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Mechanism of the reaction of acetylene with Grignard reagents

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Abstract

Kinetics of the reaction between acetylene and phenylmagnesium bromide were investigated in diethyl ether in the presence of small additions of triethylamine and without a catalyst. The mechanistic scheme suggested by Grignard et al. was supplemented with the reaction of bromomagnesiumacetylene with the Grignard reagent. The rate constants for individual reactions were determined. Triethylamine catalyzes the reactions to different extents, the conversions of bromomagnesiumacetylene being the most susceptible to the catalysis. The possible ways of the action of the catalyst were discussed and the importance of nucleophilic assistance was stressed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The reaction of acetylene with a Grignard reagent affords a mixture of bromomagnesiumacetylene and bis-bromomagnesiumacetylene, which can serve as an intermediate in the syntheses of acetylenic compounds [1]. Since the reaction proceeds slowly and the ratio of the products is predetermined by the reaction conditions, a knowledge of the reaction mechanism is desirable in order to control the process.

Grignard reagents of the type $RC{\equiv}CMgX$ were first prepared by Iotsitch [2] by the method of hydrogen displacement. The dimagnesium Grignard reagent itself was also prepared by Iotsitch by the passage of acetylene into an ethereal solution of ethylmagnesium bromide [3].

Grignard et al. [4] suggested a two-step reaction mechanism for the formation of bis-bromomagnesiumacetylene:

$$RMgX + HC{\equiv}CH \rightarrow HC \equiv CMgX + RH$$

$$2HC{\equiv}CMgX \rightleftarrows XMgC{\equiv}CMgX + HC{\equiv}CH$$

Kleinfeller and Lohmann [5] studied the kinetics of ethane evolution during the reaction of acetylene with ethylmagnesium bromide. The formation of bromomagnesiumacetylene in the first step of the reaction and its further disproportionation were confirmed. However, the authors did not follow the reaction long enough to observe the equilibrium between mono- and bis-bromomagnesium products. Jones et al. [6] also questioned the occurrence of the equilibrium and suggested the following reaction scheme:

$$RMgX + HC{\equiv}CH \rightarrow CH{\equiv}CMgX + RH$$

$$HC{\equiv}CMgX + RMgX \rightarrow XMgC{\equiv}CMgX + RH$$

$$2HC{\equiv}CMgX \rightarrow XMgC{\equiv}CMgX + HC{\equiv}CH$$

In an earlier work [7] we followed the kinetics of the reaction of acetylene with phenylmagnesium bromide by the consumption of acetylene and the evolution of benzene simultaneously. The measurements were performed in diethyl ether and THF in the presence of triethylamine and also without the catalyst. Insignificant additions of triethylamine to the solution of phenylmagnesium bromide in diethyl ether were found to largely accelerate the reaction and change the kinetic feature of the process considerably. The feeble effect of triethylamine in THF solutions revealed distinctions in the solvating power of the donors (see also discussion in Ref. [8]). However, the interpretation of the results was based upon the mechanism proposed by Grignard et al. (vide supra).

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In this paper we report the results of a reinvestigation of the reaction. A similar experimental technique was used. It appeared that Grignard's mechanism had to be supplemented with the reaction between bromomagnesiumacetylene and the Grignard reagent.

2. Experimental

2.1. Materials

All the operations with carefully purified reagents and solutions were carried out under dry argon. Phenylmagnesium bromide was prepared and analyzed in the conventional manner [9].

2.2. Kinetic measurements

The reaction of phenylmagnesium bromide with acetylene was carried out in a thermostated 100 ml glass vessel at 20°C. The reaction cell was provided with a magnetic stirrer and inlets for the injection of the reagents and the sampling of the vapor above the reaction mixture.

The reaction vessel was purged thoroughly with pure argon. Then 50 ml of diethyl ether solution of phenylmagnesium bromide (0.9–1.1 M), 5 ml of pure toluene (internal standard for GLC analyses) and a calculated amount of triethylamine (up to 5.6 mg) were introduced. The reaction mixture was refluxed for 5 min to displace the inert gas, then the condenser was quickly replaced with a silicon septum, the flask was cooled and placed into the thermostat. After the thermal equilibrium was set, the acetylene flow was turned on. A constant pressure of acetylene in the reaction cell was provided by an automatic gasometer with a continuous registration of the volume of consumed gas. First the initial volume of acetylene in the flask was registered, then the consumption of acetylene for the saturation of the solution and its further consumption were recorded. The measured volumes of absorbed acetylene were reduced to normal conditions and transformed into moles. For convenient use of the data in kinetic calculations the molar amounts of consumed acetylene were referred to the volume of the reaction mixture (mol l^{-1}).

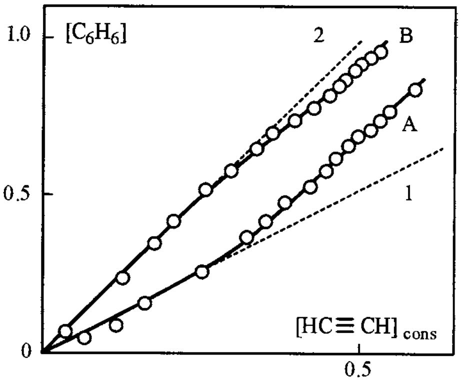


Fig. 1. Plots of benzene evolution vs. acetylene consumption (mol l^{-1}) for noncatalytic reaction (A) and in the presence of 0.03 mol% of triethylamine (B). The numerals indicate the slopes of the lines.

Aliquots (about 0.25 ml of the gas phase) were periodically withdrawn from the reaction flask and analyzed by means of GLC. The concentration of benzene in the solution was calculated by making use of the calibration data obtained from analyses of samples with known benzene content. Then kinetic curves of the evolution of benzene were plotted.

After the absorption of acetylene had practically ceased, 0.25 ml of triethylamine was added to the reaction mixture for the completion of the reaction. This accelerated the reaction sufficiently to read the final amounts of benzene and consumed acetylene after some 10 min. The final concentration of benzene in the reaction mixture corrected for the benzene concentration in the initial solution was taken for the initial concentration of the active Grignard reagent. The acidimetrically determined concentration of basic magnesium in the initial reagent exceeded the active Grignard concentration by 4–6%.

3. Results and discussion

The reaction between acetylene and phenylmagnesium bromide in diethyl ether was investigated. Both the consumption of acetylene and the evolution of benzene during the reaction were registered. Kinetic measurements were also carried out in the presence of small additions of triethylamine (up to 9.6×10^{-4} mol mol^{-1} of the Grignard reagent).

It was found that under constant acetylene concentration in the solution, the evolution of benzene during the reaction was a first-order process. The consumption of acetylene appeared to be of more complicated kinetics, the kinetic order of the process changing during the reaction. In this context plots of the molar amount of benzene evolved versus that of acetylene consumed seem to be informative as regards the reaction mechanism.

As is seen in Fig. 1 (plot A), at the beginning of the reaction one mole of benzene was evolved per mole of acetylene consumed in the absence of the catalyst. Further, 2 mol of benzene were evolved per mol of acetylene up to the end of the reaction. Apart from the enormous acceleration of the reaction, additions of triethylamine greatly alter the kinetic picture (Fig. 1, B). During the first half-period of the reaction exactly 2 mol of benzene are formed per mol of consumed acetylene. Moreover, the plot declines slightly from the straight line.

Table 1
Individual rate constants of the reaction between acetylene and phenylmagnesium bromide in diethyl ether at 20°C ($k \times 10^4$, l mol^{-1} s^{-1})

TEA × 10^4 [a]	k_1 [b]	k_1 [c]	k_2	k_3	k_4
0	0.39 ± 0.01	0.39 ± 0.03	0.11 ± 0.02	0.72 ± 0.07	0.07 ± 0.02
2.8	2.72 ± 0.08	2.72 ± 0.13	3.70 ± 0.30	1.83 ± 0.20	1.20 ± 0.20
5.0	3.94 ± 0.10	3.72 ± 0.18	11.1 ± 1.0	2.16 ± 0.22	2.4 ± 0.3
6.0	4.10 ± 0.10	3.83 ± 0.22	15.0 ± 1.1	2.22 ± 0.26	2.6 ± 0.5
8.6	6.10 ± 0.15	5.55 ± 0.28	28.7 ± 3.2	4.44 ± 0.48	4.0 ± 0.6
9.6	6.68 ± 0.20	6.68 ± 0.40	33.3 ± 2.8	4.82 ± 0.50	4.9 ± 0.6

[a] Molar ratio of triethylamine relative to the Grignard reagent.
[b] From the consumption of acetylene.
[c] From the evolution of benzene.

While the observed kinetics in the absence of the catalyst can be explained somehow in view of the mechanism proposed by Grignard et al. [4] (see Section 1), the kinetics in the presence of triethylamine are not compatible with that scheme. Therefore, it seemed wise to also include the reaction of bromomagnesiumacetylene with the Grignard reagent first suggested by Jones et al. [6].

Thus, the following reaction scheme was subjected to verification:

$$\mathrm{RMgBr + HC{\equiv}CH \xrightarrow{k_1} HC{\equiv}CMgBr + RH}$$

$$\mathrm{HC{\equiv}CMgBr + RMgBr \xrightarrow{k_2} BrMgC{\equiv}CMgBr + RH}$$

$$\mathrm{BrMgC{\equiv}CMgBr + HC{\equiv}CH \xrightarrow{k_3} 2HC{\equiv}CMgBr}$$

$$\mathrm{2HC{\equiv}CMgBr \xrightarrow{k_4} BrMgC{\equiv}CMgBr + HC{\equiv}CH}$$

For the suggested reaction scheme the following differential equations can be written

$$\frac{\mathrm{d}[\mathrm{A}]_{\mathrm{cons}}}{\mathrm{d}t} = k_1[\mathrm{A}][\mathrm{G}] + k_3[\mathrm{A}][\mathrm{I\ 2}] - k_4[\mathrm{I\ 1}]^2$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}][\mathrm{G}] + k_2[\mathrm{I\ 1}][\mathrm{G}]$$

where $[\mathrm{A}]_{\mathrm{cons}}$ stands for the molar amount of consumed acetylene referred to the volume of the reaction solution. [A], [B] and [G] are the concentrations of acetylene, benzene and the active phenylmagnesium bromide, respectively. The symbols I 1 and I 2 denote Iotsitch complexes, bromomagnesiumacetylene and bis-bromomagnesiumacetylene, respectively.

Since the concentration of acetylene in the reaction mixture was constant (0.18 M at 20°C) during the process, the differential equations can be presented as follows:

$$\frac{\mathrm{d}[\mathrm{A}]_{\mathrm{cons}}}{\mathrm{d}t} = k'_1[\mathrm{G}] + k'_3[\mathrm{I\ 2}] - k_4[\mathrm{I\ 1}]^2$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k'_1[\mathrm{G}] + k_2[\mathrm{I\ 1}][\mathrm{G}]$$

From the stoichiometry of the process we have for any point of time

$$[\mathrm{A}]_{\mathrm{cons}} = [\mathrm{I\ 1}] + [\mathrm{I\ 2}]$$

$$[\mathrm{B}] = [\mathrm{I\ 1}] + 2[\mathrm{I\ 2}],$$

therefore

$$[\mathrm{I\ 1}] = 2[\mathrm{A}]_{\mathrm{cons}} - [\mathrm{B}]$$

$$[\mathrm{I\ 2}] = [\mathrm{B}] - [\mathrm{A}]_{\mathrm{cons}}$$

and

$$[\mathrm{G}] = [\mathrm{B}]_{\infty} - [\mathrm{B}],$$

where $[\mathrm{B}]_{\infty}$ denotes the benzene concentration at the end of the reaction (for determination see Section 2).

The rate constants obtained from the numerical integration of the differential equations are presented in Table 1. A good coincidence of the values for k_1 obtained from the consumption of acetylene and from the evolution of benzene, as well as the self-consistency of the data allow the drawing of some interesting conclusions (see below) and affirm the validity of the proposed mechanistic scheme.

The catalytic effect of triethylamine for individual reactions appeared to be different. Moreover, nonlinear dependences of some rate constants on the catalyst concentration were found. The rate constants from Table 1 were treated according to the following equation:

$$k_{\mathrm{obs}} = k_{\mathrm{noncat.}} + k_{\mathrm{cat}}[\mathrm{TEA}]^n$$

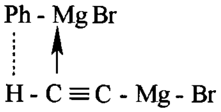
where TEA denotes triethylamine.

It appeared that the rate constants for the reactions of acetylene with phenylmagnesium bromide (k_1) and with bis-bromomagnesiumacetylene (k_3) increase linearly with the increase in the amine concentration ($n = 1$, Table 2). Obviously, the replacement of diethyl ether by a stronger donor enhances the nucleophilicity of the organic moiety bound to the magnesium atom thus accelerating the reaction with the weak acid acetylene. However, nonlinear dependences are peculiar to reactions of bromomagnesium acetylene with phenylmagnesium bromide (k_2, $n = 1.85$) or with bromomagnesiumacetylene itself (k_4, $n = 1.16$). The rather unexpected result points to a favorable effect of the

Table 2
Catalytic constants for the steps of the reaction in the presence of triethylamine

k_{obs}	$k_{\mathrm{noncat}} \times 10^4$	k_{cat}	n
k_1	0.39	0.68	0.98
k_2	0.11	1140	1.85
k_3	0.72	0.36	1.03
k_4	0.07	1.48	1.16

solvation of both of the reagents. While the rate-enhancing effect of nucleophilic solvation at the basic reagent is self evident, similar solvation of bromomagnesiumacetylene should decrease the acidity of the acetylenic reagent and should thus suppress the reaction rate. A possible explanation of the controversy stresses the importance of the nucleophilic assistance [10] by the acetylenic group. The four-center transition state of the reaction suggested by Dessy et al. [11,12] implies a nucleophilic attack at the magnesium atom by the anionic part of the carbon acid:



$$\begin{array}{l}\mathrm{Ph-MgBr} \\ \vdots \quad \uparrow \\ \mathrm{H-C{\equiv}C-Mg-Br}\end{array}$$

Evidently the accelerating effect of the nucleophilic assistance overweighs the rate decrease caused by the reduced acidity. As to the bimolecular dismutation reaction of bromomagnesium acetylene, the reason for the somewhat lower effect of triethylamine upon the rate constant k_4 in comparison with that upon k_2 is not entirely clear. It is obvious that increasing steric hindrance causes a decrease in the solvating ability of the donor. Likewise, the increasing bulkiness of the organic groups hinder complexing between the donor and the magnesium center. It has been shown that the strong Brønsted base triethylamine appeared to be a much better donor than diethyl ether for phenylmagnesium bromide but not for Grignard reagents comprising alkyl groups larger than methyl [8,13]. Our results may suggest greater steric demands of the ethynyl group over the phenyl group, but this is doubtful. On the contrary, provided that bromomagnesiumacetylene is more strongly solvated, a reduced electrophilicity of the magnesium atom and thus a decrease in the susceptibility to the nucleophilic assistance should be supposed.

Acknowledgements

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