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Solvolytic Reactions in Dipolar Aprotic Solvents. Reaction Rates of the Tertiary Aralkyl System

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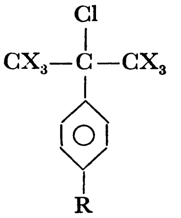
Synopsis. Solvolytic reaction rates of 2-aryl-2-chloropropanes in dipolar aprotic solvents were determined in order to obtain activation parameters, ρ-values, and β-deuterium effect. The results are compared with those in protic solvents.

Solvolytic reactions in protic media proceed through S_N1, E1, S_N2, and E2 routes depending on the structure of substrate and the nature of solvent. In some cases several reaction routes occur concurrently, while in other cases only one appears to occur. Relative ionizing powers of protic solvents have been determined so far[1] without determination of the partitions of each route. In aprotic media most reactions can proceed through the E1 route because of the slight nucleophilic character of the solvents.[2] Thus the solvolytic reaction in aprotic media may reflect the characteristics of carbonium ion type intermediates more precisely than in protic media. A few such reactions have been studied for the tertiary system, such as reactions of triphenylmethyl chloride in benzene[3] and nitromethane,[4] *t*-butyl chloride in nitromethane,[5] acetonitrile[6] and dimethylformamide,[7] and *t*-butyl nitrate in acetonitrile.[8]

We have studied the reaction rates of 2-chloro-2-phenylpropanes (cumyl chlorides) in dimethyl sulfoxide (DMSO), nitromethane, acetonitrile and dimethylformamide (DMF). The reaction was carried out in the presence of pyridine and the acid liberated was titrated with methanolic sodium methoxide solution. Constant first-order rate coefficients were obtained up to 60% reaction. Rate constants (k_H) of 2-chloro-2-phenylpropane (**1**), with activation parameters, are given in Table 1, and rate constant (k_{Br}) of 2-(4′-bromophenyl)-2-chloropropane (**2**) and their rate ratios to **1** (k_{Br}/k_H) in Table 2. Rate constants (k_D) of 2-chloro-1,1,1,3,3,3-hexadeuterio-2-phenylpropane (**3**) and sixth roots of their ratios to **1** ($\sqrt[6]{k_H/k_D}$) are also shown in Table 2. The corresponding values obtained in protic media are given in Table 3.



1; R=X=H
2; R=Br, X=H
3; R=H, X=D

The effect of solvents on the reaction rate of **1** is in the order, DMSO>nitromethane>acetonitrile>DMF. Paucity of substituents might give unreliable ρ-values. However, the fact that **1** shows almost the same ρ-values in aprotic solvents indicates a sufficient reliability.

If we compare the results obtained in aprotic solvents with those in protic media, characteristics observed can be summarized as follows. i) ρ-values are similar in both media, ii) although k_H/k_D-values are almost constant in both media, they are slightly larger in aprotic, iii) $\Delta S^{\ddagger}$-values in aprotic media are negatively larger.

Experimental

Materials. Chlorides were prepared from the corresponding alcohols by the method of Brown and Rei:[9] 2-phenyl-2-propanol,[10], bp 94—96 °C/19 mmHg; 2-(4′-bromophenyl)-2-propanol, mp 40.1 °C (lit,[11] 45.6 °C); 1,1,1,3,3,3-hexadeuterio-2-phenyl-2-propanol was prepared from acetone-d_6 and phenylmagnesium bromide,[10] bp 65 °C/2.5 mmHg, no detectable methyl H-signals in NMR. Dimethyl sulfoxide was refluxed over calcium hydride under reduced pressure and distilled (bp 48.5—50.0 °C/2.5 mmHg). Nitromethane was dried over Drierite and distilled (bp 100.5—101.8 °C). Acetonitrile was refluxed over phosphorus pentoxide and distilled (bp 80.9—82.3 °C). Dimethylformamide was distilled with benzene (about 5%) to remove impurities azeotropically. A fraction boiling at 150—152 °C was collected. Pyridine was dried over potassium hydroxide and distilled (bp 115 °C).

Rate Measurements. About 0.5 mmol of chloride was

Table 1. Rate constants and activation parameters for elimination reactions of 2-chloro-2-phenylpropane (**1**) in aprotic solvents[a)]

Solvent	Rate constant, k_H[b)]			$\Delta H^{\ddagger}$ [d)]	$\Delta S^{\ddagger}$ [e)]
	45.0 °C	35.0 °C	25 °C[c)]		
DMSO	28.2	11.45	4.41	17.0	−21.5
Nitromethane	13.75	5.25	1.895	18.2	−19.2
Acetonitrile	3.98	1.463	0.507	18.9	−19.4
DMF	2.12	0.649	0.1853	22.5	−9.4

a) [Chloride], 0.05 M; [Pyridine]; 0.05 M. b) $\times 10^5$ s^{-1}. c) Calculated from rate constants observed at 45.0 and 35.0 °C. d) kcal/mol. e) at 25 °C, eu.

TABLE 2. RATE CONSTANTS AND DERIVED DATA FOR ELIMINATION REACTION OF 2-(4′-BROMOPHENYL)-2-CHLOROPROPANE (**2**) AND ITS D_6-DERIVATIVE (**3**) IN APROTIC SOLVENTS a)

Solvent	Temp (°C)	k_{Br} b)	k_{Br}/k_H c)	(ρ d))	k_D b)	$\sqrt[6]{k_H/k_D}$
DMSO	55.0	14.28	0.22	(−4.4)		
	45.0				14.55	1.12
Nitromethane	55.0	6.77	0.21	(−4.5)		
	45.0				6.68	1.13
Acetonitrile	55.0	2.07	0.20	(−4.7)		
	45.0				1.812	1.14
DMF	55.0	1.301	0.20	(−4.7)		
	45.0				0.918	1.15

a) [Chloride], 0.05 M; [Pyridine], 0.05 M. b) $\times 10^5\ s^{-1}$. c) k_H at 55 °C were calculated from rate constants at 45.0 and 35.0 °C. d) Calculated from k_{Br}/k_H-value *vs.* σ^+.

TABLE 3. SOLVOLYSIS DATA OF 2-CHLORO-2-PHENYLPROPANES

Reaction	Temp a)	k_1 b)	$\Delta H^{\neq}$ c)	$\Delta S^{\neq}$ d)	ρ e)	k_H/k_D f)
Hydrolysis g)	35	36.1	18.8	−12.4		
(90% aq. acetone)	25	12.4			−4.54 h)	
	0	0.600				
Ethanolysis i)	50	490				
(ab. ethanol)	25	34.4	20.3	−8.3	−4.67 j)	1.06 i)

a) °C. b) $\times 10^5\ s^{-1}$. c) kcal/mol. d) eu. e) *vs.* σ^+. f) per D. g) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bouner, *J. Amer. Chem. Soc.*, **79**, 1897 (1957). h) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957). i) S. G. Smith and D. J. W. Goon, *J. Org. Chem.*, **34**, 3127 (1969). j) R. L. Buckson and S. G. Smith, *ibid.*, **32**, 634 (1967).

weighed in a 10 ml volumetric flask and 0.05 M solution of pyridine in an aprotic solvent was added. The flask was immersed in a thrmostatt. At an appropriate interval an aliquot of 1 ml was drawn out, poured into 20 ml of acetone, and titrated with a standard solution of sodium methoxide in methanol with lacmoid as an indicator.

Products. Quantitative isolation of 2-phenylpropene (**4**) was difficult because of polymerization. In the case of acetonitrile solution, the yields of **4** determined by an ultraviolet absorption at 243 nm of diluted reaction solutions with ethanol were almost quantitative based on acid formation. The yields of **4** in the other solvents deremined by ultraviolet absorption were less reproducible.

References

1) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948). See other texts, for example, E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y. (1968), p. 293.

2) Y. Pocker, "Progress in Reaction Kinetics," Pergamon Press, New York, N. Y. (1961), Vol. 1, p. 218.

3) E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *J. Chem. Soc.*, **1957**, 1256.

4) Y. Pocker, *ibid.*, **1958**, 240.

5) Y. Pocker, *ibid.*, **1959**, 1179, 3939, 3944.

6) a) D. N. Kevill and J. R. Dorsey, *Chem. Ind.* (London), **1967**, 2174, b) D. N. Kevill and J. R. Dorsey, *J. Org. Chem.*, **34**, 1985 (1969).

7) S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 4155 (1957).

8) D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc.*, *B*, **1969**, 366.

9) H. C. Brown and M. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

10) H. C. Brown, J. D. Brady, M. Grayson, and H. Bonner, *J. Amer. Chem. Soc.*, **79**, 1897 (1957).

11) H. C. Brown, Y. Okamoto, and G. Ham, *ibid.*, **79**, 1906 (1957).