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Rate and equilibrium constants for the Grignard reaction with alkoxysilanes

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Abstract. Pseudo-first-order rate constants were determined for the reactions of tetraethoxysilane with *n*-butylmagnesium chloride solvated with dibutyl ether, diethyl ether, and THF in toluene. Also isopropylmagnesium chloride and isopropyltriethoxysilane were involved in a similar investigation. Rate and equilibrium constants were calculated for the reactions and the steric effects in the reactions are discussed.

Key words: Grignard reaction, kinetics, silanes.

INTRODUCTION

Silicone production is the largest consumer of monomeric silanes. At present, the production of organosilanes by direct methods is greater than that with the Grignard process. However, the latter remains essential for a wide range of the specialty silanes [1]. Despite the viability of the Grignard process in organosilane production the quantitative aspects of the reaction have been little investigated. Until recently, only a few kinetic studies of the Grignard reaction with silanes have been published [2–4]. We have launched an extensive kinetic investigation into the Grignard reaction with silanes, the solvent problems included [5–7]. Continuation of our previous work [4] was motivated by matters emerging in Grignard technology when ether solvents were replaced by hydrocarbons of higher boiling points.

Replacement of diethyl ether by toluene significantly accelerates the reaction with alkoxysilanes, while no effect was found for the reaction with chlorosilanes [4–6]. We established that the reaction with alkoxysilanes consists of replacement of a donor molecule at the magnesium centre by the silane followed by subsequent rearrangement of the complex to products through a four-centre

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transition state [5, 6]. For detailed insight into the process, particularly for a quantitative description of the structure–reactivity relationships as well as of the solvent effects, neat rate and equilibrium constants are required.

In one of our recent publications [6] an appropriate method was fleetingly suggested. The monosolvated Grignard reagent in toluene is particularly liable to complexation with a silane. The dependence of the pseudo-first-order rate constant upon the concentration of monosolvated Grignard reagent provides a way of determining the equilibrium and rate constants separately. In this work we explore the method demonstrating its applicability to kinetic investigations.

If the reaction proceeds through replacement of a solvent molecule and subsequent rate-determining conversion of the complex to products, taking into account that alkylmagnesium chlorides are essentially dimeric species over a wide concentration range [8], it can be expressed as

$$(\mathrm{GE})_2 + \mathrm{S} \overset{K}{\rightleftarrows} \mathrm{G_2ES} + \mathrm{E}, \tag{1}$$

$$\mathrm{G_2ES} \xrightarrow{k} \text{products}, \tag{2}$$

where G denotes a magnesium compound, S the silane, and E an ether molecule, and K is the equilibrium constant and k the rate constant.

For a monosolvated Grignard reagent in toluene under pseudo-first-order conditions, the concentration of the free ether is negligible and the reaction can be rewritten as

$$\mathrm{G} + \mathrm{S} \overset{K}{\rightleftarrows} \mathrm{GS} \xrightarrow{k} \text{products}. \tag{3}$$

Assuming steady-state conditions and a fast complexation equilibrium, for this reaction Eq. 4 can be deduced

$$k_{\mathrm{obs}} = \frac{kK[\mathrm{G}]}{1+K[\mathrm{G}]}. \tag{4}$$

Equation 4 can be converted into Eq. 5, more suitable for data treatment

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k} + \frac{1}{kK[\mathrm{G}]}. \tag{5}$$

Linearity of the plot $1/k_{\mathrm{obs}}$ vs. $1/[\mathrm{G}]$ affirms the assumptions made above and then a simple calculation yields the numerical values for K and k.

An important advantage of the method consists in absence of non-specific solvation effects when specific solvation effects of donor solvents are considered.

Here we report the results for the reactions of tetraethoxysilane with *n*-butylmagnesium chloride solvated with dibutyl ether, diethyl ether, and THF, and with isopropylmagnesium chloride in the presence of diethyl ether, and also for the reaction of isopropyltriethoxysilane with *n*-butylmagnesium chloride solvated with diethyl ether.

EXPERIMENTAL

Preparation of monosolvated Grignard reagents

A round-bottomed 100 mL flask equipped with a magnetic stirrer and a back-flow condenser was charged with an adequate amount of Mg and I_2. The reaction vessel was purged thoroughly with pure argon and appropriate volumes of toluene, ether, and alkyl chloride were added. The reaction mixture was heated until the reaction was started. The alkyl halide and ether mixture (1 : 1) was added in portions to the reaction mixture over a 30 min period. Then the rest of toluene was added, the reaction mixture was stirred about 1 h at room temperature and heated to boiling. After the reaction mixture had cooled down the concentration of the Grignard reagent was determined.

Grignard reagents in ether–toluene mixtures were prepared by dilution of the stock solutions with appropriate amounts of toluene. The reagents and solutions were handled under dry argon and transferred by use of cannulas or syringes.

Kinetic measurements

Method A

The reaction vessel equipped with a magnetic stirrer and containing 40 mL of the Grignard reagent was thermostatted. According to the concentration of the Grignard reagent, 0.1–1 mL of alkoxysilane (providing a 9- to 20-fold excess of the Grignard reagent) was added into the flask to start the reaction. At appropriate times 2 mL aliquots were taken from the reaction mixture and quenched with ice-cold water. The organic layer was instantly separated, dried, and analysed using GLC.

Method B

Fast reactions were investigated in a thermostatic flask equipped with a stirrer and a thermistor. The thermistor was connected through a bridge circuit to a recording potentiometer. 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 silane was added to 15 mL of the Grignard reagent (providing a 20–40-fold excess of the Grignard reagent), and the temperature change of the reaction solution (less than 1 °C) was recorded as a plot of temperature vs. time.

RESULTS AND DISCUSSION

Pseudo-first-order rate constants for the reactions of silanes were determined in the concentration range 0.2 M to 1.0 M in the monosolvated Grignard reagents at 20 °C (Table 1).

As alkylmagnesium chlorides are essentially in a dimeric form [8], the actual concentration range of the reagents was 0.1–0.5 M. The obtained rate constants

Table 1. Pseudo-first-order rate constants in toluene at 20 °C

Silane	Grignard reagent	Titrated conc. of the Grignard reagent [R-Mg]	k_{obs}, s^{-1}	Method
$Si(OEt)_4$	n-BuMgCl · Bu_2O	0.27	$(4.65 \pm 0.08) \times 10^{-2}$	B
		0.49	$(7.32 \pm 0.06) \times 10^{-2}$	
			$(7.47 \pm 0.05) \times 10^{-2}$	
		0.66	$(8.26 \pm 0.17) \times 10^{-2}$	
			$(8.44 \pm 0.14) \times 10^{-2}$	
			$(8.83 \pm 0.12) \times 10^{-2}$	
		0.88	$(1.04 \pm 0.01) \times 10^{-1}$	
	n-BuMgCl · Et_2O	0.28	$(4.45 \pm 0.21) \times 10^{-2}$	B
			$(4.71 \pm 0.23) \times 10^{-2}$	
		0.44	$(6.50 \pm 0.11) \times 10^{-2}$	
		0.66	$(9.40 \pm 0.10) \times 10^{-2}$	
		0.67	$(9.12 \pm 0.15) \times 10^{-2}$	
		0.89	$(1.09 \pm 0.01) \times 10^{-1}$	
	n-BuMgCl · THF	0.23	$(5.2 \pm 0.42) \times 10^{-3}$	A
		0.41	$(9.13 \pm 0.21) \times 10^{-3}$	
		0.67	$(1.39 \pm 0.03) \times 10^{-2}$	
		0.9	$(1.79 \pm 0.01) \times 10^{-2}$	
	i-PrMgCl · Et_2O	0.2	$(2.27 \pm 0.09) \times 10^{-4}$	A
		0.4	$(3.84 \pm 0.29) \times 10^{-4}$	
		0.6	$(4.95 \pm 0.13) \times 10^{-4}$	
		0.8	$(5.67 \pm 0.28) \times 10^{-4}$	
i-$PrSi(OEt)_3$	n-BuMgCl · Et_2O	0.3	$(1.71 \pm 0.09) \times 10^{-4}$	A
		0.5	$(3.10 \pm 0.21) \times 10^{-4}$	
		0.7	$(4.2 \pm 0.23) \times 10^{-4}$	
		1.0	$(6.5 \pm 0.18) \times 10^{-4}$	

were treated as described in Introduction. An example is presented in Fig. 1 and the results are collected in Table 2.

The first three entries in Table 2 represent a variation of the donor solvent in the Grignard reagent. According to Eq. 1 the equilibrium constants reflect the solvating ability of donors, the strongest of them shifting the equilibrium most to the left. As the Broensted basicities of these ethers are practically similar [9], their solvating power (Lewis basicity) should be determined solely by their steric requirements (cf., e.g. [10]). Indeed, as is seen in Fig. 2, the equilibrium constants correlate well with the isosteric constants [9, 10] for the ethers. The relatively small value of the susceptibility parameter ($\delta \approx 0.4$) points at moderate steric requirements of dimeric n-butylmagnesium chloride. From the values for equilibrium constants a Lewis basicity for tetraethoxysilane close to those of alkyl ethers, at least towards n-butylmagnesium chloride, can be inferred.

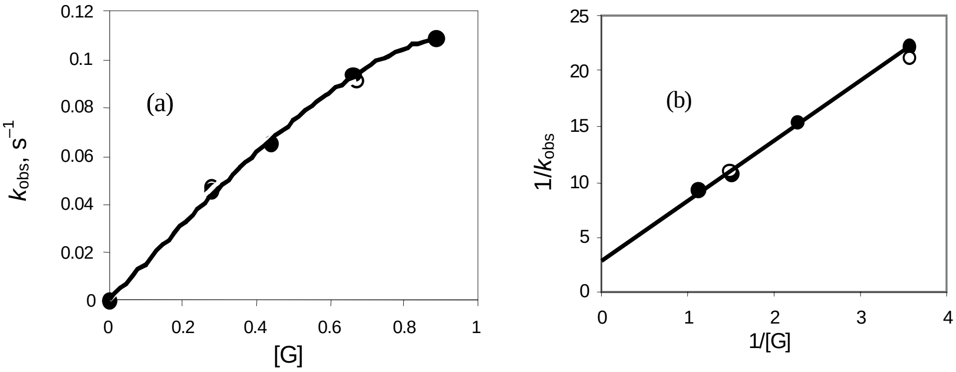


Fig. 1. (a) Pseudo-first-order rate constants k vs. the concentration of *n*-BuMgCl · Et_2O complex for reaction with tetraethoxysilane in toluene at 20°C. Full and open circles indicate the reagents from parallel preparations. (b) Determination of the equilibrium constant (K) and rate constant (k).

Table 2. Rate and equilibrium constants for the reactions of alkoxysilanes with monosolvated alkylmagnesium chlorides in toluene at 20 °C

Silane	Grignard reagent	K, L·mol^{-1}	k, s^{-1}	Method
$Si(OEt)_4$	*n*-BuMgCl · Bu_2O	2.24 ± 0.06	0.20 ± 0.02	B
	n-BuMgCl · Et_2O	1.22 ± 0.02	0.31 ± 0.01	B
	n-BuMgCl · THF	0.40 ± 0.02	0.12 ± 0.03	A
	i-PrMgCl · Et_2O	2.40 ± 0.02	$(1.17 \pm 0.04) \times 10^{-3}$	A
i-$PrSi(OEt)_3$	*n*-BuMgCl · Et_2O	0.8 ± 0.2	$(2.2 \pm 0.4) \times 10^{-3}$	A

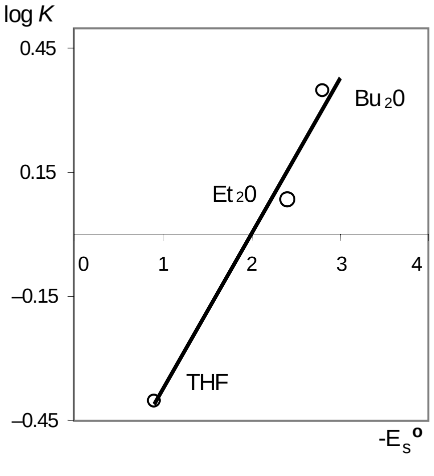
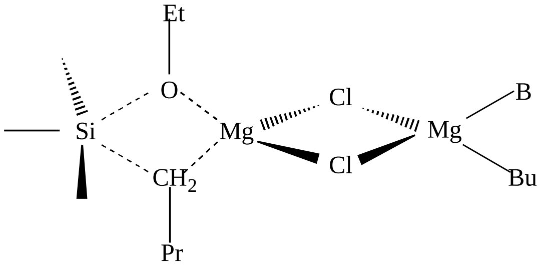


Fig. 2. Correlation of the equilibrium constants K for the reaction between monosolvated *n*-butylmagnesium chloride and tetraethoxysilane in toluene with the isosteric constants of solvating ethers.

The rate constants (Table 2) vary relatively little with the donors. This can be assigned to the remote position of the donor molecule in the transition state of the reaction (Scheme 1).



Scheme 1. Transition state of the reaction. B stands for the donor molecule.

The last two entries in Table 2 deserve attention because of the steric effects. Replacement of the *n*-butyl group by isopropyl in the Grignard reagent increases the equilibrium constant by a factor of two in accordance of increasing hindrance to coordination with the donor. On the other hand, this points at lesser steric requirements of the silane in comparison with diethyl ether. An increase in the bulkiness of the silane (last entry in Table 2) has a little 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 the silane, 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 alkoxysilanes. The rate and equilibrium data obtained in this work constitute a self-consistent set of constants fully adequate to the expected physical sense, thus manifesting the reliability of the method.

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Kiirus- ja tasakaalukonstandid Grignardi reaktsioonis alkoksüsilaanidega

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On määratud pseudomonomolekulaarsed kiiruskonstandid tetraetoksüsilaani reaktsioonis *n*-butüülmagneesiumkloriidiga, mis on solvateeritud dibutüüleetri, dietüüleetri või tetrahüdrofuraaniga tolueeni keskkonnas. Analoogilistes mõõtmistes on kasutatud ka isopropüülmagneesiumkloriidi ja isopropüültrietoksüsilaani. On arvutatud reaktsioonide kiirus- ning tasakaalukonstandid ja arutletud steeriliste efektide üle neis reaktsioonides.