

Temperature and Solvent Effects in the Neutral Hydrolysis of Methyl and Ethyl Trifluoroacetates in *sec*-Butyl Alcohol–Water Mixtures

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A conductimetric method has been employed to measure the rates of neutral hydrolysis of methyl trifluoroacetate in aqueous mixtures of *sec*-butyl alcohol in which the mole fractions of water were 0.995, 0.990, 0.985, 0.980, 0.975, 0.970, 0.965, 0.960, 0.955 and 0.950, at 2.5 K intervals from 273 K to about 320 K and the rates of neutral hydrolysis of ethyl trifluoroacetate in a *sec*-butyl alcohol–water mixture in which the mole fraction of water is 0.965 at 2.5 K intervals from 273 K to 343 K. For the first three solvent mixtures ΔC_p^\ddagger has a negative value, which does not depend on temperature. For the remaining solvent mixtures ΔC_p^\ddagger is highly temperature dependent, especially when the mole fraction of water is 0.955, for which $d\Delta C_p^\ddagger/dT$ is 41(2) J mol⁻¹ K⁻². At lower temperatures ΔC_p^\ddagger is large and negative, but increases with increasing temperature to a positive value. At $x_w = 0.965$, $d\Delta C_p^\ddagger/dT$ for the hydrolysis of ethyl trifluoroacetate [24(1) J mol⁻¹ K⁻²] is larger than that for the hydrolysis of methyl trifluoroacetate [17(1) J mol⁻¹ K⁻²]. *sec*-Butyl alcohol is the fourth known cosolvent which gives rise to a large dependence of ΔC_p^\ddagger on temperature.

The heat capacity of activation, ΔC_p^\ddagger , for the neutral hydrolysis of esters of α -halogenated carboxylic acids in aqueous solutions of organic solvents seems in most cases to be negative, independent of temperature, and to go through a minimum in the water-rich region.^{1–3} However, the activation heat capacity for this reaction in aqueous solutions of *tert*-butyl alcohol,^{4,5} 2-butoxyethanol,^{4,6,7} and 2-(2-butoxyethoxy)ethanol⁸ in some regions is highly dependent on temperature. This temperature dependence of ΔC_p^\ddagger has been explained by the formation of two microphases.^{4–7} The aim of the present work was to study the behaviour of the neutral hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures and to compare the results with the kinetic data for the hydrolysis of methyl trifluoroacetate in *tert*-butyl alcohol–, 2-butoxyethanol– and 2-(2-butoxyethoxy)ethanol–water mixtures.^{5–8} In addition, ethyl trifluoroacetate was chosen for comparison of the behaviour of the neutral hydrolysis of esters with varying hydrophobicity.

Experimental

Methyl trifluoroacetate, a *purum* grade product from Fluka AG, and ethyl trifluoroacetate, a *puriss.* grade product from Fluka AG, were redistilled before use. *sec*-Butyl alcohol was a guaranteed reagent for analysis from E. Merck AG and was used without further purification. The water

used in the kinetic experiments was deionized and distilled. Solvent mixtures were prepared by weight.

The rate constants were calculated by Guggenheim's method⁹ from conductances measured during the reactions with a Beckman RC-18 conductimeter, as described in detail earlier.¹⁰ The standard deviations of the calculated rate constants vary from 0.02 to 0.2%, but rarely more than 0.1%.

The thermodynamic activation parameters were calculated from an extended Arrhenius eqn. (1) by the method of

$$\ln k = A + (B/T) + C \ln T + DT + ET^2 \quad (1)$$

Clarke and Glew.¹¹ The calculated values are shown in Table 1.

Results and discussion

sec-Butyl alcohol as the cosolvent in water lowers the rate of hydrolysis of methyl trifluoroacetate considerably, as can be seen from Table 1. The retarding effect is evidently greater than for that in *tert*-butyl alcohol–water but much smaller than that found in 2-butoxyethanol–water and 2-(2-butoxyethoxy)ethanol–water mixtures.^{5,6,8}

The activation enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , at 298 K show almost compensatory changes. ΔH^\ddagger decreases to a

Table 1. Thermodynamic parameters of activation, calculated from eqn. (1) in its three-parametric (3) and four-parametric (4) form for the neutral hydrolysis of methyl trifluoroacetate (M) and ethyl trifluoroacetate (E) in *sec*-butyl alcohol–water mixtures at 298 K.

| | x_w | k^a | ΔH^\ddagger | $-\Delta S^\ddagger$ | $-\Delta C_p^\ddagger$ | $d\Delta C_p^\ddagger/dT$ | Temperature range/K | Number of points |
|----|-------|--------------------------|----------------------|------------------------------------|------------------------------------|------------------------------------|---------------------|------------------|
| | | 10^{-3} s^{-1} | kJ mol^{-1} | $\text{J mol}^{-1} \text{ K}^{-1}$ | $\text{J mol}^{-1} \text{ K}^{-1}$ | $\text{J mol}^{-1} \text{ K}^{-2}$ | | |
| 3M | 0.995 | 7.925 | 38.77(4) | 155.1(1) | 288(5) | | 273–316 | 45 |
| | 0.990 | 7.520 | 38.50(2) | 156.5(1) | 295(3) | | 273–326 | 59 |
| | 0.985 | 7.027 | 37.88(2) | 159.1(1) | 282(3) | | 273–326 | 67 |
| | 0.980 | 6.619 | 37.17(3) | 162.0(1) | 304(4) | | 273–328 | 68 |
| | 0.975 | 6.174 | 36.06(3) | 166.3(1) | 335(4) | | 273–328 | 72 |
| | 0.970 | 5.642 | 34.44(5) | 172.4(2) | 359(6) | | 273–328 | 80 |
| | 0.965 | 4.974 | 32.42(9) | 180.3(3) | 326(11) | | 273–333 | 71 |
| | 0.960 | 4.258 | 29.22(10) | 192.3(3) | 367(16) | | 273–321 | 52 |
| | 0.955 | 3.499 | 26.53(19) | 203.0(6) | 341(23) | | 273–313 | 55 |
| | 0.950 | 2.858 | 24.62(28) | 211.0(10) | 328(24) | | 273–303 | 38 |
| 4M | 0.995 | 7.921 | 38.71(7) | 155.3(2) | 282(8) | 2(1) | 273–316 | 45 |
| | 0.990 | 7.520 | 38.48(4) | 156.5(1) | 295(3) | 0(1) | 273–326 | 59 |
| | 0.985 | 7.027 | 37.87(6) | 159.1(2) | 282(3) | 0(1) | 273–326 | 67 |
| | 0.980 | 6.624 | 36.85(5) | 163.0(2) | 310(3) | 4(1) | 273–328 | 68 |
| | 0.975 | 6.182 | 35.74(6) | 167.4(2) | 344(3) | 4(1) | 273–328 | 72 |
| | 0.970 | 5.653 | 33.75(7) | 174.8(2) | 379(4) | 9(1) | 273–328 | 80 |
| | 0.965 | 5.027 | 30.84(7) | 185.5(2) | 401(4) | 17(1) | 273–333 | 71 |
| | 0.960 | 4.240 | 27.59(8) | 197.8(3) | 325(5) | 26(1) | 273–321 | 52 |
| | 0.955 | 3.463 | 25.48(10) | 206.6(3) | 111(17) | 41(2) | 273–313 | 55 |
| | 0.950 | 2.848 | 25.69(34) | 207.5(11) | –21(84) | 32(8) | 273–303 | 38 |
| 3E | 0.965 | 1.598 | 28.96(22) | 201.3(7) | 221(16) | | 273–343 | 84 |
| 4E | 0.965 | 1.658 | 26.73(6) | 208.5(2) | 451(6) | 24(1) | 273–343 | 84 |

^aCalculated from eqn. (1).

minimum at the mole fraction of water, x_w ca. 0.955. The minimum is deeper for the hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures than for that in *tert*-butyl alcohol–water mixtures, where it lies at x_w ca. 0.938.⁵

The heat capacity of activation, ΔC_p^\ddagger , for the neutral hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures seems to be independent of temperature from pure water to $x_w = 0.985$ (Table 1 and Figs. 1 and 2).

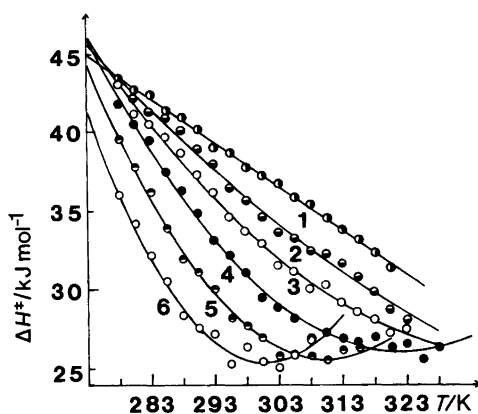


Fig. 1. Variation of ΔH^\ddagger for the neutral hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures as a function of temperature (T). The mole fraction of water is 0.985 (1), 0.975 (2), 0.970 (3), 0.965 (4), 0.960 (5), and 0.955 (6). The curves represent ΔH^\ddagger calculated from eqn. (1) in its four-parametric form. The marked dots represent ΔH^\ddagger calculated using the Arrhenius equation for ten degree intervals.

When the mole fraction of water decreases ΔC_p^\ddagger becomes gradually dependent on temperature. $d\Delta C_p^\ddagger/dT$ has a maximum value at x_w ca. 0.955, for which it is 41(2) $\text{J mol}^{-1} \text{ K}^{-2}$ (Table 1). $d^2\Delta C_p^\ddagger/dT^2$ is significant only for this hydrolysis at $x_w = 0.950$, but at this solvent mixture the temperature range is narrow, because of the limited solubility of *sec*-butyl alcohol in water at high temperatures.

The values of the enthalpy of activation can also be calculated from the Arrhenius equation for short temper-

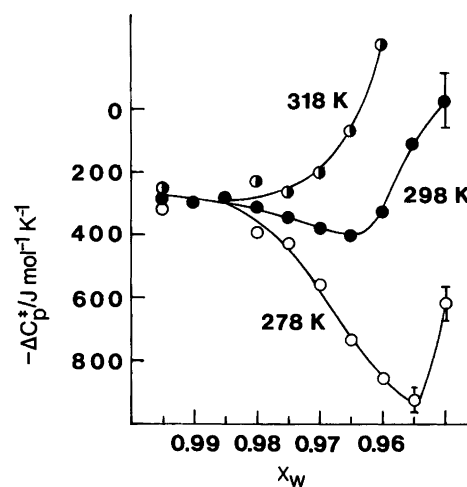


Fig. 2. Variation of ΔC_p^\ddagger , calculated from eqn. (1) in its four-parametric form, for the neutral hydrolysis of methyl trifluoroacetate as a function of the mole fraction of water (x_w) in *sec*-butyl alcohol–water mixtures at 278, 298 and 318 K.

ature intervals. These values are comparable to the values of ΔH^\ddagger calculated from eqn. (1). A visual picture for the dependence of ΔC_p^\ddagger on temperature is shown by a plot of ΔH^\ddagger vs. T (Fig. 1).

At low temperatures ΔC_p^\ddagger is large and negative, but increases with increasing temperature to a positive value. The change in mechanism from $B_{AC}3$ to S_N solvolysis is impossible in the hydrolysis of methyl trifluoroacetate. This large dependence of ΔC_p^\ddagger on temperature for the neutral hydrolysis of these esters is a property of the organic solvent component. This phenomenon, found earlier for the neutral hydrolysis of *p*-methoxyphenyl dichloroacetate,⁴ *p*-methoxyphenyl 2,2-dichloropropionate,⁴ methyl trifluoroacetate,⁷ and chloromethyl dichloroacetate⁶ in 2-butoxyethanol–water mixtures, and for that of the two last-mentioned esters in *tert*-butyl alcohol–water mixtures,⁵ and for that of methyl trifluoroacetate in 2-(2-butoxyethoxy)ethanol,⁸ has been explained by the temperature-dependent partitioning of the substrate between the two pseudo-microphases, water-rich and cosolvent-rich. Reaction occurs in both phases and at all stages of the reaction, the reactant is in equilibrium between the two microphases. A consequence is the large dependence of ΔC_p^\ddagger on temperature.¹²

At $x_w = 0.965$ (not in the minimum) $d\Delta C_p^\ddagger/dT$ for the hydrolysis of methyl trifluoroacetate is 17(1) J mol⁻¹ K⁻² but for ethyl trifluoroacetate is 24(1) J mol⁻¹ K⁻² (Table 1). This means that ΔC_p^\ddagger at high temperatures is more positive for the hydrolysis of a more hydrophobic ester. For the hydrolysis of methyl trifluoroacetate and chloromethyl dichloroacetate in 2-butoxyethanol–water mixtures Kanerva and Euranto⁶ have reported values of $d\Delta C_p^\ddagger/dT$ of 38(2) and 67(5) J mol⁻¹ K⁻², respectively. The more hydrophobic ester has a more positive value, as in this work. However, for that of the two last-mentioned esters in *tert*-butyl alcohol–water mixtures the values of this parameter seem to be almost equal. According to Holterman and Engberts⁴ the magnitude of ΔC_p^\ddagger at high temperatures is largely determined by the hydrophobicity of the substrate: a more hydrophobic substrate has a larger fraction in the cosolvent-rich microphase and leads to a more positive value for ΔC_p^\ddagger at high temperatures.

sec-Butyl alcohol, when added in a small amount to water, has a 'water structure making' effect and forms typical aqueous, TA, mixtures with water.¹³ Such a cosolvent promotes the formation of hydrogen bonds between the surrounding water molecules until a maximum water structure is reached. This maximum water structure can be seen as a minimum in the curve ΔC_p^\ddagger versus x_w .¹⁴ Larger amounts than that break the enhanced water structure. *sec*-Butyl alcohol is the fourth cosolvent in whose aqueous solutions ΔC_p^\ddagger for the neutral hydrolysis of esters depends highly on temperature. The others previously known are 2-butoxyethanol,^{4,6,7} 2-(2-butoxyethoxy)ethanol,⁸ and *tert*-butyl alcohol.⁵ These also form TA mixtures with water.¹³ For the hydrolysis of esters in aqueous mixtures of these solvents at low temperatures, ΔC_p^\ddagger passes

through a deep minimum when the mole fraction of water decreases. When the temperature is raised the minimum moves to more water-rich regions and vanishes (Fig. 2). The solvent effects on ΔC_p^\ddagger generally found in TA mixtures, are superseded by the solvent effects of the transition to a microphase structure.⁷ The position of this minimum depends on the hydrophobicity of the cosolvent for the hydrolysis of the same ester. The more hydrophobic the cosolvent, the more the minimum is shifted toward the medium richer in water. The position of the minimum at low temperatures for the neutral hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures lies at $x_w = 0.955$, but for that in *tert*-butyl alcohol–water mixtures is nearer to $x_w = 0.950$. A similar difference is noted for the positions of the minimum in the solubility of argon in these aqueous solvent mixtures.¹⁵ Also, the temperature, at which the density of an aqueous solution is at its maximum, reaches a maximum at a lower mole fraction of *sec*-butyl alcohol than for that of *tert*-butyl alcohol.¹⁶ At this mole fraction of water, where the previously mentioned minimum lies at low temperatures, ΔC_p^\ddagger for this reaction is highly dependent on temperature. $d\Delta C_p^\ddagger/dT$ for the hydrolysis of methyl trifluoroacetate in *sec*-butyl alcohol–water mixtures is 41(2), but in *tert*-butyl alcohol–water mixtures is 23(1) J mol⁻¹ K⁻².⁵

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