FIG. 3. Parameters of activation at constant pressure and constant volume, as labelled, for the solvolysis of benzyl chloride in glycerol–water mixtures.

Solvolysis of molecules solvated completely by water is faster than that of molecules partly solvated by the less solvating organic component. Consequently, most of the reaction in the dilute organic solution is reaction of molecules solvated by water. The energy required therefore depends little on the composition, but the activation entropy decreases because only a part of the reactant is contributing significantly to the rate. In less aqueous solvents, molecules partly solvated by the organic component contribute appreciably to the reaction, and the activation energy increases.

It appears then that the solvent dependence of the constant-volume parameters are easily and naturally understood. The minimum in the constant-pressure enthalpy is then to be understood in terms of this non-linear variation in the constant-volume energy of activation and a smooth and nearly linear fall in the quantity $T\alpha\Delta V^{\ddagger}/\kappa$.

Further evidence for this conclusion is that the activation parameters for the solvolysis of benzyl chloride in ethanol–water and in glycerol–water behave quite differently at constant pressure (1, 4) in that the minima in $\Delta H_p^{\ddagger}$ and $T\Delta S_p^{\ddagger}$ are several times deeper in ethanol–water. At constant volume, however, they behave in similar ways (2) in that there is little or no minimum in $\Delta U_v^{\ddagger}$.

Conclusions

There is no doubt that the effect of solvent on the activation parameters of several solvolyses is simpler and more easily understood when looked at at constant volume than when looked at at constant pressure. This does not of course prove that the constant-volume viewpoint is the more valid. Nevertheless, science has progressed by adopting the most appropriate viewpoint, and this is usually the one that gives the simplest view. There is no doubt that the simplicity of the constant-volume condition is a strong argument for its adoption at least for the reactions mentioned in this paper.

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