A Re-appraisal of the Heat Capacity of Activation and Enthalpy of Activation for t-Butyl Chloride in Water–Ethyl Alcohol Mixtures

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Summary The previously reported dependence of the heat capacity of activation for t-butyl chloride in water on mole fraction of added ethyl alcohol may be a consequence of a mechanism proposed by Albery and Robinson and the range of temperatures over which the kinetic data are obtained.

According to Albery and Robinson,[1] the large negative value for the heat capacity of activation for t-butyl chloride in water[1,2] is a consequence of a two stage mechanism [equations (1)]. Thus it follows[3] that if $\Delta C_{p1}^{\ddagger}$, $\Delta C_{p2}^{\ddagger}$, and $\Delta C_{p3}^{\ddagger}$ are zero, the heat capacity of activation calculated directly from the dependence of k on temperature[2] is related to the Albery–Robinson parameters by equation (2).

$$\mathrm{RCl} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^+Cl^-} \xrightarrow{k_3} \text{products}$$

$$k(\text{obs}) = k_1/(1+\alpha);\ \alpha = k_2/k_3 \qquad (1)$$

$$\Delta C_p^{\ddagger}\,(\text{app}) = -\,(\Delta\Delta H^{\ddagger})^2\alpha/[RT^2(1+\alpha)^2] \qquad (2)$$

$$\text{where } \Delta\Delta H^{\ddagger} = \Delta H_3^{\ddagger} - \Delta H_2^{\ddagger} \qquad (3)$$

If the Albery–Robinson mechanism[1] is correct, the conclusions drawn by Robertson and co-workers[4,5] and by others[6,7] as to the significance of the dependence of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ on solvent composition can be questioned. The kinetic data for solvolysis of t-butyl chloride in water[2,8] and in water–ethyl alcohol mixtures have been re-analysed in terms of equation (1) by writing the dependence of k(obs) on T in the form of equation (4). This non-linear equation

$$k(obs) = A_1 \exp(-\Delta E_1/RT)/[1+A_{\alpha} \exp(\Delta\Delta E_{\alpha}/RT)] \qquad (4)$$

satisfactorily fitted the experimental data, the parameters being calculated using a computer program (FORTRAN) which incorporated a modified Gauss–Newton method[9] in order to minimise $\sum_n [k - k(\text{calc})]$.[2] Among the various quantities calculated were (i) the dependence of k_1 and α on temperature, (ii) the temperature at which $\alpha = 1{\cdot}0$, (iii) the temperature at which $\Delta C_p^{\ddagger}$ (app) is a minimum together with this value of $\Delta C_p^{\ddagger}$ (app), and (iv) $\Delta C_p^{\ddagger}$ (app) at 290 K. These details are summarised in the Table together with the range of temperatures over which the kinetic data were obtained. A feature[3] of the Albery–Robinson mechanism is that $\alpha = 1$ at a temperature close to where $\Delta C_p^{\ddagger}$ (app) is

TABLE. Effect of added ethyl alcohol on the kinetics of solvolysis of t-butyl chloride in water.

Mole fraction of EtOH	Experimental temperature range/K	E_1 /kJ mol^{-1}	Es /kJ mol^{-1}	$T(\alpha = 1)$/K	$\Delta C_p^‡$ (app-max) /J mol^{-1} K^{-1}	at T /K	$\Delta C_p^‡$ (app) at 290 K /J mol^{-1} K^{-1}
0	274—293	107·1	−47·2	316·7	−672	315	−431
0·075	273—293	114·1	−36·3	280·0	−514	275	−439
0·11	266—293	116·6	−45·6	281·2	−796	280	−682
0·15	275—300	119·5	−38·4	254·5	−692	250	−186

a minimum. However, as α increases or decreases, so $|\Delta C_p^‡|$ decreases. Experimentally, as the mole fraction of ethyl alcohol, x_2, increases so the rate constant k(obs) decreases. As x_2 increases, the temperature at which $\alpha = 1$ decreases (Table) from above to below the experimental range. Hence the value of $\Delta C_p^‡$ calculated originally by Robertson and Sugamori,[4] being some averaged value obtained over the experimental range, initially decreases and then increases. The value of $\Delta C_p^‡$ (app) at 290 K (Table) shows this trend more dramatically.

The self-consistency of the above analysis lends added evidence to the Albery–Robinson mechanism. However it raises questions as to the significance of the oft-quoted analysis by Arnett and co-workers[7] of the dependence of the enthalpy of activation on x_2 in terms of initial and transition state partial molar enthalpies. The 'fortuitous'[7] independence of the latter quantity on x_2 may be a consequence of an incorrect mechanism and, thus, an invalid analysis. The data for the effect of other co-solvents on the activation parameters are currently being re-examined and will be reported elsewhere.

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