Activation Parameters for the Solvolysis of t-Butyl Chloride in Water–Ethanol Mixtures. Glycine as a Transition State Model

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Summary Variations in $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for the solvolysis of t-butyl chloride in water—ethanol mixtures are accounted for when glycine is used as a transition state model, provided that differences in molar volumes are taken into account.

The variation of activation parameters for the solvolysis of t-butyl chloride with water–ethanol solvent composition[1] has for years been the subject of considerable interest.[2–4] Arnett *et al.*,[3] from measurements on heats of solution of 1 : 1 electrolytes and non-electrolytes, have accounted for the pronounced minimum in $\Delta H^{\ddagger}$ at mol fraction ethanol

(x_2) *ca.* 0·2, but lack of suitable model substrates has so far prevented any such analysis in terms of all three parameters *G*, *H*, and *S*.

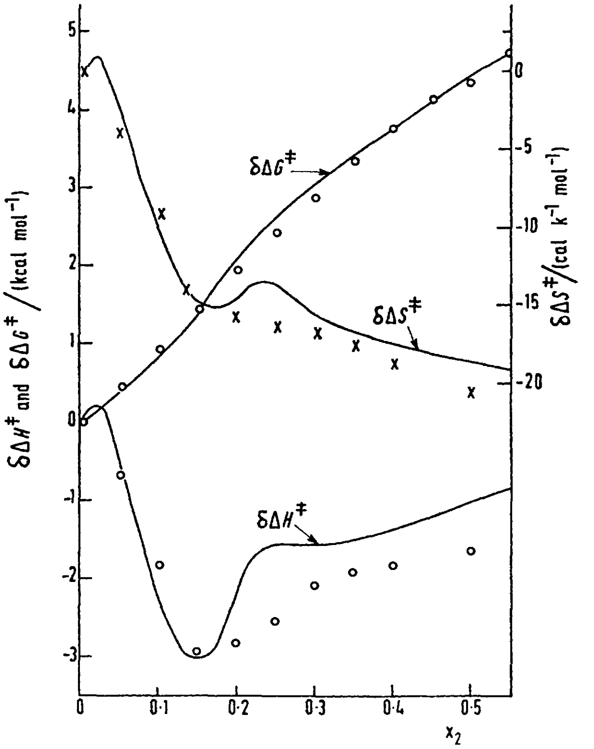

FIGURE. Variation of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ with water–ethanol composition (————). Calculated values based on equation (2): ○ for $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$, × for $\Delta S^{\ddagger}$.

We suggest that the zwitterionic α-amino acids, such as glycine, are suitable models for the highly polar solvolysis transition state. Because of differences in molar volume, it is not satisfactory merely to compare transfer parameters such as ΔG°_{t}, but to compare the electrostatic contribution to free energies of transfer, defined by equation (1) where ΔG°_{n} is the so called non-electrostatic contribution.[4,5] It

$$\Delta G^{\circ}_{t} = \Delta G^{\circ}_{e} + \Delta G^{\circ}_{n} \tag{1}$$

can be shown that because the solvolysis transition state, Tr, and ground state are of about the same molar volume, $\Delta G^{\circ}_{e}(\mathrm{Tr}) = ca.\ \delta\Delta G^{\ddagger}$ where $\delta\Delta G^{\ddagger} = \Delta G^{\ddagger}$ (water–ethanol) $-\Delta G^{\ddagger}$ (water). Since the molar volume of glycine is similar to that of ethane, we take ΔG°_{n}(glycine) $= \Delta G^{\circ}_{t}$(ethane) so that ΔG°_{e}(glycine) $= \Delta G^{\circ}_{t}$(glycine) $- \Delta G^{\circ}_{t}$ (ethane). Similar equations can be written in terms of *H* and *S*, so that comparisons of electrostatic contributions can be made through equation (2), with $P = G$, H, and S.

$$\delta\Delta P^{\ddagger} = \Delta P^{\circ}_{t}(\text{glycine}) - \Delta P^{\circ}_{t}(\text{ethane}) \tag{2}$$

Values of $\delta\Delta P^{\ddagger}$ were taken from the work of Winstein and Fainberg,[1] and ΔP°_{t}(ethane) from recent data of Yaacobi and Ben-Naim.[6] We have calculated ΔG°_{t}(glycine) from solubility data,[7] and obtained ΔH°_{t}(glycine), and hence ΔS°_{t}(glycine), from calorimetrically determined heats of solution carried out by Spink and Auker[8] and confirmed and extended in the present work. Comparisons based on equation (2) ($P = G$, H, and S) are given in the Figure. There is remarkable agreement for all three parameters,† the first time that experimental values based on a given model have been shown to reproduce the variations in $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. Thus α-amino acids can now be regarded as reasonable models for the solvolysis transition state,[9] even though their dipole moments (about 13·5 D)[10] are appreciably larger than that of the transition state (about 9 D in aqueous or alcoholic solvents).[4] Of course this will hold only for solvents (*e.g.* water–ethanol) where the acid is present mainly as the zwitterion.

(*Received*, 28*th May* 1975; *Com.* 579.)

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† The agreement in terms of *G* extends across the whole composition range, $x_2 = 0$ to $x_2 = 1$, but the slow rate of dissolution of glycine in the more ethanolic solvents has limited our calorimetric measurements to the range $x_2 = 0$ to $x_2 = 0{\cdot}5$.

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