

The α Effect. Aminolysis on a Saturated Carbon Atom^{*1}

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The rates of aminolyses of methyl, isopropyl, allyl and benzyl iodides have been determined in acetonitrile. Bases used were hydrazine, morpholine, imidazole and piperidine. The rates of all the aminolysis reactions can be correlated nicely with the basicities. Hydrazine also did not show any positive deviation from the Brønsted plots. This fact suggests that the α -effect is not operative in these displacement reactions on the saturated carbon atom.

In a number of bimolecular nucleophilic reactions, various nucleophiles having unshared electron pairs adjacent to the nucleophilic center-atom show much higher reactivities than those anticipated from their basicities. These high reactivities are generally estimated from large positive deviations from the Brønsted plots and are ascribed to so called α -effect.¹⁾ As Bruice *et al.* pointed out,²⁾ several possible explanations concerning the α -effect have been proposed. However, no satisfactory one has been presented; nor do we have sufficient data to draw any conclusion as to the origin of the α -effect.

One of the attractive approach to this problem is to focus the attention on the relation between the α -effect and the nature of the hybridization of the carbon atom of the reaction center, *i. e.*, sp , sp^2 and sp^3 . Concerning the sp and sp^2 hybridized carbon atoms, relatively large amounts of works have been carried out and large α -effects have been observed with both nonionic³⁾ and ionic^{1b,4)} nucleophiles. But in the S_N2 reactions on the sp^3 hybridized carbon atom only two data are

available, the one is the reaction of benzyl bromide with hydroperoxide anion and hydroxide anion⁵⁾ (ionic nucleophiles) and the other is the aminolysis of methyl iodide in water^{3a)} (nonionic nucleophiles). In either reaction, α -effects were rather small or negligible. From these investigations,^{1b,3a,3c,4,5)} it appears that the magnitude of the α -effect seems to depend generally on the character of the reacting site of substrate, and falls in the following order.

$$sp > sp^2 > sp^3 \text{ carbon.}$$

In general, rates of nucleophilic reaction on the sp and sp^2 carbon atoms such as nitrile⁴⁾ and carbonyl are mainly controlled by basicity rather than polarizability of the nucleophile used, while, in the case of the sp^3 carbon atom, polarizability is the more important factor than basicity. Apparently the higher the demand for stronger basicity, the larger α -effect is observed in the case with the sp and sp^2 carbon atoms whereas in the substitution reaction on the sp^3 carbon atom, the reaction requiring higher polarizable nucleophile would display a larger α -effect. Incidentally, α -effect, though small, was reported in the reaction of benzyl bromide with hydroperoxide anion in 50% acetone-water,⁵⁾ while, no α -effect was observed in the aminolysis reaction of methyl iodide in water.^{3a)} The former case is different from the latter one in that in the former reaction the nucleophile is ionic while π electrons of phenyl ring can delocalize to the reaction center in the transition state and hence the whole system is quite susceptible to polarizability.

The present work was initiated in order to examine the effect of the structural change of the substrates, in the aminolyses of methyl, isopropyl, allyl and benzyl iodides in acetonitrile.

Results and Discussion

The substrates examined were unfortunately very sparingly soluble in water, however, pK_a 's of these

^{*1} Paper VIII on "Relative Reactivities of Organic Halides in Displacement Reactions."

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3) a) M. J. Gregory and T. C. Bruice, *ibid.*, **89**, 4400 (1967). b) T. C. Bruice and S. J. Benkovic, *ibid.*, **86**, 418 (1964). c) W. P. Jencks, *ibid.*, **80**, 4585 (1958).

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TABLE 1. THE RATE CONSTANTS k_2 ($l \text{ mol}^{-1} \text{ sec}^{-1}$) OF AMINOLYSIS IN ACETONITRILE

Amines	Substrates				$pK_{a'}$ ^{m)}
	$\text{CH}_3\text{I}^{\text{a,c)}$	$i\text{-C}_3\text{H}_7\text{I}^{\text{a,d)}$	$\text{CH}_2=\text{CHCH}_2\text{I}^{\text{a,e)}$	$\text{C}_6\text{H}_5\text{CH}_2\text{I}^{\text{b,f)}$	
Imidazole ^{g)}	1.86×10^{-3}	1.17×10^{-5}	2.64×10^{-3}	3.41×10^{-3}	13.8 ⁿ⁾
Hydrazine ^{h)}	4.43×10^{-2}	1.97×10^{-4}	1.33×10^{-1}	1.47×10^{-1}	16.61
Morpholine ^{l)}	1.17×10^{-1}	1.32×10^{-4}	3.17×10^{-1}		16.61
Piperidine ^{j)}	6.81×10^{-1}	7.73×10^{-4}	3.53	1.72	18.92
Hydroxylamine ^{k)}				3.88×10^{-3}	
Benzylamine ^{l)}				6.00×10^{-2}	16.76

a) Reaction was carried out at 40°C.

c) 1.86×10^{-4} — 6.08×10^{-3} mol/l.e) 6.89×10^{-5} mol/l.g) 3.86×10^{-1} — 1.12×10^{-3} mol/l.i) 9.85×10^{-2} — 4.43×10^{-4} mol/l.k) 1.65×10^{-3} mol/l.

m) Ref. 6.

b) Reaction was carried out at 30°C.

d) 1.19×10^{-1} — 1.12×10^{-2} mol/l.f) $(1.96\text{--}3.99) \times 10^{-4}$ mol/l.h) 1.35×10^{-1} — 7.86×10^{-4} mol/l.j) 5.80×10^{-2} — 1.47×10^{-4} mol/l.l) 1.48×10^{-3} mol/l.

n) Ref. 3a.

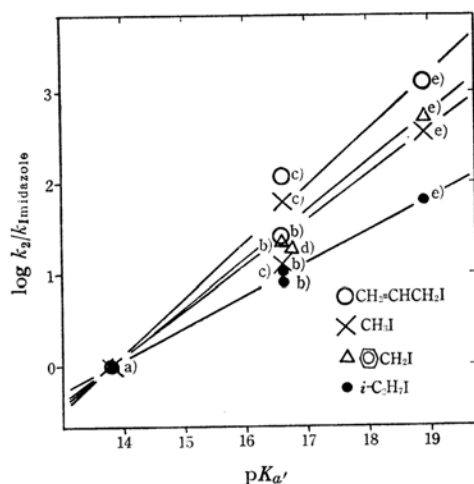


Fig. 1. Brønsted plots.

a) Imidazole. b) Hydrazine. c) Morpholine.
d) Benzylamine. e) Piperidine.

amines in acetonitrile⁶⁾ are available. Therefore we chose anhydrous acetonitrile as the solvent. The results are shown in Table 1. In all the cases fairly good correlations of logarithms of the rate constants on the $pK_{a'}$'s of the nucleophiles were observed, and no positive deviations from the Brønsted plots were observed, (Fig. 1). From the slopes, α values, the Brønsted parameter, were obtained and are listed in Table 2.

The α values obtained in the aminolysis reactions varied from 0.36 to 0.60. This means that the transition states of these reactions cover a certain range of spectrum from near S_N1 to S_N2 .⁷⁾ The α value

TABLE 2. α -VALUES OF THE AMINOLYSIS REACTIONS IN ACETONITRILE

Substrates	α -Value	°C
Allyl iodide	0.60	40
Benzyl iodide	0.55	30
Methyl iodide	0.50	40
Isopropyl iodide	0.36	40
<i>p</i> -Nitrophenyl acetate ^{a)}	0.54	30

a) See Ref. 3a.

of 0.60 in the aminolysis reaction of allyl iodide suggests that the bond forming step is the rate limiting, while α value of 0.36 of isopropyl iodide suggests the importance of bond breaking step.

It is commonly believed that the α -effect is associated with displacement reactions which are highly dependent on the basicity of the nucleophile. It would suggest then that α -effect would appear in the aminolysis reaction of allyl iodide. However, it was not the case. The aminolyses of isopropyl, methyl and benzyl iodides also showed no positive deviations from the Brønsted plots. As can be seen in Table 2, α values of *p*-nitrophenyl acetate and benzyl iodide are almost comparable and yet a large α -effect is observed in the reaction with the former compound and not with the latter.

Both benzyl and allyl iodides are considered to develop a substantial sp^2 character at the reacting center in the transition states. The lack of α -effect for these compounds may be due to the high electron delocalizations with π electrons at the transition state to kill the partial sp^2 character of the reaction center.

Experimental

Preparation of Materials. All the amines were purified according to Coetzee and Padmanabhan's

6) J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 5005 (1965).7) R. F. Hudson and R. J. Withey, *J. Chem. Soc.*, **1964**, 3513.

method.⁸⁾ Methyl iodide was purified by fractional distillation from the commercial product, bp 42.4°C. Benzyl iodide (mp 24.1°C) and allyl iodide (bp 102.5°C) were prepared from the corresponding chlorides by halogen exchange reaction in acetone.⁹⁾ Isopropyl iodide was prepared according to Stone and Shechter's method,⁹⁾ bp 89.3°C. Commercial acetonitrile was dried over calcium chloride, and then refluxed three times over phosphorus pentoxide, then distilled into freshly fused potassium carbonate, after drying, it was finally fractionally distilled,¹⁰⁾ and the center-cut fraction was used, bp 81.6°C.

Kinetic Measurement. The reactions were followed by the UV spectrophotometry using the absorption of iodide ion at 246 $m\mu$ ($\epsilon = 1.38 \times 10^4$), except for benzyl iodide, of which the absorption band of 275 $m\mu$ was followed (no iodide ion absorption at 275 $m\mu$). A desired amount of an organic iodide was weighed accurately in a 50 ml volumetric flask. After equili-

bration at a reaction temperature, it was made up to 50 ml with a desired amount of an amine solution and with the solvent at the same temperature. The flask was shaken vigorously and kept in a thermostat. Initial concentration was determined after two minutes. From time to time, 5 ml of the solution was pipetted out and diluted to a suitable concentration with acetonitrile. A typical run is shown below.

TABLE 3. REACTION OF ALLYL IODIDE WITH PIPERIDINE IN CH_3CN

Sec	O.D. ^{a)} Observed	O.D. Corrected ^{b)}	k_2 $l \text{ mol}^{-1} \text{ sec}^{-1}$	Percentage of reaction (%)
	.174			
600	.378	.242	3.57	25.4
900	.459	.338	3.67	36.1
1200	.512	.401	3.51	42.1
1800	.609	.514	3.46	54.1
2100	.658	.574	3.63	60.3
2400	.680	.600	3.45	63.2
2700	.710	.635	3.46	66.7
∞	.948			

a) Optical density at 246 $m\mu$.

b) Observed optical density was corrected, because allyl iodide has a little absorbance at 246 $m\mu$.

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