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
				$J^{allylic}_{H-F} = 0.7$ 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).

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

Thiol	δ, ppm[a] H₁	H₂	H₃	H₄	SH_2^+	$J_{H\text{-}H^+}$, cps
HSH					−6.60 (1)	. . .
1 CH_3SH	−2.95 (3)[b]				−6.45 (4)	8.0
2 1 CH_3CH_2SH	−3.37 (6)	−1.48 (3)			−6.22 (cm)	8.0
3 2 1 $CH_3CH_2CH_2SH$	−3.40 (cm)	−1.98 (cm)	−1.00 (3)		−6.37 (cm)	8.0
2 1 $(CH_3)_2\text{>}CHSH$	−3.98 (cm)	−1.73 (2)			−5.93 (2)	7.5
4 3 2 1 $CH_3CH_2CH_2CH_2SH$	−3.47 (6)	∼−1.70 (cm)	−1.70 (cm)	−0.90 (3)	−6.45 (3)	7.6
3 2 1 $(CH_3)_2\text{>}CHCH_2SH$	−3.32 (cm)	∼−2.25 (cm)	−1.03 (cm)		−6.40 (3)	8.0
3 2b 1 $CH_3CH_2CH(CH_3)SH$ 2a	−4.08 (6)	a −1.82 (2) b −2.10 (cm)	−1.15 (3)		−6.35 (2)	7.0
2a $(CH_3)_3CSH$	. . .	−1.75 (1)			−6.42 (1)	. . .
3 2b $CH_3CH_2C(CH_3)_2SH$ 2a	. . .	a −1.75 (1) b −1.97 (cm)	−1.07 (3)		−6.32 (1)	. . .

[a] From external capillary of TMS. [b] Multiplicity of peaks shown in brackets; (cm) = complex multiplet.

the methyl triplet at −1.48 ppm, a methylene sextet at −3.37 ppm, and a SH_2^+ triplet having a complex central peak at −6.22 ppm (J_{H-H} = 8.0 cps). Assignments of derived chemical shifts and coupling constants of the protonated thiols studied: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *t*-butyl, and *t*-amyl, are summarized in Table I.

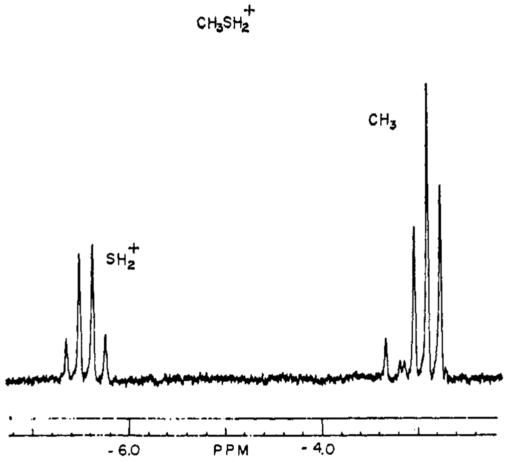


Figure 1.

The protonated thiols are surprisingly stable to increase in temperature when compared to the corresponding protonated alcohols.[3] However, the mode of sample preparation is critical. If the sample is prepared by the addition of the diluted, cooled acid to the thiol, simple protonated species are not observed. The nmr spectra indicate that protonated thiols react readily with the excess thiol still present in the solution. However, when prepared by the addition of thiol to acid, even protonated *t*-butyl thiol shows no appreciable decomposition at −60°. The small peak at −4.0 ppm in the spectrum of protonated *t*-butyl thiol (Figure 3) can be attributed to trimethylcarbonium ion and is probably due to cleavage as a consequence of local heating during sample preparation. The intensity of this peak did not increase with time at −60°. In contrast, all attempts to prepare protonated *t*-butyl alcohol results in complete formation of trimethylcarbonium ion even at −70°.

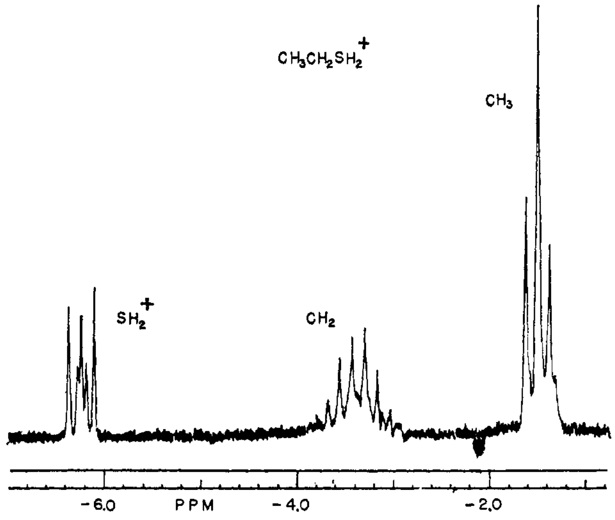


Figure 2.

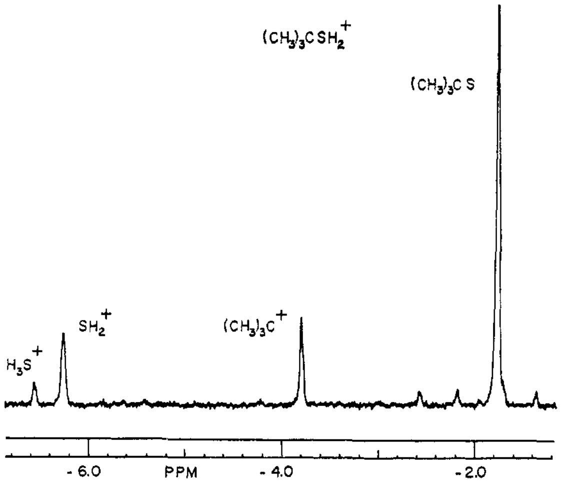


Figure 3.

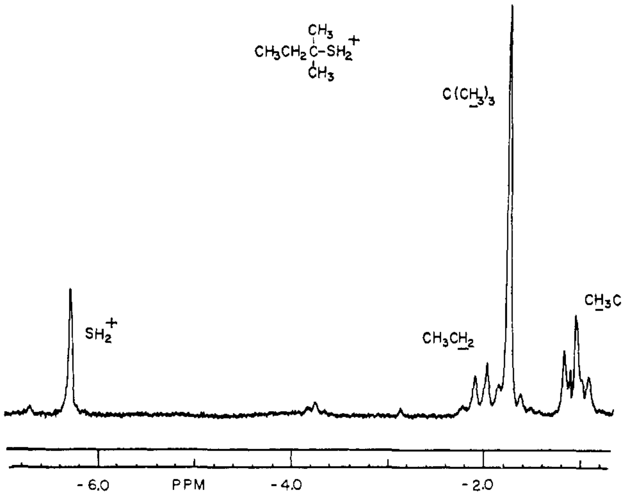


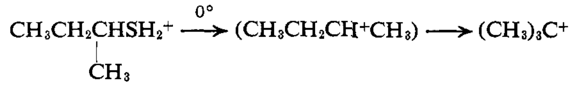
Figure 4.

Protonated *t*-butyl thiol slowly cleaves to trimethyl-

$$(CH_3)_3CSH_2^+ \xrightarrow{-30°} (CH_3)_3C^+ + H_3S^+$$

carbonium ion and protonated hydrogen sulfide when the temperature is increased to $-30°$ ($t_{1/2} \approx 15$ min). Protonated *t*-amyl thiol (Figure 4) also cleaves at this temperature to dimethylethylcarbonium ion. The spectrum of this carbonium ion can clearly be seen in Figure 5.[5]

Protonated secondary thiols are stable at higher temperatures. Protonated isopropyl thiol cleaves slowly at 0° in FSO_3H-SbF_5 (1:1) solution. No well-identified carbonium ion was found in the nmr spectra under these conditions, obviously due to the relative instability of the isopropyl cation at higher temperature giving a complex reaction mixture. Protonated *sec*-butyl thiol cleaves to trimethylcarbonium ion at this temperature.



$$\underset{\displaystyle CH_3}{CH_3CH_2\underset{|}{C}HSH_2^+} \xrightarrow{0°} (CH_3CH_2CH^+CH_3) \longrightarrow (CH_3)_3C^+$$

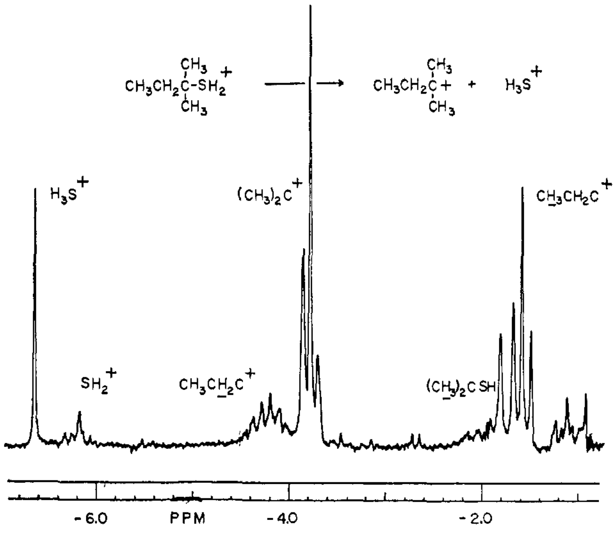


Figure 5.

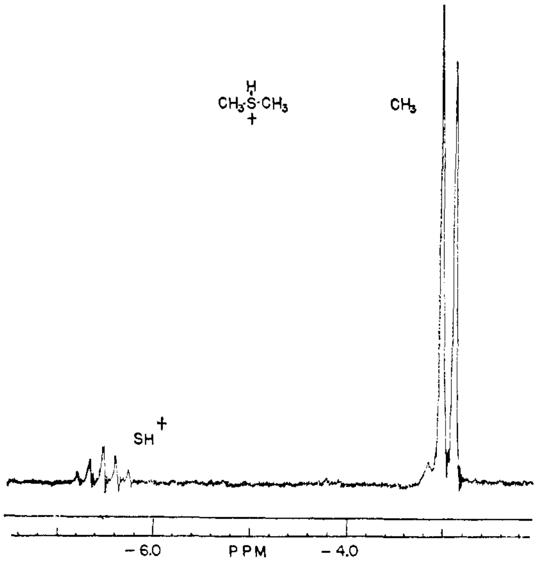
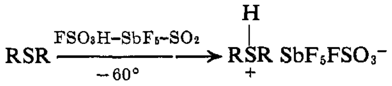


Figure 6.

Protonated primary thiols are stable at much higher temperatures. When prepared at 0° in FSO_3H-SbF_5 (1:1), protonated *n*-butyl thiol shows slight decomposition to trimethylcarbonium ion attributable to local heating during sample preparation. The intensity of the trimethylcarbonium ion peak did not increase with time at this temperature. Protonated *n*-butyl thiol slowly cleaves to trimethylcarbonium ion only at +25°.

$$CH_3CH_2CH_2CH_2SH_2^+ \xrightarrow{+25°} (CH_3CH_2CH_2CH_2^+) \longrightarrow (CH_3)_3C^+$$

Protonated Sulfides. Alkyl sulfides are quantitatively protonated in FSO_3H-SbF_5 diluted with SO_2 at $-60°$.



$$RSR \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} R\overset{\displaystyle H}{\underset{+}{S}}R\ SbF_5FSO_3^-$$

They show well-resolved nmr spectra. Protonated dimethyl sulfide (Figure 6) shows the methyl doublet at -3.08 ppm and the SH^+ septuplet at -6.52 ppm ($J_{H-H} = 8.0$ cps). Protonated diethyl sulfide (Figure 7) shows the methyl triplet at -1.67 ppm, a complex

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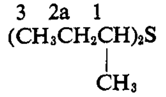
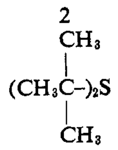
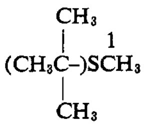
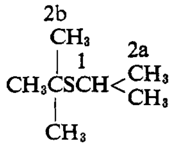
(5) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

Table II. Nmr Chemical Shifts and Coupling Constants of Protonated Sulfides at −60° in HSO_3F-SbF_5-SO_2

Sulfide	δ, ppm[a]					J_{H-SH^+}, cps
	H_1	H_2	H_3	H_4	SH^+	
1 $(CH_3)_2S$	−3.08 (2)[b]				−6.52 (7)	8.0
2 1 $(CH_3CH_2)_2S$	−3.57 (cm)	−1.67			−6.23 (5)	8.0
3 2 1 $(CH_3CH_2CH_2)_2S$	−3.33 (cm)	−2.00 (cm)	−1.07 (3)		−6.18 (5)	8.1
2a $\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\right)_2S$ 2b	−3.98 (6)	a −1.62 (2) b −1.57 (2)			−5.80 (3)	7.5
2 1a 1b $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CHSCH_3$	a − 3.89 (cm) b −2.90 (2)	−1.63 (2)			−6.07 (cm)	8.0
4 3 2 1 $(CH_3CH_2CH_2CH_2)_2S$	−3.33 (cm)	~−1.70 (cm)	~−1.70 (cm)	−1.00 (cm)	−6.13 (5)	8.0
 3 2a 1 $(CH_3CH_2\underset{CH_3}{CH})_2S$ 2b	−3.70 (cm)	a −2.00 (cm) b −1.71 (cm)	−1.10 (3)		−5.73 (cm)	7.7
 2 $(CH_3\overset{CH_3}{\underset{CH_3}{C}}-)_2S$		−1.83 (1)			−5.83 (1)	...
 $(CH_3\overset{CH_3}{\underset{CH_3}{C}}-)\overset{1}{S}CH_3$	−2.87 (2)	−1.67 (1)			−6.00 (4)	8.0
 2b $CH_3\overset{CH_3}{\underset{CH_3}{C}}S\overset{1}{C}H{<}\begin{matrix}CH_3\\CH_3\end{matrix}$ 2a	−4.05 (cm)	a−1.62 (2) b−1.73 (1)			−6.25 (2)	7.0

[a] From external capillary of TMS. [b] Multiplicity of peaks shown in brackets; (cm) = complex multiplet.

multiplet for the methylene hydrogens at −3.57 ppm, and the SH^+ quintet at −6.23 ppm (J_{H-H} = 8.0 cps). Assignments of derived shifts and coupling constants are summarized in Table II.

The proton on sulfur in the protonated thiols and sulfides is at considerably higher field (−6.52 to −5.80 ppm) than the corresponding proton on oxygen in protonated alcohols and ethers (−9.21 to −7.88 ppm).[1,2,3] It is worthy of note that protonated hydrogen sulfide appears as a sharp singlet with a similar chemical shift, −6.60 ppm, indicating that the positive charge on protonated sulfur is delocalized and little influenced by alkyl substitution.

Protonated isopropyl sulfide (Figure 8) gave an unexpectedly complex pattern for the methyl hydrogens. It showed a pair of overlapping doublets separated by 3.5 cps at −60°. It is highly unlikely that a preferred conformation can explain this multiplicity since the pair of doublets is still present at +70° in a solution of HSO_3F-SbF_5 (1:1). A more plausible explanation is the existence of intrinsic asymmetry in the $-H\ddot{S}^+-R$ group comparable to that found in ethyl isopropyl sulfoxide, diethyl sulfoxide,[6] ethyl benzenesulfonate, diethyl acetal,[7] diethyl sulfite,[8] and ethyl perfluoroisopropanesulfinate.[9] This asymmetry results in nonequivalent methylene hydrogens in the ethyl groups of the first five listed compounds and nonequivalent

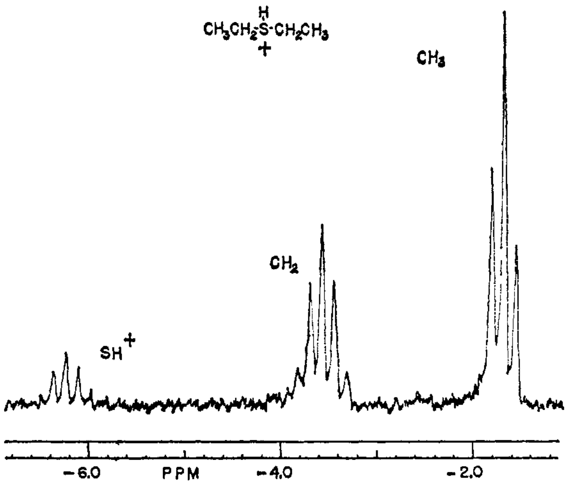


Figure 7.

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(6) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

(7) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(8) H. Finefold, *Proc. Chem. Soc.*, 283 (1960); F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961).

(9) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

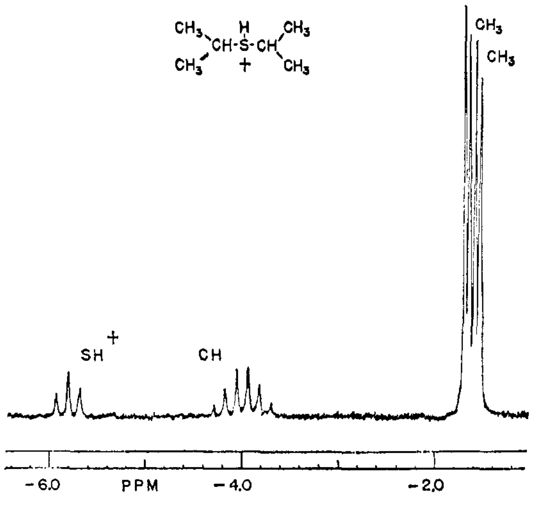


Figure 8.

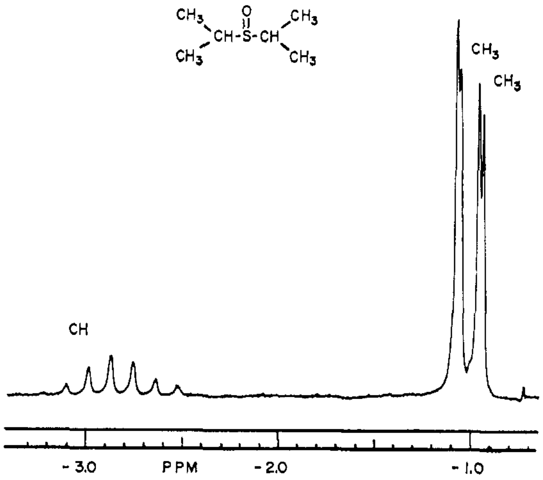


Figure 9.

perfluoromethyl groups in the F^{19} spectrum of ethyl perfluoroisopropanesulfinate. The nmr spectrum of diisopropyl sulfoxide (Figure 9) displays a nonequivalent, overlapping methyl doublets separated by 2.5 cps when dissolved in SO_2 at −60°.

It is particularly noteworthy that nonequivalent methylene hydrogens were observed in the boron hydride addition complex of diethyl sulfide, $(CH_3CH_2)_2S \cdot BH_3$.[6] This would indicate that the bonding at sulfur in this compound and in the protonated sulfides is qualitatively similar. The existence of this asymmetry further confirms the fact that the exchange of the proton is extremely slow.

In other protonated sulfides where such multiplicity might be observed, protonated methyl isopropyl sulfide gave only one isopropyl methyl doublet; protonated *t*-butyl isopropyl sulfide gave only slight broadening of the isopropyl methyl doublet; and protonated diethyl sulfide gave a complex methylene peak because of the further splitting by the proton on sulfur.

The protonated sulfides are more stable to cleavage than the corresponding protonated ethers[3] and also more stable than the protonated thiols. Protonated methyl *t*-butyl ether is completely cleaved to trimethylcarbonium ion and protonated methanol upon sample preparation even at −70°. Protonated methyl *t*-butyl sulfide is stable at −60° (Figure 10). The initial spectrum shows slight decomposition to trimethylcarbonium ion and protonated methyl thiol probably caused by local heating during sample preparation. No change in peak intensities with time was noted at −60°. When the temperature is increased to −15°, protonated methyl *t*-butyl sulfide very slowly cleaves to trimethylcarbonium ion and protonated methyl thiol.

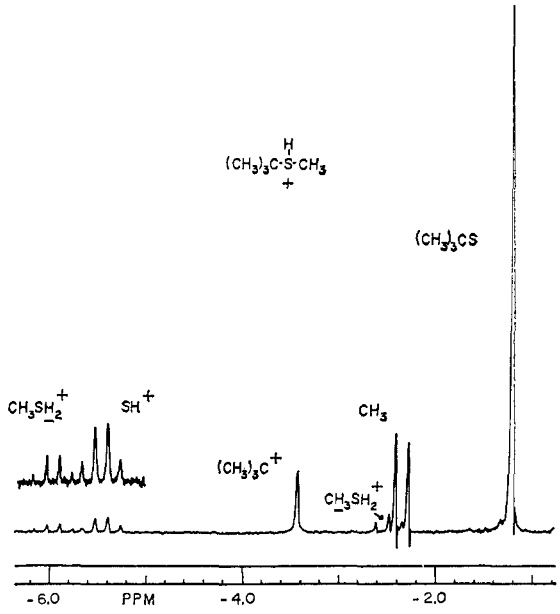


Figure 10.

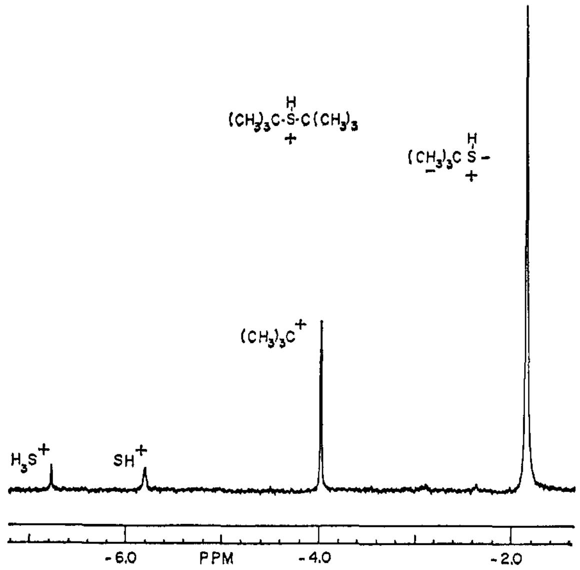
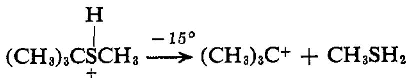
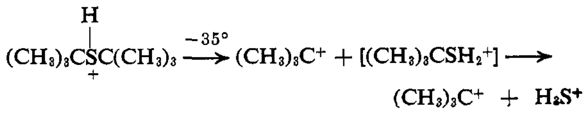


Figure 11.



$$(CH_3)_3C\overset{H}{\underset{+}{S}}CH_3 \xrightarrow{-15°} (CH_3)_3C^+ + CH_3SH_2^+$$

Protonated di-*t*-butyl sulfide shows very little cleavage at −60° (Figure 11). At −35° it cleaves slowly ($t_{1/2}$ ≈ 1 hr) to trimethylcarbonium ion and protonated hydrogen sulfide



$$(CH_3)_3C\overset{H}{\underset{+}{S}}C(CH_3)_3 \xrightarrow{-35°} (CH_3)_3C^+ + [(CH_3)_3CSH_2^+] \longrightarrow (CH_3)_3C^+ + H_3S^+$$

Protonated secondary sulfides show extraordinary stability toward the strongly acidic medium. Protonated isopropyl sulfide shows no appreciable cleavage up to +70° in a solution of FSO_3H–SbF_5 (1:1). At this temperature it slowly decomposed. No nmr identifiable products were noted at this elevated temperature.

Experimental Section

Materials. Thiols, symmetrical dialkyl sulfides, isopropyl methyl sulfide, and *t*-butyl methyl sulfide were reagent grade materials and were used without further purification.

sec-Butyl isopropyl sulfide was prepared according to the method of Vecera[10] by the reaction of *sec*-butylthiol in ethoxide–ethanol solution with isopropyl bromide. The product was purified by distillation. The fraction between 139 and 140° was used.

t-Butyl isopropyl sulfide was prepared according to the method of McAllan[11] by the reaction of *t*-butyl alcohol in 25% aqueous sulfuric acid with isopropylthiol. The product was purified by distillation. The fraction between 130 and 132° was used.

Isopropyl sulfoxide was prepared by the method of Addison[12] by the reaction of isopropyl sulfide with dinitrogen tetroxide. The product was purified by vacuum distillation. The fraction between 91 and 92° (12 mm) was used. The nmr spectra of the sulfoxide dissolved in sulfur dioxide at −60° is shown in Figure 9.

Nmr Spectra. Varian Associates Model A-56-60A and HA 60-IL nmr spectrometers with variable temperature probes were used for all spectra. Samples of S-protonated thiols and sulfides were prepared by dissolving approximately 1.5 ml of HSO_3F–SbF_5 (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −76°. The thiol or sulfide (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 excess of the sulfide or thiol as indicated by the large acid peak at −10.2 ppm. Samples undiluted with sulfur dioxide were prepared by cooling the 1:1 *M* acid to 0° and adding, with vigorous agitation, the neat, cooled sulfide or thiol. The nmr spectra of such samples showed a downfield solvent shift of about 0.3 ppm for all peaks because of the absence of sulfur dioxide.

Protonated hydrogen sulfide was prepared by passing gaseous hydrogen sulfide for a short time through a stirred solution of 2 ml of 1:1 FSO_3H–SbF_5 diluted with 2 ml of sulfur dioxide and cooled to −76°.

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

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(10) M. Vecera, J. Gasparic, D. Snobl, and M. Jurecek, *Chem. Listy*, **50**, 770 (1956); *Chem. Abstr.*, **50**, 15412*a* (1956).

(11) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **75**, 3627 (1951).

(12) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

Acid Anhydride–Free Acid Equilibria in Water in Some Substituted Succinic Acid Systems and Their Interaction with Aniline[1]

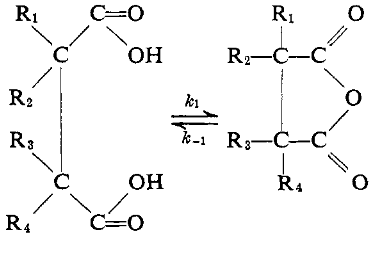
Takeru Higuchi,[2] Lennart Eberson, and John D. McRae

Contribution from the School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706. *Received November 7, 1966*

Abstract: The rates of formation of cyclic acid anhydrides in aqueous solutions of methyl-substituted succinic acids are shown to increase as expected with the degree of substitution. For the unsubstituted and mono- and disubstituted acids, at least, the estimated equilibrium concentration of the anhydride in the acid solution ranges from 1 to 50 ppm and appears to be largely determined by the rate of formation than by its hydrolysis. The aniline method was not found to be applicable to the tri- and tetrasubstituted acids because of the rapid formation of the corresponding imides.

Recent experimental evidence points to the existence of rather sluggish equilibria in water between certain sterically favored polycarboxylic acids and their corresponding cyclic internal anhydride.[3] Although such a process may be expected to be favored by, for example, alkyl substitution[4] in succinic acid, quantitative evaluation of such an effect had not been widely attempted, particularly on systems in which the relative concentration of the anhydride species would be expected to be low. The present report is concerned with results of an attempt to determine the rates of formation and the relative concentrations of these active species in aqueous solutions of methyl-substituted succinates at several temperatures.

Direct spectrophotometric determination of the forward rate of reaction 1 as carried out recently[5] was not possible in these systems since the relative concentrations of the anhydrides are always much too low to permit convenient determination. For the present purpose, the aniline method developed earlier for studies



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(3) T. Higuchi, T. Miki, A. C. Shah, and A. Herd, *J. Am. Chem. Soc.*, **85**, 3655 (1963).

(4) Recent studies in the glutaric series reflecting effects of this nature have been reported by T. C. Bruice and W. C. Bradbury, *ibid.*, **87**, 4838 (1965).

(5) L. Eberson, *Acta Chem. Scand.*, **18**, 1276 (1964).