The Kinetic Investigation of The Reactivity of Alkyl Magnesium Halides

by

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Ankara, Turquie
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The Kinetic Investigation of The Reactivity of Alkyl Magnesium Halides

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(Received April 13, 1973)

The reactivity of alkyl magnesium halides was investigated by a kinetic method and the order of the relative strength of carbon-metal bond in $S_{E1}$ reactions was given. The Zerewitinoff reaction rate constants of ethyl, propyl and butyl magnesium halides with diethyl amine in diethyl ether at 25.0°C, for which $S_{E1}$ mechanism was proposed, were measured by gas evolution method. The Taft relationship between the rate constants of alkyl magnesium bromides (k) and the polar and steric substituent constants ($\sigma^*$ and $E_\sigma$, respectively) of alkyl substituents is \( \log k/k_0 = -7.16 \sigma^* + 1.33 E_\sigma \), where $k_0$ is the rate constant of methyl magnesium bromide. The relative reactivity of alkyl magnesium halides increase in the order of chloride < bromide < iodide. A linear dependence of $\log k$ on the number of $\beta$- hydrogens ($n_H$) in the alkyl groups was also observed: $\log k/k_0 = 0.062 n_H$. In $S_{E1}$ reactions, the relative strength of the carbon-metal bond increases in the order of t-butyl < i-propyl < ethyl < s-butyl < n-butyl < n-propyl < i-butyl < methyl.

INTRODUCTION

In this work, the relative reactivity of alkyl magnesium halides (Grignard reagents) were investigated and the relative strength of carbon-metal bond in $S_{E1}$ reactions was given.

There are a few research on the relative reactivity of Grignard reagents (1,2). One of the methods for determining it consist-

* This study was financially supported by the Scientific and Technical Research Council of Turkey. (Project No.: TBAG-92).

** A more extensive summary of this study has appeared in Chimica Acta Turcica 1,113 (1973).

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ted of mixing the Grignard reagent with a small excess of some reactive substance and measuring the time necessary for the disappearance of the reagent with Gilman's negative colour test (3). Ivanoff, et al., determined the relative strength of carbon-magnesium bond by measuring the evolution rate of hydrocarbon gas in the reaction of alkyl Grignard reagents with inden (4) and chloromagnesium phenyl acetate (5). Effect of the halogen on n-butyl magnesium halides was investigated by Vavon (6). Dessy, et al., (7) measured the half times of the reactions between alkyl Grignard reagents and 1-hexyne and gave a reactivity sequence. They also investigated the effect of the changing halogen and the number of β-hydrogen atoms in the alkyl group on the reactivity. The dependence of the relative activity of Grignard reagents on their decomposition potentials and the reactivity of their mixtures were also investigated by Dessy, et al. (8, 9).

Tuulmets (10) measured the rates of three contributing parallel reactions between 1,1,1-trimethyl acetone and alkyl magnesium bromides in pseudo-first order conditions and gave three Taft relationships concerning reduction, addition and enolization rate constants.

The studies on the reactivity of organomagnesium compounds are also outlined by Abraham and Hill (11, 12).

In this work, the reactivity of alkyl magnesium halides was investigated kinetically. The solutions of ethyl, propyl and butyl magnesium halides in diethyl ether were prepared and their rate constants of Zerewitinoff reaction (13) with diethyl amine, were measured at 25.0°C. Then, Taft relationship (14, 15) concerning the reactions of alkyl magnesium bromides, were given. The effect of changing halogen in a given alkyl magnesium halide was determined. It was also found a linear dependence of log k on the number of β-hydrogen atoms.

**EXPERIMENTAL SECTION**

In this work, Grignard reagents were prepared from magnesium turnings and alkyl halides indicated below, in diethyl ether, under nitrogen atmosphere in the conventional manner (13, 16).
THE KINETIC INVESTIGATION OF THE REACTIVITY

The magnesium turnings were Fisher's Grignard quality. The solvent absolute diethyl ether was dried on sodium wire and distilled with a small amount of previously prepared ethyl magnesium halide in diethyl ether.

Alkyl chlorides and bromides were dried on Drierite or P₂O₅ and redistilled over a small amount of Na₂CO₃. B. p., °C: n-Propyl chloride: 46.7; n-propyl bromide: 71.0; i-propyl chloride: 34.8; i-propyl bromide: 59.4; n-butyl bromide: 101.6; s-butyl bromide: 91.3; i-butyl bromide: 91.4; t-butyl chloride: 50.7; t-butyl bromide: 73.3. n-Propyl iodide (B. p: 102.5 °C) was washed with aq. NaOH, then water, dried on Al₂O₃ and redistilled fractionally. i-Propyl iodide and t-butyl iodide (B. p: 89.5 and 99.0 °C) were treated with mercury, dried on Al₂O₃ and redistilled fractionally (17).

Diethyl amine was dried on KOH and distilled over CaO (B. p.: 55.5 °C).

The Zerewitinoff reaction between alkyl magnesium halides and diethyl amine in diethyl ether, at 25.0 °C,

\[ \text{RMgX + \( (\text{C}_2\text{H}_5)_2\text{NH} \rightarrow \(\text{C}_2\text{H}_5)_2\text{NMgX} + \text{RH} \) } \]

was investigated kinetically by gas evolution method which we also used in the kinetic investigation of the reaction between ethyl magnesium bromide and active hydrogen compounds (13).

In this work, rate constants were found only by pseudo-first order procedure. As Grignard reagents could be prepared in low concns. (16), their reactions could be followed up in the presence of the large excess of diethyl amine. It was not possible to follow the reaction up to 70-80 % conversion with the equiv amount of reagents in low concns. In applying pseudo-first order procedure, the concn. of Grignard reagent was held constant and the concn. of diethyl amine was taken at least 10 fold of the concn. Grignard reagent and gradually changed in a serie of reactions. Then, the second order rate constant was found from the slope of the line by plotting the pseudo-first order rate constants vs. the concn. of diethyl amine (13,18).

The uncertainty of the rate constants was found not higher than 1 %.
RESULTS AND DISCUSSION

The Taft relationship concerning the reaction of alkyl magnesium halides with diethyl amine in diethyl ether at 25.0 °C.

It was found that the reaction between alkyl magnesium halides and diethyl amine is second order overall and first order with respect to each reactant, in diethyl ether at 25.0 °C. The rate constants of alkyl magnesium bromides (k) and the polar and steric substituent constants of alkyl groups (σ* and E* respectively) are given in Table 1.

TABLE 1

The rate constants of alkyl magnesium bromides with diethyl amine (k) in diethyl ether at 25.0 °C and the polar and steric substituent constants (σ* and E*) respectively of alkyl groups.

\[
RMgBr + (C_2H_5)_2NH \overset{k}{\longrightarrow} (C_2H_5)_2NMgBr + RH
\]

<table>
<thead>
<tr>
<th>R</th>
<th>(10^4k \text{ mole}^{-1} \cdot \text{sec}^{-1})</th>
<th>σ*</th>
<th>E*</th>
<th>nH</th>
</tr>
</thead>
<tbody>
<tr>
<td>n- C_3H_7</td>
<td>11.2*</td>
<td>-0.10</td>
<td>-0.07</td>
<td>3</td>
</tr>
<tr>
<td>n- C_4H_9</td>
<td>7.2</td>
<td>-0.12</td>
<td>-0.36</td>
<td>2</td>
</tr>
<tr>
<td>i- C_5H_11</td>
<td>11.3</td>
<td>-0.19</td>
<td>-0.47</td>
<td>6</td>
</tr>
<tr>
<td>n- C_6H_13</td>
<td>8.0</td>
<td>-0.13</td>
<td>-0.39</td>
<td>2</td>
</tr>
<tr>
<td>s- C_7H_15</td>
<td>10.0</td>
<td>-0.21</td>
<td>-1.13</td>
<td>5</td>
</tr>
<tr>
<td>i- C_8H_17</td>
<td>3.5</td>
<td>-0.12</td>
<td>-0.93</td>
<td>1</td>
</tr>
<tr>
<td>t- C_9H_19</td>
<td>16.9</td>
<td>-0.30</td>
<td>-1.54</td>
<td>9</td>
</tr>
</tbody>
</table>

* From Table 4 of ref. 13.

The Taft relationship was found by using the least squares method with a correlation value of 0.11:

\[
\log k/k_0 = -7.16 \sigma^* + 1.33 E^*
\]

where \(\log k_0\) is the rate constant of methyl magnesium bromide, found equal to -2.34. The linear plot of \((\log k - 1.33 E^*)\) vs. \(\sigma^*\) is shown in Fig. 1 A. In \(S_E\) i mechanism which we proposed for Zerewitinoff reaction (13), as the electron releasing inductive effect of alkyl groups accelerate the reaction, a negative slope of the Taft plot is expected (14). And the reaction rate is affected by both inductive and steric effects of alkyl groups unlike the other types of \(S_E\) mechanism (12), resulting an activity sequence of alkyl groups ethyl > n-propyl < i-propyl < t-butyl. The sign of the inductive reaction constant, \(\sigma^* = -7.16\) and the rate constants given in Table 1 confirm the above results.
Fig. 1. A: The Taft plot concerning the reaction between alkyl magnesium bromides and diethyl amine, in diethyl ether at 25.0°C. B: The plot of log k vs. the number of $\delta$-hydrogen atoms in the same reaction.
The effect of halogen on the reactivity of alkyl magnesium halides.

n-Propyl, i-propyl and t-butyl magnesium halides which contain primary, secondary and tertiary carbon atom respectively, were chosen and their rate constants with diethyl amine in diethyl ether, at 25.0 °C were measured. The results are given in Table 2.

<table>
<thead>
<tr>
<th>RMgX + (C₂H₅)₂NH → (C₂H₅)₂NMgX + RH</th>
<th>10⁶k 1.mole⁻¹.sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMgX</td>
<td>X = Cl</td>
</tr>
<tr>
<td>n-C₃H₇MgX</td>
<td>10.8</td>
</tr>
<tr>
<td>i-C₃H₇MgX</td>
<td>4.1</td>
</tr>
<tr>
<td>t-C₃H₇MgX</td>
<td>5.5</td>
</tr>
</tbody>
</table>

As the reactivity of alkyl magnesium halides depend upon the stability of the carbamion, any effect which decreases this stability, increases the reaction rate. The electron with-drawing effect of halogen atoms decreases in the order of Cl > Br > I and the reaction rate increase in the order of RMgCl < RMgBr < RMgI. The observed rate constants agree with this result.

The effect of the number of β-hydrogen atoms on the reactivity of alkyl magnesium halides.

A linear dependence of log k to the number of β- hydrogen atoms (n_H) was found:

\[ \log k = 0.062 \, n_H - 2.30 \]

The number of β-hydrogen atoms are given in Table 1 and the linear plot of log k vs. n_H is shown in Fig. 1B. From this relationship, it can be found -2.30 for the log k of methyl magnesium bromide and it is in accordance with the value of -2.34, found from the Taft relationship. This gives k_0 = 4.5 \times 10^{-3} 1. mole⁻¹. sec⁻¹ for the rate constant of methyl magnesium bromide.

Increasing number of β-hydrogen atoms is an effect that decreases the stability of alkyl carbonion (19); There are three β-H–β-C
bonds in CH$_3$–CH$_2$ and the negative charge on β–C is inducted to the α–C, i.e. the reaction site which is now more electronegative than the α–C in H–CH$_2$. As the partial negative charge on α–C in H$_2$C–CH$_2$ is higher than in H–CH$_2$, CH$_3$–CH$_2$ reacts with active H faster than H–CH$_2$ because of its decreased stability. This is the result of chain induction from β–C to α–C by three β–H’s. In (CH$_3$)$_2$CH, the negative charge on α–C is increased much because of six β–H’s in this case to give chain induction and make the carbanion more activated than CH$_3$–CH$_2$ or H–CH$_2$. The reaction rate depending upon the inductive effect of alkyl groups, also depends upon the number of β–hydrogen atoms and a linear relationship between log k and n$_H$ was tried to explain.

The activity of alkyl carbanions in $S_{Ei}$ reactions of organometallic compounds (the relative strength of carbon-metal bond).

Depending upon the results taken in this work, the reactivity sequence of alkyl groups in $S_{Ei}$ reactions can be given as follow: t-butyl > i-propyl > ethyl > s-butyl > n-butyl > n-propyl > i-butyl > methyl. This is also the reverse order of the strength of carbon-metal bond and the stability of alkyl carbonions in $S_{Ei}$ reactions.

REFERENCES

özet

Alkil magnesium halogenürlerin nicel aktifliği kinetik metotla araştırılmış ve \( S_E \) reaksiyonlarında karbon-metal bağının bağlı değişikliği için bir sra verilmişdir. Etil, propil ve bütül magnesyum halogenürlerin dietil amine, dietil eterde, 25,0°C de ve \( S_E \) mekanizması üzerinden yürüyen Zerewitinoff reaksiyon hız sabitleri ölçülmüştür. Alkil magnesyum bromürlerin reaksiyon hız sabitleri ile alki gruplarının polar ve steric etkinlikleri arasında Taft bağlantısı vardır: \( \log k/k_o = -7,16 \sigma^* + 1,33 E_\beta \), burada \( k_o \) metil magnesyum bromürün hız sabitidir. Alkil magnesyum halogenürlerin bağlı aktiflikleri klorür < bromür < iyodür sırasında artar. Reaksiyon hız sabitlerinin log. u ile alkim grubundaki \( \beta \)-hidrojenleri sayısı \( n_H \) sırasında lineer bir bağıntı bulunmaktadır: \( \log k/k_o = 0,062 n_H \cdot S_E \) reaksiyonlarında karbon - metal bağının değişikliği t-bütlil > i-propil> etil > s-bütlil > n-propil > i-bütlil > metil sırasında azahr.
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