GRIGNARD REACTION WITH ACETYLENE IN THF

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Abstract

Kinetics of the reaction between acetylene and phenylmagnesium bromide were investigated in THF and also in the presence of triethylamine. The reaction proceeds through the formation of bromomagnesiumacetylene (1 1); its further reaction with PhMgBr providing bis(bromomagnesium)acetylene (1 2). The disproportionation equilibrium of 1 1, leading to 1 2 and acetylene, which is significant in Et_2O solutions, fails in THF. A moderate rate enhancing effect of triethylamine in THF solution was found.

Introduction

Acetylenic Grignard compounds can serve as intermediates in many syntheses of acetylenic compounds. The reaction of acetylene with a Grignard reagent affords a mixture of bromomagnesiumacetylene and bis-(bromomagnesium)acetylene, the ratio of products being predetermined by the reaction conditions [1-3].

In an earlier work [4] we investigated the kinetics of the reaction of acetylene with phenylmagnesium bromide. The measurements were conducted in diethyl ether and THF, and also in the presence of triethylamine. Catalytic amounts of triethylamine in the diethyl ether solution of phenylmagnesium bromide were found to largely accelerate the reaction [4,5]. The moderate effect of triethylamine in THF solutions revealed distinctions in the donating ability of the bases [4,6]. However, the mechanistic interpretation of the results was based on a limited number of data and for that reason we decided to revisit the topic.

Experimental

The experimental procedure in this work was similar to that described in the previous paper [7].

The reaction was carried out at 20 °C in a thermostated 100 ml glass vessel, which was provided with a magnetic stirrer and inlets for the injection of the reagents and the sampling of the vapour above the reaction mixture. The reaction cell was purged thoroughly with pure argon. Then 50 ml of about 0.95 M solution of phenylmagnesium bromide, 5 ml of pure toluene (internal standard for GLC analyses) and a calculated amount of triethylamine were introduced. The reaction mixture was refluxed for 5 minutes to displace the inert gas, then the condenser was 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. 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}).

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 the analyses of samples with known benzene content. Then kinetic curves of the evolution of benzene were plotted. 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 Grignard reagent.

Results and Discussion

Various mechanistic schemes have been proposed for the reaction of acetylene with Grignard reagents in diethyl ether [8-10]. The results of our recent work [7] proved to be more concordant with the reaction scheme (1)-(4) including the primary mechanism proposed by Grignard et al. [8], supplemented with the reaction of bromomagnesium acetylene (2) first suggested by Jones et al. [10]. The main goal of this work was to determine whether the mechanism also holds for the reaction in THF solutions.

$$\mathrm{RMgBr + HC{\equiv}CH \xrightarrow{k_1} HC{\equiv}CMgBr + RH} \quad (1)$$

$$\mathrm{HC{\equiv}CMgBr + RMgBr \xrightarrow{k_2} BrMgC{=}CMgBr + RH} \quad (2)$$

$$\mathrm{BrMgC{\equiv}CMgBr + HC{=}CH \xrightarrow{k_3} 2\ HC{\equiv}CMgBr} \quad (3)$$

$$\mathrm{2\ HC{=}CMgBr \xrightarrow{k_4} BrMgC{\equiv}CMgBr + HC{\equiv}CH} \quad (4)$$

The following differential equations can be written for the reaction scheme (1)-(4)

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

$$\frac{d[RH]}{dt} = k_1\,[A]\,[G] + k_2\,[I\,1]\,[G],$$

where $[A]_{cons}$ stands for the molar amount of consumed acetylene referred to the volume of the reaction solution. [A], [G] and [RH] are the concentrations of acetylene, the Grignard reagent, and hydrocarbon RH, respectively. The symbols I 1 and I 2 denote Iotsitch complexes, bromomagnesiumacetylene and bis-(bromomagnesium)acetylene, respectively. Grignard reagents of the type RC≡CMgX and XMgC≡CMgX were first prepared by Iotsitch [11].

Phenylmagnesium bromide was employed as the Grignard reagent in our experiments. Thus, hydrocarbon RH is benzene ([RH] = [B]), and from the stoichiometry of the process we have for any point of time

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

$$[B] = [I\,1] + 2\,[I\,2],$$

therefore

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

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

and

$$[G] = [B]_\infty - [B],$$

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

Since the concentration of acetylene in the reaction mixture was constant during the process, the differential equations can be presented as follows

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

$$\frac{d[B]}{dt} = k_1'\,[G] + k_2\,[I\,1]\,[G]$$

For a numerical integration of the system of equations differentials (dc/dt) were replaced by intervals (Δc/Δt), and the rate constants were obtained by means of the method of least squares. The results revealed, in contrast to diethyl ether solutions, the statistical insignificance of the rate constants k_3 and k_4 for the reaction in THF. Consequently, only reactions (1) and (2) occur in THF and the contribution of the disproportionation equlibrium (reactions (3) and (4)) is negligible. This conclusion is well supported by the practice of the synthesis of bromomagnesiumacetylene. While in diethyl ether it can be prepared from a Grignard reagent under an overpressure of acetylene, in THF the Grignard reagent is usually added dropwise into a reaction vessel that bubbles in acetylene in THF at the rate of consumption [3]. Hence, the reduced system of differential equations was solved and the obtained values for rate constants k_1 and k_2 are presented in Table 1. The final concentrations of the Iotsitch complexes are also given in the Table.

Benson [12] has accomplished a kinetic analysis of a formal scheme exactly corresponding to the reaction in question. It follows from his calculations that if $[G]_0k_2/[A]k_1 = 0.9$, $[I\,1]_\infty = 0.5$. In our experiments the ratio was equal to 0.86 and the final concentration of bromomagnesiumacetylene (I 1) was found to be 0.51 M. This also confirms the mechanism discussed above.

Table 1.
Individual rate constants[a] of the reaction between acetylene and phenylmagnesium bromide in THF at 20 °C (k x 10^4, l mol^{-1} s^{-1}).

TEA x 10^2[b]	k_1	k_2	Final concentrations (M) [I 1][c]	 [I 2][d]
0	3.71±0.18	1.17±0.18	0.511	0.201
0.07	3.80±0.21	1.69±0.21	0.502	0.219
19.8	9.25±0.36	3.52±0.52	0.540	0.211
37.5	14.6±0.6	5.06±0.37	0.550	0.195
71.6	24.8±1.0	8.80±0.62	0.549	0.211
96.8	32.6±1.4	11.56±0.95	0.505	0.223

[a] the mean values obtained from several runs, [b] molar ratio of triethylamine relative to the Grignard reagent, [c] bromomagnesiumacetylene, [d] bis-(bromomagnesium)acetylene.

The second-order rate constant k_1 for reaction (1) is several times greater than k_2, similarly to the reaction in diethyl ether [7], where $k_1 = 0.39 \times 10^{-4}$ l mol^{-1} s^{-1} and $k_2 = 0.11 \times 10^{-4}$ l mol^{-1} s^{-1}. However, the rate constants for the reaction in THF are about ten times greater than those in diethyl ether. Obviously the decreased acidity of bromomagnesiumacetylene in comparison with the unsubstituted acetylene lowers the reaction rate, and the stronger donating power of THF enhances the nuclephilicity of the Grignard reagent resulting in greater values of the rate constants.

Our kinetic data show a more significant contrast between the catalyses by triethylamine in THF and diethyl ether. While in diethyl ether triethylamine exerts a dramatic effect on the reaction rates, particularly for reaction (2), relatively great additions of triethylamine to the THF solution of the Grignard reagent only weakly enhance the reactivity (Table 1). Thus, it can be inferred that the very strong Brønsted base triethylamine only slightly exceeds THF by the Lewis basicity relative to phenylmagnesium bromide.

It is obvious that an increase in steric hindrance causes a decrease in the solvating ability of the donor regardless of the intrinsic (Brønsted) basicity. Likewise, an increase in the bulkiness of the organic group in the substrate hinders complexing between the donor and the magnesium center. It has been earlier shown by one of us [6] that the sequence of the relative Lewis basicity of these donors was THF>triethylamine>diethyl ether for ethylmagnesium bromide, and THF>diethyl ether>>triethylamine for diethylmagnesium. Indeed, triethylamine only had a moderate catalytic effect on the reaction of hex-1-yne with ethylmagnesium bromide in diethyl ether but did not catalyze the reaction with diethylmagnesium [13].

In summary, we have shown how the mechanism of the Grignard reaction with acetylene depends on the donating ability of the solvent. The contribution of the disproportionation equilibrium is significant in diethyl ether solutions but practically fails in THF. Triethylamine readily replaces diethyl ether at phenylmagnesium bromide but does to a lesser extent at alkylmagnesium halides. The Lewis basicity of THF is comparable to that of triethylamine while phenylmagnesium bromide is the substrate but is superior to the basicity of triethylamine when bulkier Grignard reagents are involved. Thus, a powerful catalytic effect of triethylamine can only be observed in marginal cases such as the reaction of phenylmagnesium bromide in diethyl ether.

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