[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Organosilicon Chemistry: The Mechanisms of Hydrolysis of Triphenylsilyl Fluoride and Triphenylmethyl Fluoride in 50% Water–50% Acetone Solution[1]

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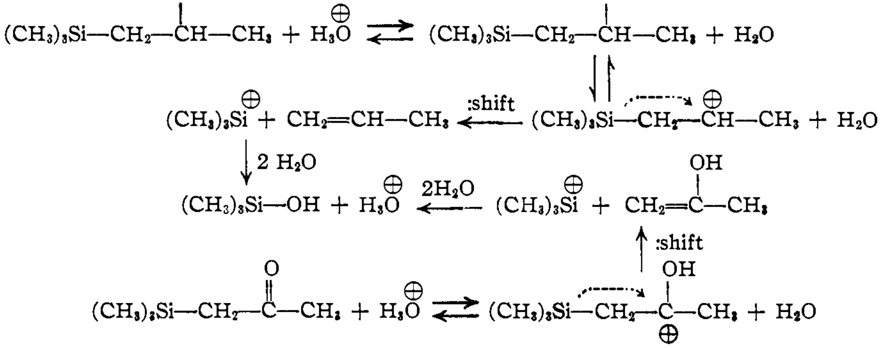
Certain of the reactions of organosilicon compounds have been written by Whitmore and coworkers as proceeding through siliconium ion intermediates, analogous to the carbonium ion intermediates well established for similar reactions of carbon compounds. For example, the fission (cleavage) of trimethyl-β-hydroxypropylsilane by dilute acids or of trimethylsilylacetone even in neutral water have been represented with siliconium ion intermediates.[2] Siliconium ions have been used by these investigators primarily as *formal* ways of explaining the products obtained, since evidence was really not available to permit evaluation of their importance or stability as reaction intermediates. It is therefore of interest to determine how stable and how common are siliconium ion intermediates relative to analogous carbonium ions.



These intermediates with a positive charge on silicon might seem particularly likely, *a priori*, in view of the fact that silicon is a more electropositive element than carbon, and even has some of the properties of the metals.[3] Therefore, one might expect silicon to form a positive ion even more readily than carbon.

The carbonium ion intermediate in the hydrolysis of triphenylmethyl (trityl) halides is one of the stablest known carbonium ions.[4] The *formally analogous* hydrolysis of triphenylsilyl (hereafter referred to as "trisyl") halides was therefore studied to see whether the same mechanism (here involving a siliconium ion intermediate) really held. The results indicate that this is not the case. Parallel kinetic experiments have been carried out with trisyl fluoride and trityl fluoride to test the effect on the rate of hydrolysis caused by variations in *p*H, *p*-substituents, concentration of inert salt, and composition of the solvent.

Data.—The results of typical runs are summarized in Table I and detailed data are given for three runs with trisyl fluoride in Table II and Fig. 3 and for one run with trityl fluoride in Table III and Fig. 4.

Trisyl fluoride reacts more than a million times as rapidly with hydroxide ion (calculated for 1 *M*) as with water in 50% water–50% acetone solution (see experimental section on procedure), whereas trityl fluoride reacts at the same rate regardless of *p*H. Fluorosilanes have been reported[5] to react only slowly with strong alkali even when heated. We observed the same results with trisyl fluoride when working in a pure water solvent, but this was due to the existence of a heterogeneous system. In solution, reaction occurs very rapidly.

Substitution of three *p*-methyl groups in trisyl fluoride *decreases* the rate of reaction with water about five-fold, whereas *p*-alkyl substitution *increases* the rate of solvolysis of trityl halides.[6]

The salt and solvent effects are positive, *i. e.*, the rate increases with concentration of inert salt or increasing polarity of the solvent, for both trisyl fluoride and trityl fluoride, although the effects are much stronger with trityl fluoride.

The activation energy for hydrolysis of trisyl

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(1) Paper presented at the St. Louis meeting of the American Chemical Society, September 6, 1948. This is paper III in the series, "Concerted Displacement Reactions"; for paper II, see Swain and Eddy, THIS JOURNAL, 70, 2989 (1948).

(2) Whitmore, *Chem. Eng. News*, 26, 672 (March 8, 1948); Whitmore, Sommer, Gold and Van Strien, THIS JOURNAL, 69, 1551 (1947).

(3) Rochow, "Chemistry of the Silicones," Wiley and Sons, Inc., New York, N. Y., 1946, pp. 3–4. From the heats of formation of Si–Si, C–C, Si–C, Si–H, C–H, and H–H single bonds, it appears that the electronegativity of silicon is 1.8 compared to 2.1 for hydrogen and 2.5 for carbon (Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, pp. 58–70).

(4) From conductivity of halides in liquid sulfur dioxide it is clear that triphenylcarbonium ion is enormously stabler than trimethylcarbonium ion (Hantzsch, *Ber.*, 54, 2573 (1921); Walden, *Z. physik. Chem.*, 43, 454 (1903)), yet even the latter is stable enough to exist as a relatively free intermediate, as indicated by the noncorrelation of product composition with rate in the solvolysis of *t*-butyl halides in water–alcohol mixtures [Bateman, Hughes and Ingold, *J. Chem. Soc.*, 881 (1938); Cooper, Hughes and Ingold, *ibid.*, 1280 (1937)].

(5) Pearlson, Brice and Simons, THIS JOURNAL, 67, 1769 (1945).

(6) Three *p*-*t*-butyl substituents increase the rate of methanolysis of trityl chloride in benzene solution at 25° thirty fold (Swain, THIS JOURNAL, 70, 1119 (1948)). One *p*-methyl substituent increases the rate of ethanolysis of trityl chloride four-fold in 40% ethanol–60% ether at 25° (Nixon and Branch, *ibid.*, 58, 496 (1936)).

TABLE I

REACTIONS OF TRIPHENYLSILYL AND TRIPHENYLMETHYL FLUORIDES

Run	Fluoride	Concn., *M*	Water, %^{a}	Temp., °C.	Method	k(min.$^{-1}$)^d
26	$(C_6H_5)_3Si$	0.0186	16.6	45	A	$0.52 \pm 0.05 \times 10^{-4}$
25	$(C_6H_5)_3Si$	.0186	33.3	45	A	$2.4 \pm .3 \times 10^{-4}$
31	$(C_6H_5)_3Si$	.0186	33.3^b	45	A	$2.9 \pm .3 \times 10^{-4}$
36	$(C_6H_5)_3Si$	.0110	40	25	A	$0.87 \pm .09 \times 10^{-4}$
27	$(C_6H_5)_3Si$	.0186	41.7	45	A	$3.5 \pm .4 \times 10^{-4}$
28	$(C_6H_5)_3Si$	.0093	50	45	A	$7.0 \pm .7 \times 10^{-4}$
29	$(C_6H_5)_3Si$	.0093	50^b	45	A	$9.1 \pm 1.0 \times 10^{-4}$
14,20	$(C_6H_5)_3Si$	.00085	50	45	C	$7.2 \pm 0.8 \times 10^{-4}$
32	$(C_6H_5)_3Si$	.0104	40	100	B	$1.35 \pm .02 \times 10^{-2}$
33	$(C_6H_5)_3Si$	.0104	40^b	100	B	$1.40 \pm .02 \times 10^{-2}$
34	$(C_6H_5)_3Si$	.0104	50	100	B	$1.73 \pm .02 \times 10^{-2}$
35	$(p\text{-}H_3C\text{-}C_6H_4)_3Si$	.00918	40	100	B	$3.0 \pm .3 \times 10^{-3}$
18	$(p\text{-}H_3C\text{-}C_6H_4)_3Si$	.00091	50	45	C	$1.3 \pm .2 \times 10^{-4}$
45	$(C_6H_5)_3C$	.00124	40	25	D	$1.25 \pm .13 \times 10^{-2}$
41	$(C_6H_5)_3C$	.00124	50	25	E	$5.3 \pm .6 \times 10^{-2}$
46	$(C_6H_5)_3C$	.00124	50	25	D	$5.2 \pm .6 \times 10^{-2}$
44	$(C_6H_5)_3C$	.00124	60	25	D	$7.9 \pm .8 \times 10^{-1}$
54	$(C_6H_5)_3O$	.00100	50	45	E	$2.3 \pm .3 \times 10^{-1}$
56	$(C_6H_5)_3C$	.00100	95^c	25	E	$8.2 \pm .9 \times 10^{-3}$
55	$(C_6H_5)_3C$	.00100	95^c	45	D	$4.2 \pm .4 \times 10^{-2}$
50	$(C_6H_5)_3C$	.00100	95^c	45	E	$4.6 \pm .5 \times 10^{-2}$

^{a} The part of the medium not indicated is acetone. ^{b} Sodium perchlorate was present to the extent of 0.52 *M*, 0.36 *M*, and 0.26 *M* in runs 31, 33, and 29, respectively. ^{c} 95% methanol, 5% acetone, no water present. ^{d} First order rate constant (equal to 0.693 divided by the half life).

TABLE II

HYDROLYSIS OF 0.0093 *M* TRIPHENYLSILYL FLUORIDE IN 50% WATER–50% ACETONE SOLUTION AT 45°, RUN 28, METHOD A

Minutes	0.0385 *N* cc. $Th(NO_3)_4$	Reaction, %
0.0	0.05	0.0
5.5	0.50	19.1
19.0	1.40	57.5
23.5	1.57	64.7
30.0	1.72	71.1
42.0	1.95	80.9
42.8	2.01	83.5
47.3	2.12	88.1
200	2.40	100.0

TABLE III

METHANOLYSIS OF 0.00100 *M* TRIPHENYLMETHYL FLUORIDE IN 95% METHANOL–5% ACETONE SOLUTION AT 25°. RUN 56, METHOD E

Minutes	0.0546 *M*, cc. $NaOCH_3$	Reaction, %
0.0	0.00	0.0
1.0	.27	1.0
4.0	.30	3.9
7.0	.33	6.7
12.5	.36	9.6
15.5	.39	12.5
21.0	.43	16.3
24.0	.45	18.3
28.0	.48	21.2
31.3	.50	23.1
35.5	.53	26.0
41.0	.56	28.8
46.0	.59	31.7
52.0	.62	34.6
57.0	.65	37.5
63.0	.68	40.4
68.0	.71	43.3
75.0	.74	46.2
82.0	.77	49.0
89.5	.80	51.9
96.0	.83	54.8
104	.86	57.6
111	.89	60.6
121	.92	63.4
131	.95	66.3
138	.97	68.8
170	1.04	75.0
195	1.11	81.7
360	1.24	94.2
720	1.30	100.0

fluoride is 13.6 ± 0.5 kcal. in 50% water–50% acetone, 15.5 ± 0.5 kcal. in 40% water–60% acetone. For solvolysis of trityl fluoride the figures are 13.0 ± 0.6 kcal. in 50% water–50% acetone and 14.9 ± 0.5 kcal. in 95% methanol–5% acetone.

Discussion.—The mechanism of hydrolysis of trisyl fluoride is evidently quite different from that of trityl fluoride. The above experimental facts can be used to disprove all but one out of the following limited group of mechanisms[7] for

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[7] This group includes the mechanisms commonly written. Other mechanisms can easily be written, but seem less probable, more complicated, or not really physically different from one of the five given. In these mechanisms all ions are understood to be hydrated and two (or more) solvent molecules are understood to play the role of reactants in solvating both anion and cation forming in each ionization step; these solvent molecules are omitted only to save space. The conjugate acid of silanol is the primary product of all these mechanisms. It will, of course, come into rapid equilibrium with silanol, water and oxonium ion, after its formation.

the hydrolysis of trisyl fluoride under our acid conditions.

$$(C_6H_5)_3SiF \xrightarrow{\text{slow}} (C_6H_5)_3Si^{\oplus} + F^{\ominus} \qquad (1a)$$

$$(C_6H_5)_3Si^{\oplus} + H_2O \xrightarrow{\text{fast}} (C_6H_5)_3SiOH_2^{\oplus}$$

$$(C_6H_5)_3SiF \overset{\text{fast}}{\rightleftarrows} (C_6H_5)_3Si^{\oplus} + F^{\ominus} \qquad (1b)$$

$$(C_6H_5)_3Si^{\oplus} + H_2O \xrightarrow{\text{slow}} (C_6H_5)_3SiOH_2^{\oplus}$$

$$H_2O + (C_6H_5)_3SiF \xrightarrow{\text{slow}} H_2\overset{\oplus}{O}Si(C_6H_5)_3 + F^{\ominus} \qquad (2)$$

$$H_2O + (C_6H_5)_3SiF \xrightarrow{\text{slow}} H_2OSi(C_6H_5)_3F \qquad (3a)$$

$$H_2OSi(C_6H_5)_3F \xrightarrow{\text{fast}} H_2\overset{\oplus}{O}Si(C_6H_5)_3 + F^{\ominus}$$

$$H_2O + (C_6H_5)_3SiF \overset{\text{fast}}{\rightleftarrows} H_2OSi(C_6H_5)_3F \qquad (3b)$$

$$H_2OSi(C_6H_5)_3F \xrightarrow{\text{slow}} H_2\overset{\oplus}{O}Si(C_6H_5)_3 + F^{\ominus}$$

There are three general possibilities for the mechanism of hydrolysis of trisyl fluoride under our acid conditions.

(1) The old bond to fluorine may break *before* the new bond to oxygen forms. This would be a two-step mechanism involving a siliconium ion intermediate. (We have subdivided this possibility into mechanisms 1a and 1b, depending on which step is rate determining.)

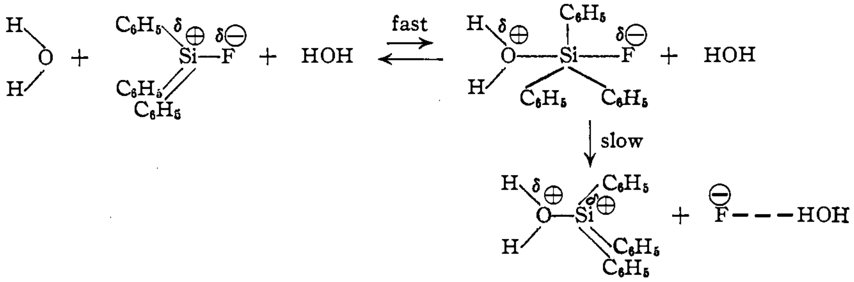
(2) Breaking the old bond and making the new bond may be exactly *simultaneous*. This would be a one-step displacement (Mechanism 2).

(3) The old bond may break *after* the new bond forms. This would be a two-step mechanism involving a pentacovalent silicon compound as an intermediate. (We have subdivided this possibility into mechanisms 3a and 3b, depending on which step is rate determining.)

The retarding effect of *p*-methyl substituents in trisyl fluoride shows that the charge on the silicon atom in the transition state is less positive than in the ground state. This eliminates mechanisms 1a, 1b and 2. The silicon atom should be increasingly positive in the series trisyl fluoride (I), triphenylsilanol conjugate acid (II), triphenyl siliconium ion (III). Hence the silicon in the transition state would be more positive than in (I) regardless of whether the transition state were half way from I to III (mechanism 1a), III to II (mechanism 1b) or I to II (mechanism 2). Only mechanisms 3a and 3b predict a less positive silicon atom in the transition state.

By mechanism 3a one would expect trisyl fluoride to be more reactive than trisyl chloride, since fluorine is a stronger electron attractor than chlorine and should give a more positive or electrophilic silicon atom. Actually, the converse appears to hold,[8] leaving mechanism 3b as the only possibility out of this group of mechanisms.

The positive salt and solvent effects show that there is greater charge or charge separation in the transition state than in the ground state. This is also consistent with mechanism 3b, where the transition state would be half way from intermediate to product.



One cannot be sure from our experiments whether the charge on silicon in the transition state, and in the pentacovalent silicon intermediate, is slightly positive or slightly negative in an absolute sense, only that it is less positive in both states than in the starting material.

These observations permit one to draw the free energy diagram of Fig. 1 to represent qualitatively the free energy of the intermediate and

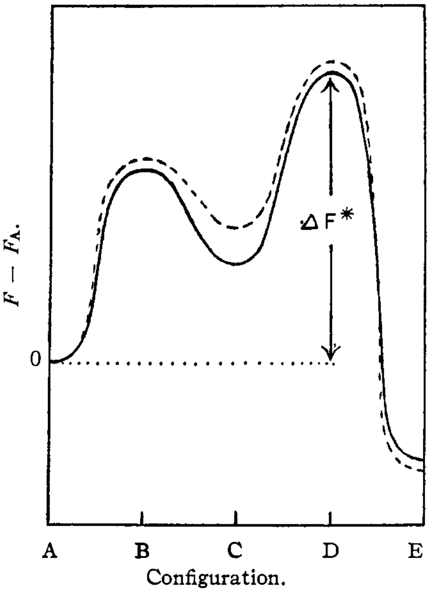


Fig. 1.—Free energy changes in the hydrolysis of triphenylsilyl fluoride: A, ground state of reactants; B, first activated state; C, pentacovalent silicon intermediate; D, second activated state; E, ground state of products.

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[8] Burkhardt, Rochow, Booth and Hartt, *Chem. Rev.*, **41**, 121 (1947); Medoks and Kotelkov, *J. Gen. Chem.* (*USSR*), **7**, 2007 (1937); Gierut, Sowa and Nieuwland, THIS JOURNAL, **58**, 897 (1936).

activated states. The solid curve represents trisyl fluoride, the dashed curve the tri-*p*-methyl substituted compound. The spread between the two curves is at all points proportional to the magnitude of the increase or decrease of the charge on silicon relative to that in the ground state (A).

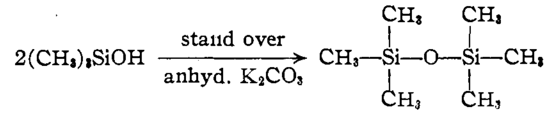
The plot for trityl fluoride would differ in the following ways. The intermediate (C) would have a more positive charge on the atom undergoing displacement than the ground state (A), rather than less positive. The first hill would represent chiefly bond breaking, the second bond making, rather than the reverse shown in Fig. 1. The first hill would be higher, not lower, than the second. The dashed curve would be everywhere below, not chiefly above, the solid curve. The separation between the curves would again be less for the activated states (B and D) than for the intermediate (C), but the separation at E would be comparable with that at C, rather than of reversed sign as in Fig. 1.

Mechanism 3 (a or b) has long been recognized as a possibility for the reaction of silicon compounds.[9] Not only are pentacovalent silicon intermediates possible and probable in view of the existence of the very stable fluosilicate ion, $SiF_6^=$, but $(C_6H_5)_3Si^{\oplus}$ or $(CH_3)_3Si^{\oplus}$ ions are improbable[10] relative to their carbon analogs because their resonance stabilization would require double bonds to silicon for which there is no stable example known. Mechanism 3 has also been advanced[9] as an attractive explanation for the remarkable ease of displacements on silicon, which are often much faster than analogous displacements on carbon, as in these examples[11]

$$\overset{\ominus}{HO:} + R_3SiH + H_2O \longrightarrow HO\text{—}SiR_3 + H_2 + :\overset{\ominus}{OH}$$

$$4\overset{\ominus}{HO:} + Cl_3SiCH_2CH_2Cl \xrightarrow[\text{dil. aq. NaOH}]{\text{titrate with}} (SiO_2)_n + CH_2{=}CH_2 + 4:\overset{\ominus}{Cl}$$

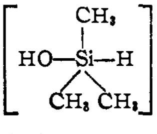
$$4CH_3MgBr + Cl_3SiCH_2CH_2Cl \xrightarrow{\text{ether}} (CH_3)_4Si + CH_2{=}CH_2 + 4MgBrCl$$



$$2(CH_3)_3SiOH \xrightarrow[\text{anhyd. }K_2CO_3]{\text{stand over}} CH_3\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}CH_3$$

$$(CH_3)_3SiNHCi(CH_3)_3 \xrightarrow[\text{dilute aq. HCl}]{\text{titrate with}} 2(CH_3)_3SiOH + NH_4Cl$$

Were a displacement like the first one above to occur on carbon, it would probably be through an unstable transition state with hydroxyl and hydrogen both only partly bonded. With silicon the following is a relatively much more stable structure due to the ability of silicon to expand its valence shell to include more than eight electrons, and this should correspondingly lower the energy of the transition state separating this intermediate from the products.



Experimental

Reagents.—Triphenylsilyl (trisyl) fluoride was prepared according to the procedure of Medoks and Kotelkov[8] by passing gaseous silicon tetrafluoride through 250 cc. of 2.8 *M*, phenylmagnesium bromide in ether for four hours at 25°. The silicon tetrafluoride was generated according to Nieuwland and Sowa[12] by adding 100 cc. of concd. sulfuric acid slowly to a mixture of 30 g. (0.16 mole) of sodium fluosilicate and 10 g. (0.17 mole) of silica (pumice) in a round-bottom glass flask while heating with a bunsen burner. After standing for a week at 25° the reaction mixture was hydrolyzed with acidified ice water and worked up as usual. The yield was 24 g. (0.086 mole, 36% based on sodium fluosilicate), b. p. 160–170° at 0.5 mm. (reported[8] 205° at 10 mm.) The distillate was crystallized twice from ether, once from acetone and again from ether, each time cooling finally with Dry Ice, to obtain a constant m. p., 61.4–61.6° (reported[8] 64°).

Tri-*p*-tolylsilyl fluoride (previously unreported) was similarly prepared starting with 29 g. (0.17 mole, b. p. 183–184°) of *p*-bromotoluene, 4.6 g. (0.19 atoms) of magnesium turnings, 200 cc. of dry ether, 7.5 g. (0.04 mole) of sodium fluosilicate, and 20 cc. of concd. sulfuric acid. The silicon tetrafluoride was passed through the Grignard solution for three hours, then the solution was allowed to stand for one hour at 25° before hydrolysis. The ether extracts were dried over sodium sulfate, evaporated on a water-bath and the residue cooled in a Dry Ice–acetone-bath to induce crystallization. The yield of crystals was 5.5 g. (0.017 mole, 28% based on sodium fluosilicate), m. p. 69–83°. This material was recrystallized from acetone by cooling with Dry Ice, then twice from petroleum ether, till a constant m. p. of 108–109° was obtained. The sample used for kinetic studies had the following analysis.

Anal. Calcd. for $C_{21}H_{21}SiF$, C, 78.71; H, 6.61. Found: 78.11; 6.69.

Triphenylmethyl (trityl) fluoride was prepared from acetyl fluoride and triphenylcarbinol (tritanol) by the procedure of Blicke.[13] The acetyl fluoride was prepared from zinc fluoride and acetyl chloride.[14] Zinc fluoride (technical grade) was heated at 150° for ten hours under oil-pump vacuum to remove all traces of water. Acetyl chloride (150 g., 2.1 moles) was added dropwise through a dropping funnel to 100 g. (0.96 mole) of the dried zinc fluoride in a well-cooled flask protected from moisture by calcium chloride tubes. After completing the addition, the water-bath around the reaction flask was warmed to 30°. All liquid boiling up to 30° was distilled through a Vigreux column and collected in a well cooled receiver. The distillate was poured into a flask containing a small amount of zinc fluoride and redistilled through the column, collecting 76 g. (1.2 moles, 63% yield), of b. p. 20–28°. In a subsequent preparation of acetyl fluoride, constant

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[9] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, pp. 159–160.

[10] It is, however, possible that siliconium ions may exist as intermediates in reactions with exceptionally electrophilic reagents such as aluminum chloride. To decide this, the effect of substituents on the rate of the reactions in question could be determined.

[11] F. Price, This Journal, 69, 2600 (1947); Sommer, Goldberg, Dorfman and Whitmore, *ibid.*, 68, 1083 (1946); Sauer, *ibid.*, 66, 1707 (1944).

[12] Nieuwland and Sowa, *ibid.*, 58, 786 (1936).

[13] Blicke, *ibid.*, 46, 1515 (1924).

[14] Meslans, *Ann. chim. phys.*, [7] 1, 411 (1894).

mechanical stirring was found to increase the speed of reaction and ease of operation. To prepare the trityl fluoride 81 cc. (1.3 moles) of acetyl fluoride was added to a cold mixture of 80 g. (0.31 mole) of tritanol, m. p. 161–162°, and 400 cc. of benzene in a round-bottom flask, stoppered securely with a rubber stopper (wired in), and allowed to stand for four days at 25° with occasional shaking. The benzene was then distilled to reduce the volume to 100 cc., petroleum ether (100 cc.) was added and the solution was cooled. The crystals were collected and recrystallized from ligroin, yielding 48 g. (0.18 mole, 59%), of m. p. 99.5–101°. Five recrystallizations from ligroin, petroleum ether, carbon tetrachloride–ligroin and petroleum ether–ligroin and drying of the crystals *in vacuo* over soda lime and paraffin raised the m. p. to 102–103° (reported m. p., 102–104).[13] Kinetics showed that about 70% of this product was trityl fluoride and 30% tritanol. It appears to be very difficult to separate trityl fluoride from tritanol by recrystallization. Acetyl fluoride was badly occluded when the material was recrystallized in its presence. Further recrystallizations from thoroughly dried solvents, or crystallizations of the mother liquor, or preparations under slightly different conditions all gave less pure products. Therefore this material was used in the kinetic studies, since the presence of tritanol should not interfere with the analytical methods nor affect the rate of reaction of trityl fluoride.

The acetone was Merck reagent grade. Stock solutions (usually 0.02 *M*) were made by weighing out the fluorides and volumetrically dissolving them in Merck reagent acetone.

Procedure.—The approximate solubility of the fluorides in water–acetone mixtures is given in Table IV. This was determined by adding water from a buret to acetone solutions until turbidity appeared.

TABLE IV

SOLUBILITIES OF TRIPHENYLSILYL AND TRIPHENYLMETHYL FLUORIDES IN WATER–ACETONE MIXTURES

Fluoride	Water, %	Solubility (*M*) at 25°	45°	100°
$(C_6H_6)_3Si$	40	0.01		
$(C_6H_5)_3Si$	50	.002	0.02	
$(C_6H_5)_3Si$	60	.0005	.01	
$(C_6H_5)_3Si$	65	.0002		
$(p\text{-}CH_3C_6H_4)_3Si$	30		.01	
$(p\text{-}CH_3C_6H_4)_3Si$	40			0.01
$(p\text{-}CH_3C_6H_4)_3Si$	50		.001	
$(C_6H_5)_3C$	45	.005		
$(C_6H_5)_3C$	60	.002		
$(C_6H_5)_3C$	80	.0005		

Temperature control was ±0.02° at 25°, ±0.1° at 45° and ±0.5° at 100°. A steam-vapor-bath at atmospheric pressure was used at 100°.

Preliminary experiments demonstrated that the reaction of trisyl fluoride with hydroxide ion is so fast that one cannot titrate aliquot samples of 0.001 *M* solutions with dilute sodium hydroxide at 25° to determine the per cent. hydrolysis without hydrolyzing the remaining trisyl fluoride. The end-points were vague and indefinite. The reaction appears to have a half life of ten seconds or less at *p*H 11, corresponding to a rate constant for reaction with hydroxide ion of over 10^{+3} liters mole^{-1} min.$^{-1}$, or ten million times that for reaction with water. This meant that the reaction with water had to be studied below *p*H 7 using analytical procedures in which aliquots were kept always below this *p*H. Methods A, B, and C served this function. The fact that good straight lines on a semi-log plot were obtained below *p*H 7 in spite of increasing acidity during the run shows that the reaction under these conditions was with water rather than with hydroxide ion.

Method A involved periodically titrating aliquot portions of the kinetic solution for fluoride ion with 0.0385 *N* thorium nitrate in acid solution using sodium alizarin sulfonate as indicator.[15] To 25 cc. of distilled water in a flask are added three drops of a saturated water solution of sodium alizarin sulfonate, two drops of 0.02 *M* nitric acid (which gives a yellow color), then 10 cc. of the solution to be titrated. The end-point is the change to a pink color. The method is accurate to ±2%. Time was counted from the moment of removal of the first aliquot, and the titer for this was used as a blank for all later aliquots. The final titer at ten times the half life was used as 100%. The thorium nitrate solution was standardized against a weighed sample of Merck reagent potassium fluoride. The blank in the standardization was 0.02 cc.

Method B used a separate sealed tube for each point, and was used for the runs at 100°. Into soft glass test-tubes previously pulled out for easy sealing, 10-cc. aliquots of a water–acetone solution of fluoride were pipetted. The sealed tubes were placed in the 100° steam-bath simultaneously. On removal each was immediately placed in ice water and the time it was in the steam-bath was recorded. Each tube was opened, emptied into a flask and titrated as in method A. The first tube was used as a zero time point and blank for all the rest.

Method C involved following the increase in acidity by using a concentration cell.[16,17] Two 150 cc. extraction flasks fitted with rubber stoppers were used. In each stopper was fitted one arm of the salt bridge, a sleeve for the glass stirrer, and a shiny platinum wire electrode. In the stopper of the titrating (dummy) cell a 5-cc. buret was also inserted. The stirrers were fitted with rubber sleeves and lubricated with glycerol to cut down evaporation and keep the solutions carbon dioxide free. They were driven by one-inch pulleys on the same belt. The salt bridge was filled with 3% agar gel saturated with potassium chloride. The galvanometer was a Leeds and Northrup No. 2420-D enclosed scale type with a sensitivity of 3 × 10^{-8} amp. mm.$^{-1}$ on a ground glass scale.

Initially 125 cc. of solution was placed in each cell. Quinhydrone (0.01 g.) was added to make the electrodes sensitive to *p*H. At zero time 5 cc. of the stock solution of fluoride was introduced into the reaction cell and 5 cc. of pure acetone into the dummy cell. To follow the reaction the cell was balanced by adding standard hydrofluoric acid to the dummy cell. The buret readings and times when the galvanometer swung through zero were recorded. The first titer was used as 0% and the final titer (at ten times the half life) as 100%.

This method is not as satisfactory for high concentrations because the platinum electrodes are gradually poisoned or desensitized by the organosilicon compounds after continued use (possibly due to coating over, although they remain bright and shiny in appearance). However, it will work with lower concentrations than the other methods.

Method D involved intermittent direct titration with sodium hydroxide of the acid liberated by the whole reacting solution.[18] This method is applicable to trityl halides since the rate of their hydrolysis is independent of the hydroxide ion concentration. Brom thymol blue was used as an indicator. The cell (Fig. 2) consisted of a 4.6 × 21 cm. test-tube, with a capillary side arm entering near the bottom for degassing with a stream of nitrogen. The shaft of a small glass stirrer rested in a depression blown in the bottom of the cell and passed through a glass sleeve in the rubber stopper in the top of the cell. It was driven at high speed by an electric motor. Small vanes, 4 cm. from the bottom, caught the gas bubbles issuing from the capillary tube, causing them to break and fill the whole solution. A thermometer graduated in 0.1° passed through a hole in the rubber stopper.

Standard sodium hydroxide solution (0.0480 *M*) was prepared from a 50% solution with freshly boiled distilled

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[15] Huckaba, Welch and Metler, *Anal. Chem.*, **19**, 155 (1947).

[16] Swain and Ross, THIS JOURNAL, **68**, 658 (1946).

[17] Ross and Swain, *ibid.*, **69**, 1325 (1947).

[18] Technique developed by Peters and Walker, *Biochem. J.*, **17**, 260 (1923).

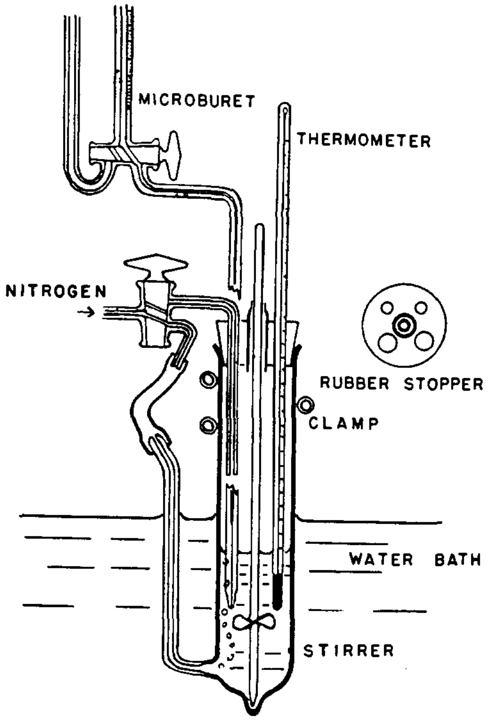


Fig. 2.—Cell used for intermittent titration in methods D and E.

water and protected from atsmospheric carbon dioxide. It was standardized against potassium acid phthalate. It was added from a 2-cc. microburet with a long fine capillary tip below the surface of the solution. For the runs in 95% methanol-5% acetone the methanol was dried over Drierite and distilled before use; in these a sodium methoxide (0.0546 *M*) solution in methanol (prepared by dissolving sodium) was used for titrating.

A cell containing the green shade of brom thymol blue to be matched was clamped in the thermostat bath next to the titration cell. A white porcelain plate was placed behind the two cells and good illumination was provided. The titration apparatus was mounted on a sliding assembly so that it could be easily raised out of the bath. By turning a stopcock the nitrogen stream could be introduced either through the solution or over the surface. Before entering the cell the nitrogen was passed through drying towers containing potassium hydroxide pellets to remove carbon dioxide and then saturated with the solvent by bubbling through two wash bottles each containing 100 cc. of 50% water-50% acetone mixture to prevent the evaporation of acetone from the reaction mixture. Before starting a run 50 cc. of water, 45 cc. of acetone, and 6 drops of 0.1% brom thymol blue were added to the cell. Nitrogen was bubbled through the solution with good motor stirring to remove carbon dioxide until the color of the kinetic cell matched the neutral green of the standard cell. Then the nitrogen stream was diverted over the surface of the liquid and 5 cc. of the stock solution of trityl fluoride was injected with a syringe pipet. The stopwatch was started when the pipet was half empty. It emptied within two seconds: The solution immediately turned yellow but excess base was added to make it blue. Each time when the solution reached a neutral green the time and buret reading were recorded and the solution immediately made basic again by adding excess base. Infinite or total hydrolysis was taken as the volume of base required at ten times the half life (99.9% hydrolysis). Dividing each volume by the total volume gave uncorrected per cent. reaction at a given time. Extrapolation back to zero time gave the initial per cent. reaction due to hydrogen fluoride impurity. This was subtracted out in obtaining corrected per cent. reaction, such as given in Table III or Fig. 4.

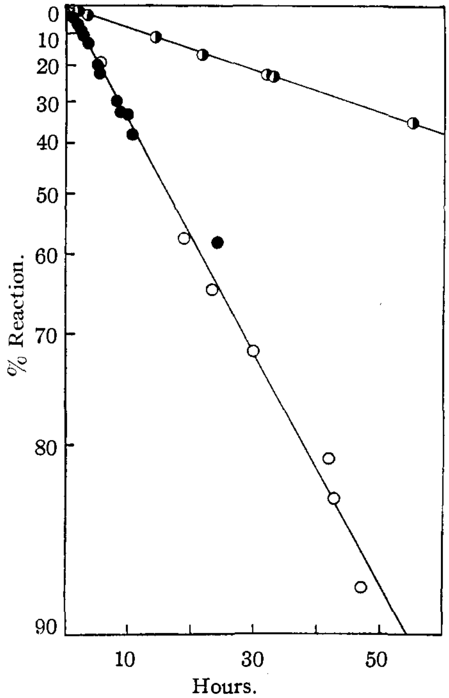


Fig. 3.—Hydrolysis of triarylsilyl fluorides in 50% water-50% acetone solution at 45°. ○, 0.0093 *M* triphenylsilyl fluoride, method A; ●, 0.00085 *M* triphenylsilyl fluoride, method C; ◑, 0.00091 *M* tri-*p*-tolylsilyl fluoride, method C.

Method E was the same as Method D except that the solution was kept acid, rather than basic, except when taking end-points. The fact that methods D and E give

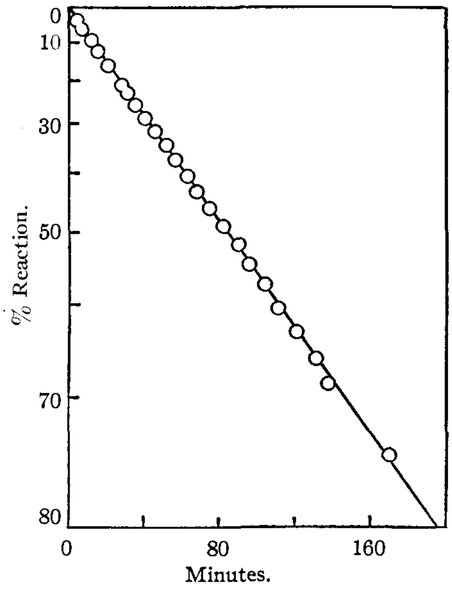


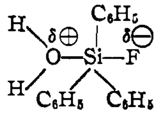
Fig. 4.—Methanolysis of 0.00100 *M* triphenylmethyl fluoride in 95% methanol-5% acetone solution at 25° by method E.

results which are identical within experimental error demonstrates that the rate of reaction of trityl fluoride is independent of *p*H.

Summary

The hydrolysis of triphenylmethyl fluoride in 50% water–50% acetone is insensitive to *p*H, is aided by *p*-alkyl substituents, and is strongly accelerated by increasing the per cent. of water. This indicates an intermediate with a more positive charge on the central carbon atom than the starting material and only three groups attached to it by predominantly covalent bonds.

The hydrolysis of triphenylsilyl fluoride in 50% water–50% acetone is more than a million times faster with hydroxide ion than with water, is retarded by *p*-alkyl substituents, and is weakly accelerated by increasing concentration of inert salt or per cent. of water. These observations are not consistent with the idea of a siliconium ion intermediate with a positive charge on silicon analogous to the "carbonium ion" intermediate in the hydrolysis of triphenylmethyl fluoride above. They indicate instead that the intermediate in the reaction with water has a less positive charge on the silicon atom than the starting material and is more closely represented by the following structure with pentacovalent silicon.



It appears that many reactions of organosilicon compounds may proceed through similar pentacovalent silicon intermediates. This constitutes an easy reaction path for displacements on silicon which is not available to displacements on carbon, since carbon lacks the ability to expand its valence shell to include more than eight electrons.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Methyldichlorosilane and its Fluorination Products[1]

BY HAROLD SIMMONS BOOTH AND ROGER LUCIEN JARRY

This investigation is a continuation of the work done in this Laboratory on the alkyl chloro silanes.[2–7] To the best of our knowledge no mention of the fluorination products, methylchlorofluorosilane and methyldifluorosilane, is made in the literature.

Experimental

Fluorination of Methyldichlorosilane.—Purification of the methyldichlorosilane[7a] prior to fluorination was accomplished by fractional distillation in a column having a total condensation head, and take-off of the design used by Whitmore and Lux. The fluorination was carried out by the Swarts reaction using antimony trifluoride as the fluorination agent, but without the use of a catalyst. The decision not to use a catalyst was made after preliminary tests indicated the possibility of chlorination of the methyldichlorosilane by antimony pentachloride; the yields of the two products without the usual catalyst were in sufficient quantity for purification and study. The apparatus and procedure for the fluorination were essentially the same as those described in previous papers from this Laboratory[8,9] with the modification of the direct condensation described by Booth and Spessard.[2] This modification entailed direct condensation in liquid-nitrogen-cooled ampules instead of the previous procedure of passing the fluorination products through a stripping column and refluxing. Since the problem of producing the intermediate fluorination product in this case was not considered difficult, as subsequent fluorinations proved, the fluorination was carried out at room temperature and atmospheric pressure. The average yields were about fifty per cent. fluorinated products, of which methyldifluorosilane comprised 70% and methyl chlorofluorosilane comprised 30%. The unfluorinated methyl dichlorosilane was repurified and refluorinated. The threshold fluorination temperature is below 20°.

Purification of the Fluorination Products.—The products of fluorination, methylchlorofluorosilane and methyldifluorosilane, were fractionally distilled in a low temperature distillation column of the type previously described[8] with the exception that the packing was a single Podbielniak Heligrid. The pressure control was a modification of the anticipator previously described[10] and will be given in a future publication. The cooling agent used in the column head was acetone cooled by a Dry Ice–acetone-bath. The methylchlorofluorosilane was distilled at pressures of 740 mm. and 300 mm. approximately; the methyl difluorosilane at 740 mm. and 250 mm. approximately.

Analysis.—Samples for analysis were taken in small sealed-glass bulbs.[11] Chlorine was determined by the Volhard method and fluorine by hydrolysis with standard base and back-titrating with standard acid with correction for the hydrochloric acid produced in the hydrolysis. The analysis of the methyldichlorosilane by the Volhard method, after hydrolysis with sodium hydroxide, gave consistently low results. To avoid this a modified Chablay method[12] was used. The results are shown in Table I.

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[1] From a thesis presented by Roger L. Jarry to the Graduate School of Western Reserve University, September, 1948, in partial fulfillment of the requirements for the degree of Master of Science, and based upon work done in connection with a research project sponsored by the Office of Naval Research.

[2] H. S. Booth and P. H. Carnell, THIS JOURNAL, **68**, 2650 (1946).

[3] H. S. Booth and H. S. Halbedel, *ibid.*, **68**, 2652 (1946).

[4] H. S. Booth and W. F. Martin, *ibid.*, **68**, 2655 (1946).

[5] H. S. Booth and J. F. Suttle, *ibid.*, **68**, 2658 (1946).

[6] H. S. Booth and D. R. Spessard, *ibid.*, **68**, 2660 (1946).

[7] H. S. Booth and A. A. Schwartz, *ibid.*, **68**, 2662 (1946).

[7a] Procured from the General Electric Company.

[8] H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939); *Ind. Eng. Chem.*, **29**, 470 (1937).

[9] H. S. Booth and W. C. Morris, THIS JOURNAL, **58**, 90 (1936).

[10] H. S. Booth and R. McNabney, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 131 (1944).

[11] H. S. Booth and W. D. Stillwell, THIS JOURNAL, **56**, 1531 (1934).

[12] H. S. Booth, W. L. Mong and P. E. Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).