Kinetics and Mechanisms of the Neutral and Acid-catalysed Hydrolyses of Chloro-substituted Alkyl Acetates in Aqueous Solutions of Constant Ionic Strength

Erkki K. Euranto* and Liisa T. Kanerva
Department of Chemistry, University of Turku, SF-20500 Turku 50, Finland
Nils J. Cleve
Section of Chemistry, Medical Faculty, University of Oulu, SF-90220 Oulu 22, Finland

The simultaneous neutral and acid-catalysed hydrolyses of different chloro-substituted alkyl acetates in water and in aqueous acetone solutions have been studied using electrolyte solutions of constant ionic strength. The mechanism of the acid-catalysed hydrolyses of monochloroesters is $A_{AC}2$. When an ester has two chloro-substituents the acid-catalysed hydrolysis takes place simultaneously by the $A_{AC}2$ and A–$B_{AC}3$ mechanisms and in the case of trihalogenated esters the mechanism is A–$B_{AC}3$, a mechanism with an unsymmetrically catalysed partition of the intermediate formed from the water-catalysed addition of water to the carbonyl group of the ester. Structural and solvent effects of these reactions are discussed.

The hydrolyses of chloromethyl chloroacetate[1,2] and methyl dichloroacetate[3] have been studied previously and were found to take place simultaneously by neutral ester hydrolysis ($B_{AC}3$) and acid catalysis. Neutral salts and acetone retard the reactions of the former ester strongly and in 2—3M perchloric acid solutions the rate passes through a flat maximum.[2] Similar results for esters of trifluoroacetic acid in dioxane + water solutions were interpreted by Bunton and Hadwick[4] as a negative salt effect both in the neutral and acid-catalysed hydrolyses. The reactions were, however, only studied in solutions of varying ionic strength so that the catalytic and electrolyte effects of an added acid could not be unambiguously separated by assuming that the difference $k_\Psi = k$ (acid) $- k$ (salt of the acid) represents the catalytic effect of an acid.[2] However, it was concluded that the initial step is the same for the neutral and acid hydrolyses.[5] In accord with this, Kurz and Farrar[6] have confirmed, on the basis of a thorough study of the hydrolysis of ethyl trichloroacetate at the constant ionic strength of 1.0, that the non-linear rate increase with increasing acidity is a consequence of an unsymmetrically catalysed partition of the intermediate formed from the water-catalysed addition of water to the carbonyl group of the ester.

The purpose of the present work was to study the simultaneous neutral and acid-catalysed hydrolyses of differently chloro-substituted alkyl acetates to separate the catalytic effect of the oxonium ion from its electrolyte effect using constant ionic strength and relatively low concentrations of added electrolytes. Owing to the partly confusing and even erroneous literature data for halogen-substituted esters the second aim was to explain the hydrolytic behaviour of these esters.

Experimental

Chloromethyl chloro- and dichloro-acetate[1,7] and methyl and isopropyl trichloroacetates[7] were prepared as described previously. Methyl and ethyl dichloroacetates (Fluka AG) and ethyl trichloroacetate (BDH) were commercial products which were redistilled before use. Reaction solutions were prepared as described previously.[1,8,9] Acetone (E. Merck AG, *pro analysi*) was used as supplied.

The hydrolysis of chloromethyl chloroacetate was followed by an argentimetric method.[1,9,10] The hydrolyses of methyl and ethyl dichloroacetates were followed by titrating acids with a standard diethylamine solution. The reactions were started by adding 0.70—0.75 ml of chloromethyl chloroacetate or 1.0—1.7 ml of the alkyl dichloroacetate to 150 ml of the reaction mixture. The hydrolyses of chloromethyl dichloroacetate and alkyl trichloroacetates were followed spectrophotometrically at 209—212 nm by a Beckman DK-2A spectrophotometer equipped with a thermostatted cuvette. Because u.v. light partly decomposed the esters the reaction solutions were held in a thermostatically controlled water-bath and the samples were transferred at appropriate time intervals to the cuvette. The ester concentration was 10^{-3}M.

The rate coefficients k_o and k_{HX} of the uncatalysed and hydrogen ion-catalysed hydrolyses, respectively, were evaluated, as described earlier,[8] from equation (1), where k_t is the time-dependent first-order rate coefficient and c_t the time-average of the hydrogen-ion concentration over the period t [equation (2)]. The values of c_t were calculated by means of the trapezoidal rule.[8]

$$k_t = k_o + k_{HX}c_t \qquad (1)$$

$$c_t = \frac{1}{t}\int_0^t c(\mathrm{H}^+)\mathrm{d}t \qquad (2)$$

In the case of dichloroacetates, the hydrogen-ion concentration $c(\mathrm{H}^+)$ was calculated from equation (3), where K is the ionization constant of dichloroacetic acid at the constant ionic strength used, c the dichloroacetic acid concentration, and c_o the initial concentration of hydrochloric acid. The values of K were calculated from equation (4), using the values of K_o determined earlier[3] and the mean activity coefficient values $f_\pm$ reported for hydrochloric acid.[11] In the case of chloromethyl chloroacetate, the ionization of chloroacetic acid had to be taken into account only when no strong acid was added initially. Because of the low ester concentrations for chloromethyl dichloroacetate and alkyl trichloroacetates the effect of the acids formed was not taken into account.

$$c(\mathrm{H}^+) = \tfrac{1}{2}\{c_o - K + (c_o + K)[1 + 4cK/(c_o + K)^2]^{\frac{1}{2}}\} \qquad (3)$$

$$K_o = Kf_\pm{}^2 \qquad (4)$$

Table 1. Kinetic data for the hydrolysis of chloromethyl chloroacetate in aqueous solutions containing electrolytes at a constant ionic strength, μ

Compound (X)	c(X)/mol l^{-1}	Temperature (°C)	μ/mol l^{-1}	c($HClO_4$)/mol l^{-1}	$\bar{c}_t$/mol l^{-1}	$10^4\ \bar{k}_t$/s^{-1}	$10^4\ k_o$/s^{-1}	$10^4\ k_{HX}$/s^{-1} M^{-1}
$LiClO_4$	0.20	25	0.2	0	0.0200[a]	0.955[a]		
	0.15			0.05	0.0673	1.024	0.932 ± 0.003	1.28 ± 0.02
	0.10			0.10	0.1188	1.083		
	0			0.20	0.2158[b]	1.207[b]		
					0.2281[b]	1.226[b]		
$NaClO_4$	0.10	25	0.1	0	0.0199	1.027		
	0.05			0.05	0.0686	1.089	1.003 ± 0.002	1.22 ± 0.03
	0			0.10	0.1211[b]	1.151[b]		
	0.20	15	0.2	0	0.0204	0.459		
	0.15			0.05	0.0689	0.484	0.448 ± 0.001	0.526 ± 0.007
	0.10			0.10	0.1188	0.512		
	0			0.20	0.2188	0.563		
	0.20	25	0.2	0	0.0262[a]	0.963[a]		
	0.15			0.05	0.0687	1.027		
					0.0691	1.029	0.936 ± 0.004	1.27 ± 0.03
	0.10			0.10	0.1228	1.092		
	0			0.20	0.2158[b]	1.207[b]		
					0.2281[b]	1.226[b]		
	0.20	35	0.2	0	0.0203	1.894		
	0.15			0.05	0.0679	2.027	1.838 ± 0.002	2.78 ± 0.01
	0.10			0.10	0.1182	2.170		
	0			0.20	0.2151	2.436		
	0.20	45	0.2	0	0.0207	3.52		
	0.15			0.05	0.0685	3.84	3.40 ± 0.01	6.11 ± 0.10
	0.10			0.10	0.1179	4.12		
	0			0.20	0.2174	4.73		
	0.50	25	0.5	0	0.0205[a]	0.795[a]		
	0.45			0.05	0.0684	0.855	0.781 ± 0.004	1.07 ± 0.01
	0.40			0.10	0.1178	0.912		
	0.30			0.20	0.2187	1.021		
	0			0.50	0.5102[b]	1.332[b]		
					0.5391[b]	1.352[b]		

[a] Reference 10. [b] Reference 1.

Table 2. Kinetic data for the hydrolysis of chloromethyl chloroacetate in aqueous acetone solutions containing electrolytes at a constant ionic strength, μ

Acetone (% w/w)	Temperature (°C)	μ/mol l^{-1}	c($NaClO_4$)/ mol l^{-1}	c($HClO_4$)/ mol l^{-1}	$\bar{c}_t$/mol l^{-1}	$10^4\ \bar{k}_t$/s^{-1}	$10^4\ k_o$/s^{-1}	$10^4\ k_{HX}$/s^{-1} M^{-1}
10	25	0.2	0.20	0	0.0203	0.518		
			0.15	0.05	0.0681	0.580	0.498 ± 0.004	1.17 ± 0.03
			0.10	0.10	0.1178	0.639		
			0	0.20	0.2183	0.751		
25	25	0.2	0.20	0	0.0206	0.1832		
			0.15	0.05	0.0683	0.2226	0.166 ± 0.002	0.855 ± 0.012
			0.10	0.10	0.1198	0.2699		
			0	0.20	0.2188	0.3519		
40	25	0.2	0.20	0	0.0178	0.0597		
			0.15	0.05	0.0710	0.0899	0.0500 ± 0.0003	0.560 ± 0.003
			0.10	0.10	0.1230	0.1193		
			0	0.20	0.2248	0.1757		
56	25	0.2	0.20	0	0.0192	0.0209		
			0.10	0.10	0.1215	0.0573	0.0144 ± 0.0006	0.349 ± 0.004
			0	0.20	0.2191	0.0906		

The activation parameters with their standard deviations were calculated by the method of least squares from the Arrhenius equation.

Results

The kinetic data for the hydrolyses of chloromethyl chloro- and dichloro-acetate and alkyl di- and tri-chloroacetates in water or acetone + water solutions are presented in Tables 1—4. Owing to the relatively high electrolyte concentrations employed in the present study it was not possible to use the conductimetric method,[12] which is the most accurate method in dilute solutions. For the hydrolysis of chloromethyl chloroacetate, perchloric acid and perchlorates were used because argentimetric titration does not give accurate results for solutions of high halide-ion concentrations. It was estimated that in this case the standard deviation of the mean $\bar{k}_t$ of the rate coefficients is of the order of 0.2%. For the hydrolyses of methyl and ethyl dichloroacetates the titration by base may cause a systematic error in rate coefficients, *e.g.*, because the base catalysis by a

Table 3. Kinetic data for the hydrolyses of methyl and ethyl dichloroacetates in water and in acetone + water solutions containing electrolytes at a constant ionic strength, μ

Ester	Acetone (% w/w)	Temperature (°C)	μ/mol l^{-1}	c(NaCl)/ mol l^{-1}	c(HCl)/ mol l^{-1}	$\bar{c}_t$/mol l^{-1}	10^5 $\bar{k}_t$/s^{-1}	10^5 k_o/s^{-1}	10^5 k_{HX}/s^{-1} M^{-1}
Methyl dichloroacetate	0	25	0.1	0.10	0	0.0213	1.89		
				0	0.10	0.1072[a]	3.15[a]	1.58 ± 0.02	14.5 ± 0.2
						0.1080[a]	3.14[a]		
	0	25	0.2	0.20	0	0.0216	1.99		
				0.15	0.05	0.0716	2.69	1.77 ± 0.04	12.2 ± 0.3
				0.10	0.10	0.1149	3.19		
				0	0.20	0.2075	4.27		
						0.2094	4.34		
	0	35	0.2	0.20	0	0.0144	3.39		
				0.15	0.05	0.0635	5.03	3.23 ± 0.22	25.8 ± 1.8
				0.10	0.10	0.1098	6.25		
				0	0.20	0.2051	8.38		
	0	45	0.2	0.20	0	0.0181	6.55		
				0.15	0.05	0.0635	9.62	5.93 ± 0.35	53.7 ± 2.9
				0.10	0.10	0.1080	12.0		
				0	0.20	0.2042	16.7		
	10	25	0.2	0.20	0	0.0145	0.997		
				0.15	0.05	0.0641	1.66	0.94 ± 0.08	10.1 ± 0.7
				0.10	0.10	0.1081	2.09		
				0	0.20	0.2044	2.95		
	25	25	0.2	0.20	0	0.0190	0.352		
				0.10	0.10	0.1175	0.979	0.24 ± 0.02	6.18 ± 0.11
				0	0.20	0.2064	1.51		
Ethyl dichloroacetate	25	25	0.2	0.20	0	0.0113	0.106		
				0.10	0.10	0.1069	0.475	0.054 ± 0.014	4.05 ± 0.11
				0	0.20	0.2021	0.878		

[a] Reference 3.

local excess of the base during the titration is possible even when diethylamine is used. Therefore, the standard deviation of $\bar{k}_t$ is higher, of the order of 1%. The rate data obtained by the spectrophotometric and titrimetric methods were essentially the same for methyl dichloroacetate at the ionic strength of 0.2 (compare, *e.g.*, the values for 10^{-4} k_o of 0.57 ± 0.07 s^{-1} and for 10^4 k_{HX} of 6.1 ± 0.6M^{-1} s^{-1} at 45 °C to those in Table 3). For chloromethyl dichloroacetate and alkyl trichloroacetates the spectrophotometric method was used because of the very fast neutral ester hydrolysis. In this case several parallel runs were performed and the pseudo-first-order rate coefficients k in Table 4 are the means of the individual k values, calculated by Guggenheim's method. Their errors are estimated to be about 4%.

The rate coefficients k_o and k_{HX} [equation (1)] with their standard deviations are also given in Tables 1—4, calculated by the method of least squares. The rate coefficients k_o and k_{HX} with their standard deviations were also calculated using the parabolic equation (5), but the second-order rate coefficient k_s

$$\bar{k}_t = k_o + k_{HX}\bar{c}_t + k_s\bar{c}_t^3 \qquad (5)$$

was not found to be statistically significant for the present data. This may be at least partly caused by the small number and low accuracy of the experimental values because all of the k_s values were found to be negative.

Discussion

The hydrolysis of chloromethyl chloroacetate in aqueous perchloric acid solutions with variable ionic strengths was previously found to have a non-linear dependence of k_t on $\bar{c}_t$ (Figure 1, broken line).[1,2] When the measurements were performed at constant ionic strength the hydrolysis was found to give a linear dependence of $\bar{k}_t$ on $\bar{c}_t$ although at the highest ionic strength employed, 0.5, the plots seem to be slightly curved (Figure 1). Further, because sodium and lithium perchlorates behave similarly (Table 1), it seems highly probable that the salt effects of added acids are eliminated by the use of a constant ionic strength. In the case of chloromethyl esters there is, however, a possibility of nucleophilic catalysis by substitution of chlorine in the alkyl group by the anion of the added electrolyte. This is improbable in the present case because of the low nucleophilicity of the perchlorate ion; in fact nucleophilic catalysis in this way was found to be insignificant.[1] Therefore, the data in Tables 1—4 do not suffer from these kinetic problems.

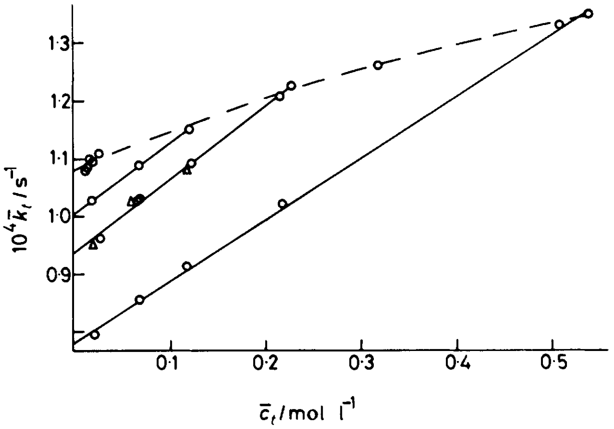


Figure 1. Plots of the rate coefficients $\bar{k}_t$ *versus* the acid concentration $\bar{c}_t$ at 25 °C for the hydrolysis of $CH_2ClCO_2CH_2Cl$ in aqueous solutions containing perchloric acid and sodium (○) or lithium (△) perchlorate. Full straight lines for the ionic strengths of 0.1, 0.2, and 0.5 mol l^{-1}; dashed line for variable ionic strength[1] (no added salt)

Table 4. Kinetic data for the hydrolyses of methyl (**1**), ethyl (**2**), and isopropyl (**3**) trichloroacetates and chloromethyl dichloroacetate (**4**) in water containing electrolytes at a constant ionic strength of 0.5 [esters (**1**), (**2**), and (**3**)] or 0.2 [ester (**4**)]

		$10^4k/s^{-1}$													
Ester	Temperature (°C)	c(HCl)/ mol l^{-1} = 0	0.05	0.075	0.10	0.15	0.175	0.20	0.25	0.30	0.35	0.40	0.50	$10^4\ k_o/s^{-1}$	$10^4\ k_{HX}/$ $s^{-1}\ M^{-1}$
(**1**)	25	7.56			8.38			8.81		9.63	9.64	10.0	10.3	7.72 ± 0.12	5.55 ± 0.39
	35	12.7			13.9			15.7		16.9		17.1	18.7	12.9 ± 0.3	11.7 ± 1.0
	45	21.8			23.9			26.4		28.5		30.6	31.6	22.0 ± 0.3	20.3 ± 1.1
(**2**)	25	2.49			2.77			3.10	3.10	3.34		3.51	3.71	2.53 ± 0.04	2.45 ± 0.14
	35	3.95			4.57			4.96		5.75		6.08	6.62	3.99 ± 0.07	5.33 ± 0.24
	45	6.91			8.20			9.43		10.3		11.5	12.4	7.07 ± 0.10	10.8 ± 0.3
(**3**)	45	2.5			2.9			3.7		3.6		3.8	3.6	2.8 ± 0.2	2.3 ± 0.8
(**4**)	25	137	143	143	149	149	153	159						137 ± 1	97 ± 11

Table 5. Kinetic data for the acid-catalysed hydrolysis of carboxylic esters in water at 25 °C

Ester	μ/mol l^{-1}	10^5 k_{HX}/s^{-1} M^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}	Mechanism
$MeCO_2Me$[a]	0.1	10.9	68.1	−92	$A_{AC}2$
$EtCO_2Me$[b]	0.02	11.7	65.9	−99	$A_{AC}2$
Me_2CHCO_2Me[c]	0.2	6.63			$A_{AC}2$
Me_3CCO_2Me[d]	0.2	1.18			$A_{AC}2$
$MeCO_2Et$[a]	0.1	10.7	67.7	−94	$A_{AC}2$
$MeCO_2CHMe_2$[c]	0.2	6.17			$A_{AC}2$
$EtCO_2Et$[a]	0.1	11.2	63.9	−106	$A_{AC}2$
$MeCO_2CH_2Cl$[e]	variable	3.54	67.5	−103	$A_{AC}2$
$EtCO_2CH_2Cl$[e]	variable	4.30	66.5	−104	$A_{AC}2$
CH_2ClCO_2Me[f]		8.45			$A_{AC}2$
CH_2ClCO_2Et[g]	0.1	8.08	64.6	−107	$A_{AC}2$
$CH_2ClCO_2CH_2Cl$[h]	variable	6.7	67.5 ± 1.5[i]	−97 ± 5[i]	$A_{AC}2 + A\text{–}B_{AC}3$
$CH_2ClCO_2CH_2Cl$	0.2	12.7	59.6 ± 0.5	−118 ± 2	$A_{AC}2 + A\text{–}B_{AC}3$
$CHCl_2CO_2Me$[j]	variable	14.8	56.2 ± 1.6[k]	−129 ± 5[k]	$A_{AC}2 + A\text{–}B_{AC}3$
$CHCl_2CO_2Me$	0.2	12.2	55.9 ± 0.7	−131 ± 2	$A_{AC}2 + A\text{–}B_{AC}3$
$CHCl_2CO_2Et$[l]		12.0			$A_{AC}2 + A\text{–}B_{AC}3$
$CHCl_2CO_2CH_2Cl$	0.5	970			$A\text{–}B_{AC}3$
CCl_3CO_2Me	0.5	55.5	48.7 ± 3.5	−142 ± 11	$A\text{–}B_{AC}3$
CCl_3CO_2Et	0.5	24.5	56.0 ± 0.5	−125 ± 2	$A\text{–}B_{AC}3$
CCl_3CO_2Et[m]	1.0	32.9			$A\text{–}B_{AC}3$

[a] Ref. 18. [b] J. L. Hockersmith and E. S. Amis, *Anal. Chim. Acta*, 1953, 9, 101. [c] M. H. Palomaa, *Ann. Acad. Sci. Fenn., Sect. AIV*, 1913. No. 2. [d] E. J. Salmi, *Ann. Acad. Sci. Fenn., Sect. A48*, 1937, No. 4. [e] Reference 8. [f] Reference 14. [g] Ref. 19. [h] Reference 1. [i] Calculated from the values of k_{HX} at 25, 35, and 45 °C. [j] Reference 3. [k] Calculated from the values of k_{HX} at 5, 25, and 45 °C. [l] E. J. Salmi, *Ber. Dtsch. Chem. Ges. B*, 1939, **72**, 1767. [m] Reference 6.

Neutral Hydrolysis.—When the neutral ester hydrolysis was studied previously low substrate concentrations without added electrolytes were employed[12] or the rate coefficients were extrapolated to zero acid concentration[1,3,8] so that the results did not include electrolyte effects. In neutral ester hydrolysis the temperature and solvent effects on the rate coefficients have been studied in detail.[1,3,12,13] In this respect, the present results do not give any new information.

Acid-catalysed Hydrolysis.—The literature data for the acid-catalysed hydrolysis of chloro-substituted acetic esters are often contradictory and even erroneous, partly because of experimental difficulties and partly because the data may include neutral hydrolysis, or at least its electrolyte effect. For instance, the third chlorine in the acyl group is now known to increase the rate although the rate of the acid hydrolysis had been stated to be unmeasurably low.[14–16]

When the most reliable data are considered, the following properties of the acid-catalysed hydrolysis of chloro-substituted alkyl acetates still remain to be explained.

(i) The first chlorine introduced to methyl acetate decreases the rate, more if it is in the alkyl component, but the next ones increase the rate.[8,17]

(ii) For esters having several chloro-substituents the rate does not increase linearly with hydrogen-ion concentration but often shows a maximum or an inflexion point.[1,2,4–6,17]

(iii) Organic co-solvents cause a considerable rate retardation in the case of esters with no chlorine, an almost negligible effect for esters with one chlorine, but a relatively strong retardation for those with two or more chlorines (Figure 2).

(iv) Added electrolytes slightly increase the rate of hydrolysis of esters with no or one chloro-substituent[8,12] but decrease the rate for esters with several chloro-substituents.[1]

(v) The solvent isotope effect $k(D_2O)/k(H_2O)$ is about 1.6 for acetates with no or one chlorine[17] but is about 0.6 for chloromethyl chloroacetate[10] and about 0.5 for ethyl trichloroacetate.[6]

(vi) The activation enthalpy ($\Delta H^‡$) is somewhat higher and the entropy ($\Delta S^‡$) less negative for esters with no or one chlorine[8,17] compared with polychloro-substituted esters (Table 5).

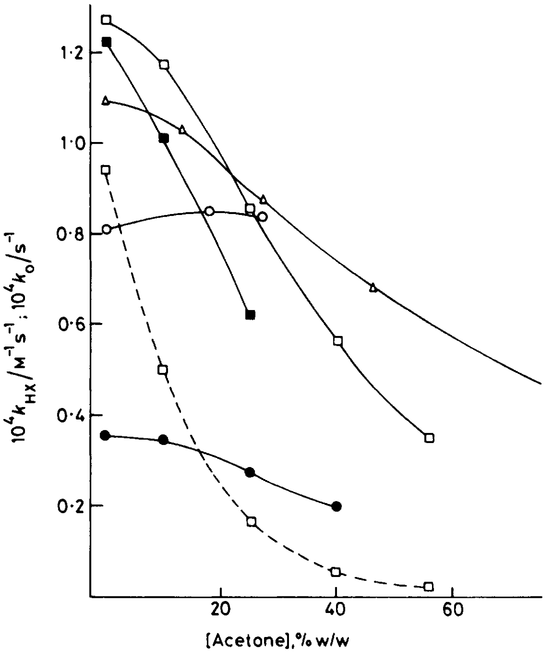
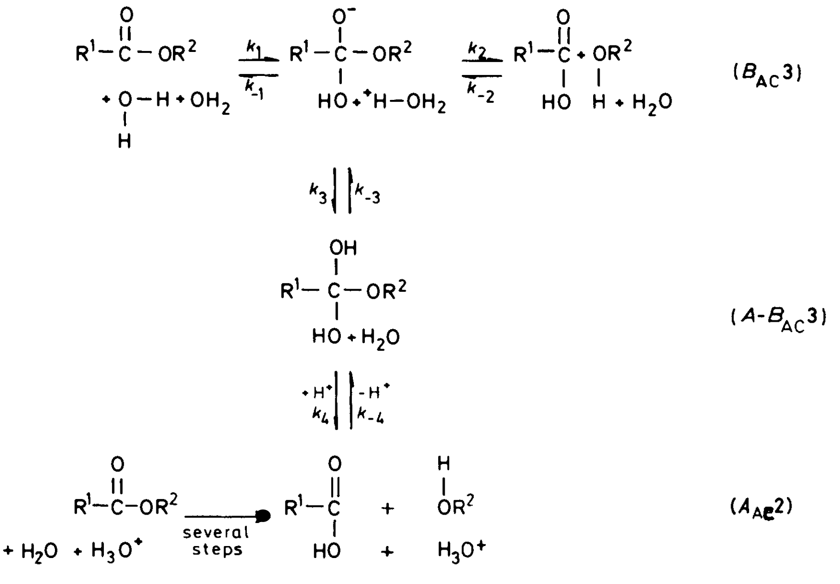


Figure 2. Plots of the rate coefficients k_{HX} (full lines) or k_o (dashed line) *versus* the concentration of acetone (% w/w) for the hydrolysis of the esters in aqueous acetone at 25 °C. △, $MeCO_2Me$;[18] ○, CH_2ClCO_2Et;[19] ●, $MeCO_2CH_2Cl$;[8] ■, $CHCl_2CO_2Me$; □, $CH_2ClCO_2CH_2Cl$

These facts led to the proposal for a change in mechanism from the common $A_{AC}2$ for unsubstituted and monochloro-substituted alkyl acetates to a mechanism where the initial state is the same as for the neutral ester hydrolysis ($B_{AC}3$) in the case of acetic esters with two or more chloro-substituents.[5,6] The new data presented in this work are in accord with this proposal.



Scheme.

Table 6. Rate ratios k_{HX}/k_o for the acid-catalysed $A\text{–}B_{AC}3$ and neutral $B_{AC}3$ hydrolyses of carboxylic esters

Ester	Temperature (°C)	μ/mol l^{-1}	$10^5\ k_o{}^a/s^{-1}$	$10^5\ k_{HX}{}^a/s^{-1}\ M^{-1}$	$(k_{HX}/k_o)/M^{-1}$
$CH_2ClCO_2CH_2Cl$	25	0.2	9.36	11.5^b	1.2
$CHCl_2CO_2Me$	25	0.2	1.77	$<11^b$	<6
$CHCl_2CO_2CH_2Cl$	25	0.5	1 370	970	0.7
CCl_3CO_2Me	25	0.5	77.2	55.5	0.7
CCl_3CO_2Me	45	0.5	220	203	0.9
CCl_3CO_2Et	25	0.5	25.3	24.5	1.0
$CCl_3CO_2Et^c$	25	1.0	12.4	32.9	2.65
CCl_3CO_2Et	45	0.5	70.7	108	1.5
$CCl_3CO_2CHMe_2$	45	0.5	28	23	0.8

[a] See Tables 1, 3, and 4. [b] Contribution of the $A_{AC}2$ mechanism substracted. [c] Reference 6.

$A_{AC}2$ *hydrolysis*. The kinetic behaviour of an $A_{AC}2$ hydrolysis is well known[17] and in accord with the above-mentioned kinetic properties of alkyl acetates with no or one chlorine. Steric effects are important in the acid-catalysed ester hydrolysis but if only one hydrogen in methyl acetate is substituted by methyl the effect on the rate is slight (Table 5). Therefore, the retarding effect of the first chlorine must be due to the negative inductive effect of chlorine on the protonation step because it should facilitate the addition of water to the carbonyl group of the protonated ester. The lower rate retardation found when the chlorine atom is in the acyl rather than in the alkyl group (Table 5) can be explained, in accord with the i.r. spectroscopic results of Laato,[20] by its diminishing effect on the ester resonance.

The introduction of additional chlorine atoms into the ester should further retard the rate of the $A_{AC}2$ mechanism because of increasing steric demands and the above-mentioned polar effects. In accord with this, it has earlier been estimated that the rate coefficient is $1.2 \times 10^{-5} M^{-1} s^{-1}$ for the $A_{AC}2$ hydrolysis of chloromethyl chloroacetate[10] in water at 25 °C. It can be roughly estimated that at least 10% of the acid-catalysed hydrolysis of methyl dichloroacetate takes place by the $A_{AC}2$ mechanism. The observed values of K_{HX} for these esters (Table 5) thus include the contributions of the $A_{AC}2$ and $A\text{–}B_{AC}3$ mechanisms. For trichloroacetates the $A_{AC}2$ hydrolysis is not kinetically significant in low acid concentrations.[6]

Dilution of water by co-solvents should diminish the rates of hydrolyses and this concentration effect is usually strengthened by the effect of reduced polarity of the solvent if the transition state is more polar than the initial state. However, the hydrolysis of ethyl chloroacetate is found initially to increase and that of chloromethyl acetate to decrease, but only slightly, with increasing acetone concentration (Figure 2). This may be understood by the increased polarity of the initial state caused by chlorine, the effect being more marked in the case of alkyl chloroacetates.

$A\text{–}B_{AC}3$ *hydrolysis*. The acid catalysis in ester hydrolysis caused by the unsymmetrically catalysed partition of the tetrahedral intermediate is called the $A\text{–}B_{AC}3$ mechanism[21] because the intermediate is the same as that of the neutral ester hydrolysis (Scheme). Structural and other kinetic effects should be similar in the two mechanisms. Thus, for the hydrolyses of chloromethyl chloroacetate and methyl dichloroacetate in acetone + water mixtures (Tables 2 and 3; Figure 2) the solvent effects on the rates of these mechanisms resemble each other, the effect being somewhat stronger on the neutral ester hydrolysis. However, the solvent effects on the $A\text{–}B_{AC}3$ hydrolyses could be even higher than that shown by the experimental results due to the contribution of the $A_{AC}2$ mechanism. Further, it is possible that acetone increases its proportion. Unfortunately no data exist about solvent effects on the acid-catalysed hydrolyses of trichloroacetates.

The rate ratios k_{HX}/k_o (Table 6) seem to be similar in spite of the high rate differences, indicating the close connection between the neutral ester hydrolysis and the A–$B_{AC}3$ mechanism. The ratio k_{HX}/k_o can be shown to be $k_b k_{-1}/k_2$, where k_b is an experimentally observable rate coefficient.[6] Only in the case of ethyl trichloroacetate are the rate constants of the individual steps in the Scheme at least approximately known on the basis of the carbonyl–^{18}O exchange measurements by Kurz and Wexler.[22] In this case, the value of k_{HX}/k_o is mainly determined by the ratio k_{-1}/k_2. Unfortunately, the low accuracy of the other rate coefficients (Table 6) does not allow further conclusions to be made on the basis of the rate ratio. The ratio k_{HX}/k_o increases with increasing temperature owing to the higher activation energy of the acid-catalysed hydrolysis and with increasing ionic strength because of strongly decreasing k_o and perhaps slightly increasing k_{HX}. A contribution of the $A_{AC}2$ hydrolysis should be seen as an increased k_{HX}/k_o ratio.

For the hydrolysis of trichloroacetic esters, the effect of the alkyl component on the rate is in the order Me > Et > Pr^i, as is usual in ester hydrolysis owing to the importance of steric factors. However, the rate ratios 1:0.32:0.13 for k_o and 1:0.5:0.1 for k_{HX}, respectively, more closely resemble the corresponding values 1:0.43:0.065 for the alkaline hydrolysis than the values 1:0.99:0.57 for the $A_{AC}2$ reactions. These results are in accord with the earlier[17] statement that structural effects are similar in the neutral $B_{AC}3$ and alkaline $B_{AC}2$ hydrolyses and the expected similarity of the $B_{AC}3$ and A–$B_{AC}3$ mechanisms.

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