ANALYTICAL FUNCTIONS AND THEIR SIGNIFICANCE

Theoretical Considerations

No strictly theoretical, analytical function describing the pressure dependence of reaction rate is available. The usual differential form of the dependence used is that given by Evans and Polanyi (6),

$$[1] \qquad \Delta V^* = -RT(\partial \ln k/\partial p)_T,$$

but the question immediately arises as to whether ΔV^* is pressure independent or not. Precisely the same question arises for the temperature dependence of rate where ΔH^* can be written

$$[2] \qquad \Delta H^* = -RT(\partial \ln k/\partial \left(\frac{1}{T}\right)_p).$$

If the pseudo-thermodynamic ΔH^* parameter has the same form as the real thermodynamic ΔH, then it is not temperature independent, since there is a non-zero value of $\Delta C_p{}^*$. In an exactly similar manner ΔV^* may be expected to be pressure dependent according to eq. [3]

$$[3] \qquad (\partial \Delta V^*/\partial p)_T = -V_0{}^* \kappa^* \exp(-\kappa^* p) + V_0{}^g \kappa^g \exp(-\kappa^g p),$$

where the first term on the right-hand side refers to the transition state with $V_0{}^*$ being the partial molal volume of the transition state at some reference pressure and κ the compressibility; the second term on the right-hand side applies similarly to the initial state. Equation [3] is unusable as an anlytical function for treating experimental rate data, since the partial molal isothermal compressibilities (κ's) cannot be determined in reacting systems.

While, therefore, there is good reason to believe that the functional dependence of rate on pressure is at least of second order with respect to pressure (just as the dependence of rate on temperature is second order in temperature), there is no theoretically deriveable form of the functional dependence which has practical utility.

Two further factors must be considered as possible contributors to the pressure dependence of rate: concentration effects and viscosity effects. In solvolytic reactions of the benzyl chloride type considered here the reaction is between the molecular species of the solvent environment and the dissolved substrate. Accordingly, if the volume of the initial and transition states is considered to be the volume of the substrate *plus* its immediate solvation shell in both states the effect of pressure on "concentration" is included in the volume of the two states as so defined. The viscosity effect would not be expected to become a major contributor until the viscosity of the system increased to a point where the diffusion rate of the reacting species was significantly reduced. This requires very high pressures as has been shown by Hamann (7) where for bimolecular reactions the rate dependence on pressure actually changes sign from positive to negative at very high pressures. Again, however, in solvolyses reactions, diffusion together of the reacting species is not an important factor, since the reacting substrate is always in immediate contact with the reactant solvent.

The Functions

In the absence of a strictly based theoretical functional form of practical utility for expressing the dependence of rate on pressure, four basic semiempirical functions have been employed. It is the purpose of this paper to examine these relations between rate and pressure from the standpoint of their utility and ability to reproduce the experimentally observed dependencies and not from the theoretical viewpoint. However, comments will be made when appropriate about the physical significance of the relationships. The first of these relationships assumes that the dependence of the logarithm of the rate constant on pressure is linear (8) (eqs. [4] and [5]). This treatment regards the activation volume as being pressure independent, and consequently neglects a possible additional activation parameter $-(\partial \Delta V^*/\partial p)_T$. The second type of function is a power series in p, usually of second order (9), which allows for the pressure dependence of the activation volume (eqs. [6] and [7]). Benson and Berson (4) have used a modified form of the Tait equation (10) to calculate both the volume of activation and the change in compressibility (eq. [8]).

Whalley has plotted the average slope of any increment of the ln k vs. p curve against the average pressure of that increment[2] (11; 2, p. 100). Extrapolation to an average pressure of zero gives an intercept which can be taken as equalling $(\partial \ln k/\partial p)_{T,p} = 0$. Such a function is given in eq. [9] in which linearity of the incremental function is assumed.

In this study we considered each of these functions in turn, using the forms shown in eqs. [4] through [9]. Here k_0 is the rate constant at atmospheric pressure, and k_{n+1} and k_n are rate constants at adjacent pressures. Equation [5] is identical to eq. [4] except that, in the former, the curve is forced to pass through the experimental ln k_0. Equations [6] and [7] also differ only in the forced intercept treatment.

$$\ln k = A + Bp \tag{4}$$

$$\ln k = \ln k_0 + Bp \tag{5}$$

$$\ln k = A + Bp + Cp^2 \tag{6}$$

$$\ln k = \ln k_0 + Bp + Cp^2 \tag{7}$$

$$\ln(k/k_0)/p = A + Bp^{0.523} \tag{8}$$

$$\ln(k_{n+1}/k_n)/(p_{n+1} - p_n) = A + B(p_{n+1} + p_n)/2 \tag{9}$$

TEST OF BENZYL CHLORIDE SYSTEM

Using our experimental data (5) for the solvolysis of benzyl chloride in water and in mixtures of ethanol and water (Table I), we calculated the various constants of eqs. [4] through [9] by the method of least squares using an IBM 1620 computer. A representative set of these constants is presented in Table II. From these we obtained the values of the activation volume which are presented in Table III. The value at atmospheric pressure is reported for those functions which take account of the pressure dependence of ΔV^*.

Our interest lies in the variation of ΔV^* with solvent composition. This dependence is shown in Fig. 1. The values of ΔV^* obtained from functions [6] and [7] are identical for all solvents except pure water, and the difference at this one point is probably within the experimental error. It appears that utilization of the experimental intercept introduces no significant error. The values from functions [4] and [5], which also differ only with regard to the forced intercept treatment, do not agree so well. However, the differences are less than 2 ml/mole. It may be noted that the ΔV^*'s from function [9] agree

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[2] *Note that refs. 11 and 2, p. 100 contain an error in the statement of the method of extracting the pressure dependence of ln k. The corrected version, as used here, is given in ref. 12.*