Organosilicon Compounds. Part IX. The Reaction between Iodine and Trisubstituted Silanes.*

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The kinetics of the reaction between iodine and some trialkyl- and triarylsilanes have been studied in carbon tetrachloride, chloroform, and benzene. The reaction is of fourth order, and the mechanism proposed involves predominant electrophilic attack by I_4 on hydrogen and a less important nucleophilic attack (or " solvation ") by I_2 on silicon.

TRIALKYLSILANES and iodine in carbon tetrachloride react according to :

$$R_3SiH + I_2 \longrightarrow R_3SiI + HI \qquad \ldots\ldots\ldots (1)$$

(Eaborn, *J.*, 1949, 2755; Nebergall and Johnson, *J. Amer. Chem. Soc.*, 1949, **72**, 4022). As briefly reported (Deans and Eaborn, *Research*, 1952, **5**, 592), we have examined the kinetics of this process for several trialkylsilanes and some triarylsilanes in weakly polar or non-polar solvents.

The iodination of triethylsilane in carbon tetrachloride at 25° was examined in most detail, and was found to be of fourth order over the concentration range studied (0·033—0·005M), the rate being given by $-d[I_2]/dt = k_4[Et_3SiH][I_2]^3$. The reaction appears to be homogeneous and chain-free, the rate being unaffected by removal or addition of oxygen or by light. Water has little effect (possibly because it is taken up by the reaction products), but small amounts of α-picoline or ethanol lead to rapid but incomplete removal of iodine. The reaction products have no influence.

The fourth-order rate constants remain satisfactorily constant within a run over the temperature range 25° to −16°, and the temperature coefficient is small and variable, as is common in high-order reactions, and there may be an inversion of the temperature coefficient below 0°, as shown by the following figures :

Temp.	−18·5°	−16·0°	−9·2°	1·1°	9·7°	25°
$10^{-3}k_4$ (mole^{-3} l.^{3} hr.$^{-1}$) ...	4·6	4·9	4·3	4·9	6·4	11·3

At 55°, however, the order within a run is between third and fourth, suggesting that a lower-order reaction, obscured at lower temperatures, has become more prominent, as in high-order aromatic halogenation and addition of halogens to olefins (Robertson and co-workers, *J.*, 1937 onwards).

Variation in Silane and Solvent.—The rates of iodination of various silanes in three solvents are shown in the following table. Satisfactory kinetics were not obtained for all the compounds in all the solvents mainly because of decomposition of the products, and for the trialkylsilanes a rate constant is given only if it remained satisfactorily constant through a run. The figures for the triarylsilanes are less reliable than those for the trialkylsilanes, but for a triarylsilane listing of a rate constant means that it remained reasonably constant throughout a run when the first 10% of reaction was neglected (a faster initial reaction may in these cases be due to traces of water, and is being investigated). However.

10^{-3} × *Fourth-order rate constants* (*mole*$^{-3}$ *l.*^{3} *hr.*$^{-1}$) *at* 25°.

Silane	CCl_4	C_6H_6	$CHCl_3$	Silane	CCl_4	C_6H_6	$CHCl_3$
Tri-*p*-chlorophenyl-	—[a]	—[a]	0·4	Tri*iso*propyl	—	14·5	—
Triphenyl-	0·1	—[b]	22	Tri-*n*-propyl-	10·9	63·6	—
Tri-*p*-tolyl-	0·5	—	—[c]	Triethyl-	11·3	278	2120
Tri*iso*butyl-	1·4	3·4	—	Tri-*n*-butyl-	18·0	75·3	5960

Too slow to be followed accurately. [b] Acid-titre low throughout. [c] Fast, but iodine returns to solution.

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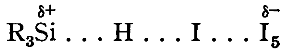
it is clear that the reactivity decreases in the order tri-*p*-tolyl-, triphenyl-, tri-*p*-chlorophenyl-silane, so that the reaction is facilitated by electron-release towards silicon. This is confirmed by the absence of detectable interaction of trichlorosilane (having three electronegative atoms attached to the silicon) with iodine in chloroform, or with iodine, and even bromine, in carbon tetrachloride at 25°.

In benzene the order of reactivity of the trialkylsilanes, R_3SiH, is (R =) $Et > Bu^n > Pr^n > Pr^i > Bu^i$ and there must be some steric hindrance, since otherwise the stronger electron-release of the *iso*propyl group would lead to a greater reactivity for tri*iso*propylsilane. However, the tri*iso*propylsilicon system has not the characteristic markedly low reactivity it shows in reactions involving predominant nucleophilic attack on silicon (cf. Eaborn, *J.*, 1952, 2840; 1953, 494; and refs.) since tri*iso*propylsilane reacts at one-fifth of the rate of the tri-*n*-propyl compound and is actually more reactive than tri*iso*butylsilane. The order of reactivity of the trialkylsilanes probably results from counteracting polar and (small) steric factors.

The reaction rate increases with polarity of the solvent, in the order: carbon tetrachloride, benzene, chloroform. In agreement with this, iodine reacts rapidly with trialkylsilanes in nitrobenzene or dioxan, but it then returns to the solution as the reaction products decompose.

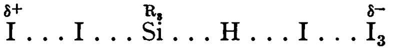
Mechanism of the Reaction.—The usual difficulties with high-order reactions preclude certainty that the reaction is exactly of fourth order and not of mixed order approximating to four. Third-order processes particularly may be playing an undetected part. The generality of the agreement with the fourth-order equation for several compounds at several concentrations and temperatures, and in three solvents, suggests that the iodination is really of fourth order. The main conclusion below, that attack is predominantly electrophilic on hydrogen, would not be affected by changing the number of iodine molecules present in the transition state.

Heterolytic fission of the Si–H bond seems always to occur in the sense Si^+H^-, as expected from relative electronegativities. The absence of a large steric factor indicates strongly that the reaction does not go exclusively by nucleophilic attack on silicon (and it should be noted that iodide ion does not attack trialkylsilanes even in aqueous ethanol which would assist separation of hydride ion) and the following rate-determining transition states must be considered. (A cyclic transition state, combining the features of all three, is sterically improbable, and would require little effect of solvent on the rate.)



$$\overset{\delta+}{R_3Si}\ldots H\ldots I\ldots \overset{\delta-}{I_5} \qquad (a)$$

$$\overset{\delta+}{I_3}\ldots I\ldots \overset{R_3}{Si}\ldots H\ldots I\ldots \overset{\delta-}{I} \qquad (b)$$



$$\overset{\delta+}{I}\ldots I\ldots \overset{R_3}{Si}\ldots H\ldots I\ldots \overset{\delta-}{I_3} \qquad (c)$$

Transition state (*a*) seems unlikely since tri*iso*propylsilane should then be more reactive than triethylsilane, and furthermore it is difficult to see why an I_6 complex should be so much more effective an electrophilic agent than an I_4 complex, particularly since the latter should be present in much greater concentration; (*b*) seems improbable in that it would lead to I^- and I_3^+ ions, whereas (*c*) would lead to the more likely I^+ and I_3^- ions. If transition state (*c*) is accepted, the order of three with respect to iodine is understandable, for one molecule is needed to attack silicon, while as an electrophilic agent the more polarizable I_4 is more powerful than I_2. Since electron-supply to silicon facilitates reaction, the electrophilic attack on hydrogen must be more important in the transition state than the nucleophilic attack on silicon. Absence of catalysis by hydrogen iodide confirms that little driving force is coming from nucleophilic attack. Indeed, the I_2 entity in the transition state could be regarded as " solvating " the forming siliconium ion rather than being attached by a partial covalent bond, its function being to stabilise the forming siliconium ion by dispersing the positive charge. If this is so, lower reaction orders would be expected in more powerfully solvating media. (The high and variable orders found in weakly polar solvents in halogenation of aromatics and addition of halogen to olefins could similarly be attributed to participation of one or more iodine molecules in "solvation" of a forming carbonium ion.)

There are several routes by which the transition state could be reached, involving various intermediate complexes; a reasonable scheme would be :

$$I_2 + I_2 \overset{\text{fast}}{\rightleftharpoons} I_4; \quad R_3SiH + I_4 \overset{\text{fast}}{\rightleftharpoons} R_3SiH,I_4; \qquad I_2 + R_3SiH,I_4 \xrightarrow{\text{slow}} R_3SiI + HI + 2I_2$$

The complex R_3SiH,I_4 is formally analogous to the R_3SiI,I_2 complex (Eaborn, *J.*, 1953, 4154), the more polarisable I_4 being required to form a complex with the less polar Si–H bond.

The conclusion that the main attack is electrophilic on hydrogen is in accord with the fact that electron-release to silicon facilitates this reaction and hinders the alkaline hydrolysis of organosilanes, in which nucleophilic attack on silicon predominates (Gilman and Dunn, *J. Amer. Chem. Soc.*, 1951, **73**, 3404; Gilman, Dunn, and Hammond, *ibid.*, p. 4499; Kaplan and Wilzback, *ibid.*, 1952, **74**, 6152; Price, *ibid.*, 1947, **69**, 2600). As expected, the latter reaction is also subject to large steric hindrance (Gilman and Brannen, *ibid.*, 1951, **73**, 4640). Because of d_π–p_π bonding between a silicon atom and an aromatic ring it is difficult to predict whether the triphenylsilyl group should release electrons more or less readily than trialkylsilyl, but the lower reactivity of triarylsilanes in iodination is in harmony with their higher reactivity in alkaline hydrolysis (Gilman and Dunn, *loc. cit.*).

Other Halogens.—Triethylsilane was found to react very rapidly with iodine monochloride in carbon tetrachloride according to $2Et_3SiH + 2ICl \longrightarrow 2Et_3SiCl + I_2 + 2HCl$. The reaction could go through either of the sequences,

$$Et_3SiH + ICl \longrightarrow Et_3SiI + HCl; \qquad Et_3SiI + ICl \longrightarrow Et_3SiCl + I_2$$

or

$$Et_3SiH + ICl \longrightarrow Et_3SiCl + HI; \qquad HI + ICl \longrightarrow HCl + I_2$$

since both hydrogen iodide and triethyliodosilane react rapidly with iodine monochloride to liberate iodine; the second sequence is more probable in view of the directions of polarisation of Si–H and I–Cl bonds.

Bromine in carbon tetrachloride reacts much more readily than iodine with trisubstituted silanes, and, contrary to a recent assertion (Gilman and Dunn, *Chem. Reviews*, 1953, **52**, 92), it reacts rapidly even with triphenylsilane, but the reaction does not go to completion, possibly because of the formation of unreactive complexes between bromine and the products.

EXPERIMENTAL

Materials.—Trialkylsilanes were fractionated in a column (12 theoretical plates) packed with glass helices. Triarylsilanes were recrystallized to constant m. p.

"AnalaR" carbon tetrachloride and chloroform were dried over and distilled from fresh phosphoric oxide. Benzene was dried over calcium hydride and distilled from phosphoric oxide.

Reaction Products.—Trialkyliodosilanes were obtained in good yield from interaction of triethyl-, tri-*n*-propyl-, and tri-*n*-butyl-silane and iodine in carbon tetrachloride. Isolation of tri*iso*butyl-, tri*iso*propyl-, and triaryl-iodosilanes was not attempted. Only when the iodine removed and acid produced (including that from hydrolysis of silicon iodides) agreed with eqn. (1) have the results been used.

With triethylsilane in carbon tetrachloride the course of the reaction was shown rigorously to conform with eqn. (1) by determination, at intervals, not only of iodine and acid but also of triethylsilane remaining (by measuring hydrogen evolved when a sample of the reaction mixture was added to excess of ethanolic alkali).

Kinetic Measurements.—Except in determination of the order with respect to each reactant in the triethylsilane–iodine reaction, initial concentrations of the reactants were accurately equal (usually 0·05—0·01M). Runs were usually carried out in sealed tubes containing 10 ml. of liquid, protected from light (Al foil). Tubes were broken under aqueous potassium iodide and the iodine was quickly extracted from the organic layer by shaking. (If the shaking was delayed, reaction proceeded at a normal rate in the organic layer.)

Faster reactions were carried out in an amber-glass vessel with ground stopper, samples (including some to give the " initial " concentration after the mixture had reached the thermostat temperature) being withdrawn by pipette. Determinations of acid for these runs were significant only up to the saturation concentration.

Titration of iodine by thiosulphate was followed by determination of the acid, either with alkali, or, more usually, by titration of iodine liberated on adding excess of potassium iodate; the acid includes that produced by hydrolysis of organosilicon iodide.

Rate constants within a run were calculated according to the equation $k_4 = (1/3t)[1/(a - x)^3 - 1/a^3]$, where a is the initial concentration of the reactants, and $(a - x)$ the concentration of iodine after time t. The rate constants quoted in the discussion were obtained from the slope of the straight-line plot of $1/(a - x)^3$ against t. An error in iodine determination is greatly magnified in the rate constant, and the rate constants quoted may be in error by as much as ±10%, although much better agreement than this was often obtained within a run and for duplicates.

Typical runs follow; the " iodine titre " is the amount of 0·025N-sodium thiosulphate solution required to discharge the iodine, and the " acid titre " is the amount to discharge the additional iodine produced on subsequent addition of potassium iodate. The sum of the " iodine titre " and " acid titre " should remain constant in a run according to eqn. (1).

Triethyliodosilane in carbon tetrachloride at 25°.

(Initially, $[I_2] = [Et_3SiH] = 0{\cdot}025$M; in tubes.)

Time, hr.	0	1/2	1	2	3	4	5	10	15	20	50	100
Iodine titre, ml.	10·00	9·22	8·65	7·90	7·35	6·50	6·00	5·42	4·84	4·44	3·35	2·66
Acid titre, ml.	0	0·60	1·30	2·00	2·45	3·40	3·95	4·55	5·10	5·55	6·55	7·35
$10^{-3} k_4$	—	11·7	11·7	10·8	10·7	11·0	11·2	11·2	11·3	11·0	10·9	11·1

From graph, $k_4 = 11{\cdot}3 \times 10^3$ mole^{-3} l.^{3} hr.$^{-1}$.

*Tri-*n*-propylsilane in benzene at* 25°.

(Initially, $[I_2] = [Pr_3SiH] = 0{\cdot}0234$M; in stoppered vessel.)

Time, min.	0	6	11	31	45	57	111	151
Iodine titre, ml.	9·32	8·56	8·21	7·12	6·60	6·22	5·29	4·67
Acid titre, ml.	0·75	0·45	1·75	2·85	—	—	—	—
$10^{-3} k_4$	—	76·6	67·2	63·5	63·6	65·6	63·7	67·8

From graph, $k_4 = 63{\cdot}6 \times 10^3$ mole^{-3} l.^{3} hr.$^{-1}$.

Triethyliodosilane and Iodine in Carbon Tetrachloride.—The reaction was of fourth order within a run and the rate constant was independent of the initial concentration within the limited range which could be studied :

Initial concn. of each reactant, M	0·0166	0·025	0·033
$10^{-3} k_4$ at 25°	11·3	11·3	10·5

Various unequal initial concentrations of iodine and silane (mole ratios 2 : 1 to 1 : 2) were used to determine the order with respect to each reactant. The slopes of the curve $[I_2]$ against t at various points were compared with those calculated, by using k_4 given above, for the expressions, $-d[I_2]/dt = k_4[Et_3SiH]^y[I_2]^{4-y}$, and y was shown clearly to be unity.

Additions were made to 10-ml. quantities of the " standard " reaction mixture (initially $I_2 = Et_3SiH = 0{\cdot}025$M) at 25°, and iodine was determined at intervals up to 7 hr. Water (0·05 g.), broken glass (equivalent to twice the surface area of the reaction vessel), or glass-wool (giving a large increase in surface area) did not affect the rate of reaction. (When moisture was present a brown deposit formed on the walls but disappeared in later stages of the reaction.) Activated alumina (0·5 g. of 200-mesh) caused a definite rate increase (*e.g.*, 60% reaction in 2 hr. compared with the usual 22% reaction). α-Picoline (either 0·05 or 0·1 g.) caused immediate loss of iodine colour when the reactants were mixed, with formation of a brown deposit containing 49—50% of the original iodine ($CH_3{\cdot}C_5H_4{\cdot}NHI,I_2$?). Ethanol (0·05 g.) caused a fast immediate reaction removing 52—46% of the original iodine, followed by a slower reaction.

Exposure to daylight and to a 100-watt lamp caused no change in rate over the first 40% of reaction. (The reaction products are decomposed by light, but relatively slowly. If a sealed tube containing reaction mixture is exposed to daylight for some weeks all the iodine returns.)

Hydrogen iodide (0·025M) or triethyliodosilane (0·025M) did not affect the rate. A mixture of triethyliodosilane (0·025M) and hydrogen iodide (0·025M) in carbon tetrachloride at 25° in tubes protected from light did not change in iodine or acid content during 10 days.

The rate was unchanged by bubbling oxygen or nitrogen through the reaction mixture for 30 sec. before the tubes were sealed, or by repeated freezing and pumping-out of the reactant solutions before mixing. When the reaction mixture was cooled to −80° and then quickly warmed to room temperature the iodine was almost completely removed; this could be caused by the increase in reactant concentrations as the solvent freezes.

Triethylsilane and Iodine in Dioxan and Nitrobenzene.—The iodine colour faded rapidly, but not completely, as equal volumes of triethylsilane (0·05M) and iodine (0·05M) in dioxan were mixed at room temperature (*ca.* 18°). About 10% of the iodine was present after 1 min., but iodine returned fairly rapidly. Titration within 1 min. of mixing equal volumes of triethylsilane (0·025M) and iodine (0·025M) in nitrobenzene at *ca.* 18° showed 50% of the iodine to be present; this increased to 80% after 40 min.

Trichlorosilane and Halogens.—Trichlorosilane in carbon tetrachloride in contact with aqueous potassium iodide produces a substance which removes iodine in the aqueous layer, and so tubes were broken under aqueous potassium iodide containing a slight deficiency of sodium thiosulphate. Trichlorosilane (0·025M) did not react detectably (<1%) with iodine (0·025M) in carbon tetrachloride or chloroform in 40 hr., or with bromine (0·025M) in carbon tetrachloride in 10 hr.

Triethylsilane and Iodine Monochloride.—When equal volumes of iodine monochloride (0·05M) and triethylsilane (0·05M) in carbon tetrachloride were mixed the colour changed immediately from brown to iodine-violet. Titration completed within 1 min. of mixing showed that 50% ± 0·5% of the halogen had been removed. Subsequently, halogen disappeared at the rate expected for the triethylsilane–iodine reaction. Dry nitrogen, bubbled through the mixture, carried off hydrogen chloride but no detectable hydrogen iodide in the first hour.

The brown colour changed immediately to iodine-violet when equal volumes of carbon tetrachloride solutions of iodine monochloride (0·05M) and triethyliodosilane (0·05M) or hydrogen iodide (0·05M) were mixed, and only hydrogen chloride was carried from the latter mixture by nitrogen.

Triphenylsilane and Bromine.—A mixture of bromine (0·025M) and triphenylsilane (0·025M) in carbon tetrachloride contained 60% and 46% of the bromine after *ca.* 1 and 2 min., respectively, at 18°, and 33% after 2 and 45 hr. at 25°. When change in bromine concentration was followed in an absorptiometer the results agreed well with those from the titration method.

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