

ORGANOSILICON COMPOUNDS. LXXXIII.*
 STRUCTURE EFFECTS IN BROMINATION
 OF SOME ORGANOSILICON HYDRIDES IN DIMETHYLFORMAMIDE**

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Kinetics of bromination of an extensive series of organosilicon hydrides by bromine in dimethylformamide in the presence of lithium bromide and lithium nitrate has been studied. The reaction was found to be first order in both reactants. The reactivity of alkyl-substituted silicon hydrides is explained in terms of inductive and steric effects of substituents. In the reactivity of fluoro-, bromo-, chloromethyl-, and phenylsubstituted derivatives, besides inductive and steric effects, also electronic interactions of the substituents with silicon $3d$ -orbitals seem to play a role. The exceptional behaviour of alkylchloro-substituted silicon hydrides is ascribed to a change in the mechanism of the reaction. The second order of the reaction in bromine observed in the case of alkoxy-substituted silicon hydrides can probably be explained by formation of molecular complexes between the hydrides and bromine.

We have recently studied¹ the kinetics of bromination of substituted phenyldimethylsilanes of the type $\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiH}$. The observed linear dependence of logarithms of rate constants of the bromination on Hammett's σ constants was accounted for by a change in the extent of the $(p-d)\pi$ bonding between the phenyl group and the silicon, which takes place in going from the ground to the transition state. The obtained results have not yielded any information on the net polar effect of the phenyl group in this reaction. Such an information would, however, make it possible evaluate quantitatively the extent to which electronegative effect of the group is compensated by oppositely operating $(p-d)\pi$ bonding.

For this reason in the present work a more detailed study of the effect of structure on the rate of bromination of a more extensive series of silicon hydrides was undertaken.

EXPERIMENTAL

Chemicals. Most of the alkylsilanes measured were reported². Other alkylsilanes were prepared by alkylation of chlorosilanes with stoichiometric amounts of the corresponding Grignard re-

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gents in the usual way. (Chloromethyl)dimethylsilane (n_D^{25} 1.4154, lit.³ n_D^{20} 1.4178), bis(chloromethyl)methylsilane (n_D^{25} 1.4482, lit.⁴ n_D^{20} 1.4495), and (dichloromethyl)dimethylsilane (n_D^{25} 1.4646, lit.⁴ n_D^{20} 1.4668) were obtained by reduction of the appropriate (chloroalkyl)chlorosilane with sodium bis(2-methoxyethoxy)aluminium hydride⁵. Methylphenylchlorosilane, methylethylchlorosilane and methyldiethylchlorosilane were prepared by alkylation of the corresponding dichlorosilanes with appropriate amount of Grignard reagents. Methylpropylfluorosilane and methylphenylfluorosilane were obtained by a reaction of the corresponding chlorosilanes with sodium phenylpentafluorosilicate in acetonitrile⁶. Diethylbromosilane and methylphenylbromosilane were prepared by a reaction of the appropriate methoxysilane with acetyl bromide⁷. Propylethoxy-substituted silicon hydrides were reported elsewhere². Other alkoxy-silanes measured were prepared in similar fashion. Dimethylformamide was purified by the described procedure². Bromine (analytical grade) was used without further purification. The purity of the silicon hydrides was checked by gas-liquid chromatography and in the case of chloro-, bromo- and fluorosilanes also by determination of the content of hydrolysable halogen. Physical properties of all the compounds agreed well with those reported.

Kinetic measurements. The rate of bromination was determined spectrophotometrically, measuring a decrease in the intensity of bromine absorption^{1,8} at 390 nm. The initial concentration of silane varied from 0.01 to 0.03 mol/l, that of bromine was about 0.001 mol/l. The temperature 25°C was kept with accuracy of ± 0.05 C. The first order rate constants $k_{1,\text{exp}}$ were determined from the slope of plot $\log A$ vs t and the second order rate constants $k_{2,\text{exp}}$ were calculated from $k_{1,\text{exp}}$ by dividing it by the initial concentration of silane (Table I). The rate constants k_2^0 for bromination of silane by free bromine were calculated from Eq. (I) where K is the dissociation constant of tribromide ion in dimethylformamide, having value¹ $2.09 \pm 0.34 \cdot 10^{-3}$ mol/l (Table II).

$$k_{2,\text{exp}} = k_2^0 K / (K + [\text{Br}^-]) \quad (I)$$

RESULTS AND DISCUSSION

The reaction is first order both in bromine and in the substrate, similarly as bromination of phenyldimethylsilanes¹. The dependence of experimental second order rate constants $k_{2,\text{exp}}$ on bromide ion concentrations is apparent from Table I. The plot of $\log k_{2,\text{exp}}$ against $K/(K + [\text{Br}^-])$, which was used to determine rate constants of bromination by free bromine, k_2^0 , (Table II) always passed through the origin. This indicates that also here tribromide ion did not participate in the reaction as a brominating agent¹. From Fig. 1 it is seen that rate constants k_2^0 for six simple trialkylsilanes correlate well with Taft σ^* constants, which are thought to be the measure of inductive effects of substituents⁹ (reaction constant $\rho^* = -0.87$, correlation coefficient $r = 0.996$). A similar correlation was already observed by Lloyd¹⁰ in halogenations of some alkylsilanes in tetrachloromethane (for chlorination $\rho^* = -4.2$). A low value of ρ^* for bromination in dimethylformamide can undoubtedly be attributed to the high polarity of the solvent¹. Whether the stabilization of the transition state by the solvent is more important than the polarization of the bonds to be broken, induced by the solvent, is not quite clear. We have found that the Si—H stretching frequency of phenyldimethylsilane, taken as an example, was within reading accuracy the same in tetrachloromethane and dimethylformamide. This might indicate that in both sol-

vents the Si—H bond is polarized to the same extent. No data are however available on solvent effect upon polarization of bromine molecule. As to the transition state of bromination in dimethylformamide we attempted to get further information on its structure by measuring deuterium isotope effect, using phenyldimethylsilane and its deuterated analogue as examples. The deuterium isotope effect is, however, small ($k_2^0/k_2^D = 1.24 \pm 0.15$). Effects of this magnitude usually occur when the transition state resembles either the reactants or the products¹¹. In both cases transition states are of low polarity. This is in harmony with our study¹ where a slightly polar three-center transition state *I*, resembling the starting compounds, has been suggested.

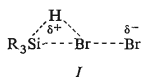
TABLE I

Dependence of $k_{2,\text{exp}}$ of Bromination of Some Alkyl-Substituted Silicon Hydrides on Bromide Ion Concentration

Dimethylformamide, temperature $25 \pm 0.05^\circ\text{C}$, ionic strength 0.3 kept by lithium nitrate, initial concentration of silicon hydride $1 - 3 \cdot 10^{-2}$ mol/l, Br^- conc. about $1 \cdot 10^{-3}$ mol/l.

Compound	$k_{2,\text{exp}}^a$, $1 \text{ mol}^{-1} \text{ min}^{-1}$, for Br^- conc.			
	0.2M	0.15M	0.10M	0.07M
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiH}$	7.80	9.30	13.80	19.08
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiH}$	9.35	12.20	16.60	25.40
$(\text{C}_2\text{H}_5)_3\text{SiH}$	11.90	14.80	21.40	29.30
$(n\text{-C}_3\text{H}_7)(\text{CH}_3)_2\text{SiH}$	7.90	10.30	12.60	—
$(n\text{-C}_3\text{H}_7)_2\text{CH}_3\text{SiH}$	10.25	13.10	19.80	27.60
$(n\text{-C}_3\text{H}_7)_3\text{SiH}$	12.10	16.50	25.60	—
$(i\text{-C}_3\text{H}_7)_3\text{SiH}$	1.57	2.19	3.05	4.40
$(i\text{-C}_4\text{H}_9)_3\text{SiH}$	4.95	6.15	9.60	—
$((\text{CH}_3)_3\text{CCH}_2)(\text{CH}_3)_2\text{SiH}$	7.14	9.42	13.84	19.32
$((\text{CH}_3)_3\text{CCH}_2)_2\text{CH}_3\text{SiH}$	2.33	2.86	4.23	—
$((\text{CH}_3)_3\text{CCH}_2)_3\text{SiH}$	0.16	0.22	0.35	0.48
$\text{ClCH}_2(\text{CH}_3)_2\text{SiH}$	—	1.92	2.46	3.72
$(\text{ClCH}_2)_2\text{CH}_3\text{SiH}$	0.36	—	0.75	1.08
$n\text{-C}_3\text{H}_7(\text{CH}_3)\text{SiHF}$	—	1.17	1.95	2.40
$\text{C}_6\text{H}_5(\text{CH}_3)\text{SiHF}$	—	0.96	1.41	1.89
$\text{C}_2\text{H}_5(\text{CH}_3)\text{SiHCl}$	13.20	—	23.72	34.54
$(\text{C}_2\text{H}_5)_2\text{SiHCl}$	—	21.00	32.42	42.61
$\text{C}_6\text{H}_5(\text{CH}_3)\text{SiHCl}$	2.52	—	5.64	7.26
$(\text{C}_2\text{H}_5)_2\text{SiHBr}$	—	3.06	4.52	6.36
$\text{C}_6\text{H}_5(\text{CH}_3)\text{SiHBr}$	—	2.40	3.60	4.90
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiD}$	—	4.80	8.28	9.75 ^b

^a The average of at least three measurements; ^b $k_{2,\text{exp}}$ at 0.03M-LiBr = $26.04 \text{ l mol}^{-1} \text{ min}^{-1}$.



Steric demands of the reaction are clearly demonstrated by the reactivity of the series of neopentyl silanes. The reactivity of neopentyl dimethylsilane differs from that expected from the Taft equation only by several percent, however, these deviations become serious when a greater number of bulky groups are attached to the silicon. The chloromethyl-substituted silanes show higher reactivity than it would be expected on the basis of their substituent constants σ . An enhanced reactivity of chloromethyl derivatives has already been observed in acid-catalyzed hydrolysis of silicon hydrides¹²⁻¹⁴ and in the chlorination of the Si—H bond in tetrachloromethane¹⁰. Steward and Pierce suggested¹² that this difference is due to dative bonding between the chloromethyl group and the silicon of the type $\text{Cl}^{(+)}\text{CH}_2=\text{Si}^{(-)}$. Effect of this type would tend to reduce the inductive effect of the chloromethyl group on a silicon atom relative to a carbon atom, and cause serious deviation from the Taft equation¹⁰. Our results can probably be explained similarly. It is noteworthy, however, that

TABLE II

Relationship between the Rate Constants k_2^0 for Bromination of Some Alkyl Silanes and Taft σ^* Substituent Constants

Dimethylformamide, temperature $25 \pm 0.05^\circ\text{C}$.

Compound	$k_2^0 (\pm 5\%)$ $1 \text{ mol}^{-1} \text{ min}^{-1}$	$\Sigma \sigma^*{}^a$
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiH}$	691.6	-0.10
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiH}$	851.5	-0.20
$(\text{C}_2\text{H}_5)_3\text{SiH}$	1055.4	-0.30
$n\text{-C}_3\text{H}_7(\text{CH}_3)_2\text{SiH}$	711.6	-0.115
$(n\text{-C}_3\text{H}_7)_2\text{CH}_3\text{SiH}$	937.6	-0.230
$(n\text{-C}_3\text{H}_7)_3\text{SiH}$	1187.2	-0.35
$[(\text{CH}_3)_3\text{CCH}_2](\text{CH}_3)_2\text{SiH}$	693.8	-0.14
$[(\text{CH}_3)_3\text{CCH}_2]_2\text{CH}_3\text{SiH}$	210.5	-0.28
$[(\text{CH}_3)_3\text{CCH}_2]_3\text{SiH}$	16.6	-0.42
$(i\text{-C}_3\text{H}_7)_3\text{SiH}$	150.7	-0.60
$(i\text{-C}_4\text{H}_9)_3\text{SiH}$	459.3	-0.385
$\text{ClCH}_2(\text{CH}_3)_2\text{SiH}$	118.7	1.05
$(\text{ClCH}_2)_2\text{CH}_3\text{SiH}$	55.0	2.10
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiH}$	520.3 ^b	0.60
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiD}$	409.6	0.60

^a Taken from ref.⁹; ^b taken from ref.¹.

a good correlation of the rates with σ^* has been observed by Schott and Werner¹⁵ in bromination of halomethylsilanes of the type $(\text{CH}_3)_{3-n}(\text{CH}_2-m\text{X}_m)_n\text{SiH}$ ($n = 1, m = 1, \text{X} = \text{Cl}, \text{Br}, \text{J}; n = 1, m = 2, \text{X} = \text{Cl}; n = 2, m = 1, \text{X} = \text{Cl}$) in tetrachloromethane.

The polar effect of the phenyl group in the bromination can best be evaluated from the reactivity of phenyldimethylsilane by means of Fig. 1. The value of σ^* so determined equals to 0.06, indicating that the electronegative inductive effect of the phenyl group (compare $\sigma^* = 0.6$ for carbon compounds)⁹ is nearly cancelled out by the oppositely operating effect of the ($p-d$) π dative bonding between the group and the reaction center. Almost the same value (0.0) was reported by Lloyd¹⁰.

A similar method has also been used to evaluate polar effects of halogen atoms attached to the silicon. Because of uncertainty in the value of σ^* for phenyl group in this case (the extent of the phenyl-silicon ($d_\pi - p_\pi$) interaction depends on the nature of the other substituents attached to the same silicon atom¹⁶), with the aim to compare both series of halogenosilanes studied we calculated the differences between experimental $\sum\sigma^*$, determined from the $\log k$ vs σ^* plot (Fig. 1), and the sum of σ^* constants of substituents¹⁷, $\sum\sigma^*_{\text{calc.}}$ ($\Delta\sum\sigma^*$, Table II). In both series the observed order of the reactivity of individual halogenosilanes ($\text{Cl} > \text{Br} > \text{F}$) does not follow the reverse order of electronegativity of the halogens ($\text{Br} > \text{Cl} > \text{F}$), as might be expected if only electronegative inductive effects of these substituents operated. The same situation was recently observed in a study on bromination of silyl-substituted phenyldimethylsilanes⁸ where these groups were in *para*-position with respect to the reaction center (Hammett σ constants for $p\text{-(CH}_3)_2\text{FSi-}$, $p\text{-(CH}_3)_2\text{ClSi-}$, and $p\text{-(CH}_3)_2\text{BrSi-}$ groups were approx. 0.170, 0.022, and 0.096, respectively). This difference is demonstrated by the $\Delta\sum\sigma^*$ values which fall in both series in the fol-

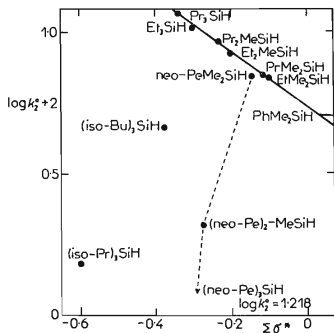


FIG. 1
Relationship between $\log k_2^0$ of Bromination of Some Alkylsilicon Hydrides in Dimethylformamide at 25°C and $\sum\sigma^*$

lowing order: $\text{Cl} > \text{F} > \text{Br}$ (Table II). The higher values of $\Delta\Sigma\sigma^*$ for all phenyl-halogenosilanes, compared with corresponding alkyl derivatives, can undoubtedly be ascribed to the fact that, similarly as in phenyldimethylsilane, also here π -electrons of the benzene ring are engaged in ($p-d$) π interaction with vacant $3d$ -orbitals of silicon. All the phenyl-substituted derivatives, except methylphenylchlorosilane, differ in their $\Delta\Sigma\sigma^*$ from the analogous alkyl derivatives by 0.6, which is practically

TABLE III

Rate Constants k_2^0 for Bromination of Some Halogenosilicon Hydrides by Free Bromine in Dimethylformamide at 25°C

Compound	$k_2^0 \pm 5\%$ $\text{l mol}^{-1} \text{min}^{-1}$	$\Sigma\sigma^{*a}$ calcd.	$\Sigma\sigma_{\text{c,exp}}^*$	$\Delta\Sigma\sigma^*$
$(n\text{-C}_3\text{H}_7)\text{CH}_3\text{SiHF}$	81.3	3.02	0.81	2.21
$(\text{C}_6\text{H}_5)\text{CH}_3\text{SiHF}$	70.3	3.62	0.84	2.78
$(\text{C}_2\text{H}_5)\text{CH}_3\text{SiHCl}$	1 134.2	2.71	-0.34	3.04
$(\text{C}_2\text{H}_5)_2\text{SiHCl}$	1 320.6	2.61	-0.42	3.03
$(\text{C}_6\text{H}_5)\text{CH}_3\text{SiHCl}$	272.7	3.41	0.39	3.02
$(\text{C}_2\text{H}_5)_2\text{SiHBr}$	220.0	2.50	0.50	2.00
$(\text{C}_6\text{H}_5)\text{CH}_3\text{SiHBr}$	174.6	3.30	0.61	2.69

^a Taft σ^* constants for halogens ($\sigma^*(\text{F}) = 3.13$, $\sigma^*(\text{Cl}) = 2.81$, and $\sigma^*(\text{Br}) = 2.70$) were calculated from corresponding σ_{I} constants²¹, using the relation²² $\sigma_{\text{I}} = 0.45\sigma^*(\text{XCH}_2)$. The obtained values were multiplied by a factor of 2.7 (coefficient for fall-off of the inductive effects of substituents through $-\text{CH}_2$ -group⁹).

TABLE IV

Third-Order Rate Constants $k_{3,\text{exp}}$ for Bromination of Alkoxysilanes in Dimethylformamide at 25°C in the Presence of 0.1M LiBr

Ionic strength 0.3 kept by lithium nitrate, the initial bromine concn. about 0.001 mol/l.

Compound	$k_{3,\text{exp}}$ $\text{l}^2 \text{mol}^{-2} \text{min}^{-1}$
$(\text{C}_2\text{H}_5)_2(\text{CH}_3\text{O})\text{SiH}$	585.3
$\text{C}_2\text{H}_5(\text{CH}_3\text{O})_2\text{SiH}$	142.5
$(n\text{-C}_3\text{H}_7)_2(\text{C}_2\text{H}_5\text{O})\text{SiH}$	1 026.3
$n\text{-C}_3\text{H}_7(\text{C}_2\text{H}_5\text{O})_2\text{SiH}$	251.2
$(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$	36.4
$\text{C}_6\text{H}_5(\text{CH}_3)\text{Si}(\text{OCH}_3)\text{H}$	202.3
$\text{C}_6\text{H}_5(\text{CH}_3\text{O})_2\text{SiH}$	96.2

the difference between the tabulated and by us and Lloyd calculated value of σ^* for the phenyl group. The reactivity of alkylchlorosilanes is extremely high. The negative value of σ^* for chlorine (-0.23), calculated from $\sum \sigma_{\text{exp}}^*$, might indicate that here the effect of $(p-d)$ π conjugation even prevails over the inductive effect of the halogen. Such an explanation seems however highly improbable. As other halogeno derivatives behaved "normally", we looked for a possible reason of this discrepancy in the known ability of chlorine atoms attached to silicon to undergo exchange reactions. If tribromide ion present in the reaction mixture participated in such an exchange, then the dibromo chloride ion formed might react with bromine, giving bromine chloride which is known to be much more efficient brominating agent than bromine itself. So, for instance, Lloyd¹⁰ reported that in tetrachloromethane the bromination of the Si—H bond by bromine chloride was four hundred times as fast as the bromination by bromine.

We were also interested in the effect of alkoxy groups, which¹⁸ show very strong tendency to $(p-d)$ π interaction with silicon. In contradistinction to previously discussed cases, the bromination of the alkoxy silanes shown in Table IV proceeded as a third-order reaction (first order in the silane and second order in bromine). The change in the order of the reaction in bromine might be caused by one of two reasons: The first one is that besides bromine molecule also tribromide ion directly participates in the reaction, *i.e.* that in the rate determining step attack by bromine molecule on the hydrogen of the Si—H bond is aided by a nucleophilic attack by tribromide ion on the silicon, these processes being more or less simultaneous. In such a case, the reaction rate is expressed by Eq. (2) (for the meaning of symbols see Eq. (1)).

$$r = -d[\text{Br}_2]_t/dt = k_2^0[\text{Br}_2]_f [\text{Br}_3^-] [\text{S}] = k_{2,\text{exp}}[\text{Br}_2]_t^2 [\text{S}] \quad (2)$$

Since¹ $[\text{Br}_2]_f = [\text{Br}_2]_t K/(K + [\text{Br}^-])$ and

$$[\text{Br}_3^-] = [\text{Br}_2]_t \{1 - K/(K + [\text{Br}^-])\}$$

then

$$k_2^0 \frac{K}{(K + [\text{Br}^-])} \left\{ 1 - \frac{K}{(K + [\text{Br}^-])} \right\} = k_{2,\text{exp}} \quad (3)$$

This derived expression was not however found to be valid in our case.

The other reason is that two bromine molecules or a dimer of bromine molecules take part in the rate-determining step of the bromination. The latter possibility seems, however, less probable. As experimental conditions were the same as in brominations previously discussed, the addition of the alkoxy silanes in so low concentrations as in our case can hardly be expected to cause serious changes in the properties of the reaction medium, which become the decisive factor determining the order in bro-

mine¹⁹. We believe that the observed order may be accounted for by a formation of complexes between bromine and the alkoxysilanes studied. With the aim to get some information on this problem, we previously studied molecular complexes of methoxymethylsilanes with iodine by UV spectroscopy²⁰. Even though convincing evidence has not been obtained, some results could be taken in support of this assumption.

The effect of alkoxy groups on the rate of bromination is apparent from Table IV. The rate decreases with increasing number of alkoxy groups attached to the silicon, undoubtedly due to gradually increasing reduction of the polarity of the Si—H bond caused by electronegative inductive effect of these groups.

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