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# The Use of Taft Relations for the Correlation of the Properties of Organosilicon Compounds. The Role of Substituent Effects

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Data for the correlations between the properties of organosilicon compounds on the basis of Taft equations are surveyed for the first time. The results for 140 relations involving reactivities, capacities for complex formation, and spectroscopic characteristics are examined. The specific features of the influence of individual effects of substituents at the silicon atom and the ability of the silicon atom and silicon-containing groups to transmit effects are discussed.
The bibliography includes 149 references.

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## I. INTRODUCTION

The only common and practically feasible approach to a quantitative description of the relations between the properties of organic compounds and their structure available at present is the Hammett–Taft theory. The fundamental postulate of the theory, based on the thermodynamic principle of linear free energy relations (LFE), presupposes that, to a first approximation, the influence of individual effects of substituents (inductive, resonance, etc.) on the given property of the molecule is additive[1–3].

Since the LFE principle is general, analogous relations are observed also for compounds where the indicator centre does not consist of carbon but of other elements. Among these, organic derivatives of phosphorus and silicon have been most widely investigated. An extremely significant feature of the electronic structures of these (and other) elements of the Third Period, responsible for their difference from carbon, is the possibility of $p_\pi$–$d_\pi$ interaction via the $d$ orbitals energetically available for combining with other reactants, which have an excess $p$- or $\pi$-electron density†. Quantum-chemical calculations on the $p_\pi$–$d_\pi$ interaction predicted its intensification with increase of the positive charge of the atom of the Third Period on $\sigma$-bonding to electronegative substituents[6]. A pronounced pair interaction between the inductive and resonance effects of the substituents was therefore to be expected in this instance. Nevertheless, in organic derivatives of phosphorus, for which experimental data concerning relations of the Hammett–Taft type have already been reliably surveyed, systematic deviations from the additivity have not been observed[7].

In this review the first attempt is made to survey the available literature data concerning the application of various modifications of the Taft equation to aliphatic organosilicon compounds. As regards the structure-property correlations for aryl derivatives of silicon, we shall only mention that the Hammett equation in its traditional form is applicable to almost all cases.

†It is noteworthy that the $p_\pi$–$d_\pi$ interaction constitutes the most widely accepted hypothesis used to account for a number of anomalies in the properties of elements with vacant $d$ orbitals. Other views have also been described[4,5].

## II. EXPERIMENTAL RESULTS

The available data on the structure–property correlations for organosilicon compounds are presented in Tables 1–3. The following numbering of the equations has been adopted:

$$A_i = A_0 + \rho^* \sum \sigma_i^*; \quad (1)$$

$$A_i = A_0 + \rho^* \sum \sigma_i^* + \delta \sum E_{s_i} \quad (2)$$

where $A_i$ are numerical characteristics of the given property, $\sigma_i^*$ are the Taft constants of the substituents, $E_{s_i}$ are the steric constants of the substituents, and $\rho^*$ and $\delta$ are the corresponding slopes.

The deviations from these equations are noted separately. The following notation is used in Tables 1–3: $r$ and $R$ are the coefficients of pair and multiple correlation respectively, $n$ is the number of compounds the values of $A_i$ for which were used in the correlation (the number of points), and $s$ is the standard error of the correlation. It is also indicated which particular steric constants ($E_S$, $E_S^C$, and $E_S^0$) or non-Taft inductive constants [$\sigma_i$ and $\sigma$(Si)] of the substituents were used in the original studies. In those cases where an independent and non-contradictory interpretation of the results exists for similar reaction series based on the same property, Tables 1–3 list only the data based on more extensive experimental results (the corresponding literature references are underlined). Certain relations (designated by an asterisk opposite the reference) were found by ourselves from literature data either for the first time or from an equation other than that given in the original communication.

Apart from the reports listed in Tables 1–3, there have been a number of publications in which the dependence of the given property on the constants of the substituents at the silicon atom was illustrated only in graphical terms. The relations between the logarithms of the rate constants and the Taft constants for the acid solvolysis of dimethylorganylsilanes[93], the cleavage of the Si–O bond in $Me_3SiOR$

**Table 1. Correlations of reactivities.**

| No. | Reaction | Quantity correlated | No. of Eqn. | $A_0$ | $\rho^*$ | $\delta$ | r(R) | n | Remarks | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $R_3SiH + H_2O \xrightarrow{EtOH,\ HCl,\ 35°} R_3SiOH + H_2$ | $\lg k$ | (1) | −2.72 | 0.77 | — | 0.96 | 14 | $s$ = 0.09, R = n-alkyl and substituted alkyl | 8 |
| 2 | ditto | $\lg k + 3$ | (2) ($E_s^c$) | 0.51 | 0.0 | 0.32 | 0.99 | 7 | R = n-alkyl, isoalkyl, or substituted alkyl | 9 |
| 3 | $R_3SiH_3 + 2H_2O \xrightarrow{EtOH,\ HCl,\ 35°} R_3Si(OH)_3 + 2H_2$ | $\lg k_1$ | (1) | −1.77 | 0.77 | — | 0.97 | 4 | $s$ = 0.06; R = H, n-alkyl, or substituted alkyl | 8 |
| 4 | $R_3SiH + H_2O \xrightarrow{EtOH,\ KOH,\ 0°} R_3SiOH + H_2$ | $\lg k_{rel}$ | (1) | — | 4.42 | — | 0.99 | 14 | R = n-alkyl or substituted alkyl but not $Ph(CH_2)_n$ | 10 |
| 5 | ditto | $\lg k_{rel}$ | (2) ($E_s^c$) | — | 1.74 | 0.39 | 0.96 | 11 | R = n-alkyl or $Ph(CH_2)_n$ ($n$ = 1,2, or 3) | 9 |
| 6 | $RSiH_3 + 3MeOH \xrightarrow[k_1,\ k_2,\ k_3]{DMF,\ KOH,\ 20°} RSi(OMe)_3 + 3H_2$ | $\lg k_1$ | (1) | −0.93 | 1.76 | — | 0.96 | 6 | R = n-alkyl, isoalkyl, substituted alkyl, or Ph | 11 |
| 7 | ditto | $\lg k_2$ | (1) | −0.21 | 1.40 | — | 0.92 | 4 | R = n-alkyl, isoalkyl, or substituted alkyl | 11 |
| 8 | » | $\lg k_3$ | (1) | −0.94 | 1.76 | — | 0.98 | 5 | R = n-alkyl, substituted alkyl, or Ph | 11 |
| 9 | $R_3SiH + O_3 \xrightarrow[-O_2]{CCl_4,\ 20°} R_3SiOH$ | $\lg k$ | (1) | 1.7 | −0.70 | — | 0.99 | 6 | R = n-alkyl or benzyl | 12, 13 |
| 10 | $R_3SiH + Br_2 \xrightarrow[-HBr]{CCl_4,\ 20°} R_3SiBr$ | $\lg k$ | (1) | 4.5 | −2.38 | — | 0.99 | 5 | $s$ = 0.22; R = n-alkyl or substituted alkyl | 14*, 15 |
| 11 | $R_3SiH + Cl_2 \xrightarrow[-HCl]{CCl_4,\ 80°,\ h\nu} R_3SiCl$ | $\lg k_{rel}$ | (1) | — | −0.11 | — | 0.99 | 5 | R = Me, Et, Ph, or Cl | 16, 17 |
| 12 | $Me_2RSiH + N_2CHCO_2Et \xrightarrow[-N_2]{90°,\ Cu} Me_2RSiCH_2CO_2Et$ | $\lg k$ | (2) ($E_s^0$) | −0.14 | −1.25 | 0.11 | 0.99 | 6 | R = n-alkyl or isoalkyl | 18 |
| 13 | $R_3SiH + Me_2SiCOPh \xrightarrow{20°} R_3SiCH(Ph)OSiMe_3$ | $\lg k_{rel}$ | (2) ($E_s$) | — | 2.13 | 0.87 | 0.99 | 4 | R = H, Ph, $PhCH_2$, or cyclo-$C_6H_{11}$ | 19 |
| 14 | $R_3SiH + CH{\equiv}CC_4H_9 \xrightarrow[-H_2PtCl_6,\ 20°]{THF,} R_3SiC_6H_{11}$ | $\lg k_{rel}$ | (2) ($E_s^0$) | 0.39 | 0.0 | 0.41 | 0.94 | 5 | $s$ = 0.12; R = n-alkyl or isoalkyl | 20 |
| 15 | $2Me_2RSiH + MeP(O)(OH)_2 \xrightarrow[-2H_2]{C_5H_5N,\ 65°} MeP(O)(OSiRMe_2)_2$ | $\lg k$ | * | −1.73 | 5.49 | 0.27 | 0.99 | 8 | $h$ = 0.27, $s$ = 0.02; R = n-alkyl or isoalkyl | 21 |
| 16 | $RSi(OCH_2CH_2)_3N$, hydrolysis (20°) | $\lg k$ | (1) | −1.54 | 4.76 | — | — | 5 | R = H, Vin, n-alkyl, or isoalkyl | 22 |
| 17 | $ROSi(OCH_2CH_2)_3N$, hydrolysis (20°) | $\lg k$ | (1) | −4.81 | 2.60 | — | — | 5 | R = n-alkyl or isoalkyl | 22 |
| 18 | ditto (HCl, 25°) | $\lg k$ | (1) | ** | −1.26 | — | 0.99 | 4 | $s$ = 0.005; R = n-alkyl or isoalkyl | 23 |
| 19 | $Me_3SiOR + MeOH \xrightarrow[-ROH]{EtNH_2,\ 20°} Me_3SiOMe$ | $\lg k_{rel}$ | (2) ($E_s$) | −0.07 | 4.64 | 0.62 | 0.96 | 7 | R = n-alkyl, isoalkyl, or substituted alkyl | 24 |
| 20 | $Me_3SiOCOR + HOCH_2Ph \xrightleftharpoons{CCl_4,\ 20°} Me_3SiOCH_2Ph + RCOOH$ | $\lg K$ | (1) | ** | −0.57 | — | 0.99 | 13 | R = n-alkyl, isoalkyl, substituted alkyl, or Ph | 25 |
| 21 | $n\,(MeRSiO)_3 \xrightarrow[(polymerisation)]{100°,\ NaOH} (MeRSiO)_{3n}$ | $\lg k_{rel}$ | (1) | — | 0.21 | — | 0.99 | 4 | R = Ph or substituted aryl | 26 |
| 22 | $(Me_2SiO)_3MeRSiO \xrightarrow[polymerisation]{KOH,DMSO,\ 50°}$ | $\lg k_{rel}$ | (1) | — | 0.43 | — | 0.93 | 5 | R = n-alkyl, Vin, Ph, or chlorophenyl | 27, 28, 29 |
| 23 | $MeRSi(CH_2CH_2)O(CH_2CH_2)SiRMe \xrightarrow[]{120°,\ KOH}$ polymerisation | $\lg k_{rel}$ | (1) | — | 0.06 | — | — | 4 | R = n-alkyl | 30 |
| 24 | $(R_3SiO)_3 + Bu_4NOH \xrightarrow{pyridine\ 25°} HO(R_3SiO)_3NBu_4$ | $E^{0,5}$, eV | (1) | −1.0 | 0.1 | — | — | 7 | R = Me, substituted alkyl, Ph, or Vin | 31 |
| 25 | $2R_3Si(OH)_2 \xrightarrow{MeOH,\ Et_3N,\ 25°} HO(R_2)SiOSi(R_2)OH + H_2O$ | $\lg k_{rel}$ | (1) | — | 4.7 | — | — | 4 | R = Me, substituted alkyl, Ph, or Vin | 32 |
| 26 | ditto (MeOH, HCl, 25°) | $\lg k_{rel}$ | (2) ($E_s^c$) | — | −0.32 | 1.02 | 0.93 | 7 | $s$ = 0.20; R = n-alkyl or substituted alkyl | 33* |
| 27 | $R_3SiCl + H_2O \xrightarrow[-HCl]{acetone,\ -45°} R_3SiOH$ | $\lg k$ | (2) ($E_s^c$) | *** | 0.62 | 0.61 | 0.99 | 5 | $s$ = 0.12; R = n-alkyl or substituted alkyl | 34 |
| 28 | $R_3SiCl + HO(Me_2)SiCB_{10}H_{10}CH + Et_3N \rightarrow R_3SiO(Me_2)SiCB_{10}H_{10}CH$ | $\lg k$ | (2) ($E_s^c$) | ** | 1.91 | 1.35 | — | 5 | R = H, n-alkyl, or substituted alkyl | 35 |
| 29 | $R_3SiCl + Me_3NSiMe_3 \xrightleftharpoons{CCl_4,\ 37°} R_3SiNMe_2 + ClSiMe_3$ | $\lg K_{rel}$ | (1) | — | 0.89 | — | 0.99 | 12 | R = n-alkyl, isoalkyl, substituted alkyl, Ph, or Vin | 36 |
| 30 | $R_3SiCl + Me_3SiOEt \xrightleftharpoons[hexamethylphosphoramide]{toluene,\ 20°} R_3SiOEt + Me_3SiCl$ | $\lg K_{rel}$ | (2) ($E_s^0$) | — | 1.02 | 0.82 | 0.98 | 6 | $s$ = 0.03; R = n-alkyl or substituted alkyl | 37 |
| 31 | $R_3SiF + MeO^- \xrightarrow{MeOH,\ 20°,\ MeONa} R_3SiOMe + F^-$ | $\lg k_{rel}$ | (1) | — | 1.44 | — | 0.99 | 5 | $s$ = 0.07; R = n-alkyl, Ph, or benzyl | 38 |
| 32 | $R_3SiF + Et_4NOH \xrightarrow{pyridine,\ 25°} R_3SiOH + Et_4NF$ | $(E_i^{0,5} - E_0^{0,5})$/ /0.059 eV | (1) | — | 1.61 | — | 0.99 | 5 | R = n-alkyl, benzyl, Ph, or Vin | 39 |
| 33 | $R_3SiNHMe + H_2SiPh_2 \xrightarrow[-H_2]{anisole} R_3SiN(Me)SiPh_2H$ | $\lg k$ | (1) | ** | 2.46 | — | 0.98 | 9 | R = n-alkyl, isoalkyl, substituted alkyl, or Vin | 40 |
| 34 | $R_3SiCB_{10}H_{10}CH + BuOH \xrightarrow[Me_2SiONa,\ 30°]{Bu_2O,\ KOH,\ 60°} R_3SiOBu + HCB_{10}H_{10}CH$ | $\lg k$ | (1) | ** | 0.92 | — | 0.93 | 6 | R = n-alkyl, substituted alkyl, or alkoxy-group | 41 |
| 35 | $R_3SiCH{=}CH_2 + AcSH \xrightarrow{ethylbenzene\ 40°} R_3SiCH_2CH_2SAc$ | $\lg k_{rel}$ | (1) | — | −0.5 | — | — | 7 | R = Me or substituted alkyl | 42 |
| 36 | $R_3Si(CH_2)_nSCH{=}CH_2$, hydrolysis (DMF, 20°) | $\lg k$ | (1) | −3.89 | −2.72 | — | 0.99 | 5 | $s$ = 0.03; R = Me or Et, $n$ = 1,2, or 3 | 43 |

*The equation $\lg k_i = \lg k_0 + \rho^*\sigma^* + \delta E_S^0 + \Delta n_H h$ was used here.
**Data not quoted in the original communication.

**Table 2.** Correlations of capacities for complex formation in terms of Eqn.(1).

| No. | Complex | Method of investigation | Quantity correlated | $A_0$ | $\rho^*$ | $r$(R) | $n$ | Remarks | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Phenol + $R_2O$ (ether) | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 263 | —90 | 0.98 | 9 | — | 44 |
| 2 | Phenol + $R_3SiOEt$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 275 | —61.3 | 0.98 | 12 | $s=6$ | 45 |
| 3 | Phenol + $(R_3Si)_2O$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 162 | —43 | 0.95 | 22 | $s=11$ | 45 |
| 4 | Phenol + $RSi(OEt)_3$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 237 | —25 | 0.99 | 5 | — | 46 |
| 5 | Phenol + $RSi(OMe)_3$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 226 | —32 | 0.96 | 6 | — | 46 |
| 6 | Phenol + $R_nSi(OCH_2C\equiv CH)_{4-n}$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 234 | —14.5 | 0.97 | 6 | $s=10$ | 47 |
| 7 | Phenol + $ROSi(Me_2)C\equiv CH$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 228 | —76 | 0.95 | 7 | $s=6.5$ | 48 |
| 8 | Phenol + $R(Me_2)SiOR'$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 272 | —47 | 0.97 | 11 | $s=5$ | 49 |
| 9 | Phenol + $Me_3SiOR$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 275 | —73 | — | 16 | *; $\rho_i^*=-75$ | 50 |
| 10 | Phenol + $Me_2SiOR$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 263 | —82 | 0.94 | 14 | $s=12$ | 50*, 51 |
| 11 | Phenol + $Me_2ClSiOR$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | ** | —88 | — | 7 | — | 51 |
| 12 | Phenol + $MeCl_2SiOR$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | ** | —39.5 | — | 7 | — | 51 |
| 13 | Phenol + $R_3SiOOSiPh_3$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 190 | —19 | 0.93 | 11 | $s=5$ | 52* |
| 14 | Phenol + $R_3SiOCMe_3$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 198 | —41 | — | 6 | — | 53 |
| 15 | Phenol + $R_3SiOOGePh_3$ | i.r.s. | $\Delta\nu$(OH) for phenol, $cm^{-1}$ | 219 | —33 | 0.89 | 7 | $s=3$ | 52* |
| 16 | $RSi(OEt)_3 \cdot SnCl_4$ | calorimetry | $q$, kcal $mol^{-1}$ | 7.85 | —1.03 | 0.95 | 4 | $q$ = heat of complex formation | 54 |
| 17 | $R_2Si(CH_2)_3$ + tetracyanoethylene (TCE) | u.v.s. | $E_{CT}$, eV | 3.56 | 2.38 | 0.99 | 8 | $s=0.015$; $E_{CT}$ = energy of first charge-transfer bands | 55 |
| 18 | Ditto | u.v.s. | $I$, eV | 9.33 | 2.77 | 0.99 | 8 | $s=0.02$; $I$ = ionisation potental of donor | 55 |
| 19 | $RSCH_2Si(OCH_2CH_2)_3N$ + TCE | u.v.s. | $I$, eV | 8.26 | 1.66 | 0.99 | 6 | | 56 |
| 20 | $R_3SiCH_2NMe_2$ | potentiometry | $pK_a$ | 9.12 | —1.76 | 0.98 | 7 | — | 56 |
| 21 | $R_3SiCH_2NEt_2$ | potentiometry | $pK_a$ | 8.60 | —1.95 | 0.99 | 6 | — | 57 |
| 22 | $R_3SiOH$ + DMSO | $^1$H NMR | $\Delta\delta$(HO) **** | 307.4 | 65.0 | 0.99 | 6 | $s=6$ | 58* |
| 23 | $R_3COH$ + DMSO | $^1$H NMR | $\Delta\delta$(HO) | 242.1 | 73.1 | 0.96 | 7 | $s=15$ | 58 |
| 24 | $Me_3SiOR + HCCl_3$ | $^1$H NMR | $\Delta\delta$(H) ***** | 0.35 | —0.41 | — | 8 | $\delta=0.26$ *** | 59 |

*The equation $\Delta\nu_i = \Delta\nu_0 + \rho^* \sum \sigma_i^* + \rho_1^* + (\sum \sigma_i^*)^2$ was used.

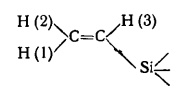
**Data not quoted in the original communication.

***Eqn.(2) was used.

****Relative to trimethylsilane; the values of $\Delta\delta$ are expressed in Hz.

*****Relative to $Me_2O$.

with the aid of butyl-lithium[94], the solvolysis of bis(trialkylsilyl) sulphides[95], the thermal decomposition of triorganyl(t-butylperoxy)silanes[96], the anionic polymerisation of cyclotetrasiloxanes $(Me_2SiO)_n[Me(CF_3CH_2CH_2)SiO]_{4-n}$, where $n = 0-3$ [97], and the dependence on the Taft constants of the constants for chain transfer by triorganylsilanes in the radical polymerisation of olefins[98], of the relative acidities of alkyl(triorganylsilyl)amines and hexaorganyldisilazanes calculated from the values of $\Delta\nu$(NH) in the infrared spectra of mixtures of the above compounds with a ligand [tetrahydrofuran (THF) and dioxan] [99], of the relative basicities of methyl(triorganylsilyl)amines determined by $^1$H NMR from the change in the chemical shift $\Delta\delta$ of the proton in chloroform in equilibrium with a mixture of the above compounds[100], of the stretching vibration frequencies of the Si–Ci bond in the infrared spectra of triorganylchlorosilanes[101], of the stretching vibration frequencies $\Delta\nu$(OH) and the corresponding values of $A^{0.5}$ in the infrared spectra of triorganylsilanols[102], of the chemical shifts $\tau(H_3-CSi)$ [but not $\tau$(H–Si)] of methyldiorganylsilanes MeRR'SiH, of the shifts $\tau(-CH_2)$ [but not $\tau(-CH_3)$] of the protons in the ethyl groups of the compounds EtRR'SiH [103], EtRR'SiVin [104] [here and subsequently Vin stands for vinyl – $CH=CH_2$ (Ed.of Translation)], and $Et_nSiX_{4-n}$ (X = halogen) [105], of the chemical shifts of the H(1) protons [but not H(3)] of the vinyl group




in the $^1$H NMR spectra of all the compounds $R_3SiVin$ [104], of the frequencies $\nu_m^{77}$ ($^{35}$Cl) in the NQR spectra of the compounds $Me_nSiCl_{4-n}$ ($n=1-4$), $(EtO)_{4-n}SiCl_n$ ($n=1-4$), and $(MeO)_{4-n}SiCl_n$ ($n=1-3$) [106], and of the dipole moments of vinylorganyldimethoxysilanes[107] were described in this way. There is a relation between the dipole moments of phenyltrialkoxysilanes ($r = 0.91$) and the $E_S^0$ of the alkyls in the alkoxy-groups but not the $\sigma^*$ of these substituents ($r = 0.55$).[108] The dependence of the logarithm of the rate constant for the addition of the trichloromethyl group in chlorobenzene to triorganylvinylsilanes $Me_2RSiVin$ ($R$ = n-, iso-, or t-alkyl) at 80 °C on the steric constants of the substituents $R$ has been demonstrated graphically[109].

We shall now consider the principal features of the influence of the substituents which are of general importance for the structure–property relations involving organosilicon compounds.

**Table 3.** Correlation of spectroscopic characteristics.

| No. | Compound | Quantity correlated | Eqn. | $A_0$ | $\rho^*$ | $r$(R) | $n$ | Remarks | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | From infrared spectra | | | | | |
| 1 | $R_3SiH$ | $\nu$(SiH), $cm^{-1}$ | (1) | 2106 | 17.5 | — | 22 | R = any substitutent | 60, 61 |
| 2 | Ditto | $\nu$(SiH), $cm^{-1}$ | (1) | 2115 | 31.5 | 0.94 | 43 | R = H, alkyl, or substituted alkyl; $s$ = 8.7 | 62, 63—65 |
| 3 | » | $\nu$(SiH), $cm^{-1}$ | * | 2141 | 24.4 | 0.99 | 43 | $a$ = −3.83; $s$ = 3.7; R = ditto | 62 |
| 4 | » | $\nu$(SiH), $cm^{-1}$ | ** | 2110 | 24.5 | 0.99 | 43 | $a$ = 11.0; $s$ = 2.7; R = ditto | 66 |
| 5 | $R_3SiOSi(Me_2)H$ | $\nu$(SiH), $cm^{-1}$ | (1) | 2117 | 8.1 | 0.91 | 9 | $s$ = 1.3; R = alkyl, substituted alkyl, or Ph | 67 |
| 6 | $XR_2SiH$, X=Cl | $\nu$(SiH), $cm^{-1}$ | (1) | 2089 | 25.8 | 0.95 | 8 | $s$ = 5; R = H, alkyl, or substituted alkyl | 68 |
| 7 | Ditto, X=Ph | $\nu$(SiH), $cm^{-1}$ | (1) | 2094 | 41 | 0.99 | 7 | $s$ = 2.2; R = ditto | 68 |
| 8 | Ditto, X=Vin | $\nu$(SiH), $cm^{-1}$ | (1) | 2091 | 46 | 0.99 | 5 | $s$ = 3.6; R = ditto | 68 |
| 9 | $X_2RSiH$, X=Cl | $\nu$(SiH), $cm^{-1}$ | (1) | 2053 | 26.5 | 0.94 | 6 | $s$ = 5.3; R = ditto | 68 |
| 10 | Ditto, X=Ph | $\nu$(SiH), $cm^{-1}$ | (1) | 2074 | 42 | 0.99 | 3 | R = ditto | 68 |
| 11 | $R_nX_{3-n}SiH$ ($n$=0, 1, 2), X=Cl | $\nu$(SiH), $cm^{-1}$ | (1) $\sigma$(Si) | 2118 | 26.9 | 0.99 | 16 | $s$ = 4.6; $\sigma$(Si) for Cl = 1.69; $\sigma$(Si) = $\sigma^*$ for "normal" substituents | 68 |
| 12 | $R_nX_{3-n}SiH$ ($n$=0, 1, 2), X=Ph | $\nu$(SiH), $cm^{-1}$ | (1) $\sigma$(Si) | 2115 | 41 | 0.99 | 12 | $s$ = 1.6; $\sigma$(Si) for Ph = 0.09 | 68 |
| 13 | ditto, X=Vin | $\nu$(SiH), $cm^{-1}$ | (1) $\sigma$(Si) | 2114 | 45.5 | 0.99 | 7 | $s$ = 2.8; $\sigma$(Si) for Vin = 0.15 | 68 |
| 14 | $R_3SiH$ | $10^{-4}A^{0.5}$($SiH_2$), litre $mol^{-1}$ $cm^{-2}$ | | 1.35 | −0.19 | 0.93 | 12 | R = alkyl or substituted alkyl; $A$ = integral intensity | 65, 69, 70—72, |
| 15 | $R_2SiH_2$ | $10^{-4}A^{0.5}$(SiH), litre $mol^{-1}$ $cm^{-2}$ | (1) | 1.72 | −0.12 | 0.92 | 7 | R = alkyl or substituted alkyl | 73 |
| 16 | $R_3SiPh$ | $\nu$(C-H) for phenyl, $cm^{-1}$ | (1) ($\sigma_1$) | 3071 | 5.57 | — | 12 | $s$ = 0.9; R = any substituent | 74 |
| 17 | $R_3SiF$ | $\nu$(Si-F), $cm^{-1}$ | (1) | 889 | 147 | 0.96 | 8 | R = alkyl or benzyl | 40, 75 |
| 18 | $HC{\equiv}C(Me)_2SiOR$ | $\Delta\nu$(SiOC), $cm^{-1}$ | (1) | 0.15 | 0.66 | 0.99 | 5 | R = alkyl | 76 |
| | | | | From NMR spectra | | | | | |
| 19 | $R_3SiH$ | $\tau$(H-Si), p.p.m. | (1) | 6.16 | −0.29 | 0.99 | 16 | R = H, alkyl, substituted alkyl, Cl, Ph, or $m$-$CF_3C_6H_4$ | 61 |
| 20 | Ditto | $J$ ($^{29}$SiH), Hz | (1) | −203.4 | 19.76 | 0.97 | 63 | $s$ = 11; R = any substituent | 77, 78 |
| 21 | Ditto | $J$ ($^{29}$SiH), Hz | *** | −181 | −12.9 | 0.98 | 63 | $\rho_1^*$ = −2.9; $s$ = 8.7; R = any substituent | 77 |
| 22 | $R_3SiOSi(Me_2)H$ | $J$ ($^{29}$SiH), Hz | (1) | −203.4 | −2.9 | 0.97 | 8 | $s$ = 0.24; R = alkyl or substituted alkyl | 67 |
| 23 | $R_nSiMe_{4-n}$ | $\tau$($CH_3$), p.p.m. | (1) | 10.0 | −0.14 | 0.94 | 26 | R = H, alkyl, substituted alkyl, or Cl | 61, 79, 80 |
| 24 | $R_nSiEt_{4-n}$ | $\tau$($CH_2$), p.p.m. | (1) | 9.38 | −0.085 | 0.96 | 6 | R = ditto | 80 |
| 25 | $R_3SiOEt$ | $\tau$($CH_3$ in OEt), p.p.m. | (1) | 8.87 | −0.077 | 0.92 | 6 | R = alkyl, substituted alkyl, or Ph | 81 |
| 26 | $R_2Si(OEt)_2$ | $\tau$($CH_3$ in OEt), p.p.m. | (1) | 8.88 | −0.039 | 0.99 | 10 | R = ditto | 81 |
| 27 | $RSi(OEt)_3$ | $\tau$($CH_3$ in OEt), p.p.m. | (1) | 8.92 | −0.038 | 0.99 | 9 | R = ditto | 81 |
| 28 | $R_3SiOEt$ | $\tau$($CH_2$ in OEt), p.p.m. | (1) | 6.41 | −0.138 | 0.99 | 6 | R = ditto | 81 |
| 29 | $R_2Si(OEt)_2$ | $\tau$($CH_2$ in OEt), p.p.m. | (1) | 6.42 | −0.104 | 0.99 | 10 | R = ditto | 81 |
| 30 | $RSi(OEt)_3$ | $\tau$($CH_2$ in OEt), p.p.m. | (1) | 6.53 | −0.101 | 0.99 | 9 | R = ditto | 81 |
| 31 | $RSi(OCH_2CH_2)_3N$ | $\tau$($H_2CO$), p.p.m. | (1) | 6.23 | −0.180 | 0.98 | 6 | R = H or alkyl | 82 |
| 32 | ditto | $\tau$($H_2C$), p.p.m. | (1) | 7.21 | −0.177 | 0.97 | 6 | R = ditto | 82 |
| 33 | $Me_3SiOR$ | $\delta$ ($^{29}$Si), p.p.m. | (1) | 14.88 | 8.11 | 0.98 | 20 | R = alkyl or substituted alkyl | 50 |
| 34 | ditto | $\delta$($^{29}$Si), p.p.m. | (1) | 14.87 | 5.21 | 0.98 | 11 | R = Ph or substituted aryl | 83 |
| 35 | $Me_3SiOCOR$ | $\delta$ ($^{29}$Si), p.p.m. | (1) | 15.14 | 4.73 | 0.99 | 10 | $s$ = 0.46; R = alkyl or substituted alkyl | 83 |
| 36 | $R_3Si^1OSi^2(Me_2)H$ | $\delta$ ($^{29}Si^2$), p.p.m. | (1) | −7.83 | 4.83 | 0.99 | 8 | $s$ = 0.28; R = ditto | 67 |
| 37 | $R(Me)SiO(Me_2SiO)_2$ | $\Delta\delta$ ($^{29}$Si), p.p.m. | (1) | — | 1.64 | 0.94 | 6 | $s$ = 0.25; R = ditto | 84 |
| 38 | $YCH_2Si(OCH_2CH_2)_3N$ | $\delta$ ($^{29}$Si), p.p.m. | (1) | −67.1 | −11.3 | 0.99 | 8 | $s$ = 0.77; Y = alkyl or substituted alkyl | 85 |
| 39 | $YCH_2Si(OEt)_3$ | $\delta$ ($^{29}$Si), p.p.m. | (1) | −45.3 | −11.3 | 0.99 | 8 | $s$ = 1.28; Y = ditto | 85 |
| 40 | $R_3SiF$ | $\tau$($^{19}$F), p.p.m. | (1) | 44.0 | −60 | 0.99 | 8 | R = alkyl | 75 |
| 41 | $R_2SiF_2$ | $\tau$($^{19}$F), p.p.m. | (1) | 63.4 | −60 | | | R = alkyl | 86 |
| 42 | $R_3SiNR_2'$ и $NH_3$ | $\tau$($^{14}$N), p.p.m. | (1) | 383.7 | −36.7 | 0.98 | 7 | R = alkyl or alkoxy-group; R' = H or $R_3Si$ | 87 |
| | | | | From NQR spectra | | | | | |
| 43 | $R_3SiCl$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 16.63 | 0.404 | 0.96 | 30 | $s$ = 0.11; R = H, alkyl, substituted alkyl, Ph, or Vin | 88, 89, 90 |
| 44 | $R_2SiCl_2$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 17.77 | 0.415 | 0.99 | 11 | $s$ = 0.08; R = ditto | 88, 89 |
| 45 | $RSiCl_3$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 18.91 | 0.484 | 0.96 | 12 | $s$ = 0.09; R = ditto | 88—90 |
| 46 | $R_3SiCH_2Cl$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 34.05 | 0.308 | 0.98 | 21 | $s$ = 0.18; R = any substituent | 91 |
| 47 | $R_3SiCHCl_2$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 35.28 | 0.279 | 0.99 | 5 | $s$ = 0.02; R = Me, Cl, or Ph | 91 |
| 48 | $R_3SiCCl_3$ | $\nu_m^{77}$($^{35}$Cl), MHz | (1) | 37.59 | 0.166 | 0.95 | 5 | $s$ = 0.21; R = Et, $PhCH_2$, Cl, OEt, or Ph | 91 |
| 49 | $R_3SiBr$ | $\nu_m$($^{81}$Br), MHz | (1) | 113.1 | 3.95 | — | 5 | $s$ = 0.81; R = alkyl, Ph, Cl, or Br | 92 |

The following equations have been used respectively:

*$\nu_i = \nu_0 + \rho^* \sum\sigma^* + a \sum(n_H + 0.4n_C)$;

**$\nu_i = \nu_0 + \rho^* \sum\sigma^* + aq$, where $q = 0$–3 is the number of silicon hydride bonds combined with the "indicator" Si–H bond;

***$J = J_0 + \rho^* \sum\sigma^* + \rho_1^*(\sigma_1^*\sigma_2^* + \sigma_2^*\sigma_3^* + \sigma_1^*\sigma_3^*)$.

## III. SPECIFIC FEATURES OF THE EFFECTS OF SUBSTITUENTS AT THE SILICON ATOM

### 1. The Inductive Effect

The vast majority of the relations presented in Tables 1–3 demonstrate the exclusive influence of the inductive effect of the substituents. In this respect organosilicon compounds exhibit a much greater similarity to normal organic compounds than to organic derivatives of phosphorus. Indeed, the inductive Taft $\sigma^*$ constants cannot be used for the $\rho,\sigma$ analysis of organophosphorus compounds owing to the considerable resonance influence of many substituted alkyl groups. As a result, whereas the Kabachnik constants $\sigma^f$ for unsubstituted alkyl groups are proportional to their $\sigma^*$ constants, for substituted alkyls (and substituents capable of $p_\pi$–$d_\pi$ conjugation with phosphorus), the constant $\sigma^f$ reflects both the inductive ($\sigma^f_I$) and resonance ($\sigma^r_R$) influence of the substituent:

$$\sigma^f = \sigma^f_I + \sigma^f_R .$$

The resonance effect of the substituted alkyls in organophosphorus compounds (and in derivatives of other elements having *d* orbitals available for bonding[110]) has been explained by an intramolecular interaction, for example, of the following type[7]:



Such bonding is possible, in principle, also in silicon compounds; nevertheless its manifestation is not typical in this instance, which has been confirmed by numerous relations involving only the Taft $\sigma^*$ constants for a wide variety of unsubstituted and substituted alkyl groups. The data for the "α-effect", which will be examined below, constitute an exception.

On the other hand, the relations for compounds with substituents capable of $p_\pi$–$d_\pi$ interaction deviate as a rule from the relations based on the $\sigma^*$ constants of other substituents (for further details, see below). At the same time, examples (Table 3, Nos.16, 20, and 21) of the dependence of certain properties solely on the inductive effect have been described in the literature for compounds with any substituents at the silicon atom. Relations Nos.20 and 21 have been most completely confirmed experimentally for the spin–spin coupling constants $J(^{29}SiH)$ for molecules of silicon hydrides on the basis of $^1H$ NMR data. These data are also consistent with theoretical ideas, according to which the extent of the short-range spin–spin interaction is determined mainly by the amount of *s* character of the corresponding bond[111]. The above relations are therefore suitable for the estimation of the inductive constants of any non-trivial substituents at the silicon atom, for which the literature values of the Taft constant are not available[77,112].

### 2. The Influence of the Steric Effect

The extreme rarity of the manifestation of the steric effect in reactions of organophosphorus compounds is most likely to be due to the fact that the most readily available derivatives containing the compact phosphoryl groups were used in most of the investigations. However, if the compound has three organic substituents at the phosphorus atom, their steric influence on the reactivity is in some cases fairly appreciable[7].

In contrast to organophosphorus compounds, compounds with three or even four organic substituents at the silicon atom have been frequently synthesised even more readily than their organic analogues. Therefore the majority of the reactions of organosilicon compounds investigated at the level of $\rho,\sigma$ analysis have been carried out using derivatives with a strongly shielded silicon atom. The influence of the steric effect of substituents at the silicon atom on the reactivity of a wide variety of organosilicon compounds has been discussed very widely in the literature at a qualitative level. Certain generalisations in this field are described in Sommer's monograph[17].

The quantitative data presented in Table 1 demonstrate a significant manifestation of the steric influence of substituents in many reactions of compounds of the type $R_3SiX$ and even $R_2SiX_2$ (R = organic substituent and X = functional group). Not a single case of correlations which do not take into account the steric effect has been described for compounds with tertiary substituents at the silicon atom. There are a few instances of such relations describing compounds with substituents having the isostructure (Table 1, Nos.6, 7, 16, 29, and 33). On the other hand, the data for some reactions of compounds with substituents having the normal structure were interpreted successfully solely in terms of an equation taking into account the steric effect (Table 1, Nos.5, 26 and 28).

The role of the steric effect diminishes as bulky substituents move further away from the reaction centre. Thus the logarithms of the equilibrium constants for the alcoholysis of trimethylacyloxysilanes $Me_3SiOCOR$, in which the substituent R is separated from the silicon atom by the group OC(O), are linearly related to the $\sigma^*_{R_i}$ for any R, including R = t-Bu (Table 1, No.20). In the remaining cases the correlations for reactions of triorganylsilanes with functional groups, which do not take into account the steric factor, are most likely to be because compounds with substituents whose steric effects differed little were used in the investigations rather than to the low value of the steric factor. This hypothesis is supported by the finding that the majority of the reactions in Table 1 are characterised by a weak inductive effect of the substituents (low values of the reaction constant $\rho^*$ in the Taft equation), which is the reason for the increased importance of other effects, including the steric effects, taken into account by any multiple correlation.

As for a number of organic compounds, the reactions of organosilicon derivatives involving acid catalysis are characterised by a much weaker influence of the inductive effect and a much stronger influence of the steric effect of the substituents than the analogous processes under the influence of a basic catalyst. Thus, although the values of $\lg k_{rel}$ for the triethylamine-catalysed condensation of diorganylsilanediols in methanol are related to the values of $\sum \sigma^*$ of the diorganyl groups by a single-parameter equation with the reaction constant $\rho^* = 4.7$ (Table 1, No.25),[32] the equation proved to be unsuitable for the analogous reaction in the presence of HCl.[33]

The result of our treatment of the data of Dejak et al.[33] in terms of an equation taking into account both $\sum \sigma^*$ and $\sum E^c_s$ (Table 1, No.26) confirmed the hypothesis of Dejak et al.[33] concerning the decisive role of the steric factor in this reaction. The results of studies[8,10] of the kinetics of the acid and alkaline solvolysis respectively of triorganylsilanes with n-alkyl, fluoroalkyl, and cyanoalkyl substituents

were evaluated from the relation between $\lg k_i$ and $\sum \sigma_i^*$ (Table 1, Nos.1 and 4). The value of $\rho^*$ for alkaline solvolysis (4.42) proved to be much higher than for acid solvolysis (0.77). However, in both cases there were appreciable deviations of the points corresponding to compounds with more bulky substituents. The experimental data[9] for the reactions indicated (without the corresponding results for compounds with fluoro- and cyano-alkyl groups, for which literature values of the steric constants are not available) were interpreted in terms of Eqn.(2), which takes into account both the inductive and steric effects of the substituents. As a result, the two-parameter correlation for the basic solvolysis made it possible to describe by a single relation a series of points differing appreciably from the theoretical values obtained with the aid of their inductive effects of the substituents alone (Table 1, No.5). Statistical treatment of the experimental data for the analogous acid solvolysis reaction showed that the rate of the process is almost wholly determined by the steric effect of the substituents (Table 1, No.2).[9]#

An analogous conclusion has been reached[20] for the hydrosilylation of hex-1-yne by triorganylsilanes (Table 1, No.14). However, in this study too a very narrow statistical selection was made (only six points were chosen for the calculation) and there are deviations of the points for $Et_3SiH$, $Pr_3SiH$, and $Me_2(Me_3CCH_2)SiH$ which cannot be accounted for by the proposed relation. Since instances of the dependence of the reaction rate exclusively on the steric effect of the substituents are extremely rare in correlation analysis, the above examples merit additional investigation.

### 3. The Influence of the Hyperconjugation Effect

Apparently owing to the abundance of different substituents containing C–H bonds at the silicon atom, many more data which can be interpreted as due to the manifestation of the hyperconjugation effect (in the given case $\sigma,d$ conjugation) have been obtained for organosilicon compounds than for phosphorus derivatives. In particular, it is believed that, precisely because of the displacement of the electrons of the C–H bonds to the d orbitals of the silicon atom, the C–Si bond is unusually weakly polarised and is chemically inert[114]. The stabilisation of the C–Si bond by $\sigma,d$ hyperconjugation has been confirmed by theoretical calculations[115,116].

Quantitative allowance for the hyperconjugation effect in the determination of the reactivity of organosilicon compounds has been based solely on kinetic data for the reactions of organylsilanes with methylphosphonic acid (Table 1, No.15). In order to establish a correlation, use was made of points for eight compounds having the general formula $RMe_2SiH$ with n-, iso-, and s-substituents as well as R = cyclohexyl. The deviation of the point for the t-butyl derivative was explained by the "saturation of hyperconjugation", i.e. by a decrease of the sensitivity of the rate of reaction to a change in the number of α-C–H bonds with increase of the latter[21].

The authors[21] (Table 1, No.9) found that the points for the compounds $R_3SiH$ (R = $PhCH_2$ or n-alkyl but not Me) and $MeR_2SiH$ form two parallel lines on the $\lg k_i - \sum \sigma_i^*$ diagram. Their relative positions suggested an increased influence of the hyperconjugation effect for methyl derivatives. The facts that the $Me_3SiCH_2$ group ($\sigma^0 = -0.20$) is significantly more electropositive than the $Me_2Si$ group ($\sigma^0 = 0.04$) [117] and that the $Et_3SiCH_2$ group is less electropositive than the $Me_2SiCH_2$ group ($\sigma^* = -0.13$ and $-0.26$ respectively) constitute very important arguments in support of the occurrence of hyperconjugation[118].

The interpretation of certain spectroscopic properties of organosilicon compounds also supports the hyperconjugation effect. Infrared spectroscopic data for organylsilicon hydrides are particularly characteristic. The values of $\nu_i$(SiH) for compounds in the $R_3SiH$, $R_2SiH_2$, and $RSiH_3$ series (R = alkyl or substituted alkyl) form three parallel lines on the correlation diagram in terms of $\sum \sigma^*(R)$.[63,64] The authors explained this finding by the different contributions of the hyperconjugation effect depending on the number of alkyl substituents at the silicon atom. The individual correlations for a series of compounds with n- or iso-groups can apparently also be accounted for by the differences between the hyperconjugation components[65]. It has been shown[62] (Table 3, No.3) that the data for all the above organylsilicon hydrides can be described by a general relation taking into account the effect of hyperconjugation. However, we should note that, when there are substituents capable of $p_\pi - d_\pi$ interaction at the silicon atom ($R_nX_{3-n}SiH$, R = H, alkyl, or substituted alkyl, X = Cl, Ph, or Vin, and $n = 1$ or 2), the hyperconjugation effect is not exhibited (Table 3, Nos.6–10). This finding was explained by competition between the substituents R and X for the *d* orbitals of the silicon atom, as a result of which the stronger $p_\pi - d_\pi$ conjugation predominates[68].

There are also certain differences between the parameters of the correlations of the integral intensities of the Si–H bond absorption bands and the Taft constants for a series of compounds differing in the structure of the alkyl substituents at the silicon atom[65] or the number of Si–H bond in the molecule[69] (Table 3, Nos.14 and 15). Plots of $\Delta A_i^{0.5}$ against $\sum \sigma_p$ for the organylsilicon hydrides $R_nX_{3-n}SiH$ (R = alkyl, X = Cl, Ph, or $XC_6H_4$, and $n = 0$, 1, or 2) give rise to three lines with identical slopes for a series of compounds differing in the values of *n*. It is believed[65] that the distances between the lines for the $X_3SiH$ series and the lines for $RX_2SiH$ or $R_2XSiH$ characterise the magnitude of the effect of the $\sigma,d$ conjugation of one or two alkyl groups respectively with the silicon atom[71].

### 4. The Influence of the α-Effect

We shall now consider recent data concerning the α-effect in certain α-substituted alkylsilanes, mainly chloromethyl derivatives. In the majority of correlations of the properties of organosilicon compounds the influence of substituents of the type $CH_nCl_{3-n}$ as well as other substituted alkyls is successfully taken into account by the usual $\sigma^*$ constant. This applies to the reactivities[30,32–37,42] and $^1H$ NMR data for organylethoxysilanes[81] and organylmethylsilanes[79], the relative basicities of hexaorganyldisiloxanes, triorganylethoxysilanes[45], organyltriethoxysilanes, and organyltrimethoxysilanes[46], the infrared spectra (position[62] and intensity[69] of the absorption band due to the Si–H bond) of organylsilicon hydrides, and the NQR spectra of many organylchlorosilanes[88,91].

# Later this relation was used to estimate the steric effects of certain non-trivial substituents at the silicon atom[113].

Furthermore, for a number of existing examples the apparent "anomaly" of the properties of compounds with α-chloroalkyl substituents, which has been usually attributed to the α-effect, has been either inadequately rigorously demonstrated or an alternative explanation is possible. Thus the unduly low reactivity, from the standpoint of relation No.1 (Table 1), of chloromethyldimethylsilane has been explained in a study of the acid hydrolysis of organylsilicon hydrides[8] by the presence of the resonance structure $^{+}ClCH_2=Si^{-}\leftrightharpoons$. However, it was found later[9] that the point for this compound does not deviate from the general relation taking into account the steric constants of the substituents (Table 1, No.2).

The relations between $\lg k_i$ and $\sum \sigma_i^*$ proposed[13,15] for the ozonisation and bromination reactions respectively do not describe a greater number of points than the number of points which deviate appreciably from them (the latter include the points for compounds with α-chloroalkyl substituents). The use of these relations for the construction of mathematical models of the corresponding processes is therefore problematical. Consequently the authors' conclusions[13,15] concerning the manifestation of the α-effect are not sufficiently well founded.

In the infrared spectra of organylsilicon hydrides with a chloromethyl group the absorption band due to the Si–H bond is frequently an unresolved doublet. The average value of ν(SiH) fits on the existing relations without deviations (Table 3, Nos.2–4). The presence of the doublet has been explained[119,120] by the equilibrium between the inner-complex (α-effect) and the usual forms of the molecules of the compounds indicated. However, this view has been criticised[121] and the phenomenon has been attributed to the presence of conformational isomers.

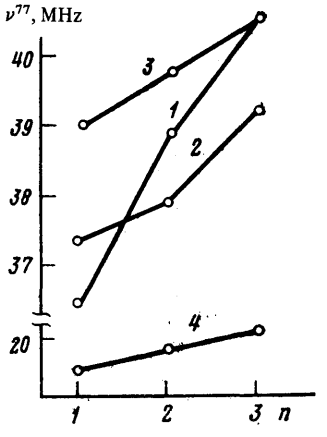



**Figure 1.** Relation between the $^{35}Cl$ NQR frequency ($\nu^{77}$) for the molecules of the $ECl_3CCl_nH_{3-n}$ series (E = C or Si) and the number of chlorine atoms n: *1*) in the $CCl_nH_{3-n}$ group with E = C; *2*) ditto with E = Si; *3*) in the $CCl_3$ group; *4*) in the $SiCl_3$ group[123].

The most extensive data on the properties of chloromethyl derivatives of silicon, attributed to the influence of the α-effect, have been obtained by NQR. As already mentioned above, the points for compounds with such substituents fit without deviations on the correlations between the values of $\nu_m^{77}$ and $\sum\sigma^*$ for the series of compounds $RR'R''SiCl$, where R is an organic substituent and R' and R'' are organic substituents or Cl (Table 3, Nos.43–45), and for compounds $RR'R''SiCH_nCl_{3-n}$, where R, R', and R'' are organic substituents, halogens, and alkoxy or siloxy-groups, and n = 0, 1, or 2 (Table 3, Nos.46–48). The following facts have been attributed to the manifestations of the α-effect. Despite the lower electronegativity of the silicon atom compared with the carbon atom, which presupposes lower Taft constants for substituents in compounds involving silicon, in the $R_3ECH_nCl_{3-n}$ series, where E = Si or C, the quantity $\nu_m^{77}$ for compounds with E = Si and low values of $\sum\sigma^*(R_3)$ is greater than in the case where M = C.[91,122–124]. Accordingly, of one begins with the relation between $\nu_m^{77}$ and σ* for the RCl series ($\nu_0 = 33.2$ and $\rho^* = 2.7$) [125], it is found that unusually high values of the σ* constant for the $R_3SiCH_2$ groups correspond to the experimental values of $\nu_m^{77}$ for the compounds $R_3SiCH_2Cl$. For example, $\sigma^* = 0.4$ has been calculated for the $Me_3SiCH_2$ group, in contrast to $\sigma^* = -0.26$ in handbooks. This phenomenon is characteristic precisely of α-derivatives, since the values of $\nu_m^{77}$ for the $R_3E(CH_2)_nCl$ series are higher in the case where E = Si only when n = 1 but not when n = 0, 2, or 3.[122]

The specific features of the NQR of chlorine in the Si–C–Cl group are clearly shown when the frequencies $\nu_m^{77}$ for compounds in the $CCl_3CCl_nH_{3-n}$ and $Cl_3SiCCl_nH_{3-n}$ series are compared (Fig.1). Whereas the frequencies for the chlorine atoms attached to the silicon in the $SiCl_3$ group are significantly lower than the corresponding frequencies $\nu_m^{77}(CCl_3)$ in the $CCl_3CCl_nH_{3-n}$ series (as might have been expected in view of the influence of the electropositive silicon), the frequencies for the groups $ECCl_nH_{3-n}$ with E = Si or C differ much less, which indicates the operation of the α-effect in the silicon-containing fragment[123]. The authors[123] also see the manifestation of the α-effect in the observation that the slope ρ* in the Taft equation for compounds of the $R_3CCl$ series without silicon (1.02) is significantly higher than for the organosilicon series $RR'(X_3Si)CCl$ (0.42). However, this view can be contrasted with the finding that the values of ρ* found from the analogous relation for organic derivatives are higher than for organosilicon derivatives also in the $R_3ECl$ series (E = C or Si) where the conditions for the manifestation of the α-effect do not exist.

Thus examination of all the data for the "unusual" properties of compounds with the Si–C–Cl group shows that the most convincing evidence has been obtained with the aid of NQR–in the form of increased NQR frequencies for organosilicon compounds compared with their carbon analogues. However, the interpretation of the findings as a manifestation of intramolecular coordination has aroused objections by Mel'nikova et al.[126] in this case also, although they do not propose any alternatives. They believe[126] that the interaction in the Si–C–Cl group within the complex can be exhibited only when other highly electronegative substituents are present at the silicon atom, while according to NQR data the greatest anomaly is shown for the region of low values of σ*.

In the study of correlations for other carbon-functional organosilicon compounds with Si–C–X groups, where X is an atom with an unshared electron pair, instances of deviations due to intramolecular coordination were still more infrequent.

Thus the "unusually" large value of $\Delta\nu(OH) = 318$ cm$^{-1}$ in the infrared spectrum of a mixture of phenol with $(Me_3SiCH_2)_2O$, initially attributed to the influence of the α-effect[127], was later shown to be satisfactorily accounted for by the relation $\Delta\nu_i = 263 - 90\ \sum\sigma_i^*$ for ethers[44] using $\sigma^*\ (Me_3SiCH_2) = -0.26$.

The higher reactivity of $Me_3SiCH_2OSiMe_3$ ($k_{rel} = 0.15$) compared with $Me_3CCH_2OSiMe_3$ ($k_{rel} = 0.049$) in the ethylamine-catalysed methanolysis of compounds in the series $R(CH_2)_nOSiMe_3$ has been explained by the intramolecular interaction between the Si and O atoms in the Si–C–O group[24]. For analogous compounds with $n = 2$, 3, or 4, the reaction rates are approximately the same. However, since the rate of this reaction is influenced appreciably by the steric effect of the substituents R (Table 1, No.19), a final conclusion concerning the causes of the feature noted above can be reached only after taking into account the steric hindrance due to the $Me_3SiCH_2$ group, the steric constant of which has not been determined so far.

The dependence of the values of $\Delta\nu(OH)$ in the infrared spectra of complexes of phenol with trimethylalkoxysilanes on the inductive constants has been described[50] by a quadratic equation (Table 2, No.9). The points for compounds with bulky substituents ($Me_3C$ and $Me_3CCH_2$) and also $CH_2Cl$ deviate from this relation. The electronegativity of the chloromethyl group, which is apparently unusually low from the standpoint of this relation, has been explained by a "specific" redistribution of electron density in the Si–O–C–Cl group. However, if the interpretation is based on the usual linear relation (Table 2, No.10), which is statistically quite reliable ($r = 0.94$ when the point for the compound with the sterically bulky group $CH_2CCl_3$ is disregarded), then the result for $Me_3SiOCH_2Cl$ no longer appears to be anomalous.

We shall consider finally the data for the characteristic features of the properties of compounds with the Si–C–N group. The basicity constants of *N*-substituted cyclic amines having the general formula $R\overline{N(CH_2)_{m-2}CH_2}$, where $m = 6$ [129,130], 5, or 7 [118], and R = organic substituent, or $R'_3Si(CH_2)_n$ ($n = 1$, 2, or 3 and R′ = alkyl) have been determined. Individual correlations $(pK_a)_i = (pK_a)_0 + \rho^*\sigma_i^*$ have been found for each heterocycle from data for organic derivatives (except for $R = Me_3CCH_2$, which deviates). The values $\sigma^*(Me_3SiCH_2) = -0.17 - -0.18$ calculated from these relations differ appreciably from the literature value $\sigma^* = -0.26$. The difference (which, however, is significantly smaller than that obtained on the basis of NQR data for the chloromethyl substituent—see above) was explained[130] by the manifestation of the α-effect in the Si–C–N group. This difference is not associated with the steric effect of the $Me_3SiCH_2$ group, because it is independent of the size of the heteroring of the amine, while the analogous difference for the neopentyl group increases with *m* and hence with enhancement of the steric hindrance in the molecule.

In contrast to these data, the basicity of $Me_3SiCH_2NR_2$ (R is an organic group) hardly differs from that calculated from the relation for organic amines $R_3N$, namely $(pK_a)_i = 7.86 + 2.7\ \sum\sigma^*$ using the usual value $\sigma^*(Me_3SiCH_2) = -0.26$.[57]

The data considered here show that the anomalies for compounds with the Si–C–X group, which have been reliably established from the standpoint of ρ,σ analysis and which can be attributed to the α-effect, have been observed only for a very small number of compounds, so that further studies in this field are of interest. Furthermore, the question why the resonance interaction is shown much more weakly and rarely for a series of substituted silicon alkyls than for the corresponding phosphorus derivatives still awaits an answer.

### 5. The Influence of the $p_\pi$–$d_\pi$ Effect

Although the problem of the $p_\pi$–$d_\pi$ interaction in organosilicon compounds has been actively discussed already for several decades[114,131–133], no general solution whereby a quantitative account could be taken of this effect have so far been proposed.

In organophosphorus compounds, the effect of the $p_\pi$–$d_\pi$ interaction can be taken into account for a wide range of substituents with the aid of the resonance constants $\sigma_R^f$.[7] The method used by Mastryukova and Kabachnik[7] to find these constants is of general validity for the estimation of resonance contributions[1–3] and consists in the determination of the difference between the real value of the measured quantity and the value calculated on the assumption that only the inductive effect of the substituent operates. This approach involves a series of assumptions. In particular, it is assumed that the resonance effect is additive and the influence of other substituent effects (steric, hyperconjugation, etc.) is neglected. The corresponding correlation equation using the Taft constants and the resonance constants $\sigma_R$ is

$$A = A_0 + \rho^*\sigma^* + \rho_R\sigma_R, \qquad (3)$$

where $\rho_R$ is a proportionality coefficient taking into account the sensitivity of the given property to the resonance effect of the substituents; for the standard series, it is assumed that $\rho_R = 1$.

It is noteworthy that attempts have been frequently made to isolate by an analogous procedure the contribution of the resonance effect (due to the $p_\pi$–$d_\pi$ interaction) of individual substituents in organosilicon compounds[13,36,41,134–136], but the results obtained did not lead to the derivation of universal organosilicon resonance constants. A critical analysis of these attempts is described below: at present we shall consider the problem of the applicability of the traditional approach to the estimation of the resonance effects of substituents at the silicon atom.

In the first place we shall attempt to test the validity of the additive rule. For this purpose, it is in principle sufficient to analyse data for the properties of a series of compounds with a variable number of certain identical substituents capable of $p_\pi$–$d_\pi$ interaction, for example, a series of the type $Me_{3-n}X_nSiY$, where X is a substituent, Y is a functional group, and $n = 0$–3. For this series, the dependence of the property on the number *n* of substituents X is expressed by the equation

$$A_n = n\rho_n(\sigma^* + \sigma_R^{Si}), \qquad (4)$$

where $\sigma_R^{Si}$ are the resonance constants of the substituents in the organosilicon compounds. Here the values of $\sigma_R^{Si}$ were taken without correction for the slope $\rho_R$, because each of these microseries can be regarded as standard. Under the condition where the given property is not influenced by the effects of the substituent X and the $CH_3$ group, which were not taken into account in Eqn.(4), a linear relation between $A_n$ and $n$ implies that $\sigma_R^{Si}$ remains constant regardless of the number of substituents X in the molecule.

Such linear relations have been obtained for the compounds $Me_{3-n}X_nSiH$ ($n = 0$–3, X = Ph, Cl, Br, $NMe_2$, C ≡ CH [137], or Vin [137,138]) from the values of ν(SiH) in the infrared spectra, for $Et_{3-n}X_nSiH$ ($n = 0$–3) with X = Ph from the relative ozonolysis rate constants[12] or with X = Vin from the solvolysis rate constants (95% EtOH) [138], for $Me_{3-n}Cl_n$·.SiOR ($n = 0$–3, R = Et or iso-Pr) [51] and $Me_{4-n}Si(OR)_n$ ($n = 1$–4, R = Me, Et, Pr, or iso-Pr) [139] from the Δν(OH) in

the infrared spectra of the complexes of these compounds with phenol, for $Me_{3-n}Cl_nSiVin$ ($n = 0-3$) from the relative rate constants for the addition of the $Cl_3C^\bullet$ radical [109], for $Me_{3-n}Cl_nSiCH_2C_6H_5$ ($n = 0-3$) from the relative chlorination rate constants[140], for $Et_{4-n}X_nSi$ ($n = 0-3$) with X = Cl [80,105] or Br [105] and for $Me_{3-n}Cl_nSiOEt$ ($n = 0-3$) [81] from the values of $\tau(CH_2)$ in $^1H$ NMR spectra, and for $Me_{3-n}X_nSiVin$ ($n = 0-3$, X = Cl, MeO, or $Me_3SiO$; $n = 0$, 1, or 2, X = Ph; $n = 0$, 2, or 3, X = OEt) from the relative rate constants for their reactions with thioacetic acid[42].

At the same time it has been found that there is no linear relation for compounds in the series $Me_{4-n}Si(OPh)_n$ ($n = 1-4$) on the basis of the $\Delta\nu$(OH) in the infrared spectra of their complexes with phenol[141], for $Me_{4-n}Si(OEt)_n$ ($n = 1-4$) on the basis of the values of $\tau(CH_2)$ and $\tau(CH_3)$ in the $^1H$ NMR spectra[81], for $Me_{3-n}F_nCH_2Ph$ ($n = 0-3$) on the basis of the relative rate constants for their chlorination[142], for $Et_{3-n}Cl_nSiH$ ($n = 0-3$) and $Pr_{3-n}(OEt)_nSiH$ ($n = 0-3$) on the basis of the rate constants for their addition to hex-1-ene[143], for $Me_{3-n}(Me_3SiO)_nSiH$ ($n = 0-3$) and $Pr_{3-n}\cdot(EtO)_nSiH$ ($n = 0-3$) on the basis of their solvolysis rate constants (95% EtOH) [144], and for $Me_{3-n}X_nSiH$ (X = F, MeO, or EtO), $Ph_{3-n}F_nSiH$, $F_nSiH_{4-n}$ [137], and $Pr_{3-n}(EtO)_n\cdot SiH$ [143,144] ($n = 0-3$ throughout) on the basis of $\nu$(SiH) in the infrared spectra.

The above list shows that almost all the substituents are capable of influencing additively the properties of the corresponding compounds. As regards the instances of a non-additive influence, one should bear in mind that the reactivity data did not take into account the steric influence of the substituents, which can distort the linear relation. In the remaining instances the absence of a linear relation is apparently caused by the non-additive influence of the electronic effects of the corresponding substituents (F and RO) when the latter accumulate in the molecule.

It would seem that these data permit the conclusion that Eqn.(3) is applicable at least to compounds with substituents which usually have an additive effect (Ph, Vin, Cl, and Br). However, there is an unexpected obstacle, which in fact has no analogies for compounds of other elements: in numerous instances the values of $\rho^*$ in analogous correlations change on passing from the $R_3SiY$ series to the $R_{3-n}X_nSiY$ series (X are substituents capable of $p_\pi$–$d_\pi$ conjugation and R are other substituents). These cases are presented in Tables 2 and 3 (see Nos.2–4, 10–12, and 13–15 in Table 2 and 6–13 and 25–30 in Table 3). In view of the fundamental importance of this process, we shall consider the most typical results in greater detail.

Fig.2 presents the dependence of the chemical shifts of the methylene protons of the ethoxy-group on the values of $\sum\sigma^*$ for the remaining three substituents at the silicon atom in the molecules of organylethoxysilanes $R_{4-n}Si(OEt)_n$ (Table 3, Nos.28–30); the points for the $Me_{4-n}Si(OEt)_n$ series are indicated separately. Evidently the linear relation (4) for this series includes only points corresponding to $n = 2$, 3, or 4, but not $n = 1$. It is also seen that, owing to the difference between the slopes of the lines for the $R_{4-n}Si(OEt)_n$ series with $n = 1$, on the one hand, and for the series with $n = 2$ and 3, on the other, the distances between them are not constant. From the standpoint of the relation for the series of compounds with $n = 1$ (Table 3, No.28), the second and third ethoxy-groups therefore influence the chemical shift via the inductive effect, which formally diminishes on passing to the region of higher values of $\sum\sigma^*$. For example, the deviation calculated in terms of the $\sigma^*$ scale from the above relation, caused by the influence of the excess ethoxy-group, is −0.43 for $Me_2Si(OEt)_2$ ($\sum\sigma^* = 1.37$) and −1.81 for $(Cl_3C)_2Si(OEt)_2$ ($\sum\sigma^* = 6.67$). Evidently, the difference between these values, each of which corresponds to the resonance effect of the ethoxy-group from the standpoint of Eqn.(3) is very considerable.

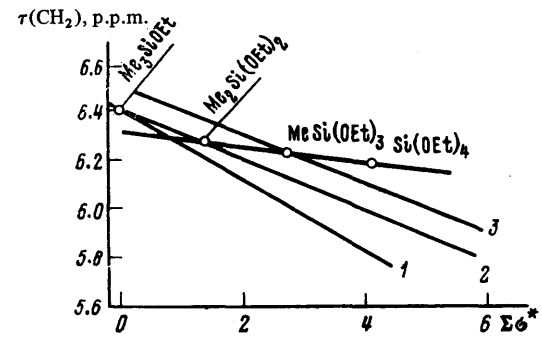



**Figure 2.** Dependence of the chemical shifts of the methylene protons of the ethoxy-group on the $\sum\sigma_i^*$ for the remaining three substituents at the silicon atom in the $R_{4-n}Si(OEt)_n$ molecules[81]: *1*) $n = 1$; *2*) $n = 2$; *3*) $n = 3$.

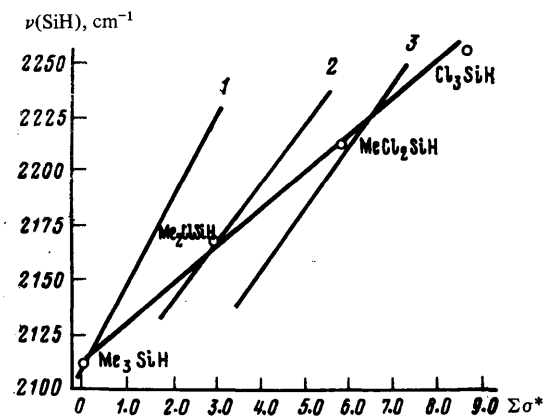



**Figure 3.** Dependence of $\nu$(SiH) on $\sigma_i^*$ for the substituents $R_3$ or $R_{3-n}Cl_n$ in the $R_3SiH$ and $R_{3-n}Cl_nSiH$ molecules[68]: *1*) $R_3SiH$; *2*) $R_2ClSiH$; *3*) $RCl_2SiH$.

The individuality of the slopes of the straight lines corresponding to correlations for the series of compounds $R_{3-n}X_nSiH$ (Table 3, Nos.6–13), which differ in the type of substituent (X = Cl, Ph, or Vin), has been demonstrated[68] in relation to the dependence of the stretching vibration frequencies of the silicon hydride bond on the $\sum\sigma^*$ for the substituents at the silicon atom. An example of such relations for the case where X = Cl and their position on the graph relative to the regression line for the $R_3SiH$ series (Table 3, No.2) are presented in Fig.3. Fig.3 also demonstrates the validity of Eqn.(4) for the $Me_nCl_{3-n}SiH$ microseries (when X = Ph or Vin, this relation also holds).

As in the previous instance, owing to the difference between the slopes of lines corresponding to the relations for $R_3SiH$ and $R_2XSiH$, here the distances between the lines, caused by the influence of the substituent X, are not the same for the entire range of values of $\sum \sigma^*$.

Since the above study[68] is the only example hitherto where series of compounds with different substituents X have been investigated by a single method, it is of particular interest to analyse the nature of the variation of the slope of the relation between $\rho^*$ and $\sigma^*$ as a function of the nature of the substituent X. The data in Table 3 show that, when X = Ph or Vin, the quantity $\rho^*$ is greater and, when X = Cl, it is smaller than in the correlation for the $R_3SiH$ series. This corresponds formally to a decrease of the resonance influence of the substituents for X = Ph or Vin on $\nu$(SiH) (i.e. the experimental values of $\nu_i$ approach those calculated from the relation for $R_3SiH$) and to an increase of the resonance influence of chlorine with increase of the values of $\sum\sigma^*(R_2X)$. Even if it is assumed that the change in the values of $\rho^*$ is caused by the mutual influence of the inductive and resonance effects of the substituents in the molecules of $R_2XSiH$, it cannot therefore be taken into account by adding an additional term to the right-hand side of Eqn.(3). This is particularly true in view of the fact that, on further increase of the number of substituents X in the molecule, the slope no longer changes. Thus, so far one can only conclude that the coefficient $\rho^*$ is specific to each substituent X; there are as yet insufficient data to formalise this phenomenon by a general correlation.

The results lead to the conclusion that in the general case the calculation of the constant $\sigma_R^{Si}$ by Eqn.(3) is erroneous, because the calculated quantities are not constant for a specific substituent X and apparently do not reflect the true resonance contribution of the latter. A comparative estimate of random deviations (for different substituents X), corresponding to the quantity $\rho_R\sigma_R$ in Eqn.(3) [44,63,73,134–136,145–148], does not therefore appear to be sufficiently fruitful.

On the grounds that the values of $\rho^*$ for the series of compounds $R_{3-n}X_nSiH$ with $n = 1$ or 2 and a constant X are virtually the same, the relations for the $R_2XSiH$ series have been used as a basis for the estimation of the $\sigma_R^{Si}$ and the deviations $\Delta\nu_i$ from these relations for compounds in the series $RX_2SiH$ were attributed to the resonance influence of the second substituent X:

$$(\sigma_R^{Si}) = \Delta\nu_i/\rho_i^*.$$

The values of the resonance constant $\sigma_R^{Si}$ found for the substituents X = Cl, Ph, and Vin were respectively −1.23, −0.51, and −0.50. The constants $\sigma$(Si), characterising the overall (effective) inductive effect of the substituents, were also calculated with the aid of the equation $\sigma^* + \sigma_R^{Si}$. Using the values of $\sigma$(Si) obtained [for substituents R which do not exhibit the resonance effect, $\sigma(Si) = \sigma^*$], the correlation parameters were calculated for the series of compounds $R_{3-n}X_nSiH$ with $n = 1$, 2, or 3 (Table 3, Nos.11–13). The high accuracy of the correlations confirm the additivity of the resonance contribution of the substituents X independently of their number in the molecule. $\sigma_R^{Si}(OEt) = -1.06$ can be found analogously from the $^1H$ NMR data for the $R_2Si(OEt)_2$ and $RSi(OEt)_3$ series discussed above; $\sigma_R^{Si}(OMe) = -0.59 \pm 0.07$ has been found from data[11] for the methanolysis of the compounds $RSiH_2(OMe)$ and $RSiH(OMe)_2$. Other results suitable for estimates of this kind are so far not available in the literature.

It is seen from the preceding discussion that a fairly rigorous allowance for the $p_\pi$–$d_\pi$ effect of the substituents at the silicon atom requires the use of extensive experimental data and is therefore difficult. Hence it is still useful to investigate the possibility of employing Eqn.(3), ignoring the possibility of a difference between the values of $\rho^*$ for the $R_3SiY$ and $R_{3-n}X_nSiY$ series, at least for an approximate comparative estimate of the extent of the $p_\pi$–$d_\pi$ effects of different substituents. The only condition which ensures the possibility of applying the scale of approximate values of $\sigma_R^{Si}$ obtained in this way is mutual proportionality of the influences of the $p_\pi$–$d_\pi$ effect on any of the properties investigated. The validity of this condition makes it possible to use the slope $\rho_R^*$ in Eqn.(3).

To test this claim, we shall consider the approximations obtained for the relative values of $\sigma_R^{Si}$ [having assumed that $\sigma_R^{Si}(Cl) = 1$] in the case of the substituents Ph, Cl, or OEt, for which the greatest amount of factual data is available (Table 4). Table 4 shows that different research techniques manifest, as it were, a selective sensitivity to the influence of individual substituents, as a result of which a mutual proportionality of the changes in the resonance contribution does not obtain. Consequently the simplified approach to the establishment of a general relation proposed above is inapplicable. Hence it becomes clear why the values of $\sigma_R^{Si}$ (or analogous quantities), frequently calculated in this way, have not been widely accepted.

**Table 4.** The relative values of $\sigma_R^{Si}$ calculated by Eqn.(3) (for $\rho_R = 1$).

| Compound and property investigated | R | | | References |
|---|---|---|---|---|
| | Ph | Cl | OEt | |
| $R_{3-n}X_nSiH$, i.r.s., $\nu$(SiH) | 0.32 | 1.0 | 0.41** | 68,134* |
| $R_2XSiVin$ + AcSH, $k_{rel}$ | 0.13 | 1.0 | 0.51 | 42 |
| $R_{3-n}X_nSiOEt$, $\tau(CH_2$ in OEt) | 0.00 | 1.0 | 0.50 | 81* |
| $R_{3-n}X_nSiOEt$ + phenol, i.r.s., $\Delta\nu$(OH) | 0.17 | 1.0 | 0.64 | (45,51,149)* |

*Calculated from data in the communications indicated.
**Here R = OMe.

Thus, although the very fact of the deviation from the relation for the $R_3SiY$ series caused by the introduction of the substituent X in $R_{3-n}X_nSiY$ can serve as an indication of the manifestation of the $p_\pi$–$d_\pi$ effect of the above substituent, the magnitude of the deviation is an extremely arbitrary characteristic of the magnitude of this effect. Furthermore, the same characteristic is not constant owing to the lack of proportionality in terms of the scales of the deviations obtained by different methods and for different models. The causes of such a significant difference in the manifestations of the resonance effects of the substituents in silicon and phosphorus compounds still remain obscure.

## IV. THE ABILITY OF THE SILICON ATOM AND OF SILICON-CONTAINING ATOMIC GROUPS TO TRANSMIT EFFECTS

The transmission coefficient $z_N$ of a structural unit N is defined[1-3] as the decrease of the inductive influence of the substituents R when the latter move away from the indicator centre Y as a result of the introduction of this particular structural unit. The values of $z_N$ are determined from the ratios of the corresponding slopes or Taft constants:

$$z_N = \rho^*_{R-N-Y}/\rho^*_{R-Y} = \sigma^*_{R-N}/\sigma^*_R .$$

The few literature values of the transmission coefficients of organosilicon structural units as well as the values which we calculated from the literature data (with the aid of the $\rho^*-\rho^*$ method) are presented in Table 5. Evidently the transmission capacity of the silicon atom (Table 5, Nos.1–3) is not constant for different compounds, in contrast to the transmission capacity of organic structural units. This indicates differences between the mechanisms of the transmission of the inductive influence of substituents via a silicon atom. Presumably this is caused by the different extents of the $p_\pi-d_\pi$ interaction in different series. The unusually high transmission coefficient of the $SiCH_2$ group (Table 5, No.4) has been attributed[57] to an additional (apart from the σ-bond) interaction of the silicon and nitrogen atom. The coefficient $z_{OSi(Me_2)} = 0.15-0.26$ (Table 5, Nos.5 and 6) is entirely comparable to the transmission coefficient of the C–O bond ($z_{C-O} = 0.26-0.34$);[1] thus the abilities of the Si–O and C–O bonds to transmit the inductive effects of substituents are approximately the same.

**Table 5.** The transmission coefficients of the silicon atom and silicon-containing structural units.

| No. | R-Y and R-N-Y series | Method of investigation and parameter investigated | $\rho^*_{(RY)}$ | $\rho^*_{(RNY)}$ | N | $z_N$ | Refs. |
|---|---|---|---|---|---|---|---|
| 1 | ROR′ and $R_3SiOEt$ | i.r.s., Δν(OH) for phenol | −90 | −61 | Si | 0.68 | 44,45* |
| 2 | R–Cl and $R_3SiCl$ | NQR, $\nu_m^{77}$($^{35}$Cl) | 2.7 | 0.4 | Si | 0.15** | 88,125* |
| 3 | $R_2NH$ and $R_3SiNHMe$ | kinetics of reaction with $Ph_2SiH_2$, $k_i$ | — | — | Si | 0.22 | 40 |
| 4 | $R_3N$ and $R_3SiCH_2NMe_2$ | potentiometry, $pK_a$ | −2.7 | −1.8 | $SiCH_2$ | 0.68 | 57 |
| 5 | $R_3SiH$ and $R_3SiOSi(Me_2)H$ | $^1$H NMR, $J(^{29}SiH)$ | 19.8 | 2.9 | $OSiMe_2$ | 0.15 | 67 |
| 6 | Ditto | i.r.s., ν(SiH) | 31.5 | 8.1 | $OSiMe_2$ | 0.26 | 67 |

*Calculated from data in the communications indicated.
**The data for the RCl and $R_3CCl$ series ($\rho^* = 1.02$) yielded $z_C = 0.37$, which is consistent with the literature value $z_{CH_2} = 0.36$.[125]

It is of interest to estimate the transmission capacity of the silicon atom compared with those of other elements in isostructural compounds. If the $\rho^*/\rho^*$ method is used in this instance, it is possible to obtain a quantitative expression for the above estimate in the form of an "isostructural" transmission coefficient, which we shall designate by $z'$:

$$z' = \rho^*(Si)/\rho^*(E),$$

where ρ*(Si) is the slope for the organosilicon series and ρ*(E) is the corresponding slope for the isostructural series in which silicon has been substituted by the element E. The values of $z'$ calculated from the literature data are listed in Table 6.

Since the silicon atom is less electronegative than the carbon atom, its isostructural substituents should have a smaller inductive effect, which is reflected also in the values of $z'$ for the silicon–carbon pair, the latter being always less than unity. However, a universal value of $z'$ is also not observed, as for the coefficient $z$(Si) discussed above. The inconstancy of the $z'$ for compounds in which silicon is linked to a substituent capable of $p_\pi-d_\pi$ interaction (Table 6, Nos.1–3 and 7–9) apparently reflects the different degrees of manifestation of the resonance effect and for the series of compounds Nos.4–6 the different influences of the α-effect. It is of interest that a value $z' < 1$ has been obtained also for the Si/Ge pair (No.10), in which the germanium atom is less capable of $p_\pi-d_\pi$ bonding than the silicon atom despite being still less electronegative.

**Table 6.** The isostructural transmission coefficient $z'$ for the silicon atom.

| No. | Isostructural series* | Method of investigation and parameter investigated | $\rho^{**}$ (M) | $\rho^{**}$ (Si) | $z'$ | Refs. |
|---|---|---|---|---|---|---|
| 1 | $R_3MCl$ | NQR, | 1.019 | 0.404 | 0.39 | 123 |
| 2 | $R_2MCl_2$ | ditto | 0.959 | 0.415 | 0.43 | 123 |
| 3 | $RMCl_3$ | » | 0.933 | 0.484 | 0.52 | 123 |
| 4 | $R_3MCH_2Cl$ | » | 0.594 | 0.308 | 0.52 | 123 |
| 5 | $R_2MCHCl_2$ | » | 0.409 | 0.279 | 0.68 | 91 |
| 6 | $R_2MCCl_3$ | » | 0.408 | 0.166 | 0.41 | 91 |
| 7 | $R_3MOH \cdot DMSO$ | $^1$H NMR, chemical shift of H in HO(Hz) | 73 | 65 | 0.89 | 58 |
| 8 | $C_6H_5MR_3$ | i.r.s., ν(CH) in $C_6H_5$ | 8.28 | 5.57 | 0.67 | 74* |
| 9 | $R(Me_2)MOR' \cdot PhOH$ | i.r.s., Δν(OH) for phenol | −54 | −47 | 0.87 | 49 |
| 10 | $Rh_3SiOOMR_3 \cdot PhOH$ | ditto | −33 | −19.4 | 0.59 | 52 |

*M = C in Nos.1–9 and M = Ge in No.10.
**The constants $\sigma_i$ were used by Knižek et al.[74] to calculate ρ* (M, Si).

We may note finally the instances of the changes in the transition capacity of the silicon atom on passing from compounds $R_3SiY$ to compounds $R_{3-n}X_nSiY$, partly discussed above. As already mentioned, the slope ρ*, characterising the relative ability of the silicon atom to transmit the inductive effect of the substituents to the indicator centre, can both decrease and increase after the introduction of different substituents. However, for highly electronegative substituents (RO, Cl), capable of effective $p_\pi-d_\pi$ conjugation with the silicon atom, the values of ρ* for the compounds $R_{3-n}X_nSiY$ are as a rule smaller than for $R_3SiX$ and tend to decrease further with increase of $n$ (Nos.2–4 and 13–15 in Table 2, and 2, 6, 9, and 25–30 in Table 3). It has been suggested[45] that the decrease of the sensitivity of the indicator centre to the influence of the inductive effect of substituents with increase of the number of substituents X in the molecule is caused by the increase of the degree of $p_\pi-d_\pi$ bonding under these conditions.

* * *

Thus the results of the application of the Taft relations in order to establish correlations between the properties of organosilicon compounds and their structure demonstrates the applicability of the usual inductive (for alkyl and substituted alkyl groups) and steric constants of the substituents. In contrast to organophosphorus compounds,

substituted alkyl groups at the silicon atom do not exhibit a resonance effect with the exception of individual instances in α-substituted derivatives. The role of the hyperconjugation effect in silicon compounds has been only slightly investigated. The most specific feature of organosilicon compounds is $p_\pi$–$d_\pi$ conjugation, the extent of which cannot in general be estimated with the aid of procedures usually employed in the calculation of resonance contributions. A preliminary estimate of the transmission coefficient of the silicon atom and silicon-containing groups showed that their ability to transmit the inductive effect of substituents is reduced compared with carbon (and germanium).

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