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Complexes PhMgBr·nMgBr$_2$·mNEt$_3$ in the reaction with acetylene

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Abstract

Kinetics of the reaction of acetylene with two phenylmagnesium bromide reagents of different magnesium bromide content (Br/Mg 1.08 and 1.27) in diethyl ether in the presence of various additions of triethylamine (TEA) were investigated. The reagent of average stoichiometry PhMgBr·2TEA reacts about 20 000 times faster than in the absence of the amine. Elevated content of magnesium bromide in the reagent enhances the accelerating effect of the amine. The complicated relationships obtained enabled us to draw conclusions on the structure and reactivity of the title complexes. At moderate magnesium bromide content species 2PhMgBr·MgBr$_2$ dominate and preferentially complex with TEA giving solvates more reactive than PhMgBr·TEA, whose formation takes place at a higher amine content. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Acetylenic Grignard compounds or the corresponding organoalkali metal derivatives are important intermediates in many syntheses of acetylenic compounds. Although deprotonation of terminal acetylenes by organolithium compounds in organic solvents or by alkali metal amides have been most frequently used, in certain cases [1,2] converting of acetylenes into Grignard reagents has advantages over these methods.

Reactions of acetylenic compounds with Grignard reagents have been investigated sporadically over many years [3]. The reaction of acetylenes is an extremely slow process, however, it was found that addition of tertiary amines accelerates remarkably the reaction of alkylmagnesium halides with 1-hexyne [4,5]. Formation of bis-bromomagnesiumacetylene in conventional ethers also proceeds sluggishly [1].

The kinetics of the reaction of acetylene with phenylmagnesium bromide were previously investigated in this laboratory [6–8]. A catalytic effect of organic bases was established, whereas secondary and aliphatic tertiary amines were found to accelerate considerably the formation of bis-bromomagnesiumacetylene. Triethylamine (TEA) appeared to be the most effective catalyst among the investigated donors [6].

Besides other findings a conspicuous effect of magnesium bromide additions was intriguing. Similarly to the one reported by Wotiz et al. [5] for the reaction of ethylmagnesiumbromide with 1-hexyne, additions of magnesium bromide to the Grignard reagent enhanced considerably the catalytic effect of triethylamine in the reaction with acetylene [8]. Such a result was bewildering on the background of a well-known suppressing effect of magnesium halides on the reaction rates of Grignard reagents with 1-hexyne [9], acetylene [8], ketones [10–13], esters [12], nitriles [14] and phosphonates [15]. Namely, it was found that in the presence of a small amount of TEA (about 0.2 equivalents per Ph–Mg) the reaction rate in diethyl ether increased almost linearly and by more than 10 times when passing from pure diphenylmagnesium (no catalytic effect) to the complex of stoichiometry 2PhMgBr·MgBr$_2$. Although complexation and solvation effects were evident, a detailed analysis of the phenomenon failed in that work.

In connection with our continuous interest in solvation effects in the Grignard chemistry, we have resuscitated our earlier investigation of the reaction of acetylene with phenylmagnesium bromide. In this work the rate constants of the reaction were determined for a wide range of triethylamine additions in the presence of both small and considerable amounts of magnesium bromide. The unexpectedly complicated relationships

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obtained enabled us to draw significant conclusions on the structure and reactivity of the system PhMgBr·nMgBr$_2$·mTEA in diethyl ether.

2. Experimental

2.1. Materials

All the operations with the reagents and solutions were carried out under dry argon. The Grignard reagents were prepared in the conventional manner. Elevated magnesium bromide content in the reagent was attained by partial replacing of bromobenzene with 1,2-dibromoethane in the synthesis. The reagents were analysed for basic magnesium concentration acidimetrically and for bromide ion concentration by the Mohr method in the same solution after the acidimetric analysis. The total magnesium content was determined by complexation titration. The material balance was always good to excellent.

2.2. Kinetic measurements

The reaction was carried out in a cylindrical glass vessel (34 cm^3) mantled with foam plastic and placed in a thermostatted housing. The equipment was sealed with a thermostatted lid. The reaction cell was provided with three tubes mounting through the lid. Two inlets were employed for a mechanical stirrer and for a thermistor, respectively, the third inlet serving for the injection of the reagents. The thermistor was connected through a bridge circuit to a recording potentiometer and the device was calibrated for the temperature range from 19.8 to 20.3°C.

All parts of the equipment as well as the reagents were thermostatted at 19.8°C. The reaction vessel was purged thoroughly with pure argon, about 30 ml of the Grignard reagent was cannulated into the cell and the stirring was started. After the thermal equilibrium was set, the temperature of the solution was adjusted to 19.8°C by introducing a thin jet of dry argon. Then about 0.6 cm^3 of dry ether saturated with acetylene was introduced, and the temperature change of the reaction solution (usually 0.4°C by the end of the reaction) was recorded as a plot of temperature (in mm) versus time. Thus the mean reaction temperature was about 20°C. Because of short reaction times ranging from tens to a few hundreds of seconds, the system was nearly adiabatic and the heat exchange with the internal part of the calorimeter caused a heat loss to an extent of a few per cent. The temperature of the reaction mixture was corrected as described earlier [16].

The pseudo-first-order rate constants were calculated from the initial rate of the reaction as

$$k_{\mathrm{I}} = \frac{v_0}{[\mathrm{C_2H_2}]_0}$$

where v_0 is the slope of the tangent to the kinetic curve in its initial point in mm s^{-1} and the initial concentration of acetylene, $[\mathrm{C_2H_2}]_0$, is expressed as the total heat of the reaction measured in mm from the thermogram corrected for the heat exchange.

3. Results and discussion

The two-step mechanism of the reaction of acetylene with a Grignard reagent

$$\mathrm{HC{\equiv}CH + RMgX \rightarrow HC{\equiv}CMgX + RH} \quad (1)$$

$$\mathrm{2\ HC{\equiv}CMgX \rightarrow XMgC{\equiv}CMgX + HC{\equiv}CH} \quad (2)$$

was suggested by Kleinfeller and Lohmann [17] and confirmed inter alia by our investigations [7]. The first step of the reaction is rate limiting. Although amines catalyse the second step more intensively [7], under a 100-fold excess of the Grignard reagent and at low acetylene concentration applied in our experiment only reaction (1) could be observed at the beginning of the process. However, the total thermal effect of the process recorded at the end of the reaction consists of heats ΔH_1 and ΔH_2 of two consecutive reactions (1) and (2), respectively. Therefore, the pseudo-first-order rate constants calculated as described in the experimental section should be corrected by a factor $(\Delta H_1 + \Delta H_2)/\Delta H_1$, but the reaction heats are not known. We could only establish that the total heat of the process was proportional to the amount of acetylene regardless of the changes in Grignard reagents or in the amine concentration. Hence, two corrections were made. The observed pseudo-first-order rate constants divided by the Grignard reagent concentration gave the second-order rate constants k_{II} and the relative rate constants k_{rel} were calculated by taking the system PhMgBr·0.087MgBr$_2$·0.01TEA for the reference point ($k_{\mathrm{rel}} = 1$). The obtained reactivity values for the Grignard–TEA systems are presented in Tables 1 and 2 and in Fig. 1.

True rate constants can be estimated from the following experimental data. The second-order rate constant for 1 molar per cent amine content in Table 1 exceeds by about 50 times the one obtained by the same method for the same reagent without amine addition [7]. Kinetic measurements both by acetylene absorption and benzene production gave coinciding results and indicated about a 100-fold rise of the rate by adding the same relative amount (1 molar per cent) of TEA [18]. Thus, the correction factor for thermographic data is about 2.0, indicating at the same time close values for ΔH_1 and ΔH_2.

Table 1
Kinetic data for the reagent $PhMgBr·0.087MgBr_2$ in the presence of different additions of triethylamine

PhMgBr ($mol\ l^{-1}$)	Amine [a] (mol%)	k_I ($10^2\ s^{-1}$)	k_{II} (10^2) [b]	k_{rel}
0.707	1.00	0.176	0.250	1.00
0.690	1.74	0.253	0.366	1.46
0.662	3.68	0.550	0.831	3.32
0.702	6.87	1.24	1.77	7.06
0.707	18.1	3.30	4.67	18.7
0.678	33.0	4.70	6.91	27.6
0.668	51.0	6.00	8.99	36.0
0.627	59.5	6.67	10.6	42.5
0.515	75.0	6.12	11.8	47.5
0.540	81.5	7.00	12.9	51.8
0.660	94.3	9.20	13.9	55.7
0.515	103.0	7.60	14.7	59.0
0.606	121.0	11.4	18.8	75.2
0.636	132.0	16.0	25.1	100.6

[a] ([TEA]/[PhMgBr]) × 100.
[b] $l\ mol^{-1}\ s^{-1}$.

Two Grignard reagents with different contents of magnesium bromide were used. Conventional Grignard reagents usually contain a slight excess of magnesium halide because of some unavoidable Wurtz coupling. In this experiment the ratio Br/Mg was equal to 1.08 and for the reagent with enhanced magnesium bromide content it equalled 1.27 Thus, the stoichiometric composition of the reagents was $PhMgBr·0.087MgBr_2$ (A) and $PhMgBr·0.37MgBr_2$ (B), respectively.

A Grignard reagent in diethyl ether is an extremely complex system [3]. Because of low solubility the magnesium bromide present must be complexed with the organomagnesium compound. At the ratio Br/Mg = 1.5 the stoichiometric complex $PhMgBr·MgBr_2$ forms and layering of the solution occurs. The same has been observed also for the ethylmagnesium bromide–magnesium bromide system [10]. Thus, at lower values of the ratio Br/Mg, complexes of lower magnesium bromide content, e.g. $2PhMgBr·MgBr_2$, should be preponderant. Quite rational structures I or II, where E stands for diethyl ether and X for the bromine atom, could be attributed to the complex.

Table 2
Kinetic data for the reagent $PhMgBr·0.37MgBr_2$ in the presence of different additions of triethylamine

PhMgBr ($mol\ l^{-1}$)	Amine [a] (mol%)	k_I ($10^2\ s^{-1}$)	k_{II} (10^2) [b]	k_{rel} [c]
0.380	1.00	0.262	0.689	2.75
0.380	5.00	0.690	1.82	7.26
0.372	9.40	1.120	3.22	12.9
0.370	20.0	2.26	6.11	24.4
0.366	40.0	4.36	11.9	47.6
0.363	60.0	6.70	18.5	73.8
0.360	80.0	9.10	25.3	101.1
0.356	100.0	9.95	27.9	111.8
0.352	120.0	10.9	31.0	123.9
0.346	140.0	13.9	39.8	159.3
0.345	160.0	17.5	50.7	202.9

[a] ([TEA]/[PhMgBr]) × 100.
[b] $l\ mol^{-1}\ s^{-1}$.
[c] For $k_{rel} = 1$ see first entry in Table 1.

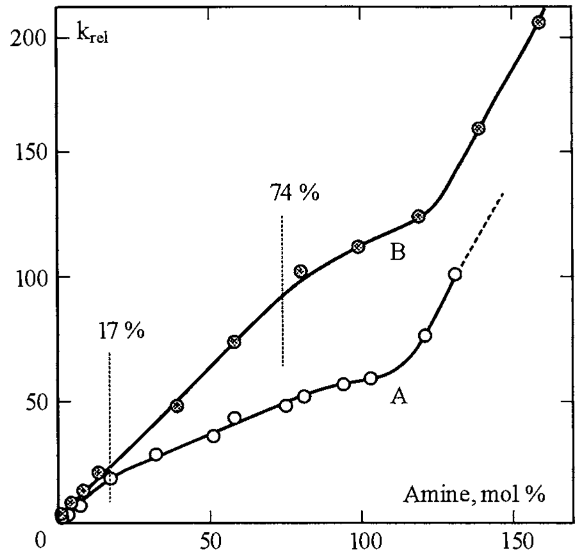
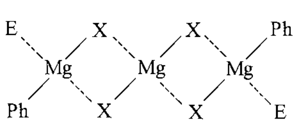


Fig. 1. Dependence of the reaction rate on the relative content of triethylamine. (A) The reagent $PhMgBr·0.087MgBr_2$; (B) the reagent $PhMgBr·0.37MgBr_2$.



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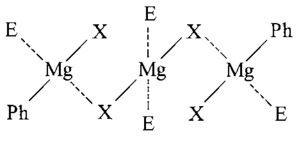


II

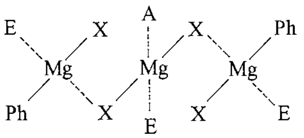
If this is true, in the Grignard reagent of the ratio Br/Mg = 1.27 (B) about 74% of PhMgBr pertains to the complex with magnesium bromide and 26% of it is unbound. For the conventional Grignard reagent (A) the figures are 17 and 83, respectively.

Let us consider now the influence of triethylamine additions on the reactivity of Grignard reagents A and B towards acetylene. It is seen from Fig. 1 that small amine additions enhance reactivity proportionally and the plots for both reagents are parallel. However, beginning from certain points on the graph the growth of reactivity decelerates. It is remarkable that the range of the bend is close to 17 mol% of amine for reagent A and to 74 mol% for reagent B, which is just in correspondence with the relative content of complexes I or II in the reagents. Further increase in reactivity is moderate and lasts for a short interval in the amine content scale for reagent B but does for quite a long one for reagent A. Then, from 120 to 130 mol% of amine the reactivity graphs of both reagents are steep again. An increase in reactivity was evident up to at least 300 mol% of amine, but our experimental facilities did not allow the performance of reliable kinetic measurements in this region.

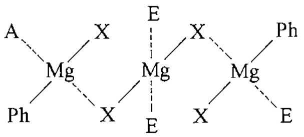
The observed experimental facts impose some conclusions on the structure and the reactivity of species comprising the systems under investigation. Obviously, the first portions of amine become bound to PhMgBr–$MgBr_2$ complexes with the formation of species more reactive than PhMgBr·TEA complexes appearing at further amine additions. A reverse order of the formation of the complexes or their opposite reactivity would not bring about the shapes of the curves shown in Fig. 1.

The conclusions drawn above can be rationalized on the basis of effective (Lewis) acidity of solvation centres and effective basicity of donors (see, e.g. discussion in Ref. [19]). It is appropriate to note here that a strong Brønstedt base TEA appeared to be a much better donor than diethyl ether and slightly better than THF for phenylmagnesium bromide but not for diphenylmagnesium. In the case of sterically more hindered diethylmagnesium TEA is even a weaker donor than diethyl ether [6,19].

In complex II the central magnesium atom is the most favourable centre to be solvated by TEA. As regards free phenylmagnesium bromide, simultaneous solvation by two donors with great steric demands, TEA and diethyl ether, is energetically less advantageous and therefore this complex forms at higher amine concentrations. Replacement of diethyl ether by TEA in complex II can lead to complexes III or IV, where A stands for the amine molecule.



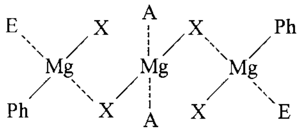
III



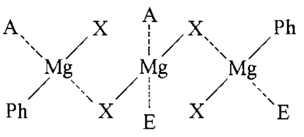
IV

Although complex III seems to be energetically more favourable, complex IV should be more reactive because of a proximate effect of the donor on the nucleophilicity of the organic group. However, a possible long-range effect of the donor in complex III should not be overlooked. According to Charton parameters [20] steric demands of the ligands line up in a sequence $Br \leq Ph < Et_2O \ll TEA$. On the other hand, Brønstedt basicity in terms of B parameters [21,22] is a little less than 100 for alkyl halides, 280 for diethyl ether, and 650 for TEA. Tetraalkylammonium halides, where the halide atom is in ionic form, show basicities comparable to or even greater than that of TEA [23]. Although magnesium bromide is not entirely ionic under these conditions, polarity of the magnesium–halide bond considerably exceeds that of alkyl halides. When the magnesium centre carries a ligand like TEA, basicity of the bromine atom may be comparable to or higher than that of alkyl ethers. Owing to low steric requirements the bromine atom in complex III can gain an unexpectedly great donating power. Similar circumstances seem to be liable for the association of Grignard reagents in the media of moderate solvating ability. We intend to publish further details on this issue elsewhere.

At an amine content of 100 mol% each PhMgBr entity is solvated by one molecule of TEA on the average. In this region complexes like V and VI should be formed.



V



VI

Further increase in the amine content involves the formation of complexes including more amine molecules and thus brings about higher reactivity of the system. Finally, at high amine contents only disolvated species PhMgBr·2TEA and $MgBr_2$·2TEA should occur. However, the equilibrium

$$PhMgBr{\cdot}Et_2O{\cdot}TEA + TEA \rightleftharpoons PhMgBr{\cdot}2\ TEA + Et_2O$$

is not necessarily shifted to the far right. It is known that the second equilibrium constant of recoordination between the complex of ethylmagnesium bromide with 1-ethoxy-2-methylbutane and TEA is about 25 times less than the first equilibrium constant [24]. This is an obvious reason for the continuing increase of k_{rel} in the region of amine additions exceeding two equivalents per phenylmagnesium bromide. The powerful effect of amine is manifested by the fact that the reagent of average stoichiometry PhMgBr·2TEA reacts with acetylene about 20 000 times faster than in the absence of the amine.

Acknowledgements

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