

Charge Separation in Transition States of Reactions Involving Neutral Molecules as Reactants

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Abstract

It is shown that the parameter m in the Grunwald-Winstein equation, $\log(k/k_0) = mY$, can be equated to z/z_0 where z_0 is the charge separation in the transition state of solvolysis of t-butyl chloride in a given pair of solvents and z is the charge separation in the transition state of a reaction in which only neutral molecules are involved as reactants in the same pair of solvents.

Introduction

We have been interested^{1,2} in the interpretation and improvement of the various empirical linear free energy equations. In this paper we show that the Grunwald-Winstein equation (equation (1)) can be used to give a quantitative measure of the charge developed in transition states of reactions in which neutral molecules are involved as reactants.

Results and Discussion

In the Grunwald-Winstein equation^{3,4}

$$\log(k/k_0) = mY \quad (1)$$

k and k_0 are the rate constants for a given reaction in a given solvent and in the reference solvent (80% ethanol) respectively, Y is calculated from $\log(k/k_0)$ for the rate constants for solvolysis of t-butyl chloride for each solvent, and m is a constant characteristic of the nature of the reactants and the pair of solvents used in the reaction being studied.³⁻⁵ We find that the parameter m can be expressed as

$$m = z/z_0 \quad (2)$$

where z_0 refers to the charge developed in the transition state of solvolysis of t-butyl chloride in a given pair of solvents and z is the charge developed in the transition state of a reaction in which only neutral molecules are involved as reactants in the same pair of solvents. The solvents are divided into three groups, namely hydroxylic,

¹ Poh, B.-L., *Can. J. Chem.*, 1977, **55**, 3721.

² Poh, B.-L., *Can. J. Chem.*, 1978, **56**, 747.

³ Grunwald, E., and Winstein, S., *J. Am. Chem. Soc.*, 1948, **70**, 846.

⁴ Fainberg, A. H., and Winstein, S., *J. Am. Chem. Soc.*, 1957, **79**, 1597.

⁵ Hine, J., 'Physical Organic Chemistry' 2nd Edn, Ch. 7 (McGraw-Hill: New York 1962).

aprotic and non-polar. This classification takes account of the observation that the z_0 values for the solvolysis of t-butyl chloride in these three groups of solvents are different. The reported values are 0.85, 0.57 and 0.48, respectively.⁶ The z values of various S_N1 and S_N2 reactions involving neutral molecules as reactants can be calculated from the reported m values in the literature and the appropriate z_0 values by equation (2). The m values for a large number of reactions have been reported and we only choose those reactions whose z values have been calculated by other methods, so that a comparison can be made. Table 1 shows that our z values calculated by equation (2) agree well with those obtained by Abraham.⁶ Thus, equation (2) provides a convenient method of calculating the charge developed in transition states of reactions in which only neutral molecules are involved as reactants.

Table 1. Comparison of z values calculated by equation (2) with literature values

No.	Reactant	Solvents	m	z (this work) ^H	z (literature) ^I
1	Me ₃ CBr	EtOH-H ₂ O	0.940 ^A	0.80	0.82
2	Me ₂ CHBr	EtOH-H ₂ O	0.544 ^A	0.46	0.51
3	PhCH ₂ Cl	EtOH-H ₂ O	0.425 ^A	0.36	0.40, 0.39 ^J
4	EtBr	EtOH-H ₂ O	0.343 ^A	0.29	0.31
5	MeBr	EtOH-H ₂ O	0.258 ^A	0.22	0.28
6	Me(CH ₂) ₃ Br	EtOH-H ₂ O	0.392 ^B	0.33	0.28
7	Ph(Me)CHCl	EtOH-H ₂ O	0.966 ^C	0.82	0.77 ^J
8	Me ₃ N+MeI	dioxan-Me ₂ CO	0.755 ^D	0.43	0.42
9	Et ₄ Sn+HgCl ₂	MeOH-H ₂ O	0.713 ^E	0.61	0.70
10	C ₅ H ₅ N+MeI	PhH-PhNO ₂	0.582 ^F	0.28	0.30
11	PhNMe ₂ +MeI	aprotic solvents	0.549 ^G	0.31	0.39

^A Winstein, S., Grunwald, E., and Jones, H. W., *J. Am. Chem. Soc.*, 1951, **73**, 2700. ^B Ref.³ ^C Ref.⁴
^D Tommila, E., and Kauranen, P., *Acta Chem. Scand.*, 1954, **8**, 1152. ^E Abraham, M. H., and Johnston, G. F., *J. Chem. Soc. A*, 1970, 188. ^F Pickles, N. J. T., and Hinshelwood, C. N., *J. Chem. Soc.*, 1936, 1353. ^G Matsui, T., and Tokura, N., *Bull. Chem. Soc. Jpn*, 1970, **43**, 1751. ^H The values⁶ of z_0 used are 0.85 (reactions 1-7, 9), 0.57 (reactions 8, 11), and 0.48 (reaction 10). ^I Values taken from ref.⁶, pp. 14, 42 and 77, unless otherwise stated. ^J Calculated from the Hammett ρ values given in Jaffe, H. H., *Chem. Rev.*, 1953, **53**, 191 according to the method in Poh, B.-L., *Can. J. Chem.*, in press.

Equation (2) has a theoretical basis since it can be derived from the sphere-in-continuum model of Born.⁷⁻⁹ According to the Born model the electrostatic contribution to the medium effect on a reaction involving neutral molecules as reactants and in which charge is produced in the transition state is given by

$$\ln \Gamma = (ze)^2(1/D_{S1} - 1/D_{S2})/rk_B T \quad (3)$$

where $\ln \Gamma$ is the medium effect due to electrostatic contribution, e is the electronic charge, z is the fraction of charge present in the reaction's transition state, D is the dielectric constant, r is the radius of the charged transition state, k_B is the Boltzman constant, T is the absolute temperature; S1 and S2 denote two different solvents.

⁶ Abraham, M. H., *Prog. Phys. Org. Chem.*, 1974, **11**, 1.

⁷ Born, M., *Z. Phys.*, 1920, **1**, 45.

⁸ King, E. J., 'Physical Chemistry of Organic Solvent Systems' p. 345 (Plenum: London 1975).

⁹ Leffler, J. E., and Grunwald, E., 'Rates and Equilibria of Organic Reactions' p. 266-7 (Wiley: New York 1963).

The two solvents should be closely related in order that the charges developed in the transition states in the two solvents are the same.¹⁰ Therefore, the medium effect on such a given reaction relative to that of the reference reaction, the solvolysis of t-butyl chloride, is given by

$$\ln \Gamma / \ln \Gamma_0 = (z^2/r)/(z_0^2/r_0) \quad (4)$$

where the subscript 0 denotes the reference reaction. Intuitively we expect the radius of the charged transition state to be proportional to the amount of charge present in the transition state because a larger r implies a greater extent of bond cleavage and, therefore, a larger amount of charge developed in the transition state. Therefore, equation (4) may be written as

$$\ln \Gamma / \ln \Gamma_0 = z/z_0 \quad (5)$$

The term $\ln \Gamma$ is related to the rate constants in the two solvents in the form⁸ of equation (6):

$$\ln \Gamma = \log(k_{s2}/k_{s1}) \quad (6)$$

A combination of equations (5) and (6) gives equation (1) with m related to z in the form of equation (2), $k_{s2} = k$, and $k_{s1} = k_0$.

Acknowledgment

The author thanks Universiti Sains Malaysia for a short-term research project grant.

Manuscript received 12 December 1978

¹⁰ Poh, B.-L., *Aust. J. Chem.*, 1979, **32**, 429.