

Kinetic Acidity of Carbon Acids: Initial and Transition State Enthalpies of Transfer from Water to Aqueous Dimethyl Sulphoxide in the Hydroxide Ion Catalysed Ionization of Acetophenone

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Enthalpies of solution of acetophenone in water, dimethyl sulphoxide, and mixtures of the two have been measured. These values, together with the enthalpies of activation and the enthalpies of transfer of hydroxide ion from water to the mixtures, have been used to calculate transition state enthalpies of transfer for the hydroxide ion catalysed ionization of acetophenone; these increase strongly with the dimethyl sulphoxide (DMSO) content of the solvent. The values are very close to those for the hydroxide ion. The enthalpically strong desolvation of the hydroxide ion on changing the solvent from water to aqueous DMSO is offset by the comparable desolvation of the transition state. For this reason the rate acceleration caused by the DMSO in the solvent is poor in the detritiation of [³H]acetophenone compared with that of [³H]chloroform.

The sensitivity of the rate of detritiation of [³H]chloroform to solvent basicity has been observed to be exceptionally high in water–dimethyl sulphoxide mixtures compared with that of other carbon acids, *e.g.* acetophenone.^{1,2} It has been shown that the localization or delocalization of the negative charge in the intermediate carbanion was not necessarily the only factor responsible for the observed difference.¹ When the negative charge in the carbanion is distributed between oxygen and carbon atoms, solvation of the activated complex, or the structuring effect of the latter on the solvent, can be expected to be comparable to that of the hydroxide ion. If that is the case, they would cancel each other almost entirely, and the accelerating effect of dimethyl sulphoxide (DMSO) should remain negligible compared with that for chloroform.

Initial and transition state solvent effects on reaction rates may be approached from the viewpoint of thermodynamic transfer functions.³ Results on thermodynamic parameters of activation showed that the increase in the rate of detritiation was brought about by the change in activation enthalpy. The observed change in the entropies of activation was rate-retarding.⁴ Enthalpies of transfer could be informative in this problem.

Enthalpies of solution of carbon acids in water and aqueous dipolar aprotic solvents, together with enthalpies of activation and enthalpies of transfer of hydroxide ion from water to the mixtures, make it possible to calculate transition state enthalpies of transfer.^{5,6} These data are available for the ionization of chloroform in DMSO mixtures.⁶

To confirm the assumption of the reason for different rate acceleration and to obtain quantitative information on the changes of solvation enthalpy of initial and transition states for different carbon acid ionizations, enthalpies of solution in aqueous DMSO were measured for acetophenone.

Experimental

Materials.—Acetophenone (Fluka AG, purum) was purified by distillation before use. DMSO was purified by distillation over calcium hydride.⁷ Mixtures of DMSO and water were prepared by weight.

Calorimetry.—The enthalpies of solution were measured with

an LKB 10700-2 Batch Microcalorimeter. The larger compartment of the reaction cell was filled with about 4 g of water or aqueous DMSO and the smaller compartment with acetophenone. The mass of acetophenone was about 5–20 mg in mixtures where *x*(DMSO) was smaller than 0.2 and 20–50 mg in solvents with more organic component, where the solubility was higher. In each solvent mixture, from two to four parallel measurements were performed. The maximum deviation of the values from each other was 200 J mol⁻¹ in the former case and 100 J mol⁻¹ in the latter. Polyethylene syringes were used to fill the compartments, and the exact masses of the liquids used were found by weighing the syringe before and after the filling procedure. The corresponding compartments of the reference cell were both filled with the studied solvent mixture so that the volumes were as close as possible to the volumes in the reaction cell compartments.

When the equipment had been equilibrated and a steady base line obtained on the recorder, the reaction run was carried out by rotating the calorimeter unit four times and the reaction curve was registered. In the correction run, which was carried out after the reaction, no heat of friction was observed and therefore no compensation was necessary. The calibration run was made with the solutions used during the reaction run left in the cells. The electrical heating during the calibration run was adjusted so that the areas below the reaction curve (representing the heat of reaction) and the calibration curve were as close to each other as possible to obtain the maximum accuracy of the calibration. The areas were measured by a digital integrator.

Results and Discussion

Enthalpies of solution for acetophenone in water and water–DMSO mixtures are presented in the Table. These values increase with DMSO content until a broad maximum is reached at DMSO mole fraction 0.2. In pure DMSO, the enthalpy of solution is nearly the same as in pure water. Jones and Fuchs⁶ measured the enthalpies of solution for chloroform in the corresponding solvent mixtures. A sharp maximum value is observed at DMSO mole fraction 0.17. In pure water the value for chloroform is higher than that for acetophenone, but the maximum value for chloroform remains smaller.

The difference of the enthalpies of solution in aqueous

Table. Enthalpies of solution for acetophenone (S) and enthalpies of transfer from water to aqueous DMSO for the initial (S) and transition (TS) states of the detritiation of acetophenone at 298 K.

| $x(\text{DMSO})$ | $\Delta_{\text{sol}}H(\text{S})/\text{kJ mol}^{-1}$ | $\Delta_{\text{tr}}H(\text{S})/\text{kJ mol}^{-1}$ | $\Delta_{\text{tr}}H(\text{TS})/\text{kJ mol}^{-1}$ |
|------------------|---|--|---|
| 0.000 | 2.33 | 0.00 | 0.0 |
| 0.025 | 4.34 | 2.01 | |
| 0.050 | 6.18 | 3.85 | |
| 0.100 | 8.52 | 6.19 | |
| 0.103 | | | 3.0 |
| 0.150 | 10.11 | 7.78 | |
| 0.200 | 10.25 | 7.92 | |
| 0.203 | | | 22.0 |
| 0.275 | 10.28 | 7.95 | |
| 0.310 | | | 34.0 |
| 0.350 | 9.64 | 7.31 | |
| 0.400 | 8.01 | 5.68 | |
| 0.402 | | | 40.0 |
| 0.450 | 7.10 | 4.77 | |
| 0.509 | | | 45.0 |
| 0.511 | 6.23 | 3.90 | |
| 0.650 | 4.39 | 2.06 | |
| 0.800 | 3.14 | 0.81 | |
| 1.000 | 2.04 | -0.29 | |

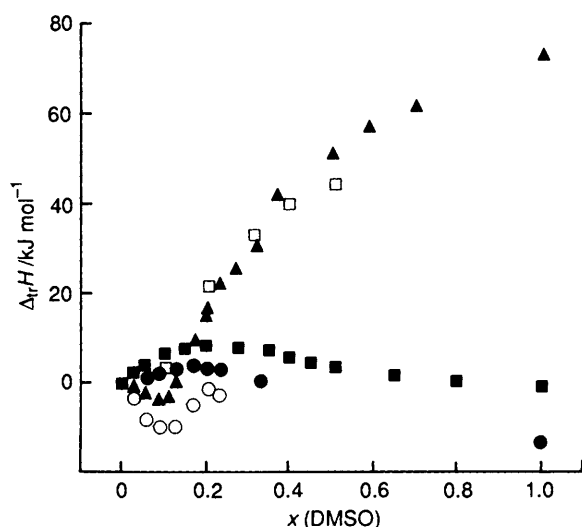


Figure. Initial and transition state enthalpies of transfer from water to water–DMSO mixtures in the hydroxide ion catalysed ionization of acetophenone and chloroform. Filled symbols refer to the initial state and open symbols to the transition state of the reactions of acetophenone (squares) and chloroform (circles; data from ref. 6). Triangles refer to the values for the hydroxide ion and are taken from refs. 8 and 11.

organic solvent mixture (denoted here as subscript s) and water gives the enthalpy of transfer from the latter to the former [equation (1)].

$$\Delta_{\text{tr}}H(\text{S})_{\text{s} \rightarrow \text{w}} = \Delta_{\text{sol}}H(\text{S})_{\text{s}} - \Delta_{\text{sol}}H(\text{S})_{\text{w}} \quad (1)$$

The enthalpies of transfer of acetophenone from water to aqueous DMSO are presented in the Table. To compare these values with those for chloroform determined by Jones and Fuchs,⁶ both are presented as the function of mole fraction of DMSO in the solvent in the Figure. The small positive values imply that acetophenone is slightly less solvated in DMSO mixtures than in pure water and that chloroform is similarly so in DMSO mole fractions smaller than 0.4. The desolvation is

stronger for acetophenone than for chloroform when changing from water to these solvent mixtures. The results indicate that the changes in solvation arise from the structure of the solvent rather than from the solute–solvent interactions. The maximum enthalpy of transition is close to the DMSO·2H₂O solvent composition at which aqueous DMSO mixtures have been shown to have maximum solvent structure.^{8–10} More energy is needed to make ‘holes’ to accommodate the molecules, and the energy required increases with the size of the hole needed.⁸ This explains the enthalpically stronger desolvation of acetophenone.

Enthalpies of transfer of hydroxide ion,^{8,11} the other species in the initial state of the ionization of carbon acids, have been calculated using the extrathermodynamic assumption $\Delta_{\text{tr}}H(\text{Ph}_4\text{P}^+) = \Delta_{\text{tr}}H(\text{Ph}_4\text{B}^-)$. The values are presented in the Figure. The changes of solvation for this negatively charged species are high compared with those for neutral molecules. The addition of DMSO to water causes first a slight increase in the solvation of the hydroxide ion, but at DMSO mole fraction ≥ 0.15 the hydroxide ion becomes increasingly desolvated.

An expression for the transition state enthalpy of transfer may be derived, seeing that the difference of activation enthalpies in different solvents is the difference of the enthalpies of transfer for the transition and initial states. In the hydroxide-ion-catalysed ionization of carbon acids, substrate and hydroxide ion represent the initial state [equation (2)].^{5,6}

$$\Delta_{\text{tr}}H(\text{TS})_{\text{s} \rightarrow \text{w}} = \Delta H_{\text{s}}^{\ddagger} - \Delta H_{\text{w}}^{\ddagger} + \Delta_{\text{tr}}H(\text{S})_{\text{s} \rightarrow \text{w}} + \Delta_{\text{tr}}H(\text{HO}^-)_{\text{s} \rightarrow \text{w}} \quad (2)$$

Activation enthalpies are available for the detritiation of acetophenone in aqueous DMSO.⁴ Transition state enthalpies of transfer for the detritiation of acetophenone are presented in the Table.

Jones and Fuchs⁶ calculated the transition state enthalpies of transfer for the hydroxide-ion-catalysed ionization of chloroform from the enthalpies of activation determined by Margolin and Long.² These data are presented together with the data for acetophenone in the Figure. The changes in solvation of the transition states of the two reactions are quite different. In the ionization of chloroform, the transition state is slightly better solvated in aqueous DMSO [$x(\text{DMSO}) < 0.2$] than in water.

Transition state enthalpies of transfer from water to aqueous DMSO for the detritiation of acetophenone increase strongly with the DMSO content of the solvent. The values are very close to those for the hydroxide ion when the DMSO content exceeds mole fraction 0.2. This indicates that the change in solvation, when going from the initial state to the transition state, is much less in the detritiation of acetophenone than in that of chloroform. In the former, the strong desolvation of the hydroxide ion and the transition state cancel each other in water–DMSO mixtures. In the latter, the effect of desolvation of the initial state is enhanced by the solvation of the transition state.

The results confirm the assumption that the low sensitivity of the rate of detritiation of [³H]acetophenone to solvent basicity in water–DMSO mixtures is due to the enthalpically strong desolvation of both the activated complex and the hydroxide ion. Furthermore, this result gives information on the transition state structure in the ionization of acetophenone. The negative charge distribution—the basic reason for the change in solvation—must be similar in the transition state to that in the hydroxide ion. This is possible in rate-determining ionization, where either triton transfer to the hydroxide ion is at an early stage in the transition state or the negative charge of the developing anion is distributed more on the carbonyl oxygen than on the carbanion carbon atom.

References

- 1 A. Kankaanperä, M. Lahti, and P. Scharlin, *Acta Chem. Scand., Ser. A*, 1986, **40**, 387.
- 2 Z. Margolin and F. A. Long, *J. Am. Chem. Soc.*, 1973, **95**, 2757.
- 3 E. Buncel and H. Wilson, *Acc. Chem. Res.*, 1979, **12**, 42.
- 4 M. Lahti, T. Kallio, M. Luukkonen, P. Scharlin, and A. Kankaanperä, *Acta Chem. Scand., Ser. A*, 1987, **41**, 447.
- 5 D. K. Jaiswal, J. R. Jones, and R. Fuchs, *J. Chem. Soc., Perkin Trans. 2*, 1976, 102.
- 6 J. R. Jones and R. Fuchs, *Can. J. Chem.*, 1977, **55**, 99.
- 7 C. G. Karakatsanis and T. B. Reddy, in 'Recommended Methods for Purification of Solvents and Tests for Impurities,' ed. J. F. Coetzee, Pergamon Press, Exeter, 1982, p. 25.
- 8 R. Fuchs and C. P. Hagan, *J. Phys. Chem.*, 1973, **77**, 1797.
- 9 J. J. Lindberg and J. Kenttämää, *Suomen Kemistil.*, 1960, **B33**, 104.
- 10 J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, 1961, **39**, 2240.
- 11 R. Fuchs, C. P. Hagan, and R. F. Rodewald, *J. Phys. Chem.*, 1974, **78**, 1509.

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