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Communication

A novel insight into the inductive effect in silicon chemistry

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ABSTRACT

A revision of quantitative literature data for the reactivity of organosilicon compounds in light of conceptions stemmed from organic chemistry has been carried out. It has been found that in structure-reactivity analysis for organosilicon compounds, differently of carbon compounds, the inductive effect of substituents, at least in nucleophilic displacement reactions at silicon, must be expressed by two terms involving that for electronegativity. A protocol for the correlation analysis in organosilicon chemistry is now available.

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The quantitative structure-reactivity analysis, basing on linear free-energy relationships and usually referred to as the correlation analysis, has been widely practised in organic chemistry since the pioneering work by Hammett [1]. Despite of the emergence of quantum chemical calculations and other complementary methods, correlation analysis has maintained its importance as a useful tool for unravelling reaction mechanisms and also for prediction of rate or equilibrium constants [2–4].

Effects of aliphatic substituents on the reactivity of organosilicon compounds have been described since long with the Taft equation (Eq. (1)) [5–7], where the two last terms express independent contributions from inductive and steric effects respectively [2,3]. Sometimes, to be fitted in with the data, the equation has been extended with a resonance term referred to the hyperconjugation effect [6].

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_S \tag{1}$$

Silicon chemists have mainly used correlations for which the substituent constants have been defined in organic reactions [5,7]. However, the steric parameters derived from reactions of organic carbonyl compounds have been but moderately suitable for description of steric effects in reactions taking place at Si atoms [8,9].

Cartledge [8] defined a set of $E_S(Si)$ parameters for alkyl groups from reaction rates of silicon compounds. Similar quantitative scales have been proposed for reactions at the silicon center by other groups [10,11]. The $E_S(Si)$ scale is closely related to the scale v' derived by Charton [12] from replacement reactions at sp^3-carbon. The scale v' was successfully applied in correlating reactivity data of alkyl substituted phosphorus compounds [13].

The σ^*-values in Eq. (1) measure the inductive effects of substituents. However, there have been numerous contributions [2,3,12,14] which denote that alkyl substituents do not exert any inductive effect. In a great number of works reactivity data for silicon compounds have been correlated with Taft's σ^* constants (see, e.g. review [6]).

However, the authors never paid attention to a close correlation between σ^* and steric E_S constants ($R = 0.865$). Thus, the correlations actually described the steric effects of alkyl substituents. We have analyzed available literature data for silicon compounds with alkyl substituents. Statistical treatment of 17 reaction series confirmed clearly that alkyl substituents contribute to the reactivity of silicon compounds exclusively with their steric effects [15].

For an analysis of electronic effects quantitative separation of inductive and resonance components is necessary. Participation of p- and d-orbitals in the structure formation of silicon compounds have been a subject of continuing debates [6,16,17]. Theoretical studies show that d-orbitals have no significant involvement in the bonding [18] and bonds between Si and H, C, O, and F are extensively polarized with significant charge transfer. Thus, a resonance interaction requiring an overlap of p- and/or d-orbitals should be considerably hindered. As an unambiguous test, correlation of kinetic data for substituted phenylsilanes with σ° constants was implicated by Chvalovsky et al. [19]. A linear correlation with purely inductive σ_o or σ_I constants rules out the conjugation of substituents with the reaction center [2]. Good correlations obtained for ten available reaction series [20] provided an evidence of insignificance of the resonance effect at least in nucleophilic displacement reactions at the silicon center.

From the brief analysis above it follows that a revision of quantitative literature data for the reactivity of organosilicon compounds in light of current conceptions is necessary. As only inductive and steric effects are operating and as steric parameters for alkyl substituents are available now, relying on scales of inductive constants determined in organic chemistry, missing steric parameters for polar substituents could be readily calculated from Eq. (1). According to this logic the susceptibility constants for inductive and steric effects can be found from rate data for substituted phenyl compounds and for alkyl compounds, respectively.

However, our attempts to calculate steric parameters for polar substituents failed entirely [20]. The values obtained for $E_S(Si)$ parameters varied by several times in case of different reaction series. We concluded that the data cannot be described by means of a two-parameter equation like Eq. (1) and apparently one more variable need to be involved [20].

Recently Exner and Böhm discovered the complex character of the inductive effect [21,22]. The principle is that a simple inductive effect can be observed only on the interaction with a charged group; when both interacting groups are less polar, the effect must be expressed in two terms. The second term is small and its physical meaning is still unclear, however, it was related to the electronegativity [21,22].

Note that the novel conception of the inductive effect stems from the carbon chemistry. If applicable to the silicon chemistry, the proportions between the components of the effect need not remain the same. The conception had never been applied to kinetic data.

We inserted the two-term expression of the inductive effect into Eq. (1) thus obtaining Eq. (2) for organosilicon reactions

$$\log k_{rel} = \rho_I \sigma_I + \xi \chi + \delta E_S(Si) \tag{2}$$

In Eq. (2), keeping to designations by Exner and Böhm, χ is the electronegativity and ζ is the corresponding reaction constant. Considering that for phenyl compounds substituted in para- or meta-position with X, $E_S(Si)_{XPh} = E_S(Si)_{Ph}$ and $\chi_{XPh} \sim \chi_{Ph}$, the susceptibility constant ρ_I can be found as the slope of the plot $\log k_{rel}$ vs. σ_I (Fig. 1). The same plot provides an intercept equal to $\zeta \chi_{Ph} + \delta E_S(Si)_{Ph}$. While δ can be found from the correlation of rate data for alkyl compounds, the reaction constant ζ and parameter $E_S(Si)_{Ph}$ remain unknown.

We used an iteration method assigning different values to $E_S(Si)_{Ph}$. Values for ζ and subsequently values of $E_S(Si)$ for polar groups were calculated from five different reaction series. For calculations inductive σ_I parameters from Ref. [23], the group electronegativities from Ref. [24], and the improved $E_S(Si)$ scale from Ref. [15] were employed [25]. In all the scales the origin was adjusted to the methyl group.

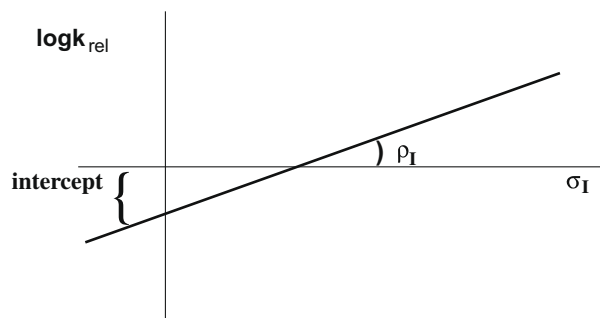It appeared that standard errors of average values for calculated $E_S(Si)$ parameters and the statistical validity of correlations according to Eq. (2) with all substituents included, were almost insensitive to initial values of $E_S(Si)_{Ph}$ set in the range between -0.5 and -0.65. Thus, $E_S(Si)_{Ph} = -0.55$ was taken as the best approximation. Calculated $E_S(Si)$ values for polar substituents together with available parameters for alkyl groups are collected in Table 1. It is obvious that the values for polar groups are placed in plausible positions among those for alkyl substituents.

In Table 2 results of correlations according to Eq. (2) with all substituents included are presented. Reaction series 1–5 were used for calculation $E_S(Si)$ values (Table 1). Series 6 and 7 were left for an independent test of the method. The results shown in Table 2 confirm the validity of our novel approach to the quantitative structure-reactivity analysis in organosilicon chemistry. The correlations are unexpectedly good if considering that the kinetic measurements feasible in organosilicon chemistry never afford the accuracy attainable with, e.g. spectrometric methods.

The last column in Table 2 deserves a special attention. It appears that the relative contribution of electronegativity varies largely and is related to both the nucleophilic reagent and the organosilicon substrate. While in reactions 1–3 the effect of electronegativity is almost negligible, in case of stronger nucleophiles (series 4 and 7) or of di- or trichlorosilanes (series 5–7) its contribution is considerable. However, the physical meaning of the rate decreasing effect of electronegativity still remains obscure, similarly as it was left open by Exner and Böhm [21,22]. Supposedly, the electronegativity term in Eq. (2) can be considered as a correction factor for the inductive constants derived in organic chemistry.

An analogue of Eq. (2) in form of Eq. (3) was applied to infrared stretching frequencies of Si–H bond in substituted dimethylsilanes RMe_2SiH [28–31].

$$A = A_0 + \rho_I \sigma_I + \xi \chi \tag{3}$$

Table 1
Steric parameters for substituents in organosilicon compounds (calculated values for polar groups are in bold).

Substituent	$-E_S(Si)$	Substituent	$-E_S(Si)$
Me	0	i-Bu	0.41
MeO	**0.12[a]**	**BrCH₂**	**0.44 ± 0.06**
EtO	**0.14[a]**	**PhCH₂**	**0.51 ± 0.15**
Et	0.15	i-Pr	0.56
n-Pr	0.22	**Ph**	**0.57 ± 0.02**
n-Bu	0.23	c-Hex	0.66
ClCH₂	**0.32 ± 0.11**	s-Bu	0.67

[a] Determined from a single reaction series (series 4 in Table 2).

Table 2
Results of correlations according to Eq. (2).

Reaction	ρ_I[a]	ξ[a]	δ[a]	n[b]	R[b]	S[b]	ξ/ρ_I
1[c]	7.51(0.59)	−0.05(0.48)	1.57(0.19)	15	0.982	0.133	−0.01
2[d]	7.25(0.49)	0.61(0.34)	1.61(0.16)	16	0.987	0.110	0.09
3[e]	7.34(0.25)	−0.72(0.20)	1.56(0.08)	15	0.996	0.056	−0.10
4[f]	8.69(0.70)	−2.51(0.24)	2.28(0.12)	16	0.989	0.154	−0.29
5[g]	7.48(0.99)	−3.95(0.68)	1.39(0.21)	15	0.958	0.140	−0.53
6[h]	15.7(2.1)	−8.6(1.3)	1.59(0.23)	11	0.976	0.099	−0.54
7[i]	6.33(0.82)	−2.92(0.63)	0.65(0.27)	10	0.960	0.116	−0.46

[a] Regression coefficients of Eq. (2), standard deviations are in parentheses.
[b] Number of compounds, correlation coefficient, and standard deviation from the regression, respectively.
[c] Reaction $RMe_2SiCl + Me_3SiOLi$ [11].
[d] Reaction $RMe_2SiCl + PhMe_2SiOLi$ [11].
[e] Reaction $RMe_2SiCl + Me_2CHOLi$ [11].
[f] Reaction $RMe_2SiCl + H_2O$ in dioxane [10].
[g] Reaction $RSiCl_3 + t\text{-}BuOLi$ [26].
[h] Acetolysis of $RSiCl_3$ [27].
[i] Reaction $RMeSiCl_2 + PhMgCl$ [20].

Fig. 1. Graphical determination of ρ_I and the intercept ($\zeta \chi_{Ph} + \delta E_S(Si)$) from data for para- and meta-substituted phenyl compounds.

These physical properties of organosilicon compounds correlate well ($R = 0.980$, $n = 13$) according to Eq. (4) [32],

$$\Delta v_i = (-1.4 \pm 2.0) + (174 \pm 15)\sigma_I + (1.4 \pm 3.7)\chi \qquad (4)$$

but interestingly, the electronegativity term seems to be insignificant in this case.

In conclusion, it has been established that in general the inductive effect in nucleophilic displacement reactions at silicon must be expressed by two terms involving the electronegativity of substituents. Additionally, a protocol for correlation analysis in organosilicon chemistry is now available.

Most probably our results are general for elements of the third period and thus can be extended to the organophosphorus chemistry. A relevant work is under way.

Acknowledgements

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