Temperature Dependence of the Neutral Ester Hydrolysis of Chloromethyl Dichloroacetate in 2-Butoxyethanol–Water Mixtures in a Wide Temperature Range

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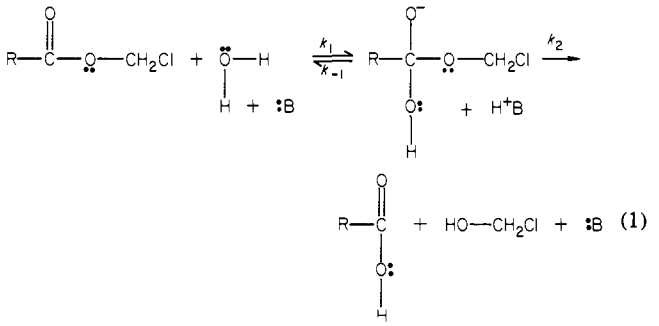
Abstract: Rates of the water-catalyzed hydrolysis of chloromethyl dichloroacetate in 2-butoxyethanol–water mixtures in the temperature range from 2.5 to 45 °C at 2.5 °C intervals were measured conductometrically when the mole fractions of water were 0.988, 0.984, 0.981, 0.980, and 0.975. The Arrhenius plots for the reactions are S shaped when the mole fraction of water is from 0.984 to 0.975. Thus the sign of the heat capacity of activation depends on temperature. At higher temperatures $\Delta C_p^{\ddagger}$ is positive, in agreement with the results obtained by Holterman and Engberts[1] for other esters. The positive $\Delta C_p^{\ddagger}$ was shown not to be caused by a change in reaction mechanism. At lower temperatures the reaction gives a negative $\Delta C_p^{\ddagger}$, in agreement with other aqueous solutions studied earlier. The estimated $\Delta C_p^{\ddagger}$ values at lowest temperatures are exceptionally negative.

Holterman and Engberts[1] recently found a large positive value for $\Delta C_p^{\ddagger} = d\Delta H^{\ddagger}/dT$ in the neutral hydrolysis of *p*-methoxyphenyl dichloroacetate ($\Delta C_p^{\ddagger} = +224$ cal K^{-1} mol^{-1}) and 2,2-dichloropropionate ($\Delta C_p^{\ddagger} = +342$ cal K^{-1} mol^{-1}) in a 2-butoxyethanol–water system at the mole fraction 0.98 of water. This is in disagreement with the negative values of $\Delta C_p^{\ddagger}$ found for different solvolytic reactions in water and aqueous solvent mixtures.[2-5] For instance, in the neutral hydrolysis of chloromethyl dichloroacetate, the value of $\Delta C_p^{\ddagger}$ has been found to be -43.5 ± 2.0 cal K^{-1} mol^{-1} in water.[5] In methanol–water mixtures there seems to be a minimum when the mole fraction of water is 0.95 ($\Delta C_p^{\ddagger} = -58.3 \pm 3.0$ cal K^{-1} mol^{-1}).[5] Like methanol, 2-butoxyethanol is a "water structure-making" (TA) solvent.[6,7] Usually the value of $\Delta C_p^{\ddagger}$ decreases when small amounts of such a solvent are added to water.[3-5] Therefore, the value of $\Delta C_p^{\ddagger}$ could be expected to be smaller in 2-butoxyethanol–water mixtures, rich in water, than in pure water. The aim of this work was to study the behavior of the neutral hydrolysis of $CHCl_2COOCH_2Cl$ in 2-butoxyethanol–water mixtures when the mole fraction of water is close to 0.98. The reaction is assumed to take place as a general-base-catalyzed ester hydrolysis, $B_{AC}3$, with a second water molecule acting as a general base :B.[8] In the case of chloromethyl esters, the mechanism can be written in the form of eq 1 and 2. The possible concurrent rate-determining nucleophilic displacement of chlorine of the chloromethyl group is insignificant in our reaction conditions.[3]



(1)

$$k_2,\ k_{-1} \gg k_1$$

$$ClCH_2OH \xrightarrow{\text{fast}} CH_2O + H^+ + Cl^- \qquad (2)$$

Experimental Section

The ester was prepared by chlorinating methyl dichloroacetate with gaseous chlorine[9] and purified by careful fractional distillation using a Todd apparatus, with all disturbing impurities being removed. The solvent mixtures were prepared by diluting a known weight of distilled water with 2-butoxyethanol (Fluka AG, purum), purified by ion exchange and redistillation, to a known volume in a volumetric flask. The initial ester concentrations were about 0.0001 M. The temperature was stable to about 0.01 K.

The reaction was followed conductometrically with a Beckman RC-18 conductometer, with concentrations of the acids being measured. In theory, the degree of reaction is not a precise linear function of conductance. It can be estimated, however, that if the concentration of the acids is such as in our kinetic experiments, the error introduced in rate coefficients is about 0.1% and is even partly compensated by Guggenheim's calculation method. Further, the effect is quite similar at different temperatures and does not affect the calculated activation parameters. Guggenheim's method[10] was used, e.g., because the final value may be in error as adsorption or desorption may cause some drift in longer time periods. Final values were measured in some cases, and the obtained rate coefficients were essentially the same. The standard deviations of the rate coefficients were in general less than 0.05% but may sometimes be about 0.1%. The conductometric method and the accuracy of $\Delta C_p^{\ddagger}$ determinations will be described in greater detail elsewhere.[11]

Results and Discussion

The experimental rate coefficients for the neutral ester hydrolysis of $CHCl_2COOCH_2Cl$ in 2-butoxyethanol–water mixtures are given in Table I, and their logarithms are plotted vs. $1/T$ in Figure 1. The plots are S shaped in four different 2-butoxyethanol–water mixtures (x_w 0.984, 0.981, 0.980, and 0.975). Thus even the sign of $\Delta C_p^{\ddagger}$ depends on the reaction temperatures used:

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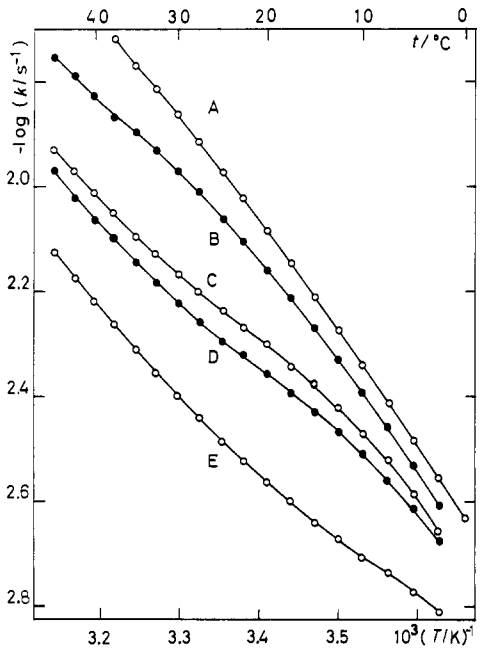

Figure 1. Arrhenius plots of $-\log k$ vs. $(1/T)$ for the neutral hydrolysis of chloromethyl dichloroacetate in 2-butoxyethanol–water. $x_w = 0.988$ (A), 0.984 (B), 0.981 (C), 0.980 (D), and 0.975 (E).

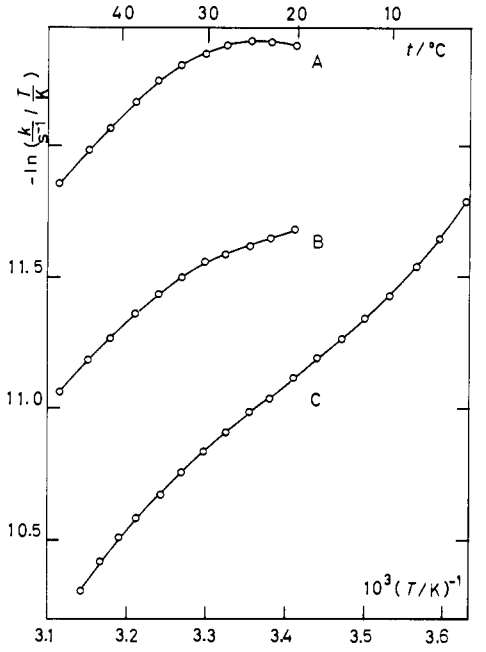

Figure 2. Eyring plots of $-\ln (k/T)$ vs. $(1/T)$ for the neutral hydrolysis of esters in 2-butoxyethanol–water at $x_w = 0.98$. Comparison of the present results (C) with those of Holterman and Engberts[1] (A and B). (A) *p*-Methoxyphenyl 2,2-dichloropropionate ($-\ln (k/t) - 3$); (B) *p*-methoxyphenyl dichloroacetate ($-\ln (k/T) - 2$); (C) chloromethyl dichloroacetate.

at higher temperatures $\Delta C_p^{\ddagger}$ is positive, but at lower temperatures negative. Further, it is seen that, in the mole fraction range studied, the smaller the water content of the solution, the wider is the temperature range that gives a positive value for $\Delta C_p^{\ddagger}$. Holterman and Engberts[1] did their experiments in the temperature range from 20 to 48 °C. So our results with a different ester confirm their positive $\Delta C_p^{\ddagger}$ (Figure 2) but also show that at lower temperatures the reaction gives a negative $\Delta C_p^{\ddagger}$, which is in agreement with other aqueous solutions studied earlier.

Positive values of $\Delta C_p^{\ddagger}$ have earlier been found for the hydrolyses of 4-methoxybenzyl trifluoroacetate[12] and bromomethyl chloroacetate.[13] In both cases the result was explained by assuming that the reaction mechanism changes when the temperature is raised, in the former case from $B_{Ac}3$ to $B_{Al}1$, in the latter from $B_{Ac}3$ to a nucleophilic substitution of bromine, S_N2. Also, Holterman and Engberts[1] considered a change in mechanism as a possible, although improbable, explanation for their results. Indeed, in their case a change in mechanism from $B_{Ac}3$ to $B_{Al}1$ is possible. Because the electronegativities of the alkyl components of their and our esters are very different, it is highly improbable that for both esters the same or some other change in mechanism takes place at the same conditions.

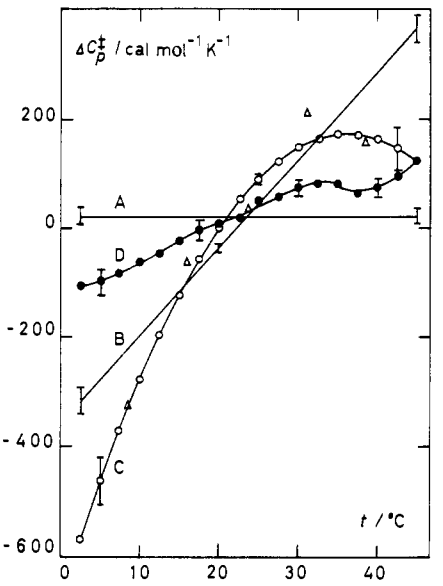

Figure 3. Values of $\Delta C_p^{\ddagger}$ at different temperatures for the neutral hydrolysis of chloromethyl dichloroacetate in 2-butoxyethanol–water with x_w 0.980, calculated by the method of Clarke and Glew,[14] with three (A), four (B), and five (C) parameters (eq 3), by the method of Blandamer et al.[15] (D), and from $\Delta H^{\ddagger}$ values for narrow temperature ranges (triangles, see text). Standard deviations for some points indicated by bars.

The Arrhenius plots (Figure 1) indicate that $\Delta H^{\ddagger}$ and even $\Delta C_p^{\ddagger}$ are temperature dependent. Their values can be estimated, e.g., by calculating $\Delta H^{\ddagger}$ for short temperature intervals. The results obtained by the method of least squares for $x_w = 0.980$ employing 5-K intervals with three temperatures are indicated in Figure 3. It is better, however, to employ eq 3 as proposed

$$R \ln k = R \ln \frac{\mathbf{k}T}{h} - \frac{1}{\theta}\Delta G_{\theta}^{\ddagger} + \left(\frac{1}{\theta} - \frac{1}{T}\right)\Delta H_{\theta}^{\ddagger} + \left(\frac{\theta}{T} - 1 + \ln \frac{T}{\theta}\right)\Delta C_{p\theta}^{\ddagger} + \frac{\theta}{2}\left(\frac{T}{\theta} - \frac{\theta}{T} - 2 \ln \frac{T}{\theta}\right)\left(\frac{d\Delta C_p^{\ddagger}}{dT}\right)_{\theta} + \frac{\theta^2}{12}\left(\frac{T^2}{\theta^2} - 6\frac{T}{\theta} + 3 + 2\frac{\theta}{T} + 6 \ln \frac{T}{\theta}\right)\left(\frac{d^2\Delta C_p^{\ddagger}}{dT^2}\right)_{\theta} + \ldots \quad (3)$$

by Clarke and Glew.[14] Calculations up to seven parameters show that the five-parametric equation (3) is flexible enough to correctly represent the data. In general, the first five parameters differ from zero at the 98% level. The values of $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ calculated from the five-parametric equation (3) are presented in Table I and $\Delta C_p^{\ddagger}$ values for the three to five parameter equations ($x_w = 0.980$) in Figure 3. Blandamer et al.[15] proposed that a method, actually based on eq 3 with three parameters, can be used to estimate $\Delta C_p^{\ddagger}$. The method was employed in the present case (Figure 3). It is seen, as stated by Blandamer et al., that the method underestimates the temperature effect on $\Delta C_p^{\ddagger}$. All three methods, however, give similar estimates for $\Delta C_p^{\ddagger}$, which is highly

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Table I. Kinetic Data for the Neutral Hydrolysis of Chloromethyl Dichloroacetate in 2-Butoxyethanol-Water Mixtures

x_w	T, °C	k_{obsd}, 10^{-3} s^{-1}	$\Delta H^{\ddagger}$, cal mol^{-1}	$\Delta C_p^{\ddagger}$, cal mol^{-1} K^{-1}
0.988	0.07	2.3261 ± 0.0003	9980 ± 150	−33 ± 35
	2.60	2.7776 ± 0.0006	9880 ± 80	−41 ± 25
	4.99	3.2691 ± 0.0006	9780 ± 40	−47 ± 17
	7.41	3.8537 ± 0.0010	9660 ± 30	−54 ± 10
	10.05	4.5452 ± 0.0014	9510 ± 40	−60 ± 5
	12.53	5.3010 ± 0.0012	9350 ± 40	−66 ± 5
	15.02	6.1362 ± 0.0016	9180 ± 30	−71 ± 6
	17.59	7.1319 ± 0.0014	8990 ± 30	−76 ± 7
	20.00	8.209 ± 0.003	8800 ± 30	−80 ± 7
	22.70	9.492 ± 0.005	8580 ± 30	−84 ± 6
	24.95	10.667 ± 0.003	8390 ± 40	−87 ± 5
	27.65	12.152 ± 0.009	8150 ± 40	−90 ± 6
	30.14	13.689 ± 0.006	7920 ± 30	−93 ± 11
	32.67	15.338 ± 0.012	7680 ± 50	−95 ± 18
	35.05	17.041 ± 0.015	7460 ± 90	−96 ± 27
	37.71	19.086 ± 0.015	7200 ± 170	−97 ± 38
0.984	2.50	2.471 ± 0.003	9650 ± 350	−12 ± 70
	5.03	2.937 ± 0.003	9570 ± 200	−54 ± 52
	7.50	3.484 ± 0.003	9390 ± 110	−89 ± 37
	7.51	3.467 ± 0.004	9390 ± 110	−89 ± 37
	10.05	4.042 ± 0.002	9130 ± 70	−119 ± 24
	12.51	4.673 ± 0.002	8810 ± 80	−140 ± 15
	15.06	5.358 ± 0.003	8430 ± 80	−156 ± 10
	17.45	6.108 ± 0.003	8040 ± 80	−165 ± 10
	20.02	6.924 ± 0.003	7610 ± 60	−168 ± 12
	22.67	7.845 ± 0.003	7170 ± 60	−163 ± 13
	24.91	8.673 ± 0.004	6820 ± 60	−153 ± 13
	27.64	9.769 ± 0.004	6420 ± 70	−135 ± 11
	30.09	10.708 ± 0.004	6120 ± 80	−111 ± 9
	32.63	11.690 ± 0.006	5880 ± 80	−80 ± 11
	35.01	12.705 ± 0.007	5730 ± 80	−44 ± 17
	37.69	13.577 ± 0.009	5670 ± 80	3 ± 29
	37.69	13.634 ± 0.018	5670 ± 80	3 ± 29
	40.04	14.912 ± 0.015	5730 ± 130	50 ± 41
	42.54	16.237 ± 0.015	5930 ± 240	107 ± 57
	42.54	16.213 ± 0.009	5930 ± 240	107 ± 57
	45.06	17.600 ± 0.009	6270 ± 390	171 ± 75
0.981	2.61	2.2101 ± 0.0006	10380 ± 210	−631 ± 44
	4.99	2.599 ± 0.002	9000 ± 130	−530 ± 33
	7.46	3.002 ± 0.003	7810 ± 70	−433 ± 24
	7.55	3.017 ± 0.003	7770 ± 70	−430 ± 23
	9.96	3.3640 ± 0.0018	6840 ± 40	−343 ± 15
	12.55	3.7731 ± 0.0019	6070 ± 50	−257 ± 9
	15.02	4.1866 ± 0.0018	5530 ± 50	−182 ± 6
	15.10	4.204 ± 0.003	5510 ± 50	−180 ± 6
	17.37	4.5277 ± 0.0013	5180 ± 50	−118 ± 6
	20.03	4.9988 ± 0.0011	4950 ± 40	−54 ± 8
	22.62	5.3823 ± 0.0013	4880 ± 30	1 ± 9
	24.95	5.8059 ± 0.0019	4930 ± 40	43 ± 8
	27.66	6.2950 ± 0.0019	5110 ± 50	83 ± 7
	30.12	6.807 ± 0.003	5350 ± 50	112 ± 6
	32.68	7.458 ± 0.002	5670 ± 60	135 ± 7
	35.02	8.005 ± 0.003	6000 ± 50	148 ± 11
	37.74	8.900 ± 0.002	6410 ± 50	156 ± 19
	40.08	9.735 ± 0.012	6780 ± 90	155 ± 27
	42.55	10.680 ± 0.011	7150 ± 160	147 ± 37
	45.04	11.745 ± 0.009	7500 ± 260	131 ± 49
0.980	2.52	2.1091 ± 0.0005	9100 ± 280	−569 ± 57
	5.04	2.4387 ± 0.0006	7800 ± 170	−462 ± 43
	7.34	2.7496 ± 0.0007	6840 ± 90	−372 ± 31
	10.01	3.0875 ± 0.0004	5980 ± 60	−277 ± 20
	12.47	3.4050 ± 0.0005	5400 ± 60	−197 ± 12
	15.00	3.7140 ± 0.0006	5000 ± 70	−122 ± 7
	17.50	4.0228 ± 0.0011	4780 ± 70	−57 ± 7
	20.04	4.3743 ± 0.0005	4710 ± 60	1 ± 9
	20.04	4.3717 ± 0.0007	4710 ± 60	1 ± 9
	22.67	4.754 ± 0.002	4780 ± 50	52 ± 11
	24.97	5.0643 ± 0.0019	4940 ± 50	89 ± 11
	27.59	5.521 ± 0.003	5220 ± 50	123 ± 9
	30.10	5.976 ± 0.005	5560 ± 60	147 ± 8
	32.66	6.544 ± 0.005	5960 ± 70	164 ± 8
	35.03	7.167 ± 0.004	6360 ± 60	171 ± 12
	37.71	7.991 ± 0.002	6820 ± 60	171 ± 20
	37.75	7.974 ± 0.004	6820 ± 60	171 ± 20
	40.06	8.621 ± 0.008	7210 ± 90	163 ± 29
	42.54	9.459 ± 0.009	7590 ± 160	147 ± 41
	45.08	10.69 ± 0.03	7940 ± 270	122 ± 55
	45.08	10.76 ± 0.02	7940 ± 270	122 ± 55
0.975	2.48	1.5408 ± 0.0006	4610 ± 240	−103 ± 50
	4.98	1.6818 ± 0.0006	4420 ± 140	−51 ± 37
	7.43	1.8369 ± 0.0011	4350 ± 80	−6 ± 27
	10.06	1.9593 ± 0.0006	4390 ± 70	37 ± 17
	12.49	2.1283 ± 0.0014	4520 ± 60	70 ± 10
	15.01	2.2888 ± 0.0012	4730 ± 60	97 ± 7
	17.59	2.5007 ± 0.0005	5010 ± 60	120 ± 7
	20.02	2.7256 ± 0.0004	5320 ± 50	134 ± 9
	22.56	2.9825 ± 0.0006	5680 ± 40	144 ± 10
	24.98	3.2595 ± 0.0009	6030 ± 40	147 ± 10
	27.64	3.6141 ± 0.0012	6420 ± 50	143 ± 8
	30.11	3.9553 ± 0.0012	6760 ± 60	134 ± 7
	32.63	4.412 ± 0.003	7080 ± 60	118 ± 8
	35.02	4.8784 ± 0.0018	7340 ± 60	98 ± 12
	37.73	5.463 ± 0.004	7570 ± 60	67 ± 21
	40.05	6.015 ± 0.004	7690 ± 90	36 ± 30
	42.55	6.669 ± 0.003	7730 ± 170	−4 ± 41
	45.09	7.482 ± 0.005	7660 ± 280	−51 ± 55

temperature dependent, $d\Delta C_p^{\ddagger}/dT$ being 19 ± 1 and 16 ± 1 cal mol^{-1} K^{-2} for x_w 0.981 and 0.980, respectively. Evidently this is the highest temperature dependence of $\Delta C_p^{\ddagger}$ ever found for solvolytic reactions.

Albery and Robinson[16] proposed a different mechanistic model to explain the deviations from the Arrhenius equation. Blandamer et al.[17] recently applied it to other solvolytic reactions. It cannot, however, be used in the present case because it always gives a negative $\Delta C_p^{\ddagger}$.

The temperature dependence of $\Delta C_p^{\ddagger}$ will be discussed more precisely elsewhere, employing other esters and other cosolvents in water. At present, we want to warn against drawing too hasty conclusions on the basis of $\Delta C_p^{\ddagger}$ values calculated from results obtained when studying a limited temperature range or using different temperature intervals.

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