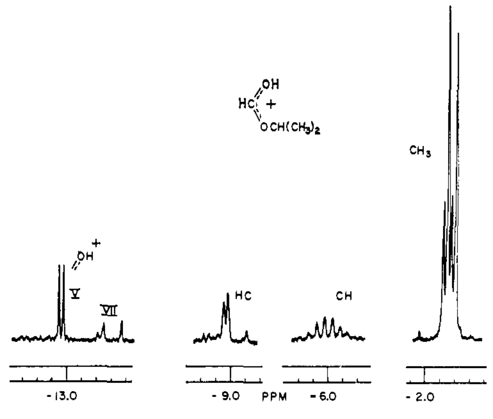


Figure 3.

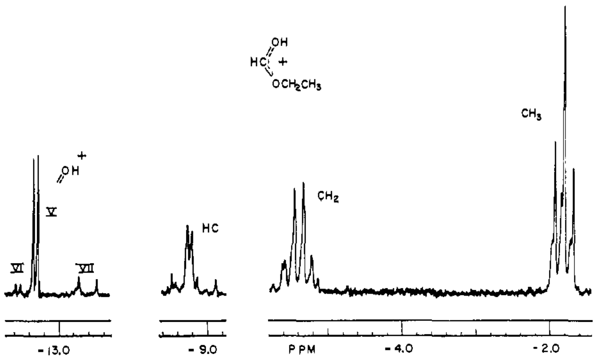


Figure 2.

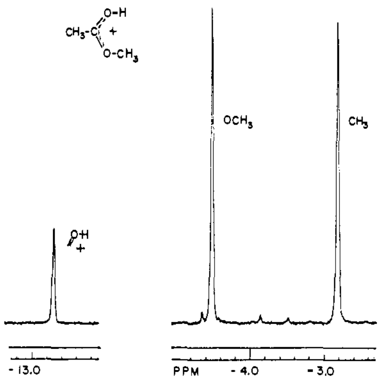
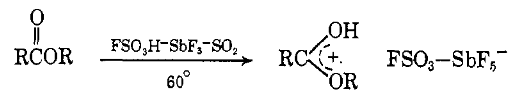


Figure 4.

HSO_3F–SbF_5 using SO_2 as diluent. Kinetics of cleavage of protonated esters, either to oxocarbonium ions and protonated alcohols *via* acyl oxygen cleavage or to protonated acids and carbonium ions *via* alkyl oxygen cleavage, allows further insight into the mechanism of ester cleavage.

Results and Discussion

Esters are protonated on the carbonyl oxygen in FSO_3H–SbF_5 solution diluted with SO_2 at −60°.



$$\overset{\mathrm{O}}{\overset{\|}{\mathrm{RCOR}}} \xrightarrow[60^{\circ}]{\mathrm{FSO_3H{-}SbF_5{-}SO_2}} \mathrm{RC}\overset{+}{\lessdot}{}^{\mathrm{OH}}_{\mathrm{OR}} \quad \mathrm{FSO_3{-}SbF_5^-}$$

The protonated esters give well-resolved nmr spectra with slow exchange rates.

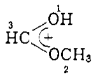
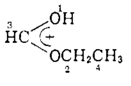
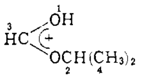
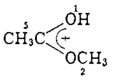
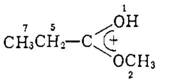
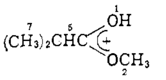
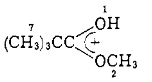
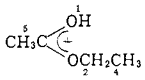
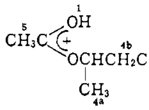
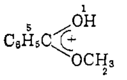
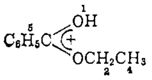
Protonated Formates. The proton on oxygen of protonated methyl formate (Figure 1) appears as a doublet at −13.50 ppm ($J_{\mathrm{H-O^+H}}$ = 3.5 Hz) coupled to the methine hydrogen. At lower temperatures (< −65°) another small doublet appears at −12.77 ppm ($J_{\mathrm{H-O^+H}}$ = 14.0 Hz). The methine hydrogen appears as a pair of overlapping quartets at −8.42 ppm, coupled to both the methyl group ($J_{\mathrm{H-CH_3}}$ = 0.9 Hz) and the proton on oxygen. In protonated ethyl formate (Figure 2) the proton on oxygen appears as three doublets. A pair of these doublets appears at −13.53 and −13.30 ppm with the same coupling constant to the methine hydrogen ($J_{\mathrm{H-O^+H}}$ = 3.5 Hz). The other doublet appears at −12.67 ppm ($J_{\mathrm{H-O^+H}}$ = 14.1 Hz). The methine hydrogen appears as a set of peaks at −9.20 ppm. The methyl group appears as a pair of overlapping triplets at −1.73 ppm. Protonated isopropyl formate (Figure 3) shows a pair of doublets for the proton on oxygen at −13.07 ppm ($J_{\mathrm{H-O^+H}}$ = 3.5 Hz), and at −12.37 ppm ($J_{\mathrm{H-O^+H}}$ = 14.2 Hz) coupled to the methine hydrogen. The methine hydrogen appears as a broad multiplet at −9.10 ppm and the terminal methyl groups as a pair of overlapping doublets at −1.67 ppm.

Protonated Acetates. Protonated acetates (Figure 4, Table I) show the proton on oxygen as a singlet at −12.47 to −12.72 ppm. No coupling of this proton with the acetyl methyl hydrogens or with the α-protons of the alkyl groups was observed.

Protonated Benzoates. The proton on oxygen in protonated benzoates appears as a singlet, slightly shielded when compared to the proton on oxygen in the corresponding acetates. Derived chemical shifts and coupling constants for the protonated esters are summarized in Table I.

The Structure of Protonated Esters. In the protonated formates studied, the main resonance due to the proton on oxygen appears between −13.50 and −13.07 ppm. At lower temperatures (−65 to −90°), smaller multiplets appear in this region, one additional doublet for methyl and isopropyl and two new doublets for ethyl formate. These smaller peaks are not caused by minor impurities or by decomposition of the formates under the condition of the experiment. These resonances were present even after repeated distillation of the formate. The primary formates show no appreciable cleavage even up to +10° in 1:1 HSO_3F–SbF_5. Furthermore, careful integration of the proton on oxygen region results in a value which is too low if

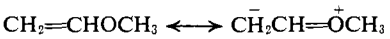
Table I. Nmr Chemical Shifts and Coupling Constants of Protonated Esters at −60° in $HSO_3F\text{-}SbF_5\text{-}SO_2$

	δ, ppm[a]						
Protonated ester	H_1 $J_{1,3}$, Hz	H_2 $J_{2,3}$, Hz	H_3	H_4	H_5	H_6	H_7
 $\overset{3}{H}C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−13.50 (2)[b] 3.6 −12.77 (2) 14.0	−4.73 (2) 0.9	−9.33 (2 × 4)				
 $\overset{3}{H}C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_2\underset{4}{C}H_3\end{matrix}\right.$	−13.53 (2) 3.5 −13.30 (2) 3.5 −12.67 (2) 14.1	−5.57 (cm)	−9.20 (2)	−1.73 (2 × 3)			
 $\overset{3}{H}C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH(\underset{4}{C}H_3)_2\end{matrix}\right.$	−13.07 (2) 3.5 −12.37 (2) 14.2	−6.00 (cm)	−9.10 (cm)	−1.67 (2 × 2)			
 $C\overset{5}{H}_3C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−12.72 (1)	−4.53 (1)			−2.83 (1)		
 $C\overset{7}{H}_3C\overset{5}{H}_2\text{—}C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−12.62 (1)	−4.68 (1)			−3.24 (4)		−1.43 (3)
 $(C\overset{7}{H}_3)_2C\overset{5}{H}C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−12.58 (1)	−4.63 (1)			−3.35 (7)		−1.48 (2)
 $(C\overset{7}{H}_3)_3CC\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−12.25 (1)	−4.60 (1)					1.50 (1)
 $C\overset{5}{H}_3C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_2\underset{4}{C}H_3\end{matrix}\right.$	−12.47 (1)	−4.95 (4)		−1.48 (3)	−2.75 (1)		
 $C\overset{5}{H}_3C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH(\underset{4a}{C}H_3)\overset{4b}{C}H_2\overset{6}{C}H_3\end{matrix}\right.$	−12.53 (1)	−5.63 (cm)		a, −1.48 (2) b, −1.80 (cm)		−0.93 (3)	
 $C_6\overset{5}{H}_5C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_3\end{matrix}\right.$	−12.47 (1)	−4.68 (1)			−8.10 (cm)		
 $C_6\overset{5}{H}_5C\left\{\begin{matrix}\overset{1}{O}H\\ +\\ \underset{2}{O}CH_2\underset{4}{C}H_3\end{matrix}\right.$	−12.23 (1)	−5.17 (4)		−1.63 (3)	−8.17 (cm)		

[a] From external capillary of TMS. [b] Figures in parentheses represent multiplicity of peaks; cm, complex multiplet.

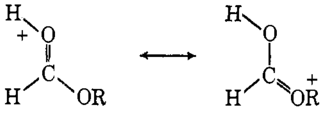
these smaller peaks are not included. Protonated isopropyl formate does cleave very slowly to protonated formic acid by alkyl oxygen cleavage (AAL1) at −70°. However, freshly distilled isopropyl formate shows a small doublet at −12.37 ppm when the spectrum of the protonated formate is taken quickly, before appreciable reaction has taken place.

It has been noted before that the size of the *cis* and *trans* coupling constants appears to be a qualitative measure of the double bond character in protonated carbonyl compounds[3–5] and protonated imines[8] as well as in conjugated alkenes.[9] In uncharged olefinic systems such as I, in which delocalization is expected, the size of the *cis* coupling constant is reduced (Table II).


$CH_2{=}CHOCH_3 \longleftrightarrow \overset{-}{C}H_2CH{=}\overset{+}{O}CH_3$

I

Although the isoelectronic protonated carbonyls differ from I by the presence of a heteroatom and a positive charge, this trend is still apparent. The *cis* coupling constant for protonated formic acid is 3.5 Hz compared to 8.7 Hz for protonated formaldehyde. In the present work, the coupling constant for protonated formates are the same as for protonated formic acid, indicating extensive delocalization throughout the system (II ↔ III). It is interesting to note that the chemical shift of the proton on oxygen in protonated esters (−12.2 to −13.5 ppm) is intermediate between that of protonated aldehydes[3] and ketones[4] (∼−15 to −16 ppm) and that of protonated ethers[10] (∼−9.0 ppm). This also demon-



II III

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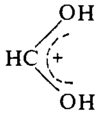
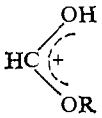
(8) G. A. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.*, **89**, 4756 (1967).

(9) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Resonance Spectroscopy," Vol. II, Pergamon Press, Inc., Oxford, 1967, pp 710–749.

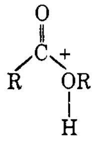
(10) G. A. Olah and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 1725 (1967).

Table II. Coupling Constants for Conjugated Alkenes and Protonated Carbonyl Compounds

Compd	J_{cis}, Hz	J_{trans}, Hz	Lit.
$H_2C{=}CHCH_3$	10.2	17.0	*a*
$H_2C{=}CHOCH_3$	6.6	14.4	*b*
$H_2C{=}\overset{+}{O}H$	8.7	21.1	3
$RHC{=}\overset{+}{O}H$	8.9	19.5	3
$RHC{=}\overset{+}{N}HR$	. . .	17.4	8
	3.5	15.0	5 and *c*
	3.5	14.1	This work

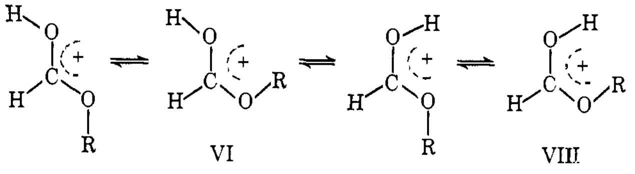
[a] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961). [b] J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962). [c] H. Hogoveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean, *Chem. Commun.*, 898 (1966).

strates the delocalization of charge and, taken together with the absence of coupling between the proton on oxygen and the α-hydrogens of the alkyl group, eliminates the presence of structure IV as a major form.



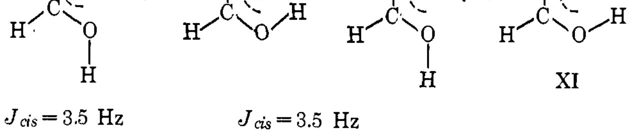
IV

The partial double bond character of both carbon-oxygen bonds and the observation of as many as three OH^+ resonances for the proton on oxygen imply the presence of isomers in protonated formates. Similar isomerization has been observed in other protonated carbonyls.[3-5] Four isomers for protonated formates can be drawn (V-VIII). When the size of the coupling



V VI VII VIII

constants for the isomers of protonated formates is compared to similar couplings for the three possible isomers of protonated formic acid (IX-XI), tentative structural assignments can be made.



$J_{cis} = 3.5$ Hz

IX

$J_{cis} = 3.5$ Hz

$J_{trans} = 15.0$ Hz

X

XI

In protonated methyl formate, one *cis* isomer (J_{H-O^+H} = 3.6 Hz) predominates and at lower temperatures ($<-70°$) there is an indication of a small amount of a *trans* isomer (J_{H-O^+H} = 14.0 Hz) (Figure 1). It is not possible to definitely assign the structure of this *cis* isomer to either V or VI. The *trans* isomer is most probably VII, since the corresponding isomer is observed in protonated formic acid (X), while the all-*trans* form for protonated formic acid (XI) was not observed. These isomers (VIII and XI) are presumed to be sterically unfavorable.

The lowest field resonance in protonated formic acid was assigned to the *cis* proton on oxygen (X). The *cis* proton of isomer IX was found 0.17 ppm to higher field.

In protonated ethyl formate (Figure 2) we observed two isomers having *cis* coupling constants of 3.5 Hz separated by 0.23 ppm. Consistent with the assignments for protonated formic acid, the smaller, low-field *cis* resonance can be assigned to isomer VI and the dominant upfield *cis* resonance to isomer V. Protonated ethyl formate also shows a small resonance due to one of the *trans* isomers, again most probably isomer VII.

Protonated isopropyl formate (Figure 3) shows one *cis* and one *trans* isomer. From the preceding discussion, it appears reasonable that the energetically favored isomer for protonated formates is represented by structure V. The isomer distribution for protonated ethyl formate was 82% for V, 12% for VI, and 6% for VII between -40 and $-80°$ and showed little variation in this temperature range.

For the other protonated esters studied, only one resonance for the proton on oxygen was observed. This appears as a singlet between -12.25 and -12.72 ppm. Because of the absence of coupling of this proton with other hydrogens in these esters, no definite isomer assignment can be made.

Cleavage of Esters. In strong acid systems, cleavage of esters is assumed to occur by a unimolecular mechanism, either with alkyl oxygen or acyl oxygen scission. In view of the fact that this cleavage corresponds to the rate-determining step in either the AAcl or the AAl1 mechanism for ester hydrolysis,[11,12] we felt it of interest to study the rates and mode of cleavage for a number of esters.

Methyl Esters. Protonated esters of primary alcohols are relatively stable even at 0° to room temperature. The nmr spectrum of protonated methyl formate showed no change indicative of cleavage even after 16 hr in 1:1 HSO_3F-SbF_5 at room temperature. Protonated methyl acetate, methyl propionate, methyl isobutyrate, and methyl pivalate are much less stable than protonated methyl formate and begin to cleave above 0° in 1:1 HSO_3F-SbF_5. At these temperatures the proton on oxygen could still be observed, indicating that the exchange rate is still slow. The kinetics of cleavage of methyl acetate, methyl propionate, methyl isobutyrate, and methyl pivalate were followed in 1:1 FSO_3H-SbF_5 between 0 and 40°. All were found to go completely to protonated methanol and the corresponding oxocarbonium ion (Figure 5). The rates were measured by following the disappearance of the protonated ester and the appearance of the oxocarbonium ion and all showed

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(11) Reference 6, p 771.

(12) A. G. Davies and J. Kenyon, *Quart. Rev.* (London), 203 (1955).

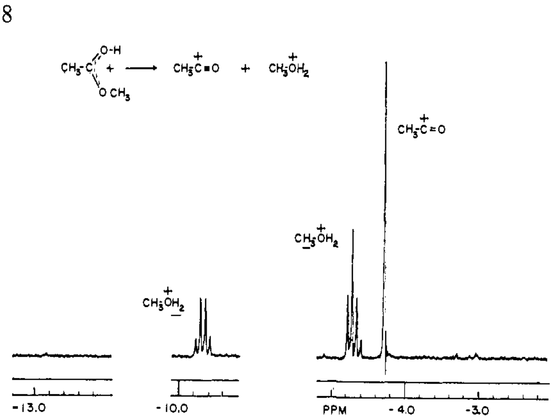
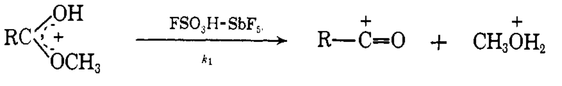


Figure 5.

first-order kinetics. The rate constants evaluated for this reaction are shown in Table III and are compared to the corresponding rates for protonated acids[5] in Table IV. The activation parameters evaluated from Arrhenius plots of the data are given in Table V.



$$\mathrm{RC}(\overset{+}{\mathrm{O}}\mathrm{H})\mathrm{OCH_3} \xrightarrow[k_1]{\mathrm{FSO_3H\text{-}SbF_5}} \mathrm{R{-}\overset{+}{C}{=}O} + \mathrm{CH_3\overset{+}{O}H_2}$$

Table III. Rates of Cleavage of Protonated Methyl Esters at 30°

Ester	$k_1 \times 10^4$, sec^{-1}	Rate relative to $\mathrm{CH_3COOCH_3}$
$\mathrm{CH_3COOCH_3}$	8.31	1.00
$\mathrm{CH_3CH_2COOCH_3}$	12.6	1.52
$\mathrm{(CH_3)_2CHCOOCH_3}$	12.2	1.47
$\mathrm{(CH_3)_3CCOOCH_3}$	3.27	0.39

Table IV. Comparative Rates of Cleavage of Protonated Esters and Acids at 13°[a]

$\mathrm{RCOOH_2^+}$ or $\mathrm{RCOOHCH_3^+}$, R	k_1(acid) $\times 10^4$ sec^{-1}	k_2(ester) $\times 10^4$ sec^{-1}	k_1(acid)/k_1(ester)
$\mathrm{CH_3}$	32.9	0.794	44.5
$\mathrm{CH_3CH_2}$	30.7	1.51	20.3
$\mathrm{(CH_3)_2CH}$	24.7	1.58	17.3
$\mathrm{(CH_3)_3C}$	14.7	0.479	30.7

[a] Extrapolated from Arrhenius plot.

Table V. Activation Parameters for Cleavage of Protonated Methyl Esters at 0°

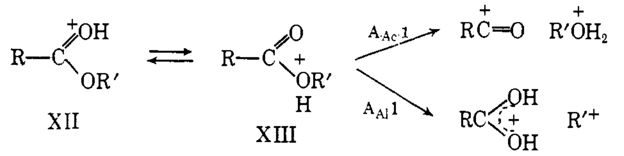
Ester	$\Delta H^{\ddagger}$,[a] kcal/mole	$\Delta S^{\ddagger}$,[b] eu	No. of points on plot
$\mathrm{CH_3COOCH_3}$	22.6	+1.4	5
$\mathrm{CH_3CH_2COOCH_3}$	20.5	−3.9	5
$\mathrm{(CH_3)_2CHCOOCH_3}$	19.8	−6.2	5
$\mathrm{(CH_3)_3CCOOCH_3}$	18.7	−12.6	6

[a] $\Delta H^{\ddagger} = E_a - RT$. [b] $\Delta S^{\ddagger} = 4.576 \log (A/T) - 49.203$.

The enthalpy of activation for cleavage of the investigated series of methyl esters is about 6 kcal/mole higher than for the corresponding carboxylic acids[5] under similar conditions. This is in accord with the electron-donor properties of the methyl group compared to hydrogen which would be expected to retard acyl oxygen cleavage.[13,14] Similarly, electron-donor groups in the acyl fragment should accelerate the reaction and the small decrease found in the enthalpy of activation in the series acetate, propionate, isobutyrate, pivalate is to be expected. In the light of this, the decrease in the rate constants in going from propionate to isobutyrate to pivalate is unexpected. Considering only the electron-donor properties of the *t*-butyl group compared to methyl, methyl pivalate would be expected to cleave with greater ease than methyl acetate. In both the protonated esters and corresponding protonated carboxylic acids, the reverse is true.

Apparently the predominant effect on the first-order rate constants for this cleavage is the entropy of activation which, while consistent with a unimolecular mechanism,[15] shows a trend toward increasing negative values for $\Delta S^{\ddagger}$ with increased branching in the acyl portion.

The proposed mechanisms for AAc1 and AAl1 hydrolysis of esters have been based on the assumption that the ester is protonated on the ether oxygen (XIII).[11]

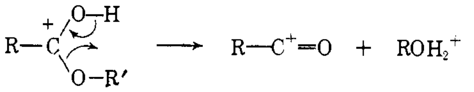


XII

XIII

In the present work, no evidence for any coupling of the proton on oxygen to the α-hydrogens of the alkyl group is observed even at temperatures as low as −90°. This indicates predominant carbonyl oxygen protonation (XII), although this does not exclude reaction *via* small, undetectable, equilibrium concentrations of XIII.

An alternative possibility is a one-step mechanism involving a simultaneous proton transfer and acyl oxygen fission.



The available data does not make it possible to differentiate between these closely similar mechanisms. A third possibility, that the reaction proceeds *via* a diprotonated species, can be ruled out on the grounds that the rate would be expected to decrease with decreasing acidity due to a reduction in the concentration of any small amount of diprotonated species. As a test of this possibility, the rate of cleavage of methyl acetate was measured in 1:1 and 2:1 $\mathrm{FSO_3H\text{-}SbF_5}$ and found to be the same.

Ethyl Esters. Studying the cleavage of ethyl acetate in $\mathrm{HSO_3F\text{-}SbF_5}$ at 20°, we noted a decrease in the first-order rate constant in going from 1:1 to 2:1 acid ($k_1 = 1.7 \times 10^{-3}$ sec^{-1} in 1:1 compared to 0.52×10^{-3} sec^{-1} in 2:1). Diluting a sample of partially cleaved protonated ethyl acetate with $\mathrm{SO_2}$ and cooling to −60°, we observe several new peaks in the nmr spectrum (Figures 6 and 7). The new peak at −3.00 ppm, close to the acyl methyl peak of the protonated ester, can be assigned to protonated acetic acid. The deshielded proton on

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(13) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, 37, 686 (1941).

(14) J. A. Leisten, *J. Chem. Soc.*, 1572 (1956).

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

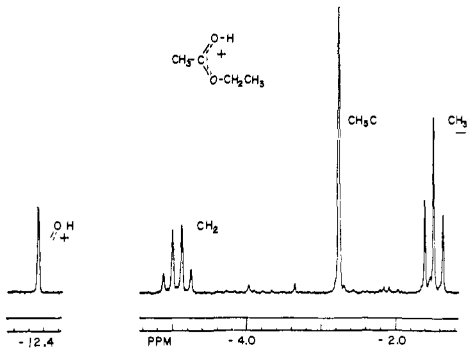
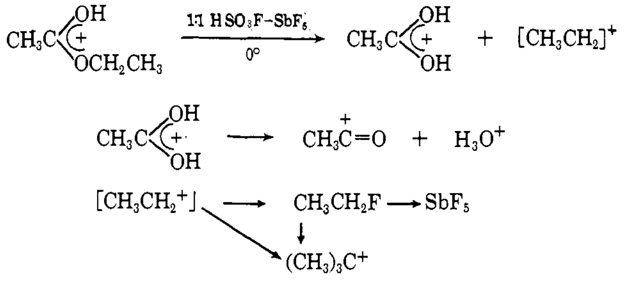


Figure 6.

oxygen of protonated acetic acid can be seen beside the proton on oxygen of the protonated ester. The large peak at −4.07 ppm can be assigned to the methyloxocarbonium ion. A new triplet appears at −2.00 ppm and a quartet appears at −6.32 ppm which can be assigned as being ethyl fluoride in the form of an exchanging donor–acceptor complex with antimony pentafluoride. Ethyl fluoride shows a triplet at −1.95 ppm and a quartet at −6.25 ppm when dissolved in 1:1 $HSO_3F-SbF_5-SO_2$ at −60°.(16) Another new quartet appears at 5.55 ppm. Its assignment is not certain but can probably be attributed to the methylene group of an ethyl compound resulting from a secondary reaction of ethyl cation (methylcarbonium ion) formed in the acid system. If the reaction is allowed to go to completion, these ethyl species react further and are replaced by a peak at −3.97 ppm which can be assigned to the trimethylcarbonium ion. It is important to note that there is no indication in the nmr spectrum of protonated ethanol when the reaction is carried out in 1:1 acid at 0°.

The first-order rate constant for the cleavage of protonated ethyl acetate, as determined by the disappearance of the acyl methyl singlet, was found to be 2.7×10^{-4} sec^{-1} at 0° in 1:1 acid. This is about ten times faster than the rate of cleavage of protonated methyl acetate under the same conditions. If protonated ethyl acetate were to cleave *via* acyl oxygen fission, the rate would be expected to be less than that of methyl acetate due to the enhanced electron-donor properties of ethyl as compared to methyl.[14] Acyl oxygen cleavage would also require the formation of protonated ethanol and this was not observed in 1:1 FSO_3H-SbF_5. The possibility that protonated ethanol is not stable under the reaction conditions was considered. It was found, however, that ethanol, either in 1:1 FSO_3H-SbF_5 alone or in the presence of ethyl acetate, gave the trimethylcarbonium ion at a rate about 100 times slower than the ethyl acetate cleavage. This demonstrates that protonated ethanol was not a product of the ethyl acetate cleavage reaction.

We rationalize these observations as showing that protonated ethyl acetate cleaves by alkyl oxygen fission giving protonated acetic acid and the ethyl cation (methylcarbonium ion). Protonated acetic acid reacts further at 0° to give methyloxocarbonium ion. The ethyl cation reacts with the acid system to form the complex of ethyl fluoride–antimony pentafluoride in the early part of the cleavage reaction. This complex and other ethyl compounds react slowly at 0° to give trimethylcarbonium ion. The reaction sequence is shown below.



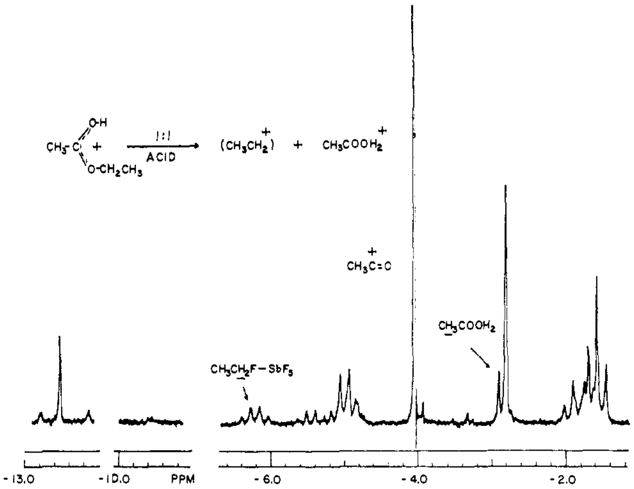


Figure 7.

The ease of alkyl oxygen cleavage (AAL1) appears to be related to the stability of the resultant carbonium ion. Thus esters of tertiary aliphatic esters hydrolyze *via* the AAL1 mechanism.[12] The alkyl oxygen cleavage of ethyl acetate is the first example of a primary aliphatic ester undergoing this mode of fission, the only other examples being the ethyl esters of 4-chloro-3-nitro- and 3,5-dinitrobenzoate in which the strongly electron-withdrawing group in the phenyl ring leads to alkyl oxygen fission being observed in 99.9% sulfuric acid.(17)

With the object of attempting to observe a transition from alkyl oxygen to acyl oxygen cleavage, we carried out the reaction in 2:1, 3:1, and 4:1 molar FSO_3H-SbF_5 at 0°. In these acid systems we observed progressively greater amounts of protonated ethanol (Figure 8) as well as the methyloxocarbonium ion. In the 4:1 acid, *t*-butyl cation was not observed. Under these acid conditions, after several days at 0° some protonated ethyl acetate remains, indicating that the cleavage does not go to completion. Thus, under conditions of lower acidity we are able to observe the slower acyl oxygen cleavage leading to the formation of protonated ethanol and methyloxocarbonium ion.

Esters of Secondary and Tertiary Alcohols. Protonated secondary esters were found to cleave exclusively by the AAL1 mechanism between −40° and −20° to protonated acids and stable tertiary carbonium ions. For example, *sec*-butyl acetate reacts cleanly at −30° to give protonated acetic acid and *t*-butyl cation (Figure 9 and 10).

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(16) G. A. Olah and M. B. Comisarow, unpublished results.

(17) D. N. Kershaw and J. A. Leisten, *Proc. Chem. Soc.*, 84 (1960).

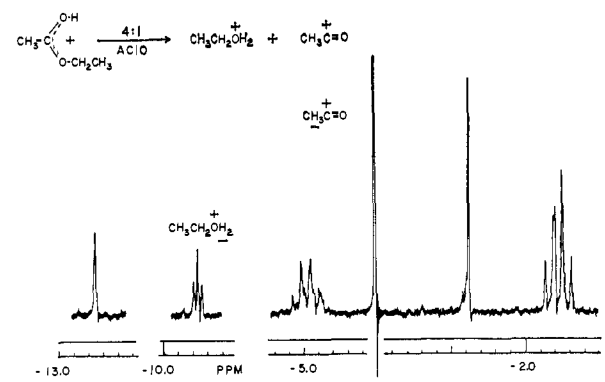


Figure 8.

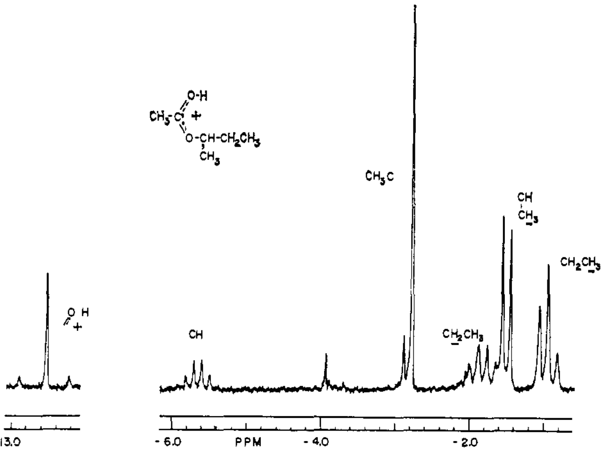
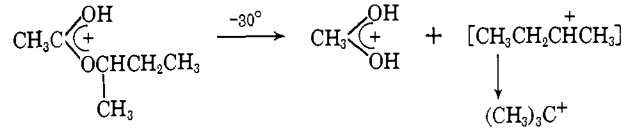


Figure 9.

The protonated acid goes to the oxocarbonium ion only very slowly under these conditions and its observation is proof of alkyl oxygen cleavage.



$$CH_3C\overset{OH}{\underset{OCH(CH_3)CH_2CH_3}{\langle\!+}} \xrightarrow{-30°} CH_3C\overset{OH}{\underset{OH}{\langle\!+}} + [CH_3CH_2\overset{+}{C}HCH_3] \longrightarrow (CH_3)_3C^+$$

Esters of tertiary alcohols were found to cleave so rapidly that only the protonated acid and the tertiary carbonium ions could be observed even at −80°.

Experimental Section

Materials. All esters were either commercially available materials or were prepared by standard literature methods and purified by distillation.

Nmr Spectra. Varian Associates Model A-56-60A and HA 60-IL nmr spectrometers with variable-temperature probes were used for all spectra. Coupling constants (Table II) are believed accurate to ±0.1 Hz.

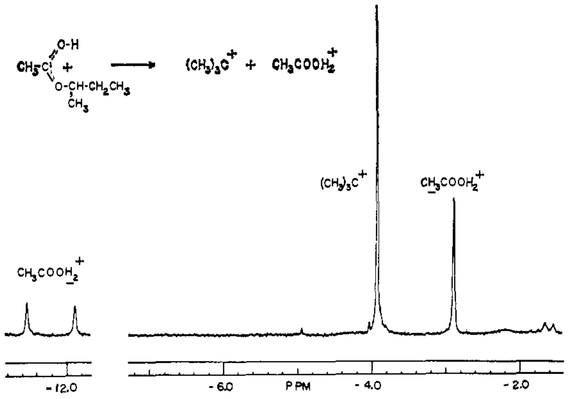


Figure 10.

Preparation of Protonated Esters. Samples of protonated esters were prepared by dissolving approximately 1.5 ml of HSO_3F-SbF_5 (1:1) molar solution in an equal volume of sulfur dioxide and cooling to −76°. The ester (approximately 0.2 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −76°, and with vigorous agitation slowly added to the acid solution. Samples prepared in this manner gave nmr spectra which showed no appreciable chemical shift differences with temperature or small concentration variations. The acid was always in large excess as indicated by the large acid peak at about −10.9 ppm. For simplicity, the acid peaks (including a minor peak at −10.3 ppm due to water as impurity in the system) were deleted from Figures 1–10.

Kinetic Measurements. Solutions of the esters for rate measurements were prepared by adding the ester to the acid solvent at −80°, in a 1:10 molar ratio. Aliquots of this solution were transferred to nmr tubes and the rates of cleavage followed at several temperatures. The rate of disappearance of the ester and appearance of the oxocarbonium ion was determined 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. Rate data were fitted to the first-order rate law in the usual manner. In all cases, plots were obtained which were linear over at least two half-lives. For the evaluation of the Arrhenius parameters, rate constants were determined for at least five different temperatures over a range of 25°. Temperature measurements were made at the beginning and end of each kinetic run by means of a calibrated thermometer constructed to fit the nmr tube used. Temperature equilibration was estimated from the initial curvature of the rate plots to be of the order of 1 min. Temperature measurements are believed to be accurate to within ±0.5°. Calculation of standard deviations of the rate constants by the method of least squares showed them to have a reliability of ±3%. Similar treatment of the Arrhenius parameters gave limits of precision for the activation energy of ±0.5 kcal and for the entropy of activation of ±2 eu.

Isomer Distribution. Because of the low concentration of two of the isomers of protonated ethyl formate, the isomer distribution was calculated between −40 and −80° from the integration of at least 16 sweeps of the proton on oxygen region using a Varian C-1024 time-averaging computer.

Acknowledgment. Support of the work by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged.