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Quantitative structure-reactivity
analysis in organosilicon chemistry



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LIST OF ORIGINAL PUBLICATIONS

- I D. Panov, A. Ploom, A. Tuulmets, Steric Effects of Alkylmagnesium Chlorides in the Grignard Reaction with Silanes, *Phosphorus, Sulfur and Silicon*, **2006**, 181, 2807–2816.
- II A. Ploom, D. Panov, A. Tuulmets, Steric effects of alkyl substituents in silicon chemistry, *Arkivoc*, **2006**, Part (V), 37–42.
- III O. Golubev, D. Panov, A. Ploom, A. Tuulmets, B.T. Nguyen, Quantitative substituent effects in the Grignard reaction with silanes, *J. Organomet. Chem.*, **2007**, 692, 3700–3705.
- IV A. Ploom, D. Panov, J. Järv, A. Tuulmets, Rate and equilibrium constants for Grignard reaction with alkoxy silanes and ketones, *J. Organomet. Chem.*, **2008**, 693, 2351–2354.
- V A. Ploom, A. Tuulmets, A novel insight into the inductive effect in silicon chemistry, *J. Organomet. Chem.*, **2009**, 694, 313–315.
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Paper IV: Responsible for all experiments and calculations. Participation in manuscript preparation.

Paper V: Responsible for data processing. Participation in manuscript preparation.

Paper VI: Responsible for all experiments, calculations and correlations. Participation in manuscript preparation.

ABBREVIATIONS

AcMe	acetone
Ac ₂ O	acetic anhydride
Bu ₂ O	dibutyl ether
diox	dioxane
DMF	dimethylformamide
Et ₃ N	triethylamine
GLC	gas-liquid chromatography
<i>i</i> -Pr ₂ O	diisopropyl ether
LFER	linear free energy relationships
MeViSiCl ₂	methylvinylchlorosilane
MTBE	methyl <i>tert</i> -butyl ether
Si(OEt) ₄	tetraethoxysilane
<i>t</i> -BuOLi	lithium <i>tert</i> -butoxide
THF	tetrahydrofuran

I. INTRODUCTION

The quantitative structure-reactivity analysis, based on linear free-energy relationships (LFER) and referred to as the correlation analysis, has been widely practiced in organic chemistry since pioneering works of Hammett [1] and Taft [2]. Besides the quantum chemical calculations and other complementary methods, the correlation analysis has still maintained its importance as a useful tool for investigating into reaction mechanisms and for prediction of rate and equilibrium constants [3–5].

In traditional organic chemistry, several protocols have been proposed for quantitative description of substituent effects in reactions taking place at the carbon atom or at its closest neighbors in the second period of elements [3–5]. However, the same substituent constants are commonly used also in correlation analysis of reactions, taking place at silicon or other atoms of elements of the third period of the periodic table. As the physical meaning of these correlations has often remained obscure, there was a clear need for their critical revision and for development of unequivocal LFER for reactions taking place at heteroatoms, including organometallic chemistry in general [6–8].

In this work, we have carried out a critical revision of quantitative data about reactivity of organosilicon compounds and compared this information with views stemmed from organic reactions at carbon atom. This analysis revealed that the classical resonance effect is insignificant in nucleophilic substitution reactions at the silicon reaction center, and the inductive effect of substituents must be expressed by two terms, involving one that describes electronegativity. Further, this analysis confirmed the original idea of Cartledge [9] that the E_s scale of steric parameters, suggested by Taft for substitution reactions at carbon atom, is not applicable for reactions taking place at silicon. We have revised the four sets of steric parameters, which were suggested for alkyl substituents in earlier works [8–12], and added some missing values into this list. It appeared that all these sets of steric parameters can be used for quantitative analysis of steric effects in organosilicon compounds. We also extended the $E_s(\text{Si})$ scale for several polar substituents, for which the data were not available hitherto.

In parallel with this theoretical analysis, we also launched practical investigations into quantitative aspects of the reactivity in the Grignard reaction with silanes. This reaction is a particular instance of nucleophilic displacement at silicon, since the Grignard reagent is one of the strongest nucleophiles applicable in common coupling reactions. A small number of kinetic studies of this reaction has been published before [13–20], however the structure-reactivity relationships for these data were analyzed for the first time in this study.

Further, we studied kinetics of the Grignard reaction with some alkoxy silanes and described kinetic mechanism of these reactions in terms of appropriate rate and equilibrium constants, and characterized the concurrent implication of steric and solvation effects in this process. These results supplemented other recent investigations in our laboratory, demonstrating that

replacement of diethyl ether by toluene significantly accelerated the reaction of alkylmagnesium halides with alkoxy silanes, while no effect has been found for the same reaction with chlorosilanes [13, 14, 16].

Besides the theoretical interest, this work was also motivated by its practical importance, emerging from technological application of the nucleophilic substitution reactions at silicon atom in production of silicones and monomeric organosilicon compounds, and from the needs of replacement of ether solvents by hydrocarbons of higher boiling points to meet the safety requirements of industrial application of the Grignard reaction.

2. STRUCTURAL EFFECTS IN ORGANOSILICON CHEMISTRY

2.1. General considerations

Distinction between steric and electronic (inductive) effects of substituents upon chemical and physical properties of organic compounds has been a generally recognized concept since their qualitative definition in pioneering works of Ingold. Later, this issue has a long history of theoretical and experimental studies and many protocols for quantitative separation of these effects have been suggested [3–5]. However, this work has been focused mainly on organic reactions taking place at the carbon reaction center.

Impact of meta- or para-substituted benzene derivatives on the reactivity of aromatic compounds is expressed by the Hammett equation [Eq. (1)] [1],

$$\log k = \log k_0 + \rho\sigma \quad (1)$$

where k_0 is the rate constant for the unsubstituted derivative and σ is the substituent constant and ρ is the reaction constant. The σ -constant includes both inductive and resonance effects (σ^0 is substituent constant for the inductive effect, determined from reactions in which the reaction center is incapable of conjugation with aromatic system), while ρ describes the susceptibility of the reaction to polar effects.

Effects of aliphatic substituents on the reactivity of organosilicon compounds have been described since long with the Taft equation [Eq. (2)] [6, 21, 22], where the two last terms express independent contributions from inductive and steric effects respectively [3, 4].

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_s \quad (2)$$

The σ^* -values measure the polar effects of substituents. However, there have been numerous contributions [3, 10, 23, 24] casting doubt on the status of σ^* -values for alkyl groups. As the main conclusion, it has been stressed that alkyl substituents do not exert any inductive effect and the σ^* -values of alkyl groups are treated as an artifact.

The Taft E_s scale of steric parameters has been derived from reactions at carbonyl group, and has been subjected to criticism from different viewpoints. Several authors [25, 26] have maintained that the Taft E_s parameters do not represent a complete separation of steric and polar effects and have attempted to improve the scale in various ways. Dubois et al. [27] have criticized the basic assumptions used in obtaining the Taft E_s scale and have proposed a revised and extended scale based on a single defining reaction. Sometimes, to be fitted in

with experimental data, the Taft equation has been extended with an additional structural effect referred to hyperconjugation [22].

Silicon chemists have mainly used substituent constants, defined from organic reactions at carbon atom [6, 21], although this has been questioned, especially for steric parameters [9], considering the greater length of C-Si bond as compared to C-C bonds. Therefore, at least some incompatibility of the Taft steric parameters could be expected in reactions at Si center.

Based on these suggestions, Cartledge [9] has defined a new set of steric parameters $E_S(\text{Si})$ for eight alkyl groups and for hydrogen proceeding from rates of acid-catalyzed hydrolysis of SiH compounds. Similar parameters have been proposed for reactions at the silicon center by other groups [8, 11, 12]. Rühlmann et al. [8, 12] applied a modified Taft scale fitted for silane reactions. Shimizu et al. [11] have analyzed this structural effect in nucleophilic displacement at silicon using the rates of solvolysis for triorganochlorosilanes. The $E_S(\text{Si})$ scale is also closely related to the scale ν' derived by Charton [10] from replacement reactions at sp^3 -carbon. The scale ν' was successfully applied in correlating reactivity data of alkyl substituted phosphorus compounds [28].

The major difference in the parameters derived from silicon compounds and those derived from carbonyl compounds (the scales by Taft or Dubois) is a greater effect of branching in α – position to the silicon center if compared with that in β – position. From this point of view, the steric parameters derived from reactions at carbon atom are not applicable in silicon chemistry.

Cartledge found that the steric effects were additive at silicon reaction center [9], which is not the case for organic reactions at carbon atom [3, 26]. Charton has concluded [10] that steric effects are more sensitive to reaction type than to the identity of the atom under attack and that a reaction involving expansion of coordination from four to five will show a different sensitivity to α and β branching than a reaction involving change of coordination from three to four.

In a great number of works reactivity data for silicon compounds have been correlated with Taft σ^* -constants (see review [22], and Refs. [29–31]). However, the authors never paid attention to a close correlation between σ^* and steric E_S parameters used in these calculations, characterized by $R = 0.865$, or even by $R = 0.950$, if Me –group is omitted from analysis. Thus, these correlations actually described the steric effects of alkyl substituents. In less numerous cases, where the two-parameter correlations including both σ^* and E_S constants were applied, the results were confused in an extent depending on the relative contribution of alkyl compounds in a reaction series. Anyhow, the physical meaning of such correlations remains obscure, and as already stressed by Cartledge [9], substantial amounts of structure-reactivity correlations in organosilicon chemistry need to be re-evaluated. Only Rühlmann's group has taken steps toward this goal [8], but the details of their results have not been published.

In this dissertation, we have undertaken systematic revision of literature data about reactivity of organosilicon compounds to ascertain the state-of-art in the

domain. Another objective of this work was to outline subsequently a general protocol for correlation analysis in organosilicon chemistry.

2.2. Steric effects of alkyl substituents

2.2.1. Steric parameters for correlation analysis

As mentioned above, several quantitative scales have been proposed for description of steric effects of alkyl substituents at silicon atom. At the same time, attempts to compose similar scales for polar substituents were entirely missing in literature. We filled this gap in this dissertation and extended the scale of steric parameters by including polar groups (see section 2.4). For this work, however, we had to re-evaluate also the steric parameters for alkyl substituents, as described below. For this analysis, we compiled and systematized available data about reactivity of silicon compounds with alkyl substituents as summarized in Table 1. Only reaction series with sufficient span of reaction rates and involving at least five different substituents were considered in our analysis. As is seen in Table 1, predominantly nucleophilic displacement reactions at silicon atom were available in literature. Alkyl substituents attached to the attacking nucleophiles have been varied in few papers [29, 32, 33] and in this study. The reaction series used in Cartledge work [9] (series X–XVII) also were included, providing comparison between the steric susceptibilities of the reactions. Series I–IX were previously not correlated with the $E_S(\text{Si})$ scale.

Chronologically, the first $E_S(\text{Si})$ scale for alkyl groups was created by Cartledge [9]. Although Cartledge was "reluctant to promote extensive use of a new set of parameters," the scale appeared to be as good as other sets under consideration (vide infra) and subsequently we compared other scales with that proposed by Cartledge. The available quantitative data concerning the reactivity of organosilicon compounds and the data for compounds with alkyl substituents were subjected to a correlation analysis with $E_S(\text{Si})$ parameters using a reduced Taft equation matched for silicon compounds,

$$\log k = a_0 + \delta E_S(\text{Si}) \quad (3)$$

where δ is the susceptibility factor for steric effects.

Table 1. Correlations of kinetic data with Cartledge steric parameters $E_S(\text{Si})$.

Reaction, solvent	n^a	δ^b	R^c	S^d
I. $\text{RMe}_2\text{SiCl} + \text{Me}_3\text{SiOLi}, \text{Et}_2\text{O}^e$	7 ^f	1.50 ± 0.30	0.911	0.184
II. $\text{RMe}_2\text{SiCl} + \text{PhMe}_2\text{SiOLi}, \text{Et}_2\text{O}^e$	6 ^{f,g}	1.23 ± 0.16	0.969	0.077
III. $\text{RMe}_2\text{SiCl} + \text{Me}_2\text{CHOLi}, \text{Et}_2\text{O}^e$	7 ^f	1.55 ± 0.11	0.989	0.064
IV. $\text{RMe}_2\text{SiCl} + \text{H}_2\text{O}, \text{H}_2\text{O}/\text{diox}^h$	8 ^f	2.28 ± 0.12	0.991	0.152
V. $\text{RSiCl}_3 + \text{Me}_3\text{SiOLi}, \text{Et}_2\text{O}^i$	7 ^f	1.54 ± 0.10	0.990	0.059
VI. RSiCl_3 acetolysis, Ac_2O^j	6	1.59 ± 0.19	0.973	0.082
VII. $\text{ROH} + \text{PhMe}_2\text{SiOH}, \text{HCl}/\text{diox}^k$	6	0.70 ± 0.07	0.981	0.030
VIII. $\text{RMgCl} + \text{MeViSiCl}_2, \text{Et}_2\text{O}$	5 ^l	1.04 ± 0.03	0.998	0.032
IX. $\text{RMe}_2\text{SiH} + \text{KOH}, \text{EtOH}/\text{H}_2\text{O}^m$	6	1.28 ± 0.06	0.996	0.028
X. $\text{R}_3\text{SiH} + \text{HCl}, \text{EtOH}/\text{H}_2\text{O}^n$	9 ^p	1.05 ± 0.02	0.998	0.058
XI. $\text{R}_3\text{SiH} + \text{KOH}, \text{EtOH}/\text{H}_2\text{O}^n$	10	1.82 ± 0.05	0.996	0.086
XII. $\text{R}_3\text{SiH} + \text{Br}_2, \text{DMF}^n$	8	0.44 ± 0.13	0.817	0.179
XIII. $\text{R}_3\text{SiH} + \text{O}_3, \text{CCl}_4^n$	10	-0.31 ± 0.04	0.928	0.133
XIV. $\text{R}_3\text{SiOph} + \text{OH}^-, \text{EtOH}/\text{H}_2\text{O}^n$	5	4.25 ± 0.15	0.998	0.156
XV. $\text{R}_3\text{SiOph} + \text{H}^+, \text{EtOH}/\text{H}_2\text{O}^n$	5	2.85 ± 0.17	0.995	0.177
XVI. $\text{R}_3\text{SiF} + \text{H}_2\text{O}, \text{H}_2\text{O}/\text{AcMe}^n$	5	1.91 ± 0.19	0.985	0.206
XVII. $\text{R}_3\text{SiH} + 1\text{-hexyne}, \text{THF}^n$	6	0.70 ± 0.16	0.907	0.123

^a Number of compounds in the correlation. ^b Regression coefficient. ^c Correlation coefficient. ^d Standard deviation of regression. ^e Ref. [8] ^f Point for *c*Hex used to correct the $E_S(\text{Si})$ value. ^g Point for Me removed. ^h Ref. [11] ⁱ Ref. [12] ^j Ref. [34] ^k Ref. [29] ^l Point for *s*Bu used to calculate the $E_S(\text{Si})$ value. ^m Ref. [35] ⁿ Ref. [9] ^p Reference series of Cartledge, corrected value of $E_S(\text{Si})$ for *c*Hex used.

Four sets of steric constants for alkyl substituents were listed in Table 2, namely $E_S(\text{Si})$ scale by Cartledge [9], v' parameters by Charton [10], E_S^{Si} constants by Shimizu et al. [11], and the set of steric constants $E_S(\text{R})$ by Rühlmann et al. [8].

Excellent correlations of series VIII with $E_S(\text{Si})$ and v' parameters enabled to calculate from our experimental data missing values of steric constants for *s*Bu group (for more details see our publication I).

It also appeared that the original $E_S(\text{Si})$ value for *c*Hex group was inaccurate. From series I and III–V a corrected value -0.66 ± 0.035 was obtained. Similarly, a correction for v' of Me-group equal to -0.124 ± 0.017 was found from series I and IV–VII. Further the scale of v' parameters was shifted to adjust the origin to methyl group. The improved sets of steric parameters were collected in Table 2. All the scales are in good correlations with each other, e.g. correlation coefficients for $E_S(\text{Si})$ vs. E_S^{Si} , $E_S(\text{R})$, and v' are equal to 0.991, 0.996, and 0.996, respectively. When remote points for H are involved, the

correlations are inferior, however, the correlation coefficients still exceed 0.90. For this reason, only results of correlations with $E_S(\text{Si})$ scale are shown in Table 1.

Table 2. Revised sets of steric substituent constants.

R	$-E_S(\text{Si})^a$	$-E_S^{\text{Si}^b}$	$-E_S(\text{R})^c$	ν^d
H	-1.12	-0.948	-1.00	-0.23
Me	0	0	0	0 ^e
Et	0.149	0.261	0.28	0.15
Pr	0.216	0.315	0.36	0.19
Bu	0.225	0.348	0.39	0.19
<i>i</i> Bu	0.405	0.400	0.55	0.32
<i>i</i> Pr	0.556	0.677	0.70	0.39
<i>c</i> Hex	0.66 ^c	0.757	0.79	–
<i>s</i> Bu	0.67 ^f	0.704	0.87	0.49 ^f
<i>t</i> Bu	1.46	1.670	–	1.00

^a Constants by Cartledge [9]. ^b Constants by Shimizu et al. [11] ^c Constants by Rühlmann et al. [8] ^d Charton parameters [10] adjusted to $\nu_{\text{Me}} = 0$. ^e Value corrected in this work (see text). ^f Calculated in Paper I.

Prevalence of good and excellent correlations in Table 1 gives an evidence that reactivity of these compounds is governed exclusively by steric influence of alkyl substituents. Likewise, additivity of the steric effects of different substituents in these reactions is obvious since parameters $E_S(\text{Si})$ defined for compounds with several alkyl groups in each molecule (series X and XI) [9] appeared to be successfully applicable to any other organosilicon reaction listed Table 1. This finding corroborates the suppositions made by Cartledge [9].

The results in Table 1 show that these reactions reveal a wide range of sensitivity against steric effect. Enhanced susceptibility against steric effect is clearly seen with sterically encumbered compounds. Moreover, interrelations between steric effect and reaction mechanism is also evident (cf., e.g. series III and IV, X and XI, or XIV and XV), giving promise of fruitful application of correlation analysis in organosilicon chemistry.

We concluded that the improved sets of steric parameters are practically equivalent and almost equally applicable for quantitative description of influence of alkyl substituents upon reactivity of organosilicon compounds. Statistical treatment of 17 reaction series confirmed clearly that alkyl substituents contribute to the reactivity of silicon compounds exclusively via their steric effects.

2.2.2. Steric effects in the Grignard reaction with silanes

The importance of steric effects in organosilicon chemistry has been stressed in many papers [21, 22, 36, 37], but attempts of quantitative description of these effects were not numerous [8, 9, 11, 12, 21, 22, 38] and this analysis has never been done for the Grignard reaction with organosilicon compounds. Therefore, we studied the steric effect of alkyl groups in reactions of Grignard reagents [39] with chlorosilanes and alkoxy silanes and correlated these kinetic data with the improved scale of the $E_S(\text{Si})$ parameters. This reaction was selected because only a small number of kinetic studies have been published about the Grignard reaction with silanes [13–20], and significant amount of these results has been produced in our laboratory [13–15, 20].

The kinetic experiments were made under the pseudo-first order conditions at excess of the Grignard reagent over the silane concentration [40], and alkyl substituents were varied in both reagents. For more experimental details, see Papers I and III. The rate constants obtained were collected in Table 3.

Table 3. First order rate constants ($k \times 10^4$, s^{-1}) for Grignard reactions with chlorosilanes, in diethyl ether at 20°C and corresponding substituent constants $E_S(\text{Si})$. Concentration of Grignard reagents 0.5 M.

R in RMeSiCl ₂ or RMgCl	EtMgCl	PhMgCl	MeViSiCl ₂	$E_S(\text{Si})^a$
Me	2.00	10.33	–	0
Et	–	7.58	0.917	–0.149
<i>n</i> Bu	0.618	–	0.800	–0.225
<i>i</i> Bu	0.467	5.72	0.492	–0.405
<i>i</i> Pr	0.157	4.17	0.400	–0.556
<i>s</i> Bu	0.123	–	0.272	–0.67
<i>t</i> Bu	–	–	0.040	–1.46
Vi	8.83 ^b	7.00 ^b	–	–
ClCH ₂	18.3 ^b	41.7 ^b	–	–
Cl	–	61.6 ^b	–	–
Ph	4.50	4.25	–	–
4-MePh	–	3.40	–	–
4-MeOPh	–	3.50	–	–
3-MeOPh	–	6.00	–	–
4-ClPh	–	11.3	–	–
3-ClPh	–	13.5	–	–

^a Steric constants by Cartledge [9] (see previous section). ^b Thermographic method.

These rate constants were analyzed by means of the reduced Taft equation (3), as described in section 2.2.1. It can be seen in Table 4 that in the case of selected reactions the rate constants correlated well with the $E_S(\text{Si})$ parameters. These correlations were also illustrated in Fig. 1. Results of our analysis corroborated the former suggestion that alkyl substituents contribute to the reactivity of silicon compounds exclusively via their steric effects.

Table 4. Correlations of rate data with Cartledge steric parameters $E_S(\text{Si})$.

Reaction ^a	n ^b	δ^c	R ^d
RMgCl + MeViSiCl ₂	6	1.04 ± 0.03	0.998
RMeSiCl ₂ + PhMgCl	4	0.64 ± 0.11	0.970
RMeSiCl ₂ + EtMgCl	5	1.81 ± 0.18	0.985

^a R = Alkyl, solvent Et₂O. ^b Number of compounds in the correlation. ^c Regression coefficient. ^d Correlation coefficient.

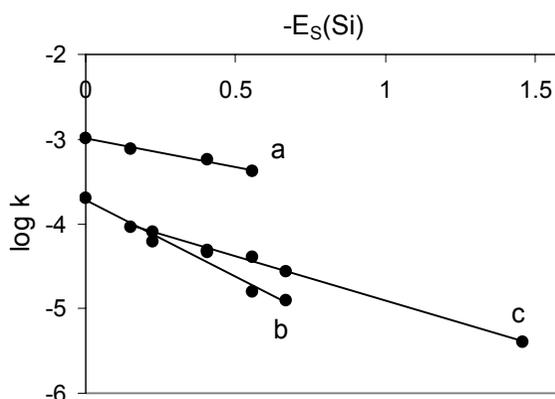


Figure 1. Correlation of rate data for the reactions between Grignard reagents and chlorosilanes with steric constants $E_S(\text{Si})$. (a) RMeSiCl₂ + PhMgCl, (b) RMeSiCl₂ + EtMgCl, (c) RMgCl + MeViSiCl₂.

The observed large dissimilarity between the steric effects in reaction series of PhMgCl and EtMgCl was somewhat unexpected, as such a great differences can hardly be explained merely by structural diversities between ethyl and phenyl groups. Provisionally, we tend to assign the extremely small steric influence in the reaction with phenylmagnesium chloride to a rather early transition state of the reaction. This assumption is consistent with the considerable nucleophilicity of the reagent and does not contradict a remarkable charge development in the transition state manifested by strong substituent effects of polar groups (cf. the data in Table 3). As a whole, these few

susceptibility parameters calculated from these Grignard reactions fit with the range of available δ values obtained for other reactions of organosilicon compounds discussed above (see previous section).

In the following part of this study, the rate constants for tetraethoxysilane reaction with RMgCl were determined in diethyl ether. Six Grignard reagents were involved to cover primary, secondary and tertiary alkyl groups. The pseudo-first order rate constants determined were listed in Table 5. For comparison, kinetic data for the corresponding reactions with chlorosilane were also included.

Table 5. Rate constants ($k \times 10^5$, s^{-1}) for the coupling reaction of silanes with alkylmagnesium chlorides, RMgCl, in diethyl ether at 20°C.

R	MeViSiCl ₂	Si(OEt) ₄	E _S (Si)
Et	9.17	1700 ^a	-0.149
<i>n</i> Bu	8.00	200	-0.225
<i>i</i> Bu	4.92	4.67	-0.405
<i>i</i> Pr	4.00	2.55	-0.556
<i>s</i> Bu	2.72	0.85	-0.67
<i>t</i> Bu	0.40	0.0147	-1.46

^a A rough estimation from previous data [20].

This reaction revealed remarkable sensitivity against steric effect if compared with that in reaction with methylvinylchlorosilane. To some extent, this could be referred to greater steric requirements of the substituents in alkoxy silane in comparison with the chlorosilane [20].

It can be seen in Fig. 2 that no linearity between logarithms of the rate constants for the reaction of alkylmagnesium chlorides with tetraethoxysilane and methylvinylchlorosilane exists. In general, this can be considered as an evidence of diverse reaction mechanisms [5]. Indeed, it has been found that the Grignard reaction with alkoxy silanes consists of replacement of a donor molecule at the magnesium center by the silane, followed by subsequent rearrangement of the complex to products through a four-center transition state, while chlorosilanes react differently without solvent molecule replacement [13, 14].

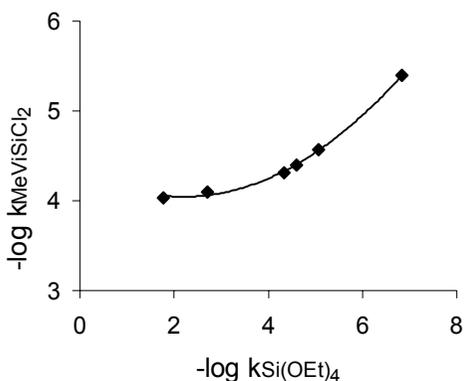


Figure 2. A LFE analysis of the reaction of alkylmagnesium chlorides with tetraethoxysilane and methylvinylchlorosilane.

Further the kinetic data for tetraethoxysilane were correlated with $E_S(\text{Si})$ parameters (Fig. 3). Differently of the reaction with chlorosilanes the data do not correlate in this case. However, the points lay well on two intersecting lines, pointing to the possibility of a change in reaction mechanism [5]. Validity of this conclusion, as well as details of the mechanisms under consideration, can only be elucidated by independent experiments.

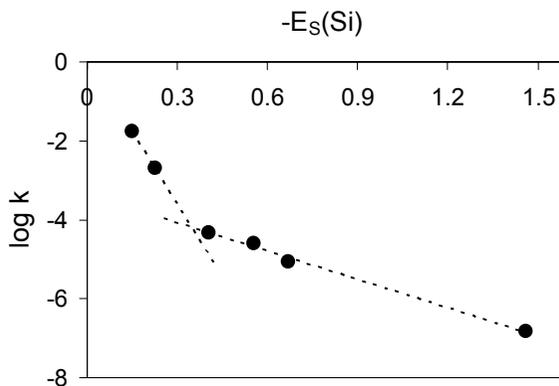


Figure 3. Correlation of rate data for the reaction with tetraethoxysilane with steric parameters $E_S(\text{Si})$.

In summary, results of our experiments confirm conclusions drawn in section 2.2.1, viz., that alkyl substituents govern reactivity of silicon compounds exclusively through their steric effects and the $E_S(\text{Si})$ scale of alkyl substituents is applicable for description of these steric effects in the Grignard reaction with silanes.

2.3. The resonance effect

Subsequently we exploited the Grignard reaction with chlorosilanes for testing the significance of the resonance effect of substituents, using correlation of kinetic data for the reaction of PhMgCl with substituted methylphenyldichlorosilanes by using σ° (the same reaction series as in section 2.2.2).

According with the current understandings [41], the polar effect can be divided into inductive and resonance components. In the conventional organic chemistry this issue has a long history and several protocols for quantitative separation of these effects have been suggested [3, 42]. In the case of silicon compounds, however, the participation of d-orbitals in these interactions has been a subject of continuing debates [22, 43, 44]. Theoretical studies of the $S_N2(\text{Si})$ reaction and pentacoordinate silicon intermediates or transition states show that d-orbitals are unlikely to have any significant involvement in the bonding in such species [43, 44]. Streitwieser et al. [45] found that bonds between Si and H, C, O, and F are extensively polarized with significant charge transfer. As a result of this effect, the Si-O and Si-F bonds should have dominating ionic interactions, and Si-H and Si-C bonds should have an importantly strong ionic character. As any resonance interaction require an overlap of p- and/or d-orbitals, this interaction should be considerably hindered at Si reaction center. As an unambiguous experimental test of these theoretical considerations, correlation of kinetic data for substituted phenylsilanes with σ° constants was implicated by Chvalovský et al. [46]. By definition [3], the σ° constants measure the inductive effect of substituted phenyl groups at the reaction center. A linear correlation with purely inductive σ° rules out the conjugation of substituents with the reaction center.

Table 6. First order rate constants for PhMgCl with methylphenyldichlorosilanes substituted in phenyl group, and corresponding substituent constants σ° .

R in RMeSiCl ₂	$k \times 10^4, \text{s}^{-1}$	σ° [3]
Ph	4.25	0
4-MePh	3.40	-0.15
4-MeOPh	3.50	-0.16
3-MeOPh	6.00	0.06
4-CIPh	11.3	0.27
3-CIPh	13.5	0.37

Correlation of these rate constants for the reaction between phenylmagnesium chloride and substituted methylphenyldichlorosilanes (data from Table 6) with σ° constants is shown in Fig 4. The regression coefficient $\rho^\circ = 1.12 \pm 0.10$ ($R = 0.985$) was found from this correlation. The good linear

interrelationship indicated that the contribution of the resonance effect of substituents could not be observed in this case. This conclusion was also confirmed by results of correlation of other published data listed in Table 7. Due to limited amount of available experimental data, this analysis included also reaction series consisting of three compounds. Taking together, all these results provided good evidence that the resonance effect of substituents at the silicon reaction center has negligible role, at least in nucleophilic substitution reactions occurring at this reaction center.

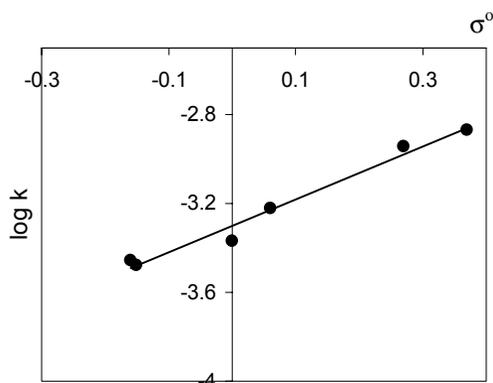


Figure 4. Correlation of rate data for the reaction between phenylmagnesium chloride and methylphenyldichlorosilanes substituted in phenyl group with inductive σ° constants.

Table 7. Correlation data for nucleophilic displacement reactions at the silicon center.

Reaction, Solvent	Induction effect		
	n^a	ρ°	R^b
I. $\text{RMe}_2\text{SiCl} + \text{Me}_3\text{SiOLi}, \text{Et}_2\text{O}$ [8]	3	0.73 ± 0.02	0.999
II. $\text{RMe}_2\text{SiCl} + \text{PhMe}_2\text{SiOLi}, \text{Et}_2\text{O}$ [8]	5	0.74 ± 0.09	0.976
III. $\text{RMe}_2\text{SiCl} + \text{Me}_2\text{CHOLi}, \text{Et}_2\text{O}$ [8]	3	1.11 ± 0.08	0.997
IV. $\text{RMe}_2\text{SiCl} + \text{H}_2\text{O}, \text{diox}$ [11]	3	1.20 ± 0.11	0.996
V. $\text{RSiCl}_3 + t\text{-BuOLi}, \text{Et}_2\text{O}$ [12]	5	1.02 ± 0.08	0.990
VI. RSiCl_3 acetolysis, Ac_2O [34]	6	1.85 ± 0.16	0.989
VII. $\text{RMe}_2\text{SiCl} + t\text{-BuOLi}, \text{Et}_2\text{O}$ [12]	5	0.83 ± 0.08	0.987
VIII. RMe_2SiH acidic solvolysis [47]	3	0.35 ± 0.04	0.994
IX. RMe_2SiH alkaline solvolysis [46]	6	2.41 ± 0.06	0.999
X. $\text{RMeSiCl}_2 + \text{PhMgCl}, \text{Et}_2\text{O}^c$	6	1.12 ± 0.10	0.985

^a Number of compounds in the correlation. ^b Correlation coefficient. ^c This work.

2.4. Steric effects of polar substituents

2.4.1. Calculation of steric constants

For alkyl substituents, appropriate scales of steric parameters have been developed for reactions at silicon atom and these data were discussed in section 2.2.1. However, this analysis has never been extended to cover steric effects of polar substituents at silicon atom. Therefore, we made an attempt to fill this gap.

This analysis was made proceeding from the fact that only inductive and steric effects are operating at the silicon reaction center, presented by Eq. (2) in section 2.1. In this analysis we used the σ^* constants introduced by Taft [3, 42] for polar aliphatic substituents, and the σ^o constants defined for substituted phenyl groups. A correlation for substituted phenyl groups with σ^o constants will give ρ^o parameter, which can be taken for ρ^* in Eq. (2), provided σ^* values for phenyl substituents are calculated as

$$\sigma^*(XC_6H_4-) = \sigma^o(XC_6H_4-) + \sigma^*(C_6H_5-).$$

Within a reaction series susceptibility to the steric effect (δ) can be determined from a variety of alkyl substituents.

Following these preparations Eq. (2) was rearranged for straightforward calculation of the novel parameters characterizing the steric interaction between polar substituents and silicon reaction center.

$$E_s(Si) = \frac{\log k - \log k_0 - \rho^* \sigma^*}{\delta} \quad (4)$$

Table 8. Correlation data for nucleophilic displacement reactions at the silicon center.

Reaction, Solvent	Induction effect			Steric effect		
	n ^a	ρ^o	R ^b	n ^a	δ	R ^b
I. RMe ₂ SiCl + Me ₃ SiOLi, Et ₂ O [8]	3	0.73 ± 0.02	0.999	7	1.59 ± 0.29	0.924
II. RMe ₂ SiCl + PhMe ₂ SiOLi, Et ₂ O [8]	5	0.74 ± 0.09	0.976	6	1.31 ± 0.16	0.971
III. RMe ₂ SiCl + Me ₂ CHOLi, Et ₂ O [8]	3	1.11 ± 0.08	0.997	7	1.62 ± 0.11	0.988
IV. RMe ₂ SiCl + H ₂ O, diox [11]	3	1.20 ± 0.11	0.996	8	2.30 ± 0.11	0.993
V. RSiCl ₃ + <i>t</i> -BuOLi, Et ₂ O [12]	5	1.02 ± 0.08	0.990	7	1.61 ± 0.09	0.992
VI. RSiCl ₃ acetolysis, Ac ₂ O [34]	6	1.85 ± 0.16	0.989	6	1.59 ± 0.19	0.973
VII. RMe ₂ SiCl + <i>t</i> -BuOLi, Et ₂ O [12]	5	0.83 ± 0.08	0.987	–	–	–
VIII. RMe ₂ SiH acidic solvolysis [47]	3	0.35 ± 0.04	0.994	–	–	–
IX. RMe ₂ SiH alkaline solvolysis [46]	6	2.41 ± 0.06	0.999	–	–	–
X. RMeSiCl ₂ + PhMgCl, Et ₂ O ^c	6	1.12 ± 0.10	0.985	4	0.64 ± 0.11	0.970

^a Number of compounds in the correlation. ^b Correlation coefficient. ^c This work.

Table 9. Calculated steric constants $E_S(\text{Si})$ for several polar substituents. Numeration of the reaction series is the same as in Table 8.

Substituent	I	II	III	IV	V	VI	X
Ph	-0.301	-0.356	-0.557	-0.683	-0.952	-1.45	-1.46
X-C ₆ H ₄ - ^a	-0.322	-0.368	-0.542	-0.658	-0.967	-1.39	-1.29
ClCH ₂ -	0.038	-0.028	-0.288	-0.313	-0.394	-	-0.64
Cl ₂ CH-	0.023	-0.003	-	-0.623	-0.724	-	-
BrCH ₂ -	-0.031	-0.105	-0.205	-	-	-	-
PhCH ₂ -	-0.538	-0.750	-0.489	-0.356	-0.293	-	-

^a Average value for substituted phenyl groups.

The reaction series for which this algorithm was applied were listed in Table 8 and the results of these calculations were summarized in Table 9. It can be seen in this Table that the obtained results varied significantly if different reaction series were compared. Therefore, the results obtained did not match with the context the procedure, used to calculate the $E_S(\text{Si})$ parameters. Further examination of these results led us to conclusion that the data cannot be described by means of a two-parameter equation [Eq. (2)], and probably one more variable is needed to unravel the structure-reactivity relationships in this particular field.

2.4.2. Complex nature of the inductive effect

As the simple algorithm used for calculation of steric constants for polar substituents has failed (see previous section), we considered this result as an indication of a more complex nature of the phenomenon. This was in agreement with the arguments discussed in more recent papers [48, 49]. These arguments have been focused on the principle that the genuine inductive effect can be observed only in the case substituents, which interact with a charged group. When both interacting structural fragments are less polar, the overall effect must be expressed by two terms. The second term might be small and its physical meaning is still unclear, however it has been related to electronegativity of the substituent [48, 49]. Note that this novel concept of the inductive effect stems from carbon chemistry, and if adopted for reactions at silicon atom, the proportions between the components of these two contributions need not remain the same. Secondly, this approach has never been applied to kinetic data. Nevertheless, we decided to test this approach in the case of organosilicon compounds.

Following the principles stated above, we used a two-term expression to describe the contribution of the inductive effect in Eq. (2), and obtained the following correlation equation for organosilicon reactions.

$$\log k_{rel} = \rho_I \sigma_I + \zeta \chi + \delta E_S(Si) \quad (5)$$

In Eq. (5), keeping the designations given by Exner and Böhm [48, 49], χ is the electronegativity and ζ is the corresponding reaction constant. Considering that for substituted phenyl groups, where substituent X stands in para or meta positions, we can use the approximations $E_S(Si)_{XPh} = E_S(Si)_{Ph}$ and $\chi_{XPh} \sim \chi_{Ph}$, the susceptibility constant ρ_I can be calculated as the slope of the $\log k_{rel}$ vs. σ_I plot (Fig. 5). The same plot provides an intercept equal to $\zeta \chi_{Ph} + \delta E_S(Si)_{Ph}$. Finally, if the δ value is calculated from the correlation of rate data for alkyl compounds, the reaction constant ζ and $E_S(Si)_{Ph}$ remain unknown.

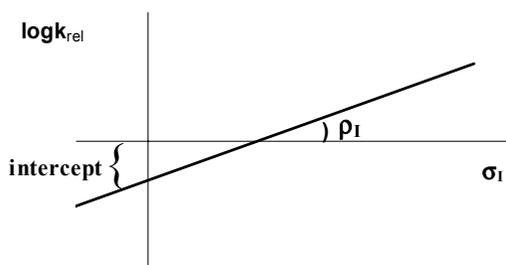


Figure 5. Graphical determination of ρ_I and the intercept [$\zeta \chi_{Ph} + \delta E_S(Si)$] from data for para- and meta-substituted phenyl compounds.

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 the inductive σ_I parameters from Ref. [50], the group electronegativities from Ref. [51], and the improved $E_S(Si)$ parameters from our paper II were employed [52]. In all 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 . The $E_S(Si)_{Ph} = -0.55$ was used on these calculations as the best approximation.

The $E_S(Si)$ values calculated for polar substituents together with available parameters for alkyl groups were collected in Table 10. It is obvious that these steric constants of polar groups are placed in plausible positions among those for alkyl substituents.

Table 10. Steric parameters for substituents in organosilicon compounds (Calculated values for polar groups are in bold).

Substituent	$-E_S(\text{Si})$	Substituent	$-E_S(\text{Si})$
Me	0	<i>i</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>i</i> Pr	0.56
<i>n</i> Pr	0.22	Ph	0.57 ± 0.02
<i>n</i> Bu	0.23	<i>c</i> Hex	0.66
ClCH₂	0.32 ± 0.11	sBu	0.67

^aDetermined from a single reaction series (Series IV in Table 11).

Table 11 lists the results of all correlations made according to Eq. (5). The reaction series I–V were used for calculation of the $E_S(\text{Si})$ values for polar groups (Table 10), and the series VI and VII were used for test of the method. The latter series is the reaction of PhMgCl with substituted methyl-dichlorosilanes (see section 2.2.2 and 2.3). These results confirm the validity of our novel approach to the quantitative structure-reactivity analysis in organosilicon chemistry.

Table 11. Results of correlations according to Eq. (5).

Reaction	ρ_I^a	ζ^a	δ^a	n^b	R^b	S^b	ζ/ρ_I
I. ^c	7.51(0.59)	-0.05(0.48)	1.57(0.19)	15	0.982	0.133	-0.01
II. ^d	7.25(0.49)	0.61(0.34)	1.61(0.16)	16	0.987	0.110	0.09
III. ^e	7.34(0.25)	-0.72(0.20)	1.56(0.08)	15	0.996	0.056	-0.10
IV. ^f	8.69(0.70)	-2.51(0.24)	2.28(0.12)	16	0.989	0.154	-0.29
V. ^g	7.48(0.99)	-3.95(0.68)	1.39(0.21)	15	0.958	0.140	-0.53
VI. ^h	15.7(2.1)	-8.6(1.3)	1.59(0.23)	11	0.976	0.099	-0.54
VII. 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. (5), standard deviations are in parenthesis. ^b Number of compounds, correlation coefficient, and standard deviation from the regression, respectively. ^c Reaction $\text{RMe}_2\text{SiCl} + \text{Me}_3\text{SiOLi}$ [8]. ^d Reaction $\text{RMe}_2\text{SiCl} + \text{PhMe}_2\text{SiOLi}$ [8]. ^e Reaction $\text{RMe}_2\text{SiCl} + \text{Me}_2\text{CHOLi}$ [8]. ^f Reaction $\text{RMe}_2\text{SiCl} + \text{H}_2\text{O}$ in dioxane [11]. ^g Reaction $\text{RSiCl}_3 + t\text{-BuOLi}$ [12]. ^h Acetolysis of RSiCl_3 [34]. ⁱ Reaction $\text{RMeSiCl}_2 + \text{PhMgCl}$ (this work).

The last column in Table 11 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 I–III the effect of electronegativity is almost negligible, in the case of stronger nucleophiles (series IV, VII) or in reaction of di- or trichlorosilanes (series V–VII) its contribution is considerable. However, the physical meaning of the rate decreasing effect of electronegativity still remains obscure, as it was left open by Exner and Böhm [48, 49]. Supposedly, the electronegativity term in Eq. (5) can be considered a correction factor for the inductive constants derived in organic chemistry.

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

3. SOLVENT EFFECTS IN THE GRIGNARD REACTION WITH ALKOXYSILANES

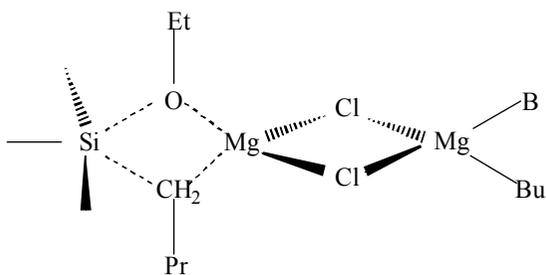
A comprehensive kinetic investigation of the Grignard reaction with silanes was extended in our laboratory to elucidate the relationships between Grignard reagent solvation and its reactivity [13–16], since solvation effects have decisive role in this reaction [53]. Besides theoretical interest, this research was strongly motivated by practical needs, as the use of conventional Grignard reagents in ether solutions in large-scale organomagnesium syntheses in industry is hazardous [39]. Therefore, the replacement of readily flammable solvents by those of high boiling points is desirable. Replacement of highly volatile and flammable ethers with hydrocarbon solvents offers also other advantages since they are cheap and non-hygroscopic. Employment of toluene as a solvent is also important environmentally.

Replacement of diethyl ether by toluene significantly accelerated the reaction with alkoxy silanes, while no effect was found in the reaction with chlorosilanes [13, 14]. It has been established that the reaction with alkoxy silanes consists of replacement of a donor molecule at the magnesium center by the silane, and is followed by subsequent rearrangement of the complex to products through a four-center transition state [13, 14]. For detailed insight into the mechanism of this process, particularly for a quantitative description of the structure-reactivity relationships as well as solvent effects, the appropriate rate and equilibrium constants are required.

In one recent publication from our laboratory [14], an appropriate method for separation of equilibrium and rate constants was fleetingly suggested (see next section). In this work, we applied this method to examine involvement of steric and solvation effects in the Grignard reaction with alkoxy silanes. This method has also been exploited successfully for investigating the Grignard reaction with diisopropyl ketone (more details in Paper IV).

3.1. The method for separation of equilibrium and rate constants

This method is based on understanding that the reaction proceeds through complexation of the Grignard reagent with silane, which replaces the donor molecule (commonly ether) bound at the magnesium centre. Subsequently, this complex is involved in formation of the reaction products through a four-centre transition state (Scheme 1) [13, 14].



Scheme 1. Transition state for the reaction of *n*-butylmagnesium chloride with an alkoxy silane. B stands for the donor molecule.

As alkylmagnesium chlorides exist essentially as dimeric species, which are stable over a wide concentration range [40], the overall reaction scheme can be presented as follows:



where G denotes magnesium compound, S silane, and E is an ether molecule, $(GE)_2$ is the dimeric monosolvated Grignard reagent, and G_2ES is the substitution complex. The parameters K and k are the equilibrium and rate constants, respectively.

In the presence of an excess of Grignard reagent, the reaction sequences (6) and (7) should follow the first order rate equation under steady-state conditions. From these kinetic data, the pseudo-first order rate constant k_{obs} can be calculated. Assuming that the complex formation step (6) is a fast equilibrium and concentration of the free ether is negligible, the following equation can be derived for the observed rate constant k_{obs} :

$$k_{\text{obs}} = \frac{kK[G]}{1+K[G]}. \quad (8)$$

This equation can be converted into the following linear form:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{1}{kK[G]}. \quad (9)$$

which can be used for data processing in coordinates $1/k_{\text{obs}}$ vs. $1/[G]$ and provides illustrative possibility for validation of the presumptions made above about the reaction mechanism (an example in Fig. 6). An important advantage of the method consists also in absence of non-specific solvation effects, while specific solvation effects of donor solvents are considered.

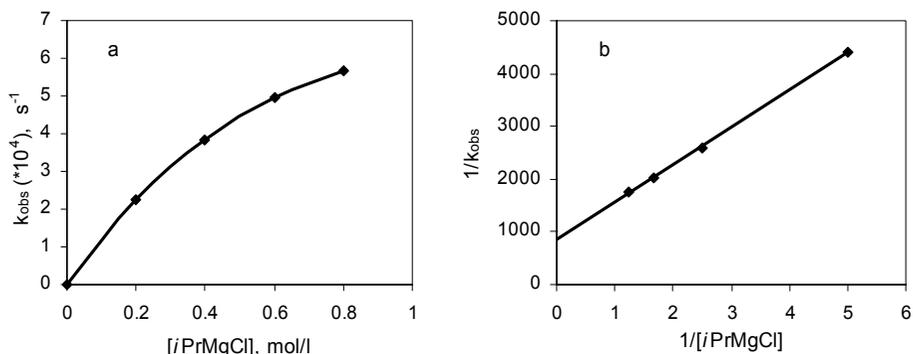


Figure 6. (a) Pseudo-first order rate constants k vs. the titrated concentration of *i*-PrMgCl-Et₂O complex for the reaction with tetraethoxysilane in toluene at 20°C. (b) Determination of the equilibrium constant (K) and rate constant (k).

3.2. Results of experiments with monosolvated Grignard reagents

Kinetics of alkoxy silane reactions with Grignard reagents, specifically solvated with various ethers, was studied in toluene. In separate experiments, thermodynamic parameters were determined for rate and equilibrium constants, measured for the reaction of tetraethoxysilane with *n*-butylmagnesium chloride solvated with dibutyl ether in toluene, and also in bulk dibutyl ether (for more details see IV).

For kinetic measurements of fast reactions, a thermographic method was used. In the case of slow reactions the composition of reaction products was determined by means of GLC. In all experiments only the first replacement at the silicon center was observed, because the further substitutions were extremely slow. Yields of the syntheses of monosolvated reagents were well reproducible considering the complexity of this experiment (for more details see papers IV and VI).

Concentrations of the monosolvated Grignard reagents changed from 0.15 M to 1.0 M and the exact values were determined by titration. As alkylmagnesium chlorides are essentially in dimeric form [40], the actual concentration range of the reacting species was two times smaller than the titrated concentration. The pseudo-first order rate constants determined at a great excess of Grignard

reagent were used for separation of the appropriate equilibrium and rate constants. Measurements were made at 20°C, but also at 30°C and 40°C when the thermodynamic parameters were determined [IV]. The rate constants measured with solutions from different batches were in excellent agreement between different experiments. Determinations of rate and equilibrium constants were carried out at least in duplicate.

3.2.1. Variation of donor solvents

Kinetics of tetraethoxysilane reaction with *n*-butylmagnesium chloride, stoichiometrically monosolvated with dibutyl ether, diethyl ether, THF, isopropyl ether, methyl *tert*-butyl ether, and triethylamine, was studied in toluene. The results are collected in Table 12.

Table 12. Rate and equilibrium constants for the reaction^a of tetraethoxysilane with monosolvated *n*-butylmagnesium reagents in toluene at 20°C.

Grignard reagent	K, L·mol ⁻¹	k, s ⁻¹
<i>n</i> -BuMgCl·THF ^b	0.40 ± 0.10	0.12 ± 0.03
·Et ₂ O ^c	1.22 ± 0.19	0.31 ± 0.05
·Bu ₂ O ^c	3.30 ± 0.66	0.33 ± 0.05
·MTBE ^{c,d}	3.95 ± 0.19	0.13 ± 0.01
· <i>i</i> -Pr ₂ O ^c	6.15 ± 0.31	0.10 ± 0.01
·Et ₃ N ^b	0.76 ± 0.06	(1.70 ± 0.13) × 10 ⁻³

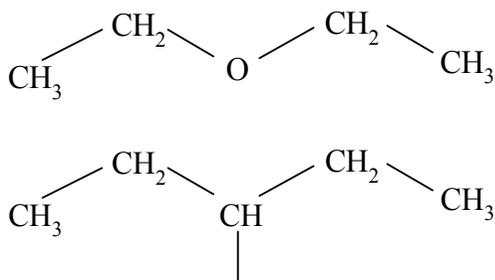
^a Si(OEt)₄ + BuMgCl → BuSi(OEt)₃ + EtOMgCl. ^b A GLC method was used. ^c Thermographic method was used. ^d Methyl *tert*-butyl ether.

According to Eq. (6) the equilibrium constants K should reflect the solvating ability of donors, the strongest of them shifting the equilibrium most to the left. As the Broensted basicities of used ethers are practically similar [54], their solvating power (Lewis basicity) should be determined solely by their steric effect. Indeed, the equilibrium constants aligned well in line with the presumable steric properties of the ethers. Triethylamine is largely stronger Broensted base than the used ethers, however, its great steric requirements evidently lead to a moderate solvating power.

On the other hand, the rate constants k varied relatively little with variation of the donor ethers. This can be explained by the remote positioning of the retained donor molecule in the transition state of the reaction (see Scheme 1 in section 3.1).

In order to quantify the structure-reactivity relations for the equilibrium (6), logarithms of the equilibrium constants were contrasted with corresponding

isosteric constants in Table 13. The ethers were considered as substituents at the magnesium center and following the principle of isostericity the oxygen atom of the ether was taken to be equivalent to CH-group in the corresponding alkyl substituents, as shown in Scheme 2.



Scheme 2. Ethyl ether and the corresponding isosteric 3-pentyl group.

Table 13. Logarithms of the equilibrium constants from Table 12 and the corresponding isosteric constants.

Ether ligand	log K	$-E_S^{\prime a}$	$-E_S(\text{Si})^b$
THF	-0.40	0.41	0.66 ^c
Et ₂ O	0.086	2.00	0.78
Bu ₂ O	0.52	2.08	0.87
MTBE	0.60	3.21	0.98
<i>i</i> -Pr ₂ O	0.79	5.01	0.99

^a Constants from Ref. [27]. ^b Calculated in this work (see text). ^c Approximated with *cyclo*-hexyl group (from Paper II).

The appropriate constants E_S^{\prime} were taken from the revised and extended analysis by Dubois et al. [27], made by default for carbon compounds. The corresponding isosteric $E_S(\text{Si})$ constants were not available in literature. However, extensive kinetic data for the hydrolysis of alkyldimethylchlorosilanes published by a Japanese group [11] and their unexpectedly good additive scheme for calculation of the missing rate data [55] enabled us to obtain the rate constants for silanes with the required alkyl substituents. Further, excellent correlation for alkyl substituents from the same reaction with $E_S(\text{Si})$ scale and a significant susceptibility of the reaction to steric effects permitted calculation of the values of the isosteric constants listed in Table 13.

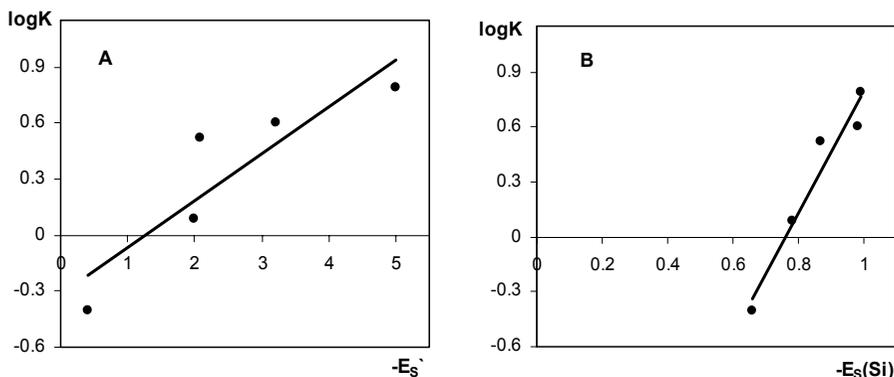


Figure 7. Correlation of equilibrium constants with isosteric parameters E_S' (A) and $E_S(\text{Si})$ (B).

As seen in Fig. 7 correlation of the equilibrium constants with the isosteric E_S' parameters was hardly satisfactory ($R^2 = 0.804$), while $E_S(\text{Si})$ constants provided an excellent correlation ($\delta = -3.34 \pm 0.45$; $R^2 = 0.950$). Thus, the steric effect of substituents on the reaction of ligand replacement taking place at this center can be reliably expressed by $E_S(\text{Si})$ constants.

One can conclude that the $E_S(\text{Si})$ scale of steric parameters, derived from organosilicon chemistry, proved to be pertinent in case of organomagnesium compounds and this seems to be true also for organophosphorus compounds (in form of the equivalent ν' scale) [28]. Thus, it is greatly plausible that these constants are inherent to all of the third period of elements.

3.2.2. Variation of steric requirements in Grignard reagents and in alkoxy silanes

In this study, variation in structure of both reagents was made. Kinetics of tetraethoxysilane reaction with *n*-butylmagnesium chloride, specifically solvated with diethyl ether, was studied in toluene. In addition, isopropylmagnesium chloride and isopropyltriethoxysilane were involved in a similar investigation. Some of these structural alterations had rather significant effect on reactivity of these compounds.

It was observed (Table 14) that replacement of the *n*-butyl group by isopropyl in the Grignard reagent increases the equilibrium constant by a factor of two in accordance with increasing hindrance to coordination with the donor.

Table 14. Rate and equilibrium constants for reactions of ethoxysilanes with monosolvated alkylmagnesium chlorides^a in toluene at 20°C.

Silane ^b	Grignard reagent ^c	K, L·mol ⁻¹	k, s ⁻¹	Method ^d
Si(OEt) ₄	<i>n</i> -BuMgCl·Et ₂ O	1.22 ± 0.19	0.31 ± 0.05	B
	<i>i</i> -PrMgCl·Et ₂ O	2.40 ± 0.08	(1.17 ± 0.04) × 10 ⁻³	A
<i>i</i> -PrSi(OEt) ₃	<i>n</i> -BuMgCl·Et ₂ O	0.8 ± 0.2	(2.2 ± 0.4) × 10 ⁻³	A

^a Si(OEt)₄ + RMgCl → RSi(OEt)₃ + EtOMgCl. ^b Initial concentration of silane in method B 0.015 M, in method A 0.01 M to 0.10 M. ^c Initial concentration from 0.2 M to 1.0 M.

^d Method A is the GLC method, Method B is the thermographic method.

An increase in the bulkiness of the silane has smaller effect, but still shifting the equilibrium in the expected direction. However, the steric effects upon the rate of the reaction are more impressive. Replacement of an ethoxy group by isopropyl in silane molecule, and particularly the substitution of alkyl groups in the Grignard reagent, leads to a decrease in rate constants by more than two powers of ten.

In conclusion, we have elaborated an experimental method for determination of rate and equilibrium constants for the Grignard reaction with alkoxy silanes, and these parameters were determined for several sets of reactants. The results obtained constitute a self-consistent and adequate set of kinetic parameters, remaining in good agreement with the expected physical meaning of the process, involving fast complex formation before the reaction step. Most probably this kinetic method can be extended to other Grignard reactions, in which the reaction step is also preceded by complex formation, consisting of replacement of the donor molecule at the metal atom.

4. CONCLUSIONS

1. Structure-reactivity relationships in reactions at silicon and carbon atoms revealed the following differences:
 - the conventional scale of steric parameters E_S is not applicable for silicon compounds,
 - the resonance effect is insignificant in the S_N reactions at the silicon center,
 - the inductive effect of substituents at silicon atom must be expressed by two terms, involving one that describes electronegativity.
2. Statistical treatment of kinetic data for 17 reaction series of organosilicon compounds revealed that:
 - alkyl substituents contribute to the reactivity of silicon compounds exclusively through steric influence,
 - the steric effects of alkyl groups at silicon atom are additive,
 - the scale of steric parameters $E_S(\text{Si})$ for alkyl groups was extended for polar substituents at silicon center.
3. From kinetic data for the Grignard reaction with silanes:
 - excellent correlations of the rate data with steric constants $E_S(\text{Si})$ were obtained for reactions of chlorosilanes,
 - linear correlations with break point were obtained for the tetraethoxysilane reaction, referring to the change in the reaction mechanism.
4. Kinetics of the reaction between monosolvated Grignard reagents and tetraethoxysilane was studied and:
 - kinetic method for separation of the rate and equilibrium constants was elaborated for the two-step reaction, where the reaction step was preceded by formation of a coordination complex.
5. It was found that the parameters $E_S(\text{Si})$ derived from organosilicon chemistry were applicable in case of organomagnesium compounds and also with organophosphorus compounds. Thus, these constants may be inherent to all elements of the third period.

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SUMMARY IN ESTONIAN

Kvantitatiivne struktuuri-reaktsioonivõime analüüs räniorgaanilises keemias

Käesolevas töös tegeleti struktuuriefektide uurimisega räniorgaaniliste ühenditega toimuvates reaktsioonides korrelatsioonanalüüsi meetodil, mis annab võimaluse ennustada tasakaalu- või kiiruskonstante ning välja selgitada reaktsioonimehhanismi detaile.

Elkõige vaadati üle räniorgaaniliste ühendite reaktsioonivõime andmed ja töödeldi olemasolevat andmestikku korrelatsioonivõrrandite meetodil, mille tulemusena selgus, et Tafti steerilised konstandid E_S , mis on määratud süsiniku tsentris toimuvatest reaktsioonidest, ei sobi steeriliste efektide kirjeldamiseks ränitsentri juures toimuvates reaktsioonides, resonantsiefekt on ebaoluline vähemalt ränitsentri juures toimuvates nukleofiilsetes asendusreaktsioonides ning asendusrühmade induktsiooniefekti tuleb kirjeldada kahe liikmega, kaasates ka liikme, mis iseloomustab asendaja elektronegatiivsust.

Samuti täiendati ja parandati olemasolevaid alküülrühmade steeriliste konstantide skaalasisid, mille tulemusena saadi neli praktiliselt ekvivalentset alküülühmade steeriliste parameetrite skaalat, mis kirjeldavad kvantitatiivselt alküülrühmade mõju ränitsentris toimuvatele reaktsioonidele. 17 reaktsiooni-seeria statistiline töötlus näitas, et alküülrühmad avaldavad mõju reaktsioonivõimele ainult steeriliste efektide kaudu ning steerilised efektid on räniorgaanilistes reaktsioonides aditiivsed.

Järgnevalt sai laiendatud Cartledge konstantide skaalat $E_S(\text{Si})$ ka polaarstele asendajatele, mille kohta kirjanduses andmed puuduvad. Seega on meil nüüd võimalik uurida struktuuriefekte korrelatsioonanalüüsi meetodil ränitsentri juures toimuvates reaktsioonides, kasutades sobivaid parameetrite skaalasisid.

Peale selle tegeletakse meie grupis Grignard'i reaktiivi ja silaanide vahelise reaktsiooni struktuuriefektide uurimisega. Käesolevas töös korreleeriti saadud kineetilisi andmeid Cartledge $E_S(\text{Si})$ parameetritega, mis näitas, et skaala kirjeldab alküülrühmade steerilist toimet ka Grignard'i reaktiivi ja silaanide vahelistes reaktsioonides. LFE analüüsi abil tuli ilmsiks Grignard'i reaktiivi reaktsioonis tetraetoksüsilaaniga, et steerilise takistuse kasvades valib reaktsioon teise tee, mis on vähem tundlik steerilistele efektidele.

Grignard'i reaktiivi ja silaanide vaheliste reaktsioonide kineetika uurimist oleme laiendanud ka solvendi efektide uurimisele keskendudes käesolevas töös eeskätt sellele, kuidas mõjutab solvent monosolvateeritud Grignard'i reaktiivi reaktsioonivõimet reaktsioonides alkoksüsilaanidega. Solvendi efektide uurimiseks sai välja töötatud meetod, mis võimaldab Grignard'i reaktsioonis alkoksüsilaanidega tasakaalu- ja kiiruskonstante eraldi määrata. Saadud tasakaalu- ja kiiruskonstandid alkoksüsilaanide reaktsioonis monosolvateeritud Grignard'i reaktiividega olid kooskõlas füüsikalise arusaamaga antud protsessist, kus enne reaktsiooni toimub komplekseerumine, mille käigus toimub

Grignard'i reaktiivi magneesiumtsentri juures doonormolekuli asendumine silaani molekuliga.

Monosolvateeritud Grignard'i reaktiivi ja tetraetoksüsilaani vahelise reaktsiooni solvendiefektide uurimisel selgus, et alküülrühmade steeriliste konstantide skaala $E_S(\text{Si})$, mis on määratud räni tsentri juures toimuvatest reaktsioonidest on kasutatav ka magneesium- ja fosfororgaaniliste ühendite juures. Seega tõenäoliselt on need parameetrid rakendatavad kõigile kolmanda perioodi elementidele.

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Konverentsid

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