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Kinetics of the Grignard Reaction with Silanes in Diethyl Ether and Ether−Toluene Mixtures

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Kinetics of the reactions of butylmagnesium chloride and phenylmagnesium bromide with tetraethoxysilane and methyltrichlorosilane was investigated in diethyl ether and diethyl ether−toluene mixtures. Replacement of ether by toluene significantly accelerates the reaction with alkoxysilanes, while no effect was found for the reaction with chlorosilanes. We established that the reaction with alkoxysilanes 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. Chlorosilanes react differently without solvent molecule replacement but also via a four-center transition state. Large negative activation entropies are consistent with formation of cyclic transition states. Small activation enthalpy values together with remarkable exothermicity point to early transition states of the reactions.

Introduction

Silicone production is the largest consumer of monomeric silanes. The monomeric organosilicon compounds are also important components in a wide range of other applications apart from silicone chemistry. Although a number of direct methods have been developed, Grignard chemistry remains a vital and versatile method for the production of organosilanes.[1] However, despite the increasing industrial use of the reaction, only a few investigations into the kinetics have been implemented.[2] To date, Reid and Wilkins have disclosed only the activation parameters for the reactions of trimethylhalosilanes with methylmagnesium halides.[2a] Previously, we had confined ourselves to some particular cases of the reaction with ethoxysilanes.[2b,c]

Continuation of our investigation[2d] was motivated by matters emerging in Grignard technology when ether solvents were replaced by hydrocarbons of higher boiling points.

Now it is well documented that organomagnesium compounds can be obtained not only in conventional ethers, but also in nonpolar hydrocarbon media in the presence of minor amounts of donor solvents[3] or even in the absence of donor solvent. This has opened wide possibilities for industrial applications, as hydrocarbons are relatively cheap, nonhygroscopic, and environmentally less dangerous solvents if compared with readily flammable and hazardous ethers. The significance of those factors becomes apparent with the growing importance of organomagnesium compounds in the synthesis of silicone monomers and other chemical processes.

Synthesis of unsolvated organomagnesium halides, i.e., their preparation in the absence of the donor solvents, is limited to primary alkyl and aryl compounds. In the presence of minor amounts of complexing agents, e.g., ethers and tertiary amines, a greater variety of organomagnesium compounds can be obtained in hydrocarbon media.[3] Primary, secondary, and tertiary alkylmagnesium chlorides in toluene solutions, containing less than 1 equiv of organic base, have been prepared recently.[3d−f] More generally, toluene has been proved to be a particularly suitable solvent for synthesis of Grignard reagents, as rather concentrated (1 M and above) solutions of these compounds can be obtained in this solvent.[3e,f]

Whereas the Grignard reagents are solvated at least by two solvent molecules per atom of magnesium in donor solvents, the reagents obtained in the presence of smaller molar amounts of donor substances are only partially solvated. The chemical features of the conventional Grignard reagents and partially solvated organomagnesium compounds can be rather different, e.g., the reactions of partially solvated alkylmagnesium chlorides and bromides with carbonyl compounds in benzene or toluene give better yields of addition products in comparison with those in ethers.[4]

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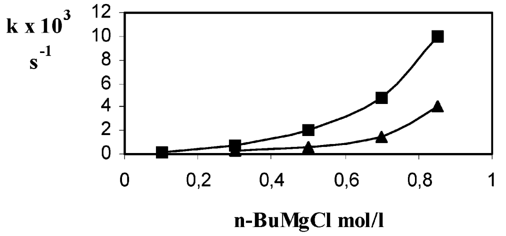

FIGURE 1. Dependence of pseudo-first-order rate constants on Grignard reagent concentration for the reaction of butylmagnesium chloride with tetraethoxysilane (■) and butyltriethoxysilane (▲) in diethyl ether at 20 °C. Method A (see Experimental Section).

The rate of the reaction of Grignard reagents with hydrazones is greatly increased when free ether is replaced by toluene.[5] Kinetic investigations have revealed that additions of toluene accelerate the reaction of phenylmagnesium bromide with hex-1-yne in both diethyl ether and THF.[6] The same was observed for the reaction between ethyltriethoxysilane and ethylmagnesium chloride. At a molar ratio of 0.8 for toluene in ether, the reaction proceeded 12 times faster than in pure ether.[2b] The reagent *n*-BuMgCl·Et$_2$O in toluene, in comparison with *n*-BuMgCl in diethyl ether, was predominantly reactive toward tetraethoxysilane.[2c] However, this did not prove to be valid for the reactions with chlorosilanes.[2d] Here we report the results of a detailed kinetic investigation of the Grignard reaction with both alkoxy and chlorosilanes in diethyl ether and diethyl ether−toluene mixtures. Also, the issues concerning the reaction mechanism, raised in our preliminary communication,[2d] will be discussed.

In the kinetic investigation, methyltrichlorosilane and tetraethoxysilane were chosen for model silanes, while phenylmagnesium bromide and *n*-butylmagnesium chloride served as model Grignard reagents.

Results and Discussion

Alkoxysilanes. Kinetics of the Grignard reaction with alkoxysilanes should obey the second-order law; therefore, the pseudo-first-order rate constants determined with a great excess of the Grignard reagent should depend linearly upon the concentration of the reagent. However, this is not the case, as seen in Figure 1.

Nevertheless, higher kinetic orders in the Grignard reagent do not appear to be pertinent to the reaction. A similar dependence has been observed for the reaction of ethyltriethoxysilane with ethylmagnesium chloride in diethyl ether.[2b] At that time, a semiquantative interpretation was given on the basis of the association equilibria in the Grignard reagent solution and assuming that only the tetramers were reactive.

However, these phenomena can be explained more straightforwardly by the necessity to substitute a donor molecule at the magnesium center by the substrate. The concept of replacement of an ether molecule by a carbonyl compound as the first step in its reaction is generally accepted.[7] We have shown using density functional theory calculations that for the Grignard reaction with alkynes, preliminary replacement of a solvent molecule is energetically preferable.[6a,8] The magnitude of the calculated equilibrium constants is about 10^{-6}. Experimentally, the estimated complexation constants for ketones and esters range from unity to 14 l/mol.[9] Alkoxysilanes probably lie somewhere between since due to both electronic and steric reasons they should be slightly weaker Lewis bases than ethers or carbonyl compounds. Thus, replacement of the donor solvent by a nondonating one, e.g., diethyl ether by toluene, shifts the complexing equilibrium toward a more favorable position, thereby enhancing the reaction rate. The same appears to be the case in more concentrated Grignard solutions where the concentration of free ether is decreased.

If the reaction proceeds through replacement of a solvent molecule and subsequent rate-limiting conversion of the complex to products, the rate of the reaction can be expressed as

$$\mathrm{G\cdot 2E} + \mathrm{S} \overset{K}{\rightleftharpoons} \mathrm{GS\cdot E} + \mathrm{E}$$

$$\mathrm{GS\cdot E} \xrightarrow{k} \text{product} \tag{1}$$

$$v = k\,[\mathrm{GS\cdot E}] = kK\frac{[\mathrm{G\cdot 2E}][\mathrm{S}]}{[\mathrm{E}]} \tag{2}$$

where G denotes a magnesium compound, S the silane, and E an ether molecule.

Under pseudo-first-order conditions ([G·2E] = constant)

$$k_{\mathrm{obs}} = kK\,\frac{[\mathrm{G\cdot 2E}]}{[\mathrm{E}]} \tag{3}$$

and

$$kK = \frac{k_{\mathrm{obs}}[\mathrm{E}]}{[\mathrm{G\cdot 2E}]} \tag{4}$$

Taking advantage of the Grignard reagent density determinations published by the authors,[2b] we recalculated their kinetic data for the reaction between ethylmagnesium chloride and ethyltriethoxysilane. According to the extensive investigations into the association phenomena in Grignard solutions,[10] alkylmagnesium chlorides are essentially dimeric species over a wide concentration range. Thus, in the calculation of the free ether concentration, ethylmagnesium chloride was considered

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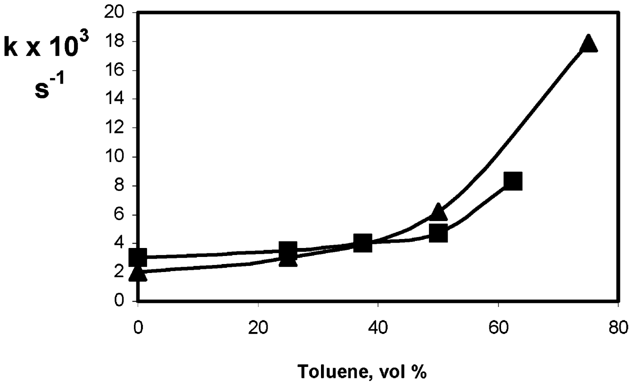


FIGURE 2. Rate of the Grignard reaction with tetraethoxysilane in diethyl ether–toluene mixtures at 20 °C: (■) PhMgBr, (▲) *n*-BuMgCl. Method B (see Experimental Section).

TABLE 1. Recalculation of Rate Constants for the Reaction of Ethyltriethoxysilane with Ethylmagnesium Chloride

EtMgCl (M)	k_{obs} (s^{-1})	Et_2O (M)	kK
0.9	0.014	8.35	0.130
1.09	0.016	8.10	0.119
1.45	0.035	7.60	0.183
2.03	0.040	6.75	0.133
2.16	0.054	6.50	0.163
2.32	0.063	6.30	0.171
3.22	0.088	4.60	0.126
		kK(av) = 0.146 ± 0.03	

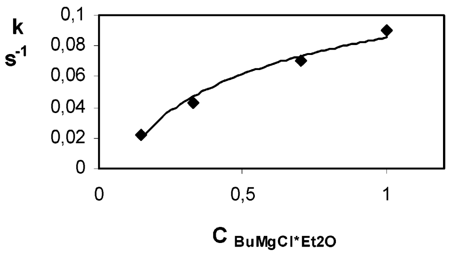


FIGURE 3. Pseudo-first-order rate constants vs the concentration of $BuMgCl\cdot Et_2O$ complex for the reaction with tetraethoxysilane in toluene at 20 °C. Method B (see Experimental Section).

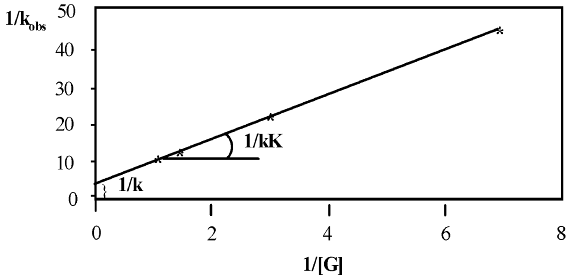


FIGURE 4. Determination of the equilibrium constant (K) and rate constant (k) for the reaction of tetraethoxysilane with *n*-$BuMgCl\cdot Et_2O$ complex in toluene at 20 °C.

to be monosolvated. The results in Table 1 clearly demonstrate the validity of the assumptions made above. Similarly, the rate enhancement caused by the replacement of diethyl ether by toluene (Figure 2) can be quantitatively ascribed to shifts in the complexation equilibrium as shown in Table 2.

The monosolvated Grignard reagent in toluene is particularly liable to complexation with a silane, this matter being reflected in the rather high reaction rates. The dependence of the pseudo-first-order rate constant upon the concentration of monosolvated Grignard reagent (Figure 3) provides a way of determining the equilibrium and rate constants separately.

Assuming steady-state conditions and a fast complexation equilibrium, for the reaction 1 we deduce eq 5

$$k_{obs} = \frac{kK[G]}{1 + K[G]} \qquad (5)$$

Equation 5 can be converted into eq 6, more suitable for data treatment.

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{1}{kK[G]} \qquad (6)$$

The obtained linear plot in Figure 4 affirms the assumptions made above and yields the numerical values $K = 1.03$ l mol^{-1} and $k = 0.17$ s^{-1}. Actually, because of the dimeric nature of the reagent, the Grignard reagent concentration should be halved and then $K \approx 2$. The rate constant remains unchanged.[11]

Apart from the solvent system diethyl ether–toluene, increasing the solvating power of the solvents is unfavorable for complexing between the reagents and in this way suppresses the reaction rate. This has been clearly demonstrated by a distinct sequence of the rates of the reaction between *n*-BuMgCl and tetraethoxysilane in solvents methyl *tert*-butyl ether > diethyl ether > THF.[2d] Similarly, additions to ketones or nitriles and oxirane ring openings, in which complexation with the metal precedes the reaction, are slower in more coordinating solvents.[7,12] Consequently, replacement of the donor

TABLE 2. Recalculation of Rate Constants for the Grignard Reactions of Alkoxysilanes in Diethyl Ether–Toluene Mixtures (Temperature 20 °C, Method B)

PhMgBr (0.5 M) + $(EtO)_4Si$				BuMgCl (0.5 M) + $(EtO)_4Si$				BuMgCl (0.5 M) + $Bu(EtO)_3Si$			
toluene (vol %)	free ether [E] (M)	$k \times 10^3$ (s^{-1})	$k[E] \times 10^2$	toluene (vol %)	free ether [E] (M)	$k \times 10^3$ (s^{-1})	$k[E] \times 10^2$	toluene (vol %)	free ether [E] (M)	$k \times 10^3$ (s^{-1})	$k[E] \times 10^2$
0	8.9	3.00	2.65	0	8.9	2.00	1.78	0	8.9	0.64	0.57
25	6.45	3.50	2.25	25	6.45	3.00	1.94	25	6.45	0.86	0.55
37.5	5.29	4.04	2.14	50	4.00	6.20	2.47	50	4.00	1.90	0.76
50	4.00	4.70	1.89	75	1.48	17.9	2.65	75	1.48	6.00	0.89
62.5	2.83	8.30	2.35	95[a]	0	60.0					
95[a]	0	40.0									
		av = 2.26 ± 0.27				av = 2.21 ± 0.4				av = 0.69 ± 0.2	

[a] Monosolvated reagent.

TABLE 3. Rate Constants for the Grignard Reactions of Methyltrichlorosilanes in Diethyl Ether−Toluene Mixtures at 20 °C[a]

PhMgBr (0.5 M) toluene, vol %	$k \times 10^3$, s^{-1}
0	1.62
25	1.50
37.5	1.70
50	1.60
62.5	1.90
75	1.45
	av 1.63 ± 0.16

[a] Method B (see Experimental Section).

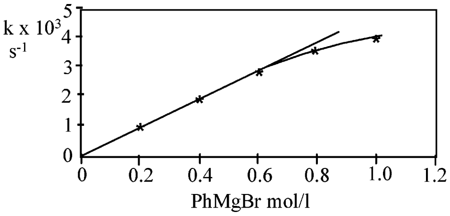
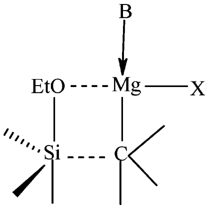


FIGURE 5. Plot of pseudo-first-order rate constants vs phenylmagnesium bromide concentration in diethyl ether for the reaction with methyltrichlorosilane at 20 °C. Method B (see Experimental Section).

SCHEME 1



molecule and the four-center transition state with an S_Ei mechanism at the carbon atom generally accepted for Grignard reactions with carbonyl compounds[7] can be adopted for the Grignard reaction with alkoxysilanes (Scheme 1)

Chlorosilanes. Solvent effects in the reactions with methyltrichlorosilane reveal different behaviors of chlorosilanes. A reverse sequence of solvent effects, in comparison with alkoxysilanes, THF > diethyl ether > methyl *tert*-butyl ether, was found for the reaction with phenylmagnesium bromide.[2d] In contrast to alkoxysilanes, the reaction rate increases with the increasing solvating power of ethers, and replacement of ether by toluene does not affect the reaction rate as seen from the data in Table 3.

Kinetics of the reaction obey the second-order law as seen from Figure 5. The pseudo-first-order rate constants depend linearly on the Grignard reagent concentration. A slight deviation from linearity at higher reagent concentrations can be attributed to a decrease in the Grignard reagent activity because of intensive self-association of phenylmagnesium bromide in diethyl ether solutions.[10]

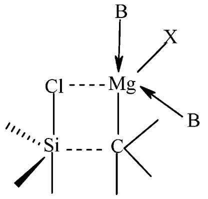
The findings described above exclude the substitution of an ether molecule in the Grignard reagent as the first step of the reaction with chlorosilanes. The data also point to the decisive role of the donor solvent in determining the nucleophilicity of the carbon center. Thus, the mechanism of the Grignard reaction with chlorosilanes is different from that with alkoxysilanes. An S_Ei mechanism, common for electrophilic substitution reaction with organometallic compounds,[13] can be assumed (Scheme 2). A cyclic transition state with magnesium−halogen coordination, followed by concerted formation of the silicon−carbon bond and rupture of the silicone−halogen bond, has been suggested by Reid and Wilkins[2a] on the basis of a thorough analysis of activation energies

TABLE 4. Determination of the Activation Parameters

reaction and solvent	*t* (°C)	$k \times 10^3$ (s^{-1})	activation parameters[a]
$Si(OEt)_4 + BuMgCl$ (1.0 M)	0.5	1.6	$\Delta H^\ddagger = 39.1 \pm 7.8$
diethyl ether[b]	11	4.4	$\Delta S^\ddagger = -154 \pm 17$
	20	4.7	
	30	10.8	
$Si(OEt)_4 + BuMgCl\cdot Et_2O$ (0.6 M)	11	55.2	$\Delta H^\ddagger = 34.2 \pm 3.3$
toluene[c]	20	72.8	$\Delta S^\ddagger = -149 \pm 8$
	30	123	
	40	219	
i-$PrSi(OEt)_3 + BuMgCl$ (1.0 M)	9	0.013	$\Delta H^\ddagger = 51.8 \pm 2.3$
diethyl ether[b]	20	0.030	$\Delta S^\ddagger = -154 \pm 8$
	30	0.066	
i-$PrSi(OEt)_3 + BuMgCl\cdot Et_2O$ (1.0 M)	9.5	0.30	$\Delta H^\ddagger = 41.9 \pm 2.7$
toluene[b]	20	0.64	$\Delta S^\ddagger = -163 \pm 9$
	30	1.20	
	40	1.80	
$MeSiCl_3 + BuMgCl$ (0.5 M)	12	0.092	$\Delta H^\ddagger = 37.6 \pm 2.7$
diethyl ether[b]	20	0.15	$\Delta S^\ddagger = -190 \pm 9$
	30	0.27	
$MeSiCl_3 + PhMgBr$ (0.63 M)	12	2.5	$\Delta H^\ddagger = 22.2 \pm 1.5$
diethyl ether[b]	17	2.7	$\Delta S^\ddagger = -216 \pm 5$
	20	3.5	
	30	4.0	
$MeSiCl_3 + PhMgBr\cdot Et_2O$ (0.55 M)	11	2.0	$\Delta H^\ddagger = 33.1 \pm 3.4$
toluene[b]	20	3.6	$\Delta S^\ddagger = -179 \pm 11$
	30	6.0	
	40	8.0	

[a] $\Delta H^\ddagger$ in kJ mol^{-1}, $\Delta S^\ddagger$ in J mol^{-1} K^{-1}. [b] Method A. [c] Method B.

SCHEME 2



and entropies for the reactions of halogenotrimethylsilanes with methylmagnesium halides in diethyl ether.

The activation parameters for the reactions presented in Table 4 are very similar to those published by Reid and Wilkins.[14] The large entropy losses during the activation found in this work and by Reid and Wilkins[2a] are consistent with formation of cyclic transition states in the reactions of both alkoxysilanes and chlorosilanes. Low activation energy values, together with the significant exothermicity of the reactions, point to transition states occurring rather early in the reaction coordinate. This provides an explanation of almost total absence of nonspecific medium effects in these reactions (Tables 2 and 3). Indeed, in an early transition state, the charge distribution may differ insignificantly from that in the reagents, thus displaying no considerable changes in polarity during activation.

Introduction of a bulky isopropyl group into the alkoxysilane does not cause any noticeable change in the activation entropy (Table 4) but gives rise to a considerably greater activation energy of the reaction.

A certain difference in activation entropy values for the reactions of alkoxysilanes and chlorosilanes (Table 4) is evident. Relatively lower entropy losses for alkoxysilanes may involve the release of a solvent molecule during the reaction; however, rather large entropy values for chlorosilane reactions probably manifest the steric encumbrance in the transition state, particularly at the magnesium atom site (see Scheme 2).

Conclusions

We have carried out a kinetic investigation of solvent effects in the Grignard reaction with silanes. We have established that the reaction with alkoxysilanes 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. Chlorosilanes react differently without solvent molecule replacement but also via a four-center transition state. The Grignard reaction with silanes can be carried out in diethyl ether−toluene mixtures. The reaction with alkoxysilanes becomes significantly accelerated when ether is replaced by toluene. Use of monosolvated Grignard reagents provides a convenient way to determine separately the equilibrium and rate constants for the reactions with alkoxysilanes.

Experimental Section

Grignard reagents were obtained by conventional methods.[15] Monosolvated Grignard reagents in toluene were prepared as described earlier.[3e,f] Grignard reagents in diethyl ether−toluene mixtures were prepared by dilution of concentrated stock solutions in diethyl ether with appropriate amounts of the ether and/or toluene. The reagents and solutions were handled under dry argon and transferred by use of cannulas or syringes.

Kinetic Measurements. Method A. Flasks (7−8 for each run) equipped with magnetic stirrers and containing 8 mL of the Grignard reagent were thermostated. To start the reaction, 0.1−0.2 mL of alkoxysilane (providing a 9−20-fold excess of the Grignard reagent) was injected into each flask. At appropriate times, the reaction mixtures were quenched with ice cold water. The organic layer was promptly separated, dried, and analyzed by use of 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. To a 15 mL sample of the Grignard reagent was added 0.05 mL of silane (providing a 20−40-fold excess of the Grignard reagent), and the temperature change of the reaction solution (up to 1 °C) was recorded as a plot of temperature versus time. Use of a differential method for calculation of rate constants eliminated the contribution of heat exchange with the reaction vessel.

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[11] Preliminary experimental data for the same reaction with isopropyltriethoxysilane afford an estimation of $K \approx 0.4$ and $k \approx 0.0022$, which are well in line with the supposedly small steric hindrances for the complexation and considerable steric requirements of the substitution at the silicon atom.

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[14] For instance, $\Delta H^{\ddagger} = 33.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = -201$ J mol^{-1} K^{-1} for the reaction of MeMgCl with Me_3SiCl or $\Delta H^{\ddagger} = 33.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -189$ J mol^{-1} K^{-1} for the reaction of MeMgBr with Me_3SiCl were found.[2a]

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