COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 20 B — ANNÉE 1973

The Kinetic Investigation of The Reactivity of Alkyl Magnesium Halides

by

CELÂL TÜZÜN and ENDER ERDİK

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences
de l'Université d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté: Mathématiques pures et appliquées, Astronomie, Physique et Chimie théorique, expérimentale et technique, Géologie, Botanique et Zoologie.

La Revue, à l'exception des tomes I, II, III, comprend trois séries

Série A : Mathématiques, Physique et Astronomie.
Série B : Chimie.
Série C : Sciences naturelles.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adresse: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara; Turquie.

The Kinetic Investigation of The Reactivity of Alkyl Magnesium Halides * **

CELÂL TÜZÜN and ENDER ERDİK

*Department of General Chemistry, Faculty of Science, Ankara University, Ankara, Turkey****

(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_Ei 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_Ei 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 (σ^* and E_s respectively) of alkyl substituents is $\log k/k_0 = -7.16\sigma^* + 1.33 E_s$, 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 β– hydrogens (n_H) in the alkyl groups was also observed: $\log k/k_0 = 0.062\, n_H$. In S_Ei 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_Ei reactions was given.

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

* 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).

*** Mailing address: A. Ü. Fen Fakültesi, Ankara, Turkey.

ted of mixing the Grignard reagent with a small excess of some reactive substance and measuring the time necessary for the dissappearance 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 aceton and alkyl magnesium bromides in pseudo-fist 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 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 P_2O_5 and redistilled over a small amount of Na_2CO_3. 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 Al_2O_3 and redistilled fractionally. i-Propyl iodide and t-butyl iodide (B. p: 89.5 and 99.0 °C) were treated with mercury, dried on Al_2O_3 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,

$$RMgX + (C_2H_5)_2\,NH \longrightarrow (C_2H_5)_2NMgX + RH$$

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 concn.s. (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 concn.s. 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 grups (σ^* and E_s respectively) are given in Table 1.

TABLE 1

The rate constants of alkyl magnesium bromides wity diethyl amine (k) in diethyl ether at 25.0°C and the polar and steric substituent constants (σ^* and E_s respcctively) of alkyl groups.

$$RMgBr + (C_2H_5)_2NH \xrightarrow{k} (C_2H_5)_2NMgBr + RH$$

R	10^3k l.mole^{-1} . sec^{-1}	σ^*	E_s	n_H
n- C_2H_5	11.2*	-0.10	-0.07	3
n- C_3H_7	7.2	-0.12	-0.36	2
i- C_3H_7	11.3	-0.19	-0.47	6
n- C_4H_9	8.0	-0.13	-0.39	2
s- C_4H_9	10.0	-0.21	-1.13	5
i- C_4H_9	3.5	-0.12	-0.93	1
t- C_4H_9	16.9	-0.30	-1.54	9

* From Table 4 of ref. 13.

The Taft relationship was found by using the least squares method with a correlation value of 0,11:

$$\log k/k_0 = -7.16\ \sigma^* + 1.33\ E_S$$

where log k_0 is the rate constant of methyl magnesium bromide, found equal to -2.34. The linear plot of (logk- 1.33 E_s) vs. σ^* is shown in Fig. 1 A. In S_Ei 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 grous 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, $\rho^* = -7.16$ and the rate constants given in Table 1 confirm the above results.

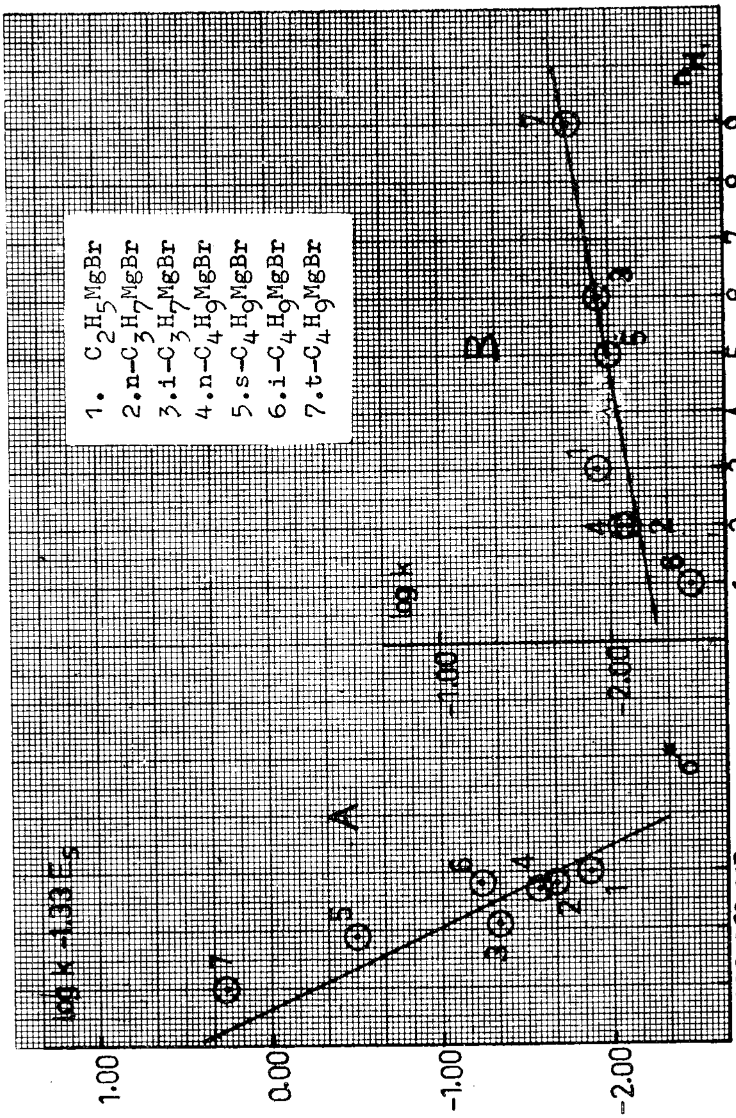

Fig. 1. A: The Taft plot concerning the reaction between alkyl magnesium bromides and diethyl amine, in diethyl ether at 25.0°C. B: The plot of log k vs. the number of β- hydrogen atoms in the same reaction.

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 2

The rate constants of n-propyl, i-propyl and t-butyl magnesium halides with diethyl amine (k) in diethyl ether at 25.0°C.

$$RMgX + (C_2H_5)_2\ NH \xrightarrow{k} (C_2H_5)_2\ NMgX + RH$$

RMgX	10^3k l.mole^{-1}.sec^{-1}		
	X = Cl	X = Br	X = I
n–C_2H_5MgX	10.8	7.2	12.9
i–C_3H_7MgX	4.1	11.3	17.9
t–C_4H_9MgX	5.5	16.9	8.9

As the reactivity of alkyl magnesium halides depend upon the stability of the carbanion, 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 $k_0 = 4.5\ 10^{-3}$ l. 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_3C-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 $(CH_3)_2CH$, 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 $S_E i$ reactions of organometallic compounds (the relative strength of carbon-metal bond).

Depending upon the results taken in this work, the reactivity sequence of alkyl gruups 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

[1] M. S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice Hall, New York, 1954, Chap. II.

[2] S. T. Ioffe and A. N. Nesmeyanov, Methods of Elemento-organic Chemistry, North Holland, Amsterdam, 1967, Chap. 2.

[3] Gilman, H., et al., Rec. Trav. Chim. 49, 212 (1930)

[4] Ivanoff, D. and A. Spassoff, Bull. Soc. Chim. France, 51, 619 (1932).

[5] Ivanoff, D. and I. Abdouloff, Comptu. Rend., 196, 491 (1933).

[6] Vavon, G., et al., Bull. Soc. Chim. France, 5, 1, 806 (1934).

[7] Dessy, R. E., C. H. Wotiz and C. A. Hollingsworth, J. Am. Chem. Soc., 77, 103 (1955)

[8] Dessy, R. E., C. H. Wotiz and C. A. Hollingsworth, ibid., 77, 4410 (1955).

[9] Smalley G. W. and C. A. Hollingworth, J. Org. Chem., 27, 760 (1962)

[10] Tuulmets, A., C. A. 69: 43202 j.

[11] Abraham, M. H. and J. A. Hill, Chem. Ind., 561 (1965).

[12] Abraham, M. H. and J. A. Hill, J. Organometal. Chem., 7, 11 (1967).

[13] Tüzün C. and E. Erdik, Comm. Fac. Sci. Ankara, 19 B, 2 (1972).

[14] J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, John Wiley, New York, 1963, Chap. 7

[15] R. D. Wells, Linear Free Energy Relationships, Academic Press, London, 1968, Chap 2. 2.

[16] S. T. Ioffe and A. N. Nesmeyanov, loc. cit., p 23.

[17] J. Riddick and G. Toops, Organic Solvents, Vol VII in Technique of Organic Chemistry, Interscience, New York, 1967, p. 404.

[18] S. L. Friess, Lewis and A. Weissberger. Investigation of Rates and Mechanisms of Reactions, Part I, Vol. VIII in Technique of Organic Chemistry, Interscience, New York, 1967, p. 196.

[19] D. J. Cram, Fundemantals of Carbanion Chemistry, Academic Press, 1956, Chap. I.

ÖZET

Alkil magnezyum halojenürlerin nicel aktifliği kinetik metodla araştırılmış ve S_Ei reaksiyonlarında karbon-metal bağının bağıl gevşekliği için bir sıra verilmiştir. Etil, propil ve bütil mağnezyum halojenürlerin dietil aminle, dietil eterde, 25,0°C de ve S_Ei mekanizması üzerinden yürüyen Zerewitinoff reaksiyon hız sabitleri ölçülmüştür. Alkil magnezyum bromürlerin reaksiyon hız sabitleri ile alkil gruplarının polar ve sterik etkinlikleri arasında Taft bağıntısı vardır: $\log k/k_o = -7{,}16\,\sigma^* + 1{,}33\,E_s$, burada k_o metil mağnezyum bromürün hız sabitidir. Alkil mağnezyum halojenürlerin bağıl aktiflikleri klorür $<$ bromür $<$ iyodür sırasında artar. Reaksiyon hız sabitlerinin log. u ile alkil grubundaki β- hidrojenleri sayısı (n_H) arasında linear bir bağıntı bulunmuştur: $\log k/k_o = 0.062\, n_H$. S_Ei reaksiyonlarında karbon - metal bağının gevşekliği t-bütil $>$ i-propil $>$ etil $>$ s-bütil $>$ n-propil $>$ i-bütil $>$ metil sırasında azalır.

Prix de l'abonnement annuel

Turquie : 15 TL; Étranger: 30 TL.

Prix de ce numéro : 5 TL (pour la vente en Turquie).

Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi–1973