

THE INTERPRETATION OF ΔC_p^\ddagger FOR S_N DISPLACEMENT REACTIONS IN WATER

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The treatment of the temperature/rate data for ionogenic S_N displacement reactions according to transition state formalism and assumptions invariably yields a negative temperature coefficient of ΔH^\ddagger i.e., ΔC_p^\ddagger (1). In mixed solvents this coefficient has a value close to $-30 \text{ cal mol}^{-1} \text{ deg}^{-1}$. In water the corresponding values of ΔC_p^\ddagger range from -30 to $-150 \text{ cal mol}^{-1} \text{ deg}^{-1}$, depending on the nature and the charge on the anion at the transition state (2-4). These differences in ΔC_p^\ddagger values have been attributed to the unusual nature of aqueous solutions of weakly polar solutes and to the assumed requirement for reorganization of the temperature dependent solvation shell in the activation process(2). This qualitative hypothesis seemed adequate until it was found that the value of ΔC_p^\ddagger for hydrolysis by a limiting mechanism was more negative than $-130 \text{ cal mol}^{-1} \text{ deg}^{-1}$ (3,4). The latter values were well outside the estimated effect of the isolated anion on the structural heat capacity in aqueous solutions (5-6).

The large negative values of ΔC_p^\ddagger for limiting S_N displacement reactions in water together with the uniformly small values of k_{H_2O}/k_{D_2O} , which showed no correlation with the corresponding ΔC_p^\ddagger values, lead to a reinterpretation of the temperature coefficient of ΔH^\ddagger and reinterpretation of the role of bond making and solvation in such reactions.

The fact that the kinetic solvent isotope effect is small (1.1-1.2 (7)) for solvolytic displacement reactions in water and independent of the degree of bond breaking as judged by the variation in values of ΔC_p^\ddagger leads to the conclusion that the transition state for hydrolysis in water by an S_N^2 mechanism corresponds to initiation of bond making (see Kurz (8)). Subsequent electronic reorganization is rapid compared to the rate controlling step. Hence solvent reorganization following bond initiation is unimportant kinetically and the assumption that bond making compensates bond breaking thus reducing ΔH^\ddagger and accounting for the lack of correlation between ΔH^\ddagger and bond strength appears to be superfluous. Further the above evidence is now seen to be incompatible with the hypothesis that ΔC_p^\ddagger , as calculated, is derived from the temperature dependence of that component of ΔH^\ddagger required to reorganize the temperature dependent solvation shell (2).

Rather, the evidence cited above supports the conclusion that the arrangement of the solvent about the anionic moiety at the moment of activating collision of the substrate with a water molecule which initiates bond making determines anion-solvent interaction. If the solvent order is more favorable for stabilization of the activated complex at lower temperatures, a negative component will be imposed on the normal increase in rate with increasing temperature. Aqueous solutions of weakly polar solutes are known to give evidence of such an effect of temperature on the solvation shell (9) and hence the range of ΔC_p^\ddagger values found for hydrolysis of RX in water

in contrast to those in mixed solvents can be attributed in part if not wholly to the effect of temperature on the order of the solvation shell. It follows that these differences in ΔC_p^\ddagger characteristic of ionogenic reactions in water are to be attributed to the effect of temperature on solvent order existing at the time of collision. The ramifications of this conclusion will be dealt with in greater detail elsewhere.

References

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