Solvent Effect on Activation Parameters for the Neutral Hydrolysis of Phenyl Trifluoroacetates in Aqueous Acetonitrile

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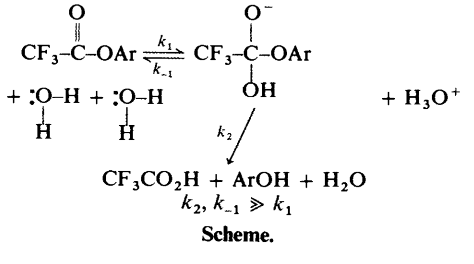
Rates of neutral hydrolysis of phenyl, 4-nitrophenyl, and 2,4-dinitrophenyl trifluoroacetates in acetonitrile–water mixtures (x_{MeCN} = 0.39—0.97) have been measured. The free energies of activation increase smoothly upon increasing the acetonitrile content of the medium while the enthalpies and entropies of activation show a more complex but partially compensating behaviour. For phenyl trifluoroacetate both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ pass through an inflexion point around x_{MeCN} = 0.6. For 4-nitrophenyl and 2,4-dinitrophenyl trifluoroacetates a minimum value possibly occurs both in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ around x_{MeCN} = 0.9—0.95, but it is clearly observed in $\Delta H^{\ddagger}$ at x_{MeCN} = 0.92 for the former ester and in $\Delta S^{\ddagger}$ at x_{MeCN} = 0.94 for the latter ester. The activation parameters are discussed in terms of solvent structure. The extreme values are mainly attributed to changes in the thermodynamic functions of transfer of the transition state of the hydrolysis reaction from water to acetonitrile–water mixtures.

Much current research is focused upon the elucidation of kinetic solvent effects on organic reactions in binary mixtures of water with organic solvents.[1–3] It is possible in binary mixtures to change the hydrogen-bonded structure of water by gradually increasing the mole fraction (x) of the organic component. This continuous change in the microenvironment of the reactant and transition state elucidates the importance of solvent effects on organic reactions.[2]

Mixed aqueous solvent effects on organic reactions have often been examined in terms of changes in the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. However, previous studies have mainly been limited to highly aqueous binaries.[1,2] This paper describes the study concerning solvent and temperature effects on the neutral hydrolysis of phenyl trifluoroacetates in acetonitrile–water mixtures containing low concentrations of water. The crystallographic evidence of low content of water at the active sites of enzymes has previously promoted some solvation studies concerning the imidazole-catalysed hydrolysis of 4-nitrotrifluoroacetanilide in poorly aqueous acetonitrile.[4] Gopalakrishnan and Hogg[5] studied the effect of solvent composition on the neutral hydrolysis of 1-acetyl-3-methylimidazolium ion in acetonitrile–water binaries including cosolvent-rich mixtures.

As demonstrated by the strongly negative and highly solvent-dependent entropies of activation, the neutral hydrolysis of acyl-activated aryl esters is very sensitive to solvation changes in highly aqueous media.[6] A single-step reaction mechanism involving water-catalysed nucleophilic attack of water on the ester carbonyl has been suggested for the neutral hydrolysis of 4-nitrophenyl and 4-methoxyphenyl dichloroacetates in aqueous solutions.[2,6] Similar mechanism is proposed for substituted phenyl trifluoroacetates in poorly aqueous acetonitrile–water mixtures with the exception that in the latter case the reaction evidently proceeds through a tetrahedral addition intermediate, and the C–OAr bond-breaking does not seem to contribute to the rate-limiting step (Scheme).[7] The continuous increase of the mole fraction of the organic cosolvent in acetonitrile–water binaries is concluded to produce significant changes in the solvent structure,[1b,8,9] which should be reflected by the kinetic behaviour of the present reaction.[1,2,3,6]



Scheme.

The effect of variation of a binary mixture on the thermodynamic activation parameters can be considered in terms of how the thermodynamic quantities of transfer of the reactants change as the medium is altered from one of its pure components to the mixtures under study. This method yields the transfer functions of the transition state. The difference in solvation between reactants and the transition state depends on the difference between their hydrophobicity and polar character as well as on the organic cosolvent used. If the solvent effects are sufficiently different for the transition state and reactants, extreme values can be observed in the activation parameters upon variation of the composition of a binary mixture.[2]

For water-catalysed hydrolysis of activated esters and amides, the most typical behaviour of the thermodynamic activation parameters in highly aqueous binaries involves a smooth increase in $\Delta G^{\ddagger}$ while $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ show large and partially compensating changes and pass through extrema when the mole fraction of the organic component is increased. However, the size of the minima and maxima in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ varies, and in some cases no extrema are observed.[1a,2,6,10] Different kinetic patterns are observed in typically aqueous (TA) and in typically non-aqueous (TNA) mixtures.[1,2,3,10b] In TA mixtures (*e.g.* t-butyl alcohol–water), the substantial changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with change in solvent composition presumably reflect reactant-state stabilization through hydrophobic interactions with the cosolvent.[2,3,10b,c] Dominating specific solvation effects and a minor contribution of hydrophobic effects in TNA mixtures (*e.g.* acetonitrile–water) lead to a smaller variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[2,10b] Further, the size of the extrema in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is clearly dependent on the substrate hydrophobicity.[2,10b,c]

Experimental

Materials.—Phenyl trifluoroacetate, a commercial product (Pierce Chemical Company), was redistilled before use. 4-Nitrophenyl and 2,4-dinitrophenyl trifluoroacetates were prepared as described earlier.[7]

Acetonitrile (Merck; max. H_2O 0.03%) was used as received. The solvent mixtures were prepared by diluting a known weight of distilled water with acetonitrile to a known volume in a volumetric flask.

Kinetics.—Reaction rates were determined by following the increase in absorption owing to the formation of the phenolic product (phenol, 270 nm; 4-nitrophenol, 310 nm; 2,4-dinitrophenol, 290 nm). The reactions were followed with a Perkin-Elmer 46 spectrophotometer as described earlier.[7] The first-order rate coefficients were calculated by Guggenheim's method[11] and they were reproducible to within ±3%.

Results and Discussion

Before examining the present results, it is necessary to consider some facts relevant to acetonitrile–water mixtures. There have been arguments for[12] and against[1b,8,13] the proposal that the network structure of water is enhanced by the initial addition of acetonitrile. However, the overall trend for this cosolvent appears to be to disrupt water–water interactions.[1b,8,9] Moreau and Douhéret[9a] have considered that it is likely that several different structural regions exist in acetonitrile–water mixtures. The composition variation of the water proton chemical shift suggests that there may be five structurally distinct regions.[9b]

In the water-rich region water–acetonitrile interactions are weak. The water proton chemical shift variation,[9b] tracer diffusion coefficient data,[9c] and the composition dependence of the empirical solvent polarity parameter E_T[9d] for the acetonitrile–water binary system suggest that near the composition $x_{MeCN} =$ 0.15—0.20 there occurs a pronounced change in the solvent structure. It has been concluded by Easteal *et al.*[9b—d] that at this composition the water network becomes 'saturated' with acetonitrile molecules and progressive disruption of the water structure occurs. In terms of the Naberukhin–Rogov structural model, further addition of the organic cosolvent results in the formation of two 'microphases'; the structured water phase, *i.e.* globules, which contains a small amount of acetonitrile and the disordered phase consisting of acetonitrile molecules associated with some individual water molecules.[9b—d] In the composition region $x_{MeCN} \approx$ 0.6—0.95, acetonitrile–acetonitrile interactions begin to be effective and progressive formation of the acetonitrile liquid structure occurs.[9b—d] The combined diffusion coefficient and viscosity data indicate that the acetonitrile microphase has a maximum disorder at $x_{MeCN} = 0.95$.[9c] The composition dependence of the water proton chemical shift[9b] as well as the tracer diffusion coefficient data[9c] suggest that at low concentrations in acetonitrile (beyond $x_{MeCN} \approx 0.95$) water is in a similar state to that in which it exists in water vapour. In the light of i.r. spectra and other evidence, water is monomeric in acetonitrile up to $[H_2O] \approx$ 0.5—1M, beyond which concentration it begins to undergo self-association, *i.e.* dimer formation.[14] This water concentration corresponds to $x_{MeCN} \approx$ 0.95—0.97.

Rate Coefficients and Activation Parameters for Phenyl Trifluoroacetates.—First-order rate coefficients and the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the neutral hydrolysis of phenyl trifluoroacetates investigated are given in Tables 1 and 2. The activation parameters $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are plotted against the mole fraction of acetonitrile (x_{MeCN}) in the Figure.

As reflected by the gradual increase of the $\Delta G^\ddagger$ values the rates of hydrolysis are retarded with increasing mole fraction of acetonitrile. This is the expected effect of the organic cosolvent on the rate of the neutral hydrolysis of activated esters.[2,6,10a,b] As usual for organic reactions in mixed aqueous solvents,[1,2,6,10] the enthalpy and entropy of activation show a partially compensating behaviour for all three esters. For phenyl trifluoroacetate both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ decrease and pass through an inflexion point when the mole fraction of acetonitrile increases from 0.4 to 0.8, the inflexion points falling around $x_{MeCN} = 0.6$. The decrease in $\Delta H^\ddagger$ implies that the increase in $\Delta G^\ddagger$ is dominated by an entropy effect. In water-rich binaries solvent effects on organic reactions often are dominated by an entropy effect.[2] For 4-nitrophenyl trifluoroacetate there occurs a minimum in $\Delta H^\ddagger$ at $x_{MeCN} = 0.92$ and possibly also in $\Delta S^\ddagger$ around $x_{MeCN} = 0.95$. For 2,4-dinitrophenyl trifluoroacetate the experimental values are few but they indicate the occurrence of a minimum in $\Delta S^\ddagger$ around $x_{MeCN} = 0.94$ and possibly also in $\Delta H^\ddagger$ around $x_{MeCN} = 0.93$. The rates of the reactions investigated have limited the solvent regions used for each ester. However, if it is assumed that the form of the curves shown in the Figure are similar for 4-nitrophenyl and 2,4-dinitrophenyl trifluoroacetates, the conception of the occurrence of a minimum both in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is confirmed.

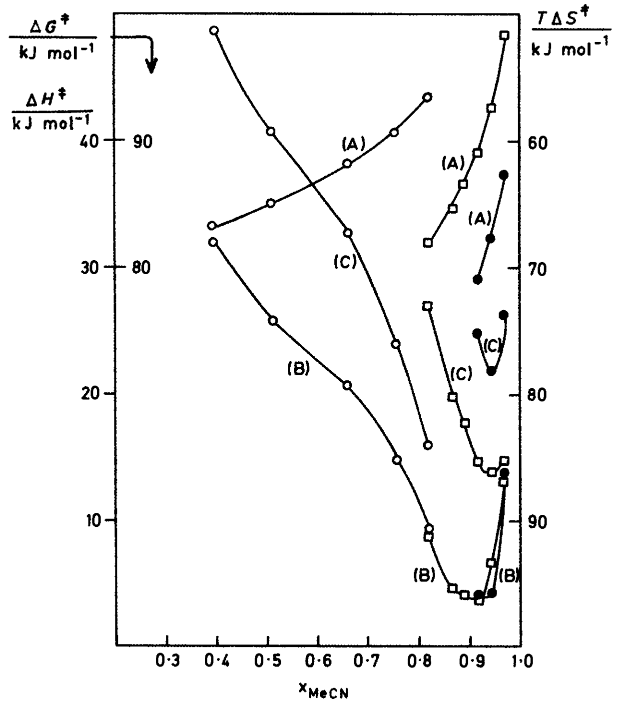


Figure. Plots of $\Delta G^\ddagger$ (A), $\Delta H^\ddagger$ (B), and $-T\Delta S^\ddagger$ (C) for the neutral hydrolysis of phenyl trifluoroacetate (○), 4-nitrophenyl trifluoroacetate (□), and 2,4-dinitrophenyl trifluoroacetate (●) in acetonitrile–water mixtures as a function of solvent composition at 298.2 K

The smooth decrease in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the hydrolysis of phenyl trifluoroacetate in the region $x_{MeCN} =$ 0.4—0.8 possibly reflects the progressive disruption of the water liquid structure. The inflexion points of the functions are located at the same mole fraction, $x_{MeCN} = 0.6$, where there occurs an inflexion point in the plot of the E_T values of acetonitrile–water mixtures against the mole fraction of acetonitrile.[9d] It has been suggested that near this composition the highly structured microphase, consisting predominantly of water, has disappeared and the solution contains only the disordered microphase composed of acetonitrile molecules and individual water molecules associated with them.[9d]

In the neutral hydrolysis of 4-nitrophenyl and 2,4-dinitrophenyl trifluoroacetates there occur pronounced changes both in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at low concentrations of water in acetonitrile (Figure). A similar $\Delta H^\ddagger/\Delta S^\ddagger$ pattern at low concentrations of water has been observed *e.g.* in the hydrolysis of benzenesulphonic acid esters in acetone–water and dioxane–water mixtures[15a] as well as in the hydrolysis of arylsulphonylmethyl perchlorates in t-butyl alcohol–water mixtures.[15b] As discussed

Table 1. Rate coefficients for the neutral hydrolysis of substituted phenyl trifluoroacetates CF_3CO_2Ar in acetonitrile–water mixtures[a]

Ar	x^b_{MeCN}	T/K	10^3k_{obs}/s^{-1}
Ph	0.394	298.2	13.77 ± 0.03
		303.2	17.99 ± 0.04
		308.2	21.96 ± 0.04
		313.2	27.07 ± 0.05
		318.2	33.42 ± 0.05
	0.510	298.2	6.539 ± 0.015
		303.2	8.383 ± 0.020
		308.2	9.672 ± 0.018
		313.2	11.60 ± 0.02
		318.2	13.61 ± 0.04
	0.663	298.2	1.961 ± 0.004
		303.2	2.341 ± 0.003
		308.2	2.701 ± 0.005
		313.2	3.155 ± 0.010
		318.2	3.530 ± 0.009
	0.756	298.2	0.665 ± 0.002
		303.2	0.785 ± 0.002
		308.2	0.861 ± 0.003
		313.2	0.995 ± 0.002
		318.2	1.018 ± 0.002
	0.819	298.2	0.2225[c] ± 0.0005
		308.2	0.2593 ± 0.0017
		318.2	0.3016 ± 0.0013
C_6H_4-4-NO_2	0.819	298.2	23.52[c] ± 0.03
		303.2	25.39 ± 0.04
		308.2	26.94 ± 0.02
		313.2	29.25 ± 0.04
		318.2	31.43 ± 0.05
	0.867	298.2	7.72[c] ± 0.02
		308.2	8.74 ± 0.01
		318.2	9.55 ± 0.02
		328.2	10.16 ± 0.01
		338.2	10.87 ± 0.02
	0.891	298.2	3.631[c] ± 0.004
		308.2	4.047 ± 0.003
		318.2	4.403 ± 0.004
		328.2	4.728 ± 0.008
		338.2	4.975 ± 0.004
	0.917	298.2	1.317[c] ± 0.001
		308.2	1.456 ± 0.001
		318.2	1.575 ± 0.002
		328.2	1.700 ± 0.001
		338.2	1.767 ± 0.002
	0.944	298.2	0.3074[c] ± 0.0007
		308.2	0.3481 ± 0.0005
		318.2	0.3828 ± 0.0021
		328.2	0.4345 ± 0.0005
		338.2	0.4721 ± 0.0017
	0.971	288.2	0.025 72[c] ± 0.000 06
		298.2	0.031 92[c] ± 0.000 11
		308.2	0.037 53[c] ± 0.000 20
		318.2	0.048 23[c] ± 0.000 32
C_6H_3-2,4-$(NO_2)_2$	0.917	298.2	72.2 ± 0.3
		303.2	75.1 ± 0.2
		308.2	79.0 ± 0.2
		313.2	82.5 ± 0.2
		318.2	84.4 ± 0.3
	0.944	298.2	19.37 ± 0.04
		303.2	20.15 ± 0.03
		308.2	21.26 ± 0.05
		313.2	22.04 ± 0.03
		318.2	22.96 ± 0.09
	0.971	298.2	2.514[c] ± 0.005
		303.2	2.871[c] ± 0.004
		308.2	3.062[c] ± 0.011
		313.2	3.511[c] ± 0.004
		318.2	3.813[c] ± 0.015

[a] Errors shown are standard deviations. [b] The mole fraction of acetonitrile. [c] Ref. 7.

Table 2. Activation parameters for the neutral hydrolysis of substituted phenyl trifluoroacetates CF_3CO_2Ar in acetonitrile–water mixtures[a]

Ar	x^b_{MeCN}	$\Delta H^‡$/ kJ mol^{-1}	$-\Delta S^‡$/ J mol^{-1} K^{-1}
Ph	0.394	32.0 ± 0.8	172 ± 3
	0.510	25.8 ± 1.3	199 ± 4
	0.663	20.8 ± 0.7	226 ± 2
	0.756	14.8 ± 2.0	255 ± 6
	0.819	9.5 ± 0.2	282 ± 1
C_6H_4-4-NO_2	0.819	8.9 ± 0.3	245 ± 1
	0.867	4.6 ± 0.5	269 ± 1
	0.891	4.1 ± 0.4	276 ± 1
	0.917	3.8 ± 0.4	286 ± 1
	0.944	6.6 ± 0.3	289 ± 1
	0.971	13.1[c] ± 1.1	287[c] ± 1
C_6H_3-2,4-$(NO_2)_2$	0.917	3.9 ± 0.4	252 ± 1
	0.944	4.3 ± 0.2	262 ± 1
	0.971	13.8[c] ± 0.9	248[c] ± 3

[a] Errors shown are standard deviations. [b] The mole fraction of acetonitrile. [c] Ref. 7.

above, the different response of the thermodynamic functions of transfer of the reactant state and transition state to the solvent composition leads to the marked changes observed for the thermodynamic activation parameters. As shown by Cox,[16] for different non-electrolytes such as ethyl acetate, ethyl vinyl ether, acetone, and benzene, the trends in the enthalpies (ΔH^0_{tr}) and entropies (ΔS^0_{tr}) for transfer from water to mixtures of water–dimethyl sulphoxide (DMSO) are similar in their gross features in the composition region x_{DMSO} = 0—1.0, the net result being a small decrease in free energy.* The initial addition of the cosolvent increases both enthalpy and entropy of transfer. The major increase in both terms occurs during the addition of the first 0.2—0.3 mole fraction of the cosolvent, and further addition of the organic component results in a small decrease in ΔH^0_{tr} while ΔS^0_{tr} remains approximately constant.[16] Similar behaviour was found for transfer of ethyl acetate from water to binaries of water with acetonitrile or dioxane.[16] In acetonitrile–water mixtures with mole fractions of x_{MeCN} = 0.4, 0.6, 0.8, and 1.0 the value for ΔH^0_{tr} is 10 kJ mol^{-1} in all cases and the values for $T\Delta S^0_{tr}$ at 298 K are 17, 18, 19, and 19 kJ mol^{-1}, respectively.[16] The initial increase followed by subsequent levelling off of ΔH^0_{tr} was observed in the water-rich region (x_{org} = 0—0.15) for transfer of 4-nitrophenyl acetate from water to dioxane–water or acetonitrile–water mixtures.[2] If the slight variation of ΔH^0_{tr} and ΔS^0_{tr} observed in the cosolvent-rich region for ethyl acetate for transfer from water to acetonitrile–water mixtures[16] is valid also for phenyl trifluoroacetates, the pronounced changes in $\Delta H^‡$ and $\Delta S^‡$ (Figure) must mainly reflect changes in thermodynamic functions of transfer for the transition state. However, although the enthalpies for transfer of the substrate from water to the acetonitrile–water mixtures under study can stay approximately constant, the progressive decrease in the water content of the medium may change the activity of water and thereby affect the enthalpy of activation.

In the neutral hydrolysis of 1-acetyl-3-methylimidazolium ion, there occurs a gradual decrease in $\Delta H^‡$ when the solvent composition is progressively changed from water to an acetonitrile–water mixture with x_{MeCN} = 0.9.[5] The entropy of activation exhibits only small changes as the mole fraction of acetonitrile changes from 0 to 0.5 but there occurs a striking decrease in $\Delta S^‡$ when x_{MeCN} changes from 0.5 to 0.9. These

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* ΔH^0_{tr} and ΔS^0_{tr}, respectively, denote the enthalpy and enthopy for transfer of a solute from water to a mixture of water and an organic solvent.

effects have been explained by the preferential solvation of the transition state by water.[5] As shown by Cox *et al.*,[17] both the enthalpies and entropies for transfer of alkali metal halides from water to acetonitrile–water mixtures decrease smoothly upon increasing the acetonitrile content and then show a sharp minimum at x_{MeCN} *ca.* 0.95. The alkali metal and halide ions are preferentially solvated by water in acetonitrile–water mixtures and the observed changes in the enthalpies and entropies for transfer of the electrolytes from water to aqueous mixtures of acetonitrile were explained by specific interactions between the ions and the neighbouring solvent molecules as well as by the effect of the solvated ions on the bulk solvent properties.[17] The transition state for the addition–elimination mechanism assumed for the present reaction probably resembles the addition intermediate, has fairly localized charges, and is preferentially solvated by water in acetonitrile–water mixtures. Thus the marked changes and minimum values at low concentrations of water proposed for the enthalpy and entropy of transfer of the transition state for the neutral hydrolysis of 4-nitrophenyl and 2,4-dinitrophenyl trifluoroacetates from water to acetonitrile–water mixtures are compatible with the results of Cox *et al.*[17]

For the mole fraction $x_{\mathrm{MeCN}} = 0.95$, the maximum disorder of the acetonitrile microphase has been suggested.[9c] At this composition the diffusion of water is proposed to be less hindered by interactions with acetonitrile molecules than it is in solutions with a higher content of acetonitrile. Beyond this mole fraction water is suggested to reach a similar state to that in which it exists in water vapour.[9c] Therefore, the occurrence of the minimum values in the thermodynamic functions of transfer for the species preferentially solvated by water and in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values discussed above at the composition region $x_{\mathrm{MeCN}} = 0.9$—0.95 is reconcilable with the specific solvent structure and specific solute–solvent interactions.

Conclusions

The main emphasis in this study has been the recognition of the specific patterns of the kinetic solvent effects on the neutral ester hydrolysis in poorly aqueous acetonitrile–water mixtures. As previously observed for water rich aqueous binaries, the water structure effects which have a smooth influence on $\Delta G^{\ddagger}$ consist of large and mutually compensating effects on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Due to the lack of the relevant thermodynamic functions of transfer, the detailed analysis of interaction mechanisms between the reactant and transition state and the solvent mixture is not possible. However, the observed minimum values in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the region $x_{\mathrm{MeCN}} = 0.9$—0.95 are assumed mainly to reflect the occurrence of minimum values in the enthalpy and entropy of transfer of the transition state for the present hydrolysis reaction from water to acetonitrile–water mixtures.

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