627. *Organosilicon Compounds. Part VI.* The Kinetics of the Acid-catalysed Cleavage of* p-*Methoxyphenyltrimethylsilane.*

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The rates of cleavage of the Si–C bond of *p*-methoxyphenyltrimethylsilane by hydrochloric and perchloric acid in aqueous methanol, and by the former acid in aqueous dioxan have been studied spectrophotometrically. The reaction is of first order in the silane, and for a given solvent the rate of reaction is governed by the acidity function of the system; this indicates the rapid formation of an intermediate, probably one in which a proton is attached to the aromatic carbon atom joined to silicon. Changes of rate caused by variation of the water content of the solvent suggest that nucleophilic attack on silicon may be involved in the rate-determining decomposition of the intermediate.

Aromatic groups are readily cleaved from silicon by acids, particularly by concentrated sulphuric acid (*e.g.*, Kipping, *J.*, 1907, 211; 1921, 647). The effects of nuclear substituents on the ease of cleavage appear to parallel those on ease of electrophilic aromatic substitution, since the Si–C_6H_4·NH_2-*p* link is readily, and the Si–C_6H_4·NH_2-*m* link much less readily, cleaved by acids, while the Si–C_6H_4·NO_2 link, whether *meta* or *para*, is very stable to acids (Kipping and Cusa, *J.*, 1935, 1088). Furthermore, for cleavage by hydrogen chloride in glacial acetic acid the ease of removal of groups from silicon is in the order, 2-thienyl > *p*-methoxyphenyl and *p*-dimethylaminophenyl > *p*-tolyl > phenyl > *p*-chlorophenyl (Gilman and Marshall, *J. Amer. Chem. Soc.*, 1949, **71**, 2066). *p*-Methoxyphenyltrimethylsilane is now found to be cleaved much more easily than trimethylphenylsilane in aqueous-methanolic hydrochloric acid.

Kinetics in Aqueous Methanol.—The overall course of the acid-catalysed cleavage of *p*-methoxyphenyltrimethylsilane is represented by

$$p\text{-}Me_3Si{\cdot}C_6H_4{\cdot}OMe + ROH \xrightarrow{H^+} Me_3Si{\cdot}OR + C_6H_5{\cdot}OMe$$

(R = Me or H). The silanol or silicon ester is quickly converted into hexamethyldisiloxane. In 9 vol.-% of water in methanol, with hydrochloric acid as catalyst, the reaction is of first order in *p*-methoxyphenyltrimethylsilane throughout a run, and the first-order constant is independent of the initial concentration of the silane. As the concentration of acid is

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* Part V, *J.*, 1953, 494.

increased from 0·04 to 1·1M the rate constant, k, increases rapidly, and the variation can be represented approximately by a relation of the form $k = k'[\mathrm{HCl}]^{1 \cdot 67}$ over the range 0·2—0·7M, or by $k = k''[\mathrm{HCl}] + k''[\mathrm{HCl}]^2/3$ over the range 0·1—0·8M. These equations fail to keep pace with the rate increase at higher acid concentrations.

With perchloric acid as catalyst the rates are higher than for hydrochloric acid at corresponding concentrations, and the rate rises even more rapidly with increasing acid concentration. This indicates that the rate-equation does not, in fact, involve a square term in acid, for while chloride ion could conceivably be concerned in nucleophilic attack in a transition state in which a proton makes electrophilic attack, giving rise to such a term, the weakly nucleophilic perchlorate ion is very unlikely to participate in this way.

The explanation of the results emerged when the acidity functions H (Braude, *J.*, 1948, 1971) of the reaction media were determined, for a plot of log k against H is a straight line of unit slope over the range of hydrochloric acid concentrations studied, as shown in the following table

Solvent : 9 vol.-% water in methanol. Temp. 49·7°.

[HCl],† M	11·68	7·65	6·43	5·74	4·27	3·38	2·31	1·08	0·498
10^2k, min.$^{-1}$	6·78	2·25	1·75	1·41	0·836	0·598	0·329	0·138	0·42
$-H$	0·220	0·666	0·815	0·888	1·113	1·257	1·484	1·911	—
$-(\log k - H)$	0·95	0·98	0·94	0·96	0·97	0·97	1·00	0·96	—

† This refers to the concentration of aqueous acid, 1 ml. of which was added to 10 ml. of methanolic solution of the silane.

Values of log $k - H$ are similarly constant for the perchloric acid solutions, and agree reasonably well with those for hydrochloric acid.

Solvent : As above. Temp. : 49·7°.

$[\mathrm{HClO_4}]$,* M	5·74	4·12	2·17	0·918
10^2k, min.$^{-1}$	2·01	1·13	0·404	0·124
$-H$	0·779	1·046	1·486	1·968
$-(\log k - H)$	0·92	0·90	0·91	0·94

* See footnote to previous table.

Increase in the water content of the solvent from 9 to 27 vol.-% at a given concentration of hydrochloric acid slows the reaction, particularly at higher acid concentrations. The fall in rate is paralleled by a fall in the acidity function, but while the values of log $k - H$ remain satisfactorily constant as the acid concentration is varied in the 27% water–methanol, they are significantly greater than those in the less aqueous solvent. Water thus has an accelerating effect on the reaction which counteracts the fall in acidity function.

Solvent : 27 vol.-% of water in methanol. Temp. : 49·7°.

[HCl],* M	7·63	6·43	5·74	3·38
10^2k, min.$^{-1}$	1·70	1·25	1·09	0·507
$-H$	0·993	1·106	1·171	1·505
$-(\log k - H)$	0·78	0·80	0·79	0·79

* See footnote to first table.

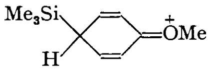
Kinetics in Aqueous Dioxan.—In 45·5 vol.-% water in dioxan the reaction is again of first order in *p*-methoxyphenyltrimethylsilane, and log $k - H$ is satisfactorily constant. When, however, the water content of the dioxan is increased over the range 8—25M(14—52 vol.-%) water the rate constant falls less rapidly than is required by the fall in H, so that the value of log $k - H$ increases. The values of log $k/[\mathrm{H_2O}] - H$ are more nearly constant for 8—25M-water, while those of log $k/a_{\mathrm{H_2O}} - H$ are satisfactorily constant over this range. and reasonably so over the whole range which could be studied.

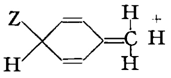
Solvent : Water–dioxan. Temp. : 49·7°.

$[\mathrm{H_2O}]$, M	8·12	10·11	12·64	15·17	20·22	25·28	26·90	28·77	25·28	25·28	25·28
[HCl], M	0·278	0·526	0·664	0·789	1·045	1·055	0·870	0·973	0·794	1·324	0·526
10^2k, min.$^{-1}$	0·167	0·391	0·507	0·631	1·20	1·43	0·974	1·44	0·765	0·231	0·032
$-H$	1·520	1·204	1·125	1·113	0·964	0·864	0·996	0·874	1·080	0·636	1·468
$-(\log k) - H$	1·26	1·20	1·16	1·11	0·96	0·98	1·01	0·97	1·04	1·00	1·03
$-(\log k/a_{\mathrm{H_2O}}) - H$	2·40	2·41	2·43	2·45	2·40	2·50	2·55	2·54	—	—	—

The Mechanism of the Reaction.—Constancy of log $k - H$ for an acid-catalysed reaction is usually interpreted as indicating the existence of a fast reversible proton transfer from the solvent to the substrate before the rate-determining step (*e.g.*, Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, p. 275; Braude and Stern, *J.*, 1948, 1982; Long and Purchase, *J. Amer. Chem. Soc.*, 1950, **72**, 3272). Since the effects of substituents on the acid cleavage of silicon–aryl bonds appear to parallel those on aromatic substitution, it seems probable that the *p*-methoxy-group activates through its $+E$ effect, so that an intermediate with a proton on the ether oxygen is unlikely to be effective in the cleavage reaction, but it cannot be finally rejected. An acceptable intermediate would be that having (as one mesomeric form) the structure (I). Ions of the analogous form (II) (with resonance variations) have been postulated to exist in the complexes formed by aromatic hydrocarbons and hydrogen chloride in the presence of aluminium chloride ($Z = H^+$; Brown and Brady, *ibid.*, 1952, **74**, 3570) and by these hydrocarbons with hydrogen fluoride in presence of boron trifluoride ($Z = H$; McCaulay and Lien, *ibid.*, 1951, **73**, 2013), and as intermediates produced in the rate-determining step of aromatic nitration ($Z = NO_2$; Hughes, Ingold, and Reed, *J.*, 1950, 2400). The polarity $\overset{\delta+}{\mathrm{Si}}$–$\overset{\delta-}{\mathrm{C}}$ should facilitate the formation of the intermediate (I). If an intermediate of type (I) is general for acid-catalysed cleavage of silicon–aryl bonds, nuclear substituents which supply electrons to the carbon atom attached to silicon would increase the rate of cleavage by increasing the concentration of the intermediate, and the rules for aromatic substitution would apply to the cleavage. Furthermore, the particular effectiveness of concentrated sulphuric acid would be understandable, since the acidity functions of this medium are exceptionally high (Hammett, *op. cit.*, p. 268).

(I)





(II)

The protonated intermediate could decompose unimolecularly to form anisole and a siliconium ion, which would then quickly react with the solvent. In this case no molecule of water would be involved in covalency change in the transition state and log $k - H$ might be expected to remain reasonably constant as the water content of the medium is varied. However, the silicon atom is very susceptible to nucleophilic attack, and should be especially so in a positively charged complex. The reaction sequence could be:

$$p\text{-}\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}OMe} + \mathrm{H^+} \overset{\text{fast}}{\rightleftharpoons} p\text{-}\mathrm{Me_3Si{\cdot}\overset{+}{C}_6H_5{\cdot}OMe}$$

$$p\text{-}\mathrm{Me_3Si{\cdot}\overset{+}{C}_6H_5{\cdot}OMe} + \mathrm{H_2O} \xrightarrow{\text{slow}} \mathrm{Me_3Si{\cdot}\overset{+}{O}H_2} + \mathrm{C_6H_5{\cdot}OMe}$$

$$\mathrm{Me_3Si{\cdot}OH_2} \xrightarrow{\text{fast}} \mathrm{Me_3Si{\cdot}OH} + \mathrm{H^+}$$

Such a scheme is formally analogous to that postulated by Keading and Andrews (*J. Amer. Chem. Soc.*, 1952, **74**, 6189) for the acid hydrolysis of *p*-nitrobenzophenone diethyl ketal in aqueous ethanol, in which constancy of log $k/a_{H_2O} - H$, expected on the assumption of rate-determining attack of a water molecule on the oxonium salt of the ketal, was experimentally demonstrated. In the present case log $k/a_{H_2O} - H$ gives better constancy than log $k - H$ in aqueous dioxan, while log $k - H$ in 27% water–ethanol is higher than in the more weakly nucleophilic 9% medium. In the absence of evidence to the contrary it seems reasonable to suppose that nucleophilic attack on silicon is involved in the decomposition of the protonated intermediate, but no definite conclusion is possible.

Acidity Functions, and the Activity of Water in Dioxan.—The values of the acidity function of hydrochloric acid in aqueous methanol appear to be somewhat higher than in the corresponding ethanolic solutions (Braude and Stern, *J.*, 1948, 1976). The acidity functions of solutions of perchloric acid in 9% water–methanol are higher than those of hydrochloric acid of the same concentration, as is the case for more concentrated aqueous solutions (Hammett, *op. cit.*, p. 269).

Values of the activities of water in dioxan containing hydrochloric acid are not available. Since the mole fractions of hydrochloric acid present in the kinetic studies were relatively low, the activity coefficients of water in dioxan were used as an approximation. These were calculated from the partial vapour pressures of water in dioxan at 25° (listed by Hovorka, Schaefer, and Dreisbach, *ibid.*, 1936, **58**, 2264), according to the method of Butler, Thomson, and Maclennan (*J.*, 1933, 674), with the following results :

Water, mole fraction	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
f_{H_2O}	4·28	3·00	2·25	1·85	1·60	1·48	1·39	1·32	1·21

EXPERIMENTAL

p-*Methoxyphenyltrimethylsilane.*—Chlorotrimethylsilane (54 g.) was boiled under reflux for 7 hr. with the Grignard reagent from *p*-methoxyphenyl bromide (100 g.) and magnesium (14 g.) in ether (200 ml.). Hydrolysis, followed by fractionation of the ethereal layer, gave p-*methoxyphenyltrimethylsilane* (31 g.), b. p. 222·5—223·5°. The product was redistilled in nitrogen, and a middle sample (of *ca.* 2 g.), $n_D^{13·5}$ 1·5073, was used (Found : C, 66·7; H, 9·1. $C_{10}H_{16}OSi$ requires C, 66·6; H, 8·9%).

Cleavage of p-*Methoxyphenyltrimethylsilane and Trimethylphenylsilane.*—Methanol (46 ml.) *p*-methoxyphenyltrimethylsilane (11·5 g.), and hydrochloric acid (5·4 ml.; s.g. 1·18; sufficient to make the mixture about 1N in acid) were boiled for 3½ hr. The mixture was poured into water; drying and fractionation of the ether extract gave hexamethyldisiloxane (4·0 g., 80%) and anisole (6·5 g., 93%).

Trimethylphenylsilane under the same conditions gave small amounts of hexamethyldisiloxane and benzene, and 93% of unchanged material.

Ultra-violet Absorption Spectra.—A Unicam S.P. 500 spectrophotometer was employed. In methanol (redistilled " AnalaR " material, probably slightly aqueous) the absorption curves of anisole and *p*-methoxyphenyltrimethylsilane are similar in shape but that of the latter is displaced by *ca.* 30 Å towards the visible and the extinction coefficients at both maxima are less. The maxima are : anisole; 2710 (ε, 1780), 2775 (ε, 1530), and 2647 Å (inflexion); *p*-methoxyphenyltrimethylsilane; 2735 (ε, 1380), 2805 (ε, 1260), and 2664 Å (inflexion). The curves cross at 2757 (ε, 2120) and 2733 Å (ε, 1370). The presence of dioxan ($<$10%) displaces the curves slightly. The wave-lengths chosen for spectrophotometric assay in the rate studies were 2700 Å [ε = 1720 (anisole) and 1160 (*p*-methoxyphenyltrimethylsilane)], 2820 Å (ε, 240 and 980, respectively), and either 2757 or 2755 Å depending upon whether the runs were in methanol or dioxan.

Trimethylsilanol, hexamethyldisiloxane, and methoxytrimethylsilane do not absorb in this spectral region.

General.—For kinetic measurements, " AnalaR " methanol was dried by Bjerrum and Zechmeister's method (*Ber.*, 1923, **56**, 894), and dioxan was purified by Eigenberger's method (*J. pr. Chem.*, 1931, **130**, 75) and dried by boiling it with sodium.

Volume changes on mixing have been neglected except in calculating the activity coefficients of water in dioxan: " 20% water–methanol " refers to a solution consisting of 20 ml. of water made up to 100 ml. with methanol.

Kinetic Measurements.—All runs were carried out in a thermostat at 49·7° ± 0·02°.

For the runs in aqueous methanol, 1 ml. of aqueous acid of known strength was added to 10 ml. of an 0·02M solution of *p*-methoxyphenyltrimethylsilane in methanol or 20% water–methanol contained in the thermostat. At intervals, 1-ml. samples of the mixture were withdrawn and made up to 10 ml. with methanol, and the optical density, *D*, of the resulting solution was determined against the appropriate solvent blank at 2700, 2757, and 2820 Å, 0·5-cm. cells and a fixed slit width of 0·3 mm. being used. Since evaporation of the reaction mixture was serious during long periods, the values of D_∞ were obtained with the appropriate solution of anisole. When an 0·2M-solution of the silane was used, with hundredfold dilution of the 1-ml. sample for assay, the rate constant was unaffected.

For runs in dioxan, 1 ml. of an 0·2M solution of the silane in dioxan was added to 10 ml. of aqueous dioxan of known acid concentration. The 1-ml. portions withdrawn were *added* to 10 ml. of methanol, and the optical density was determined as before, but at 2700, 2755, and 2820 Å. Values of D_∞ were again determined by use of anisole, but in sample checks these agreed well with figures for the reaction mixture after a time equal to ten times the half-life.

For runs in methanol the optical density at 2757 Å was used only to indicate whether evaporation was serious, and a run in which it changed by more than 5% was rejected. For runs in dioxan the optical density at 2755 Å was used to correct the *D* (2820 Å) figures for errors in volume (particularly pipette-drainage errors) involved in rapid withdrawal of the 1-ml. samples. The *D* (2700 Å) values could not be accurately determined at the concentrations employed and were used only to confirm that the reaction was following the expected course. Reactions were followed to more than 60% completion.

The rate constant is given by

$$k_t = 2{\cdot}303 \log [D_0(2820\ \text{Å}) - D_\infty(2820\ \text{Å})]/[D_t(2820\ \text{Å}) - D_0(2820\ \text{Å})]$$

Values of *k* were obtained from the slope of the straight-line plot of log $[D_t(2820\ \text{Å}) - D_\infty(2820\text{Å})]$ against time, but rate constants calculated throughout the reaction are included in the following typical runs. (The figures in parentheses for zero and infinity readings were determined by use of anisole solutions.)

(*a*) Solvent; 9 vol.-% water in methanol: [HCl] (added), 6·43N: temp., 49·7°.

Time, min.	0	9	17	28	38	52	76	∞
10^3D(2757 Å)	—	1117	1142	1122	1142	1150	1142	—
10^3D(2700 Å)	(1100)	1176	1257	1304	1372	1430	1486	(1620)
10^3D(2782 Å)	890	797	718	633	567	498	405	(230)
10^4k, min.$^{-1}$	—	172	179	177	173	175	175	—

k from graph, 175 × 10^{-4} min.$^{-1}$.

(*b*) Solvent: 45·5 vol.-% water in dioxan: [HCl], 0·794N: Temp., 49·7°.

Time, min.	0	16	31	48	65	92	120	200	∞
10^3D(2755 Å)	(1055)	1062	1062	1055	1043	1058	1052	1054	—
10^3D(2700 Å)	(972)	1038	1092	1129	1166	1240	1287	1375	(1480)
10^3D(2820 Å)	—	780	724	660	606	547	490	378	—
10^3D(2820 Å) corr.*	(847)	775	719	662	613	546	491	378	(247)
10^4k, min.$^{-1}$	—	792	772	768	762	756	750	751	—

k from graph, 764 × 10^{-4} min.$^{-1}$. * *D*(2820 Å) corr. = *D*(2820 Å) × 1·055/*D*(2755 Å).

Determination of Acidity Functions.—Braude's method (*loc. cit.*) was employed, *p*-nitroaniline being used as indicator (B). The solutions were made up as for the reaction media, so that for the methanolic solutions 1 ml. of aqueous acid of strength c_A was added to 10 ml. of anhydrous methanol or 20% water–methanol containing the indicator (4 × 10^{-4}M) or nitrobenzene (0·025M). For measurements in aqueous dioxan, 1 ml. of a solution of the indicator (1·4 × 10^{-3}M) or of nitrobenzene (0·33M) in dioxan was added to 10 ml. of aqueous dioxan (11*x*/10 ml. of water in 100 ml. of solution) containing hydrochloric acid of concn. $11c_A'/10$M. Because volume-additivity is assumed, and because pipettes were not calibrated for all the solutions, the values of the indicator ratio, $I = [BH^+]/[B]$, are more accurate than the absolute values of the extinction coefficients. Measurements were at *ca.* 18°. In the following tables

(*a*) Solvent, 9% water-methanol. Acid, hydrochloric. $\lambda_N = \lambda_A = 374$ mμ. ε_N, 15,950. ε_S, 60.

c_A, N	11·40	7·63	6·43	5·74	4·27	3·38	2·306	1·451	1·079
ε_A	2,820	5,460	6,740	7,400	9,440	10,670	12,330	13,850	14,370
I	4·75	1·94	1·38	1·16	0·693	0·497	0·295	0·152	0·111
− *H*	0·277	0·666	0·815	0·888	1·113	1·257	1·484	1·771	1·911

(*b*) Solvent, 27% water–methanol. Acid, hydrochloric. $\lambda_N = \lambda_A = 380$ mμ. ε_N, 15,770. ε_S. 40.

c_A, N	7·630	6·43	5·74	4·27	3·38
ε_A	8,260 *	9,270	9,830	11,260	12,320
I	0·914	0·705	0·607	0·402	0·281
− *H*	0·993	1·106	1·171	1·350	1·505

* $\lambda_A = 381$ mμ.

(*c*) Solvent, 9% water–methanol. Acid, perchloric. $\lambda_N = \lambda_A = 374$ mμ. ε_N, 15,950. ε_S, 60.

c_A, N	5·74	4·12	2·17	0·918
ε_A	6,420	8,840	12,340	14,550
I	1·50	0·809	0·294	0·097
− *H*	0·779	1·046	1·486	1·968

(*d*) Solvent, x% water–dioxan. Acid, hydrochloric.

x	c'_A, N	λ_N, mμ	ε_N	ε_A	λ_A, mμ	ε_S	I	$-H$
14·5	0·278	369	16,790	13,280	369	90	0·266	1·43
14·5	0·421	369	16,790	10,670	367	90	0·573	1·20
18·2	0·526	370	16,790	10,780	370	80	0·561	1·20
23·2	0·666	371	16,740	9,870	372	80	0·674	1·13
27·3	0·789	374	16,650	9,860	374	70	0·693	1·11
36·0	1·045	377	16,621	8,440	376	60	0·976	0·96
45·5	1·055	380	16,280	7,330	380	50	1·230	0·86
45·5	0·794	381	16,500	10,010	381	50	0·652	1·14
45·5	1·324	381	16,280	5,310	381	50	2·08	0·64
45·5	0·526	380	16,500	12,650	378	60	0·306	1·47
47·3	0·870	380	16,500	8,680	381	50	0·906	1·00
51·8	0·973	381	16,310	7,260	382	40	1·26	0·86

λ_N and ε_N refer to the wave-length and molecular-extinction coefficients of the indicator at the absorption peaks in neutral solution, λ_A and ε_A are the corresponding values in acid solution, and ε_S refers to that of the nitrobenzene solution at λ_A. The acidity function is given by $H = \log I - 0{\cdot}954$, where $I = (\varepsilon_N - \varepsilon_A)/(\varepsilon_A - \varepsilon_S)$.

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