

Kinetics of the Reaction of Benzyl Bromides with Thiourea

by

Soo Dong Yoh, Dae Soo Lee*, and Soon Yung Hong

Department of Chemistry, Kyungpook National University, Taegu, Korea

(Received May 8, 1969)

Benzyl Bromide 類와 Thiourea 의 反應에 關한 反應速度論的 研究

慶北大學校 文理科學部 化學科

呂 壽 東 · 李 大 秀* · 洪 淳 瑛

(1969. 5. 8 接受)

ABSTRACTS

The kinetics of the reaction of *m*- or *p*-substituted benzyl bromides with thiourea in methanol at 35.0° were determined by an electric conductivity method. According to a plot of log *k* against the Hammett substituent constants, C-Br bond cleavage in benzyl bromide is postulated to be a rate determining step at the SN₂ reaction of benzyl bromide with thiourea. Both electron-donating substituents and electron-withdrawing substituents quantitatively affected the rate of reaction, but each in a different manner. A mechanistic possibility was proposed to account for the results. Some activation parameters were also calculated.

要 約

Methanol을 溶媒로 한 thiourea와 *m*- 또는 *p*-置換 benzyl bromide 類의 反應速度를 電氣傳導度法으로 測定하였다. Hammett 置換基定數와 Log *k* 와의 關係를 調査한 結果 benzyl bromide 에 對한 thiourea 의 SN₂ 反應에 있어서 C-Br 結合의 解離가 이 反應의 律速段階임을 알 수 있었다. 電子供與基와 電子吸引基는 다같이 反應速度에 定量的인 影響을 주었으나 그 樣式은 서로 달랐다. 이 結果에 符合되는 反應 메카니즘을 考察하였다. 몇 가지 熱力學的 파라미터도 求하였다.

INTRODUCTION

Kinetic studies of the reactions of thiourea with *m*- or *p*-substituted phenacyl bromides¹, or those of thiourea with ring-substituted heterocyclic bromoketones² showed that the substituent constants and reaction rates were well correlated according to the Hammett equation. In both cases, electron-withdrawing substituents

accelerate the reaction. Before these studies, Pearson, *et al.*³, reported the second-order rate constants for the reaction of pyridine or thiourea with a number of organic bromides including benzyl bromide. But they have not investigated the effect of substituent to the rate of reaction.

The present work was undertaken to determine quantitatively the effects of various ring-substituents to the rate of reaction of thiourea with *m*- or *p*-substituted

*Sung Kyun Kwan University, Seoul, Korea

benzyl bromides. A mechanism of this reaction was also discussed.

EXPERIMENTAL SECTION

Materials. 3-Methoxybenzyl bromide and 4-methoxybenzyl bromide were prepared from their corresponding benzyl alcohols. The other bromides and thiourea were purchased from the Aldrich Chemical Company, Inc., Milwaukee, Wis., U. S. A., and were used without further purification. Methanol was dried over magnesium turnings before use.

Preparation of *s*-Benzylisothiuronium Bromide. According to the procedure of *s*-benzylisothiuronium

product was collected by filtration and recrystallized twice from ethanol. Obtained colorless needles with mp 155-156°.

Anal. Calcd for $C_8H_{11}N_2SBr$: C, 38.83; H, 4.48; N, 11.34; Br, 32.38. Found: C, 38.03; H, 4.53; N, 11.78; Br, 32.95.

IR Spectrum. The sample was determined as a mull by Beckman IR 5A spectrophotometer. The spectrum (Fig. 1) showed an $-NH_3^+$ (stretching vibration) band at $3300-3150\text{ cm}^{-1}$ (m, multiple)⁵ and an $>C=N-$ (stretching vibration) band at 1630 cm^{-1} (s).

NMR Spectrum. The nmr spectrum was recorded on a Varian A-60(60Mc) spectrometer using TMS as an internal standard. As a solvent, D_2O was employed.

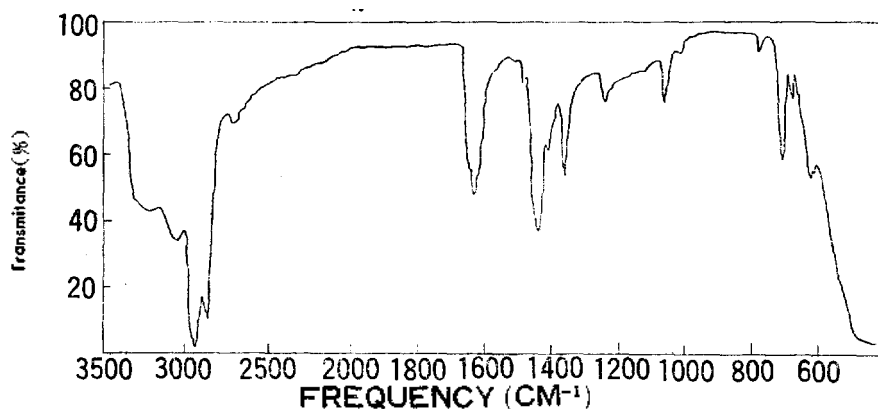


Fig. 1. IR Spectrum of *s*-benzylisothiuronium bromide.

chloride preparation⁴, a mixture of 0.1mole of benzyl bromide, 0.1mole of thiourea, and 300 ml of ethanol was refluxed at 90-95° for an hour. The precipitated

The spectrum (Fig. 2) provided almost conclusive conformation of structure(IV) on page 10. The five protons at 7.36 ppm ($\tau=2.64$, singlet) corresponding

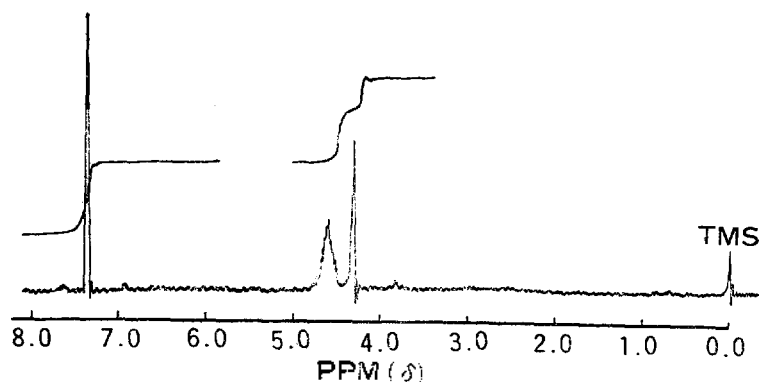


Fig. 2. Nmr spectrum(60 Mcps) of *s*-benzylisothiuronium bromide in D_2O with TMS as internal standard. Intensities are above the peaks.

to the five benzene-ring protons, four protons at 4.60 ppm ($\tau=5.40$, multiplet, broad) supposed to be four protons of imino and ammonium groups, and two protons at 4.34 ppm ($\tau=5.66$, singlet) corresponding to methylene group substituted by a phenyl and an isothiuronium group were observed.

Kinetics. The kinetic apparatus utilized for the rate studies of the reaction of substituted benzyl bromide with thiourea is shown in Figure 3. It is composed of a water bath, a long-necked reaction vessel in which two platinum-black electrodes (round, $d=1.0$ cm) are inserted through mercury tubes, and an electric conductivity outfit (Yanagimoto MY-7). The bath temperature was maintained to $\pm 0.1^\circ$.

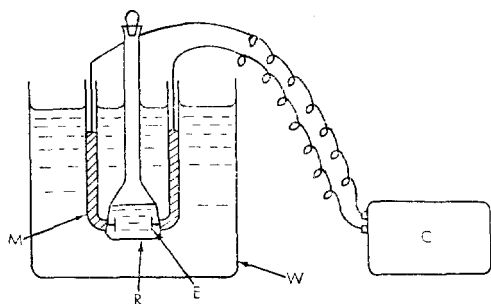


Fig. 3. Kinetic apparatus.

- M: Mercury tube
E: Electrode (Platinum-black)
R: Reaction vessel
W: Water bath
C: Electric Conductivity outfit

First the electric conductivity of 10 ml of 0.005 mole methanol solution of thiourea (K_a) and that of 10 ml of 0.005 mole methanol solution of benzyl bromide (K_b) were measured respectively. The two solutions, then, were mixed and the electric conductivity (K) was checked at appropriate times. The second-order reaction rates (k 's) were derived from equation(1) below. The initial electric conductivity (K_0) was obtained from equation(2).

$$kC_0t = \frac{K_\infty - K_0}{K_\infty - K} - 1 \quad (1) \quad K_0 = \frac{K_a + K_b}{2} \quad (2)$$

C_0 : Initial concentration of the mixture of two solutions

K_∞ : Electric conductivity at the terminal period

The electric conductivity at the terminal period, K_∞ , is that measured after 3 days from the initiation of the reaction. This value was almost the same as the value obtained measuring the electric conductivity of the solution of *s*-benzylisothiuronium itself (10 ml of 0.0025 mole methanolic solution). Two examples of the results obtained by the above procedure are summarized in Tables 1 and 2.

TABLE 1. Rates of reactions benzyl bromide with thiourea in methanol at 35.0° ($C_0=0.005$ mole/l, $K_a=10.2 \times 10^{-6}$)

t(min)	K(10^{-6})	kC ₀ t	k(l/mole · min)
10	27.3	0.031	1.24
20	41.1	0.059	1.18
40	74.1	0.132	1.05
60	89.9	0.168	1.12
100	121.6	0.254	1.02
140	155.5	0.361	1.03
180	194.9	0.512	1.14
240	227.5	0.658	1.09
3days	555.6		mean: 1.10

TABLE 2. Rates of reactions of *p*-Nitrobenzyl bromide with thiourea in methanol at 35.0° ($C_0=0.0025$ mole/l, $K_a=3.25 \times 10^{-6}$)

t(min)	K(10^{-6} Ω)	kC ₀ t	k(l/mole · min)
10	15.3	0.024	0.94
20	26.9	0.047	0.95
40	47.6	0.093	0.93
60	68.5	0.143	0.95
80	86.9	0.191	0.95
100	102.0	0.233	0.93
120	117.7	0.280	0.93
140	135.1	0.337	0.96
180	156.2	0.413	1.03
220	188.7	0.549	0.99
260	212.7	0.668	1.03
3days	526.3		mean: 0.96

RESULTS AND DISCUSSION

Temperature dependent kinetic data for the reaction of benzyl bromide with thiourea are summarized in Table 3. The calculated activation parameters for this reaction are $E_a=13.16$ kcal/mole and $\Delta S^\ddagger 25^\circ = -17.64$ eu.

reaction. In the latter case, however, C-Br bond cleavage is more important than S-C bond formation since the Hammett slope still shows negative.

REFERENCES

- 1) J. Okamiya, *Nippon Kagaku Zasshi*, **86**, 315 (1965).
- 2) J. Okamiya, *ibid.*, **87**, 594 (1966).
- 3) R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, **74**, 5130 (1952).
- 4) J. J. Donleavy, *ibid.*, **58**, 1004 (1936).
- 5) R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 66.
- 6) E. A. Guggenheim and J. E. Prue, *Physicochemical Calculations* North-Holland Publishing Co., Holland, 1955, Sec. 156.
- 7) C. D. Ritchie and W. F. Sager, *Progress in Phys. Org. Chem.*, **2**, 323 (1964).
- 8) K. B. Wiberg, *Physical Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1964, p. 407.