

Temperature and Solvent Effects on the Neutral Hydrolysis of Methyl Trifluoroacetate in 2-(2-Butoxyethoxy)ethanol–Water Mixtures

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The influence of organic solvents as a cosolvent in water on the activation parameters for the neutral hydrolysis of methyl trifluoroacetate has been studied earlier.^{1–3} On the basis of these studies the heat capacity of activation for this reaction seems in most cases to be negative, independent of temperature, and to go through a minimum in the water-rich region. So far only two cosolvents, *tert*-butyl alcohol and 2-butoxyethanol, are known, in whose aqueous solutions the heat capacity of activation, ΔC_p^\ddagger , for the neutral hydrolysis of esters is highly dependent on temperature.^{4–7} The temperature dependence of ΔC_p^\ddagger has been explained by the formation of two microphases. The aim of this work was to study the behaviour of the neutral hydrolysis of methyl trifluoroacetate in 2-(2-butoxyethoxy)ethanol–water mixtures.

Experimental

Methyl trifluoroacetate was a *purum* grade product from Fluka AG and was used without further purification. 2-(2-Butoxyethoxy)ethanol (Fluka AG *purum*) was purified by ion exchange, shaken with iron(II) chloride containing sulfuric acid, and distilled. 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 method⁸ from conductances measured during the reactions with a Beckman RC-18 conductimeter as described in detail earlier.⁹ The standard deviations of the calculated rate constants vary between 0.02 and 0.2%.

The thermodynamic activation parameters were calculated from an extended Arrhenius equation (1):

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

by the method of Clarke and Glew.¹⁰ The calculated values are shown in Table 1.

Results and discussion

The heat capacity of activation, ΔC_p^\ddagger , for the hydrolysis of methyl trifluoroacetate in 2-(2-butoxyethoxy)ethanol–water mixtures seems to be independent of temperature when the mole fraction of water (x_w) is 0.995, 0.990 and 0.965 (Table 1A and Figs. 1 and 2). For mole fractions of water from 0.985 to 0.970 $d\Delta C_p^\ddagger/dT$ is highly significant, especially when $x_w = 0.980$, for which $d\Delta C_p^\ddagger/dT$ is 18.3(4) J mol⁻¹ K⁻² (Table 1B). In addition, $d^2\Delta C_p^\ddagger/dT^2$ is significant for the hydrolysis at $x_w = 0.985$ and 0.975 (Table 1C).

A visual picture for the dependence of ΔC_p^\ddagger on temperature is shown by a plot of the enthalpy of activation, ΔH^\ddagger , vs. T (Fig. 1). The values of ΔH^\ddagger can also be calculated from Arrhenius equation for short temperature intervals. These values are comparable to the values of ΔH^\ddagger calcu-

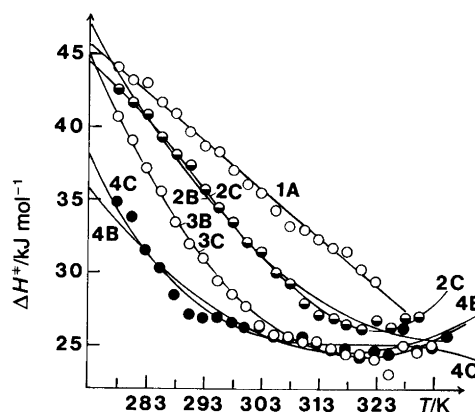


Fig. 1. Variation in ΔH^\ddagger for the neutral hydrolysis of methyl trifluoroacetate in 2-(2-butoxyethoxy)ethanol–water mixtures as a function of temperature (T), $x_w = 0.990$ (1), 0.985(2), 0.980(3) and 0.975(4). The curves represent ΔH^\ddagger calculated from eqn. (1) in its three- (A), four- (B), and five- (C) parametric form. The marked dots represent ΔH^\ddagger calculated using the Arrhenius equation for ten-degree intervals.

Table 1. Thermodynamic parameters of activation, calculated from eqn. (1) in its three-parametric (A), four-parametric (B) and five-parametric (C) form, for the neutral hydrolysis of methyl trifluoroacetate in (2-butoxyethoxy)ethanol–water mixtures at 298 K.

x_w	k^a	ΔH^\ddagger	$-\Delta S^\ddagger$	$-\Delta C_p^\ddagger$	$d\Delta C_p^\ddagger/dT$	$d^2\Delta C_p^\ddagger/dT^2$	Temperature range/K	Number of points	
	10^{-3} s^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-1}$	$\text{J mol}^{-1} \text{ K}^{-2}$	$\text{J mol}^{-1} \text{ K}^{-3}$			
A	0.995	7.600	38.03(3)	157.9(1)	321(4)		273–323	73	
	0.990	6.866	37.22(3)	161.5(1)	330(4)		273–328	76	
	0.985	5.939	34.03(6)	173.4(2)	366(7)		273–336	86	
	0.980	4.772	30.57(10)	186.8(3)	310(11)		273–338	86	
	0.975	3.551	27.74(9)	198.8(3)	139(8)		273–341	77	
	0.970	2.760	27.65(4)	201.2(1)	97(5)		273–333	71	
	0.965	2.172	28.48(4)	200.4(1)	81(4)		273–333	64	
B	0.995	7.598	37.90(8)	158.4(3)	320(4)	1.7(11)	273–323	73	
	0.990	6.866	37.06(7)	162.0(2)	332(4)	2.0(8)	273–328	76	
	0.985	5.972	32.99(7)	176.8(2)	410(4)	10.9(7)	273–336	86	
	0.980	4.837	28.64(5)	193.2(2)	408(3)	18.3(4)	273–338	86	
	0.975	3.602	26.75(7)	202.0(2)	222(6)	10.9(6)	273–341	77	
	0.970	2.765	27.12(7)	202.9(2)	117(4)	5.9(7)	273–333	71	
	0.965	2.174	28.31(9)	200.9(3)	89(6)	1.8(8)	273–333	64	
C	0.995	7.603	37.89(9)	158.4(3)	335(17)	1.9(11)	0.3(3)	273–323	73
	0.990	6.872	37.08(7)	162.0(2)	352(13)	1.5(9)	0.4(2)	273–328	76
	0.985	5.995	33.32(7)	175.7(2)	473(9)	6.0(8)	1.0(1)	273–336	86
	0.980	4.834	28.60(6)	193.3(2)	401(7)	18.9(7)	-0.1(1)	273–338	86
	0.975	3.592	26.34(9)	203.4(3)	179(8)	16.6(10)	-0.7(1)	273–341	77
	0.970	2.759	27.00(7)	203.4(2)	80(10)	8.1(9)	-0.6(2)	273–333	71
	0.965	2.179	28.47(10)	200.4(3)	124(14)	-0.8(12)	0.6(2)	273–333	64

^aCalculated from eqn. (1).

lated from eqn. (1) which thus provides a test of the chosen equation. As anticipated, ΔH^\ddagger , calculated from the five-parametric eqn. (1), fits the values best. The four-parametric eqn. (1), however, correlates satisfactorily. There are only small deviations at low and high temperatures, where the experimental accuracy is low.

At low temperatures ΔC_p^\ddagger is large and negative, but increases with increasing temperature to zero or to a slightly positive value (Fig. 2). Positive values of ΔC_p^\ddagger arise from the change in mechanism from $B_{AC}3$ to S_N solvolysis

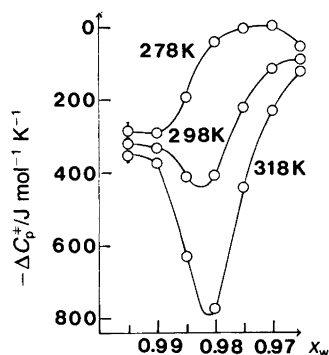


Fig. 2. Variation of ΔC_p^\ddagger , calculated from eqn. (1) in its four-parametric form, for the neutral hydrolysis of methyl trifluoroacetate as a function of the mole fraction of water (x_w) in 2-(2-butoxyethoxy)ethanol–water mixtures at 278, 298 and 318 K.

when the temperature is raised, as in the neutral hydrolysis of bromomethyl chloroacetate.¹¹ The corresponding change in mechanism is impossible in the neutral hydrolysis of methyl trifluoroacetate.

The large dependence of ΔC_p^\ddagger on temperature for the neutral hydrolysis of esters in 2-butoxyethanol–water and *tert*-butyl alcohol–water mixtures has been interpreted on the basis of the formation of microphases or aggregates when the temperature is raised. Holterman and Engberts⁴ have examined the hydrolysis of *p*-methoxyphenyl dichloroacetate and 2,2-dichloropropionate in 2-butoxyethanol–water mixtures. When the mole fraction of water is 0.980, ΔH^\ddagger increases with increasing temperature. This may indicate that a possible minimum in the plot of ΔH^\ddagger vs. T is below the temperature at which the reactions were studied. They explained such behaviour by taking into account a temperature-dependent partitioning of the substrate between the two microphases. The magnitude of ΔC_p^\ddagger 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 .

Kanerva and Euranto^{5–7} have observed for the hydrolysis of methyl trifluoroacetate and chloromethyl dichloroacetate in *tert*-butyl alcohol–water⁵ and 2-butoxyethanol–water^{6,7} mixtures, when the mole fraction of water is about 0.95 and 0.98, that ΔC_p^\ddagger is highly temperature dependent. According to Kanerva,⁷ the solvent effects on ΔC_p^\ddagger , gener-

ally found in typical aqueous (TA) solutions, are surpassed by the effects of the transition to a microphase structure when the temperature is raised.

The heat capacity of activation is a sensitive indicator of solvent effects. ΔC_p^\ddagger for the hydrolysis of methyl trifluoroacetate in 2-(2-butoxyethoxy)ethanol–water mixtures goes through a very deep minimum when the mole fraction of water is about 0.980 (Fig. 2). 2-(2-Butoxyethoxy)ethanol, when added in small amounts to water, has a ‘water-structure making’ effect and forms TA mixtures with water as glycol ethers.¹² Usually ΔC_p^\ddagger for the solvolysis in TA mixtures has a minimum at the mole fraction of water, where the breaking of the solvent structure occurs.¹³ The minimum in the plot of ΔC_p^\ddagger vs. x_w becomes more shallow and moves to the higher water content when the temperature is raised. This is observed also for the hydrolysis of methyl trifluoroacetate in 2-butoxyethanol–water⁷ and *tert*-butyl alcohol–water⁵ mixtures. Roux *et al.*¹⁴ have found that the pseudo-microphase-transition concentration decreases with increasing temperature for 2-butoxyethanol–water mixtures. The mole fraction of water, where the maximal values for the temperature dependence of ΔC_p^\ddagger is observed, is approximately similar, but is not necessarily identical in these solvent mixtures.

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