291. *Organosilicon Compounds. Part XVII.* The Acidic Solvolysis of Organosilicon Hydrides.*

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A kinetic study has been made of the decomposition of organosilicon hydrides by hydrogen chloride in aqueous ethanol or aqueous dioxan. It is concluded that the reaction involves nucleophilic attack by a solvent molecule on the silicon atom of the Si–H bond and electrophilic attack by an oxonium ion on the hydrogen atom.

There is a linear relation over the whole range of acid concentrations between the logarithm of the velocity constant for a given organosilane and the logarithm of the ratio of conjugate acid to free base for *p*-nitroaniline.

TAKETA, KUMADA, and TARAMA [1] concluded that the rate of acidic ethanolysis of triethyl-silane is proportional to the square of the mean activity of hydrogen chloride, and thus to the product of the activities of chloride and oxonium ion. The implication of this, either that both chloride ion and oxonium ion are involved in the rate-determining step, or that catalysis is by undissociated hydrogen chloride, seemed to us improbable, and our view is confirmed by the work described below.

Dependence of Rate on Acid Concentration.—To avoid difficulties with traces of water which are formed in solutions of strong acids in ethanol, we used aqueous 95% ethanol as solvent, and to facilitate measurements in dilute acid we used the reactive di-*n*-propyl- and *cyclo*hexyl-silane.

The acidic solvolysis of di-*n*-propylsilane takes place stepwise. The first Si–H bond is broken some 18 times as quickly as the second, and first-order rate constants, k_1 and k_1', for the two steps may be obtained from a single run, but only k_1 is of interest. (The rate constant k_1' probably refers to the hydrogen evolution from *s*-tetra-*n*-propyldisiloxan.)

Table 1 shows that below 0·5M-acid, k_1 is accurately proportional to the hydrogen chloride concentration, and thus to the concentration of oxonium ion, since dissociation is complete in this medium.[2] (In agreement with this, the rates are not significantly different when perchloric acid is used.) At higher concentrations k_1 increases more rapidly with acid concentration, the variation in the range 0·6—1·4M being expressed roughly by the equation $10^4 k_1 = 87[\text{HCl}] + 68[\text{HCl}]^2$.

* Part XVI, *J.*, 1955, 4023.

[1] Taketa, Kumada, and Tarama, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1953, **31**, 260.

[2] Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330.

Table 1 also shows that there is an exact linear relation between $\log k_1$ and $\log I$, where I is the indicator ratio (at 18°) for *p*-nitroaniline (*i.e.*, the ratio of the concentration of the conjugate acid of *p*-nitroaniline to that of the free base). This linearity covers the whole range of acid concentration, and not just the lower part in which both $\log k_1$ and $\log I$ are proportional to $\log$ [HCl].

TABLE 1. *Solvolysis of di-n-propylsilane in aqueous-ethanolic hydrogen chloride at* 34·9°.

[HCl] (M)	0·109	0·195	0·390	0·651	0·977	1·302	1·954
$10^3 k_1$ (min.$^{-1}$)	1·31	2·43	4·94	8·57	14·4	22·2	48·8
I	0·035(4)	0·104	0·314	0·782	1·795	3·796	12·17
$10^3 k_1$/[HCl]	12·0	12·5	12·7	13·2	14·8	17·1	25·0
$-(\log k_1 - 0·62 \log I)$	1·98	2·00	2·00	2·00	2·00	2·01	1·98

The range of low acid concentration was investigated more accurately with *cyclo*hexylsilane. The initial rate of hydrogen evolution was used as a measure of the rate of reaction and could be determined with accuracy because it remained constant during the evolution of 20% of the hydrogen available. (The apparent zero-order nature of the hydrogen evolution must result from similar reactivites of all three available hydrogen atoms in the stepwise decomposition. The initial rate is, in fact, proportional to the initial concentration of the organosilane.) Again (Table 2), the rate of reaction (expressed as a zero-order rate constant, k_0, which is the rate of hydrogen evolution arbitrarily divided by the volume of hydrogen which would be obtained from complete reaction of one Si–H bond of the *cyclo*hexylsilane), is proportional to the acid concentration below 0·6M. Above this the variation in rate has the same form as that for di-*n*-propylsilane, $\log k$–[HCl] plots for the two hydrides being superimposable. It follows that $\log k_0$–$\log I$ plots for *cyclo*hexylsilane are linear, as confirmed by the constancy of ($\log k_0$–0·6 $\log I$) in Table 2.

TABLE 2. *Solvolysis of* cyclo*hexylsilane in aqueous-ethanolic hydrogen chloride at* 34·9°.

[HCl] (M)	0·0245	0·049	0·098	0·131	0·163	0·196	0·327	0·490	0·654	0·980	1·300
$10^3 k_0$ (min.$^{-1}$)	0·125	0·257	0·513	0·677	0·835	0·996	1·68	2·56	3·53	5·61	8·52
$10 k_0$/[HCl]	0·51	0·52	0·52	0·52	0·51	0·51	0·51	0·52	0·54	0·57	0·66
I *	—	—	0·030	0·051	0·075	0·105	0·232	0·460	0·784	1·802	3·79
$-(\log k_0 - 0·6 \log I)$	—	—	1·38	1·40	1·40	1·41	1·39	1·39	1·39	1·40	1·42

* Obtained by interpolation from experimental values in Table 1.

It appears that the form of dependence of rate on acid concentration is not much influenced by the organosilicon hydride employed, and similar results would be expected for triethylsilane. It is thus interesting to re-examine Taketa, Kumada, and Tarama's data [1] for its reaction in anhydrous ethanolic hydrogen chloride, and the variation in k_1/([HCl] × f)^2 (where f is the activity coefficient of hydrogen chloride) shows (Table 3)

TABLE 3. *Reaction of triethylsilane with ethanolic hydrogen chloride at* 50°. (Kinetic data from Taketa, Kumada, and Tarama.[1])

[HCl] (M)	0·0425	0·085	0·127	0·170	0·525	1·05	1·57	2·10
$10^3 k_1$ (min.$^{-1}$)	0·06	0·158	0·255	0·362	1·12	3·74	7·70	13·30
k_1/([HCl] × f)^2	2·30	2·28	2·01	1·72	1·25	1·54	1·59	1·78
$10^3 k_1$/[HCl]	(1·42)	1·86	2·02	2·13	2·13	—	—	—
I	0·88	1·81	2·72	3·65	8·50	22·42	—	—
$-(\log k_1 - 1·27 \log I)$	4·15	4·13	4·14	4·15	4·15	4·15	—	—

that the rate is not proportional to the activity of hydrogen chloride as they claim. A k_1–[HCl] plot is a straight line for the four lowest acid concentrations, but does not pass through the origin, and we suggest that the rate is in fact proportional to the acid concentration but that there is a small constant experimental error in k_1 (possibly associated with the "induction period"). This will be most serious for the weakest acid, and if the figure for this is neglected, k_1/[HCl] is reasonably constant up to 0·525M-acid. Further,

over the whole range of concentration for which values of I may be obtained by interpolation from Braude's data,[3] values of $(\log k_1 - 1.27 \log I)$ are reasonably constant.

Addition of Water and Salts.—Increase in the water content of the medium from 5% to 10% causes a decrease in the rate of reaction, this decrease being relatively greater the higher the concentration of acid, as revealed in Table 4, which refers to the reaction of di-*n*-propylsilane at 34·9°.

TABLE 4.

[HCl] (M)	1·954	1·302	0·977
$10^3 k_1$ (min.$^{-1}$) (in 95% EtOH)	48·8	22·2	14·4
$10^3 k_1$ (min.$^{-1}$) (in 90% EtOH)	31·0	18·0	12·7

Inhibition by added water is common for acid-catalysed reactions in alcoholic solvents,[4] and is associated with the replacement of ethoxonium ions by the less reactive hydroxonium ions. The increase in the effect as the acid concentration is raised may reasonably be related to the greater lowering of $\log I$ by added water at higher acid concentrations.[4]

As shown in Table 5 (which refers to the reaction of di-*n*-propylsilane in 95% ethanol at 34·9°) additions of lithium chloride or tetraethylammonium bromide increase the rate of reaction (but the former rather less than would be expected if the equation $10^4 k_1 = 87[\text{HCl}] + 68[\text{H}^+][\text{Cl}^-]$ applied). In view of the low dielectric constant of the medium, which magnifies salt effects, there is no reason to doubt that the rate changes are purely medium effects, chloride or bromide ions not entering into the reaction. Though both salts raise the reaction rate, the lithium salt raises the value of $\log I$ while the tetraethylammonium salt lowers it, probably because both salts raise the activity coefficient of the organosilane while the former raises, and the latter lowers, the activity coefficient of *p*-nitroaniline.[5]

TABLE 5.

[HCl] (M)	0·977	0·977	0·977	0·977	0·710	0·710	0·710	0·710
Salt	—	LiCl	LiCl	LiCl	—	Et$_4$NBr	Et$_4$NBr	Et$_4$NBr
[Salt] (M)	—	0·263	0·469	0·960	—	0·129	0·285	0·479
$10^3 k_1$ (min.$^{-1}$)	1·37	1·45	1·56	1·90	0·98	1·00	1·03	1·11
$\log I$	0·27	0·29	0·43	—	−0·04	−0·06	−0·08	−0·13

Solvent Isotope Effect.—The reaction of *cyclo*hexylsilane is 2·25 times as fast in protium oxide–dioxan as in deuterium oxide–dioxan, as shown in Table 6 which refers to 0·490M-hydrogen chloride at 34·9°.

TABLE 6.

	Protium oxide				Deuterium oxide	
Vol. % of H$_2$O (or D$_2$O)	0	10	20	20	20	20
k_0 (min.$^{-1}$)	<0·0002	0·0089	0·0133	0·0134	0·0059(3)	0·0058(9)

This means that proton transfer occurs in the rate-determining step and not in a prior fast reversible step. The assumption involved, *viz.*, that acids are more dissociated in protium oxide–dioxan than in deuterium oxide–dioxan, has been experimentally justified in the case of the conjugate acid of *p*-nitroaniline (unpublished work by Mr. J. B. Hurd).

Variation of Structure.—The rate constants at two temperatures for several triorgano-monosilanes, R$_3$SiH, at the same hydrogen chloride concentration (1·430M) in 95% ethanol are shown in Table 7 along with approximate activation energies, E (the variations in which are not significant). All the reactions were of first order in organosilane.

The effects of *para*-substitution show that electron release to silicon slightly hinders the reaction. The low reactivity of tri*iso*propylsilane compared with that of the normal compound (relative reactivities, 1 : 10) is probably mainly a steric effect, comparable with that in alkaline hydrolysis in which the reactivity ratio is 1 : 20 but in which electron release by the *iso*propyl group contributes more to the inhibition.

[3] Braude, *J.*, 1948, 1971.
[4] Braude and Stern, *J.*, 1948, 1976.
[5] Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3243.

TABLE 7.

R_3 in R_3SiH	Et_3	Pr^n_3	Bu^n_3	Bu^i_3	Pr^i_3	Ph_3
$10^3 k_1$ (34·9°)	1·19	0·745	0·70	0·20	0·07	0·40
$10^3 k_1$ (45·0°)	3·03	2·07	1·95	—	—	—
E, kcal./mole	18·1	19·8	19·9	—	—	—
Relative rates (34·9°) *	1	0·63	0·59	0·17	0·06	0·3

R_3 in R_3SiH	$(p\text{-}C_6H_4Cl)_3$	$(p\text{-}C_6H_4Cl)Me_2$	$PhMe_2$	$(p\text{-}C_6H_4Me)Me_2$
$10^3 k_1$ (34·9°)	1·5	2·58	2·13	1·82
$10^3 k_1$ (45·0°)	—	—	5·52	5·02
E, kcal./mole	—	—	18·5	19·7
Relative rates (34·9°) *	1·3	2·2	1·8	1·5

* At this acid concentration, the relative reactivities of $C_6H_{11}SiH_3$, $Pr^n_2SiH_2$ (first Si–H), and Et_3SiH are 120 : 22 : 1.

The variation in reactivity of the organosilicon hydrides examined is small compared with that in other reactions.[6,7]

Mechanism of the Reaction.—The observed solvent isotope effect and the first-order dependence of rate on acid concentration in dilute acid mean that electrophilic attack by an oxonium ion on the hydrogen atom of an Si–H bond is involved in the rate-determining step. However, since the reaction is hindered by electron-release to the silicon atom, the latter must be more negatively charged in the transition state than in the ground state, and thus there must also be nucleophilic attack on silicon, normally by a solvent molecule. In agreement with this, reaction is very slow in anhydrous dioxan (although the proton-availability, as measured by I, is quite high [3]); a much faster reaction occurs when water is added, and the rate increases with the water concentration even though the value of I falls.[4]

Since in alkaline hydrolysis, in which electrophilic attack on the incipient hydride ion of the Si–H bond is by a water molecule, $SiH \cdots HOH$ bonding is considerable in the transition state,[8] the analogous $SiH \cdots H\overset{+}{O}H_2$ bonding should be even stronger in acid catalysis when attack is by the positively charged oxonium ion. This explains the relatively small solvent isotope effect, since the loss of zero-point energy from the $H-^+OH_2$ bond is partially compensated by the gain in zero-point energy in the $H \cdots H$ bond of the transition state.

A two-stage mechanism fits the facts, the first step being fast and reversible and the second rate-determining :

$$\equiv\!SiH + H_2O \rightleftharpoons H_2\overset{+}{O}\!-\!\overset{-}{Si}H \; ; \; H_2\overset{+}{O}\!-\!\overset{-}{Si}H + H-\overset{+}{O}H_2 \longrightarrow H_2OSi\!\equiv + H_2 + H_2O$$
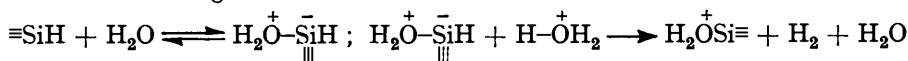
(There will be a subsequent fast proton loss from $\equiv\!Si\overset{+}{O}H_2$.) In the rate-determining transition state the silicon atom is more negative than in the (original) ground state even if the Si–H bond is considerably stretched. The transition state could be reached without formation of an intermediate, in a synchronous process in which the new bond to silicon is slightly more formed than the Si–H is broken, but this would involve a termolecular collision.

Since the rapid increase in rate in more concentrated acids is paralleled by increase in the indicator ratio, I, it is reasonable to attribute it to a medium effect rather than to a change in mechanism, but the possibility of intervention by chloride ion or undissociated hydrogen chloride has not been experimentally excluded. Since dissociation is substantially complete in the solvent used, undissociated hydrogen chloride would need to be very reactive for its intervention to cause the rate increase.

Acidity Functions in Organic Solvents.—Braude [3] first measured the indicator ratios for solutions of p-nitroaniline in anhydrous or aqueous ethanol, acetone, or dioxan, and derived acidity functions H, by means of the relation $H = \log I - \log K_B^{H_2O}$ which holds in aqueous solutions ($K_B^{H_2O}$ being the indicator constant in dilute aqueous solution). Gutbezahl and Grunwald [9] point out, however, that values of f_{BH+}/f_B (which determine I for a given base,

[6] Baines and Eaborn, *J.*, 1955, 4023.
[7] (a) Deans and Eaborn, *J.*, 1954, 3169; (b) Eaborn, *J.*, 1955, 2517.
[8] Kaplan and Wilzbach, *J. Amer. Chem. Soc.*, 1955, **77**, 1297.
[9] Gutbezahl and Grunwald, *ibid.*, 1953, **75**, 559.

and hence *H*), where f_B is the activity coefficient of the neutral base and f_{BH^+} that of its conjugate acid, are not independent of the base in solutions of low dielectric constant, and thus the acidity function concept has no application in alcoholic solvents.

Use of acidity functions for a given solvent containing varying amounts of acid would be empirically justified by a unit-slope straight-line plot of log *I* for one base against log *I'* for another base, but in 27% water in methanol, for example, the log *I*–log *I'* plot even for the related bases *p*- and *o*-nitroaniline, while it is a straight line, has a slope of 0·82 (unpublished work by Mr. J. B. Hurd). It follows that the unit slope of the log *k*–*H* plot in acidic cleavage of *p*-methoxyphenyltrimethylsilane in this solvent [10] is fortuitous, depending on the choice of *p*-nitroaniline as indicator.

The significance of the linearity of log *k*–log *I* and log *I*–log *I'* plots is not clear; either non-linearity or unit-slope linearity would be expected. Slopes of up to 1·4 for straight-line log *k*–*H* plots in aqueous solutions have been explained as salt effects, log *k*–(*H* — constant × c_A) plots (c_A is the concentration of acid) being unit-slope straight lines, but no such plot fits our data. [Plots of log *k*–log *I* and log *k*–(log *I* — constant × c_A) can both be linear only if log *I* is proportional to c_A, and this is not even approximately true in 95% ethanol.]

It is tempting to infer that when log *k*–log *I* relations are of the same type as log *I*–log *I'* relations, then the transition state of the reaction is the conjugate acid of the ground-state molecule, but in the acidic solvolysis of organosilyl hydrides the transition complex also contains solvent molecules. Perhaps the only reasonable inference, and this tentative, is that variations in *k* with acid concentration (outside those expected for simple proportionality) are caused by the medium effects which account for the variations in *I*, and not by mechanistic changes.

<div align="center">EXPERIMENTAL</div>

Materials.—p-*Chlorophenyldimethylsilane*, b. p. 199·5°, n_D^{20} 1·5188 (Found : C, 56·6; H, 6·7. $C_8H_{11}ClSi$ requires C, 56·3; H, 6·5%), was prepared by treating trichlorosilane (1 mol.) successively with *p*-chlorophenylmagnesium bromide (1 mol.) and methylmagnesium iodide (2 mol.) in ether. To remove a fuming impurity the product was dissolved in methanol and recovered after ½ hr.

Dimethyl-p-*tolylsilane*, b. p. 181—182°, n_D^{20} 1·5000 (Found : C, 71·7; H, 9·2. $C_9H_{14}Si$ requires C, 71·9; H, 9·4%), was prepared by reduction of fluorodimethyl-*p*-tolylsilane with excess of lithium aluminium hydride. The product was free from unchanged fluoride.

Rate Measurements.—Reactions were carried out in the twin-limbed vessels previously described,[7(b)] supersaturation and the apparent induction period [1] thus being avoided.

(i) *With aqueous-ethanolic hydrochloric acid.* The " 95% ethanol " was a water–ethanol mixture of s.g. 0·8161 at 60° F (5 vol.-% of water), and dry hydrogen chloride was dissolved in it as required. Usually 5 ml. of a *ca.* 0·20M-solution of the organosilane were mixed with 10 ml. of the acid solution, but because of limited solubilities larger volumes of more dilute solutions were used for triarylsilanes.

The following typical runs illustrate procedures. The volumes of hydrogen, V_t, were measured over water at the temperature and pressure given in parentheses, and the infinity values, V_∞, are the theoretical volumes expected.

(a) Et_3SiH (initially) 0·0673M, [HCl] 1·430M; 34·9°.

Time (*t*) (min.)	0	29	64	94	129	169	236	292	389	449	∞
V_t (ml., 20°, 747 mm.)	0	0·83	1·91	2·63	3·75	4·77	6·33	7·50	9·52	10·57	25·30
$10^3 k_1$ * (min.$^{-1}$)	—	1·15	1·22	1·16	1·25	1·24	1·22	1·20	1·21	1·21	—

<div align="center">* $k_1 t = \ln[V_\infty / V_\infty - V_t)]$.</div>

(b) $Pr^n_2SiH_2$ (initially) 0·0337M, [HCl] 1·430M; 34·9°.

Time (*t*) (min.)	0	3	5	10	18	23	28	60	226	299	343	403	486	∞
V_t (ml., 20°, 758 mm.)	0	0·94	1·52	2·84	4·56	5·55	6·44	10·29	15·76	16·76	17·28	17·88	18·62	24·82
$10^3 k_1$ * (min.$^{-1}$)	—	26·3	26·1	26·0	25·4	25·8	26·1	—	—	—	—	—	—	—
$10^3 k_1'$ * (min.$^{-1}$)	—	—	—	—	—	—	—	—	1·42	1·44	1·42	1·44	1·44	—

<div align="center">* $k_1 t = \ln [12·42/(12·42 - V_t)]$; $k_1' t = \ln [12·42/(24·84 - V_t)]$, it being assumed that after 226 min. only the second Si–H bond is reacting.</div>

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[10] Eaborn, *J.*, 1953, 3148.

(c) $C_6H_{11}SiH_3$ (initially) $0.0663M$, [HCl] $0.980M$; $34.9°$.

Time (t) (min.) ...	0	1	2	3	4	5	6	7	8	9	10	13.5	∞
V_t (ml., 21°, 759 mm.)	—	1.38	2.78	4.14	5.50	6.68	8.26	9.62	10.94	12.23	13.48	17.60	73.8
V_t/t (min.$^{-1}$)	—	1.38	1.39	1.38	1.38	1.37	1.38	1.37	1.37	1.36	1.35	1.30	—

$$k_0 = 3V_t/tV_\infty = 0.0557 \text{ min.}^{-1}.$$

(ii) *Aqueous-ethanolic perchloric acid.* The acid solution was made by mixing 5 ml. of aqueous acid with 95 ml. of ethanol. The reaction mixture thus contains slightly less than 5 vol.-% of H_2O but this is unimportant at the acid concentrations involved (see Table 4). The rate constants in parentheses are those for corresponding concentrations of hydrochloric acid.

[HClO$_4$] (M)	0.374	0.311	0.272
10^3k_1 (min.$^{-1}$)	4.90 (4.7)	4.05 (3.9)	3.50 (3.4)

(iii) *In aqueous dioxan.* The silane in dioxan (5 ml.) was added to 3 ml. of a $1.633M$-solution of hydrogen chloride in dioxan (purified,[11] and dried by prolonged boiling with sodium) either with 2 ml. of water or with 1 ml. of water and 1 ml. of dioxan. Deuterium oxide was the 99.8% material.

Indicator Ratios.—These were measured in 95% ethanol by standard spectrophotometric techniques and the symbols below have the usual meaning.[3, 10] The values of λ_N and ε_N are 378 and 15,425 respectively.

10^3 [HCl] (M)	109	195	390	651	977	1302	1954
λ_A (mμ)	378	378	378	378	378	375	371
ε_S	47	47	48	48	48	57	73
ε_A	14,900	13,975	11,750	8675	5550	3260	1290
10^3I	35.(4)	104	314	782	1795	3796	12,170

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[11] Eigenberger, *J. prakt. Chem.*, 1931, **130**, 75.