Stable Carbonium Ions. LXXV.[1] Protonated Thiocarboxylic Acids, S-Alkyl Esters, and Their Cleavage in Fluorosulfonic Acid–Antimony Pentafluoride Solution. Thio Analogs of Protonated Carbonic Acid

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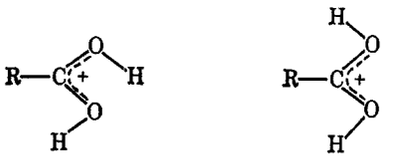
Thiocarboxylic acids were protonated in fluorosulfonic acid–antimony pentafluoride solution. Three isomers of protonated thioacids were found and identified by nmr spectroscopy. The rates of cleavage to oxocarbonium ions and H_3S^+ were compared with the corresponding rates of the oxygen analogs and the results are discussed in terms of the mechanism of the reaction. The protonation of a series of thioacid esters and the rates and mechanism of their cleavage was also investigated. Primary and secondary S-alkyl thioacetates cleave *via* acyl–sulfur fission, whereas alkyl–sulfur fission was found for S-*t*-alkyl thioacetates. Only S-*t*-alkyl thioformates could be cleaved in the acid system yielding *t*-alkylcarbonium ions and protonated thioformic acid. The generation of the sulfur analogs of protonated carbonic acid is also described.

A number of reports have appeared concerning the protonation of carboxylic acids in super acid systems.[3-9] In the case of both formic and acetic acids the existence of two isomers have been shown (I and II), the evidence for the assignments of these structures being based on the coupling constants between the methine and hydroxyl protons in protonated formic acid.[8]

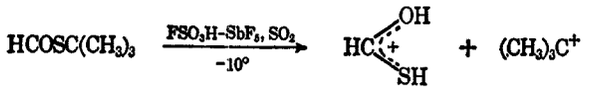


I II

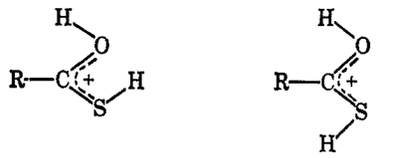
Isomer I is the predominant species in both of these systems, and in protonation of higher homologs isomer II is not found. Our continued interest in cations of this type led us to study the protonation of thiocarboxylic acids. In addition we have compared the rates of cleavage of protonated thioacids and their S-alkyl esters with the rates of cleavage of their oxygen analogs and present data which enables some conclusions to be drawn regarding the mechanism of these cleavage reactions. Owing to the biological importance of thioesters, particularly in enzymatic catalysis, we felt it of particular interest to study the mechanism and cleavage of thio esters.

Results and Discussion

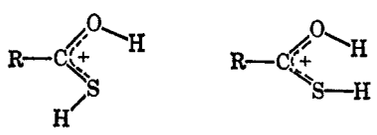
Protonated Thio Acids.—Protonated thioformic acid was generated by cleavage of S-*t*-butyl thioformate (*vide infra*) in 1:1 molar HSO_3F–SbF_5 solution containing an equal volume of SO_2 as diluent. The



100-MHz nmr spectrum at −70° (Figure 1) showed OH absorptions between δ 13.0 and 14.0, SH absorptions between δ 7.0 and 7.4, and methine proton absorptions between δ 10.0 and 10.5. The latter were almost completely obscured by the acid solvent peak at δ 10.25. Analysis of the spectrum was achieved with the aid of double-irradiation experiments and showed the presence of three isomers. The spectral parameters found for the isomers are summarized in Table I. In only one isomer (IV) was coupling between the SH and OH protons found (3.0 Hz). This provides strong evidence that in this isomer both the SH and OH protons are *cis* to the methine proton (IV, R = H) since of the four possible isomers (III–VI, R = H) this is the only one in which a favorable planar W coupling path exists between these protons. Such a configuration is known to lead to coupling constants of the same order of magnitude through both sp^3- and sp^2-hybridized centers.[10] The two *cis* couplings with the methine proton in this isomer are larger than those found in protonated formic acid (3.5 Hz)[8] and have values closer to those for *cis*-HCOH couplings found in protonated aldehydes (8.5–9.0 Hz).[11] The other two isomers each have two vicinal couplings, one small and one large. The larger coupling indicates a *trans* relationship between the methine and hydroxyl or thiol proton and the smaller coupling constant a *cis* relationship. On this basis, the isomers are assigned as shown (R = H), the isomer distribution being 60:30:10 for III, IV, and V, respectively. No evidence for isomer VI was found for protonated thioformic acid.



III IV



V VI

Protonated thioacetic acid, at −60° gave an nmr spectrum (Figure 2) having three methyl peaks at

(1) Part LXXIV: G. A. Olah, D. H. O'Brien, and C. Y. Lui, *J. Amer. Chem. Soc.*, **91**, 701 (1969).

(2) (a) National Institutes of Health Predoctoral Research Investigator, 1967–1968; (b) National Institutes of Health Postdoctoral Research Investigator, 1967–1968.

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

(4) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. Maclean, *Chem. Commun.*, 898 (1966).

(5) H. Hageveen, *et al.*, *Rec. Trav. Chim. Pays-Bas*, **86**, 687 (1967).

(6) H. Hogeveen, *ibid.*, **86**, 809 (1967).

(7) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967).

(8) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

(9) G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967).

(10) S. Sternhall, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

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

TABLE I

NMR SPECTRAL PARAMETERS OF PROTONATED THIO ACIDS, $RCOSH_2^+$

Isomer	Rel abundance	Chemical shifts[a] CH_3	Chemical shifts[a] CH_2	Chemical shifts[a] OH	Chemical shifts[a] SH	Coupling constants[b] J_{OH}^3	Coupling constants[b] J_{SH}^3	Coupling constants[b] J^4
R = H[g]								
III	60			13.23	7.33	7.5	13.0	
IV	30			13.47	7.03	8.0	7.5	3.0
V	10			13.86	7.36	16.5	7.0	
R = CH_3[h]								
III	60	3.23[c]		12.97	7.20[d]			
IV	20	3.37		13.17	6.88			3.0
		or						
V	20	3.45		13.45	7.30			
R = CH_3CH_2[i]								
III	70	1.74[e]	3.47[f]	12.65	7.09			
IV	10			12.84	6.86			3.0
V	20			13.43	7.18			

[a] δ in parts per million from external TMS for spectra obtained at $-70°$. [b] In hertz; J_{OH}^3 and J_{SH}^3 refer to coupling of the methine protons with the OH and SH protons, respectively. J^4 refers to the coupling between the SH and OH protons. [c] Doublet, $J = 1$ Hz. [d] Quartet, $J = 1$ Hz. [e] Triplet, $J = 7$ Hz. [f] Quartet, $J = 7$ Hz. [g] Registry no.: 19214-46-1. [h] Registry no.: 19214-47-2. [i] Registry no.: 19214-48-3.

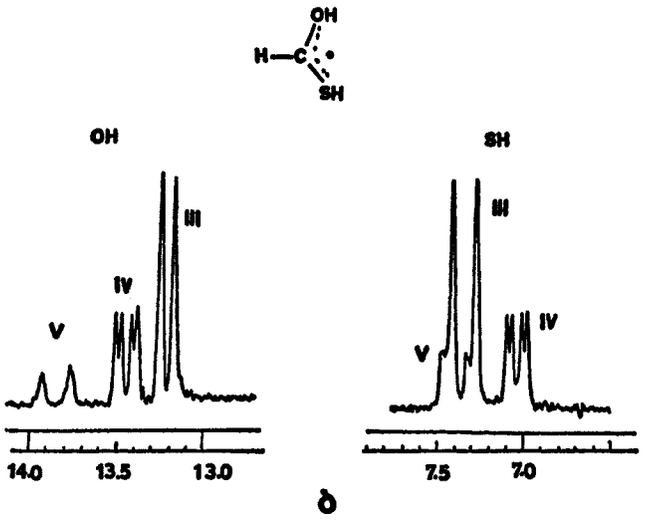


Figure 1.—Nmr spectrum (100 MHz) of protonated thioformic acid in fluorosulfonic acid–antimony pentafluoride–sulfur dioxide solution at $-70°$. III, IV, and V refer to the isomers assigned in Table I. The region between δ 10.0 and 11.0, where the solvent and methine protons absorb, is not shown.

δ 3.23, 3.37, and 3.45 of relative areas of 3:1:1, indicating, as in the case of thioformic acid, that three isomeric species are present. The pmr spectral parameters are summarized in Table I. The ion having the structure IV is assigned on the basis of the coupling between the SH and OH protons of 3.0 Hz, the reason for this assignment being the same as in the case of the related isomer of protonated thioformic acid. We tentatively assign the other two isomers on the basis of the OH chemical shift and comparison with protonated thioformic acid. With this assignment, isomer III is the most abundant (60%) and IV and V are present in approximately equal amounts (20–20%). One fact appears to contradict the assignment of III and V, and that is the 1-Hz coupling observed between the methyl and the SH protons in the most abundant species. While no corresponding couplings have been observed in protonated acetic acid,[8] protonated aldehydes,[11] and ketones[12] do show a four-bond coupling of about 1 Hz for alkyl groups *cis* to the hydroxyl proton. Using this coupling constant for comparison to assign the isomers is, we feel, less proper than comparison of the chemical shifts, since the π character of the C–O bond in protonated ketones is considerably greater than that of the C–S bond in the present example. As a justification for ignoring this coupling in assigning the spectrum, methyl four-bond coupling through a carbon–carbon double bond is greatest for a *cis* configuration (*cis*-allylic coupling) while for a saturated carbon skeleton a *trans* configuration leads to the largest coupling.[10]

Thiopropionic acid, when protonated in 1:1 HSO_3F–SbF_5–SO_2 solution again shows three isomers. Assigning isomers in an identical manner with that described for protonated thioacetic acid leads to isomer ratios of 70:10:20 for III, IV, and V (R = CH_3CH_2), respectively (see Table I).

Protonated thiobenzoic acid shows only single peaks for the OH and SH protons at δ 12.91 and 6.65. A similar observation was made in the case of protonated benzoic acid and is believed due to a low barrier to rotation about the C–OH bonds[8,9] which cannot be "frozen out" on the nmr time scale in the accessible temperature range studied ($-85°$).

The isomer ratios observed are relatively independent of the nature of the group R in the series R = H, CH_3, CH_3CH_2, and, furthermore, energetically the three isomers must be very similar. This indicates that steric interaction between the R group and either the proton or lone pairs on sulfur or oxygen is not very significant, although it probably accounts for the reduction in the proportion of isomer IV as the size of R is increased. The preponderance of isomer III over V suggests some hydrogen-bonding interaction between the SH proton on sulfur and the neighboring oxygen in spite of the resultant, unfavorable, four-membered ring. This interaction would be expected to be greater in III than in V since hydrogen bonding to oxygen should be favored over hydrogen bonding to sulfur.

Cleavage of Protonated Thiocarboxylic Acids to Oxocarbonium Ions.—On warming solutions of protonated thio acids in fluorosulfonic acid–antimony pentafluoride

(12) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967).

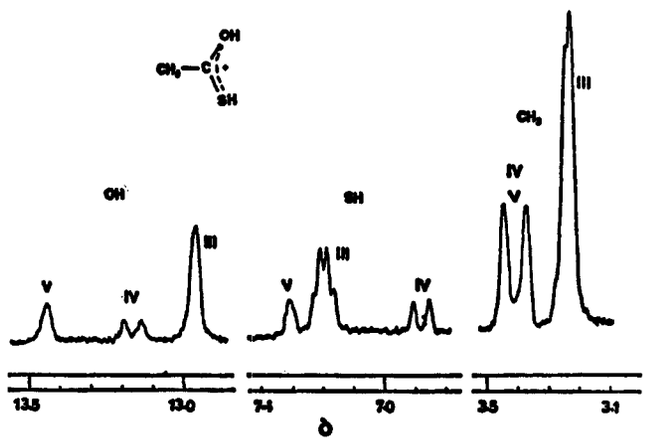
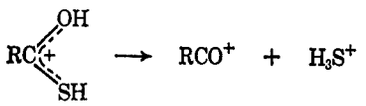


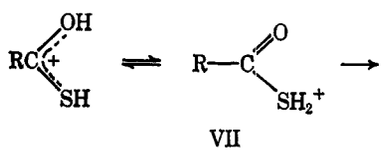
Figure 2.—Nmr spectrum (60 MHz) of protonated thioacetic acid at −60°.

solution to between −10 and 0°, cleavage of the carbon–sulfur bond occurred to give oxocarbonium ions and protonated hydrogen sulfide. Protonated hydrogen



sulfide is unstable under these conditions;[13] however, a small amount of H_3S^+ could be detected in the nmr spectrum as a peak at δ 6.60.

The rates of cleavage of protonated thioacetic and thiopropionic acids to the methyl- and ethyloxocarbonium ions were measured by the method described previously for protonated carboxylic acids[8] and their alkyl esters.[14] The rates were found to be slower than those for the oxygen analogs in both cases by a factor of 50 when compared under the same conditions at 0°.[14] A mechanism which accounts for this rate decrease is one involving a preequilibrium with a sulfur-protonated species (VII).



VII

$$RCO^+ + H_2S \xrightarrow{H^+} H_3S^+$$

Comparing the sulfur and oxygen protonated acids, the concentration of the intermediate VII should be lower in the sulfur case due to the lower basicity of sulfur. The subsequent cleavage of VII should be easier for sulfur owing to the fact that carbon–sulfur bonds are weaker than carbon–oxygen bonds.[15] It has been found, however, that protonated thiols cleave to carbonium ions less easily than do protonated alcohols.[13,16] Since this cleavage is closely related to the present case under discussion this result suggests that the cleavage of VII should be slower for sulfur than for the oxygen analog. This rate difference, in seeming contradiction to the bond strength order, may be due to interaction with a second proton in the transition state of this cleavage reaction, the interaction being greater for oxygen than for sulfur.

$$RSH_2^+ \longrightarrow R^+ + H_2S \xrightarrow{H^+} H_3S^+$$

In an earlier paper we discussed the mechanism of the cleavage of protonated esters and concluded that we could not distinguish between the preequilibrium mechanism and a four-center mechanism.[14] In the present study of the cleavage of protonated thio acids and thio esters the results still do not allow this distinction to be made since the difference between these two mechanisms lies in whether VII and X (see subsequent discussion) is an intermediate or a transition state. While we favor the preequilibrium mechanism, verification of this must await detection of VII; so far, this has not been accomplished.

Protonated S-Alkyl Thio esters.—Details of the nmr spectra obtained for solutions of a series of S-alkyl thioformates and thioacetates in 4:1 molar FSO_3H–SbF_5 diluted with SO_2 [17] are given in Tables II and III. In both series, carbonyl protonation was observed, the OH proton appearing between δ 12.6 and 12.8 (Figure 3).

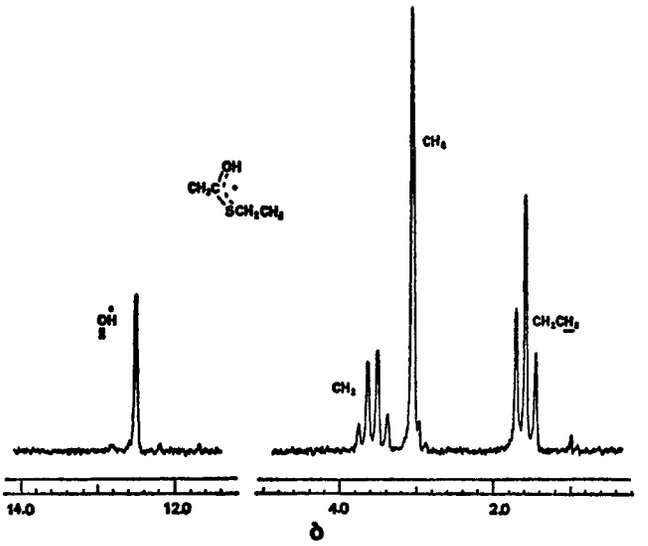
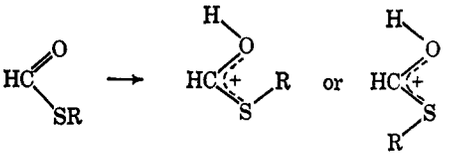


Figure 3.—Nmr spectrum (60 MHz) of protonated S-ethyl thioacetate at −60°.

In the thioformate series, the OH proton appeared as a doublet coupled by 8 Hz to the methine proton, the latter appearing at δ 10.2. Within the limits of the sensitivity of the nmr method, only a single isomeric species could be detected in all the thioesters studied. The magnitude of the coupling observed in the thioformate series shows that the OH and methine proton must have a *cis* relationship to each other and therefore the isomer observed must be either VIII or IX.



VIII IX

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

(14) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5494 (1967).

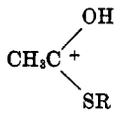
(15) The acid-catalyzed bimolecular hydrolysis of thioacetic acid has been shown to proceed slower than the oxygen analog by a factor of *ca.* 10: J. Hipkin and D. P. N. Satchell, *Tetrahedron*, **21**, 835 (1965).

(16) G. A. Olah, E. Namanworth, and J. Sommer, *J. Amer. Chem. Soc.*, **89**, 3576 (1967).

(17) A 4:1 molar concentration of FSO_3H–SbF_5 was used in preference to the 1:1 molar acid since, in the latter solution, spectra were less well resolved particularly at higher temperatures. The spectra obtained in both acids were (in other respects) identical.

TABLE II

NMR SPECTRAL PARAMETERS FOR PROTONATED THIOACETATES[a] AT −60°

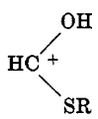


		Nmr			
				R	
R	Registry no.	OH	CH_3 (acetyl)	CH_3	CH_2 and CH
CH_3	19227-67-9	12.75	3.10	3.03	
CH_3CH_2	19214-49-4	12.70	3.12	1.66, t (8.0)	3.65, q
$(CH_3)_2CH$	19214-50-7	12.68	3.05	1.63, d (7.5)	4.46, m
$(CH_3)_3C$	19214-51-8	12.73	3.00	1.80	

[a] Chemical shifts in parts per million from external TMS. Coupling constants in hertz are given in parentheses following the multiplicities: d = doublet, *t* = triplet, q = quartet, m = multiplet.

TABLE III

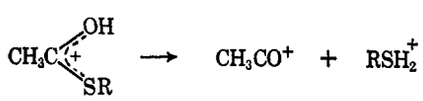
NMR SPECTRAL PARAMETERS FOR PROTONATED THIOFORMATES[a]



			Nmr			
					R	
R	Registry no.	Temp, °C	OH	CH (formyl)	CH_3	CH_2 and CH
$CH_3(CH_2)_2$	19214-52-9	−60	12.78, d (7.7)	10.23, d	1.23, t (7.0)	2.06, m; 3.68, t (7.0)
$(CH_3)_2CH$	19214-53-0	−60	12.75, d (7.7)	10.16, d	1.67, d (7.0)	4.53, m
$(CH_3)_3C$	19214-54-1	−70	12.82, d (8.0)	10.16, d	1.90	

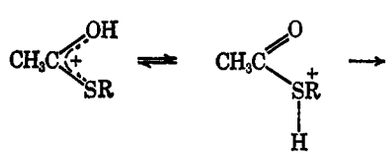
[a] Chemical shifts in parts per million from external TMS. Coupling constants in hertz are given in parentheses following the multiplicities: d = doublet, t = triplet, q = quartet, m = multiplet.

On raising the temperature of solutions of protonated S-alkyl thioacetates to between −20 and 10°, methyl, ethyl, isopropyl, isobutyl, and *sec*-butyl thioacetates underwent acyl–sulfur cleavage giving the methyloxocarbonium ion and the corresponding thiol, the nmr spectra of which have been reported previously[13] (Figure 4).



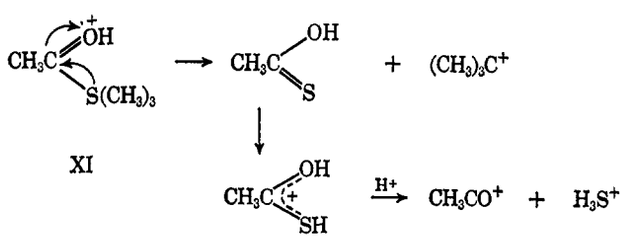
The rates of this reaction were measured by following the disappearance of the nmr signals of the protonated thioacetate and appearance of that of the methyloxocarbonium ion. In all cases the reaction was first order in protonated thioacetate and went to completion. First-order rate constants determined in 4:1 molar FSO_3H–SbF_5 and at 5.5° are reported in Table IV.

The small increase in the first-order rate constants found in the series, methyl, ethyl, and isopropyl thioacetate is consistent with a mechanism analogous to that proposed for the cleavage of thio acids. Changing the electronic properties of the group R should affect the concentration of the S-protonated intermediate X and the rate of its cleavage in opposite senses, the over-all effect on the observed rate being small.



X

In contrast to the behavior of these thioacetates, *t*-butyl thioacetate underwent alkyl–sulfur cleavage. At −45° the formation of *t*-butyl cation and protonated thioacetic acid could be observed. At higher temperatures, the protonated thioacetic acid undergoes further reaction and *t*-butyl cation and the methyloxocarbonium ion are the observed products.



XI

At 5.5° protonated S-methyl thioacetate reacts at half the rate of protonated methyl acetate, reaction in both cases involving cleavage of the acyl group. The rate of alkyl cleavage of protonated S-*t*-butyl thioacetate, on the other hand, is considerably slower than the corresponding rate for *t*-butyl acetate. The latter reaction

TABLE IV

FIRST-ORDER RATE CONSTANTS FOR THE CLEAVAGE OF THIOACETATES IN 4:1 MOLAR FSO_3H–SbF_5 SOLUTION AT 5.5°

Thioacetate	$K_1 \times 10^4$
S-Methyl	0.63
S-Ethyl	1.46
S-Isopropyl	1.63
S-*t*-Butyl	4.20

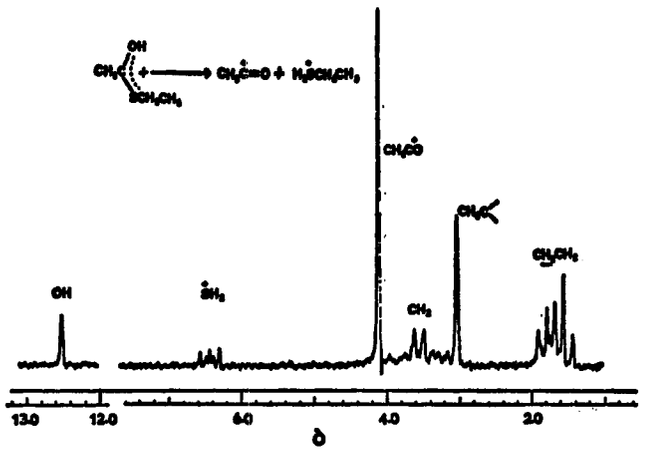
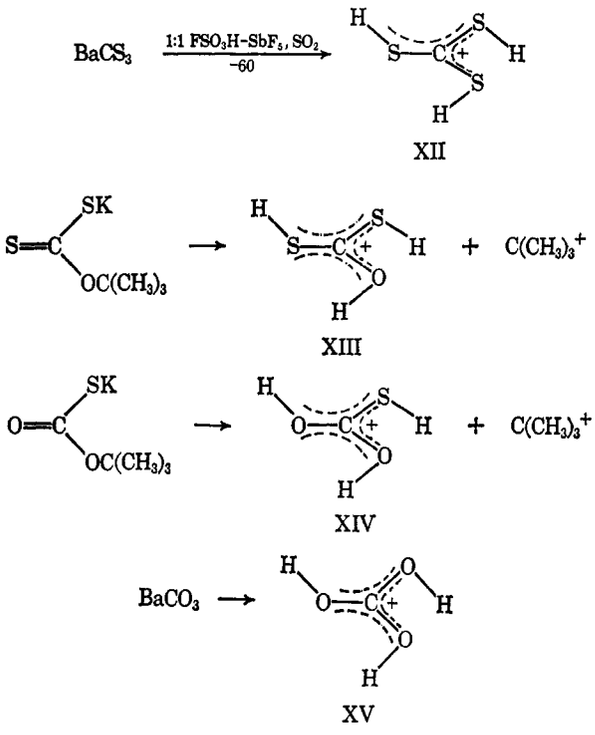


Figure 4.—Nmr spectrum (60 MHz) of protonated S-ethyl thioacetate at −60° after partial acyl–sulfur cleavage at −10°.

occurs immediately on protonation of the ester at −78°, whereas the rate of fission of protonated S-*t*-butyl acetate has a half-life of 15 min at 0°.[14] The considerably enhanced rate of cleavage of protonated *t*-butyl acetate is understandable due to the fact that in the protonated ester a much greater degree of positive charge character is associated with the alkoxy oxygen than is associated with the sulfur in the protonated thio ester. The loss of *t*-butyl cation will thus be greatly facilitated in the case of *t*-butyl acetate compared with the sulfur analog. The result suggests that, whereas the acyl–sulfur cleavage proceeds *via* an S-protonated intermediate X, alkyl–sulfur cleavage occurs directly through the O-protonated species XI, as indicated in the reaction scheme. It is of interest that studies of the acid-catalyzed bimolecular hydrolysis of thioacetates in aqueous acetone[18] have shown that S-*t*-butyl thioacetate, under these conditions, undergoes acyl–sulfur cleavage and, to observe alkyl–sulfur cleavage, the alkyl group has to be a potentially more stable carbonium ion such as triphenylmethyl.

Of the protonated thioformates studied only the *t*-butyl ester underwent cleavage giving the *t*-butyl cation and protonated thioformic acid at −10°. Neither the *n*-butyl or isopropyl esters could be cleaved, even when solutions of the protonated esters were heated to temperatures as high as 100°. This result demonstrates the stability of the methyl oxocarbonium ion compared with the formyl cation.[19]

Thiol Analogs of Protonated Carbonic Acid.—Protonated carbonic acid (trihydroxycarbonium ion) (XV) has been generated in 1:1 FSO_3H–SbF_5 solution at low temperatures.[20] In connection with this present study of the behavior of thiocarboxylic acids and their esters in super acid solutions, we also observed the formation of mono-, di-, and trithiol analogs of protonated carbonic acid. Protonated trithiocarbonic acid (XII) was formed in solutions of barium trithiocarbonate in 1:1 molar FSO_3H–SbF_5– with SO_2 at low temperature (−60°). Protonated dithiocarbonic acid (XIII) was generated under the same conditions from potassium *t*-butylxanthate and protonated thiocarbonic acid (XIV) from O-*t*-butyl S-potassium thiocarbonate.



It was found that generation of XIII and XIV by the routes indicated led mainly to ions XII and XV, XIV being present only to the extent of about 10% at −60°. It proved impossible to generate the ions at a lower temperature owing to the insolubility of the precursors, and the mechanism of this dissociation has not been established. It is possible that the reaction involves transient formation of protonated carbon dioxide, carbonyl sulfide, or carbon disulfide and this possibility is currently being further investigated.

The nmr shifts found for the OH and SH protons in protonated thiocarbonic acids are summarized in Table V. The increased deshielding of both the OH and SH protons as the number of thiol groups in the ion is increased is consistent with the lesser ability of sulfur compared with oxygen to delocalize the positive charge on the central carbon atom.

TABLE V
CHEMICAL SHIFTS OF THE THIOL ANALOGS OF PROTONATED CARBONIC ACID[a]

	Registry no.	OH	SH
$C(OH)_3^+$	19227-68-0	11.55	
$C(OH)_2SH^+$	19214-55-2	11.99	6.73
$C(SH)_2OH^+$	19214-56-3	12.56	7.19
$C(SH)_3^+$	19214-57-4		7.66

[a] In external TMS at −60°. All peaks observed were sharp singlets

Experimental Section

Materials.—The thio acids used were commercially available reagents and were purified before use by repeated fractional distillation under reduced pressure. Thioacetates were prepared by the reaction of the appropriate mercaptan with either acetyl chloride or with acetic anhydride and sodium acetate.[21] The

(18) (a) P. N. Rylander and D. S. Tarbell, *J. Amer. Chem. Soc.*, **72**, 3021 (1950); (b) B. K. Morse and D. S. Tarbell, *ibid.*, **74**, 416 (1952).

(19) Some evidence for the formyl cation, CHO^+, was obtained in SbF_5–SO_2 solution of formyl fluoride at −70° showing a single nmr peak at δ 15.8 The formyl ion is an unstable species, cleaving even at this temperature with evolution of carbon monoxide.

(20) G. A. Olah and A. M. White, *ibid.*, **90**, 1884 (1968).

(21) F. W. Wenzel, Jr., and E. E. Reid, *ibid.*, **59**, 1089 (1937).

thioformate esters were prepared by reaction of formyl fluoride with the appropriate mercaptan in ether solution at 0°.[22] Fluorosulfonic acid and antimony pentafluoride were distilled prior to their use.

Nmr Spectra.—Varian Associates Model A-56/60A and HA 100 nmr spectrometers were used for all spectra. Chemical shifts are reported in parts per million (δ) from external (capillary) tetramethylsilane.

Preparation of Solutions and Kinetic Measurements.—The procedure used for the preparation of solutions of the protonated thioacids and thioesters was identical with that described previously.[14] The same procedure as was used in studies of the cleavage of protonated carboxylic acid esters[14] was used in the present work to determine rate constants for the cleavage reactions studied.

Registry No.—Fluorosulfonic acid, 7789-21-1; antimony pentafluoride, 7783-70-2.

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(22) G. A. Olah and S. J. Kuhn, *ibid.*, **82**, 2380 (1960).

Organophosphorus Compounds. XI.[1a] ^{1}H and ^{31}P Nuclear Magnetic Resonance Study of the Protonation of Phosphines

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Symmetrical trialkyl (triaryl) phosphines, as well as diphenylphosphine and phosphine itself were protonated in fluorosulfuric acid. ^{1}H and ^{31}P nmr spectra of the phosphines and the corresponding phosphonium ions were studied. The one-bond coupling constant, J_{PH}, is inversely related to the bulkiness of the alkyl substituents. J_{PH} and the three-bond coupling constant, J_{HPCH}, are directly related. An empirical correlation of the phosphorus chemical shifts of the protonated phosphines with substituent constants was found.

A long-recognized characteristic of phosphines is their basicity, analogous to the basicity of amines. Although many phosphines have been studied by nuclear magnetic resonance (nmr) spectroscopy,[2] only a few protonated phosphines (which are phosphonium ions containing one or more hydrogen atoms attached directly to phosphorus) have been similarly examined. The trimethylphosphonium ion has been investigated thoroughly.[3] A pmr study of other methylphosphonium ions and the triethylphosphonium ion has been published.[3d] The unsubstituted phosphonium ion (PH_4^+) has only recently been observed spectrally.[4] Phosphorus chemical shifts have also been reported for the tributylphosphonium ion[5a] and the triphenylphosphonium ion.[5b]

We undertook a systematic nmr study of a series of alkyl- (aryl-) phosphines and the protonation of these phosphines in strong acid solution. Eight symmetrically trisubstituted alkyl- (aryl-) phosphines, diphenylphosphine, and phosphine itself (PH_3) were used in our studies. We found that neat fluorosulfuric acid served well both as a proton donor to the phosphines and as a solvent for the phosphonium ions which were formed. ^{1}H and ^{31}P nmr spectra of the phosphines and their corresponding phosphonium ions in excess fluorosulfuric acid were obtained. We were particularly interested in the effect of protonation on the phosphorus chemical shifts, and in the nmr spectral parameters of the proton which became bonded to the phosphorus atom. We also wanted to investigate the possible empirical correlations of phosphorus shifts in phosphonium ions with substituent constants.

Results

The phosphines and phosphonium ions which were studied, their phosphorus chemical shifts, and nmr spectral parameters of the proton(s) bonded directly to phosphorus are listed in Table I. Except where otherwise noted, the phosphines were examined as neat liquids. Each phosphine (except PH_3), when mixed with a fivefold molar excess of fluorosulfuric acid, yielded a stable solution of the corresponding phosphonium ion. A concentration of 1 mol of PH_3 in 31.5 mol of fluorosulfuric acid was sufficient for obtaining nmr spectra. The excess fluorosulfuric acid appeared in each proton spectrum as a sharp singlet at δ 11.1 to 12.6 (parts per million (ppm) downfield from external tetramethylsilane). The proton(s) attached to phosphorus appeared as widely separated doublets; each component had additional fine structure in those cases where three-bond coupling with other protons was possible. In the 60-MHz proton spectra of the trialkylphosphonium ions, the upfield component of the doublet due to the phosphonium proton was always hidden under peaks due to the alkyl protons. Taking spectra at 100 MHz usually separated this upfield component from the interfering peaks. In the two cases (triisopropylphosphonium ion and tricyclohexylphosphonium ion) where the upfield component remained hidden, the change in position of the downfield component upon switching from 60 to 100 MHz permitted calculation of the proton shift of the phosphonium proton and the one-bond coupling constant, J_{PH}. The trisubstituted phosphines all showed a change in the 24.3 MHz phosphorus spectra from a single broad peak to two widely separated components

(1) (a) Part X: S. J. Kuhn and G. A. Olah, *Can. J. Chem.*, **40**, 1951 (1962); (b) National Institutes of Health Predoctoral Research Fellow, 1968.

(2) Recent summaries of nmr spectra of phosphorus compounds are by (a) G. Mavel in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. I, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Long Island City, N. Y., 1966, Chapter 4; and by (b) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance," John Wiley & Sons, Inc., New York, N. Y., 1967.

(3) (a) B. Silver and Z. Luz, *J. Amer. Chem. Soc.*, **83**, 786 (1961); (b) P. Haake, W. B. Miller, and D. A. Tyssee, *ibid.*, **86**, 3577 (1964); (c) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964); (d) H. Dreeskamp, H. Elser, and C. Schumann, *Ber. Bunsenges. Phys. Chem.*, **70**, 751 (1966); (e) K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

(4) G. M. Sheldrick, *Trans. Faraday Soc.*, **63**, 1077 (1967).

(5) (a) Reference 2b, p 197; (b) J. E. Lancaster in ref 2b, p 381.