qualitatively the properties of the compound were found to be in agreement with reactions (10) and (11). A solution of an oxidizing agent reported to be composed of sulfur tetroxide was prepared by the action of fluorine on bisulfate according to the method of Fichter and Humpert.[14] The alleged sulfur tetroxide liberated oxygen containing ozone very rapidly at 50° in solutions of *p*H greater than 0, but in 3 *M* perchloric acid solution it formed Caro's acid quantitatively.

It should be pointed out that the proposed mechanism predicts the kinetics given by equation (4) only if the $HS_2O_8^-$ ion is a strong acid. Measurement of the *p*H of solutions of potassium persulfate in 0.01 *M* HCl has shown that K_a for the $HS_2O_8^-$ ion has a value of 1 or greater. Therefore, $HS_2O_8^-$ is a much stronger acid than HSO_4^-. The proposed mechanism also accounts for the fact that the oxygen formed by the acid-catalyzed decomposition of persulfate is derived from the persulfate while the oxygen liberated by the uncatalyzed reaction comes from the water.

According to reaction (6) the rate-determining step of the uncatalyzed reaction involves the thermal rupture of the O–O bond. The activation energy for this reaction was found to be 33.5 kcal. per mole. Although Palmer[15] has reported a value of 57 kcal. for the energy of the O–O bond in persulfate it is believed that the energy of the O–O bond in the solvated persulfate ion cannot be much different from the activation energy for the uncatalyzed thermal decomposition of the persulfate ion, namely, 33.5 kcal. per mole.

[14] F. Fichter and K. Humpert, *Helv. Chim. Acta*, **9**, 602 (1926).

[15] W. G. Palmer, "Valency," London, 1945.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. I. Organosilicon Compounds[1]

BY H. HARRY SZMANT, ORA MAE DEVLIN AND GENE A. BROST

Tetraphenyl- and tetrabenzylsilane are cleaved in sulfuric acid to the corresponding sulfonic acid and partially sulfated polysilicic acid. While tributylsilicon fluoride ionized only to the tributylsilicyl sulfate and protonated hydrogen fluoride, the triphenyl- and tribenzylsilicon fluorides ionize with cleavage of the carbon–silicon bonds. Evidence is presented that the fluorine on cleavage is converted in sulfuric acid to protonated hydrogen fluoride rather than fluosulfonic acid.

The reported studies of the cryoscopic behavior of organosilicon compounds in the solvent sulfuric acid were limited in the past to relatively simple alkyl siloxanes,[2,3] alkoxy silanes and silanols.[3] In view of the interest in cleavage reactions of more complex organosilicon compounds brought about by hydrogen chloride[4] or sulfuric acid,[5] the results of cryoscopic studies using aryl and benzylsilanes, as well as several substituted fluorosilanes, are reported in this paper.

Procedure and Data

The apparatus and experimental procedure employed were similar to those described by Newman, *et al.*[6] The temperatures were measured by a platinum resistance thermometer (Leeds and Northrup No. 709,899) which was calibrated by the National Bureau of Standards. All the compounds studied were prepared according to procedures described in the literature and purified with care by several crystallizations and/or distillations. Several series of measurements were made with each of the compounds under study, and each series consisted of at least two determinations using different portions of solute. The reliability of the apparatus and technique was periodically checked by determining the freezing point depression caused by addition of pure benzoic acid. Table I lists representative experimental results obtained in this study and the calculated van't Hoff factor *i*. In view of the slow dissolution of most of the compounds in sulfuric acid, and since slow secondary changes in the initially formed products were suspected, the variation of the freezing point depression with time was also observed.

Isolation of Benzene- and Benzylsulfonic Acids.—Benzenesulfonic acid was isolated from the reaction mixture of tetraphenylsilane (or triphenylfluorosilane) by pouring the sulfuric acid solution on ice and neutralizing by the addition of sodium carbonate. Sodium chloride was also added to ensure the precipitation of the sodium benzenesulfonate. The solid was separated by filtration, dried, and extracted in a Soxhlet apparatus with absolute ethanol. On removal of the alcohol, the residue was dissolved in a small amount of water and treated with benzylthiuronium hydrochloride. The resulting product was recrystallized from 50% ethanol to a constant m.p. 144–145°. The melting point of this product was not depressed by admixture with an authentic sample of the S-benzylthiuronium salt of benzenesulfonic acid.

Benzylsulfonic acid was isolated from the reaction mixture of tetrabenzylsilane by pouring the sulfuric acid solution on ice. On standing for 24 hours there were obtained the crystals of benzylsulfonic acid, m.p. 110–111°, the melting point of which was not depressed by an authentic sample of benzylsulfonic acid.

Attempted Isolation of Fluosulfonic Acid.—First we convinced ourselves that fluosulfonic acid could be separated by distillation from a synthetic mixture of 100% sulfuric acid and fluosulfonic acid in essentially quantitative amounts. Then the equivalent distillation experiments were performed on solutions obtained from the interaction of sulfuric acid with sodium fluoride, or benzotrifluoride. No fluosulfonic acid was detected in either one of the two reaction mixtures. The reaction mixture of benzotrifluoride and the sulfuric acid also did not produce any distillate boiling in the range expected of benzoyl fluoride, and the behavior of benzotrifluoride in the presence of sulfuric acid was rather unexpected. The first portion of benzotrifluoride did not react with cold sulfuric acid and formed a clear layer which slowly disappeared only when the sulfuric acid was heated. However, the second portion of the benzotrifluoride reacted progressively more vigorously with the sulfuric acid and it was accompanied by the liberation of hydrogen fluoride and etching of the glassware. Thus, it appears that the initial

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[1] Presented in part before the Organic Division, American Chemical Society, Philadelphia, April, 1950.

[2] F. P. Price, THIS JOURNAL, **70**, 871 (1948).

[3] M. S. Newman, *et al.*, *ibid.*, **71**, 869 (1949).

[4] (a) H. Gilman, *et al.*, *ibid.*, **71**, 2066 (1949); (b) **72**, 2629 (1950).

[5] (a) B. N. Dolgov and Yu. Vol'nov, *J. Gen. Chem.*, (*U. S. S. R.*), **63**, 91 (1931); (b) Flood, THIS JOURNAL, **55**, 1735 (1933); (c) W. I. Patnode and F. C. Schmidt, *ibid.*, **67**, 2272 (1945); (d) L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946); (e) C. A. Burkhard, *ibid.*, **72**, 1078 (1950).

[6] M. S. Newman, *et al.*, *ibid.*, **67**, 704 (1945).

Table I

Freezing Point Depression Measurements

Δm	Time (hr.)	F.p., °C. (initial)	ΔT	i[a]
Tetraphenylsilane				
0.003618	144	9.47	0.22	9.9
.008909	135	10.04	.55	10.0
.004666	22		.29	10.1
.01262[b]	27	10.17[b]	.72	9.3
	47		.76	9.8
Tetrabenzylsilane				
0.003785	50	10.29	.23	9.9
.01137	96	10.21	.70	10.0
Tributylfluorosilane				
0.001369	22	10.19	.28	3.3
.001574	46	9.50	.32	3.3
Triphenylfluorosilane				
0.005697	98	10.00	.21	6.0
0.02346	96	10.28	0.85	5.9
.01050	48–501[c]	10.04	0.38–0.75	5.5–11.6
Tribenzylfluorosilane				
0.004200	58	10.16	0.28	10.8
.01931	75	10.20	1.25	10.5
.01202	53	10.20	0.79	10.7
Hexaphenyldisiloxane				
0.005868	19.5	9.97	.51	14.1
	50		.57	15.8
	120		.61	16.9
Sodium Fluoride				
0.02896	69	10.05	.83	4.7
.009718	2	10.12	.30	5.0
Fluosulfonic Acid				
0.09736	5	9.82	.52	0.87

[a] Calculated according to the method of ref. 6. [b] This experiment was carried out by first adding 0.30 g. of potassium bisulfate to the batch of 72.30 g. of sulfuric acid. The initial freezing point is that of the resulting solution. [c] The reaction mixture was intermittently heated to 50° before the many freezing point measurements.

slow decomposition of benzotrifluoride continued until the sulfuric acid was well saturated with hydrogen fluoride (dissolved as H_2F^+), and the reaction became vigorous when catalyzed by either free hydrogen fluoride or bisulfate ions.

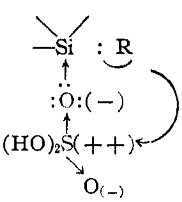
Discussion

It is apparent from inspection of Table I that tetraphenyl- and tetrabenzylsilane caused considerable freezing point depressions of the solvent sulfuric acid. The interpretation of the van't Hoff i factor calculated on the basis of the experimental data leads to the conclusion that the silanes under discussion are completely cleaved. The following equation can be written for the reactions of the silanes in sulfuric acid

$$R_4Si + 8H_2SO_4 \longrightarrow 4RSO_3H + 1/x[SiO(OSO_3H)_2]x + 3H_2O^+ + 3HSO_4^- \quad (1)$$

The degree of sulfation of the polymeric silicic acid is based on the work of Price.[2] If the reaction product were silica the i value would be 8, if it were monomeric sulfated orthosilicic acid the value would be 13. The cleavage of aryl and benzyl groups attached to silicon was demonstrated by Kipping[7] with bases, aluminum chloride, nitric acid and bromine. The cleavage of phenyl and benzyl groups under our experimental conditions is substantiated by the isolation of the corresponding sulfonic acids.[8]

In the cases of the tetraphenylsilane and tetrabenzylsilane it was observed that successive portions of the solute dissolved considerably faster than the first portion of the solute. We believe that this observation indicates the operation of a cleavage mechanism which involves the nucleophilic attack of the sulfuric acid (or bisulfate ion) on the silicon atom, with subsequent rearrangement of the substituent from silicon to sulfur:



The acceleration of the dissolution (*i.e.* reaction) of the samples in the presence of bisulfate ions corresponds to the million-fold increase in the nucleophilic reaction of hydroxide ions as compared to water, in the hydrolysis of triphenylfluorosilane.[9] To test the above ideas tetraphenylsilane was dissolved in sulfuric acid containing potassium acid sulfate, and the rate of dissolution was indeed found to have doubled (Table I).[10]

The solutions of hexaphenyldisiloxane in sulfuric acid would be expected to give values of i ranging from 12 to 22 depending on the degree of sulfation of the silicic acid. Assuming partial sulfation of silicic acid the equation for the complex ionization (2) yields an i factor of 16.

$$(Ph_3Si)_2O + 15H_2SO_4 \longrightarrow 6PhSO_3H + 2/x[SiO(OSO_3H)_2]_x + 5H_3O^+ + 5HSO_4^- \quad (2)$$

It is apparent from the results shown on Table I that the values of i approached a value lying near that of 16, and that the initial rates of dissociation of the disiloxane were high when compared to those of the tetraphenyl- or benzylsilanes.

The comparison of the behavior of trialkylsilicon fluoride with the corresponding triphenyl and tribenzyl compounds reveals the relatively greater stability of the alkylsilicon bonds. Thus, while tributylsilicon fluoride[11] undergoes ionization according to equation (3), the corresponding phenyl and benzyl compounds gave more complex reactions due to carbon–silicon bond cleavage. The reactions of the latter compounds can be represented by equation (4). The experimental results

$$Bu_3SiF + 2H_2SO_4 \longrightarrow Bu_3SiOSO_3H + H_2F^+ + HSO_4^- \; (i = 3) \quad (3)$$

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(7) F. S. Kipping and co-workers, *J. Chem. Soc.*, 1427, 1431 (1928); 2774 (1931); 2205 (1932); 1040 (1933); 1088 (1935).

(8) Benzenesulfonic and benzylsulfonic acids are assumed to have i values of unity on the basis of the observations of Hantzsch (*Z. physik. Chem.*, **65**, 41 (1908)).

(9) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, This Journal, **71**, 965 (1949).

(10) The observation of Gilman (ref. 4) that cleavage of carbon–silicon bonds by means of hydrogen chloride occurred readily in glacial acetic acid but failed in benzene or carbon tetrachloride can be explained in the same manner. Of the above three solvents, acetic acid has the greatest ion solvating ability and therefore the concentration of the highly nucleophilic chloride ion should be greatest in that solvent.

(11) Tributylsilicon fluoride behaves similarly to trimethylsilicon chloride which, on treatment with sulfuric acid, was reported to give the normal trimethylsilyl sulfate (Patnode and Schmidt, This Journal, **67**, 2272 (1945)).

$$R_3SiF + 8H_2SO_4 \longrightarrow 3RSO_3H + H_2F^+ + 1/x[OSi(OSO_3H)_2]_x + 2H_3O^+ + 3HSO_4^- \quad (i = 9) \quad (4)$$

indicate that the benzyl compound undergoes complete cleavage[12] and that the degree of sulfation and polymerization of the silicic acid lies between the extreme situations which would give i values of 7 and 12.

The initial results with triphenylsilicon fluoride were obtained when the reaction period was limited to approximately one hundred hours, and the average i value of these experiments was less than that expected on the basis of equation (4). In view of the observation that the sample of triphenylsilicon fluoride in sulfuric acid deposited a gel-like mass, and since the latter refused to dissolve on standing, the low i values could be attributed to the formation and insolubility of a phenylpolysiloxane structure. To test this hypothesis the initial deposit was allowed to stand for long periods of time, and the solution process was aided by intermittent warming of the mixture. The reaction mixture remained colorless throughout the experiment and the i values gradually increased until a constant value of 11.5 (between 400 and 500 hours) was obtained. The distinct behavior of triphenylsilicon fluoride (when compared to that of tetraphenylsilane or hexaphenyldisiloxane) is surprising since the initial cleavage reaction in all three cases should yield the same triphenylsilyl group. It may be that the insoluble condensation product is formed only in the case of triphenylsilicon fluoride because of a combination of reaction rates particularly favorable for this reaction.

Triphenyl- and tribenzylsilicon fluorides dissolved considerably faster than tetraphenyl- and tetrabenzylsilane.[13] The greater reaction rate of the fluorosilanes may be attributed to the more positive fractional charge of the silicon atom as a result of the high electronegativity of the fluorine atom and thus, a greater reactivity with respect to the nucleophilic reagent. There exists, however, also the possibility that the initial breakdown of a fluorosilane occurs by way of a hydrogen bond formation in the transition state

$$R_3Si^{+\delta} \cdots\cdots F{-}H \cdots\cdots {}^{-\delta}OSO_3H$$

In view of the recent work of LeFave[14] on the mechanism of the conversion of benzotrifluorides to the corresponding benzoic acids in sulfuric acid, a few experiments were made to test the theory that the fluorine atoms on cleavage are converted to fluosulfonic acid. Since the i factor of fluosulfonic acid was found to be nearly unity it must be concluded that the fluosulfonic acid simply dissolves in the solvent without further cleavage. The determination of the i factor for sodium fluoride gave values in the range 4.2–5.0. Two of the possible ways in which sodium fluoride reacts in the solvent sulfuric acid are represented by equations (5) and (6).

$$Na^+ + F^- + 2H_2SO_4 \longrightarrow Na^+ + H_2F^+ + 2HSO_4^- \quad (i = 4) \quad (5)$$

$$Na^+ + F^- + 3H_2SO_4 \longrightarrow Na^+ + 2HSO_4^- + FSO_3H + H_3O^+ \quad (i = 5) \quad (6)$$

Unfortunately, when the samples of sodium fluoride were introduced inside small glass capsules into the apparatus some of the hydrogen fluoride which was initially liberated caused *slight* etching of the walls of the capsules. The lowest i factor was obtained when the etching was almost invisible and this occurred when the widest of the three capsules was employed. Thus, it is permissible to conclude that the etching caused by hydrogen fluoride was a function of the speed with which it came in contact with sulfuric acid. Since the products of the interaction of the hydrogen fluoride with glass would considerably raise the experimental i factor, and since in no case the i factor exceeded the value of five, we believe that sodium fluoride reacted with sulfuric acid according to equation (5). This conclusion is supported by the fact that no fluosulfonic acid could be detected from the reactions of either sodium fluoride or benzotrifluoride with sulfuric acid (see Experimental).

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(12) It is curious that Gilman and Marshall (ref. 4) were unable to bring about cleavage of benzyl groups by means of hydrogen chloride in glacial acetic acid. Steel and Kipping (*J. Chem. Soc.*, 1431 (1928)) showed that the treatment of dibenzylsiloxane with water of piperidine caused cleavage of the carbon–silicon bond with the formation of toluene. Also Evanson and Kipping (*J. Chem. Soc.*, 2774 (1931)) demonstrated that tetrabenzylsilane as well as tetraphenylsilane were cleaved by means of aluminum chloride.

(13) We are comparing here only the initial fast reaction of triphenylsilicon fluoride and not the slow process by which the insoluble condensation product is gradually dissolved.

(14) G.M. LeFave, THIS JOURNAL, **71**, 4148 (1949); Abstracts of the Philadelphia Meeting of the American Chemical Society, April, 1950, 66 L.