DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 15, No. 5, 1971
Printed in Republic of Korea

브롬화벤질의 알코올에 의한 용매분해에 관한 반응속도론적 연구

임용진 · 여수동 · 홍순영*
경북대학교화학과

(1971. 1. 18 접수)

Kinetics of the Solvolysis of Benzyl Bromides in Alcohols

Yong-Jin Lim, Soo-Dong Yoh and **Soon-Yung Hong***
Department of Chemistry, Kyungpook National University

(Received Jan. 18, 1971)

Abstract The kinetics of the solvolysis of benzyl and *p*- or *m*-substituted benzyl bromides in various alcohols have been determined by an electric conductivity method.

From these reactions, a curved Hammett plot is obtained and a mechanism is proposed to account for the nonlinear behavior observed.

In addition, effects of solvent polarity on the activation parameters for the solvolysis of benzyl bromides are discussed.

Introduction

For the solvolysis of benzyl halide, a number of investigations on the quantitative correlation of rates with solvents or with substituents have been carried out[1-11]. In most cases, the Hammett plot[12], log k/ko vs. σ, for nucleophilic reactions of benzyl halides, is smoothly curved rather than linear[13-15]. This deviation from linearity will arise when the mechanism of a reaction changes because of the presence of certain substituents or when the measured rate constant is actually a composite quantity depending on the rate and equilibrium constant of several reaction steps.

The present paper describes another case of nonlinear behavior of the Hammett plot for the solvolysis of *p*- or *m*-substituted benzyl bromides in methanol. A correlation between the solvent polarity and the activation parameter has also been discussed.

Experimental Section

Materials *p*-Methoxybenzyl bromide and *m*-methoxybenzyl bromide were prepared from their corresponding benzyl alcohols by a procedure of Quelet and Allard[16]. Aldrich Chemical Co. reagent grade *p*-methylbenzyl bromide, *m*-methylbenzyl bromide, *p*-bromobenzyl bromide, *p*-nitrobenzyl bromide, and benzyl bromide were fractionated under reduced pressure or recrystallized. Fisher reagent grade methanol, ethanol

---

* Department of Chemistry, Hanyang University, Seoul

1-propanol, 2-propanol, and 1-butanol were fractionated and dried over magnessium turnings before use.

Kinetics Pseudo-first-order rate constants of alcoholysis of benzyl and substituted benzyl bromides were obtained by an electric conductivity method. The kinetic apparatus and procedure were the same as those used previously[17]. Pseudo-first-order rates, k_1'*s*, were derived from equation 1 below[18,19]. An example of the results obtained by the above procedure is summarized

$$\ln\frac{C_\infty - C_o}{C_\infty - C_t} = k_1' t \qquad (1)$$

C_o: Initial elecric conductivity of a 0.005 mole/1 alcoholic solution of the reagent

C_∞: Electric conductivity at the terminal period which is measured after 3 days from the initiation of the reaction

C_t: Electric conductivity at time t

in *Table I*. The plot of log $(C_\infty - C_o)/(C_\infty - C_t)$ against time shows good linearity (*Fig.* 1).

Table I. Solvolysis of benzyl bromide in methanol at 35.0°.

t(min)	$C_t(10^{-6}\Omega)$	$\log(C_\infty - C_o)/(C_\infty - C_t)$
0	7.7	
10	12.6	0.00260
20	19.1	0.00561
40	34.2	0.01326
60	45.9	0.01953
80	61.0	0.02735
100	71.6	0.03302
120	84.0	0.03981
140	97.0	0.04689
160	108.8	0.05346
180	120.5	0.05994
220	142.8	0.07298
260	172.4	0.09061
300	191.9	0.10278
3days	881.8	

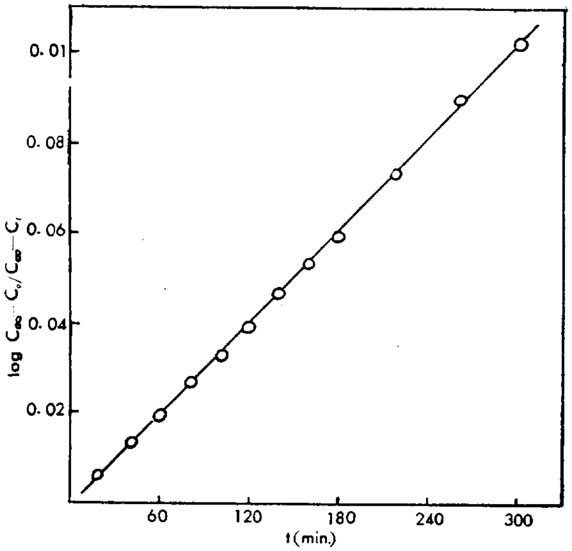


Fig. 1. The plot of log $(C_\infty - Co)/(C_\infty - Ct)$ vs. reaction time, t, for the solvolysis of benzyl bromide in methanol at 35.0°.

Results

Correlation between substituent and rate of solvolysis Pseudo-first-order rate constants (k_1'*s*) of solvolysis of benzyl and substituted ben-

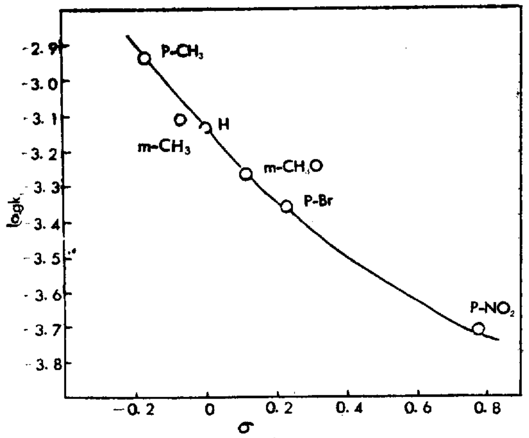


Fig. 2. Hammett plot of pseudo-first-order rate constants for methanolyses of benzyl and substituted benzyl bromides at 35.0°.

Table II. Rate constants of solvolysis of benzyl bromides in methanol at 35.0°.

Benzyl Bromides	Substituents	Pseudo-first-order rate constant^a, k_1' sec^{-1} $\times 10^5$
p-Methoxybenzyl Bromide	*p*-CH_3O	Could not be obtained^b
p-Methylbenzyl Bromide	*p*-CH_3	115.20
m-Methylbenzyl Bromide	*m*-CH_3	77.74
Benzyl Bromide	H	75.17
m-Methoxybenzyl Bromide	*m*-CH_3O	54.25
p-Bromobenzyl Bromide	*p*-Br	43.80
p-Nitrobenzyl Bromide	*p*-NO_2	19.67

a. Duplicate runs were made in each reaction studied.

b. The rate of reaction was too fast to measure by this experimental apparatus.

zyl bromides in methanol are given in *Table II.* The Hammett plot for these reactions is shown in *Fig.* 2. Hammett substituent constants are taken from Ref. 20.

Activation energy and entropy of activation for solvolysis of benzyl bromide Rate constants of solvolysis of benzyl bromide with various alcohols are given in *Table III.* The Arrhenius plots for these reactions show good linearities (*Fig.* 3) and activation parameters derived from these plots are summarized in *Table IV.*

Table III. Pseudo-first-order. rate contants of benzyl bromide in various alcohols, k_1' sec^{-1} $\times 10^5$.

Solvents	Temperature		
	25.0°	35.0°	45.0°
Methanol	37.76	72.65	110.42
Ethanol	32.48	57.13	73.93
2-Propanol	29.92	37.32	44.62
1-Propanol	37.24	41.85	55.40
1-Butanol	35.99	43.44	53.53

Table IV. Activativation energy, *Ea*, and entropy of activation, $\Delta S^{\neq}$ 25°, for solvolysis of benzyl bromide in various alcohols.

Solvents	*Ea*(Kcal)	$\Delta S^{\neq}$ 25°(eu)
Methanol	10.118	−42.255
Ethanol	7.809	−50.299
2-Propanol	3.688	−64.288
1-Propanol	3.804	−64.433
1-Butanol	3.509	−64.522

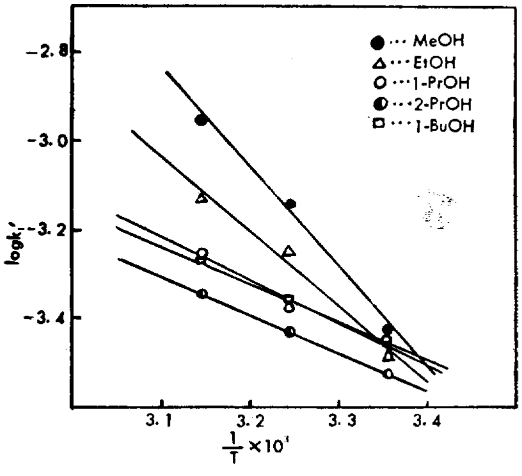
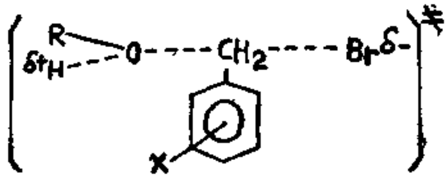


Fig. 3. Plots of log k_1' vs. $1/T$ for the solvolysis of benzyl bromide in varions alcohols.

Discussion

The Hammett plot for the solvolysis of benzyl bromides shows a smooth concave upward curvature rather than a straight line (*Fig.* 2). This behavior, as explained by Thornton[21], would be interpreted as reflecting changes in the relative importance of bond-making and bond-breaking caused by different substituents in the S_N2-type transition state. If bond-making were more complete than bond-breaking, the benzylic carbon atom would bear a net negative charge in the transition state, which would be stabilized by an electron-withdrawing substituent, *e. g.*, a *p*-methoxy or *p*-methyl group. If bond-breaking were more complete than bond-making, the carbon atom would bear a net positive charge in the transition state, which would be stabilized by an electron-donating substituent,



e. g., a *p*-bromo group. This type of behavior has been noted before for benzyl derivatives and has been interpreted in terms of increasing nucleophilic participation in the displacement as the electron-donating power of the substituent decreases[22].

As for the effect of solvent, the Arrhenius activation energy and entropy of activation of the solvolysis of benzyl bromides in alcohol, as expected, are greater in the more polar alcohol. The same phenomena have been observed by Hackett and Thomas in their solvolytic study of *p*-nitrobenzyl bromide[23], and discussed by Gould[24], Frost and Pearson[25].

References

1) J. W. Baker, *J. Chem. Soc.*, 987(1934).
2) C. G. Swain and R. W. Eddy, *J. Am. Chem. Soc.*, **70**, 2989(1948).
3) S. Winstein, E. Grunwald and H. Walter Jones, *ibid.*, **73**, 2700(1951).
4) C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731(1955).
5) C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3737(1955).
6) J. W. Hill and A. Fry, *ibid.*, **84**, 2763(1962).
7) J. B. Hyne, R. Wills and R. E. Wonkka, *ibid.* **84**, 2914(1962).
8) B. L. Murr, Jr. and V. J. Shiner, Jr., *ibid.*, **84**, 4672(1962).
9) C. W. L. Bevan, E. D. Hughes and C. K. Ingold, *Nature*, **171**, 301(1953).
10) I. Lee, *This Journal*, **9**, 8(1965), and preceding series of this paper.
11) E. S. Lee and S. K. Lee, *University Journal*, Pusan National University, Korea, **10**, 345(1969).
12) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, pp. 184-207.
13) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813(1951).
14) R. Fuchs and A. Nisbet., *ibid.*, **81**, 2371(1959).
15) R. Fuchs and D. M. Carlton., *ibid.*, **85**, 104 (1963).
16) R. Quelet and J. Allard, *Bull. Soc. Chim. France*, **4**, 1468(1937).
17) S. D. Yoh, D. S. Lee and S. Y. Hong, *This Journal*, **13**, 215(1969).
18) E. A. Guggenheim, *Phil. Mag.* Vol. i, 538 (1926).
19) R. E. Robertson, *Can. J. Chem.*, **33**, 1536(1955).
20) C. D. Ritchie and W. F. Sager, *Progress in Phys. Org. Chem.*, **2**, 323(1964).
21) E. R. Thornton, *Solvolysis Mechanism*, The Ronald Press Co., New Yor, 1964, Chapters 3 and 5.
22) For references to the other examples and and an excellent discussion of this matter, see J. O. Schreck, *J. Chem. Educ.*, **48**, 103(1971).
23) J. W. Hackett and H. C Thomas, *J. Am. Chem. Soc.*, **72**, 4962(1950).
24) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart and Winston, New York, 1959, p. 181.
25) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, 2nd Ed., John Wiley and Sons, Inc., New York, 1961, p. 137.