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Kinetics of the Reaction of Benzyl Bromides with Thiourea

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Benzyl Bromide類와 Thiourea의 反應에 關한 反應速度論的 硏究

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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와의 反應速度를 電氣傳導度法으로 測定하였다. Hammett 置換基定數와 Log k와의 關係를 調査한 結果 benzyl bromide에 對한 thiourea의 SN_2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 bromides[1], or those of thiourea with ring-substituted heterocyclic bromoketones[2] 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

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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-Benzylisothiouronium Bromide. According to the procedure of *s*-benzylisothiouronium chloride preparation[4], 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 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) showd an $-NH_3^+$(stretching vibration) band at 3300-3150 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.

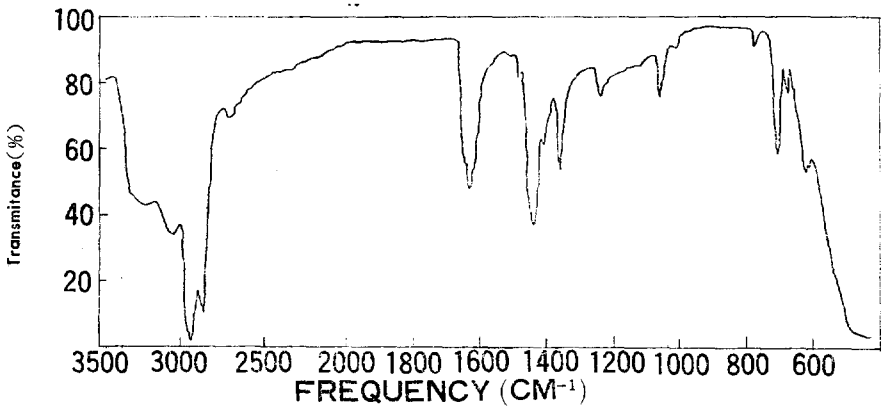


Fig. 1. IR Spectrum of s-benzylisothiouronium bromide.

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

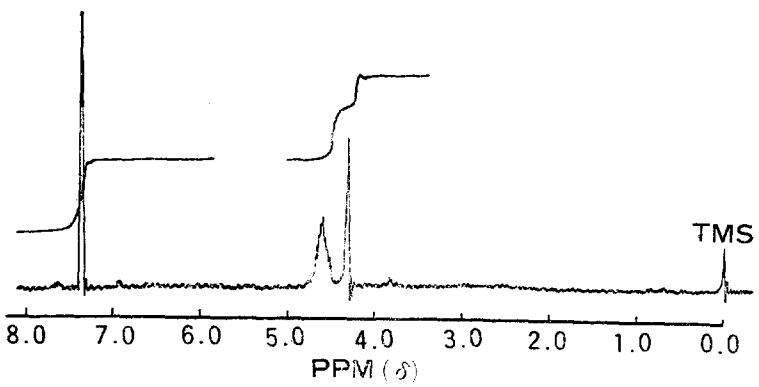


Fig. 2. Nmr spectrum(60 Mcps) of s-benzylisothiouronium bromide in D_2O with TMS as internal standard. Intensities are above the peaks.

to the five benzene-ring protons, four protons at 4.60 ppm(τ=5.40, multiplet, broad) supposed to be four protons of imino and ammonium groups, and two protons at 4.34 ppm (τ=5.66, singlet) corresponding to methylene group substituted by a phenyl and an isothiouronium 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±0.1°.

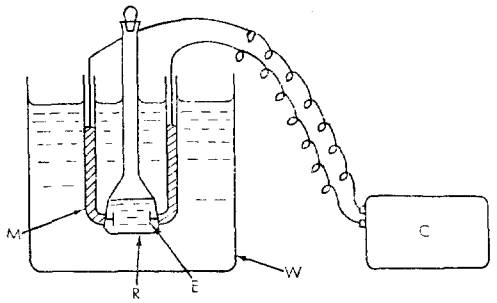


Fig. 3. Kinetic apparatus.
M: Mercury tube
E: Electrode (Platinum-black)
R: Reaction vessel
W: Water bath
C: Electric Conductivity outfit

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)[6] below. The initial electric conductivity (K_o) was obtained from equation(2).

$$kC_ot=\frac{K_\infty-K_o}{K_\infty-K}-1 \quad (1) \qquad K_o=\frac{K_a+K_b}{2} \quad (2)$$

C_o: 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*-benzylisothiouronium 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_o= 0.005 mole/1, K_o=10.2×10^{-6})

t(min)	K(10^{-6})	kCot	k(1/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_o=0.0025 mole/l, K_o=3.25×10^{-6})

t(min)	K(10^{-6}℧)	kC$_o$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 kineticd ata for the reaction of benzyl bromide with thiourea are summarized in Table 3. The calculated activation parameters for this reaction are Ea=13.16 kcal/mole and $\triangle S^{\neq}25°$ =−17.64 eu.

TABLE 3. Kinetic data for the reaction of benzyl bromide with thiourea in methanol

Point	Second-order rate Constant, k(l/mole · min)	Temp. (±0.1°)
1	0.57	25
2	0.52	25
3	1.10	35
4	1.03	35
5	2.28	45
6	2.12	45

The rates of reaction of *m*- or *p*-substituted benzyl bromide with thiourea in methanol at 35.0°C are given in Table 4. The Hammett plots based on these data are shown in figure 4; the σ-constants employed were taken from the compilation of Rithchie and

TABLE 4. Rates of reactions of Benzyl bromides with thiourea in methanol at 35.0°

Benzyl Bromides	Substituents	Second-order rate constant[a], k(l/mole · min)
p-Methoxybenzyl Bromide	*p*-CH_3O	Unsuccessful to obtain[b]
p-Methylbenzyl Bromide	*p*-CH_3	2.12
m-Methylbenzyl Bromide	*m*-CH_3	1.28
Benzyl Bromide	H	1.03
m-Methoxybenzyl Bromide	*m*-CH_3O	0.99
p-Bromobenzyl Bromide	*p*-Br	0.97
p-Nitrobenzyl Bromide	*p*-NO_2	0.96

[a] Duplicate runs were made in each reaction studied.
[b] The rate of reaction as too fast and was out of scale in this experimental apparatus.

Sager[7]. These reactions are second-order reactions since the time-dependent rate constant k, derived from equation(1) which is based on the second-order reaction kinetics, showed a good constancy. Pearson, *et al.*[2] also suggested this reaction to be a second-order. Hence the reaction could be best described as an SN_2 displacement with the methylene carbon of benzyl bromide as the reaction center. The transition state structure can be drawn as Ⅲ in equation (3) below. According to this, the rate of reaction could be ruled either by C-Br bond cleavage or by S-C bond formation, or by both C-Br bond cleavage and S-C bond formation. If the rate is influenced by these two factors, the rate constant would be given by the equation[8], k=ka+kb, and the Hammett equation then would take the form log

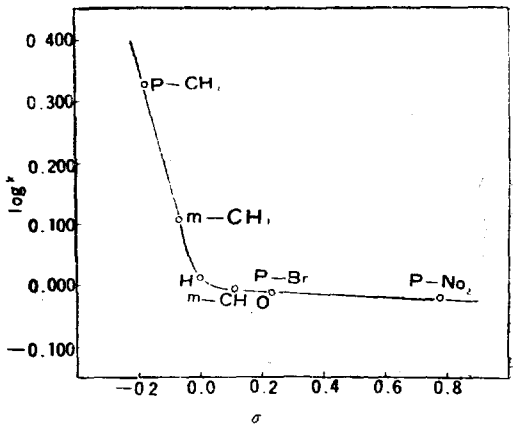
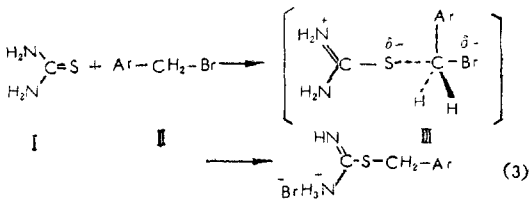


Fig. 4. Hammett plot for the rates of reactions of benzyl bromides with thiourea in methanol at 35.0°.

k=log(ka+kb). A normal Hammett plot will be obtained when the two rate constants, ka and kb, are similarly affected by substituents, or when one rate constant which is affected by substituents predominate over the other. Let ka be a reaction rate determined



by C-Br cleavage and kb determined by S-C formation. In light of structure Ⅲ, if the reaction rate is determined by C-Br cleavage and is influenced by substituents, the Hammett plot will show negative slope: meanwhile, the plot will show positive slope if the rate is determined by S-C formation. In other words, ka will be increased by electron-donating substituents; on the other hand, kb will be decreased by these groups.

According to the present investigation, the Hammett plot showed two different slopes(Fig. 4); $\rho=-3.8$ for the negative σ groups and $\rho=-0.06$ for the positive σ groups. This suggests that the S_N^2 reaction of benzyl bromide with thiourea is dominated by C-Br bond cleavage when electron-donators are substituted on the benzene-ring of benzyl bromide. And by changing the substituents with electron-with-drawers, the factor of S-C bond formation is gradually participated in the

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.

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