

formed, and Color Test I¹⁵ became negative. The reaction mixture was filtered by suction, and the solid residue was extracted with hot benzene. The benzene extract was evaporated to give 1.2 g. of white solid melting at 217–222°. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 0.7 g. (14%) of colorless fine needles melting at 229–230°. From the ethereal solution of the reaction mixture a large amount of gummy residue was obtained from which only a small amount of impure product could be isolated.

Anal. Calcd. for C₃₈H₃₄Si₂: Si, 10.28. Found: Si, 10.31, 10.33.

The same product was obtained from the reaction of triphenylsilylpotassium with phenyldi-*p*-tolylchlorosilane (equation 2) to give an 85% crude yield of 1,1,1,2-tetraphenyl-2,2-di-*p*-tolylidisilane melting at 228°. One recrystallization from a mixed solvent of benzene-petroleum ether (b.p. 60–70°) gave 72% of pure product melting at 229–230°. A mixed melting point determination with the product obtained from 1,1,1,2-tetraphenyl-2,2-dichlorodisilane and *p*-tolyllithium was not depressed.

Pentaphenyl-*p*-tolylidisilane (equation 5).—An ethereal solution containing 0.011 mole of *p*-tolyllithium was added rapidly to 4.8 g. (0.01 mole) of pentaphenylchlorodisilane.⁶ The reaction mixture became more and more turbid, but very little heat was evolved. After 16 hours of stirring at room temperature, Color Test I¹⁵ was negative. The reaction mixture was hydrolyzed with water and filtered to separate 2.8 g. (53%) of white powder melting at 270° to a turbid liquid. Two recrystallizations from benzene yielded small needles (1.5 g., 28%) melting at 283–285°.

Anal. Calcd. for C₃₇H₃₂Si₂: Si, 10.55. Found: Si, 10.50, 10.47.

The same product, pentaphenyl-*p*-tolylidisilane, was obtained in an 82% crude yield (m.p. 276–282°) and a 77% pure yield (m.p. 283–285°) by the reaction of triphenylsilylpotassium with diphenyl-*p*-tolylchlorosilane (equation 2). A mixed melting point determination of these two products showed no depression.

AMES, IOWA

[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

Kinetics and Mechanism of Methyl-Silicon Cleavage by Sulfuric Acid¹

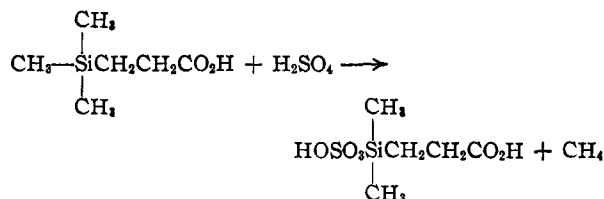
BY LEO H. SOMMER, WALTER P. BARIE AND JACK R. GOULD

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The kinetics of the reaction of β -trimethylsilylpropionic acid with sulfuric acid to give selective cleavage of one methyl group from silicon as methane has been studied. A mechanism involving electrophilic attack on carbon and formation of a siliconium ion in the rate-determining step is advanced.

Introduction

The reaction of certain organosilicon structures with concentrated sulfuric acid to give selective cleavage of one methyl group from trimethylsilyl, Me₃Si, as methane, has provided an important synthetic route to new types of aliphatic organofunctional siloxanes.^{2,3} Thus, the mechanism of this reaction is of interest from both theoretical and practical standpoints. The present paper reports a kinetic study of the methyl-silicon cleavage given by β -trimethylsilylpropionic acid. The reaction is homogeneous, and quantitative.



Discussion and Results

The pseudo first-order character of the reaction (sulfuric acid in large excess) is clearly shown for sulfuric acid concentrations of 85–97% by Fig. 1. *These good straight-line plots were obtained after initial difficulty, due to the formation of supersaturated solutions of methane in sulfuric acid, was overcome by more efficient stirring.* This somewhat surprising phenomenon is well-illustrated by Fig. 2 in the experimental part.

(1) Paper 34 in a series on organosilicon chemistry; for 33 see *THIS JOURNAL*, **75**, 2932 (1953).

(2) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *ibid.*, **73**, 882 (1951).

(3) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **73**, 2932 (1953).

Having established the fact that the reaction follows a pseudo first-order rate law, *e.g.*, is first order in the silicon acid, it was of interest to determine whether the decrease of rate with decreasing concentration of sulfuric acid could be correlated in terms of a simple mechanism.

No correlation between the pseudo first-order rate constants and stoichiometric concentration of sulfuric acid was available.

In order to determine whether the concentration of molecular or non-ionized sulfuric acid might be the critical factor use was made of the (approximately correct) assumption that the following reaction proceeds to completion⁴

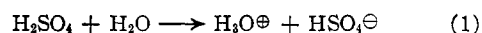


Table I gives the pseudo first-order rate constants, the concentrations of molecular sulfuric acid calculated on the above approximation, and also lists values of second-order rate constants obtained by dividing out the concentration of molecular sulfuric acid. These latter values have been calculated for the range 87–97% sulfuric acid since equation (1) becomes seriously in error below 87% sulfuric acid.⁴ Taking into consideration the approximations involved in calculating the concentration of molecular sulfuric acid, as well as the very serious medium effects to be expected on changing the solvent-reactant from 97% sulfuric acid to 87% sulfuric acid, the relative constancy of the second-order rate constants is here considered to be quite good. For example, a change from 87 to 97% sulfuric acid increases the pseudo first-order constant by a factor of 4.7, the same change

(4) For a good discussion and pertinent references see J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

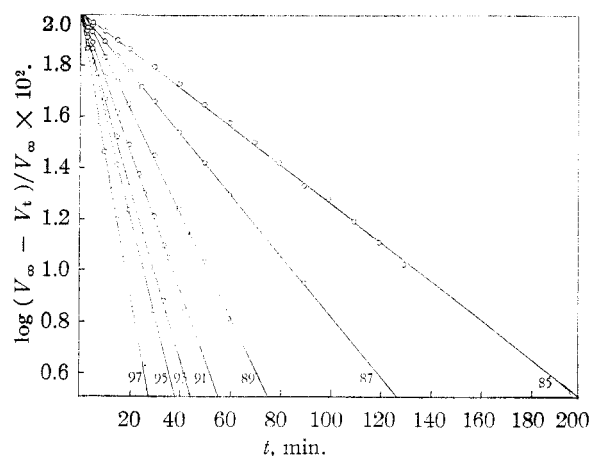


Fig. 1.— V_{∞} = final volume of methane; V_t = volume of methane at time t ; $(V_{\infty} - V_t)$ = concn. of Si acid at time t .

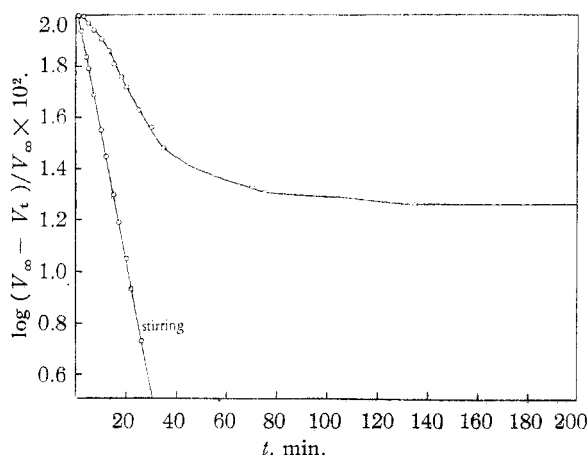


Fig. 2.

corresponds to an increase in the concentration of molecular sulfuric acid by a factor of 5.1.

TABLE I
H₂SO₄-H₂O MIXTURES AT 20.00°

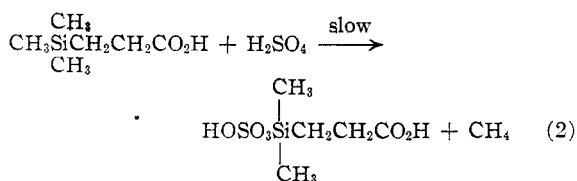
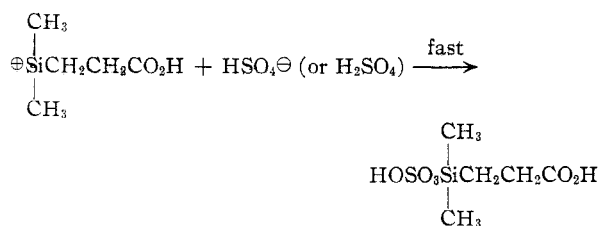
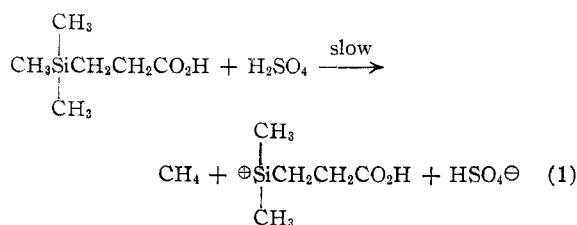
Si acid, moles/l.	H ₂ SO ₄ , %	$k_1 \times 10^4$ sec. ⁻¹	Un-ionized H ₂ SO ₄ , moles/l.	$k_2 \times 10^4$ (l. mole ⁻¹ sec. ⁻¹) ^a
0.0572	97	21.64	15.37	1.41
.0508	96	19.75	13.80	1.43
.0278		19.53		1.42
.0415		19.00		1.38
.0538	95	15.23	12.67	1.20
.0498	94	13.11	11.55	1.14
.0525	93	12.98	10.18	1.27
.0438	92	11.97	8.92	1.34
.0420	91	10.83	7.88	1.38
.0525	90	7.95	6.58	1.21
.0480	89	7.53	5.37	1.40
.0550	88	6.23	4.15	1.50
.0502	87	4.53	2.95	1.54
.0556	86	3.67	1.78	
.0563	85	2.88	0.60	

^a $k_2 = k_1/\text{concn. un-ionized H}_2\text{SO}_4$.

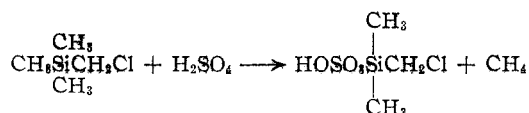
To the above should be added the fact that the reaction does not proceed at all in a reasonable time at concentrations of sulfuric acid below 80%, and that addition of bisulfate ion as sodium bi-

sulfate has an erratic effect on the rate, as shown in Table II in the Experimental part.

The above data do not permit a decision between reaction mechanisms (1) and (2)



However, a basis for choosing between the above alternates is, in our opinion, available from the following considerations. Firstly, there is the significant fact that the reaction involves cleavage of only *one* methyl group from silicon although there remain two more such groups on silicon in the product of the reaction. Secondly, we have demonstrated that the reaction of chloromethyltrimethylsilane with concentrated sulfuric acid gives selective cleavage of one of the methyl-silicon bonds, *viz.*



This experiment is important from a mechanism standpoint because of the unequivocal demonstration that the reactions of bases with chloromethylsilicon compounds involve nucleophilic attack on silicon and give selective cleavage of the chloromethyl group from silicon.⁵ Thus, nucleophilic attack at a silicon atom to which are linked chloromethyl and methyl groups gives, as expected, cleavage of the more electronegative substituent. These reactions may be classified as S_N2. From the facts concerning the reaction of chloromethyltrimethylsilane with sulfuric acid, it is therefore clear that the transition state for the sulfuric acid reactions cannot involve to any appreciable extent nucleophilic attack on silicon. The alternate, which seems the only reasonable one, is to classify these reactions as involving electrophilic attack on carbon. This hypothesis is, of course, completely in harmony with one of the most important aspects of the reaction from a synthetic standpoint,

(5) Cf. R. H. Krieble and J. R. Elliott, *THIS JOURNAL*, **67**, 1810 (1945).

namely, the fact that the reaction stops with the cleavage of one methyl group. The presence of a highly electronegative substituent such as a bisulfate group would be expected to inhibit greatly the removal of a second methyl group by mechanism (1). Other acids, expected to be less effective in mechanism (1), such as phosphoric, hydrochloric and acetic did not give methyl-silicon cleavage in the present study. Thus, we favor a siliconium ion mechanism involving electrophilic attack on carbon over nucleophilic attack on silicon and electrophilic attack on carbon by the same molecule of sulfuric acid. Reaction by mechanism (1) is made possible by the partial ionic character, *ca.* 12%, of the silicon-carbon bond which corresponds to an electronegativity difference between the two elements of 0.7 on the Pauling scale.⁶ It is of some interest to note that on this same scale carbon and chlorine differ in electronegativity by 0.5.

In support of siliconium ions as reaction intermediates in a sulfuric acid solvent we may cite the demonstration by Price, from cryoscopic measurements, that these ions are formed in appreciable concentration in the reaction of substances such as hexamethyldisiloxane with 100% sulfuric acid.⁷ In fact, the substances from which the siliconium ions derive by ionization are organosilicon bisulfates similar to the product of the reaction dealt with here. Further evidence for siliconium ions as real entities is provided by a recent communication in which conductance measurements and reactions show clearly that organochlorosilanes are significantly ionized to siliconium ions in the solvent dimethylformamide.⁸

Experimental

β -Trimethylsilylpropionic Acid.—The apparatus for the kinetic studies consisted of a 3-necked reaction flask equipped with a mercury-sealed stirrer and connected to a mercury-filled gas buret and manometer. In each run, the volume of sulfuric acid used was 50 cc., and the reaction mixture was maintained at 20.0° by a thermostat. Weighed samples of β -trimethylsilylpropionic acid were introduced all at once by means of a glass capsule. The silicon-containing acid is quite soluble in sulfuric acid, and all of the reactions studied were homogeneous.

In view of the homogeneity of the reaction systems being investigated, it might be supposed that stirring would have little or no effect on the rate of evolution of methane with a given concentration of acid. That such a conclusion is completely in error is shown by Fig. 2 which compares the rate of methane evolution from 96% sulfuric acid with and without stirring. In fact it was found after considerable experimentation that *efficient agitation of the reaction mixture is absolutely essential if decrease in rate due to supersaturation of methane is to be avoided.* In all of the runs an efficient paddle-type glass stirrer driven by an electric motor

was used. The effect of added bisulfate on the rate for 96% H₂SO₄ is shown in Table II.

TABLE II

Si acid, moles/l.	Added (HSO ₄ ⁻), moles/l.	$k_1 \times 10^4$ sec. ⁻¹
0.0508	0.0000	19.75
.0543	.1385	18.95
.0569	.3560	18.40
.0557	.6991	19.79
.0544	.8000	19.92
.0552	2.2900	22.68

It can be seen that the results of the added bisulfate show an erratic sort of behavior. The only run which shows a decided increase in rate is that involving 2.29 M NaHSO₄ added. It shows an increase of about 15%, whereas the others vary from less than 1% to about 7% deviation from the reference run with no bisulfate added. Attempts were made to increase the concentration of added bisulfate ion, but due to the insolubility of the NaHSO₄ in the sulfuric acid solutions, this was impossible.

Chloromethyltrimethylsilane.—Sixty-two grams, 0.5 mole, of chloromethyltrimethylsilane and 200 g., 2 moles, of concentrated (95.7%, Baker) sulfuric acid were placed in a 500-cc., three-necked flask which had been equipped with a mercury-sealed stirrer, a bulbled reflux condenser and a thermometer in liquid. The top of the condenser was connected to two Dry Ice-acetone traps and one liquid air trap in series. Stirring at room temperature caused no apparent reaction. While stirring rapidly, the flask was then heated with a Glas-Col mantle until, somewhat above 70°, slow reflux began, followed by frothing of the reaction mixture (first mild; then sufficiently vigorous to fill the entire flask with foam). Heating was stopped and the reaction allowed to continue spontaneously. The temperature remained at 85–86° for 15 minutes. Sufficient heat was then applied to maintain reflux until the temperature had risen to 105°, after which the mantle was removed and the contents of the flask, now completely homogeneous, allowed to cool to room temperature. This solution was then poured slowly into 350 g. of cracked ice to give two layers. The lower, aqueous layer was extracted with 100 cc. of ether, in two portions, and these extracts combined with the main product. Washing with 25 cc. of water and with 25 cc. of dilute sodium carbonate was followed by drying over anhydrous sodium sulfate. Fractionation gave 46.1 g., 0.20 mole, 80% yield of *sym*-bis-(chloromethyl)-tetramethyldisiloxane, b.p. 92° (21 mm.), n_D^{20} 1.4389.⁹

Anal. Calcd. for C₄H₁₆Si₂OCl₂: Cl, 30.6; mol. wt., 231.2. Found: Cl, 30.5, 30.8; mol. wt., 229.0.

Examination of the Dry Ice-acetone traps revealed that less than 1 cc. of liquid had been collected; however, the liquid air trap contained a considerable quantity of liquid which consisted largely of methane. Removal of all dissolved air and determination of the molecular weight (Dumas method) were most kindly performed by Dr. T. J. Brice of this Department.

Anal. Calcd. for CH₄: mol. wt., 16.04. Found: mol. wt., 16.2, 16.0.

Acknowledgment.—We thank Dr. R. W. Taft, Jr., and Dr. N. C. Deno for helpful discussions. Special thanks are due Dr. J. D. Roberts for his help in connection with supersaturation of methane in sulfuric acid.

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(9) R. H. Krieble and J. R. Elliott, *THIS JOURNAL*, **67**, 1810 (1945).

(6) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940, p. 70.

(7) F. P. Price, *THIS JOURNAL*, **70**, 871 (1948).

(8) E. G. Rachow, K. Gingold, D. Seyferth, A. Smith and R. West, *ibid.*, **74**, 6306 (1952).