The Mechanism of the Reaction of Molecular Bromine with Organosilicon Hydrides

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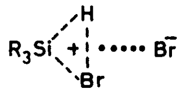
The kinetics of the bromination of 7 triarylsilanes and 14 other organosilicon hydrides by molecular bromine in CCl_4 have been determined by the stopped flow method. For triethylsilane, Arrhenius parameters have been measured in octane and CCl_4, and solvent effects determined in other solvents of different polarity. The results accord with a molecular mechanism involving one molecule of bromine and one of the organosilicon hydride, with partial positive charge build-up on silicon in the transition state.

The reaction of bromine with triorganosilanes according to equation (1) is very rapid compared with the corresponding bromination of alkanes, and is of considerable mechanistic interest in defining pathways for reaction at silicon which may not be available for reactions at carbon.

$$R_3SiH + Br_2 \longrightarrow R_3SiBr + HBr \qquad (1)$$

Using additional data from halogenations by Cl_2 and BrCl, Sommer[1] postulated that the reaction involved attack of a bromine molecule on the organosilicon hydride to give an intermediate (or transition state) of type 1 with charge separation as indicated. Studies of optically active silicon compounds showed that the reaction involves retention of stereochemistry at the silicon atom.[2] The reaction of phenyldimethylsilane[3] showed a primary deuterium isotope effect of only 1.24 ± 0.15, indicating that the transition state involves little breakage of the Si–H bond; a ρ^* value of -0.87 for alkyl-substituted silanes[3] and ρ of -0.77 for XC_6H_4-$SiMe_2H$[4] accord with the positive charge build-up, as in (1).



(1)

Results and Discussion

Previous studies of the rapid reaction of bromine with organosilicon hydrides have used bromide ion in dimethylformamide to complex the free bromine reversibly,[3,4] and thus reduce the rate of reaction. Our experiments to determine the kinetics of such reactions in carbon tetrachloride directly have involved the use of stopped flow for reactions which are too fast to measure conventionally.

Triethylsilane was used as a model compound to determine the order of reaction. Triethylsilane and bromine concentrations were varied over a 100-fold range with at least a tenfold excess of silane over bromine. The disappearance of bromine followed pseudo-first order kinetics over at least 75% of the reaction. The results (Table 1) show that for solutions which contain no more than 0.1M-Et_3SiH, the reaction is of first order in the organosilane as well, indicating a second order process, first order with respect to both triethylsilane and bromine. For higher concentrations of silane (and bromine), deviations from these simple kinetics take place: the bromine appears to have an order greater than unity. Schott and Werner found a dependence on $[Br_2]^2[R_3SiH]$ in similar brominations in more concentrated solutions, and postulated a prior reversible complexation of a bromine molecule with R_3SiH, followed by reaction of this complex with another bromine molecule to give products.[5] In the remainder of the experiments described in this paper, dilute solutions have been used to avoid this problem.

Table 1. Bromination of triethylsilane in carbon tetrachloride at 25 °C

Et_3SiH/M	Br_2/M	k_1/s^{-1}
1.0	0.1	17.95
1.0	0.01	12.05
1.0	0.001	8.09
0.1	0.01	1.34
0.1	0.001	1.31
0.01	0.001	0.141

Table 2. Bromination of organosilicon compounds[a] in CCl_4 at 25 °C

Organosilicon compound	k_2/l mol^{-1} s^{-1}	$k_{rel.}$
$(CH_3)_3SiH$	1.10	1.00
$(CH_3)_2C_2H_5SiH$	2.24	2.04
$CH_3(C_2H_5)_2SiH$	4.95	4.52
$(C_2H_5)_3SiH$	13.4	12.2
$(CH_3)_2C_6H_5SiH$	0.70	0.64
$CH_3(C_6H_5)_2SiH$	0.28	0.26
$(C_6H_5)_3SiH$	0.084	0.077
$(C_6H_5CH_2)_3SiH$	0.083	0.075
$(n\text{-}C_3H_7)_3SiH$	12.8	11.7
$(i\text{-}C_3H_7)_3SiH$	27.1	24.7
Cl_3SiH	0.0	0.0
$(CH_3)_3SiCH_2Si(CH_3)_2H$	6.77	6.17
$\{(CH_3)_3Si\}_3CSi(CH_3)_2H$	14.7	13.4
$n\text{-}C_8H_{17}SiH_3$	0.31	0.28
$C_6H_5SiH_3$	0.65	0.59
$(CH_3)_3SiSi(CH_3)_3$	1.26	1.15

[a] Initial concentrations: silane 0.1M; bromine 0.01M.

Variation of the Alkyl Groups.—To ascertain the effects of variation of the structure of the organosilicon hydride on the rate of bromination, we measured the second-order bromination rates of the sixteen compounds listed in Table 2.

All simple trialkylsilanes brominate faster than trimethylsilane: this accords with a positive charge build-up at Si in the transition state, which will be stabilized by electron-releasing alkyl groups. Sequential replacement of methyl by ethyl in trimethylsilane causes increases in rate of bromination by factors of 2.0, 2.2, and 2.7, respectively. This slightly rising sequence of numbers indicates that steric effects must be unimportant for these compounds, and the effect is just that of the inductive effect of replacement of H by CH_3 on going

Table 3. Bromination of substituted triphenylsilanes [a] $(XC_6H_4)_3SiH$ in CCl_4 at 25 °C

Substituent (X)	k_2/l mol^{-1} s^{-1}	σ
p-CH_3O	1.45×10	−0.28
p-CH_3	8.90×10^{-1}	−0.14
H	8.41×10^{-2}	0.0
p-F	6.73×10^{-3}	0.06
p-Cl	2.70×10^{-3}	0.24
m-Cl	1.28×10^{-3}	0.37
m-CF_3	3.46×10^{-4}	0.46

[a] Initial concentrations: silane 0.1M; bromine 0.01M.

Table 4. Reaction of triethylsilane (0.1M) with molecular bromine (0.01M) in different solvents at 25 °C

Solvent	k_2/ l mol^{-1} s^{-1}	$E_T(30)$ [a]
Octane	1.45	30.9
CCl_4	13.4	32.5
$CHCl_3$ (0.06 mol) : CCl_4 (0.94 mol)	32.6	32.9
$CHCl_3$ (0.23 mol) : CCl_4 (0.77 mol)	122	34.0
$CHCl_3$ (0.55 mol) : CCl_4 (0.45 mol)	861	36.1

[a] $E_T(30)$ values are from ref. 12. Octane is assumed to have the same $E_T(30)$ value as hexane, and values for mixtures of $CHCl_3$ and CCl_4 are obtained by interpolation between the $CHCl_3$ and CCl_4 values using the molar proportions of the two solvents.

from methyl to ethyl. Tri-n-propylsilane brominates at virtually the same rate as triethylsilane, as would be expected for changes in structure remote from the reaction centre.

Tribenzylsilane, in which three hydrogen atoms in trimethylsilane have been replaced by phenyl groups, reacts 13.3 times more slowly than trimethylsilane, in accord with the inductive electron-withdrawing effect of the phenyl group.

Tri-isopropylsilane reacts about twice as fast as triethylsilane, but this is a much smaller increase than the factor of 12.2 expected from the analogous variation in structure from trimethylsilane to triethylsilane. Thus it appears that steric factors begin to become important for tri-isopropylsilane, even though they are not for triethylsilane.

(Trimethylsilylmethyl)dimethylsilane brominates about six times faster than trimethylsilane. This increase in reactivity is probably due to the polar effect of the trimethylsilylmethyl group, which is known to be a moderately strong electron-donating group.[6] Tris(trimethylsilyl)methyldimethylsilane shows a reactivity towards bromination of only *ca.* 13.4 times greater than that shown by trimethylsilane. Its reactivity is about 18 times less than would be expected from the polar effect of three Me_3Si groups. This large decrease suggests strongly that steric effects are very important for this very bulky group, according with other work on compounds of this type.[7]

Replacement of the three methyl groups in trimethylsilane by electron-withdrawing chlorine atoms causes the rate of bromination to fall to an immeasurably low value. Successive replacement of methyl groups by phenyl groups causes reductions in rate of a factor of 0.64, 0.40, and 0.30, respectively: both polar and steric effects are likely to be operational here. Steric effects should be at their minimum for the compounds octylsilane and phenylsilane: phenylsilane reacts 2.1 times faster, indicating that the phenyl group can stabilize the positive charge in the transition state by some measure of conjugation. In contrast, phenyldimethylsilane brominates 3.2 times more slowly than ethyldimethylsilane, indicating that in these more crowded compounds, steric repulsion is more important. If we take the $PhSiH_3 : C_8H_{17}SiH_3$ ratio as indicative of a steric-free effect of the phenyl group, assume that higher alkyl groups have a similar effect to ethyl, and take the difference for ethyl from methyl from the $EtMe_2SiH : Me_3SiH$ ratio, the effect of replacing methyl by phenyl can be estimated as an increase of a factor of 4.3. Using this value for the electronic effect, the steric effect of replacement of each successive methyl group in Me_3SiH by phenyl can be calculated to be a decrease in rate by factors of 7, 11, and 14, respectively. Increasing steric effects on successive substitution by bulky groups are expected, as favourable conformations for reaction are successively eliminated. A greater steric effect of phenyl compared with isopropyl groups is to be expected on the basis of the equatorial/axial conformational preferences of these groups in cyclohexane derivatives.[8]

The bromination rate of hexamethyldisilane is included for comparison. Although this compound has no Si–H bond to facilitate approach of the bromine, two strong Si–Br bonds are formed during the reaction, and the exothermicity will act as a powerful driving force.

Bromination of Substituted Triphenylsilanes.—To investigate the effects of substituents on this reaction further, we studied the kinetics of bromination of seven substituted triphenylsilanes in carbon tetrachloride at 25 °C. The kinetics were second order, first order with respect to both silane and bromine. The results are shown in Table 3.

Hammett plots (of log k against three times the relevant substituent constant[9]) showed a better relationship with σ than with σ^+, with $\rho = -2.0$, according with the build-up in positive charge in the transition state discussed above. A Yukawa–Tsuno treatment of the data gave $\rho = -2.2$ and $r = 0.22$, indicating some contribution of σ^+, but the fit was not noticeably improved in spite of the extra parameter. Chvalovský and co-workers[4] obtained a ρ value of −0.77 for the bromination of substituted phenyldimethylsilanes: their smaller value reflects the fact that the reactions were carried out in the more polar solvent dimethylformamide.

Arrhenius Parameters, Solvent Effects and Alternative Mechanistic Possibilities.—Rate constants were determined for the bromination of triethylsilane in octane and in carbon tetrachloride at temperatures varying from 5 to 46 °C. Good Arrhenius plots were obtained, giving $\log_{10} (A/\text{l mol}^{-1} \text{s}^{-1}) = 3.97 \pm 0.33$ and $E/\text{kJ mol}^{-1} = 21.68 \pm 1.92$ for the reaction in octane, with corresponding values of 4.91 ± 0.10 and 21.62 ± 0.56, respectively, in carbon tetrachloride. The reaction is faster in CCl_4 than in octane over the entire range of temperature, but the difference in rate is due to differences in the A factor rather than the activation energy.

A low A factor is expected for reactions between two neutral molecules in which charge is developed in the transition state: electrostriction of the solvent by the developing charge results in a substantially negative entropy of activation. Similar low A factors are observed in other reactions in which two neutral molecules react to give a charged transition state, for example the quaternization of tertiary amines by iodoalkanes.[10] An increase in rate in more polar solvents is expected (see below), but it is interesting that in our experiments, the increase is virtually entirely due to change in the A factor. In other examples reported in the literature,[11] both A and E vary.

In addition to our experiments on the bromination of triethylsilane in octane and CCl_4, we extended the solvent range to mixtures of $CHCl_3$ and CCl_4 to increase the range of solvent polarities, as shown in Table 4. A plot of log k_2 against the solvent polarity parameter $E_T(30)$ (ref. 12) shows a fairly good linear relationship ($r = 0.991$) over a 600-fold variation in rate constants. This regular increase in reaction rate with increase in solvent polarity confirms the build-up of charge in the transition state.

The second-order kinetics observed for our brominations do not in principle rule out the possibility of a free radical mechanism. Provided that bimolecular initiation by a process such as reaction (2) took place and that reactions (3) and (4) have approximately the same rate, then approximately

$$R_3Si{-}H + Br{-}Br \longrightarrow R_3Si^{\bullet} + H{-}Br + Br^{\bullet} \qquad (2)$$

$$R_3Si^{\bullet} + Br{-}Br \longrightarrow R_3Si{-}Br + Br^{\bullet} \qquad (3)$$

$$Br^{\bullet} + R_3SiH \longrightarrow R_3Si^{\bullet} + H{-}Br \qquad (4)$$

$$2X^{\bullet} \longrightarrow X_2\ (X = R_3Si \text{ or } Br) \qquad (5)$$

second-order kinetics should be observed, first order with respect to both $[R_3SiH]$ and $[Br_2]$. The overall activation energy will be given by $E_{obs} \simeq \frac{1}{2}[E_2 + E_3 + E_4 - E_5]$. For radical combination, $E_5 \sim 0$, and even if E_3 and E_4 are low, E_2 (and hence $2 \times E_{obs}$) cannot be less than the endothermicity of reaction (2). ΔH_2 can be estimated from thermochemical data[13] to be *ca.* +203 kJ mol^{-1}, and thus E_{obs} should be at least 102 kJ mol^{-1}. Our observed value of 22 kJ mol^{-1} thus makes this mechanism very unlikely.

Further evidence for a non-radical mechanism comes from experiments on the reaction of bromine with mixtures of triphenylsilane and trichlorosilane in the dark and in the light. In the dark, from the proportions of the silanes which reacted, $k^{Cl_3SiH}/k^{Ph_3SiH} = 0$, in accord with the kinetic results (Table 2). In the light, $k^{Cl_3SiH}/k^{Ph_3SiH} \simeq 1$, indicating that a different, unselective process was taking place, most probably involving steps analogous to reactions (3) and (4), initiated by the photo-produced bromine atoms. Thus the selective dark reaction is unlikely to be a radical process.

Thus our evidence supports a molecular mechanism for the bromination of organosilanes by bromine, involving attack of one molecule of bromine on one of organosilane under our conditions. A partial positive charge builds up at silicon in the transition state, as is shown by substituent and solvent effects. Steric effects are unimportant for simple aliphatic groups such as methyl, ethyl, and n-propyl, but become important for bulky groups such as isopropyl, phenyl, and tris(trimethylsilyl)methyl.

Experimental

Kinetic determinations were carried out spectrophotometrically at 420 nm, using a Cary 210 spectrophotometer with a thermostatically controlled cell-holder for the slow reactions, and a Nortech Canterbury SF-3A stopped flow apparatus for the fast reactions. The rate constants tabulated are the means of at least three runs: additional results for the reaction of Et_3SiH (0.1M) and Br_2 (0.01M), used in the evaluation of Arrhenius parameters are as follows: (results given in the form: solvent, temp. °C, k_2/l mol^{-1} s^{-1}): octane: 11.4, 1.01; 20.5, 1.32; 27.6, 1.50; 40.0, 2.17; 42.6, 2.62. CCl_4: 5.5, 7.04; 23.2, 12.6; 25.0, 13.4; 46.2, 23.1.

Photobromination of Ph_3SiH–Cl_3SiH *Mixtures.*—Solutions containing Ph_3SiH (0.025M), Cl_3SiH (0.025M), and Br, (0.025M) in CCl_4 were placed 10—15 cm from a 200 W tungsten lamp. The bromine colour disappeared in about 30 s. Analysis of the residual silanes by integration of the n.m.r. Si–H peaks showed that approximately half of each silane had disappeared, and application of the Ingold–Shaw equation gave $k^{Cl_3SiH}/k^{Ph_3SiH} = 1.03$, 0.94, and 1.06. For solutions left in the dark, only the triphenylsilane reacted.

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Received 19*th November* 1982; *Paper* 2/1942