

Steric effects of alkyl substituents in silicon chemistry

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Dedicated to Professor Edmunds Lukevics on his 70th birthday

Abstract

Reactivity data for a number of reactions taking place at Si atoms in organosilicon compounds containing a variety of alkyl groups have been examined for statistical correlations with steric parameters. Four practically equivalent sets of parameters are now available for quantitative description of steric effects of alkyl substituents in organosilicon compounds. Alkyl substituents contribute to the reactivity exclusively with their steric effects. Steric effects in silicon compounds are additive.

Keywords: Correlation analysis, silicon compounds, steric effects, substituent constants

Introduction

To correlate structural effects with chemical and physical properties it is necessary to differentiate between steric and electronic effects in relation to a property. In traditional organic chemistry this issue has a long history and protocols for quantitative separation of the effects are available,¹⁻⁴ however, in organometallic chemistry a general and unequivocal approach still needs to be developed.^{5,6}

The importance of steric effects in organosilicon chemistry has always been stressed⁷⁻¹⁰ and several attempts of quantitative description of the effects have been done.^{8,10-14}

Effects of aliphatic substituents on the reactivity of organosilicon compounds have been described since long with the Taft equation (Eq.1),^{8,10} where the two last terms express the independent contributions from polar (inductive) and steric effects respectively.^{1,3}

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_s \quad (1)$$

The σ^* -values measure the polar effects of substituents. However, there have been numerous contributions^{2,3,15,16} 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 an artifact.

Also the Taft E_s scale of steric parameters has been subjected to criticism from different viewpoints. Several authors^{17,18} 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.¹⁹ 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.

Silicon chemists have mainly used correlations for which the substituent constants have been defined in organic reactions.^{5,8,10} However, the steric parameters derived from reactions of organic carbonyl compounds have been moderately suitable for description steric effects in reactions taking place at Si atoms. Considering the greater length of C-Si as compared to C-C bonds some incompatibility of Taft type scales with reactions at Si center could be expected.

Cartledge¹¹ defined a set of $E_s(\text{Si})$ parameters for eight alkyl groups and for H from rates of acid-catalyzed hydrolysis of SiH compounds. For eight reaction series the correlation with $E_s(\text{Si})$ was better or comparable with these where Taft type constants were involved. The Cartledge scale of $E_s(\text{Si})$ constants appeared to be in a good correlation with ν' parameters derived by Charton²⁰ for correlation of the nucleophilic substitution at four-coordinate carbon.

Shimizu et al.¹² have proposed a quantitative scale for the structural effect on reactivity toward nucleophilic displacement at silicon using the rates of solvolysis for triorganochlorosilanes. The steric constants E_s^{Si} by Shimizu et al. for alkyl groups correlate with Cartledge $E_s(\text{Si})$ constants as well as with ν' parameters by Charton. Rühlmann et al.^{13,14} apply a modified Taft scale fitted for silane reactions.

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 than that of branching in β -position. Cartledge found the steric effects in silicon reactions to be additive.¹¹ Interestingly, this is not the case for organic reactions.^{3,18} Charton has concluded²⁰ 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, e.g. at carbonyl carbon.

In a great number of works reactivity data for silicon compounds have been correlated with Taft σ^* -constants (see review,¹⁰ and refs.²¹⁻²³). However, the authors never paid attention to a close correlation between σ^* and steric E_s constants ($R = 0.865$, or without Me-group $R = 0.950$). Thus, the correlations actually described the steric effects of alkyl substituents. In less numerous cases, where alkyl and polar groups were involved and two-parameter correlations including both σ^* and E_s constants were applied, the results are confused in an extent depending on the relative contribution of alkyl compounds in a reaction series. Anyhow, the physical sense of such correlations remains obscure. Therefore, as already stressed by Cartledge,¹¹ substantial amounts of reactivity data in organosilicon chemistry need to be reexamined and reinterpreted. So far, this

is only Rühlmann group which has taken steps toward this goal,¹³ however, details of the work have not been published.

We have undertaken a revision of quantitative literature data for the reactivity of organosilicon compounds in order to ascertain the state-of-art in the domain and to outline subsequently a general protocol for correlation analysis in organosilicon chemistry. In this work we confine ourselves to steric effects of alkyl substituents. A reliable quantitative description of the reactivity of alkyl compounds is necessary for further separation of polar and steric effects in silicon chemistry.

Results and Discussion

As mentioned above, several quantitative scales have been proposed for description of steric effects by alkyl substituents on organosilicon compounds. Chronologically, the first among them is the $E_s(\text{Si})$ scale by Cartledge.¹¹ 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 compare other scales with that proposed by Cartledge.

Only reaction series with a sufficient span of reaction rates and involving at least five different substituents were considered in our analysis. As is seen in Table 1 the reactions are predominantly nucleophilic displacements at silicon atom. Alkyl substituents in attacking nucleophiles have been varied in few works.²³⁻²⁶ Two of them are involved in Table 1. Also the reaction series used in Cartledge work¹¹ X-XVII are included to provide a comparison between the steric susceptibilities of the reactions. Series I-IX were primarily not correlated with the $E_s(\text{Si})$ scale.

Four sets of steric constants for alkyl substituents were considered, namely $E_s(\text{Si})$ scale by Cartledge,¹¹ v' parameters by Charton,²⁰ E_s^{Si} constants by Shimizu et al.,¹² and the set of steric constants $E_s(\text{R})$, by Rühlmann et al.¹³

Excellent correlations of series VIII with $E_s(\text{Si})$ and v' parameters²⁶ enabled to calculate missing values of steric constants for *s*-Bu group (Table 2). It appeared that the original $E_s(\text{Si})$ value for *c*-Hex group was inaccurate. From series I and III-V a corrected value -0.687 ± 0.031 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. The improved sets of steric parameters are collected in Table 2. All the scales are in good correlations with each other, e.g. $E_s(\text{Si})$ for alkyl groups has correlation coefficients with E_s^{Si} , $E_s(\text{R})$, and v' equal to 0.991, 0.996, and 0.996 respectively. When remote points for H are involved, the correlations are slightly 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.

Prevalence of good and excellent correlations in Table 1 is an evidence of exclusively steric effects of alkyl substituents. Likewise, additivity of the steric effects is obvious since parameters $E_s(\text{Si})$ defined¹¹ from experimental data for compounds with several different or

multiple alkyl groups in each (series X and XI) appeared to be successfully applicable to any organosilicon reaction in Table 1 thus corroborating the supposition by Cartledge.¹¹

The results in Table 1 show a great diversity of susceptibilities to steric effects. Applicability of this kind of correlation analysis to such a wide range of mechanistically distinct reactions is impressive. In the absence of reliable quantitative data for polar effects on the reactions an extensive analysis of structure-reactivity relationships involving polar substituents seems to be premature. However, enhanced susceptibility of reactions with sterically encumbered compounds is obvious. Also, interrelations between reaction mechanisms and steric effects are evident (cf., e.g. series III and IV, X and XI, or XIV and XV), thus giving promise of fruitful application of correlation analysis in organosilicon chemistry.

Table 1. Correlations of rate 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. $\text{R}_3\text{SiOPh} + \text{H}^+, \text{EtOH}/\text{H}_2\text{O}^n$ | 5 | 2.85 ± 0.17 | 0.995 | 0.177 |
| XV. $\text{R}_3\text{SiOPh} + \text{OH}^-, \text{EtOH}/\text{H}_2\text{O}^n$ | 5 | 4.25 ± 0.15 | 0.998 | 0.156 |
| 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 |

^aNumber of compounds in the correlation. ^bRegression coefficient. ^cCorrelation coefficient.

^dStandard deviation of regression. ^eRef.¹³ ^fPoint for *c*-Hex used to correct the $E_s(\text{Si})$ value.

^gPoint for Me removed. ^hRef.¹² ⁱRef.¹⁴ ^jRef.²⁷ ^kRef.²³ ^lPoint for *s*-Bu used to calculate the $E_s(\text{Si})$ value. ^mRef.²⁸ ⁿRef.¹¹ ^pReference series of Cartledge, corrected value of $E_s(\text{Si})$ for *c*-Hex used.

Table 2. Revised sets of steric substituent constants

| R | $-E_s(\text{Si})^a$ | $-E_s^{\text{Si}^b}$ | $-E_s(\text{R})^c$ | v^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 | 0.69 ^e | 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 |

^aConstants by Cartledge.¹¹ ^bConstants by Shimizu et al.¹² ^cConstants by Rühlmann et al.¹³

^dCharton parameters²⁰ adjusted to $v_{\text{Me}} = 0$. ^eValue corrected in this work (see text). ^fCalculated in ref.²⁶

Conclusions

Available quantitative literature data concerning the reactivity of organosilicon compounds were collected and the data for compounds with alkyl substituents were subjected to a correlation analysis. Four sets of steric constants for alkyl substituents of silicon compounds were considered. Some missing values were calculated and several corrections were made. It appears that the improved sets of parameters are practically equivalent and almost equally applicable for quantitative description of steric effects exerted by alkyl substituents upon the reactivity of organosilicon compounds. Statistical treatment of 17 representative reaction series lead to results corroborating former suppositions that (i) alkyl substituents contribute to the reactivity exclusively with their steric effects, and (ii) steric effects in silicon compounds are additive.

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