

Kinetic Studies of Chlorine Exchange between Benzyl Chloride and Radioactive Chloride Ion.

by

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Benzyl Chloride 의 Chlorine 交換反應

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要 約

90% ethanol solution 에서 benzyl chloride 와 radioactive chloride ($^{36}\text{Cl}^-$) 와의 exchange 를 反應速度論的으로 研究하였으며 그 結果로 이 交換反應은 typical bimolecular reaction 임을 알았고 그 activation parameter 들은 각 기 다음과 같았다. $\Delta H^\ddagger = 18.50 \text{ Kcal}$ $\Delta S^\ddagger = -22.09 \text{ e.u.}$ 특히 本實驗 結果와 여러 다른 實驗結果를 綜合討議함 으로써 反應速度는 attacking anion 의 nucleophilic ability 에 크게 관계 됨을 입증할 수 있었으며 또한 exchange reaction 에 있어서 halide 들의 reactivity 의 순서는 bond dissociation energy 의 차로써 보다는 오히려 Swain 의 nucleophilic parameter(n)로써 설명함이 더욱 타당함을 알았다.

Abstract

Halogen exchanges between benzyl chloride and chloride ion have been studied in 90% ethanol-water mixture, and activation parameters in the exchange reaction have been determined; $\Delta H^\ddagger = 18.50 \text{ Kcal}$ and $\Delta S^\ddagger = -22.09 \text{ e.u.}$ Results indicated that the reaction proceeded via a typical bimolecular mechanism. The importance of nucleophilic ability of attacking anion in S_N2 process has been stressed giving some experimental evidence. The order of reactivity of halides in the exchange reaction is better explained with the Swain's nucleophilic parameter than with the bond dissociation energies.

Introduction

Extensive studies on halogen exchange have been reported by Johnston and coworkers¹⁾ for haloacetic acid-halide and haloacetate-halide systems. They were able to show that in every reaction systems the exchange was characterized as typical S_N2 process. They further showed that reactivity of halogen exchange could be rationalized simply by the differences

in bond dissociation energies of the C-X bond, which are in order of, $-\text{I} < -\text{Br} < -\text{Cl}$. Thus the activation energies of the exchange reaction were to be in the same order.

Halogen exchanges have also been investigated for benzyl halides systems in various solvents^{2,3)}, reaching essentially the same conclusion as to its bimolecular nature of mechanism.

On the other hand, these halogen exchanges are

complicated by the parallel solvolytic reactions within the systems. Luehr et al.,⁴⁾ treated the isotopic exchange in non-stable systems theoretically and derived a general expression to represent the progress of exchange in a homogeneous system undergoing simultaneous chemical conversion of exchanging species.

We have investigated in this work chlorine exchange between benzyl chloride and chloride ion in 90% ethanol solution. Employing a modified form of Luehr's expression we have determined the bimolecular rate constant and the activation parameters.

Experimental

1. Materials:

Benzyl chloride was purified by distillation. b. p. $s = 52^\circ$ (lit. b. p. $= 179^\circ$), $n_D^{15} = 1.5419$ (lit.⁵⁾ $n_D^{15} = 1.5415$). The solvent ethanol was Merck GR grade. Radioactive chlorine-36 was obtained from the Radiochemical Centre, Amersham, England, as NaCl^* aqueous solution. The stock solution was prepared by diluting this solution to specific activity of $1 \mu\text{C}/\text{ml}$.

2. Kinetic runs:

Weighed amount of benzyl chloride was dissolved in a volumetric flask with absolute ethanol and desired amount of stock active solution was added. Double distilled water was then added to make up 90% ethanol by volume and the flask was filled to the mark with absolute ethanol. Temperature was kept constant at $20^\circ\text{C} (\pm 0.05^\circ)$ during these operations. This solution was divided into nine, 5ml. portions each and sealed in ampoules. One 5ml. portion was kept for blank activity test and $(\text{Cl}^-)_0$ determination. Negligible exchange and solvolysis were found normally to occur during these processes. Thermostatic bath containing the sealed ampoules was kept to better than $\pm 0.05^\circ\text{C}$. At timed intervals, ampoules were withdrawn from the bath and immediately the reaction was quenched by immersing ampoules into ice-water mixture. 5ml. sample solution was pipetted out from the ampoule and extracted with 10 ml. of *n*-heptane, 1 ml. portion of which was counted under G-M tube in a round Al counting tray covered with cellophane tape. Two 1 ml. portions were counted for each extracted *n*-heptane solution, and average value was taken. Counting rate was high enough to require only few minutes counting for the counting error of less than 2%. The total counting rate for 5 ml. reactant solution in a given set was

obtained by direct counting of an aliquot of original solution. Since this solution differs from the heptane solution in density, hence in β -absorption efficiency, corrections were applied by multiplying by density of the solvent, i.e., for 90% ethanol, 0.83 and for *n*-heptane, 0.68, to the observed counting rate. This converts the specific activity into cpm/ml. for the two solution.

On the other hand, extraction of benzyl chloride by *n*-heptane was not complete, and correction was necessary using the distribution coefficient determined separately. The increase of chloride ion concentration due to solvolysis was titrated by Volhard method.

3. Determination of distribution coefficient:

U.V. absorption curves were obtained for benzyl chloride in 90% ethanol and purified *n*-heptane and a maximum absorption wave length was determined (260 $m\mu$). General shapes were nearly the same for the two solutions and agreement was good with the literature value⁶⁾. Maximum molar extinction coefficient, ϵ , was then determined for each solution taking the value of more than three determinations for varying concentration of benzyl chloride. The results are shown in Table I, where we can see that the Beer's law is obeyed in both solutions. 10^{-3}M benzyl chloride in 90% ethanol was then extracted with *n*-heptane and the benzyl chloride content of each layer was determined by the absorbances at 260 $m\mu$ peak and ϵ obtained above. Distribution coefficient K was obtained as an average of 0.774, at room temperature, 30°C .

$$K = \frac{(\phi\text{CH}_2\text{Cl}) \text{ in } 90\% \text{ ethanol}}{(\phi\text{CH}_2\text{Cl}) \text{ in } n\text{-heptane}}$$

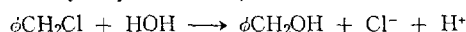
Table I Molar extinction coefficient of benzyl chloride.

90% ethanol solution			n-heptane solution		
$(\phi\text{CH}_2\text{Cl})$ mole/l $\times 10^3$	absor- bance	$\epsilon \times 10^{-2}$	$(\phi\text{CH}_2\text{Cl})$ mole/l $\times 10^3$	absor- bance	$\epsilon \times 10^{-2}$
2.070	0.510	2.465	4.526	0.857	1.89
6.076	1.50	2.469	2.241	0.43	1.919
4.880	1.193	2.450	3.83	0.726	1.90
average		2.46	average		1.90

(maximum absorption peak at 260 $m\mu$).

4. Determination of rate constant:

For hydrolysis reaction,



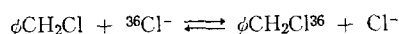
$$\frac{d(\text{Cl}^-)}{dt} = -\frac{d(\phi\text{CH}_2\text{Cl})}{dt} = \alpha(t) \quad (1)$$

$$(\text{Cl}^-)_t = (\text{Cl}^-)_0 + \int_0^t \alpha(t) dt = a + \rho(t) \quad (2)$$

$$(\phi\text{CH}_2\text{Cl})_t = (\phi\text{CH}_2\text{Cl})_0 - \int_0^t \alpha(t) dt = b - \rho(t) \quad (3)$$

where a and b are the initial concentrations of chloride ion and benzyl chloride.

For exchange reaction,



The rate is then,

$$\begin{aligned} R_x(t) &= k_x (\text{Cl}^-)^m (\phi\text{CH}_2\text{Cl})^n \\ &= k_x [a + \rho(t)]^m [b - \rho(t)]^n \quad (4) \end{aligned}$$

On the other hand,

$$\ln(1-F) = - \int_0^t \frac{R_x(t)(a+b)}{[a+\rho(t)][b-\rho(t)]} dt \quad (5)$$

therefore,

$$\begin{aligned} \ln(1-F) &= -k_x(a+b) \int_0^t [a+\rho(t)]^{m-1} \\ &\quad \cdot [b-\rho(t)]^{n-1} dt \quad (6) \end{aligned}$$

If the exchange rate is first order with respect to each reacting species,

$$\begin{aligned} \ln(1-F) &= -k_x(a+b)t \\ \therefore k &= -\frac{2.303}{(a+b)} \times \frac{\log(1-F)}{t} \quad (7) \end{aligned}$$

where

$$\begin{aligned} F &= \frac{\text{specific activity of benzyl chloride at } t}{\text{specific activity of total chlorine}} \\ &= \frac{e/d}{c/a+b} \end{aligned}$$

a ; $(\phi\text{CH}_2\text{Cl})_0$, moles in 5 ml.

b ; $(\text{Cl}^-)_0 + ({}^{36}\text{Cl}^-)_0$, moles in 5 ml.

c ; total activity in 5 ml. of reactant solution obtained by counting an aliquot of the original solution.

d ; concentration of extracted benzyl chloride in 10 ml. *n*-heptane, determined by applying K to $b-\rho(t)$.

e ; activity of extracted benzyl chloride in 10 ml. *n*-heptane at t .

Equation (7) is the normal bimolecular isotopic exchange equation, and a linear plot may be obtained between $\log(1-F)$ and t . Thus it can be transformed into,

$$k_x = \frac{2.303}{-(a+b)} \times \text{slope} \quad (8)$$

Rate constant, k_x was determined by equation (8), with the slope obtained by the plot of $\log(1-F)$ versus t . A typical result is shown in Table II and Fig. 2. Rate was normally followed to about 50% exchange, where the rate reached maximum as shown in Fig. 1. After this maximum, solvolysis rate becomes faster than the exchange rate and the counting rate begins to decrease.

5. Determination of activation parameters:

Table III lists the rate constants determined at 55°, 62.35° and 70°C.

Table II Kinetic data of chlorine exchange in benzyl chloride at 55°C in 90% ethanol solution.

Reaction time (hr.)	a cpm	b $(\phi\text{CH}_2\text{Cl}) \times 10^6$	c (Cl^-)	F_t	d slope	k_x (1/mole, hr)
0	10525	6.280	0	0		
1	163	6.245	0	0.0359		
2	319	6.245	0.00102	0.0707		
3	436	6.243	0.00102	0.0966		
4	590	6.210	0.00210	0.1078	0.0131	0.170
5	725	6.115	0.00463	0.1315		
6	858	6.075	0.00574	0.1954		
23	2002	5.570	0.01968	0.4970		

Initial concentration of benzyl chloride: 0.1742 Mole/l.

Initial concentration of sodium chloride: 3.54×10^{-3} Mole/l.

a ; Corrected for back ground and dead time.

b ; Extracted $(\phi\text{CH}_2\text{Cl})$ in 10 ml. *n*-heptane solution, Mole/l.

c ; Hydrolyzed concentration of sodium chloride, Mole/l.

d ; Slope of the plot, $\log(1-F)$ vs. t .

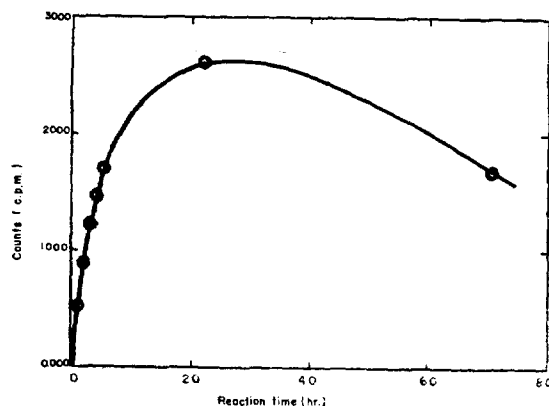


Fig. 1 Exchange rate of chlorine in benzyl chloride in 90% ethanol at 62.35°C.

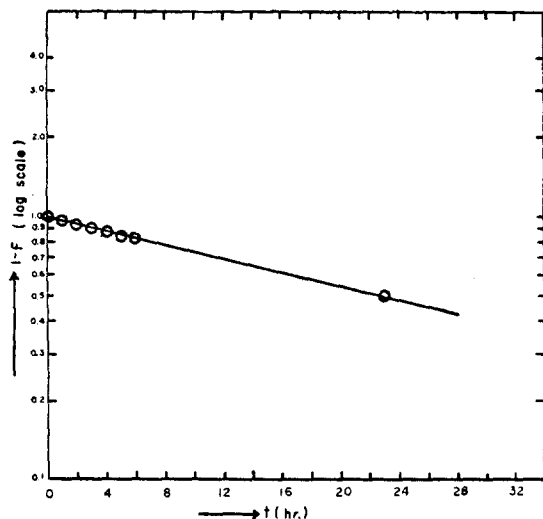


Fig. 2 Typical plot of $\log(1-F)$ vs. t ; for 90% ethanol at 55°C.

Table III Summary of rate constants of chlorine exchange in benzyl chloride in 90% ethanol solution.

°K		Benzyl chloride (mole/l)	Sodium chloride (mole/l) $\times 10^3$	Slope $\times 10^2$	k_x (l./mole-hr.)	$*k_x$ (mean)
328.16	1	0.532	3.38	3.87	0.167	0.169
	2	0.342	3.45	2.41	0.161	
	3	0.174	3.54	1.31	0.170	
	4	0.348	33.06	2.96	0.179	
	5	0.348	17.06	2.63	0.166	
335.51	6	0.348	3.47	4.97	0.325	0.325
343.16	7	0.348	3.52	1.03	0.674	0.690
	8	0.348	3.88	1.08	0.706	

* Accuracy is estimated to be better than $\pm 6\%$.

Arrhenius activation energy, $E_a = 19.49$ kcal, was determined from the slope of the linear plot of $\log k_x$ versus $1/T$, as shown in Fig 3.

Enthalpy and entropy of activation, ΔH^\ddagger and ΔS^\ddagger were calculated by the following relationships,

$$k_T = (kT/h)_{\text{exp}} [\Delta S^\ddagger/R]_{\text{exp}} [-\Delta H^\ddagger/RT]$$

$$\Delta H^\ddagger = E_a - RT$$

The result are: $\Delta H^\ddagger = 18.50$ kcal, $\Delta S^\ddagger = -22.09$ e.u.

Discussion

Reaction constant of the exchange, k_x , was found to be constant within experimental error over wide ranges of reactant concentrations as shown in Table

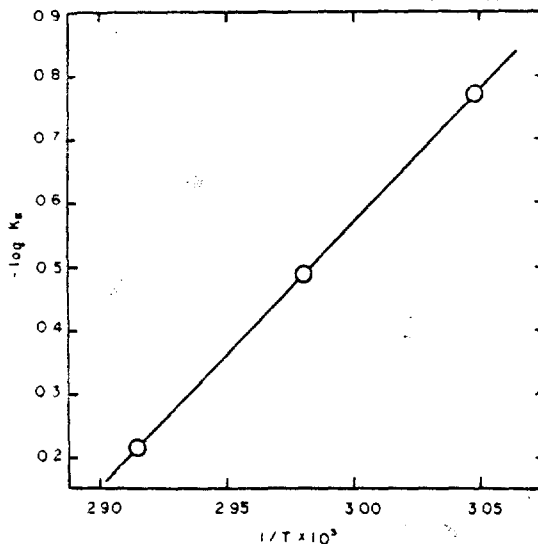


Fig. 3 Plot of $-\log k$ vs. $1/T$ for the exchange reaction. $E_A = 19.49$ kcal/mole.

III. The calculated activation energy and frequency factor now give the following expression for the rate constant,

$$k_x = 2.77 \times 10^8 \exp(-19500/RT), \text{ 1. mole}^{-1} \text{ sec.}^{-1}$$

From Table III, it can be concluded that the reaction is first order with respect to each reacting species and is a typical bimolecular displacement reaction, S_N2 ⁷⁾.

This is in accord with the results obtained in acetone²⁾ and water³⁾ solution by other workers. The rate of solvolysis was generally slow compared to that of the exchange as can be seen from Table II and Fig. 1, and the rates of the two processes become equal at about 50% exchange which took nearly 24 hours at 62.35°C as shown in Fig. 1.

This showed that it would not be of great value to follow the reaction after this peak rate, and therefore we normally followed the reaction up to about 50% completion. Separately determined activation parameters for the solvolysis of benzyl chloride in 90% ethanol-water mixture⁸⁾ were, $\Delta H^\ddagger = 23.48$ kcal and $\Delta S^\ddagger = -13.13$ e.u.. Comparing these data with those of exchange reaction, $\Delta H^\ddagger = 18.50$ Kcal and $\Delta S^\ddagger = -22.09$ e.u., we can conclude that the difference in rates is mainly an enthalpy effect since the large difference in ΔH^\ddagger is more than enough to compensate the effect of ΔS^\ddagger on rate. Since both the exchange and the solvolysis proceed with S_N2 mechanism⁸⁾, the difference in enthalpy can be explained with the

energy needed in the bond-formation⁷⁾. The more nucleophilic the attacking anion, the greater will be its tendency to form a stable covalent link, and the smaller in consequence will be the activation enthalpy needed to effect the substitution. The nucleophilic reactivity was expressed in quantitative way by Swain⁹⁾, who introduced a constant, n , called the nucleophilic parameter. According to his report the constant n for ethanol is about equal to that of water, for which he set n to be zero arbitrarily, and n for Cl^- was 3.04. Generally speaking n values for halides

(Br^- : 3.89 and I^- : 5.04, in addition to the value given above for Cl^-) are larger than those of neutral molecules of solvent. Therefore we can see the reason why the solvolysis rates were invariably slow compared to the halogen exchange rates. In Table IV we have tabulated halogen exchange reactions of interest, and solvolysis data available. Reports cited in Table IV showed that the rates of solvolysis are slow compared to the exchange rates, which is in accord with the magnitudes of ΔH^\ddagger except one, (b).

Table IV Comparison of activation parameters for halogen exchange reaction.

Reaction	ΔH^\ddagger (Kcal)		ΔS^\ddagger (e. u.)	
	Exchange	Solvolysis	Exchange	Solvolysis
a $\phi\text{CH}_2\text{Cl} + \text{Cl}^-$ in 90% ethanol	18.50(55°)	23.48	-22.09	-13.13
b $p\text{-NO}_2\phi\text{CH}_2\text{Br} + \text{Cl}^-$ in 90% dioxane(wt.)	16.5	15.4	-20.8	-44.2
c $\text{CH}_2\text{ClCOOH} + \text{Cl}^-$ in water	23.8	24.1	-10.6	-18.0
d $\text{CH}_2\text{ClCOOH} + \text{Cl}^-$ in 50% ethanol	23.0(Ea)	—	-14.0	—
e $\text{CH}_2\text{BrCOOH} + \text{Br}^-$ in water	18.98	23.07	-13.4	—
f $\text{CH}_2\text{ICOOH} + \text{I}^-$ in water	15.98	22.58	-14.6	—
g $\text{CH}_2\text{ClCOO}^- + \text{Cl}^-$ in water	26.4	27.9	-8.9	—
h $\phi\text{CH}_2\text{Cl} + \text{Cl}^-$ in acetone	17.62(55°)	—	-20.21(55°)	—
i $\text{CH}_2\text{BrCOO}^- + \text{Br}^-$ in water	19.7	—	-16.6	—
j $\text{CH}_2\text{ICOO}^- + \text{I}^-$ in water	15.9	—	-19.3	—
k $\text{CH}_3\text{CHBrCOOH} + \text{Br}^-$ in water	20.25(55°)	—	-20.45	—

a; This research and Ref. (8). b; J. W. Hackett, O. P., and H. C. Thomas, *J. Am. Chem. Soc.* **72**, 4962 (1950). c; R. A. Kenney and F. J. Johnston, *J. Phys. Chem.* **63**, 1426 (1959). d; J. H. Hinton and F. J. Johnston, *ibid.*, **66**, 1368 (1962). e; and f; J. F. Hinton and F. J. Johnston, *ibid.*, **67**, 2557 (1963). g; F. J. Johnston, *ibid.*, **66**, 1719 (1962). h; P. B. D. de la Mare and E. D. Hughes, *J. Chem. Soc.* 845 (1956). i; F. J. Johnston, *J. Phys. Chem.* **68**, 2370 (1964). j; R. C. Bond, M. S. Thesis, Univ. of Georgia, 1963. k; W. Koskowski, R. W. Dodson and R. C. Fowler, *J. Am. Chem. Soc.* **63**, 2149 (1941).

Johnston et al, explained the order of ΔH^\ddagger for halide-haloacetic acid exchanges by the order of bond dissociation enthalpy which is $D_{\text{C-Cl}} > D_{\text{C-Br}} > D_{\text{C-I}}$, and formulated the relationship as $\Delta H^\ddagger = 0.29 D_{\text{C-X}}$, where $D_{\text{C-X}}$ is the standard dissociation enthalpy at 25°C. In view of the importance of bond-formation step in transition state for S_N2 process⁷⁾, however, we prefer the argument of nucleophilicity difference

of halide ion as expressed by the Swain's n , to that of $D_{\text{C-X}}$. Other conditions being equal, the rates, or ΔH^\ddagger , should be in the reverse order of n , which is quite consistent to the experimental results (Table IV).

If on the other hand, ΔH^\ddagger were to follow $D_{\text{C-X}}$ as proposed by Johnston, ΔH^\ddagger values for the reactions (e) and (k) in Table IV should be reversed, since it is reasonable to assume that $D_{\text{C-X}}$ is in reverse order**.

* Generally speaking, rate or free energy of activation can not be judged solely by enthalpy of activation. However in this case the entropies of activation also show the same trend as the enthalpies of activation and thus it is justified to compare the rates with ΔH^\ddagger alone.

** No bond dissociation energy data are available for C-Br bonds in CH_2BrCOOH and $\text{CH}_3\text{CHBrCOOH}$. However literature survey¹⁰⁾ shows that $D_{\text{C-X}}$ decreases as the carbon atom concerned is successively methylated. In propionic acid the carbon atom has an extra CH_3 group and it can be reasonably assumed that $D_{\text{C-Br}}$ of propionic acid is less than that of α -bromoacetic acid.

This is however easily explained by our argument of bond-formation energy. Considering the developed positive charge density (δ^+) on the central carbon atom, α -carbon on propionic acid has less δ^+ than that on acetic acid and the reaction (k) should require more energy than the reaction (e). The charge density can be judged from the Taft's polar substituent constant σ^* , which is zero for CH_3 —while it is +0.49 for $-\text{H}$ ¹¹⁾ (Two compound CH_2BrCOOH and $\text{CH}_3\text{CHBrCOOH}$ differ only in substituents on α -carbon, which is $-\text{H}$ for the former and CH_3 — for the latter).

Comparing the activation parameters for reaction(h) with those of the present work, (a), we may conclude that the medium effect is not very large, in support of S_N2 mechanism proposed. We have dealt the relations between mechanism of reaction and the magnitude of solvent effect in a separate report⁸⁾, where we have shown that the magnitude of a' in eq. (9) determines the magnitude of solvent effect and hence the mechanism of reaction. This criterion requires a small a' for S_N2 reaction as the benzyl chloride-chloride exchange. It is hoped that we will be able to show this aspect by further studies.

$$\delta_M \Delta H^\ddagger = a'Y + b\delta_M \Delta S^\ddagger \dots\dots\dots (9)$$

where δ represents the effect of solvent on activation parameters following the symbol, a' is the substrate constant and b is a constant for the reaction system, and Y measures the ionizing power of the solvent¹²⁾.

In this experiment, NaCl concentration was varied up to 10-fold and found no significant changes in rate constant. This shows the nonexistence of an ionic st-

rength effect for this system as expected for an S_N2 reaction.

References

- 1) F. J. Johnston, *J. Phys. Chem.* **68**, 2370(1960), and the references cited therein. See the footnote of Table IV.
- 2) P. B. P. de la Mare and E. D. Hughes, *J. Chem. Soc.* 845(1956).
- 3) K. Tanabe and T. Sano, *J. Res. Inst. Catalysis, Hokkaido Univ.* **10**, 165(1962).
- 4) C. P. Luehr, G. E. Challenger and B. J. Masters, *J. Am. Chem. Soc.* **78**, 1314 (1956).
- 5) *Handbook of Chemistry and Physics*, 33rd Ed., (Chemical Rubber Publishing Co., 1951)
- 6) W. F. Hamner and F. A. Masten, *J. Am. Chem. Soc.* **70**, 2482(1948).
- 7) J. Hine, *Physical Organic Chemistry*, (McGraw Hill Book Co. Inc., New York, 1962)
- 8) To be published in this Journal.
- 9) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.* **73**, 2813(1951); C. G. Swain and Scott, *ibid.*, **75**, 141(1953).
- 10) E. W. R. Steacie, *Atomic and Free Radical Reactions*, Vol. I (Reinhold Publishing Corp., New York, 1954.), Chapter III.
- 11) R. W. Taft, (*Steric Effects in Organic Chemistry*, (John Wiley and Sons, Inc., New York, 1956), Chapter 13.
- 12) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.* **70**, 846(1948).