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Constant-Volume Parameters of Activation for the Hydrolysis of Benzyl Chloride in Ethanol–Water Mixtures

Sir: Recent measurements of the volume of activation $\Delta V^{\ddagger}$ for the spontaneous solvolysis of benzyl chloride in ethanol–water mixtures,[1] when combined with earlier measurements[2] of the enthalpy $\Delta H_p^{\ddagger}$ and entropy $\Delta S_p^{\ddagger}$ of activation at constant pressure, allow a calculation of the internal energy $\Delta U_v^{\ddagger}$ and entropy $\Delta S_v^{\ddagger}$ of activation at constant volume according to the formula

$$\Delta H_p^{\ddagger} - \Delta U_v^{\ddagger} = T\Delta S_p^{\ddagger} - T\Delta S_v^{\ddagger} = T\alpha\Delta V^{\ddagger}/\kappa$$

where T is the temperature, and α and κ are the thermal expansivity and compressibility of the reaction mixture. The values of α and κ for the pure solvent can be used without causing significant error. The thermal expansivities were obtained from published data.[3] The compressibilities were Moesveld's[4] values at 25°; the compressibilities of mixtures of water and organic solvents are little dependent on temperature between 25 and 60°, and this approximation should be unimportant. The values of α, κ, $\Delta V^{\ddagger}$, and $T\alpha\Delta V^{\ddagger}/\kappa$ are listed in Table I.

Table I: Thermal Expansivity and Compressibility of Ethanol–Water Mixtures, and Volumes of Activation for the Hydrolysis of Benzyl Chloride in These Mixtures

% v/v of ethanol	$10^6\alpha/\text{deg}^{-1}$ (Temp 51.0°)	$10^6\kappa/\text{bar}^{-1}$ (Temp 25°)	$\Delta V^{\ddagger}/\text{cm}^3\ \text{mole}^{-1}$ (Temp 50.25°)	$(T\alpha\Delta V^{\ddagger}/\kappa)$ cal mole^{-1}
0	465	44.2	−8.5	−692
26.5	813	40.4	−16.4	−2551
44.8	917	46.2	−20.4	−3129
58.2	976	54.0	−22.8	−3185

The parameters of activation relative to the values in pure water are plotted in Figure 1. There is no minimum in $\Delta U_v^{\ddagger}$, and only a small minimum (~0.7 kcal mole^{-1}) in $T\Delta S_v^{\ddagger}$, in contrast to minima of 1.8 and 2.8 kcal mole^{-1} in $\Delta H_p^{\ddagger}$ and $T\Delta S_p^{\ddagger}$. It was reported earlier[5] that the minima in the constant-pressure parameters for the acid-catalyzed hydrolysis of methyl acetate at 35° that occur at about 35% v/v of acetone in water are not present in the constant-volume parameters. The constant-volume parameters are undoubtedly simpler functions of the solvent composition in both systems. In addition, the entropy–energy compensation is a good deal smaller in the constant-volume parameters for both systems, and also for the

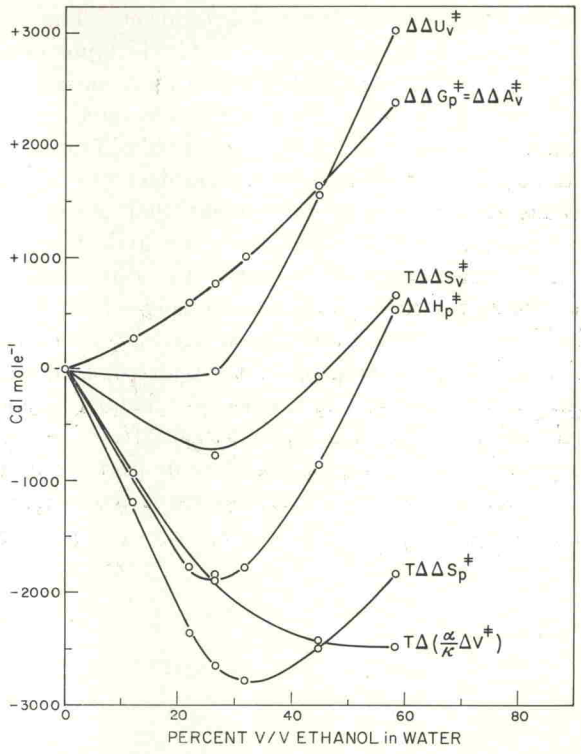


Figure 1. Changes with solvent of the parameters of activation for the hydrolysis of benzyl chloride.

acid-catalyzed enolization of acetone and of acetophenone in ethanol–water mixtures.[6]

Although there are no compelling reasons for preferring one set of parameters over the other, it was suggested[5] that the relative simplicity in the variation of the constant-volume parameters was reflected in a relative simplicity of fundamental processes. Specifically, it was suggested that a large part of the minima was due to the use of water as one component, which causes a large variation of the thermal expansivity α with composition (see Table I), and so causes $\Delta H_p^{\ddagger} - \Delta U_v^{\ddagger}$ $(= T\alpha\Delta V^{\ddagger}/\kappa)$, to be strongly solvent dependent. It seems likely that for the hydrolysis of benzyl chloride in ethanol–water mixtures, the constant-volume parameters are the simpler, and the minima in the constant-pressure parameters can be ascribed to the high effect of solvent composition on both the thermal

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expansivity and the volume of activation. The effect of solvent on the compressibility is of little importance.

If this view is accepted, the solvent variation of $\Delta U_v^{\ddagger}$ and $T\Delta S_v^{\ddagger}$ can be simply interpreted. When ethanol is added, some of the benzyl chloride has some of its neighboring water molecules replaced by ethanol. Because ethanol is a poorer solvent than water for a polar transition state, such molecules hydrolyze comparatively slowly. Consequently, the rate decreases, but because the reaction is carried essentially by benzyl chloride wholly solvated by water, $\Delta U_v^{\ddagger}$ changes little, and $\Delta S_v^{\ddagger}$ decreases. At higher concentrations more of the reaction is carried by benzyl chloride partly solvated by ethanol, and then $\Delta U_v^{\ddagger}$ increases. Presumably, $\Delta S_v^{\ddagger}$ for benzyl chloride partly solvated by ethanol is less negative than when it is solvated by water only, so that $\Delta\Delta S_v^{\ddagger}$ increases at the higher concentrations, and there is a minimum value. The minimum in $\Delta H_p^{\ddagger}$ is caused by the superposition of this "concave" variation of $\Delta U_v^{\ddagger}$ and a nearly linear variation of $T\alpha\Delta V^{\ddagger}/\kappa$ (see Figure 1), and the minimum in $T\Delta S_p^{\ddagger}$ is caused in a similar way.

Are the minima in $\Delta H_p^{\ddagger}$ and $T\Delta S_p^{\ddagger}$ closely related to mechanism? There is undoubtedly a relation, but it appears that the concave variation in $\Delta U_v^{\ddagger}$ and the small minimum in $T\Delta S_v^{\ddagger}$ are more directly related, and should be considered as more fundamental.

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