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STERIC PARAMETERS FOR SUBSTITUENTS BOUND TO ATOMS OF SILICON AND SOME OTHER ELEMENTS OF THE THIRD PERIOD

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The kinetics of a tetraethoxysilane reaction with n-butyilmagnesium chloride, stoichiometrically monosolvated with isopropyl ether or with methyl tert-butyl ether, was studied in toluene. 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. Equilibrium constants for five alkyl ether ligands at the magnesium center are in an excellent correlation with isosteric $E_S(\text{Si})$ parameters. It was concluded that these constants should be applicable to all elements of the third period of the periodic table.

Keywords Grignard reaction; isosteric parameters; silanes; solvation effects

INTRODUCTION

The quantitative structure–reactivity analysis, also known as correlation analysis, has been widely practiced in organic chemistry since the pioneering work of Hammett and Taft. Besides the quantum chemical calculations and other complementary methods, the correlation analysis has maintained its importance as a useful tool for investigating reaction mechanisms and for the prediction of rate and equilibrium constants.^{1–3}

In traditional organic chemistry, several protocols for the quantitative description of polar and steric effects of substituents are available.^{1–3} However, these protocols have been elaborated mostly for reactions taking place at the carbon atom or its closest neighbors in the second period. Therefore an unequivocal approach still needs to be developed for other reaction centers, including organometallic chemistry in general.^{4–6}

Recently we have carried out a revision of quantitative data regarding the reactivity of organosilicon compounds in light of views that stem from organic reactions at the carbon atom.^{7–10} It was found that in structure–reactivity analysis for organosilicon compounds, as opposed to carbon compounds, the Taft E_S scale of steric parameters is not applicable,^{7,8} and the inductive effect of substituents must be expressed by two terms, involving one that describes electronegativity.¹⁰

Cartledge¹¹ has defined a set of $E_S(\text{Si})$ parameters for alkyl groups from reaction rates of silicon compounds, and these constants appeared to be in a good correlation with

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ν' parameters derived by Charton¹² from replacement reactions at sp^3 -carbon. The scale of ν' was thereafter successfully applied in correlating reactivity data of alkyl substituted phosphorus compounds.¹³ The major difference between these parameters, derived for silicon compounds, and those derived previously for carbonyl compounds by Taft, can be observed if the effect of substituent branching in α and β positions is compared. Charton has concluded¹² that expansion of coordination from four to five at the reaction center will show different sensitivity to α and β branching than a reaction involving change of coordination from three to four, as we observe in the case of carbonyl compounds.

We have shown that the sets of parameters $E_S(\text{Si})$ and ν' are practically equivalent and almost equally applicable for quantitative description of steric effects exerted by alkyl substituents upon the reactivity of organosilicon compounds.⁸ Further we extended the $E_S(\text{Si})$ scale for several polar substituents, the data for which were not previously available.¹⁰

The novel protocol for the correlation analysis in organosilicon chemistry proved to be applicable to all available experimental data for nucleophilic replacements and some other reactions at the silicon center,^{8,10} including acid- and base-catalyzed hydrolyses, bromination, Grignard reactions, etc.

As far as the difference between reactivities of silicon and carbon compounds is mostly related to differences in atomic dimensions and in the electron structure, the question can be raised as to whether the conclusions above can be extended to other elements of the third period of the periodic table.

In this report, we show that $E_S(\text{Si})$ parameters also are suitable to express the steric effect of substituents at the magnesium atom. To this end, we correlate equilibrium constants for the replacement of ethers as donor ligands at the magnesium center in Grignard reagent for an alkoxy silane as a donor using the isosteric parameters of the ethers. It has been quantitatively proven¹⁴ that donor ligands at the magnesium atom in Grignard reagents can be considered as substituents equally to other groups at the center. Kinetic data for the reaction between *n*-butylmagnesium chloride and tetraethoxysilane in toluene solution in the presence of various alkyl ethers were exploited to calculate the needed equilibrium constants.

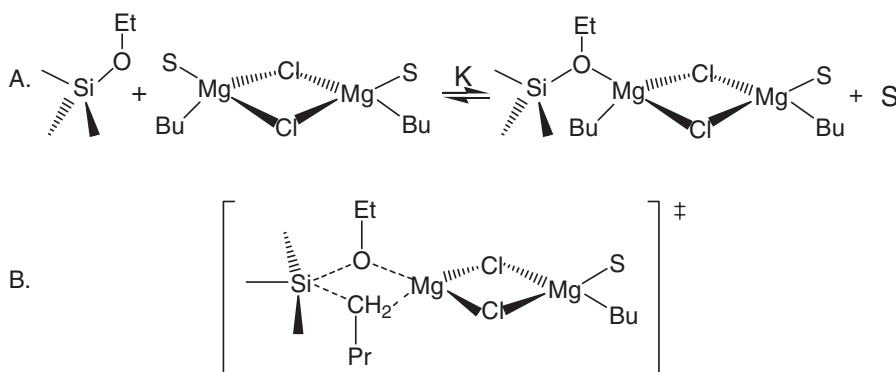
RESULTS AND DISCUSSION

We have elaborated an experimental method determining rate and equilibrium constants for the Grignard reaction with alkoxy silanes.¹⁵ The method is based on understanding that the reaction proceeds through complexation of Grignard reagent with silane, which replaces the donor molecule bound at the magnesium center (Scheme 1). Subsequently, this complex rearranges to reaction products through a four-center transition state.^{16,17}

As alkylmagnesium chlorides exist essentially as dimeric species, which are stable over a wide concentration range,¹⁸ the overall reaction can be presented as follows:



where G denotes the magnesium compound, S is silane, E is the ether molecule, $(\text{GE})_2$ 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.



Scheme 1 (A) Schematic representation of the replacement of the donor molecule at the magnesium center (donor bonds are not distinguished separately). (B) The transition state for the reaction of *n*-butylmagnesium chloride with an alkoxy-silane. In (A) and (B), S stands for the donor solvent molecule.

In the presence of an excess of Grignard reagent, the reaction follows a first-order rate equation.¹⁷ Assuming that the complexation Equilibrium (1) is fast, according to the principle of steady state kinetics,^{19,20} Eq. (3) can be deduced for the observed rate constant.

$$k_{\text{obs}} = \frac{kK[G]}{1 + K[G]}. \quad (3)$$

Eq. (3) can be converted into the linear form Eq. (4), suitable for data processing in coordinates $1/k_{\text{obs}}$ vs. $1/[G]$.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{1}{kK[G]}. \quad (4)$$

The pseudo-first-order rate constants of the reaction between tetraethoxysilane and monosolvated with alkyl ethers *n*-butylmagnesium chloride were measured in toluene using a large excess of the Grignard reagent. An important advantage of such an approach consists in preclusion of nonspecific solvation effects when the effects of donor solvents are considered.

In all experiments, only the first replacement at the silicon center was observed, because at the temperature used (20°C), further substitutions are extremely slow. Concentrations of the monosolvated Grignard reagents changed from 0.15 M to 0.5 M, and the exact values were determined by titration. As alkylmagnesium chlorides are essentially in dimeric form,¹⁸ the actual concentration range of the reacting species was two times smaller than the titrated concentration. The obtained rate constants were analyzed as described above, and an example is shown in Figure 1. The results are collected in Table I together with data obtained in our previous work.¹⁵

According to Eq. (1), the equilibrium constants *K* should reflect the solvating ability of donors, the strongest of them shifting the equilibrium most to the left (see Scheme 1A). As the Brønsted basicities of the ethers used are practically similar,²¹ their solvating power (Lewis basicity) should be determined solely by their steric effects. Indeed, the equilibrium constants aligned well with the presumable steric properties of the ethers.

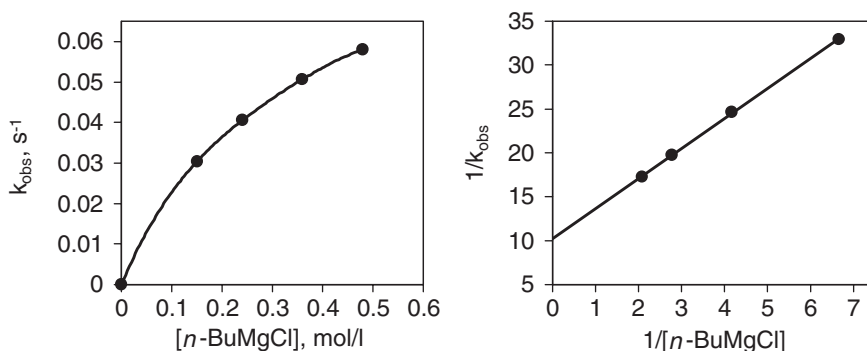
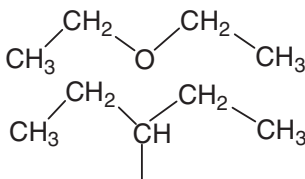


Figure 1 (a) Pseudo-first order rate constants k_{obs} vs. the titrated concentration of $n\text{-BuMgCl}$ $i\text{-Pr}_2\text{O}$ complex for the reaction with tetraethoxysilane in toluene at 20°C. (b) Determination of the equilibrium constant (K) and rate constant (k).

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 1B).

In order to quantify the structure–reactivity relations for the Equilibrium (1), logarithms of the equilibrium constants were contrasted with corresponding isosteric constants in Table II. 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 the CH-group in the corresponding alkyl substituents, as shown in Scheme 2.



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

The appropriate constants E_S' were taken from the revised and extended analysis by MacPhee et al.²² made by default for carbon compounds. The corresponding isosteric

Table I Rate and equilibrium constants calculated from Eq. (4) for the reaction^a of tetraethoxysilane with monosolvated $n\text{-butylmagnesium}$ reagents in toluene at 20°C

Grignard reagent	K , $\text{L}\cdot\text{mol}^{-1}$	k , s^{-1}
$n\text{-BuMgCl}\cdot\text{THF}^{b,c}$	0.40 ± 0.10	0.12 ± 0.03
$\cdot\text{Et}_2\text{O}^b$	1.22 ± 0.19	0.31 ± 0.05
$\cdot\text{Bu}_2\text{O}^b$	3.30 ± 0.66	0.33 ± 0.05
$\cdot\text{MTBE}^d$	3.95 ± 0.19	0.13 ± 0.01
$\cdot i\text{-Pr}_2\text{O}$	6.15 ± 0.31	0.10 ± 0.01

^a $\text{Si}(\text{OEt})_4 + \text{BuMgCl} \rightarrow \text{BuSi}(\text{OEt})_3 + \text{EtOMgCl}$.

^bFrom Ref.¹⁵, standard errors recalculated.

^cA GLC method was used, see Ref.¹⁵

^dMethyl *tert*-butyl ether.

Table II Logarithms of the equilibrium constants from Table I and the corresponding isosteric constants

Ether ligand	log K	-E _S ^a	-E _S (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 ^d	0.60	3.21	0.98
<i>i</i> -Pr ₂ O	0.79	5.01	0.99

^aConstants from Ref.²²

^bCalculated in this work (see Results and Discussion section).

^cApproximated with *cyclo*-hexyl group (from Ref.⁸).

^dMethyl *tert*-butyl ether.

E_S(Si) constants were not available in the literature. However, extensive kinetic data for the hydrolysis of alkyldimethylchlorosilanes published by Shimizu et al.,²³ and their unexpectedly good additive scheme for calculation of the missing rate data,²⁴ enabled us to obtain the rate constants for silanes with the required alkyl substituents. For the hydrolysis reaction, empirical Eqs. (5) and (6) have been derived,²⁴ where S(R) denotes the structural effect of a group R at silicon, defined as log k_{rel} for RMeSiCl₂.

$$S(RCH_2) = 0.20 S(R) - 0.57 \quad (5)$$

$$\log k_{rel}(R^1 R^2 R^3 Si) = S(R^1) + 1.15 S(R^2) + 1.35 S(R^3) \quad (6)$$

In Eq. (6), the structural effect of an alkyl group Rⁱ in R¹R²R³Si is assumed to be the largest with R¹ and the smallest with R³. Further, excellent correlation for compounds with alkyl substituents from the same reaction with E_S(Si) scale^[8] was obtained

$$\log k_{rel} = (-0.09 \pm 0.07) + (2.28 \pm 0.12) E_S(Si), R = 0.991 \quad (7)$$

and a significant susceptibility of the reaction to steric effects permitted reliable calculation of the values of the isosteric constants, as shown in Table III.

For the THF ligand, data for the isosteric *cyclo*-pentyl group are not available. However, we consider the approximation with *cyclo*-hexyl group (Table II) appropriate, because in both *cyclo*-hexyl and *cyclo*-pentyl groups, branching in α- or β-positions relative to Mg or Si center is the same (for the branching effects, see Refs.^{8,11,12}).

Table III Calculation of isosteric constants for the ether ligands

Ether ligand	Corresponding isosteric alkyl group	log k _{rel} ^a		-E _S (Si) ^d
		Obs. ^b	Calc. ^c	
Et ₂ O	Et ₂ CH-	-1.71	-1.77	0.78
Bu ₂ O	Bu ₂ CH-	—	-1.99	0.87
<i>i</i> -Pr ₂ O	<i>i</i> -Pr ₂ CH-	—	-2.26	0.99
MTBE ^e	<i>t</i> -BuMeCH-	—	-2.23	0.98

^aFor the hydrolysis of alkyldimethylchlorosilanes.²³

^bFrom Ref.²³

^cCalculated from Eq. (6).

^dCalculated from Eq. (7).

^eMethyl *tert*-butyl ether.

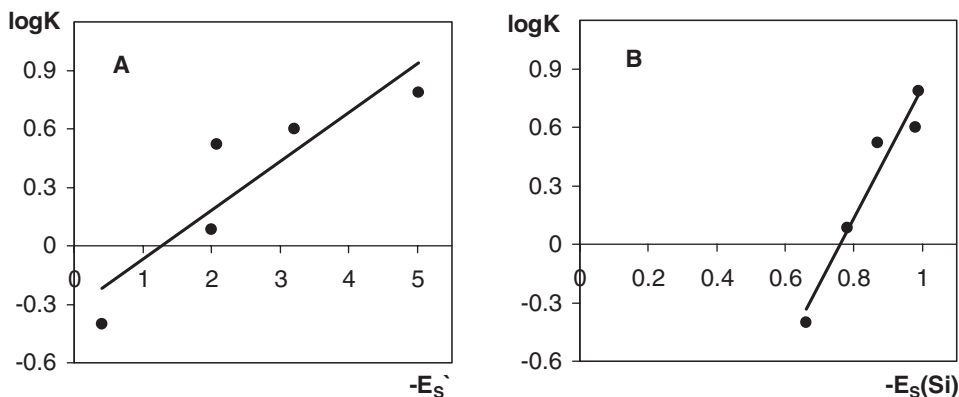


Figure 2 Correlation of equilibrium constants with isosteric parameters E_s' (A) and $E_s(\text{Si})$ (B).

As seen in Figure 2, correlation of the equilibrium constants with the isosteric E_s' parameters is hardly satisfactory ($R^2 = 0.804$), while $E_s(\text{Si})$ constants provide an excellent correlation ($\delta = -3.34 \pm 0.45$; $R^2 = 0.950$). Thus the steric effect of substituents on reactions taking place at the Mg center can be reliably expressed by means of $E_s(\text{Si})$ constants.

In conclusion, the scale $E_s(\text{Si})$ of steric parameters derived from organosilicon chemistry proved also to be pertinent in the case of organomagnesium compounds.

Charton and Charton¹³ have extensively investigated substituent effects in organophosphorus chemistry. Rate constants for the reaction of 22 sets of $\text{XZ}(\text{PO})\text{Cl}$ with water, and rate constants for sets of some other reactions, were successfully correlated with the steric parameters ν' by means of the modified Taft equation. The results were in agreement with the transition state of trigonal-bipyramidal geometry, similar to the replacement reactions at the silicon center. As already stressed in the Introduction section, we have shown⁸ that the scale ν' is equivalent to the $E_s(\text{Si})$ scale ($R = 0.996$). Therefore it can also be concluded that the scale $E_s(\text{Si})$ can be equally used for organophosphorus compounds. And moreover, as far as the scale $E_s(\text{Si})$ was proved to be applicable for magnesium, silicon, and phosphorus compounds, it is reasonable to assume that the same parameters can be applied also for aluminum and sulfur compounds, if these will be available.

EXPERIMENTAL

Preparation of Monosolvated Grignard Reagents

Toluene solutions of *n*-butylmagnesium chloride stoichiometrically monosolvated with isopropyl ether or MTBE (methyl *tert*-butyl ether) were prepared in a stainless-steel autoclave equipped with a magnetic stirrer, a thermometer, and a manometer. The autoclave was charged with an adequate amount of Mg powder, and iodine was used as activator. The reaction vessel was purged thoroughly with argon, then calculated volumes of toluene, donor ether, and *n*-butyl chloride were added and the autoclave was sealed. The reaction mixture was heated until the reaction began. With isopropyl ether, the induction period lasted several hours, and the synthesis was accomplished in 2 h at 90°C. In the

case of MTBE, the induction period was short, and the preparation was performed at 50°C.

After the reaction mixture was cooled down, the concentration of the Grignard reagent was determined. For kinetic measurements, these solutions were diluted with the appropriate amounts of toluene. The reagents and solutions were handled under dry argon and transferred by use of cannulae or syringes. Yields of the syntheses of monosolvated reagents (about 90%) were very reproducible, and the rate constants measured with solutions from different batches were in excellent agreement between different experiments.

Kinetic Measurements

Reactions were investigated in a thermostatic flask equipped with a stirrer and a thermistor. The thermistor was connected through a bridge circuit to a PC. The reaction vessel was purged thoroughly with pure argon. All parts of the equipment and the reagents were thermostatted. After the thermal equilibrium was set, 0.05 mL of tetraethoxysilane was injected into 15 mL of the Grignard reagent (providing at least a 10-fold excess of Grignard reagent), and the temperature change of the reaction solution (up to 0.5°C) was recorded as a plot of temperature vs. time. The pseudo-first-order rate constants were calculated from these kinetic data (Table IV).

Table IV Pseudo-first order rate constants for the reaction of tetraethoxysilane with monosolvated *n*-butylmagnesium reagents in toluene at 20°C

Solvent	Titred conc. of the Grignard reagent	$k_{\text{obs}} \times 10^2, \text{s}^{-1} \text{ }^a$
THF ^{b,c}	0.23	0.52 ± 0.01
	0.41	0.91 ± 0.02
	0.67	1.39 ± 0.03
	0.90	1.79 ± 0.01
Et ₂ O ^c	0.28	4.60 ± 0.10
	0.44	6.50 ± 0.11
	0.66	9.26 ± 0.10
	0.89	10.9 ± 0.10
Bu ₂ O ^c	0.44	13.9 ± 0.40
	0.66	17.0 ± 0.60
	0.88	19.8 ± 0.14
MTBE ^d	0.17	3.19 ± 0.10
	0.28	4.60 ± 0.12
	0.42	5.72 ± 0.19
	0.51	6.35 ± 0.09
<i>i</i> -Pr ₂ O	0.15	3.05 ± 0.07
	0.24	4.05 ± 0.10
	0.36	5.07 ± 0.02
	0.48	5.80 ± 0.16

^aMean values at least three determinations.

^bA GLC method was used, see Ref.¹⁵

^cInitial kinetic data from the work Ref.¹⁵

^dMethyl *tert*-butyl ether.

REFERENCES

1. J. Shorter, *Correlation Analysis of Organic Reactivity* (Wiley, Chichester, 1982).
2. O. Exner, *Correlation Analysis of Chemical Data* (Plenum Press, New York, 1988).
3. A. Williams, *Free Energy Relationships in Organic and Bio-organic Chemistry* (RSC, Cambridge, 2003).
4. V. I. Galkin, R. D. Sayakhov, and R. A. Tcherkasov, *Usp. Khim.*, **60**, 1617 (1991).
5. D. White and N. J. Coville, *Adv. Organomet. Chem.*, **36**, 95 (1994).
6. K. K  ppler, U. Scheim, K. R  hlmann, and A. Porzel, *J. Organomet. Chem.*, **441**, 15 (1992).
7. D. Panov, A. Ploom, and A. Tuulmets, *Phosphorus, Sulfur, and Silicon*, **181**, 2807 (2006).
8. A. Ploom, D. Panov, and A. Tuulmets, *Arkivoc*, 37 (2006).
9. O. Golubev, D. Panov, A. Ploom, A. Tuulmets, and B. T. Nguyen, *J. Organomet. Chem.*, **692**, 3700 (2007).
10. A. Ploom and A. Tuulmets, *J. Organomet. Chem.*, **694**, 313 (2009).
11. F. K. Cartledge, *Organometallics*, **2**, 425 (1983).
12. M. Charton, *J. Am. Chem. Soc.*, **97**, 3694 (1975).
13. M. Charton and B. J. Charton, *J. Org. Chem.*, **43**, 2383 (1978).
14. A. Tuulmets, *Organic Reactivity (USSR)*, **11**, 81 (1974).
15. A. Ploom, D. Panov, J. J  rv, and A. Tuulmets, *J. Organomet. Chem.*, **693**, 2351 (2008).
16. A. Tuulmets, D. Panov, and M. Sassian, *Tetrahedron Lett.*, **44**, 3943 (2003).
17. A. Tuulmets, B. T. Nguyen, D. Panov, M. Sassian, and J. J  rv, *J. Org. Chem.*, **68**, 9933 (2003).
18. F. W. Walker and E. C. Ashby, *J. Am. Chem. Soc.*, **91**, 3845 (1969).
19. L. P. Hammett, *Physical Organic Chemistry* (McGraw-Hill, New York, 1970), 2nd ed., Chap. 4.
20. E. A. Moelwyn-Hughes, *The Chemical Statics and Kinetics in Solutions* (Academic Press, London, 1971), Chap. 4.
21. I. A. Koppel and V. A. Palm, In *Advances in Linear Free Energy Relationships*, N. B. Chapman and J. Shorter, eds. (Plenum Press, New York, 1972), Chapter 5.
22. J. A. MacPhee, A. Panaye, and J. E. Dubois, *Tetrahedron*, **34**, 3553 (1978).
23. N. Shimizu, N. Takesuke, A. Yamamoto, T. Tsutsumi, S. Yasuhara, and Y. Tsuno, *Chem. Lett.*, 1263 (1992).
24. N. Shimizu, N. Takesuke, S. Yasuhara, and T. Inazu, *Chem. Lett.*, 1807 (1993).