

ORGANOSILICON COMPOUNDS. LXXIX.*

HAMMETT SUBSTITUENT CONSTANTS

OF SOME SILYL GROUPS**

Z. PLZÁK^{a,***}, F. MAREŠ^a, J. HETFLÉJŠ^a, J. SCHRAML^a, Z. PAPOUŠKOVÁ^a, V. BAŽANT^a,
E. G. ROCHOW^b and V. CHVALOVSKÝ^a

^a*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Science, Prague - Suchbát*

^b*Department of Chemistry,
Harvard University, Cambridge, Massachusetts, U.S.A.*

Received September 1st, 1970

Hammett's σ constants of the $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}$ - ($\text{X} = \text{OSi}(\text{CH}_3)_3$, $n = 0-3$; $\text{X} = \text{F}$, $n = 1$) and $(\text{CH}_3)_3\text{SiOCH}_2$ -groups were determined *a*) from the rate constants of esterification of substituted benzoic acids with diphenyldiazomethane in toluene, dioxane and dimethylformamide, *b*) from the carboxylic proton chemical shifts in the PMR spectra of these acids in pyridine and *c*) by a potentiometric titration of the acids in dimethylformamide. Solvent effects on the σ constants of the groups studied were found to be negligible. The values of σ constants of *m*-(*p*-)trimethylsilyl and of *m*-(*p*-)trimethylsiloxymethyl groups indicate a significant (*p*-*d*) π interaction between silicon and the aromatic ring. The inductive effect of the trimethylsiloxy group is lower than that of the methoxy group. Side reactions of some of the silyl groups preventing the determination of their σ constants are discussed.

Although much information concerning the problem of (*p*-*d*) π bonding in organosilicon compounds has been collected in literature, there are still some questions to be answered: it is above all that of the relative tendency towards the formation of (*p*-*d*) π bonds in different atoms and groups attached to silicon, of influencing the (*p*-*d*) π character of a bond by the inductive effects of the other substituents attached to silicon, as well as that of mutual influence of such bonds on a single silicon atom.

Hammett σ constant may be regarded as a quantitative measure of polar effect exerted by substituents in a given model system. Unfortunately, the only reliable σ

* Part LXVIII: This Journal 36, 2785 (1971).

** This work was published in part concerning PMR spectroscopy by E. G. Rochow and J. Schraml in Technical report, National Science Foundation, Department of Chemistry, Harvard University, February 1966; the short summary of the work was given in a lecture on *II^e Symposium international sur la Chimie des composés organiques du Silicium, Bordeaux 1968* (Résumés des communications, p. 127).

*** Present address: Institute of Inorganic Syntheses, Prague - Řež.

constants so far reported for silyl substituents are those for alkyl- and phenylsilyl groups. It seemed thus desirable to determine σ constants for silyl groups of the type $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}$ - (X = halogen, alkoxy group, hydrogen, perfluoroalkyl, amino, and trimethylsiloxy group, $n = 1-3$). We presumed that the knowledge of σ constants for silyl groups would make it possible to compare quantitatively polar effects of these groups with those of the carbon analogues, and further that from the dependence of σ constants on the substitution degree n some conclusions could be drawn on the tendency of silicon to form ($p \rightarrow d$) π dative bonds with a greater number of atoms or groups capable of such an interaction.

Classical model compounds for the determination of σ constants are *m*- and *p*-substituted benzoic acids. In the present work we used this model in the determination of σ constants for some of the silyl groups mentioned above and that trimethylsilyloxy- and methylfluorosilyl ones.

The most frequently employed methods are the measurement of $\text{p}K$'s of dissociation of benzoic acids in water or 50% aqueous ethanol at 25°C and the esterification of the acids with diphenyldiazomethane in alcohols. We made use of both methods with the exception that an aprotic solvent was employed in place of the common protic system, because of the instability of some silicon bonds in the latter. As an independent method we have chosen the measurement of carboxylic proton chemical shifts in PMR spectra of substituted benzoic acids, which were found to be linearly dependent on the σ constants of substituents.¹

EXPERIMENTAL

Compounds Used

The preparation of *p*-silylsubstituted benzoic acids Ia—d and IIa—c was reported in the previous papers^{1,2}. *m*-Silylsubstituted benzoic acids IIIa—d were prepared in a similar fashion. The acids were purified by distillation under reduced pressure (0.05 Torr) and by crystallization from dry *n*-hexane at -30°C. Their physical properties and elemental analyses are given in Table I. The other benzoic acids used were purified by a crystallization from acetic acid, aqueous ethanol, *n*-heptane or benzene and stored in a vacuum desiccator over phosphorus pentoxide. Their melting points were in accordance with those reported in literature. The molecular weights of the acids determined by alkalimetric titration agreed well (within 1%) with the calculated ones.

p-Trimethylsiloxymethylsilylbenzoic acid (V). *p*-Bromomethylbenzoic acid (21 g; 0.107 mol), prepared in the usual way³, was dissolved in 400 ml of concentrated hydrochloric acid and the solution was heated for 10 hours to 105°C. The precipitated crystalline product was filtered off and then dissolved in an equivalent amount of 10% aqueous sodium hydroxide solution. The resulting mixture was brought to boiling and then made alkaline by adding an additional amount of the sodium hydroxide solution (phenolphthalein was used as indicator). The acidification of the mixture afforded crude product which was crystallized from water. Melting point of the product (179—180°C) was identical with that recorded⁴ for *p*-hydroxymethylbenzoic acid. To a solution of 2.0 g (13 mmol) of this compound and 2.1 g (26 mmol) of pyridine in 50 ml of ether were added with stirring 4.36 g (40 mmol) of trimethylchlorosilane; stirring was continued for additional 4 hours. The reaction mixture was extracted with water, the organic layer was

separated and dried by standing over anhydrous magnesium sulphate. After removal of the solvent a crystallization of the crude product from light petroleum at -40°C afforded trimethyl-

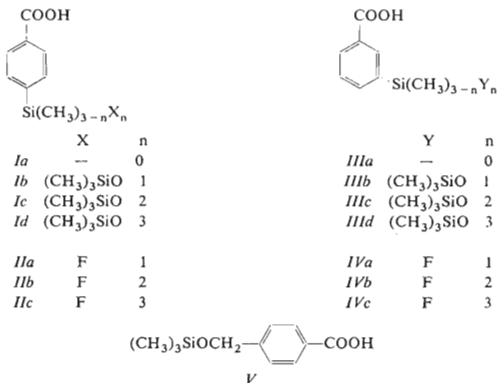


TABLE I
m-Silylsubstituted Benzoic Acids

Compound	M.p., $^{\circ}\text{C}$	Formula	M.w.	Calculated/Found	
			calculated found ^a	% C	% H
<i>IIIa</i>	111.5–112 ^b	$\text{C}_{10}\text{H}_{14}\text{O}_2\text{Si}_1$	194.3	61.81	7.26
			196.4	61.98	7.25
<i>IIIb</i>	67–68	$\text{C}_{12}\text{H}_{20}\text{O}_3\text{Si}_2$	268.5	53.69	7.51
			270.1	53.54	7.43
<i>IIIc</i>	72–73	$\text{C}_{14}\text{H}_{26}\text{O}_4\text{Si}_3$	342.6	49.07	7.65
			344.3	49.04	7.66
<i>IIId</i>	99–100	$\text{C}_{16}\text{H}_{32}\text{O}_5\text{Si}_4$	412.8	46.11	7.71
			422.3	46.22	7.75
<i>IVa</i>	86	$\text{C}_9\text{H}_{11}\text{FO}_2\text{Si}$	198.3	54.52	5.59
<i>IVb</i>	— ^c	$\text{C}_8\text{H}_8\text{F}_2\text{O}_2\text{Si}$	202.2	54.61	5.61
				47.51	3.98
<i>IVc</i>	— ^c	$\text{C}_7\text{H}_5\text{F}_3\text{O}_2\text{Si}$	206.2	47.49	4.18
				40.77	2.44
				41.01	2.54

^a Determined by alkalimetric titration. ^b Reported² m.p. 113.7–114.2 $^{\circ}\text{C}$. ^c Compound sublimes.

siloxymethylbenzoic acid, m.p. 89–91°C, in 60% yield. The structure of the acid was checked by IR spectroscopy. For $\text{Si}_1\text{C}_{11}\text{H}_{16}\text{O}_3$ (224.3) calculated: 58.89% C, 7.19% H; found: 59.12% C, 7.14% H. Its molecular weight determined by alkalimetric titration equaled to 225.3.

Diphenyldiazomethane was obtained from hydrazone of benzophenone⁵ by Miller's method⁶ in 90% yield. The crude product was purified by a crystallization from petroleum ether and anhydrous methanol at –30°C. The crystalline diphenyldiazomethane was filtered off, freed of the solvent by evaporating it at –20°C, and then dried *in vacuo* (0.01 Torr) at room temperature. Only the samples stored at –60°C for less than 10 days were used for kinetic measurements.

Tetrabutylammonium methoxide. Tetrabutylammonium iodide (20 g, 54.2 mmol) dissolved in 100 ml of anhydrous methanol was shaken with 10 g (43.3 mmol) of silver oxide for 2.5 hours. After that period test for the presence of iodide ions in solution was negative. The precipitate, separated by filtration, was washed with 200 ml of dry benzene, and then the solvents were evaporated *in vacuo* at room temperature. The evaporation residue was successively washed with 100 ml of dry benzene and freed of the solvent, this procedure being three times repeated. All the operations were carried out under the atmosphere of dry nitrogen. The benzene solution of the methoxide used (0.25M) for the potentiometric titrations was stored in a refrigerator at 0°C. Its concentration was determined by a potentiometric titration with benzoic acid.

Solvents. N,N-Dimethylformamide was purified by azeotropic distillation with benzene and water under reduced pressure (100 Torr) through a 60 TP column, then dried by standing over Nalsit 4 A molecular sieve. Prior to its application the solvent was neutralized with a benzene solution of tetrabutylammonium methoxide and redistilled under reduced pressure. Pyridine was purified by shaking it with solid sodium hydroxide for two days. After boiling over calcium oxide for 6 hours, the solvent was distilled on a 20 TP column. Toluene, dioxane, cyclohexane, and benzene were dried in the usual way, distilled on a 60 TP column and stored over Nalsit 4 A molecular sieve. The content of water in all the solvents used did not exceed 0.003% (determined by K. Fisher method). The purity of the solvents was checked by determination of their refractive indices, which were found to be in excellent agreement with those recorded⁷.

TABLE II

Dependence of the Rate Constants k_2 of the Esterification of a Selected Set of Substituted Benzoic Acids with Diphenyldiazomethane in Toluene, Dioxane and Dimethylformamide on σ Constants

Substituent	$k_2, \text{l mol}^{-1} \text{ min}^{-1}$			σ (ref. ¹⁰)
	toluene ^a	dioxane ^b	dimethylformamide ^c	
<i>m</i> -NO ₂	—	1.02	0.673	0.710
<i>m</i> -Br	3.65	0.234	—	0.391
<i>m</i> -Cl	3.63	—	0.209	0.373
<i>p</i> -Br	—	0.141	0.139	0.265
H	0.462	0.046	0.045	0.000
<i>p</i> -CH ₃	0.194	0.026	0.029	–0.129

^a Temperature $20 \pm 0.05^\circ\text{C}$; reaction constant $\rho = 2.44 \pm 0.35$, $\log k_2^0 = -0.370 \pm 0.098$, correlation coefficient $r = 0.999$, standard deviation $s_{yx} = 0.0375$. ^b Temperature $30 \pm 0.05^\circ\text{C}$; $\rho = 1.89 \pm 0.04$, $\log k_2^0 = -1.338 \pm 0.017$, $r = 1.000$, $s_{yx} = 0.009$. ^c Temperature $30 \pm 0.05^\circ\text{C}$; $\rho = 1.63 \pm 0.12$, $\log k_2^0 = -1.308 \pm 0.043$, $r = 0.999$, $s_{yx} = 0.0236$.

TABLE III

Rate Constants k_2 of the Esterification of Silylsubstituted Benzoic Acids with Diphenyldiazomethane in Toluene, Dioxane and Dimethylformamide and Calculated σ Constants

Substituent	$k_2 \cdot 10^2, \text{l mol}^{-1} \text{min}^{-1}$				σ	
	toluene ^a	dioxane ^b	dimethylformamide ^b	toluene		dioxane
$m\text{-(CH}_3)_3\text{Si}$	49.1	4.96	4.63	0.024 ± 0.050	0.017 ± 0.012	-0.016 ± 0.038
$m\text{-}[(\text{CH}_3)_3\text{SiO}]/(\text{CH}_3)_2\text{Si}$	42.9	4.51	4.02	0.001 ± 0.052	-0.004 ± 0.012	-0.017 ± 0.038
$m\text{-}[(\text{CH}_3)_3\text{SiO}]_2\text{Cl}_3\text{Si}$	36.8	4.15	4.35	-0.026 ± 0.054	-0.023 ± 0.013	-0.033 ± 0.039
$m\text{-}[(\text{CH}_3)_3\text{SiO}]_3\text{Si}$	29.3	3.11	4.23	-0.067 ± 0.057	-0.089 ± 0.014	-0.040 ± 0.039
$p\text{-(CH}_3)_3\text{Si}$	42.9	4.15	4.61	0.001 ± 0.052	-0.029 ± 0.013	-0.034 ± 0.039
$p\text{-}[(\text{CH}_3)_3\text{SiO}]/(\text{CH}_3)_2\text{Si}$	45.1	4.34	5.06	0.010 ± 0.052	-0.013 ± 0.012	0.007 ± 0.037
$p\text{-}[(\text{CH}_3)_3\text{SiO}]_2\text{CH}_3\text{Si}$	48.1	4.32	5.38	0.021 ± 0.050	-0.014 ± 0.013	0.024 ± 0.037
$p\text{-}[(\text{CH}_3)_3\text{SiO}]_3\text{Si}$	48.7	4.39	5.73	0.023 ± 0.050	-0.010 ± 0.013	0.040 ± 0.036
$m\text{-(CH}_3)_2\text{FSi}$	20.5	8.69	7.17	0.118 ± 0.047	0.146 ± 0.011	0.100 ± 0.035
$m\text{-(CH}_3)_2\text{Si}$	—	17.4	11.41	—	0.36	0.224 ± 0.034
$p\text{-(CH}_3)_3\text{SiOCH}_2$	35.4 ^c	3.80	3.89	-0.033 ± 0.054	-0.043 ± 0.013	-0.063 ± 0.040

^a Temperature $20 \pm 0.05^\circ\text{C}$. ^b Temperature $30 \pm 0.05^\circ\text{C}$. ^c Because of poor solubility of the acid, the initial concentration $5.55 \cdot 10^{-2} \text{ mol/l}$ was used in place of $5.62 \cdot 10^{-2} \text{ mol/l}$ applied in the other cases.

Esterification of Benzoic Acids with Diphenyldiazomethane

The reaction rate was measured in toluene, dioxane and dimethylformamide at a constant concentration ($5.62 \cdot 10^{-2}$ mol/l) of the acid and the concentration of diphenyldiazomethane of about $5.6 \cdot 10^{-3}$ mol/l. Up to now to follow the loss of diphenyldiazomethane either spectrophotometric or polarographic method have been applied. We decided to follow the evolution of nitrogen by a volumetric method using a Warburg apparatus which was proved to be a very handy and precise method for the kinetic measurements of the Si—H bond solvolysis⁸.

During our measurements 1 ml of $2.2 \cdot 10^{-2}$ M solution of diphenyldiazomethane and 3 ml of $7.5 \cdot 10^{-2}$ M solution of substituted benzoic acid in the appropriate solvent were transferred by means of calibrated pipettes into separated arms of a reaction vessel. The solutions were thermostated for 15 minutes and then the reaction was started by mixing the solutions together. The changes in the level of the manometric liquid (silicon oil having d_{4}^{25} 0.9553 and viscosity 10 cP) were registered together with time. As the reaction vessel is a very sensitive thermometer and barometer we corrected the reading for changes in temperature and atmospheric pressure by means of a thermobarometer (a vessel containing only the solvent) introduced into the same thermostat bath. The pseudofirst order rate constants k_1 were calculated from the slopes of the $\log V_{\infty}(V_{\infty} - V_t)$ versus time plot where V and V_t is the volume of the nitrogen evolved in the time reaching infinity and a time t , respectively. The reproducibility of the rate constants was $\pm 3\%$. Second order rate constants k_2 presented in Tables II and III were calculated from the constants k_1 by dividing them by the initial concentration of the benzoic acid used for the kinetic measurements.

Potentiometric Measurements

The titration was carried out in dimethylformamide at $25.0 \pm 0.1^{\circ}\text{C}$ kept by a thermostat. Prior to its application the glass electrode (Radiometer Copenhagen) was kept in dimethylformamide for several days. In the reference electrode (calomel electrode) the aqueous potassium chloride solution was exchanged for a saturated lithium chloride solution in dimethylformamide. In this way the irreproducibility of the junction potentials was eliminated and at the same time a contamination of the titrated solution by water, which could solvolyse some of the investigated Si—X bonds, could be removed. The potentials were measured with a pH meter PHK-1 (Development Workshops of Czechoslovak Academy of Science) with a precision of 1 mV. The volume of 0.25M tetrabutylammonium methoxide solution in benzene was recorded with a precision of 2 microliters. The titration was carried out in a nitrogen atmosphere. The nitrogen was dried and freed of carbon dioxide, bubbled through dry dimethylformamide and then introduced into the titration vessel. The titrated solution was stirred by an electromagnetic stirrer. Tetrabutylammonium iodide (in conc. $2 \cdot 10^{-3}$ M) was added to the titrated solution to accelerate the arrestment of the potential. The amount of an acid needed for one titration amounted to approx. $5 \cdot 10^{-4}$ mol. The potential of half neutralization was calculated from the plot of the potential against the amount of the consumed base in the usual manner.

The potentials of half neutralization could not be exactly reproduced. However, the difference between the potentials of half neutralization of benzoic acid and those of other investigated acids were always reproducible with a precision of 3 mV. We therefore checked the potential of benzoic acid at least three times a day. The σ constants given in the present work are based only on the differences in the potentials of half neutralization and not on their absolute value.

NMR Measurements

For the NMR determination of σ constants the method of Kondo and coworkers¹ was employed. The method uses the linear dependence of carboxylic proton chemical shift upon the Hammett σ constant in dry pyridine at infinite dilution.

Since the chemical shifts of isolated COOH and H₂O protons are considerably different and since the molecular weight of water (two protons) is about one tenth of that of the acids (one COOH proton), the measured chemical shift of COOH proton which exchanges fast with any H₂O proton present in the sample is very strongly dependent on the moisture content. The moisture shifts the signal to higher magnetic field (e.g. according to our experience if the solutions were prepared in a dry box with remaining 5–10% relative humidity the COOH line might be shifted up to 2 p.p.m. upfield). For this reason the following satisfying procedure for sample preparation was developed.

NMR samples were prepared on a vacuum line where the solid acid had been dried. Dry pyridine (prepared as described above) with 10% of cyclohexane was introduced into the vacuum system through a column filled with an active molecular sieve and the distilled on the acid. The samples were sealed off under vacuum (approx. 10^{-4} Torr). The concentration of acids was kept under 3 mol. %, so that the chemical shifts obtained could be regarded as infinite dilution shifts¹.

The spectra of *para*-derivatives were measured on a Varian A 60 instrument while those of *meta*-derivatives on a modified Tesla BS 477 spectrometer. The chemical shifts were measured in reference to the line of the cyclohexane at 23°C. Using repeated measurements the shifts were established with an error of ± 0.002 p.p.m.

For the purpose of checking our experimental arrangement the following acids with known σ constants were measured: *p*-chlorobenzoic, *p*-toluic, *m*-bromobenzoic, and benzoic acid. While the results obtained on the Tesla spectrometer agreed with the measurements of the authors of the method¹, the downfield shifts obtained on the other spectrometer were somewhat smaller (by some 0.06 p.p.m.) than those reported¹. The values of σ constants for the silyl groups were read off from the plot given in ref.¹ with an appropriate correction in the case of *para*-derivatives.

RESULTS AND DISCUSSION

It is evident from the data given in Table II that the Hammett relation is excellently fulfilled with all the reaction systems chosen. The table presents the values of correlated quantities, calculated reaction constant and those of statistical quantities characterizing their accuracy as well the accuracy of single correlations. For the correlations we used the set of σ constants recommended by van Bekkum and coworkers⁹ and the selection of standard substituents was made in accordance with the views of the authors as far as the solubility of recommended benzoic acids and their availability in required purity made it possible.

The validity of the Hammett equation for esterifications of benzoic acids with diphenyldiazomethane in dimethylformamide and dioxane was already proved¹⁰ under experimental conditions identical with those chosen by us. Our results are in good agreement with those reported (for dioxane¹⁰ $\rho = 2.00$, $\log k_0 = -1.385$, $r = 1.000$; for dimethylformamide¹⁰ $\rho = 1.555$, $\log k_0 = -1.275$, $r = 0.998$), particularly if one takes into account that the results were obtained with the different and very limited set of substituents. The esterification of benzoic acids in toluene

has been so far studied at temperatures higher than 25°C, so that a direct comparison of the reported results with those obtained by us cannot be made. With regard to the fact that in this case the linear dependence of ρ on $1/T$ has not been found¹¹, only a qualitative comparison of the reliability of the value of reaction constant ρ given here is possible. Hancock¹¹ reported that the reaction constant ρ decreases with increasing temperature (the value of ρ being 2.22, 2.13 and 2.12 at 25, 35 and 45°C, respectively). The ρ constant found in this work (2.44) follows this trend.

In the determination of σ constants for the silyl groups from the corresponding rate constants k_2 we used the calculated values of the constants of regression lines, *i.e.* the values of the slope ρ and of the $\log k_2^0$. We regarded this procedure as fully justified since the value of r^2 is very close to one. In the usual way we calculated also the standard deviation for obtained σ constants and from this deviation the confidence interval at 95% significance level. The results are summarized in Table III. The σ constants are given with the corresponding confidence limits. The use of the three solvents of different polarity enabled us to estimate the effect of solvent polarity on the values of σ constants of the silyl groups studied. As these are bulky, solvation may substantially affect the value of their σ constants. Our results show that the differences in σ constants obtained for single substituent in different solvents are not statistically significant. The same can be said also for the σ constants of standard substituents which in fact are presupposed⁹ to be essentially independent of the nature of solvent.

As the second method for the determination of Hammett constants of the silyl groups we used potentiometric titration of the corresponding benzoic acids in dimethylformamide. As follows from data presented in Table IV the difference between the potentials of half neutralization of standard benzoic acids and that of the parent compound, $\Delta E_{1/2}$, are linearly dependent on σ constants. The σ constants for the

TABLE IV

Dependence of the Values of $\Delta E_{1/2}$ for the Selected Set of Substituted Benzoic Acids on σ Constants of Substituents

Slope of regression line $a = 168.0 \pm 14.4$, $E_{1/2}^0 = 0.3 + 5.4$ mV, correlation coefficient $r = 0.998$, standard deviation $s_{yx} = 3.49$.

Substituent	$\Delta E_{1/2}$, mV	σ (ref. ¹⁰)
<i>m</i> -NO ₂	117	0.710
<i>m</i> -Br	69	0.391
<i>m</i> -Cl	51	0.373
<i>p</i> -Cl	45	0.238
H	0	0.000
<i>p</i> -CH ₃	-24	-0.129

silyl groups studied were calculated from the values of $\Delta E_{1/2}$ of corresponding silylsubstituted benzoic acids (Table V) using the calculated constants of the regression line (the values of the slope and $E_{1/2}^0$, see Table IV), *i.e.* in the same way as in the determination of σ constants from the rate constants k_2 . The obtained σ constants together with the corresponding limit of their confidence intervals are presented in Table V.

The results of NMR measurements are summarized in Table VI. In contradistinction to other methods employed in this work no statistical treatment of the NMR data was performed. The σ constants were read off from the plots given by Kondo and coworkers¹, who used slightly different values of σ constants for a few of the standard substituents. These differences could not affect the obtained value of σ constants and therefore were neglected. The confidence interval given for the σ constants in Table VI represents rather pessimistic estimate of non-systematic errors. However, since this method is extremely sensitive to the traces of water, any small amount of it in a sample would shift the final σ constant to lower values. For this reason several samples were prepared for each of the compounds and the highest of thus obtained values of the σ constants is reported.

The values of the chemical shift of *para*- and *meta*-trimethylsilylbenzoic acids call for a comment. In a paper published recently by Fenton and Zuckerman¹² the COOH shifts were presented for these acids. Unfortunately, of the acids studied by the last mentioned authors only benzoic and *para*-trimethylsilylbenzoic acids were measured at concentrations (0.5M) comparable to the concentration employed here as required by the method of Kondo and coworkers¹. The shifts they gave¹² are much smaller than those observed by us and Kondo¹, the signals being shifted to a higher magnetic field. With increasing concentration (to 2M) the signals shifted to

TABLE V
Values of $\Delta E_{1/2}$ for Silylsubstituted Benzoic Acids and Calculated σ Constants

Substituent	$\Delta E_{1/2}$, mV	σ
<i>m</i> -(CH ₃) ₃ Si	- 3	-0.020 ± 0.047
<i>m</i> -[(CH ₃) ₃ SiO](CH ₃) ₂ Si	- 4	-0.026 ± 0.048
<i>m</i> -[(CH ₃) ₃ SiO] ₂ CH ₃ Si	- 8	-0.050 ± 0.049
<i>m</i> -[(CH ₃) ₃ SiO] ₃ Si	-10	-0.061 ± 0.049
<i>p</i> -(CH ₃) ₃ Si	- 6	-0.038 ± 0.048
<i>p</i> -[(CH ₃) ₃ SiO](CH ₃) ₂ Si	- 3	-0.020 ± 0.047
<i>p</i> -[(CH ₃) ₃ SiO] ₂ CH ₃ Si	- 4	0.021 ± 0.046
<i>p</i> -[(CH ₃) ₃ SiO] ₃ Si	6	0.034 ± 0.045
<i>p</i> -(CH ₃) ₃ SiOCH ₂	-13	-0.079 ± 0.050

a lower field but even then their signals reported for 2M concentrations of *para*- and *meta*-trimethylsilylbenzoic acids are shifted considerably to higher fields as compared to our results. Moreover, the discussion in the paper of Fenton and Zuckerman¹² stresses on the order of the chemical shifts in *meta*- and *para*-derivatives which is opposite to the order observed for these shifts in the present study. Our values of σ constants of trimethylsilyl groups agree with the prediction of Fenton and Zuckerman¹² that they should be negative but they are not greater in magnitude than those for the tert-butyl group as these authors suggested.

If one compares the values of σ constants obtained by the three methods employed one can conclude that there is no statistical dependence of the σ constants for the silyl groups on the nature of the reaction center, the type of the reaction and the chosen solvent, as well on the method chosen. It should be stressed, however, that due to limited set of the data such effects cannot be quite generally excluded.

The use of the above reaction systems for the determination of σ constants was in the case of some silyl groups accompanied with difficulties that arose from the reactions of the groups with reagent or reaction medium. As an example the reaction of methylfluorosilylsubstituted benzoic acids with diphenyldiazomethane proceeds not only on the carboxylic group but also on the silyl group. The latter side reaction readily takes place with difluoro- and especially trifluorosilyl groups. So for instance phenyltrifluorosilane reacts with diphenyldiazomethane in all the solvents used here, methylphenyldifluorosilane undergoes this reaction in toluene and dioxane¹³. The rate of these reactions is comparable with that of the esterification. We first assumed that this side reaction consists of the insertion of diphenyldiazomethane into the silicon-

TABLE VI

σ Constants and Chemical Shifts of Carboxylic Protons in p -[(CH₃)₃SiO]_n(CH₃)_{3-n}SiC₆H₄.COOH

Position	n	Chemical shift ^a	σ^b
<i>para</i>	0	14.513	-0.06
	1	14.536	-0.05
	2	14.575	-0.03
	3	14.638	0.02
<i>meta</i>	0	14.623	-0.02
	1	14.538	-0.05
	2	14.539	-0.06
	3	14.513	-0.09

^a The values are in p.p.m. downfield relative to the line of cyclohexane, they are precise within ± 0.002 p.p.m. ^b The values should be considered as precise within ± 0.03 .

fluorine bond, analogously as the reaction of the silicon–chlorine bond¹⁴. However, this assumption did not turn out to be justified. Svoboda¹⁵ found that the reaction of diphenyldiazomethane with phenylfluorosilanes proceeds as the first order reaction in diphenyldiazomethane and yields polyphenylmethylene as the only reaction product. The decomposition of the diazo-compound is catalyzed by hydrogen fluoride. The reaction of silicon tetrafluoride with diazomethane was reported to proceed in the similar way, yielding polymethylene¹⁶.

Therefore, the method used for determination of the reactivity of methylfluorosilylbenzoic acids towards diphenyldiazomethane does not make it possible either to differentiate kinetically between both the reactions, or to determine their relative rates. For this reason Table III presents the values of σ constant for dimethylfluorosilyl group, which was found not to react with diphenyldiazomethane, the values for difluoromethylsilyl group are only estimates.

Similarly, the potentiometric titration of methylfluorosilylbenzoic acids yields anomalous titration curves with indistinct potential jumps, and the consumption of the titrating agent in the end point of the titration is higher than that calculated under assumption that only the carboxylic group is titrated. This shows that a partial hydrolysis of the silicon–fluorine bonds, catalyzed by a strong base (titrating agent), takes place during the titration. This finding precluded to employ the potentiometric titration in the determination of σ constants of the methylfluorosilyl groups.

Let us proceed to the discussion of the relation between σ constants and structure of silyl groups. As it was mentioned earlier, we have not found any statistically significant dependence of the calculated σ constants for the silyl groups studied on reaction medium, the type of reaction or on the sort of reaction center. In Table VII are therefore given the average values of the σ constants obtained by the three methods employed.

TABLE VII
Average Values of σ Constants for Some Silyl Groups

Substituent	σ_m	R^a	σ_p	R^a
$(\text{CH}_3)_3\text{Si}$	0.00	0.04	-0.03	0.05
$[(\text{CH}_3)_3\text{SiO}](\text{CH}_3)_2\text{Si}$	-0.01	0.03	0.00 ^b	0.03
$[(\text{CH}_3)_3\text{SiO}]_2\text{CH}_3\text{Si}$	-0.03	0.02	0.01	0.04
$[(\text{CH}_3)_3\text{SiO}]_3\text{Si}$	-0.06	0.05	0.02	0.05
$(\text{CH}_3)_2\text{FSi}$	0.12	0.05	0.16	0.03

^a The interval of the σ values determined by individual methods. ^b For *p*- $(\text{CH}_3)_3\text{SiOCH}_2$ calculated $\sigma_p = -0.054$ ($R = 0.05$).

The first question we should like to deal with is that of the nature of an interaction between silicon and the π -system of the benzene ring. The inductive effect of a substituent (I) can be – in terms of the extrathermodynamic correlations used – expressed by the constant σ_1 . The difference $\sigma - \sigma_1$ is a measure of the contribution of mesomeric interaction taking place between the substituent and the aromatic ring (M) to the overall polar effect of the substituent. If we compare the values of σ_1 constants for trimethylsilyl group¹⁷ (-0.13) and (trimethylsiloxy)dimethylsilyl group¹⁷ (-0.13) with the values of σ constants determined for these groups by us we obtain for trimethylsilyl group $\sigma_m - \sigma_1 = 0.13$ and $\sigma_p - \sigma_1 = 0.10$, and for trimethylsiloxydimethylsilyl group $\sigma_p - \sigma_1 = 0.13$. It should be mentioned that the use of σ_1 constants, derived originally for aliphatic compounds, in expressing the inductive effects of substituents attached to the aromatic ring is fully justified^{18,19}. It can be thus said that the above differences convincingly speak for +M effect of these two silyl groups. The same conclusion can be arrived at also by comparing the σ constant of trimethylsilyl group with that of tert-butyl group ($\sigma_m = -0.067$, $\sigma_p = -0.136$). Assuming that only the inductive effect of trimethylsilyl group is operating, the value of σ constants for the silyl group should be equal to or higher than the value for tert-butyl group. However, this is not the case.

The value of σ_p constant for trimethylsiloxyethyl group (-0.054) deserves comment, too. On the basis of the known higher acidity of silanols^{20,21} relative to alcohols, and lower basicity of siloxanes²², compared to ethers, one may expect that the σ constant for trimethylsiloxyethyl group will be comparable with or more positive than the corresponding constant for methoxyethyl group ($\sigma_p = 0.03$; ref.³). The value of σ constant of trimethylsiloxyethyl group found in this work (-0.054) seems to indicate that in this group the trimethylsilyl substituent affects the oxygen predominantly by its inductive effect.

The dependence of σ constants on substitution for individual types of the silyl substituents studied is also of interest. In the case of the m -trimethylsiloxyethylsilyl groups of the type $[(CH_3)_3SiO]_n(CH_3)_{3-n}Si-$ ($n = 0-3$) this dependence is surprising. Assuming that only polar effects of substituents are operative, this dependence would mean that the introduction of the electronegative substituent increases the electropositivity of the group. However, such a conclusion is evidently wrong. We believe that in this case fundamental condition for successful application of the Hammett relation (the rigidity of molecule which ensures that substituent affects the rest of molecule only by its polar effects²³ is not met due to the bulkiness of trimethylsiloxyethylsilyl groups).

In the case of the p -trimethylsiloxyethylsilyl groups a successive replacement of the methyl groups with the trimethylsiloxy ones has no measurable effect on the value of σ constant, presumably as the result of the small inductive effect of the trimethylsiloxy group. The value of σ constant for the trimethylsiloxyethyl group indicates that the substitution of one hydrogen atom in the methyl group for the

trimethylsiloxy group brings about the change in the value of σ constant of about 0.08. In the case of trimethylsilyloxydimethylsilyl group this change is substantially less, presumably as the result of a ($p \rightarrow d$) π interaction between the substituent (trimethylsiloxy group) and the central silicon atom.

In contrast, the change in the σ constant brought about by the substitution of one methyl substituent in the trimethylsilyl group for the fluorine atom is comparable with that calculated for carbon analogues ($\Delta\sigma_m = 0.17$; $\Delta\sigma_p = 0.25$ (ref.^{23,24})). The difference for carbon analogues was calculated because of the lack of the corresponding value for the 1-fluoro-1-methylethyl group. In the calculation it was assumed that σ constants of the carbon analogues are linearly dependent on the substitution number n . From the value of σ constant for the dimethylfluorosilyl group one could be inclined to conclude that the inductive effect of fluorine atom plays a predominant role in the silicon-fluorine bond. However, for such an interpretation to be made, further experimental data are necessary.

A partial financial support from National Science Foundation (Grant GP 2723) is gratefully appreciated.

REFERENCES

1. Kondo Y., Kondo K., Takemoto T., Ikenone T.: *Chem. Pharm. Bull. (Tokyo)* **14**, 1322 (1966).
2. Roberts J. D., McElhill E. L., Armstrong R.: *J. Am. Chem. Soc.* **71**, 2923 (1949).
3. Exner O., Jonáš J.: *This Journal* **27**, 2296 (1962).
4. Case F. H.: *J. Am. Chem. Soc.* **47**, 1143 (1925).
5. Talvik A., Zuman P., Exner O.: *This Journal* **29**, 1266 (1964).
6. Miller J. B.: *J. Org. Chem.* **24**, 560 (1959).
7. Weissberger A., Proskauer E. S., Riddick J. A., Toops E. E.: *Techniques of Organic Chemistry*, Vol. VII. Interscience, New York 1955.
8. Hetflejš J., Mareš F., Chvalovský V.: *This Journal* **30**, 1643 (1965).
9. van Bekkum H., Verkade P. E., Wepster B. M.: *Rec. Trav. Chim.* **78**, 815 (1959).
10. Buckley A., Chapman N. B., Dack M. R. J., Shorter J., Wall A. M.: *J. Chem. Soc. (B)* **1968**, 631.
11. Hancock C. K., Foldway E.: *J. Org. Chem.* **30**, 1180 (1965).
12. Fenton D. E., Zuckerman J. J.: *Inorg. Chem.* **7**, 1323 (1968).
13. Bílek Z., Mareš F.: Unpublished results.
14. Seyferth D.: *Chem. Rev.* **55**, 1155 (1955).
15. Svoboda L., Hetflejš J.: Unpublished results.
16. Jakubovič A. J., Ginsberg V. A.: *Ž. Obšč. Chim.* **22**, 1783 (1952).
17. Charlton M.: *J. Org. Chem.* **29**, 1222 (1964).
18. Ritchie C. D., Sager W. F. in the book: *Progress in Physical Organic Chemistry* (S. G. Cohen, Ed.) Vol. 2, p. 339. Wiley, New York 1964.
19. Exner O.: *This Journal* **31**, 65 (1966).
20. Wells P. R.: *Chem. Rev.* **63**, 171 (1963).
21. Eaborn C.: *Organosilicon Compounds*, p. 94. Butterworths, London 1960.
22. West R., Baney R. H.: *J. Inorg. Nucl. Chem.* **7**, 297 (1958).
23. Exner O.: *Chem. listy* **53**, 1302 (1959).
24. Palm V. A.: *Uspechi Chim.* **30**, 1070 (1961).

Translated by the author (J. H.).