897. *Aromatic Reactivity. Part II.* The Cleavage of Aryltrimethylsilanes by Bromine in Acetic Acid.*

By C. Eaborn and D. E. Webster.

A kinetic study has been made of the reaction between bromine and substituted phenyltrimethylsilanes in acetic acid containing 1·5% of water. This bromodesilylation † reaction, which is an electrophilic aromatic substitution, is of approximately first order in bromine at the concentrations studied (initially, 0·02—0·004M) and is of lower order than the bromination of anisole under similar conditions. Effects of salts and hydrogen bromide are similar to those in aromatic bromination in acetic acid. As in the latter reaction the effective electrophilic reagent is believed to be molecular bromine.

The effects of nuclear substituents on the reactivity of phenyltrimethylsilane form a pattern similar to that in aromatic nitration and protodesilylation,† but somewhat different from that in aromatic molecular halogenation. The reason for this may lie in the availability at the reaction site of the π-electrons of the aryl–Si bond.

Cleavage of Si–aryl bonds by bromine in absence or presence of solvents and of catalysts (usually iron filings) has long been known,[1] and has been used to identify the position of attachment of silicon to a substituted phenyl group,[2] bromine-water then frequently being employed. High yields of products have been obtained from the reaction $\mathrm{Me_3Si{\cdot}C_6H_5 + Br_2 \longrightarrow Me_3SiBr + C_6H_5Br}$.[3] Benkeser and Torkelson studied the kinetics of bromine cleavage of some aryltrimethylsilanes in carbon tetrachloride and nitrobenzene and stressed the close similarity between the cleavage and aromatic bromination.[4]

Substituent effects have been reported [5] for acid cleavage of phenyltrimethylsilane (" protodesilylation "), in which the electrophilic reagent is positively charged, and we now describe substituent effects in bromine cleavage (" bromodesilylation ") in acetic acid containing 1·5 wt. % of water, in which, as we shall show, the reagent is molecular bromine. The overall reaction is

$$\mathrm{Me_3Si{\cdot}C_6H_4R + Br_2 \xrightarrow{H_2O} Me_3Si{\cdot}OH + Br{\cdot}C_6H_4R + HBr}$$

with the silanol probably condensing rapidly to hexamethyldisiloxane.

Order of Reaction.—Because bromide ion is formed during the bromodesilylation and removes bromine as inactive tribromide ion, the apparent order of reaction rises during a

$$\mathrm{Br_2 + Br^- \rightleftharpoons Br_3^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

run as in aromatic bromination.[6] By comparing times for disappearance of the first 20% of the bromine at various initial concentrations of reactants (cf. ref. 6) the order of the reaction between phenyltrimethylsilane and bromine was found to be between 2·0 and 2·2. By varying the concentrations of each reactant separately the order with respect to each was found to be 1·0 ± 0·1 for bromine concentrations below 0·005M.

We have also measured the value of the equilibrium constant, K, for the equilibrium

---

* Part I, *J.*, 1956, 4858. † For nomenclature see Part I.

[1] Ladenburg, *Ber.*, 1907, **40**, 2274; Gruttner and Cauer, *Ber.*, 1918, **51**, 1283; Kipping, *J.*, 1921, **119**, 647.

[2] *E.g.*, Kipping and Blackburn, *J.*, 1932, 2200; Kipping and Cusa, *J.*, 1935, 1088; Benkeser and Brumfield, *J. Amer. Chem. Soc.*, 1951, **73**, 4770; Yakubovitch and Motsarev, *J. Gen. Chem. U.S.S.R.*, 1956, **26**, 611.

[3] Pray, Sommer, Goldberg, Kerr, Di Giorgio, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 433.

[4] Benkeser and Torkelson, *ibid.*, 1954, **76**, 1252.

[5] Eaborn, *J.*, 1956, 4858.

[6] Robertson, *Sci. Prog.*, 1955, **43**, 418.

(1), and used this to calculate reasonably satisfactory integrated second-order rate constants, k_2, for runs in absence and presence of added bromide ion, using the equation given by Bradfield, Jones, and Orton.[7] Since formation of hydrogen bromide should, by a primary salt effect, lead to a slight increase in k_2 throughout a run, the fall in k_2 found for runs in absence of added bromide at higher bromine concentrations may be real. Since, moreover, the value of k_2 falls somewhat as the initial reactant concentrations are decreased, and since the orders determined by the initial rate method are slightly but consistently greater than 2, it seems that there is a small contribution from a reaction of order higher than second. The values of k_2 for given initial reactant concentrations are higher in presence of added bromide, as expected from operation of a salt effect of a magnitude similar to that observed with lithium chloride.

The order of reaction has not been determined for each of the substituted phenyltrimethylsilanes, but for a pair of compounds examined at the same initial concentrations of reactants the ratio of the times for disappearance of specific fractions of the bromine is approximately constant from 20 to 70% of reaction (with a possible exception noted in the Experimental section), and thus the order of reaction is much the same for both compounds. Since many of the compounds have been directly compared with phenyltrimethylsilane in this way it is likely that the reactions of them all are of approximately first order in bromine for initial bromine concentrations of <0·01M.

On the other hand, the reaction between bromine and anisole shows a markedly greater fall-off in rate as reaction proceeds. The overall order was found to be *ca.* 2·7 at an initial bromine concentration of *ca.* 0·0025M, which agrees with figures for bromination of aromatic compounds in pure acetic acid at similar bromine concentrations.[6]

The apparent activation energy (*ca.* 12·5 kcal. for phenyltrimethylsilane in the range 25—40°) of the bromodesilylation is similar to that for aromatic brominations at low bromine concentrations.[8]

Salt Effects, and the Nature of the Electrophilic Reagent.—Brominations in pure and aqueous acetic acid have been shown to involve molecular bromine and not positively charged species such as Br^+, $H_2\overset{+}{O}Br$, $H\overset{+}{O}AcBr$.[6, 9] Since we use the same arguments to conclude that bromodesilylation also involves molecular bromine we need only outline them. They are: (i) The effect of bromide ion added or formed during a run can be quantitatively accounted for by removal of molecular halogen as tribromide ion. If Br^+ or similar unstable positively-charged entities were involved, the presence of bromide ion would cause a far greater fall in rate.[9] (ii) Acid does not accelerate the reaction, added hydrogen bromide having the same effect as lithium bromide on the rate.

The effects of salts are similar to those in aromatic bromination.[9, 10] Salts accelerate in the order $LiClO_4 > LiCl \approx NaOAc$, the order reflecting the order of dissociation of the salts. Since sodium acetate is a base in acetic acid, the absence of catalysis by it beyond the expected salt effect has been held to indicate in aromatic bromination that detachment of a proton from carbon does not occur in the rate-determining process,[6, 10] which is thus formation of the intermediate (I) rather than its destruction.* If this reasoning is accepted, it follows that removal of the trimethylsilyl group is not involved in the rate-determining step of bromodesilylation, which probably then involves formation of the intermediate (II).

However, by analogy with the mechanism suggested for aromatic dedeuteration, sulphonation, and desulphonation,[11] the separation of the proton from complex (I) could

* Hammond (*J. Amer. Chem. Soc.*, 1955, **77**, 334) has pointed out the uncertainty in interpreting kinetic isotope effects, which have also been held to indicate that destruction of (I) is not rate-determining.

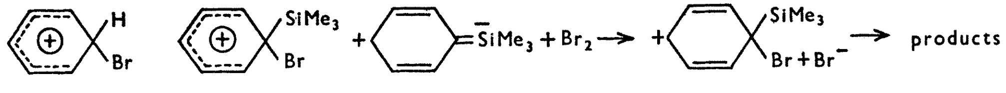
[7] Bradfield, Jones, and Orton, *J.*, 1929, 2810.

[8] Robertson, de la Mare, and Johnson, *J.*, 1943, 276.

[9] Robertson, *J.*, 1954, 1267.

[10] (*a*) Robertson, Dixon, Goodwin, McDonald, and Scaife, *J.*, 1949, 294; (*b*) Keefer, Ottenberg, and Andrews, *J. Amer. Chem. Soc.*, 1956, **78**, 255.

be the rate-determining step, but to give a π-complex, a process which would not be base-catalysed, though the subsequent rapid proton loss from this complex would be. Bromodesilylation could similarly involve rate-determining formation of a complex involving interaction of a siliconium ion with the π-electrons of the ring.



(I) (II) (III) (IV)

Substituent Effects.—The relative reactivities of two $R{\cdot}C_6H_4{\cdot}SiMe_3$ compounds can be measured by comparing the times needed for removal of various fractions of the bromine at identical initial concentrations. By overlapping in the pairs, the reactivity, k_{rel}, of each compound relative to phenyltrimethylsilane can be determined, and the results are shown in Table 1 along with the corresponding values, k'_{rel}, observed in protodesilylation.[5]

TABLE 1. *Relative reactivities of* $R{\cdot}C_6H_4{\cdot}SiMe_3$ *compounds.*

R	Bromodesilyln. k_{rel}	Protodesilyln. k'_{rel}
p-Me	49	21·1
p-Et	45	19·5
p-Pr^i	32·5	17·2
p-Bu^t	29	15·6
m-$Me_3Si{\cdot}CH_2$...	9	6·2
p-Me_3Si	3·0(5)	2·5
m-Me	~2.5	2·3
H	1	1
p-F	0·68	0·75
p-Cl	0·092	0·13
p-I	0·088	—
p-Br	0·071	0·10
m-Cl	0·003 *	~0·012

* ±0·0002.

In Table 2 the effects of substituents on the reactivity of a single C–H bond of benzene in nitration and molecular halogenation are given for comparison.

TABLE 2. *Partial rate factors in aromatic substitution.*

R [1]	Me	Bu^t	Me_3Si	*m*-Me	H	F	Cl	Br	I	*m*-Cl
Chlorination	870 [2]	—	—	5·0 [2]	1	6·3 [3]	0·4 [3]	0·25 [3]	—	—
Bromination	2420 [4]	780 [5]	—	5·5 [4]	1	4·6 [6]	0·14 [6]	0·06 [6]	0·08 [6]	0·00064 [6]
Nitration [7] ...	54	—	3·1	3·1	1	0·85	0·15	0·10	0·46	0·00106

[1] Substituent *para* unless otherwise indicated. [2] Brown and Stock (*J. Amer. Chem. Soc.*, 1957, **79**, 1421). [3] de la Mare, *J.*, 1954, 4450. [4] Brown and Stock (*loc. cit.*). [5] Calculated from rate factor for *p*-Me [Brown and Stock (*loc. cit.*)] and relative factors for *p*-Me and *p*-Bu^t given by Robertson, de la Mare, and Swedlund (*J.*, 1953, 782). [6] Illuminati and Marino (*J. Amer. Chem. Soc.*, 1956, **78**, 4975). [7] Data listed by Roberts, Sandford, Sixma, Cerfontain, and Zagt (*ibid.*, 1954, **76**, 4525), except for *p*-Me_3Si (Speier, *ibid.*, 1953, **75**, 2930).

The pattern of substituent effects in bromodesilylation differs markedly from that in molecular halogenation, the reaction it might have been expected most to resemble. Halogenation is a much more electron-demanding process as shown by the greater spread of rates and by the greater relative importance of the $+T$ effects of the *para*-halogen atoms which make these much less deactivating relative to the activation by *para*-alkyl groups (*p*-F actually activates). The pattern of substituent effects in bromodesilylation resembles rather closely that in nitration and protodesilylation, and indeed there is quantitative correlation, as shown for the second case by the straight-line log k_{rel}–log k'_{rel} plot in the Figure. As far as comparison may be made, the substituent effects in bromodesilylation also resemble those in bromination by Br^+ or $Br\overset{+}{O}H_2$[12] (in the latter reaction the rate factors are *p*-Me, 59; *m*-Me, 2·5; *p*-Bu^t, 38·5) and would be wholly consistent with the participation of a positively charged brominating agent as the effective electrophilic

---

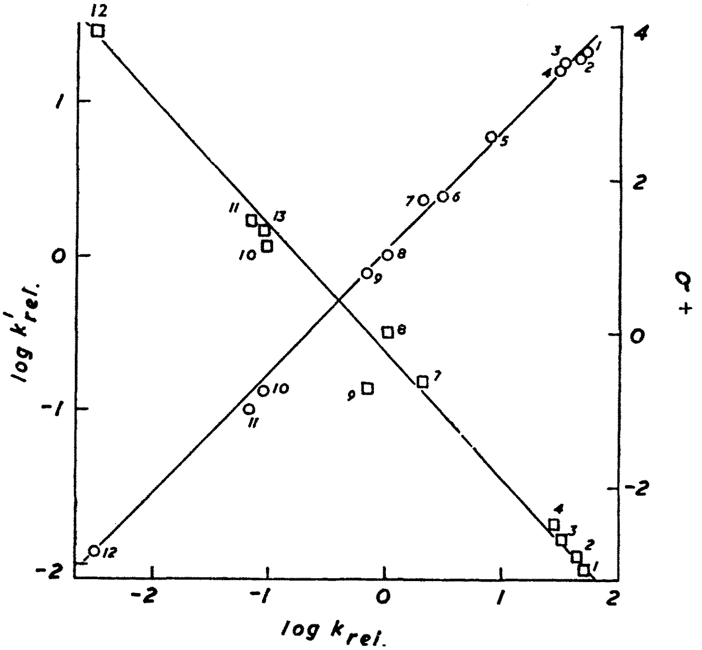
[11] Gold and Satchell, *J.*, 1956, 1635.
[12] de la Mare and Harvey, *J.*, 1957, 131; *J.*, 1956, 36.

entity in bromodesilylation. This possibility seems to be ruled out, however, by the kinetic results discussed above.

Two details of the substituent effects in bromodesilylation are noteworthy. (*a*) Alkyl groups activate in the hyperconjugative order Me > Et > Pr^i > Bu^t, as in protodesilylation, molecular halogenation, and bromination by Br^+ or $BrOH_2^+$ (for the last two only the order Me > Bu^t has been established). Anomalously, the order Bu^t > Me applies in nitration.[13] (*b*) *para*-Halogen atoms deactivate, the rate sequence being F > Cl > Br < I. The same order is found in nitration, halogenation, and brominolysis of phenylboronic acids,[14] and results from opposition of the $-I$ and $+T$ effects of the halogens.

Molecular Bromination and Bromodesilylation.—Because the spread of rates is much greater in molecular halogenation than in nitration, and because conjugative effects of substituents (*e.g.*, of the halogens) are more important in the former process, bromination is regarded as the more electron-demanding process. A review of explanations of this has been given by Berliner and Berliner,[15] whose interpretation we use now. This is that in nitration the entity which enters the ring, *i.e.*, the nitronium ion, is available independently of the aromatic compound, and being highly reactive attacks the nucleus with little assistance from time-variable electromeric effects of the aromatic compound, whereas in bromination the entering entity, Br^+, must be torn from a bromine molecule, with separation of a bromide ion. For this a powerful supply of electrons to the reaction site is necessary, and the electromeric effects of the ring and of conjugated substituents are called fully into play. Furthermore, fission of the bromine molecule has to be assisted by a second electrophilic entity which pulls off bromide ion, *e.g.*, by an additional bromine molecule.

Plot of ○ log k_{rel} (*bromodesilylation*) *against* log k'_{rel} (*protodesilylation*).



□ log k_{rel} *vs.* σ^+. Substituents: 1, *p*-Me; 2, *p*-Et; 3, *p*-Pr^i; 4, *p*-Bu^t; 5, *m*-Me_3SiCH_2; 6, *p*-Me_3Si; 7, *m*-Me; 8, H; 9, *p*-F; 10, *p*-Cl; 11, *p*-Br; 12, *m*-Cl; 13, *p*-I.

---

[13] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.
[14] Kuivila and Benjamin, *J. Amer. Chem. Soc.*, 1955, **77**, 4834.
[15] Berliner and Berliner, *ibid.*, 1954, **76**, 6179.

It is reasonable to assume that the difference between bromodesilylation and bromination arises from a greater availability of electrons at the reaction site in the former process. This could originate partly in inductive release of electrons from the trimethylsilyl group to the neighbouring ring carbon atom, but because of p_π-d_π bonding between the ring and the silicon atom the overall supply of electrons to the ring is, in fact, very small (and in certain structures the trimethylsilyl group withdraws electrons from the ring).[17] It may be that the availability at the reaction site of the π-electrons of the Si–C bond leads to polarisation of the attacking bromine molecule without large assistance from the time-variable effects of the ring and of substituents, the effect being clearly revealed if, for simplicity, the silicon compound is regarded as reacting in one of its extreme mesomeric forms (III). The electron-availability in the C–Si bond could also lead to fission of the bromine molecule without the need for an additional bromine molecule to pull away bromide ion, and thus to a reaction of lower order than aromatic bromination.

Substituent Constants for Electrophilic Aromatic Substitution.—Brown and Okamoto [16(b)] have recently described a set of substituent constants (σ^+-constants) analogous to Hammett σ-constants [18] but applicable to electrophilic nuclear and side-chain reactions. A plot of log k_{rel} for bromodesilylation against these σ^+-constants is an excellent straight line (see Fig.) and provides further justification for Professor H. C. Brown's approach to substituent effects in aromatic substitution.

While recognising the value of this approach, we would point out that the correlations so obtained should not be allowed to obscure important differences between the reactions. Since the σ^+ constants seem effectively to cover nitration, halogenation, protodesilylation, bromodesilylation, and other reactions,[16(b)] one might conclude that there are no anomalies in the substituent effects, whereas the differences between the pattern of substituent effects in nitration and molecular halogenation, for example, are of considerable significance in considering detailed mechanisms (cf. ref. 15).

EXPERIMENTAL

Materials.—Acetic acid was purified [19] and fractionated, and water was added to give a f. p. of 13·60°. This corresponds with a water content of 1·50 wt. % (confirmed by Karl Fischer titration).

Bromine was distilled from potassium bromide. Hydrogen bromide was prepared from bromine and tetralin and was passed through tetralin bubblers and cold traps into the solvent, the bromide ion content then being determined by titration.

The dried lithium salts gave neutral solutions in water.

Phenyltrimethylsilanes.—Gas–liquid chromatography showed these to contain only traces of impurities, except for *p*-bromophenyltrimethylsilane from which an impurity (<3%) could not be removed. This impurity, probably *p*-di(trimethylsilyl)benzene, caused an initial fast removal of a small amount of bromine in the rate studies.

p-*Iodophenyltrimethylsilane*, prepared in *ca.* 30% yield from iodine and the Grignard reagent from *p*-bromophenyltrimethylsilane and magnesium in ether, had b. p. 155°/50 mm., n_D^{20} 1·5652 (Found: C, 39·3; H, 4·8. $C_9H_{13}ISi$ requires C, 39·1%; H, 4·7%).

Rate Studies.—The bromine solution was standardised and an organosilane solution of appropriate (usually equal) concentration was prepared. Equal volumes of the solutions, both at thermostat temperature (25·00° ± 0·02°), were mixed, the point of half-addition being taken as zero time. Samples removed by automatic pipette were added to aqueous potassium iodide and the liberated iodine was titrated against sodium thiosulphate solution by a potentiometric (dead-stop end-point) technique. Titrations were accurate to 0·005 ml. of 0·005N-thiosulphate.

Loss of bromine by volatilisation or by reaction with the acetic acid was insignificant except for the slowest runs, involving *m*-chlorophenyltrimethylsilane, in which appropriate corrections were made.

---

[16] (*a*) de la Mare, *J.*, 1954, 4450; (*b*) Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

[17] Chatt and Williams, *J.*, 1954, 4403; Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421; Eaborn and Parker, *J.*, 1954, 939.

[18] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[19] Orton and Bradfield, *J.*, 1927, 983.

The organosilanes were shown spectrophotometrically [5] not to react with the solvent at a significant rate. Some were cleaved by added hydrogen bromide, but not at a rate which was significant in any of the runs reported.

Runs were initially carried out in blackened vessels but this was later found to be unnesessary.

Determination of Order.—Phenyltrimethylsilane was used, and Table 3 shows the effect on the times, *t* (in sec.), for removal of 10, 20, and 50% of the bromine of halving the initial (equal) concentrations of both reactants. The order, *n*, of the reaction calculated from these times is also shown. These runs are only to be used in the pairs shown, as relative rather than absolute accuracy was sought.

TABLE 3.

10^3 × Concn. (M)	$t_{10\%}$	$t_{20\%}$	$t_{50\%}$	$n_{10\%}$	$n_{20\%}$	$n_{50\%}$
4·45	1150	2975	13,950	2·08	2·07	2·00
8·9	545	1415	7000			
10·13	330	1020	6120	2·09	2·06	2·00
20·25	155	490	3060			
20·95	120	360	2790	~2·12	2·17	1·98
41·9	~55	160	1410			

By varying the concentration of each reactant separately, and taking times to 10% of reaction as proportional to initial rates, the order with respect to each reactant was found to be 1·0 ± 0·1 for <0·005M-bromine.

In the following typical runs (Table 4) the times were taken from smoothed curves, and the integrated rate constants, k_2, calculated from the formula given by Bradfield, Jones, and Orton,[7] or from a special form (kindly derived by Mr. C. A. Haywood) applicable to runs involving equal concentrations of reactants in absence of added bromide, *viz.*,

$$\frac{ktK}{2\cdot303} = 2\log\left(\frac{2\upsilon_0 + K}{2\upsilon + K}\right) - \left(2 - \frac{K}{2\alpha}\right)\log\frac{\upsilon_0}{\upsilon} - \frac{K(\upsilon - \upsilon_0)}{2\cdot303\upsilon_0\upsilon} - \left(\frac{K}{2\alpha}\right)\log\left(\frac{\upsilon_0 + 2\alpha}{\upsilon + 2\alpha}\right)$$

where *a*, *c*, and *b* are the initial concentrations of bromine, organosilane, and added lithium bromide, respectively, and the other symbols are as previously used.[7] The value of *K* is 0·0055 (see below).

TABLE 4.

(i) $a = 0\cdot0125$M. $c = 0\cdot0250$M. $b = 0$.

Br_2 used (%)	10	20	30	40	45	50	55	60	70
Time (sec.)	160	370	670	1100	1390	1765	2180	2730	4330
10^2k_2 (sec.$^{-1}$ mole^{-1} l.)	2·8	2·8	2·80	2·75	2·70	2·58	2·57	2·52	2·52

(ii) $a = c = 0\cdot003172$M. $b = 0$.

Br_2 used (%)	10	20	30	40	50	65
Time (sec.)	1260	3720	6510	10,560	16,380	32,700
10^2k_2 (sec.$^{-1}$ mole^{-1} l.)	2·17	2·21	2·21	2·18	2·17	2·15

(iii) $a = 0\cdot0125$M. $c = 0\cdot025$M. $b = 0\cdot050$M.

Br_2 used (%)	10	20	30	40	45	50	60	65
Time (sec.)	1290	2880	4950	7500	9030	10,830	15,600	18,600
10^2k_2 (sec.$^{-1}$ mole^{-1} l.)	2·86	2·82	2·81	2·80	2·80	2·78	2·78	2·78

(iv) $a = 0\cdot0125$M. $c = 0\cdot025$M. $b = 0\cdot10$M.

Br_2 used (%)	10	20	30	40	45	55	60
Time (sec.)	2130	4860	7980	12,210	14,970	21,060	24,960
10^2k_2 (sec.$^{-1}$ mole^{-1} l.)	3·38	3·32	3·23	3·37	3·33	3·32	3·23

Runs involving added hydrogen bromide were identical within experimental error with those involving lithium bromide.

In the reaction between anisole (0·0033M) and bromine (0·0033M), 10 and 20% of the bromine was used up in ~80 and 240 sec., respectively. With both anisole and bromine initially 0·00165M, the corresponding times were 275 and 800 sec. These figures correspond with an order of 2·8 and 2·7 based on 10 and 20% of reaction, respectively.

Salt Effects.—Table 5 shows the effects of salts on the reaction between phenyltrimethylsilane (initially 0·025M) and bromine (initially 0·0125M). The time for removal of half of the bromine is given in each case along with the "relative rate," which is the average ratio of the times for removal of specific fractions (20—70%) of the bromine in absence and in presence of salts. Variations of this ratio from the average during a run were small (<±2%) and random.

TABLE 5.

Salt	—	$LiClO_4$	$LiClO_4$	$LiClO_4$	LiCl	LiCl	LiCl	NaOAc	NaOAc	NaOAc
10^2Salt (M)	—	2·50	5·0	10·0	2·50	5·0	10·0	2·50	5·0	10·0
$t_{\frac{1}{2}}$ (sec.)	1760	1485	1285	990	1600	1560	1450	1560	1495	1440
Rel. rates ...	1	1·17	1·36	1·76	1·08	1·13	1·24	1·15	1·19	1·24

Table 6 shows the effect of added hydrogen bromide on the instantaneous rate, $v_{30\%}$, of the reaction between phenyltrimethylsilane (0·025M) and bromine (0·0125M) after removal of 30% of the bromine (the rates being given by the slopes of the time–titre curves). The ratios of the rates in presence and absence of added hydrogen bromide are shown. The concentrations, $[Br_2]_{30\%}$, of free bromine at 30% reaction (calculated by using 0·0055 as the value of K) are also given, along with the ratio of these concentrations in presence and in absence of added bromide. The two ratios are in reasonable agreement, the rate ratio rising slightly relative to the free-bromine ratio as the amount of added hydrogen bromide is increased, as expected from the operation of a salt effect similar to that of lithium chloride.

TABLE 6.

[HBr] (added) (M)	0	0·0125	0·0250	0·050	0·100
$10^7v_{30\%}$ (mole sec.$^{-1}$)	4·03	1·89	1·09	0·66	0·37
Rel. rate	1	0·47	0·27	0·16	0·09
$10^3[Br_2]_{30\%}$ (free) (M)	6·69	3·01	1·76	0·94	0·48
Rel. free Br_2 concn.	1	0·45	0·26	0·14	0·07

Reaction Rates.—For each substituted phenyltrimethylsilane, $R{\cdot}C_6H_4{\cdot}SiMe_3$, the following list shows the half-life of one reaction involving equal initial concentrations of silane and bromine. The substituent, R (*para* unless otherwise specified) is given along with 10^3 × initial concn. of both reactants (M) and the half-life time in sec: Me, 2·495, 431; Bu^t, 4·10, 540; Pr^i, 4·10, 490; Et, 4·10, 345; Me_3Si, 8·80, 2100; *m*-$Me_3Si{\cdot}CH_2$, 13·1, 492; F, 25·3, 3540; Cl, 25·4. 28,200; I, 15·31, 33,500; Br, 32·5, 26,820; *m*-Cl, 78·2, 219,600.

Relative Reactivities.—Solutions of two organosilanes were prepared to be of exactly the same concentration as a standardised bromine solution. The times for disappearance of specific fractions of the bromine were compared directly, usually for 20—70% of reaction. The typical comparison (Table 7) refers to *p*-trimethylsilylphenyl- and phenyl-trimethylsilane ([Silane] = $[Br_2]$ = 0·0135M).

TABLE 7.

Reaction (%)	20	30	40	50	60	70
Time (sec.) (R = H)	715	1410	2430	4110	7020	13,500
Time (sec.) (R = *p*-Me_3Si)	235	460	800	1350	2305	4440
10^2 × Rel. rate	304	306	304	304	305	304

Table 1 is based mainly on the following direct comparisons. For each pair of $R{\cdot}C_6H_4{\cdot}SiMe_3$ compounds (substituents *para* unless otherwise indicated) the average inverse ratio of times for disappearance of specific fractions of bromine is given along with the limits of variation in the ratio during 20—70% of reaction: Me/H, 48·8 ± 0·5; Pr^i/Bu^t, 1·12 ± 0·03; Me/Et, 1·07(5) ± 0·01(5); Et/Bu^t, 1·54 ± 0·02; Pr^i/*m*-Me, 13·1 ± 0·3; Pr^i/H, 32·5 ± 0·3; *m*-$Me_3Si{\cdot}CH_2$/H, 9·1 ± 0·5; Me_3Si/H, 3·05 ± 0·01; H/F, 1·47 ± 0·04; F/Cl, 7·3 ± 0·2; Cl/Br, 1·29 ± 0·03; I/Br, 1·26(5) ± 0·01(5); H/I, 11·3 ± 0·1; Cl/I, 1·04 ± 0·01; Cl/*m*-Cl, 31 ± 2.

(For the *m*-Me/H pair the ratio varied more seriously. Because of this effect, which is being investigated, only an approximate reactivity is given for the *m*-Me compound in Table 1.)

Equilibrium Constant for Formation of Tribromide Ion.—The equilibrium constant, K (*i.e.*, $[Br^-][Br_2]/[Br_3^-]$), was determined by the spectrophotometric method,[10(b),20] a series of solutions containing lithium bromide (0·004—0·02M) and bromine (6×10^{-5}—3×10^{-4}M) in 98·5% acetic acid being used. Optical densities were determined at 340, 350, and 360 mμ in 1 cm. cells at 25·00° ± 0·02° against a solvent blank. Table 8 shows the values of K determined, along with the molar extinction coefficient of tribromide ion and of bromine ($\varepsilon_{Br_3^-}$ and ε_{Br_2} respectively) at each wavelength.

[20] Ketelaar, van der Stolpe, Goudsmit, and Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

TABLE 8.

λ(mμ)	ε_{Br_2}	$\varepsilon_{Br_3^-}$	K	λ(mμ)	ε_{Br_2}	$\varepsilon_{Br_3^-}$	K	λ(mμ)	ε_{Br_2}	$\varepsilon_{Br_3^-}$	K
340	42	2340	0·0055	350	68	1460	0·0056	360	100	1050	0·0057

We thank the Department of Scientific and Industrial Research for a maintenance grant to one of us (D. E. W.), and Imperial Chemical Industries Ltd. for a grant towards the cost of chemicals.

THE UNIVERSITY, LEICESTER.

[*Received, June 4th,* 1957.]