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Benzyl Bromide-Amine Reaction in Nitrobenzene-Ethanol Mixtures

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The reactions between benzyl bromide and various bases as well as *p*-nitrobenzyl bromide and various bases have been studied in nitrobenzene-ethanol mixtures (80 : 20 v/v). The reaction is total second order as stated earlier. Comparison is made with the previous work on the same reaction with benzyl chloride and *p*-nitrobenzyl chloride.

In our earlier communications[1,2] we reported the kinetics of reaction of benzyl chloride as well as of *p*-nitrobenzyl chloride with bases in nitrobenzene-ethanol mixtures. We report here the kinetics of reaction of benzyl bromide as well as of *p*-nitrobenzyl bromide with bases in nitrobenzene-ethanol mixtures (80 : 20 v/v).

Experimental

Materials. All substances are of AnalaR grade. Nitrobenzene is also of AnalaR grade.

Rate Measurements. The reactions were followed as per the procedure stated earlier.[1,2] Solvolysis correction was also done with benzyl bromide reaction.

TABLE 1

Solvent: Nitrobenzene-Ethanol (80 : 20 v/v)
Substrate: Benzyl bromide

Base	$10^2 \times k$ l mol^{-1}min^{-1} 80°C	70°C	pK_a*
Aniline	47.20	29.90	4.25
N-Methylaniline	95.70	63.60	4.85
β-Naphthylamine	36.00	23.40	4.11
p-Toluidine	85.60	59.90	5.07
m-Toluidine	56.90	38.00	4.67
o-Toluidine	25.70	15.90	4.38
p-Chloroaniline	24.60	14.10	3.81
m-Chloroaniline	15.50	8.80	3.32
n-Butylamine	436.00	308.00	10.61†
Benzylamine	284.00	—	9.34†
Diethylamine	526.00	375.00	11.10†

* Braude and Nachod, "Determination of Organic Structures by Physical Methods," Vol. 1 (1955).
† Lange, "Handbook of Chemistry" (1961).

Discussion

The second order rate constants for benzyl bromide and bases are given in Table 1. A glance at the table indicates that all the aliphatic amines react much faster than the aromatic amines. All the compounds react in consonance with their basicity except for a few where other factors seem to operate, such as the *ortho* effect. A plot of log *k* *vs.* pK_a showed linearity.

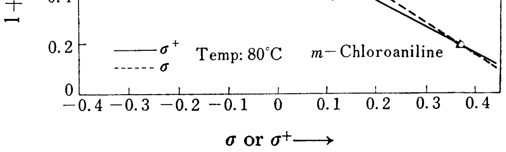

Fig. 1

Where ever σ and σ^+ are different σ and σ^+ points are indicated by △ and ○ respectively.

To analyze the data a correlation was made with Hammett's substituent constants for aromatic amines. A plot of log *k* *vs.* σ and σ^+ showed linearity (Fig. 1). The slopes were −1.4 and −1.1 respectively. All these establish that the attack by amine on the benzyl bromide is facilitated by electron releasing groups in the base and retarded by electron attracting groups in the substrates.

p-Nitrobenzyl bromide was also subjected to react with all these bases. The reactions were uniformly slower compared to benzyl bromide. This establishes that electron withdrawing groups

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[1] P. S. Radhakrishnamurti and G. P. Panigrahi, *J. Indian Chem. Soc.*, **45**, 323 (1968).

[2] P. S. Radhakrishnamurti and G. P. Panigrahi, *Israel J. Chem.*, **6**, 137 (1968).

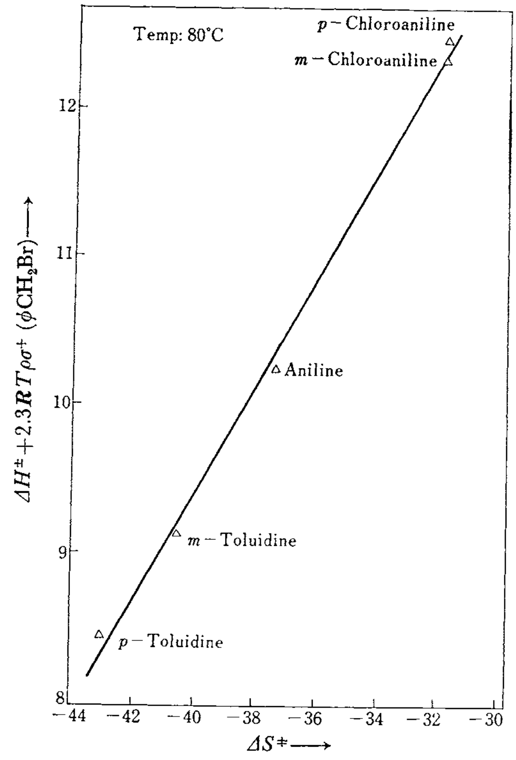

Fig. 2

either in the substrate or in the attacking base retard the process. The important features in these reactions are: (1) Anionisation of the halogen, (2) the coordination of the basic nitrogen atom with the adjacent methylene group by means of the unshared electron pair. These two are affected in turn by electron withdrawing substituents and hence retardation. The rate constants are given in Table 2.

log k *vs.* pK_a as well as log k *vs.* σ and σ^+ showed linearity. The ρ values are -1.75 and -1.4 respectively. The most reactive base is diethylamine. The two aliphatic primary amines react quite in consonance with their electron availability.

Table 2

Solvent: Nitrobenzene-Ethanol (80:20 v/v)
Substrate: *p*-Nitrobenzyl bromide

Base	$10^2\times k$ l mol^{-1}min^{-1}	
	80°C	70°C
Aniline	25.50	16.60
N-Methylaniline	40.00	26.70
β-Naphthylamine	18.90	12.40
p-Toluidine	41.50	27.60
m-Toluidine	30.70	19.00
o-Toluidine	10.80	6.89
p-Chloroaniline	9.41	5.11
m-Chloroaniline	6.11	3.28
n-Butylamine	276.00	196.00
Benzylamine	135.00	93.00
Diethylamine	390.00	290.00

Table 3

Solvent: Nitrobenzene-Ethanol (80 : 20 v/v)
Temperature: 80°C
Base: Aniline

Substrate	$10^2\times k$ $l$mol^{-1}min^{-1}
Benzyl chloride	0.755
Benzyl bromide	47.20
p-Nitrobenzyl chloride	0.356
p-Nitrobenzyl bromide	25.50

In the aromatic series, *N*-methylaniline certainly reacts faster than aniline as the pK_a values indicate. All toluidines react faster than the corresponding chloro compounds. Similar reasoning explains the reactivity of these bases with *p*-nitrobenzyl bromide.

Comparison of the Reactivity of Benzyl Chloride and Benzyl Bromide. It is interesting to note that bromide derivative reacts faster than the chloride derivative (Table 3). This is quite in accord with the well known theories of substituent effects.3)

Mechanism of the Process. It was postulated that it is possible to rationalize the inactivity of benzyl chloride with primary aromatic amines in pure nitrobenzene on the basis of a four centered transition state. It was also suggested that alternatively the abnormality could be due to specific solvent influences. The present work with benzyl bromide and *p*-nitrobenzyl bromide rules out the possibility of a likely four centered transition state. All these reactions, in general, are through a three centered transition state. Any inactivity or abnormality is to be traced to solvation phenomena.

Our arguments are based on the following facts: (1) Benzyl chloride and *p*-nitrobenzyl chloride are unreactive in pure nitrobenzene medium but reactive in nitrobenzene-ethanol mixture, nitrobenzene-dimethylformamide mixture, nitrobenzene-dimethylsulfoxide mixture and nitrobenzene-acetic acid mixture. This reaction did not occur in nitrobenzene-benzene, nitrobenzene-chlorobenzene, nitrobenzene-dioxane and nitrobenzene-acetonitrile mixtures. The relative reactivity in the solvent mixtures is nitrobenzene-DMSO (80 : 20 v/v) > nitrobenzene-ethanol (80 : 20 v/v) > nitrobenzene-acetic acid (80 : 20 v/v) > nitrobenzene-DMF (80 : 20 v/v).

(2) Benzyl bromide and *p*-nitrobenzyl bromide did react in pure nitrobenzene medium but crystallization occured at a very early stage of the reaction.

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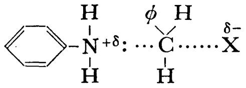
3) E. S. Gould, "Mechanism and Structure in Organic Chemistry" (1965), pp. 260—261.

Hence the kinetics of these derivatives were studied in nitrobenzene-ethanol mixtures. A complete analysis of solvent influence on bromide derivatives will be dealt with in a separate communication.

These two facts put together mean that the abnormal inactivity noticed with benzyl chloride and *p*-nitrobenzyl chloride is due to greater ground state solvation. The bromide derivatives react in nitrobenzene indicating greater transition state solvation though crystallization occurs.

A plot of log *k* of benzyl chloride *vs.* log *k* of benzyl bromide is perfectly linear indicating a similar process in both chlorides and bromides. The mechanism as mentioned earlier is a three centered transition state as follows:



(Three centered transition state)
X=Cl, Br, *etc.*

The reaction is an S_N2 reaction having a dominant S_N1 character.

Thermodynamic Parameters. The values of activation energies, frequency factor and other derived thermodynamic constants for benzyl bromide-amine reaction are collected in Tables 4 and 5. Both the parameters E and $\log_{10} PZ$ tend to increase together. Linearity is obtained by plotting $\log_{10} PZ$ against $1/\sqrt{E}$ as it should be on the basis of thermodynamic considerations[4] (Fairclough-Hinshelwood relationship) if both the Arrhenius parameters are the controlling factors of the rate. The small frequency factors would mean that standard entropy of activation $\Delta S^{\pm}$ has a relatively larger negative value or that the transmission coefficient is small.

Table 4

Solvent: Nitrobenzene-ethanol (80:20 v/v)
Temperature: 80°C
Substrate: Benzyl bromide

Base	E kcal/mol	$\log_{10} PZ$	$-\Delta S^{\pm}$	$\Delta H^{\pm}$ kcal/mol
Aniline	10.95	4.67	37.42	10.25
N-Methylaniline	9.82	4.28	39.35	9.12
β-Naphthylamine	10.33	4.17	39.80	9.63
p-Toluidine	8.60	3.48	42.98	7.90
m-Toluidine	9.72	3.99	40.61	9.02
o-Toluidine	11.22	4.57	37.96	10.52
p-Chloroaniline	13.40	5.90	31.86	12.70
m-Chloroaniline	13.70	5.89	31.93	13.00
n-Butylamine	9.44	4.73	37.25	8.74
Diethylamine	8.13	3.98	40.88	7.43

Table 5

Solvent: Nitrobenzene-ethanol (80:20 v/v)
Temperature: 80°C
Substrate: *p*-Nitrobenzyl bromide

Base	E kcal/mol	$\log_{10} PZ$	$-\Delta S^{\pm}$	$\Delta H^{\pm}$ kcal/mol
Aniline	10.32	4.02	40.51	9.62
N-Methylaniline	9.56	3.74	41.78	8.86
β-Naphthylamine	10.16	3.79	41.57	9.45
p-Toluidine	9.82	3.92	40.97	9.12
m-Toluidine	11.60	4.90	36.52	10.90
o-Toluidine	10.74	3.90	41.04	10.04
p-Chloroaniline	14.60	6.23	30.37	13.90
m-Chloroaniline	14.95	6.26	30.24	14.25
n-Butylamine	8.24	3.76	41.67	7.54
Benzylamine	8.93	3.88	41.12	8.23
Diethylamine	7.14	3.23	44.11	6.43

Enthalpy-Entropy Relationship. It was of interest to examine the relationship between activation enthalpy and entropy. The possibility of correlation between $\Delta S^{\pm}$ and $\Delta H^{\pm}$ was investigated by a conventional isokinetic plot. It appears that the plot showed a tendency of scatter which is discriminating and characteristic of the nature and position of the groups. This observation together with ideas put forward by Hepler[5a,b,c] and others suggested that if the enthalpy and entropy changes are resolved into external and internal components a relationship may exist between the external parameters. In this treatment external contributions to enthalpy and entropy are associated with solvent interactions, and the internal contributions arise from differences in enthalpy and entropy within the reactant molecules and the transition state. If the reasonable assumption is made that the internal motions of the substituents do not contribute to the free energy, *viz.*, internal entropy changes are zero, the following equation[6a,b] may be used as a test of external entropy and enthalpy relationship.

$$(\delta\Delta H^{\pm}+2.303\boldsymbol{R}T\rho\sigma^{+}) = b\delta\Delta S^{\pm}$$

where δ and Δ operator symbols represent the effect of the substituents and of chemical reaction on the activation enthalpy and entropy, σ^{+} is the electrophilic substituent constant of Brown and Okamoto, ρ is the Hammett reaction constant which is -1.1 at 80°C for benzyl bromide-amine reaction; b is a constant characteristic of the reaction and can be obtained from the slope of a plot of $\delta\Delta H^{\pm}+2.303\boldsymbol{R}T\rho\sigma^{+}$ against $\delta\Delta S^{\pm}$. The plot

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[4] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, **1937**, 538.

[5] a) L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963). b) K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1725 (1959). c) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

[6] a) I. Lee, *J. Korean Chem. Soc.*, **7**, 211, 238 (1963). b) I. Lee, *Chem. Abstr.*, **61**, 5015e, 7770e (1964).

shows perfect linearity (Fig. 2). The right hand side of the equation represents external entropy change. Since $\delta\Delta S^{\pm}=\delta\Delta S(\text{internal})+\delta\Delta S(\text{external})$, then for $\delta\Delta S(\text{internal})=0$, $\delta\Delta S^{\pm}=\delta\Delta S(\text{external})$. Similarly the left hand side of the equation represents the external enthalpy changes due to the substituents, provided that the term "$2.303\ \boldsymbol{R}T\rho\sigma^{+}$" may be identified with $\delta\Delta H$ (internal). This assumption is consistent with Hammett's original concept in which substituent constants represent changes in the potential energy of the system.

It is pertinent to refer to the work of Campbell and Hogg⁷⁾ wherein they found, in their reactions of electrophilic additions to alkenes, that there is no alteration of the reaction mechanism with changes in solvent polarity.

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7) D. S. Campbell and D. R. Hogg, *J. Chem. Soc.*, *B*, **1967**, 889.