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BROMINATION OF SILYLSUBSTITUTED PHENYLDIMETHYLSILANES AND σ CONSTANTS OF SILYL GROUPS

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Hammett's σ constants of the silyl groups $(CH_3)_{3-n}X_nSi-$ (X = Cl, Br, OCH₃; $n = 0-3$) were determined by measuring the rate constants of bromination of p- and m-substituted phenyldimethylsilanes in dimethylformamide. From the obtained σ values of the silyl groups it was deduced that the bromine bonded to the silicon exerts only the inductive effect. The dependences of σ constants of the other silyl groups studied (X = Cl or OCH₃) on the degree of substitution n were interpreted in terms of the inductive effects of the substituents and the concept of a $(p-d) \pi$ dative bond between the substituent X and the silicon.

In our laboratory we are interested in the estimation of polar effects of the silyl groups of the type $(CH_3)_{3-n}X_nSi-$ (X = halogen, alkoxy group, hydrogen, perfluoroalkyl group, alkylamino group, and trimethylsiloxy group). As the quantitative measure of the polar effect of the group we took the value of its σ constant. In the preceding paper[1] a classic Hammett's model — substituted benzoic acids — was employed in determining σ constant of some of the above groups (trimethylsiloxymethylsilyl and methylfluorosilyl groups). This model can be however used only for such groups which do not react with the carboxyl group. Thus the study of groups containing the silicon–chlorine or the silicone–bromine bonds is made impossible due to the fact that the corresponding model compounds cannot be prepared. For the determination of the σ constants of such groups for which the classic Hammett's model cannot be employed, one can however make use of the finding that the dependence of the rate constants of bromination of *meta-* and *para-*substituted phenyldimethylsilanes on σ constants excellently obeys[2] the Hammett equation[3] (correlation coefficient =

= 0·995, for six derivatives). The use of this model enabled us to extend the series of the silyl substituents so far studied to those possessing the silicon–halogen and silicon–alkoxy bonds.

EXPERIMENTAL

Compounds Used

The preparation of *p*-silylsubstituted phenyldimethylsilanes was described in the previous work[4], along with the synthesis of (*m*-trifluoromethyl)phenyldimethylsilane added to the set of the standard compounds. The purity of these compounds was checked by gas–liquid chromatography and by comparison of their physical properties with the literature data.

[*m*-(Dimethylsilyl)phenyl]methylchlorosilanes were prepared by reaction of *m*-(dimethylsilyl)-phenylmagnesium bromide with an appropriate methylchlorosilane. Although this procedure is in no way the best one for preparing the compounds in a high yield, it yields the required compounds in purity needed for kinetic measurements. Experimental conditions, physical properties and analytical data are summarized in Table I.

[*m*-(Dimethylsilyl)phenyl]trichlorosilane was obtained by adding [*m*(dimethylsilyl)phenyl]-trichlorosilane (20·0 g, 74 mmol) to an ethereal solution of methylmagnesium iodide prepared from magnesium (5·8 g, 0·24 mol) and methyl iodide (34 g, 0·24 mol). The reaction mixture was boiled for one hour and then worked-up in the usual manner[4]. Rectification afforded the pure product (b.p. 92·5°C/11 Torr, n_D^{25} 1·4919) in 75·8% yield. For $Si_2C_{11}H_{20}$ (208·5) calculated: 63·38% C, 9·67% H; found: 63·22% C, 9·50% H.

[*m*(-Dimethylsilyl)phenyl]methylmethoxysilanes were prepared by reaction of an appropriate chlorosilane with methanol in the presence of pyridine, analogously to the *p*-substituted methoxy-silyl derivatives (see[4]). The purity of the compounds was checked by gas–liquid chromatography and by IR spectroscopy. Experimental conditions, along with physical properties and analytical data are given in Table II.

Kinetic Measurements

The rate constants of the bromination of the compounds studied were determined by the method described in detail in previous paper[2]. As most of the compounds studied are readily hydrolyzable the careful drying of the solvent (dimethylformamide) was necessary. The content of water (determined by K. Fischer method) in all the solutions used did not exceed 0·003%.

RESULTS AND DISCUSSION

The kinetics of this reaction was discussed in one of our previous papers[2]. Dimethyl formamide was chosen as the most convenient medium and the reaction was followed at 25°C in the presence of different bromide ion concentrations and ionic strength kept constant by lithium nitrate. Under these conditions the reaction was proved to be second-order (first order in both silane and bromine). The second-order rate constant k_{2exp} calculated from that equation is related to the bromide ion concentration $[Br^-]$ by Eq. (*1*)

$$k_{exp} = k_2^0 K/(K + [Br^-]),\qquad(1)$$

TABLE I

Preparation of [m-(Dimethylsilyl)phenyl]methylchlorosilanes

| Compound | Starting | | | Yield % | B.p. °C/Torr | Formula (M.w.) | Calculated/(found) | |
	m-bromophenyldimethylsilane mol	methylchlorosilane (mol)	Magnesium mol				% C	% H
m-(CH₃)₂HSiC₆H₄Si(CH₃)₂Cl	0·88	(CH₃)₂SiCl₂ (1·77)	1·0	18·5	117/18	C₁₀H₁₇ClSi₂ (228·88)	52·48 (52·65)	7·48 (7·52)
m-(CH₃)₂HSiC₆H₄(CH₃)Cl₂	0·88	CH₃SiCl₃ (1·77)	1·0	21·7	116—17/12	C₉H₁₄Cl₂Si₂ (249·31)	43·36 (43·08)	5·66 (5·55)
m-(CH₃)₂HSiC₆H₄Cl₃	0·88	SiCl₄ (1·77)	1·0	25·7	108/10	C₈H₁₁Cl₃Si₂ (269·73)	35·62 (35·56)	4·11 (4·07)

TABLE II

Preparation of [m-(Dimethylsilyl)phenyl]methylmethoxysilanes

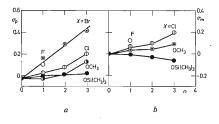| Compound | Starting | | | Yield % | B.p. °C/Torr | n_D^{25} | Formula (M.w.) | Calculated/(found) | |
	chlorosilane mmol	methanol mmol	Pyridine mmol					% C	% H
m-(CH₃)₂HSiC₆H₄Si(CH₃)₂OCH₃	87·0	87·0	87·0	71·5	124/25	1·4918	C₁₁H₂₀O₁Si₂ (224·45)	58·86 (58·94)	8·98 (8·84)
m-(CH₃)₂HSiC₆H₄SiCH₃(OCH₃)₂	80·0	170	170	66·9	125/16	1·4833	C₁₁H₂₀O₂Si₂ (240·46)	54·94 (55·12)	8·38 (8·31)
m-(CH₃)₂HSiC₆H₄Si(OCH₃)₂	110	360	360	66·4	130/12	1·4781	C₁₁H₂₀O₃Si₂ (256·46)	51·52 (51·68)	7·86 (7·86)

where k_2^0 is the rate constant for the bromination of silane by a free molecule of bromine and K is the equilibrium constant of the dissociation of tribromide ion.

The bromination of the substituted phenyldimethylsilanes studied in the present work was carried out under the same experimental conditions as in our previous study[2]. In determining the reaction constant ϱ we used the reported[2] rate constants of bromination for p-trifluoro-, m- and p-chlorophenyldimethylsilane and the parent compound, along with the rate constant for m-trifluorophenyldimethylsilane determined in this study, and the corrected value of the rate constant for p-tolyldimethylsilane. The selection of substituents and of the set of σ substituent constant was made in accordance with the views of van Bekkum and coworkers[5] in order to ensure the same way of treatment of data for all the reaction systems studied. As follows

TABLE III
Dependence of the Rate Constants k_2^0 of Bromination of Substituted Phenyldimethylsilanes on σ Temperature 25°C, dimethylformamide. Reaction constants $\varrho = -0.85 \pm 0.10$, correlation coefficient $r = 0.996$, standard deviation $s_{yx} = 0.0216$.

Substituent	k_2^0 $l\ mol^{-1}\ min^{-1}$	σ
p-CH$_3$	624·2	−0·129
H	520·3	0·000
p-Cl	329·9	0·238
m-Cl	251·5	0·373
m-CF$_3$	189·6	0·467
p-CF$_3$	182·0	0·532

Fig. 1

Dependence of σ Constants of the $(CH_3)_{3-n} . X_n Si$ Groups on the Number of Substituents X
    a p-Substituted silylbenzenes; b m-substituted silylbenzenes.

from the data given in Table III the dependence of the rate constants on σ conforms well to the Hammett equation. The value of reaction constant ϱ obtained by us (-0.85) is in good agreement with the value found earlier[2,6,7] (0.769), as can be easily shown by comparison of the confidence intervals of the given values. The difference between the two values is caused by the use of the different sets of substituents and of the values of σ. The calculated constants of the regression line were

TABLE IV
Dependence of $k_{2\,exp}$ of Bromination of Substituted Phenyldimethylsilanes $RC_6H_4Si(CH_3)_2H$ on Concentration of Bromide Ions
   Dimethylformamide, temperature $25 \pm 0.05°C$.

R	$k_{2\,exp}{}^a$, l mol^{-1} min^{-1}		
	$[Br^-] = 0.1^b$	$[Br^-] = 0.07^b$	$[Br^-] = 0.03^b$
p-$(CH_3)_3Si$	11·43	16·32	35·90
p-$(CH_3)_2CH_3OSi$	10·55	16·35	33·75
p-$CH_3(CH_3O)_2Si$	10·85	14·88	32·10
p-$(CH_3O)_3Si$	8·23	11·35	25·30
p-$(CH_3)_2FSi$	7·69	10·55	23·50
p-CH_3F_2Si	6·89	10·05	20·60
p-F_3Si	9·55	16·50	33·30
p-$(CH_3)_2ClSi$	10·71	13·80	31·40
p-CH_3Cl_2Si	8·53	12·78	28·24
p-Cl_3Si	8·13	10·06	21·96
p-$(CH_3)_2BrSi$	8·79	11·32	27·60
p-CH_3Br_2Si	6·41	8·46	18·30
p-CH_3Si	5·45	7·30	14·38
m-$(CH_3)_3Si$	10·18	16·25	32·19
m-$(CH_3)_2CH_3OSi$	10·00	13·62	30·18
m-$CH_3(CH_3O)_2Si$	10·69	14·10	30·08
m-$(CH_3O)_3Si$	9·30	12·92	27·06
m-$(CH_3)_2ClSi$	9·30	13·29	28·68
m-CH_3Cl_2Si	8·54	11·95	27·84
m-Cl_3Si	8·08	10·49	22·25

^{a} An average value of five measurements. ^{b} The expression $1/(K + [Br^-])$ attains the following values 9·79; 13·87; 31·16 l mol^{-1}.

then directly used in the determination of σ constants. This approach is fully justified since the value of correlation coefficient does not differ significantly from 1. In Table IV are presented the rate constants of bromination for different bromide ion concentrations, which were used in the calculation of the rate constant k_2^0. In all cases the kinetics of the bromination could be well described by Eq. (1). The values of k_2^0 calculated by the least square method together with the σ constants obtained are summarized in Table V (the values of σ constants are given with the limits of confidence interval for 95% level of significance). The results obtained in the bromination of fluoromethylsubstituted phenyldimethylsilanes are difficult to explain by commonly

TABLE V
Rate Constants k_2^0 of Bromination of Silylsubstituted Phenyldimethyl Silanes[a] and Calculated σ Constants of the $(CH_3)_{3-n}X_nSi$ Groups
Temperature 25°C.

$(CH_3)_{3-n}X_nSi$	k_2^0 $l\ mol^{-1}\ min^{-1}$	σ
p-$(CH_3)_3Si$	553·6	$-0\cdot047 \pm 0\cdot058$
p-$(CH_3)_2FSi$	362·5	$0\cdot170 \pm 0\cdot047$
p-CH_3F_2Si	322·5	$0\cdot230 \pm 0\cdot045$
p-F_3Si	516·8	$0\cdot011 \pm 0\cdot055$
p-$(CH_3)_2ClSi$	484·4	$0\cdot022 \pm 0\cdot053$
p-CH_3Cl_2Si	433·5	$0\cdot079 \pm 0\cdot050$
p-C_3Si	343·3	$0\cdot198 \pm 0\cdot046$
p-$(CH_3)_2BrSi$	419·2	$0\cdot096 \pm 0\cdot049$
p-CH_3Br_2Si	285·1	$0\cdot294 \pm 0\cdot046$
p-CH_3Si	229·0	$0\cdot406 \pm 0\cdot049$
p-$(CH_3)_2CH_3OSi$	525·0	$-0\cdot020 \pm 0\cdot056$
p-$CH_3(CH_3O)_2Si$	498·9	$0\cdot007 \pm 0\cdot054$
p-$(CH_3O)_3Si$	390·0	$0\cdot134 \pm 0\cdot047$
m-$(CH_3)_3Si$	504·7	$0\cdot001 \pm 0\cdot054$
m-$(CH_3)_2ClSi$	444·2	$0\cdot066 \pm 0\cdot051$
m-CH_3Cl_2Si	424·4	$0\cdot089 \pm 0\cdot049$
m-Cl_3Si	348·8	$0\cdot190 \pm 0\cdot046$
m-$(CH_3)_2CH_3OSi$	466·3	$0\cdot041 \pm 0\cdot052$
m-$CH_3(CH_3O)_2Si$	470·2	$0\cdot037 \pm 0\cdot051$
m-$(CH_3O)_3Si$	423·1	$0\cdot091 \pm 0\cdot049$

[a] Calculated from experimental rate constants k_{2exp} given in Table IV.

accepted concepts on the character of polar effects of silyl substituents. From Fig.1 and the σ constants of fluoromethylsilyl groups (Table V) it is evident that the introduction of the third fluorine atom on the silicon brings about a marked decrease in the overall electronegativity of the group and thus distinct rate enhancement over the range of bromide ion concentrations used. This fact may be accounted for by the formation of a complex with pentavalent silicon atom as the result of the presence of three strongly electronegative fluorine atoms attached to the central atom. There are two particles in the reaction system which are capable of forming such a complex. The first one is the solvent itself (dimethylformamide), the stable complexes of which with silicon tetrafluoride were already observed. One cannot exclude however even in advance an interaction of the bromide ion with the silicon atom, unfortunately there are no relevant data available which would allow us to draw any conclusion concerning a possibility of the occurrence of such an interaction in the case studied here. The coordination of either the nitrogen atom of dimethylformamide or bromide ion to the silicon atom might account for the reduced electronegativity of the trifluorosilyl group. To decide whether the formation of the above complex occurs also in the case of the methyldifluorosilyl group and thus affects the value of its σ constants is even more difficult. With the dimethylfluorosilyl group this possibility can be likely discarded since the comparison of the σ constant of dimethylfluorosilyl group obtained in this work with those determined from the rate constants of esterification of the corresponding benzoic acid in all the solvents used showed that there are no significant differences between these values. The differences between the value of σ for trimethylsilyl group obtained by measuring the rate of the bromination and those determined using trimethylsilylbenzoic acid as the model compound are also statistically insignificant. This finding may be taken as indicative of relative independency of the σ constants of silyl substituents on the type of reaction and of reaction center as well as on the solvent used.

The bromination of substituted phenyldimethylsilanes cannot be employed for determination of σ constants of substituents containing silicon–nitrogen bonds, since the cleavage of these bonds by bromine rapidly proceeds. We have found that the bromination of tris(dimethylamino)phenylsilane and hexamethyldisilazane is completed within ten seconds.

With regard to an insignificant difference between the σ constant of trimethylsilyl group found in this work and those obtained using the classic Hammett model one can conclude that also in our model compounds a significant $(p - d)\pi$ dative bonding takes place between the central atom of trimethylsilyl group and the aromatic ring.

We have attempted at estimating the mesomeric effect of silyl substituents with the aid of the relation suggested by Exner[8]:

$$\log k_p - \log k^0 = \lambda \left(\log k_m - \log k^0 \right). \qquad (2)$$

This relation, similar in nature to the Hammett equation, is as a rule valid for dipolar substituents exerting only the inductive effect when a reaction center is incapable of acting as an electrondonor in conjugative bonding with the aromatic ring. If one draws a straight line passing through the point for an unsubstituted derivative and having the slope $\lambda = 1{\cdot}14$ (see[9]), then all the substituents exerting $+M$ effect lie on the one side and those exhibiting $-M$ effect on the other side of this line. Thus, the nature of mesomeric effect of a given group can easily be established. Similar treatment of the rate constants of the bromination of the substituted phenyldimethylsilanes has not, however, yielded unambiguous results due to the fact that the experimental errors in the determination of the rate constants were comparable with the deviations of the points from the straight line.

Let us turn our attention to the dependence of σ constants of the silylsubstituents on the degree of substitution. In Fig. 1 we included also the results for trimethylsiloxymethyl groups obtained on the basis of the study of the corresponding silylsubstituted benzoic acids[1]. It is evident that of the substituents studied only the σ constants of p-bromosilyl groups show a linear dependence on the number of substituents X attached to the silicon, the dependence for the other substituents, in particular p-methylmethoxysilyl and p-methylchlorosilyl groups, being rather a curve.

According to commonly accepted concepts the linear dependence of σ on substitution degree is to be expected for substituents exhibiting the inductive effect only. In this connection it should be stressed that the change in σ constant $(\Delta\sigma)$ brought about by the replacement of all the methyl groups on the silicon by substituent X $(X = CH_3O, Br, Cl)$ is, except bromine, by far smaller than that found for the corresponding carbon analogues (e.g. for chlorine[10] $\Delta\sigma_m = 0{\cdot}51$ and $\Delta\sigma_p = 0{\cdot}65$, and for fluorine[10] $\Delta\sigma_m = 0{\cdot}53$ and $\Delta\sigma_p = 0{\cdot}74$). As the σ constant of tert-butyl group is very close to that of methyl group, the change in σ constant brought about by replacement of one methyl group by substituent X can be roughly estimated from the analogical change $(\Delta\sigma')$ after substitution of hydrogen atom of the methyl group for substituent X (e.g.[11] for bromine $\Delta\sigma'_p = 0{\cdot}28$ and for methoxy group $\Delta\sigma'_p = 0{\cdot}19$). The corresponding differences in σ constants of the silyl groups are comparable with those of the carbon analogues only in the case of bromosilyl groups $(\Delta\sigma_p = 0{\cdot}23)$. With other substituents these are distinctly smaller.

From the foregoing discussion it follows that predominantly the inductive effect of bromine is operative in the silicon–bromine bond. We believe that the non-linearity of the dependences of σ on substitution degree, as well as relatively small changes in σ observed for the silyl groups $(CH_3)_{3-n}X_nSi$ $(X = Cl, OCH_3)$ may be attributed to a $(p - d)\,\pi$ dative bond taking place between substituent X and the silicon. Assuming that a $(p - d)\,\pi$ bonding in each Si—X bond becomes less extensive when the number of substituents X increases, the greatest change in σ constant is to be expected after the introduction of the third substituent X, since here the inductive effect of the substituent X is least reduced by the opposite effect of the $(p - d)\,\pi$

dative bond. The dependences of σ on substitution degree obtained for the *p*-methyl-chlorosilyl and *p*-methylmethoxysilyl groups support this assumption.

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