Stable Carbonium Ions. XXXIII.[1a] Primary Alkoxycarbonium Ions

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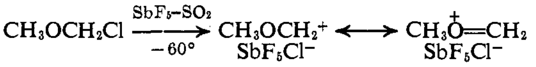
Abstract: Several primary alkoxy- and alkoxyhalocarbonium ions were directly observed by nmr spectroscopy in the solvent system antimony pentafluoride–sulfur dioxide. Methoxychloro- and methoxyfluorocarbonium ions were found to exist in isomeric forms indicating a rotational barrier around the C–O bond. In the nmr spectra of methoxy- and chloromethoxycarbonium ions nonequivalence of the methylene protons was not observed. Chloromethoxycarbonium ion exhibited a temperature-dependent spectrum because of intermolecular exchange.

Secondary and tertiary alkoxycarbonium ions were first prepared by Meerwein, *et al.*,[2] by alkylation of ketones, esters, and lactones with trimethyloxonium or triethyloxonium tetrafluoroborate or by abstraction of hydride ion from acetals and orthoesters. Recent papers by Ramsey and Taft,[3] Hart and Tomalia,[4] Dimroth and Heinrich,[5] and Kabuss[6] reported on the direct observation (nmr) or isolation of a series of additional secondary and tertiary alkoxycarbonium ions.

We would like to report now our results relating to the observation of stable primary alkoxy- and haloalkoxycarbonium ions. No primary alkoxycarbonium ions were known from the literature. The only other stable long-lived primary carbonium ions reported are benzyl cations.[7]

Results and Discussion

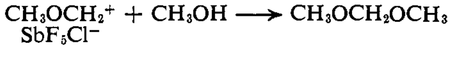
When chloromethyl methyl ether is dissolved in antimony pentafluoride diluted with sulfur dioxide, a stable clear solution is obtained. The pmr spectrum of this solution at −60° (Figure 1) clearly indicates the formation of the methoxycarbonium ion (I).



$$CH_3OCH_2Cl \xrightarrow[-60^\circ]{SbF_5-SO_2} \underset{SbF_5Cl^-}{CH_3OCH_2^+} \longleftrightarrow \underset{SbF_5Cl^-}{CH_3\overset{+}{O}{=}CH_2}$$

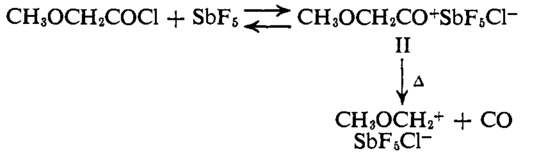
I

The ion nature of I was deduced from the following observations. (1) The pmr spectrum shows substantial deshielding of both the methylene ($\delta = -9.94$ ppm) and methoxy ($\delta = -5.66$ ppm) protons. (2) The long-range coupling, giving rise to a triplet and a quartet, indicates formation of an sp^2 center. (3) Methanolysis of the solution of I gave a high yield of dimethoxymethane.



$$\underset{SbF_5Cl^-}{CH_3OCH_2^+} + CH_3OH \longrightarrow CH_3OCH_2OCH_3$$

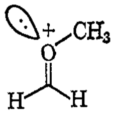
Ion I could also be observed to arise from the decarboxylation of the methoxyacetyl cation [methoxymethyloxocarbonium ion (II)] which is formed when methoxyacetyl chloride (fluoride) is treated with antimony pentafluoride in sulfur dioxide solution.



$$CH_3OCH_2COCl + SbF_5 \rightleftarrows \underset{\text{II}}{CH_3OCH_2CO^+SbF_5Cl^-} \xrightarrow{\Delta} \underset{\text{I}}{\underset{SbF_5Cl^-}{CH_3OCH_2^+}} + CO$$

If a solution of II is maintained at −60° decarbonylation is very slow and the pmr spectrum of the oxocarbonium ion is observed. Near −20° decarbonylation is very fast and ion I is quantitatively generated.

We had anticipated that in ion I the positive charge will be substantially located on oxygen and therefore a high rotational (inversional) barrier would exist about the methylene–oxygen bond (Ia). Ramsey and Taft[3] reported an activation energy of nearly 11 kcal/mole for the coalescence of the two nonequivalent methoxyl groups in the dimethoxymethylcarbonium ion, (CH$_3$O)$_2$-C$^+$CH$_3$. However, the same authors found only line broadening but not separation, indicative of an observable rotational barrier, in the triethoxy-, dimethoxy-, and diethoxycarbonium ions.



Ia

The multiplicity of the absorptions observed for the methoxycarbonium ion, *i.e.*, a quartet and a triplet, would seem to indicate that this ion is freely rotating. This appears unreasonable in view of the 11-kcal activation energy measured by Taft and Ramsey[3] for coalescence of the two nonequivalent methoxy groups in dimethoxymethylcarbonium ion and the *cis–trans* isomerism observed by us for the halomethoxycarbonium ions (subsequent discussion). One would anticipate a considerably larger activation energy for rotation in a primary alkoxycarbonium ion than in a tertiary one. We therefore suggest that the spectrum observed for the methoxycarbonium ion corresponds to an AA′X$_3$ spectrum which is deceptively simple and that the observed coupling is an average of the *cis*

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[1] (a) Part XXXII: J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Am. Chem. Soc.*, **89**, 156 (1967). (b) National Science Foundation Postdoctoral Research Investigator, 1966–1967.

[2] H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960); H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *ibid.*, **635**, 1 (1960).

[3] B. G. Ramsay and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **88**, 3058 (1966).

[4] H. Hart and D. Tomalia, *Tetrahedron Letters*, 3383, 3389 (1966).

[5] K. Dimroth and P. Heinrich, *Angew. Chem.*, **78**, 714 (1966).

[6] S. Kabuss, *ibid.*, **78**, 714 (1966).

[7] C. A. Cupas, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **88**, 361 (1966).

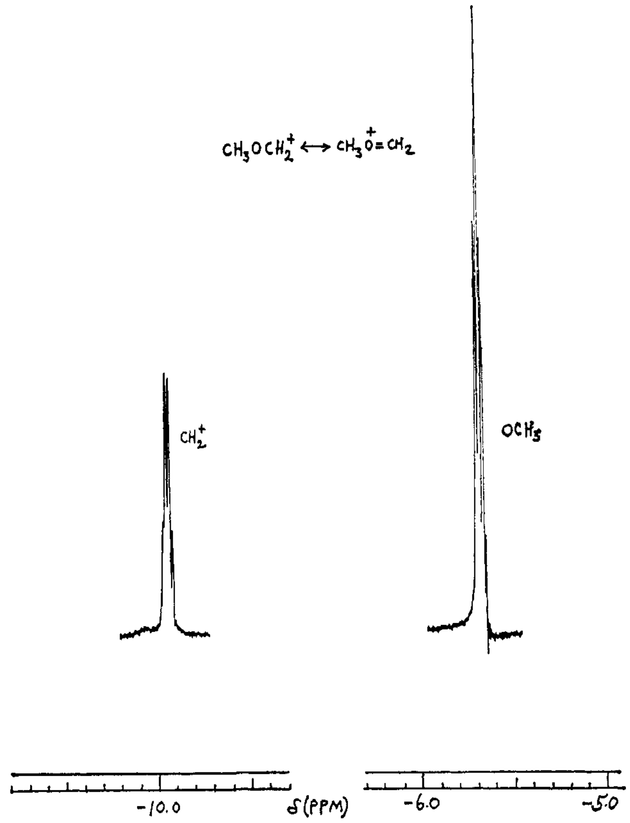


Figure 1.

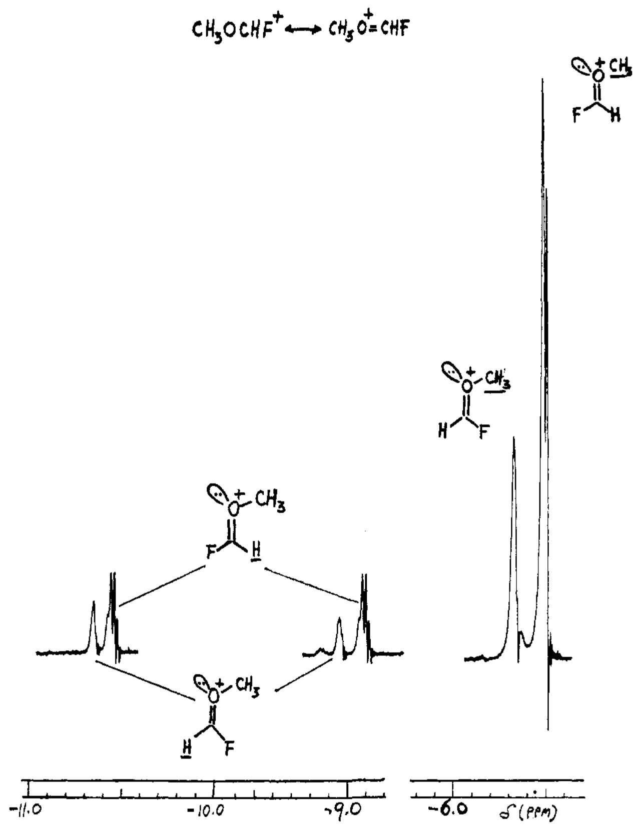


Figure 3.

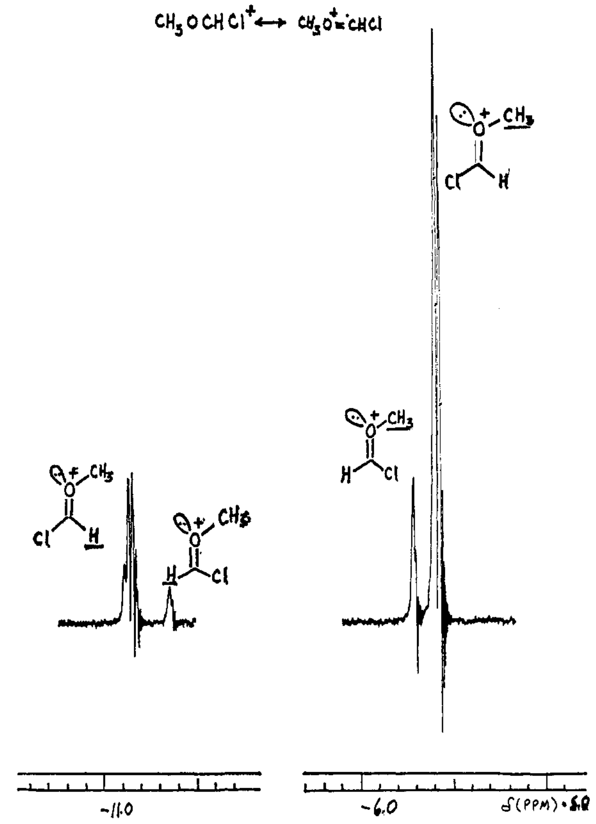


Figure 2.

and *trans* allylic couplings. This interpretation requires that the methyl group and the lone electron pair (see Ia) have the same effect on their respective nearest protons causing the same chemical shift for these two methylene protons.

Similar considerations also apply to chloromethoxycarbonium ion. Bis(chloromethyl) ether in $SbF_5–SO_2$ solution is ionized to form the chloromethoxycarbonium ion III. The pmr spectrum of III (Figure 4) at −80°

$$\mathrm{ClCH_2OCH_2Cl} \xrightarrow{\mathrm{SbF_5–SO_2}} \underset{\mathrm{SbF_5Cl^-}}{\mathrm{ClCH_2OCH_2^+}} \longleftrightarrow \underset{\substack{\mathrm{SbF_5Cl^-}\\ \mathrm{III}}}{\mathrm{ClCH_2\overset{+}{O}{=}CH_2}}$$

consists of two triplets at −9.82 and −6.76 ppm, J_{H-H} = 1.2 Hz. This ion is very sensitive to the manner of preparation, and a temperature-dependent spectrum can readily be obtained. This effect is illustrated in Figure 5 showing the coalescence of the CH_2Cl and CH_2 peaks on raising the temperature. Coalescence was also observed simply by adding a small amount of additional bis(chloromethyl) ether. This indicates that in ion III intermolecular exchange may take place (between ion III and un-ionized bis[chloromethyl] ether). Our data do not, however, rule out intramolecular exchange.

$$\mathrm{CH_2ClOCH_2^+} \rightleftarrows \mathrm{CH_2^+OCH_2Cl}$$

$$\mathrm{CH_2ClOCH_2Cl} + \mathrm{^+CH_2OCH_2Cl} \rightleftarrows \mathrm{^+CH_2OCH_2Cl} + \mathrm{ClCH_2OCH_2Cl}$$

It should be mentioned, as in the case of ion I, that there is no noticeable nonequivalence of the methylene protons of ion III. Thus there is not an observable barrier to rotation in the oxonium form of III and IV, although again we believe this to be a result of coincidental chemical shifts and deceptive simplicity.

When α,α-dichloromethyl ether is dissolved in $SbF_5–SO_2$ at −60°, the pmr spectrum (Figure 2) indicates

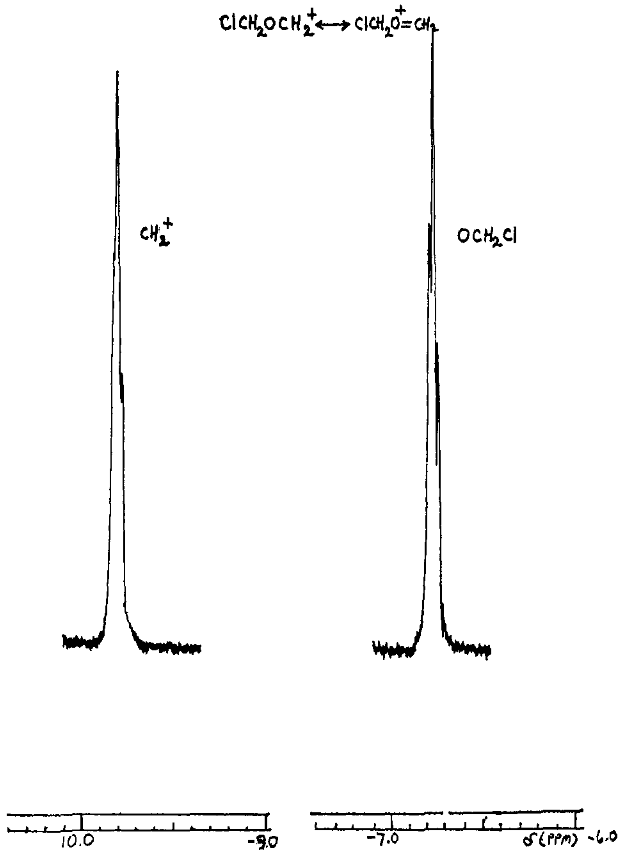


Figure 4.

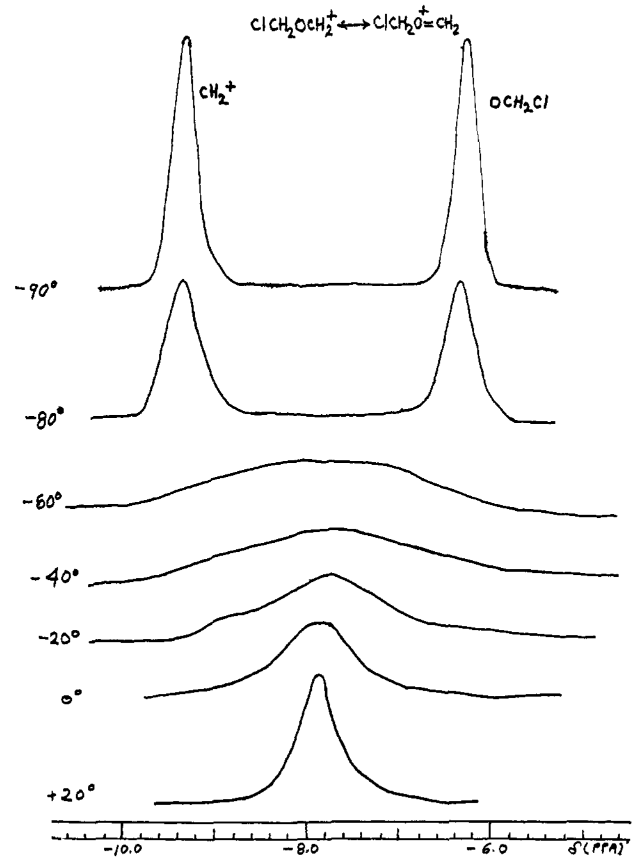
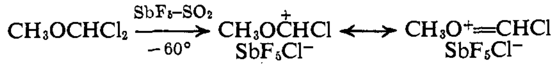


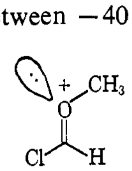
Figure 5.

the formation of the methoxychlorocarbonium ion IV. This ion exists in two conformational forms IVa and b, of which 81% is IVa and 19% is IVb (measured by integration of the pmr spectrum). This assignment is made on the basis of the larger coupling expected for a *cis* allylic coupling.[8] (We found $J = 1.2$ Hz for the *cis* allylic coupling in IVa and $J = 0.7$ Hz for the *trans* allylic coupling in IVb). No change in the relative amounts of the two species was found between −40 and −90°.

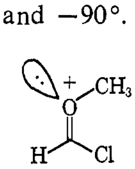


$$\mathrm{CH_3OCHCl_2} \xrightarrow[-60^\circ]{\mathrm{SbF_5\text{-}SO_2}} \underset{\mathrm{SbF_5Cl^-}}{\mathrm{CH_3O\overset{+}{C}HCl}} \longleftrightarrow \underset{\mathrm{SbF_5Cl^-}}{\mathrm{CH_3O^+{=}CHCl}}$$

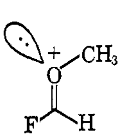
IV



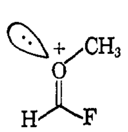
IVa



IVb

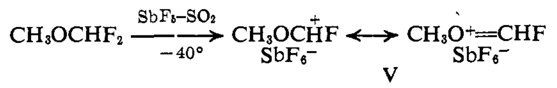


Va



Vb

This interpretation is supported by observation of the methoxyfluorocarbonium ion V prepared by ionization of α,α-difluoromethyl methyl ether[9] in antimony pentafluoride–sulfur dioxide solution.



$$\mathrm{CH_3OCHF_2} \xrightarrow[-40^\circ]{\mathrm{SbF_5\text{-}SO_2}} \underset{\mathrm{SbF_6^-}}{\mathrm{CH_3O\overset{+}{C}HF}} \longleftrightarrow \underset{\mathrm{SbF_6^-}}{\mathrm{CH_3O^+{=}CHF}}$$

V

The pmr spectrum of V at −40° (the ion was poorly soluble at lower temperatures; near −20° it decomposed with gas evolution), shown in Figure 3, is again a composite of 70% Va and 30% Vb (by integration of both the proton and the fluorine spectra). Again, on the basis of the larger coupling found in Va, this species is assigned the *cis* allylic proton conformation. It is of interest that the fluorine atom does not show detectable coupling with the methoxy group in Va. However, the methoxy group of Vb on expanded sweep width can be seen to be a triplet with 0.7-Hz separations. In this conformation the fluorine atom couples with the methoxy group with the same value as the hydrogen atom. The geminal H–F coupling in both conformations is 98 Hz and provides support for the sp^2 nature of the carbon atom,[10] as do the large downfield shifts of the fluorine atoms observed for both species ($\mathrm{CF_2HOCH_3}$ appears as a doublet, $J_{\mathrm{H-F}} = 75$ Hz, at +89.7 ppm; Va appears as a doublet, $J_{\mathrm{H-F}}^{\mathrm{gem}} = 98$ Hz, at −49.9 ppm and Vb appears as a doublet further split into quartets, $J_{\mathrm{H-F}}^{\mathrm{gem}} = 98$ Hz, $J_{\mathrm{H-F}}^{\mathrm{allylic}} = 0.7$ Hz, at −41.8 ppm, all from external $\mathrm{FCCl_3}$ at −40°).

Observations of *cis–trans* isomerism in the halomethoxycarbonium ion shows that structures such as Ia, IVa and b, Va and b, etc., are obviously the important contributing resonance structure of alkoxy ions. On the other hand, the very substantial deshielding of the methylene protons in the methoxy- and chloromethoxycarbonium ions indicates that substantial charge is localized on the methylene carbon atom, and I and III can be considered as stable primary carbonium ions.

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(8) S. Sternbell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(9) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957).

(10) H. M. McConnel, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956), find $J_{\mathrm{H-F}} = 81$ Hz in 1,1-dichlorofluoroethylene. G. A. Olah and E. B. Baker (in "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1964, pp 1182–1183) found 182.5 Hz for $J_{\mathrm{H-F}}$ in formyl fluoride.

Table I. Nmr Data of Alkoxycarbonium Ions[a]

Starting material in CCl_4, internal TMS			Ion in SbF_5–SO_2 (−60°), external TMS in $DCCl_3$	
CH_3OCH_2Cl	3.47 (s), CH_3O		I, 5.66 (t), CH_3O	J = 1.0 Hz
	5.42 (s), CH_2		9.94 (q), CH_2	
$ClCH_2OCH_2Cl$	5.58 (s), CH_2		III, 6.76 (t), CH_2	J = 1.1 Hz
			9.82 (t), CH_2	
CH_3OCHCl_2	3.67 (s), CH_3O		IVa, 5.60 (d), CH_3O	J = 1.2 Hz
	7.33 (s), CH		10.90 (q), CH	
			IVb, 5.72 (d), CH_3O	J = 0.7 Hz
			10.66 (q), CH	
CH_2OCHF_2	3.54 (s), CH_3	J_{H-F} = 75 Hz	Va,[b] 5.46 (d), CH_3O	J_{H-F} = 98 Hz
	6.14 (t), CH		9.76 (2q), CH	J_{H-H} = 1.2 Hz
			Vb,[b] 5.64 (t), CH_3O	J_{H-F} = 98 Hz
			9.86 (2q), CH	J_{H-H} = 0.7 Hz
				J_{H-F}^{allylic} = 0.7 Hz

[a] (s), singlet; (d), doublet; (t), triplet; (q) quadruplet. [b] At −40°.

The pmr data of ions I, III, IV, and V are summarized in Table I. All integrations were in accord with assigned structures.

Experimental Section

All of the halo ethers except α,α-difluoromethyl methyl ether were commercially available and used as obtained. α,α-Difluoromethyl methyl ether was prepared by the method of Hine.[9]

Solutions of the carbonium ions were obtained in the following way. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Portions (2 ml) of this solution were cooled to −78°, causing some antimony pentafluoride to crystallize from solution. To this suspension was added dropwise with stirring approximately 0.3 g of the appropriate halo ether. Slight warming was required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were approximately 10%. These operations were carried out in the laboratory atmosphere. This procedure provides a simply way to generate carbonium ions in a highly reproducible manner.

Spectra were recorded either on a Varian Model A56-60A spectrometer with external TMS in deuteriochloroform as reference (0.5 ppm has been added to these chemical shifts to correct them to TMS in a capillary as reference) or on a Varian Model HA-60 spectrometer with TMS in a capillary as reference.

Methanolysis of the carbonium ions was accomplished by adding slowly the solution of the carbonium ion in sulfur dioxide to a suspension of methanol and potassium carbonate at −78°. Product isolation was accomplished by drowning the resulting suspension in water and extracting with pentane. Identification of products was made by glpc comparison of retention times with authentic samples and by nmr and infrared spectroscopy. None of the dihalo ethers retained halogen in the quenching experiments.

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

Stable Carbonium Ions. XL.[1a] Protonated Aliphatic Thiols and Sulfides and Their Cleavage to Carbonium Ions

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received January 21, 1967

Abstract: A series of protonated aliphatic thiols and sulfides have been studied in HSO_3F–SbF_5–SO_2 solution. S-protonation was observed at −60° by nmr spectroscopy with negligible exchange rates. At higher temperatures, protonated thiols cleave to carbonium ions. Protonated sulfides, except for tertiary alkyl ones, are resistant to cleavage up to +70°.

We have previously reported the nmr observation of protonated alcohols[2,3] and ethers.[4] We wish now to report the observation of S-protonated thiols and sulfides in the extremely strong acid, FSO_3H–SbF_5, at −60° and their cleavage to carbonium ions.

Results and Discussion

Protonated Thiols. Aliphatic thiols are quantitatively protonated in FSO_3H–SbF_5 diluted with SO_2 at −60°.

$$RSH \xrightarrow[-60^\circ]{FSO_3H\text{–}SbF_5\text{–}SO_2} RSH_2^+\ SbF_5\text{–}FSO_3^-$$

They show well-resolved nmr spectra with very slow exchange rates. Protonated hydrogen sulfide itself shows a sharp singlet at −6.60 ppm. Protonated methyl thiol (Figure 1) shows the methyl triplet at −2.95 ppm and a SH_2^+ quartet at −6.45 ppm (J_{H-H} = 8.0 cps). Protonated ethyl thiol (Figure 2) shows

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[1] (a) Part XXXIX: G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2227 (1967). (b) National Science Foundation, Postdoctoral Research Investigator, 1966–1967. (c) National Science Foundation, Postdoctoral Research Investigator, 1965.

[2] G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966).

[3] G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, in press.

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