Temperature Dependence of Activation Parameters in the Neutral Ester Hydrolysis in Acetone+Water Solutions

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The kinetics of the neutral hydrolyses of methyl trifluoroacetate, 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate in acetone+water solutions over a wide temperature range have been studied. $\Delta C_p^{\neq}/J \; mol^{-1} \; K^{-1}$ for methyl trifluoroacetate at x_w about 0.971 and for 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate at x_w about 0.986 has the minimum values −285, −224 and −204, respectively. The minima of $\Delta C_p^{\neq}$ occur in the neighbourhood of the water concentration where the enhancement of water structure in acetone+water solutions is known to be at its maximum. The difference between the values of $\Delta C_p^{\neq}$ from water to the minimum seems to be about 40, 20 and 10 J $mol^{-1} \; K^{-1}$ for methyl trifluoroacetate, chloromethyl dichloroacetate and 2-methoxyethyl trifluoroacetate, respectively.

We have previously studied the solvent effects on activation parameters, activation enthalpy ($\Delta H^{\neq}$), activation entropy ($\Delta S^{\neq}$) and especially the heat capacity of activation ($\Delta C_p^{\neq}$) for the neutral ester hydrolysis in aqueous acetonitrile,[1-3] dimethyl sulfoxide,[4] acetone,[1,2] 2-butanone[5] and alcohols.[6-9] The kinetic parameters have been interpreted in terms of the Clarke-Glew method[10] although the reactions are assumed to take place as a general base-catalysed ester hydrolysis, $B_{AC}3$, with a tetrahedral intermediate.[11] On the basis of the consideration of Kurz and Ehrhardt[12] the partitioning of the intermediate is known to have only a negligible effect on the heat capacity of activation. Blandamer et al.[13,14] recently criticized this interpretation and preferred the two-step Albery-Robinson mechanism.[15] However,

as we recently showed,[16] there seems to be no reason, based on experimental data, why the Albery-Robinson model should be preferred to the Clarke-Glew method, when the non-Arrhenius behaviour of solvolytic reactions is studied.

The aim of the present work was to study the neutral hydrolyses of methyl trifluoroacetate, 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate in water-rich acetone solutions. Kinetic data for the neutral hydrolyses of methyl trifluoroacetate and chloromethyl dichloroacetate in various acetone+water solutions have been previously published by Cleve.[1,2] Some peculiar results found when trying to expand the study of the hydrolysis of the latter ester to additional acetone+water solutions, led us to reinvestigate also the hydrolysis of the former ester and to check some of the results independently in two laboratories (Universities of Turku and Oulu).

EXPERIMENTAL

Methyl trifluoroacetate, a commercial product, (E. Merck AG, *zur Synthese*), was redistilled before use. 2-Methoxyethyl trifluoroacetate and chloromethyl dichloroacetate were prepared as described previously.[17,18] The solvent mixtures were prepared by diluting a known weight of distilled water with acetone (E. Merck AG, zur Analyse) to a known volume in a volumetric flask and weighing the mixture to obtain the accurate mole fraction of water (x_w). The initial ester concentrations were about 10^{-4} M. The temperature was stable to about 0.01 K.

Table 1. Temperature range (T/K), number of kinetic runs (N), calculated first-order rate coefficients (k/s^{-1}), activation enthalpies ($\Delta H^{\ddagger}$/J mol^{-1}), activation entropies ($\Delta S^{\ddagger}$/J mol^{-1} K^{-1}) and the heat capacities of activation ($\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1}), calculated from eqn. (1) in its three-parameter form for the neutral hydrolysis of methyl trifluoroacetate in acetone+water solutions with the mole fraction of water (x_w) at 298.15 K.

x_w	T	N	$10^3 k$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$-\Delta C_p^{\ddagger}$
A. (The present work)						
1.000	273−313	24	8.459	39700(40)	151.4(1)	245(5)
	273−321	20	8.422	39760(40)	151.3(1)	249(6)
0.986	273−321	20	7.062	39050(60)	155.1(2)	254(8)
0.971*	273−321*	20*	5.778*	38150(80)*	159.8(3)*	275(11)*
	273−321*	70*	5.703*	37620(20)*	161.7(1)*	285(3)*
0.945	273−321	20	3.960	36630(110)	168.1(4)	263(16)
0.914	273−321	20	2.553	34920(90)	177.5(3)	241(13)
0.857	273−321	22	1.069	34050(90)	187.6(3)	238(14)
	273−321	20	1.044	34490(80)	186.3(3)	244(12)
0.790	273−321	20	0.377	35020(110)	193.0(4)	185(16)
B. (Cleve[2])						
1.000	273−308	19	8.54	39760(140)	151.2(5)	266(13)
0.971	273−308	10	5.65	36400(320)	166.0(10)	338(33)
0.914	273−318	12	2.50	34190(160)	180.0(5)	316(21)
0.790	253−318	16	0.386	34870(200)	193.3(7)	246(11)
0.683	268−318	6	0.112	36110(190)	199.4(6)	200(20)

* Kinetic measurements made independently at the Universities of Turku and Oulu.

The reaction was followed conductometrically as described previously.[19] Actually the concentrations of trifluoroacetic acid in the hydrolyses of methyl and 2-methoxyethyl trifluoroacetates and that of hydrochloric and dichloroacetic acids in the hydrolysis of chloromethyl dichloroacetate were measured.

The rate coefficients were calculated using Guggenheim's method.[20] The thermodynamic activation parameters were calculated by an extended Arrhenius eqn. (1),

$$\ln k = A + B/T + C \ln T + DT + \dots + \varepsilon \qquad (1)$$

employing the method of Clarke and Glew[10] after an orthogonalization procedure.

The kinetic data in Tables 1A and 3A differ somewhat from the earlier data in Tables 1B and 3B. It is not easy to explain these differences. Of course, the kinetic method has been improved during the past years, *e.g.*, some of the earlier measurements were performed using a different conductivity cell. Further, the kinetic measurements are now performed at a higher number of temperatures, more evenly distributed over the temperature range used. However, the agreement between the older and redetermined data

has been generally found to be good as recently shown in the case of the neutral hydrolysis of methyl trifluoroacetate in dimethyl sulfoxide+water solutions.[19] One explanation might be found from the behaviour of acetone+water solutions itself. Thus the reproducibility of the rate coefficients is not quite as good in aqueous acetone solutions as, *e.g.*, in aqueous alcohols and dimethyl sulfoxide, although the calculated standard errors of the rate coefficients are similar (clearly less than 0.1 %).[6-9,19] The evaporation of acetone from its water-rich solutions during the mixing of the ester with the solvent system may be of importance, especially at higher temperatures. On the other hand, the evaporation of acetone from the 5-litre storage bottle (at 298 K), when aliquots of the solution were transferred to the conductivity cell, was shown to increase systematically the rate coefficients in an experimental series containing 150 runs for the hydrolysis of 2-methoxyethyl trifluoroacetate in the acetone+water solution at x_w 0.914. To minimize this kind of systematic errors in rate coefficients, the acetone+water solutions used in this work have been prepared to ½-litre or 1-litre volumetric flasks. Thus the solvent mixtures for the parallel determinations

Table 2. Temperature range (T/K), number of kinetic runs (N), calculated first-order rate coefficients (k/s^{-1}), activation enthalpies ($\Delta H^{\ddagger}$/J mol^{-1}), activation entropies ($\Delta S^{\ddagger}$/J mol^{-1} K^{-1}) and the heat capacities of activation ($\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1}), calculated from eqn. (1) in its three-parameter form for the neutral hydrolysis of 2-methoxyethyl trifluoroacetate in acetone+water solutions with the mole fraction of water (x_w) at 298.15 K.

x_w	T	N	$10^3 k$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$-\Delta C_p^{\ddagger}$
A. (The present work)						
1.000	273–318	23	8.433	38140(40)	156.7(1)	224(6)
	273–318	10	8.418	38090(70)	156.9(2)	212(10)
0.995	273–318	11	7.661	37630(40)	159.2(1)	223(6)
0.986	273–318	10	6.845	37410(60)	160.9(2)	224(8)
0.971	273–328	12	5.396	36750(60)	165.1(2)	223(8)
0.945	273–333	13	3.545	35790(90)	171.8(3)	202(10)
0.914	273–333	14	2.251	34890(60)	178.6(2)	213(7)
0.857	273–333	13	0.924	34960(110)	185.7(4)	218(13)
	273–328	14	0.902	34950(110)	186.0(4)	176(15)
0.790	273–333	17	0.324	36270(130)	190.1(4)	158(14)
B. (Cleve[17])						
1.000	273–338	13	8.32	37710(80)	158.3(3)	234(8)

have been prepared separately and may occasionally differ somewhat from each other (see Tables 1–3).

RESULTS AND DISCUSSION

Kinetic data at 298.15 K for the neutral hydrolyses of methyl trifluoroacetate, 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate in the acetone+water solutions studied together with the previous data for methyl trifluoroacetate and chloromethyl dichloroacetate are given in Tables 1–3. As seen from the Tables, acetone decreases the rates of the hydrolyses considerably, the retarding effect being greatest for chloromethyl dichloroacetate and very similar for the two esters of trifluoroacetic acid.

In solvent mixtures, rich in water, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ usually counteract each other first decreasing to a minimum. It has been generally thought that the occurrence of the minimum and its position as a function of x_w are connected with the water structure. In accordance with this, there seems to be a minimum in the concentration dependence of $\Delta H^{\ddagger}$ for the hydrolyses of the present esters in acetone+water solutions (Tables 1–3). The position of the minimum occurs at x_w about 0.86, 0.91 and 0.96 at 298 K

for the hydrolyses of methyl trifluoroacetate, 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate, respectively, the depth of the minimum being largest for methyl trifluoroacetate and smallest for chloromethyl dichloroacetate. On the other hand, $\Delta S^{\ddagger}$ for the neutral hydrolysis of chloromethyl dichloroacetate at 298 K goes through a minimum value at x_w about 0.91, but for the esters of trifluoroacetic acid $\Delta S^{\ddagger}$ decreases continuously in the acetone+water solutions used. This behaviour of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ vs. x_w has been found to be typical for the hydrolyses of methyl trifluoroacetate and chloromethyl dichloroacetate in aqueous methanol, 2-butanone, dimethyl sulfoxide and acetonitrile solutions, too.[1-5,9]

The present work confirms that the heat capacity of activation for the neutral hydrolysis of methyl trifluoroacetate has a minimum in acetone+water solutions in the neighbourhood of the mole fraction 0.971 of water (Tables 1A and 1B). Also the two other esters behave similarly, the minimum values of $\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1} at x_w about 0.986 being -224 and -204 for the neutral hydrolyses of 2-methoxyethyl trifluoroacetate and chloromethyl dichloroacetate, respectively (Tables 2A and 3A). This is in accordance with the well-known fact that acetone in its dilute aqueous solutions behaves as a

Table 3. Temperature range (T/K), number of kinetic runs (N), calculated first-order rate coefficients (k/s^{-1}), activation enthalpies ($\Delta H^{\ddagger}$/J mol^{-1}), activation entropies ($\Delta S^{\ddagger}$/J mol^{-1} K^{-1}) and the heat capacities of activation ($\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1}), calculated from eqn. (1) in its three-parameter form for the neutral hydrolysis of chloromethyl dichloroacetate in acetone+water solutions with the mole fraction of water (x_w) at 298.15 K.

x_w	T	N	$10^3 k$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$-\Delta C_p^{\ddagger}$
A. (The present work)						
1.000	273–303	11	14.60	39180(90)	148.7(3)	182(8)
0.995	273–306	17	13.07	38750(90)	151.0(3)	191(10)
0.986	273–308	13	11.41	38080(60)	154.4(2)	204(7)
0.971	273–308	12	8.61	37400(40)	159.0(1)	203(5)
0.963	273–308	11	7.37	37200(100)	161.0(3)	197(10)
0.956	273–308	8	6.21	37180(90)	162.5(3)	186(9)
0.914	273–308	15	2.97	37830(160)	166.4(5)	138(17)
0.790	273–328	12	0.386	44600(110)	160.7(4)	110(15)
B. (Cleve [1])						
1.000	273–308	11	14.58	38070(670)	152.3(21)	222(67)
0.914	268–308	9	2.93	37530(580)	167.4(21)	293(46)
0.683	267–328	24	0.283	45560(250)	159.8(8)	234(25)

"typically aqueous" (TA) solute, enhancing water-water interactions through hydrophobic hydration.[21] There are a number of indications that this enhancement of water structure is at a maximum at x_w about 0.95 at 298 K, *i.e.*, at about the water concentration where $\Delta C_p^{\ddagger}$ has its minimum values for the neutral hydrolyses of the present esters in the acetone+water solutions studied (Tables 1–3).

According to the present results in Tables 1A–3A, the difference between the values of $\Delta C_p^{\ddagger}$ from water to the minimum, $\Delta\Delta C_p^{\ddagger}=\Delta C_p^{\ddagger}$(H$_2$O)$-\Delta C_p^{\ddagger}$(minimum), becomes smaller when the ester is changed from methyl trifluoroacetate through chloromethyl dichloroacetate to 2-methoxyethyl trifluoroacetate, $\Delta\Delta C_p^{\ddagger}$ being about 40, 20 and 10 J mol^{-1} K^{-1}, respectively. These results are in accordance with the minimum values of $\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1} -324 ± 6 at x_w 0.843 ($\Delta\Delta C_p^{\ddagger}$ about 80 J mol^{-1} K^{-1}) for methyl trifluoroacetate and -244 ± 13 at x_w 0.950 ($\Delta\Delta C_p^{\ddagger}$ about 60 J mol^{-1} K^{-1}) for chloromethyl dichloroacetate in another TA solvent system, methanol+water.[9] For the hydrolysis of methyl trifluoroacetate in 2-butanone+water solutions, $\Delta C_p^{\ddagger}$ has the minimum value -314 ± 5 J mol^{-1} K^{-1} at x_w 0.990 ($\Delta\Delta C_p^{\ddagger}$ about 70 J mol^{-1} K^{-1}).[5]

For the neutral hydrolysis of the esters now studied in acetone+water solutions, $\Delta C_p^{\ddagger}$ is

usually independent of the temperature on the confidence level of 95 % according to the Student's t-test. An exception is the neutral hydrolysis of chloromethyl dichloroacetate at x_w 0.986 and 0.963 for which $\Delta C_p^{\ddagger}$ seems to depend on temperature over the temperature range given in Table 3A, d$\Delta C_p^{\ddagger}$/dT being -5.7 ± 1.6 and $+6.3\pm2.3$ J mol^{-1} K^{-2}, respectively. Taking into account the limited temperature range and achieved accuracy in the kinetic measurements, it is usually found to be unjustifiable to use eqn. (1) in its four-parameter form. Therefore, the kinetic parameters in Tables 1–3 have been calculated only with three parameters. However, if also rate data measured at temperatures higher than 308 K are included, $\Delta C_p^{\ddagger}$ for the hydrolysis of chloromethyl dichloroacetate in acetone+water solutions becomes temperature dependent at some additional mole fractions of water. Thus $\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1} calculated from the four-parameter form of eqn. (1) increases from -233 ± 25 at 273 K to -157 ± 25 at 313 K at x_w 0.971, from -279 ± 27 at 273 K to -68 ± 27 at 318 K at x_w 0.963 and from -266 ± 23 at 273 K to -43 ± 23 at 323 K at x_w 0.956. However, when interpreting these effects one must take into account, *e.g.*, the possible evaporation of acetone at higher temperatures or some other systematic errors. On the other hand, the recent results for the neutral

ester hydrolysis in *tert*-butyl alcohol+water and 2-butoxyethanol+water solutions, have shown extraordinary solvent effects on $\Delta C_p^{\ddagger}$ in accordance with the microphase separations which take place in the vicinity of the water concentrations where the hydrophobic hydration of these solutions is at its maximum.[6-8]

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