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Short Communication

Aqueous Sulfolane as a Highly Basic Medium in the Ionization of Carbon Acids

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In the detritiation of chloroform-*t* in aqueous dimethyl sulfoxide (DMSO) highly positive activation entropies show a tendency to decrease with increasing x(DMSO).[1,2] This is also the case in highly basic aqueous hexamethylphosphoric triamide (HMPTA).[3] These results are in accordance with the change from internal return [reaction (2) rate-limiting] to rate-determining ionization [reaction (1) rate-determining] with the increase in the mole fraction of dipolar aprotic solvent in the reaction mixture.

$$RT + HO^- \rightarrow R^- \cdot TOH \quad (1)$$

$$R^- \cdot TOH \rightarrow R^- + TOH \quad (2)$$

To obtain additional evidence for this mechanistic change, kinetic measurements were extended to a less basic solvent system, aqueous sulfolane (tetramethylene sulfone), the acidity function of which increases from an H_--value of 12 to 20 (hydroxide ion concentration 0.011 mol dm^{-3}) when going from pure water to a mixture with x(sulfolane) = 0.95.[4–6] These equilibrium basicities are anomalous in the range x(sulfolane) = 0.05–0.10, where H_--values are almost independent of solvent composition. As additional evidence for this anomaly is not available, kinetic measurements for the detritiation of chloroform-*t* and acetophenone-*t* were extended, especially to mixtures of relatively low x(sulfolane). Previously only a few kinetic measurements have been performed in aqueous sulfolane. Alkaline hydrolysis of 2,4-dinitroanisole and 2-methoxy-5-nitropyridine[7] has been studied kinetically, but only in mixtures with x(sulfolane) between 0.3 and 0.7.

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Experimental

Sulfolane, produced by Aldrich (99%), was purified by distillation over sodium hydroxide, and the fraction at 98–103 °C (1–2 Torr) was collected. Commercial acetophenone (Fluka AG) was purified by distillation. Acetophenone and chloroform were labelled with tritiated water as described previously.[2,10] Kinetic methods have been described earlier.[11] Kinetic measurements were usually performed at four temperatures between 263 and 308 K in the detritiation of chloroform-*t* and between 288 and 328 K in the detritiation of acetophenone-*t*. 0.011 mol dm^{-3} tetramethyl ammonium hydroxide was used as the catalyst. Standard errors of the rate coefficients varied between 0.2 and 1%. Enthalpies of solution of acetophenone were measured at 298 K with an LKB 10700-2 batch microcalorimeter as described earlier.[9] The larger compartment of the reaction cell was filled with about 4 g of aqueous sulfolane and the smaller compartment with acetophenone. The amount of acetophenone varied in the measurements between 5 and 25 mg. The measured enthalpies were found to be independent of the amount of the substrate, and thus the values refer to infinite dilution. Two parallel measurements were performed in each solvent mixture.

Results and discussion

Dependence of rate coefficients on solvent composition. In Table 1 the second-order rate coefficients for the detritiation of chloroform-*t* and acetophenone-*t* in water–sulfolane mixtures at 298.15 K were calculated from the plots of lg(k/dm^3 mol^{-1} s^{-1}) vs. $1/T$ by the method of least squares. The susceptibility of the rate of detritiation to solvent composition can be described by the slope of the plot of lg(k/mol^{-1} dm^3 s^{-1}) vs. mole fraction of the

Table 1. Activation parameters in the detritiation of chloroform-*t* and acetophenone-*t* in aqueous sulfolane with 0.011 mol dm^{-3} tetramethyl ammonium hydroxide as the catalyst.[a]

x(sulfolane)	$\Delta H^{\ddagger}_m$/ kJ mol^{-1}	$\Delta S^{\ddagger}_m$/ J K^{-1} mol^{-1}	k(298.15 K)/ 10^{-2} dm^3 mol^{-1} s^{-1}
Substrate: chloroform			
0.000[b]	97.1	+64.9	16.5
0.0298	92.7±0.7	+56.8±2.5	32.6±0.6
0.0502	89.0±1.3	+47.8±4.4	49.2±2.0
0.0632	86.7±1.0	+41.6±3.4	59.2±1.8
0.102	86.3±0.5	+44.0±1.7	93.4±1.5
0.125	89.1±1.1	+56.9±3.8	145±3
0.148	90.1±2.2	+63.1±7.9	199±9
0.202	89.7±1.6	+65.7±5.6	321±10
0.261	86.7±3.2	+61.9±11.4	695±53
0.303	86.6±1.6	+65.0±6.1	1050±41
0.348	88.8±2.8	+78.3±10.4	2104±108
Substrate: acetophenone			
0.000[c]	63.8±1.7	−73.9±5.4	0.565±0.006
0.169	66.8±0.4	−62.0±1.4	0.723±0.008
0.303	66.1±0.6	−60.2±2.0	1.16±0.02
0.411	68.6±0.1	−46.8±0.4	2.145±0.006
0.499	70.8±0.8	−36.1±2.8	3.11±0.07
0.611	69.4±1.4	−33.9±4.6	7.24±0.30
0.697	68.7±1.7	−30.9±6.0	13.7±0.4

[a] Supplementary information on measured rate coefficients is available from the authors. [b] Ref. 1. [c] Ref. 2.

dipolar aprotic solvent. The logarithms of the rate coefficients in water–sulfolane mixtures are compared with those in dimethyl sulfoxide–water mixtures[1,2] in Fig. 1. In the detritiation of chloroform-*t* the logarithms of the rate coefficients first increase linearly with *x*(sulfolane) but only to a mole fraction of about 0.06. The slope of this plot, 8.9±0.5, is only slightly lower than the corresponding slope in water–DMSO mixtures,

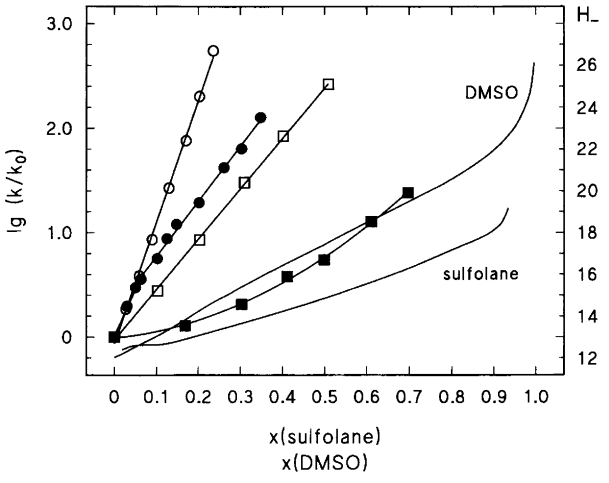

Fig. 1. Logarithms of the second-order rate coefficients for the detritiation of chloroform-*t* (circles) and acetophenone-*t* (squares) in aqueous sulfolane (filled symbols) and DMSO[1,2] (open symbols). H_--Values of sulfolane[6] and DMSO[8] in 0.011 mol dm^{-3} aqueous tetramethyl ammonium hydroxide are also given in the plot.

11.6±0.2.[1] Thus the increase in basicity of a water–sulfolane mixture with *x*(organic solvent) is comparable to that of water–DMSO mixtures when the mole fraction of dipolar aprotic solvent is relatively low. In mixtures with *x*(sulfolane) higher than 0.06 the increase in the rate coefficients of the detritiation of chloroform-*t* diminishes significantly, as the slope of the plot of $\lg(k/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})$ vs. *x*(sulfolane) is only 5.3±0.1. Thus it is evident that the increase in basicity is significantly lowered when *x*(sulfolane) exceeds 0.06, and consequently water–sulfolane systems remain less basic than the corresponding water–DMSO mixtures, especially when the mole fraction of organic component is relatively high. In spite of the intersecting point at a mole fraction of 0.06 the increase in basicity is continuous, and thus the kinetic results do not support the assumption based on previous H_--values, on the basis of which the basicity would be independent of solvent composition in the *x*(sulfolane) region 0.05–0.10.

Transfer enthalpies. As shown previously[2,3] in the detritiation of acetophenone-*t*, the slopes of the plots of $\lg(k/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})$ vs. *x*(DMSO) or *x*(HMPTA) are markedly lower than in the detritiation of chloroform-*t*. This is due to the fact that in the detritiation of acetophenone-*t* the transition state is hydroxide-ion-like, and as a result of this similarity changes in solvation of hydroxide ion and transition state partially cancel each other in eqn. (3), where the γ are activity coefficients in aqueous dipolar aprotic solvent as compared to that in water.

$$k(\text{obs}) = k_0\{\gamma(\text{HO}^-)\gamma(\text{RT})/\gamma(\neq)\} \qquad (3)$$

Thus a low rate increase is also expected in the detritiation of acetophenone-*t* in water–sulfolane mixtures. Therefore, the observation that in this medium the rate coefficients are almost independent of solvent composition when the mole fraction of sulfolane is relatively low (Fig. 1) cannot be explained only on the basis of medium effects on hydroxide ion and the transition state of the reaction. Thus it is evident that in aqueous sulfolane medium effects on uncharged species, acetophenone RT, must also be taken into account in addition to those of charged species, hydroxide ion and transition state of the reaction. To show that this assumption is well founded, enthalpies of solution of acetophenone were determined in water–sulfolane mixtures. The enthalpy of transfer of acetophenone from water to water–sulfolane mixtures was calculated from eqn. (4).

$$\Delta_{tr}H_m(\text{water–sulfolane} \leftarrow \text{water}) = \Delta_{sol}H_m(\text{water–sulfolane}) - \Delta_{sol}H_m(\text{water}) \qquad (4)$$

The results are compared with those in aqueous dimethyl sulfoxide in Fig. 2. The measured transfer enthalpies are negative, in contrast to those in aqueous DMSO, which means that acetophenone is enthalpically more solvated in water–sulfolane mixtures than in water. The change in solvation discontinues when *x*(sulfolane) exceeds the

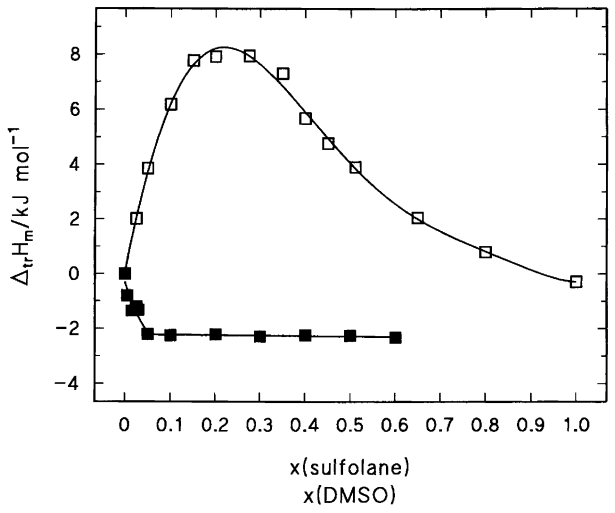

Fig. 2. Enthalpies of transfer of acetophenone from water to aqueous sulfolane (filled squares) and aqueous DMSO[9] (open squares) at 298 K.

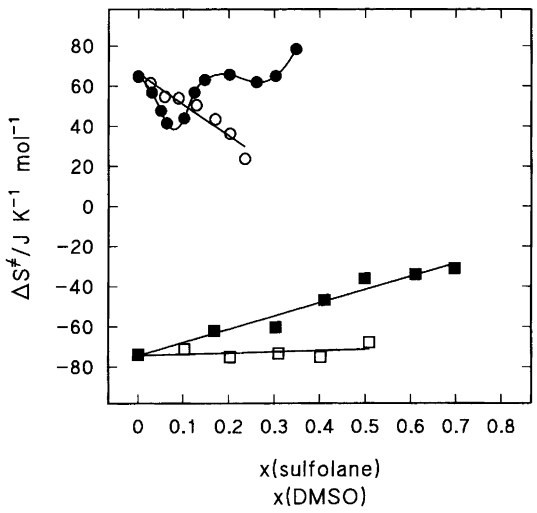

Fig. 3. Entropies of activation for the detritiation of chloroform-*t* (circles) and acetophenone-*t* (squares) in aqueous sulfolane (filled symbols) and DMSO[1,2] (open symbols).

value of 0.06. In solutions containing more sulfolane, transfer enthalpies of acetophenone are almost independent of solvent composition. The changes in solvation of acetophenone decrease the rate of detritiation when x(sulfolane) increases from 0 to 0.06, and thus the observed independence of rate coefficients on solvent composition is understandable. At higher x(sulfolane) the solvation of acetophenone remains almost constant, and therefore it no longer compensates the accelerating effect arising from the small difference in the solvation of the charged species in eqn. (3). Thus it is evident that rate coefficients of detritiation of acetophenone-*t* do not immediately give information on solvent basicity.

Activation entropies. In the detritiation of acetophenone-*t* in aqueous sulfolane activation entropies increase slightly with x(sulfolane), unlike those observed in aqueous dimethyl sulfoxide (Fig. 3). However, the measured values are negative, in accordance with bimolecular ionization [eqn. (1)]. In the detritiation of chloroform-*t* in aqueous sulfolane the measured activation entropies in Fig. 3 are highly positive, in accordance with the unimolecular internal return mechanism. Although these values first decrease slightly when x(sulfolane) increases from 0 to 0.06, the mechanistic change from internal return to rate-determining ionization, observed in aqueous dimethyl sulfoxide and hexamethylphosphoric triamide, can be excluded in aqueous sulfolane.

Activation enthalpies. Changes in activation enthalpies in the detritiation of chloroform-*t* and acetophenone-*t* are also exceptional. On the basis of kinetic results in aqueous dimethyl sulfoxide[1,2] (Fig. 4) a continuous decrease in activation enthalpy is expected with x(sulfolane). However, this is the case only in the detritiation of chloroform-*t* in the range x(sulfolane) = 0–0.06. In mixtures containing more sulfolane $\Delta H^{\neq}$-values are almost

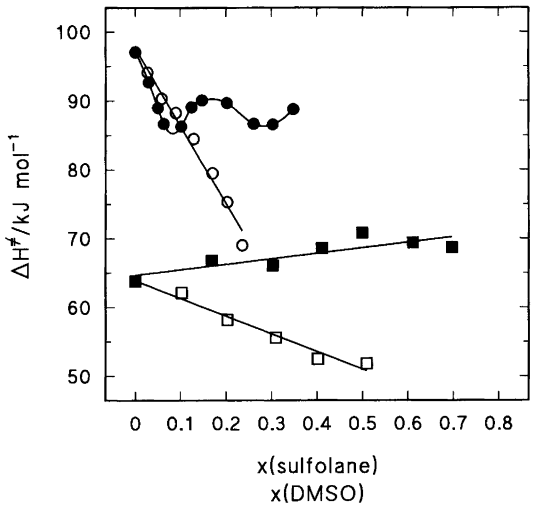

Fig. 4. Enthalpies of activation for the detritiation of chloroform-*t* (circles) and acetophenone-*t* (squares) in aqueous sulfolane (filled symbols) and DMSO[1,2] (open symbols).

independent of solvent composition. In the detritiation of acetophenone-*t*, the activation enthalpy in aqueous sulfolane is even rate-detarding as compared to that in water. Thus the observed increase in the rates of detritiation of acetophenone-*t* with x(sulfolane) is due to an increase in activation entropy and a decrease in order when going from the initial state to the transition state of the reaction.

On the basis of the present data aqueous sulfolane seems to be very capable of being used as a highly basic medium. The basicity of this system is, however, a little lower than that of the corresponding water–DMSO system, especially in mixtures containing mainly a dipolar aprotic solvent.

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