



Rate and equilibrium constants for Grignard reaction with alkoxy silanes and ketones

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ABSTRACT

Kinetics of tetraethoxysilane reaction with *n*-butylmagnesium chloride, specifically solvated with dibutyl ether, diethyl ether, THF, and triethylamine, was studied in toluene. Also isopropylmagnesium chloride, isopropyltriethoxysilane, and diisopropylketone were involved in a similar investigation. The pseudo-first-order rate constants determined at a great excess of these organomagnesium compounds were used for separation of the appropriate equilibrium and rate constants. An advantage of the method consists in preclusion of non-specific solvation effects when effects of donor solvents are considered. 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. The implication of steric and solvation effects on this reaction is discussed.

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1. Introduction

Grignard reaction is widely used in industrial synthesis of monomeric organosilanes, which are starting materials for silicone production [1]. However, despite of the technological significance of this reaction, its mechanism and especially the quantitative aspects of organosilane formation have not well understood. Proceeding from this fact we have launched an extensive program of kinetic investigation of this reaction, focussing incidentally on the influence of Grignard reagent solvation on its reactivity [2–6]. Besides theoretical interest, this latter aspect was strongly motivated by practical needs, emerging from technological application of the Grignard reaction under conditions, where ether solvents are replaced by hydrocarbons of higher boiling points to meet the safety requirements of this technology.

Our initial investigations have revealed 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 [2,3,5]. However, for a more detailed insight into the mechanism of this process, as well as for understanding the role of solvent in organosilane formation reaction, explicit rate and equilibrium constants describing this process are required. In one of our previous publications [3] an appropriate method for these kinetic measurements was suggested.

This method is based on understanding that the reaction proceeds through complexation of 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) [2,3].

As alkylmagnesium chlorides exist essentially as dimeric species, which are stable over a wide concentration range [7], the overall reaction scheme can be presented as follows:



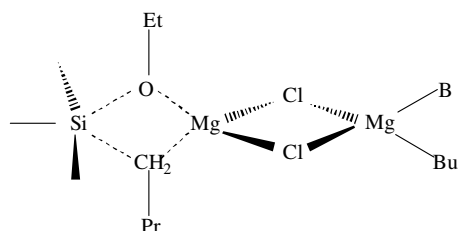
where G denotes a magnesium compound, S the silane, and E an ether molecule, $(\text{GE})_2$ is the dimeric monosolvated Grignard reagent, and G_2ES is the substitution complex. The parameters K and k are the equilibrium and rate constants, respectively.

In the presence of an excess of Grignard reagent, the reaction sequences (1) and (2) should follow a 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 (1) 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} :

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

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

This equation can be converted into the following linear form:

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

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

In this work, we explored this method for kinetic analysis of the following reactions in toluene:

–Tetraethoxysilane reactions with *n*-butylmagnesium chloride, solvated with dibutyl ether, diethyl ether, THF, and triethylamine, and isopropylmagnesium chloride solvated with diethyl ether.

–Isopropyltriethoxysilane, methylvinylchlorosilane, and diisopropylketone reactions with *n*-butylmagnesium chloride, solvated with diethyl ether.

Thermodynamic parameters were determined separately for the rate and equilibrium constants k and K of tetraethoxysilane reaction with *n*-butylmagnesium chloride, solvated with dibutyl ether in toluene, and also in bulk dibutyl ether.

2. Experimental

2.1. Preparation of monosolvated Grignard reagents

A round-bottomed 100 mL flask equipped with a magnetic stirrer and a backflow condenser was charged with an adequate amount of Mg and I_2 . The reaction vessel was purged thoroughly with argon and appropriate volumes of toluene, donor solvent, and alkyl chloride were added. The reaction mixture was heated until the reaction was started. The alkyl halide and donor solvent 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 the room temperature and heated to boiling. After the reaction mixture had cooled down the concentration of the Grignard reagent was determined.

Grignard reagents for kinetic measurements were prepared by dilution of this stock solution with appropriate amounts of toluene. The reagents and solutions were handled under dry argon and transferred by use of cannulae or syringes.

2.2. Kinetic measurements

2.2.1. 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 silane (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 for the silane using GLC.

2.2.2. 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 or ketone 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.

3. Results and discussion

Pseudo-first-order rate constants for the reactions of silanes with Grignard reagents were measured in toluene, using excess of differently solvated organomagnesium compounds. Measurements were made at 20 °C, but also at 30 °C and 40 °C when the thermodynamic parameters were determined. In all experiments, only the first replacement at the silicon center was observed because at these temperatures further substitutions are extremely slow. Concentrations of the monosolvated Grignard reagents were changed from 0.2 M to 1.0 M and the exact values were determined by titration. As alkylmagnesium chlorides are essentially in dimeric form [7], the actual concentration range of the reaction complexes was 0.1–0.5 M.

The pseudo-first-order rate constants determined at a great excess of organomagnesium compounds reveal hyperbolic plots on concentrations of the reagents. These data confirm the reaction mechanism, containing a fast complex formation of the reagents and subsequent rate-limiting reaction step of product formation. The obtained rate constants were analyzed as described in Section 1, and an example is shown in Fig. 1.

To test the reliability of the method the reaction with methylvinylchlorosilane was engaged. Formerly, we have concluded [2,3] that the Grignard reaction with chlorosilanes is an $\text{S}_{\text{N}}2$ reaction at the silicon atom without prior complexation of the reagents. Therefore a linear dependence of pseudo-first-order rate constants on the Grignard reagent concentration could be expected. Indeed, in Fig. 2 a neat linear plot can be seen. Moreover, this is an evidence against any further association of the Grignard dimers within this concentration range.

Determinations of rate and equilibrium constants were carried out at least in duplicate and the results are collected in Table 1.

In this study variation in structure of both reagents was made, and in case of Grignard reagent also the donor molecule was changed. Some of these structural alterations had rather significant effect on reactivity of these compounds.

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. As the Brønsted basicities of used ethers are practically similar [8], their solvating power (Lewis basicity) should be determined solely by their steric effect. Indeed, the equilibrium constants align well in the sequence of steric requirements of the ethers. Triethylamine is largely stronger Brønsted base than the used ethers, however, its great steric requirements evidently lead to a moderate solvating power.

The rate constants k for *n*-butylmagnesium chloride complexes in the reaction with tetraethoxysilane vary also relatively little with the donor ethers. This can be assigned to the remote position of the donor molecule in the transition state of the reaction (Scheme 1).

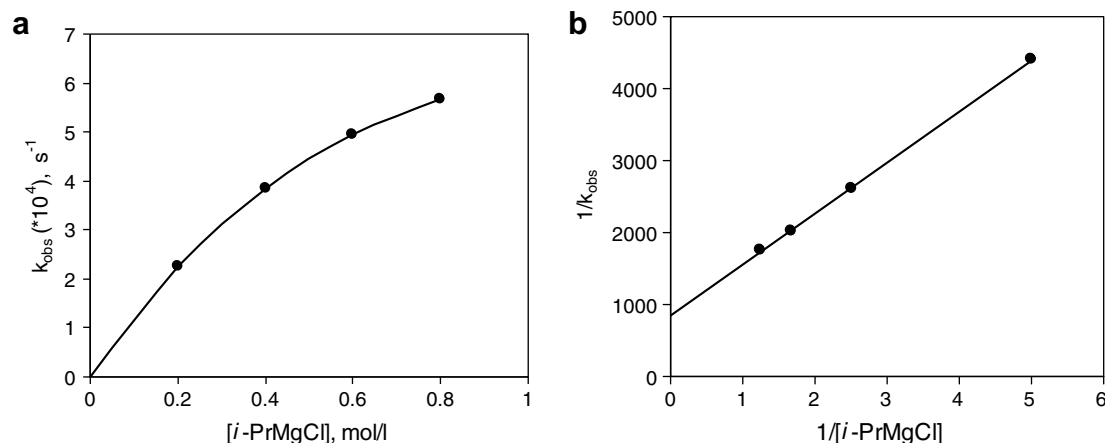


Fig. 1. (a) Pseudo-first-order rate constants k vs. the titrated concentration of i -PrMgCl · Et₂O complex for the reaction with tetraethoxysilane in toluene at 20 °C. (b) Determination of the equilibrium constant (K) and rate constant (k).

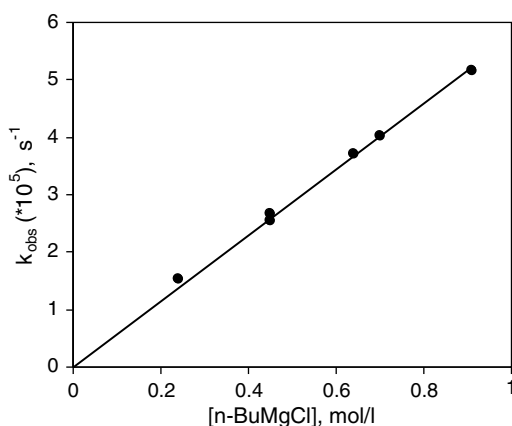


Fig. 2. Plot of the pseudo-first-order rate constants for the reaction of methylvinylchlorosilane with n -BuMgCl · Et₂O vs. Grignard reagent concentration in toluene at 20 °C.

There are two entries in Table 1, where reagents containing i -Pr group are involved. These data deserve special attention because of stronger steric influence of this substituent. It can be observed 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. 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 10.

The calculated second-order rate constants are also listed in Table 1. In general, these values reflect the same structural features and solvation effects discussed above.

Finally, thermodynamic parameters for the equilibrium and rate steps were determined. The first three entries in Table 1 represent the rate and equilibrium constants for the reaction between tetraethoxysilane and n -butylmagnesium chloride at three temperatures. Dibutyl ether appeared to be the most convenient donor for this kinetic study, made at 20 °C, 30 °C and 40 °C in toluene, but also in bulk dibutyl ether (see data in Table 2).

For the reaction in toluene the following thermodynamic parameters were calculated.

For the replacement of the equilibrium:

$$\Delta H = -48 \pm 9 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S = -153 \pm 10 \text{ JK}^{-1} \text{ mol}^{-1}.$$

For the activation process of the reaction

$$\Delta H^\ddagger = 39.8 \pm 2.4 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S^\ddagger = -118 \pm 8 \text{ JK}^{-1} \text{ mol}^{-1}.$$

From the results above a very low or even negative activation energy for the overall reaction can be predicted. Indeed, the activation parameters estimated from the second-order rate constants in Table 1 support the prediction (Table 3, first entry).

Table 1

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	k_{II}^d , L mol ⁻¹ s ⁻¹	Method
Si(OEt) ₄	n -BuMgCl · Bu ₂ O	3.30 ± 0.02	0.33 ± 0.01	1.09	B
	n -BuMgCl · Bu ₂ O ^e	1.23 ± 0.03	0.63 ± 0.01	0.78	B
	n -BuMgCl · Bu ₂ O ^f	0.95 ± 0.04	0.99 ± 0.05	0.94	B
	n -BuMgCl · Et ₂ O	1.22 ± 0.02	0.31 ± 0.01	0.38	B
	n -BuMgCl · THF	0.40 ± 0.02	0.12 ± 0.03	0.048	A
	n -BuMgCl · Et ₃ N	0.76 ± 0.06	(1.70 ± 0.02) × 10 ⁻³	0.0013	A
	i -PrMgCl · Et ₂ O	2.40 ± 0.02	(1.17 ± 0.04) × 10 ⁻³	0.0028	A
i -PrSi(OEt) ₃	n -BuMgCl · Et ₂ O	0.8 ± 0.2	(2.2 ± 0.4) × 10 ⁻³	0.0018	A

^a Si(OEt)₄ + RMgCl → RSi(OEt)₃ + EtOMgCl.

^b Initial concentration of silane in method B 0.015 M, in method A 0.01–0.10 M.

^c Initial concentration from 0.2 M to 1.0 M.

^d $k_{II} = Kk$.

^e At 30 °C.

^f At 40 °C.

Table 2

Pseudo-first-order rate constants for the reaction between tetraethoxysilane and *n*-butylmagnesium chloride (0.88 M) in dibutyl ether

<i>t</i> , °C	<i>k</i> , s ⁻¹
20	0.0353
30	0.0382
40	0.0407

Table 3

Thermodynamic activation parameters for the reaction between tetraethoxysilane and *n*-butylmagnesium chloride in various media

Grignard reagent	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹
<i>n</i> -BuMgCl · Bu ₂ O, toluene	-8 ± 11	-275 ± 38
<i>n</i> -BuMgCl, dibutyl ether	3.0 ± 0.3	-263 ± 2
<i>n</i> -BuMgCl · Et ₂ O, toluene [3]	34.2 ± 3.3	-149 ± 8
<i>n</i> -BuMgCl, diethyl ether [3]	39.1 ± 7.8	-154 ± 17

As seen in Table 3, where the activation parameters are listed for the same reaction in bulk dibutyl ether, this phenomenon is not much affected by solvent change, as very low activation energy can be observed.

For comparison, corresponding parameters concerning diethyl ether complexes from our previous work [3] are presented in Table 3.

It can be inferred that the activation parameters for the overall reaction are rather similar independently of whether the complex is dissolved in the same donor solvent or in toluene. However, an examination of these parameters separately for the equilibrium and the reaction makes visible the contribution of the ligand exchange equilibrium as the first step of the reaction, as well as the decisive importance of solvating power of the donor: the potential well on the reaction path is deeper if the donor is weaker. This permits prediction of apparently negative activation energies for complexes with donors of lesser solvating power than dibutyl ether. If alkyl ethers are regarded, the ethers with greater steric bulk like diisopropyl ether should be considered.

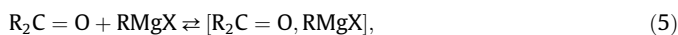
As an extension of the method, kinetic measurements were carried out for the reaction of diisopropyl ketone with *n*-BuMgCl–diethyl ether complex in toluene at 20 °C (method B). The calculated equilibrium and rate constants for the range of concentrations of this Grignard reagent from 0.29 M to 0.92 M were: $K = 8.83 \pm 0.4 \text{ L mol}^{-1}$ and $k = 0.76 \pm 0.02 \text{ s}^{-1}$.

No corresponding data for reactions of ketones with monosolvated Grignard reagents are available, however, we have found [9] for sterically similar *t*-butyl methyl ketone and *n*-propylmagnesium chloride in diethyl ether solution at 20 °C $K = 3.8 \pm 1.2 \text{ L mol}^{-1}$ and $k = 1.09 \pm 0.20 \text{ s}^{-1}$.

Several attempts have been made to determine analogous data for alkylmagnesium bromides [9–11]. However, the results of these experiments are not very reliable because of the known propensity of organomagnesium bromides to form associates at higher reagent concentrations. Contribution of this effect cannot be easily taken into account, thus it may lead to increased values for the equilibrium constants. However, the data above can be compared with the result of experiments, made with a very dilute ether solution of methylmagnesium bromide, thus the reagent existing in

monomeric state, and 2-methylbenzophenone, used in great excess [12]. These studies have yielded the K value 1.35 L mol^{-1} .

Somewhat confusing is the widely accepted way to express the complexation equilibria in ether solutions in the form of Eqs. (5) and (6) [13,14]:



$$K_{\text{eq}} = \frac{[\text{R}_2\text{CO}, \text{RMgX}]}{[\text{R}_2\text{C} = \text{O}], [\text{RMgX}]}. \quad (6)$$

As a rule, the replacement of a solvent molecule has not been considered in these equilibria. However, additions of Grignard reagents to ketones or nitriles and oxirane ring openings, in which complexation with the metal precedes the reaction, are slower in more coordinating solvents [15], this fact being an evidence of the donor molecule replacement. Hence, equilibrium constants determined in this way are solvent concentration dependent and therefore are not straightforwardly compatible with data for monosolvated reagents.

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.

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