Mechanistic Interpretation of the Simultaneous Hydrolysis and Methanolysis of Chloromethyl Chloroacetate in Weakly Acidic Aqueous Methanol Solutions of Varying Solvent Composition.

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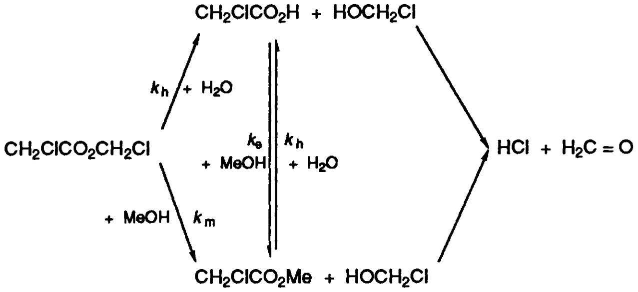
The simultaneous hydrolysis and methanolysis of chloromethyl chloroacetate in aqueous methanol at x_w from 1.00 to 0.50 in 0.01 to 0.06 mol dm^{-3} perchloric acid solutions have been studied. The methanolysis of the ester in anhydrous and in highly alcohol-rich methanolic hydrogen chloride solutions up to 0.2 mol dm^{-3} acid has also been studied. Under the reaction conditions, the neutral $B_{Ac}3$ reactions are accompanied by the acid-catalysed reactions. The kinetic data are in accord with the conclusion that the acid-catalysed reactions take place simultaneously by the $A_{Ac}2$ and A–$B_{Ac}3$ mechanisms, at least at x_w >0.5. The extent to which the $A_{Ac}2$ mechanism operates with increased methanol content and in methanol the reaction takes place solely by the $A_{Ac}2$ mechanism.

The hydrolyses of chloromethyl mono-, di-, and tri-chloroacetates in water are known to proceed by the neutral ester hydrolysis mechanism, $B_{AC}3$.[1,2] The hydrolyses and methanolyses of these esters are formally similar and, based on the experimental data, the methanolyses of the two last-mentioned esters in methanol were previously proposed to proceed by this mechanism.[3,4] On this basis, it is reasonable to assume that in aqueous methanol the simultaneous hydrolysis and methanolysis of an ester take place separately by the $B_{AC}3$ pathway. In the case of chloromethyl chloroacetate at higher temperatures (above 65 °C), however, the S_N2 solvolysis of the chlorine of the chloromethyl group may also be of importance.[1]

In acid solutions, the $B_{AC}3$ hydrolysis and methanolysis of an ester are accompanied by an acid-catalysed reaction. As previously proposed,[4–8] the acid-catalysed reaction may proceed either by the exceptional A–$B_{AC}3$ mechanism, or by the normal $A_{AC}2$ mechanism, or simultaneously by the two acid-catalysed reaction mechanisms. Because the neutral $B_{AC}3$ and the acid catalysed A–$B_{AC}3$ mechanisms are assumed to go through the same rate-limiting step (the water- or alcohol-catalysed addition of ROH to the carbonyl group of the ester), factors which favour the decomposition of an ester by the $B_{AC}3$ pathway should also favour its acid-catalysed reaction by the A–$B_{AC}3$ mechanism and *vice-versa.* Thus, an increase in the number of halogen substituents in the ester is known to increase the proportion of the A–$B_{AC}3$ mechanism at the expense of the $A_{AC}2$ pathway while organic cosolvents, added to water, exert the opposite effect.[5–7]

In aqueous methanol, α-haloalkyl esters react with both of the solvent components (Scheme). Although under the reaction conditions of this work the possibility of solvolysis of the α-halogen atom is excluded, the three mechanisms ($B_{AC}3$, A–$B_{AC}3$, and $A_{AC}2$) are still possible in dilute acid solutions. In the present work, the kinetics of the simultaneous neutral and acid-catalysed reactions of chloromethyl chloroacetate were studied in aqueous methanol solutions (the mole fraction of water x_w = 1.00–0.50) containing up to 0.06 mol dm^{-3} perchloric acid. Also the methanolysis of the ester in wet and anhydrous methanolic hydrogen chloride solutions up to 0.2 mol dm^{-3} acid was studied. The experimental data obtained were employed to evaluate the respective data for the simultaneous hydrolysis reactions.



$$H_2C=O + H_2O \rightleftharpoons H_2C(OH)_2$$

$$H_2C=O + MeOH \rightleftharpoons H_2C(OH)OMe \xrightarrow{MeOH} H_2C(OMe)_2 + H_2O$$

Scheme.

Experimental

Chloromethyl chloroacetate was prepared as described previously.[9] Aqueous methanol solutions were prepared by diluting a known weight of distilled water with methanol (Merck AG, *getrocknet, pro analysi*) to a known volume in a volumetric flask. Distilled 5-methylhexan-2-one (Fluka AG, *purum*) as an internal standard and perchloric acid (Merck AG, etwa 70%) were added. The water content of the solutions was corrected by the amount of water originating from the acid. Methanolic hydrogen chloride solutions were prepared by passing dry gaseous hydrogen chloride into methanol. The final water content of the solutions was determined by the Karl Fischer water titration. The acid concentrations were detected by titration.

The total reaction of chloromethyl chloroacetate was followed by an argentometric method[1] by addition of 0.16 cm^3 of the ester to 80 cm^3 of the reaction mixture. The time-dependent first-order rate coefficients, k_t, and the time averages, c_t, of the hydrogen-ion concentration were calculated as described previously.[5]

The methanolysis of chloromethyl chloroacetate in the water-rich aqueous methanol solutions was followed by a gas-

Table 1. The first-order rate cofficients k_T^o, k_m^o, and k_h^o for the neutral total reaction and for the methanolysis and hydrolysis of chloromethyl chloroacetate at 25 °C in aqueous methanol. x_w = mole fraction of water.

x_w	$k_T^o/10^{-5}$ s^{-1}	$k_m^o/10^{-5}$ s^{-1}	$k_h^o/10^{-5}$ s^{-1}
1.000[a]	10.82 ± 0.09		10.82
0.907	6.18 ± 0.07	1.50 ± 0.07	4.68
0.790	3.64 ± 0.07	1.70 ± 0.07	1.94
0.690	2.47 ± 0.06	1.52 ± 0.07	0.95
0.600	1.82 ± 0.04	1.28 ± 0.10	0.60
0.500	1.33 ± 0.03	1.15 ± 0.06	0.18

[a] Reference 6.

Table 2. Rate coefficients k_T^H, k_m^H, and k_h^H for the acid-catalysed total reaction and for the methanolysis and hydrolysis of chloromethyl chloroacetate at 25 °C in aqueous methanol. x_w = mole fraction of water.

x_w	$k_T^H/10^{-5}$ dm^3 mol^{-1} s^{-1}	$k_m^H/10^{-5}$ dm^3 mol^{-1} s^{-1}	$k_h^H/10^{-5}$ dm^3 mol^{-1} s^{-1}
1.000[a]	19.5 ± 0.1		19.5
0.907	17.3 ± 1.5	4.7 ± 1.4	12.6
0.790	14.9 ± 1.2	8.6 ± 1.6	6.3
0.690	14.0 ± 0.7	12.0 ± 1.5	2.0
0.600	13.5 ± 0.7	11.7 ± 2.0	1.8
0.500	13.4 ± 0.6	12.3 ± 1.2	1.1
0.143	20.1 ± 0.3		
0.044	46.5 ± 0.7	46.5 ± 0.7	
0.010	92.8 ± 1.9	92.8 ± 1.9	
0	134 ± 4.4	134 ± 4.4	

[a] Reference 6.

Table 3. Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the neutral total reaction (T) and for the neutral methanolysis (m) of chloromethyl chloroacetate at 25 °C in aqueous methanol. x_w = mole fraction of water.

x_w	$\Delta H_T^\ddagger$/kJ mol^{-1}	$-\Delta S_T^\ddagger$/J mol^{-1} K^{-1}	$\Delta H_m^\ddagger$/kJ mol^{-1}	$-\Delta S_m^\ddagger$/J mol^{-1} K^{-1}
1.000[a]	49.4	155		
0.907	47.4 ± 0.6	165 ± 2	53 ± 10	162 ± 30
0.790	48.8 ± 2.4	165 ± 8	50.1 ± 0.7	168 ± 2
0.553[b]	52.3 ± 2.4	160 ± 8	61.9 ± 0.2	132 ± 1

[a] Reference 1. [b] The value of k^o at 25 °C approximated from Figure 1.

chromatographic method. Samples taken at intervals from the reaction mixture were analysed by use of a Hewlett–Packard 5710A gas chromatograph equipped with a packed column (10% Silicone XE 60 on Chromosorb W 60/100). The instrument was calibrated by dichloromethane (Merck AG, *zur Analyse*) solutions, containing known concentration ratios of chloromethyl (E_1) or methyl (E_2) chloroacetates and 5-methylhexan-2-one (S). The area ratios (E_1/S) and (E_2/S) were measured by using a Hewlett-Packard 3380S integrator. The time-dependent first-order rate coefficients, $k_{m(t)}$, were evaluated from equation (1), where k_t is the mean value for the rate

$$k_{m(t)} = k_t\ [(E_2/S)_t - (E_2/S)_0)]/[(E_2/S)_0 - (E_1/S)_t] \quad (1)$$

coefficients of the total reaction of chloromethyl chloroacetate under the reaction conditions and the subscripts *t* and 0 refer to the times *t* and zero, respectively.

In aqueous methanol, the consecutive reactions, the esterification of chloroacetic acid with methanol and the acid-catalysed hydrolysis of methyl chloroacetate (Scheme), may also be of some importance. Thus, the rate coefficients 16.8 and 5.9 × 10^{-5} dm^3 mol^{-1} s^{-1} were previously observed for the acid-catalysed esterification and hydrolysis of the acid and the ester, respectively, at 25 °C in a 1:1 methanol–water solution.[10] That is why attempts were made to correct the concentration ratios $(E_2/S)_t$ at time *t* with the aid of the trapezoidal rule[11] by following the consecutive reactions gas-chromatographically under the same reaction conditions.

To minimize further the effects of the consecutive reactions, only the first 30 to 40% of the methanolysis reaction was taken into account. Because of the complicated experimental procedure several parallel runs (5–8) were performed in each acid solution. Within the limits of the experimental accuracy, however, the corrected and uncorrected mean values of $k_{m(t)}$ seemed to be equal.

For the methanolysis of chloromethyl chloroacetate in anhydrous or in concentrated aqueous methanol solutions, 10 mm^3 of the ester was added into 4 cm^3 of methanolic hydrogen chloride. The reactions were followed by a gas-chromatographic method described previously.[4]

Results

The rate coefficients k_T^o and k_T^H and k_m^o and k_m^H for the total reaction (T) and for the methanolysis (m) of chloromethyl chloroacetate in aqueous methanol were evaluated from equation (2). The letters o and H now refer to the neutral and

$$k = k^o + k^H[H^+] \quad (2)$$

acid-catalysed reactions, respectively. It has been previously shown that the acid-catalysed reactions that take place by the A–B_{AC}3 pathway do not follow the linear equation (2).[6,8] Owing to the limited acid concentration range used and taking into account the experimental accuracy, the use of this simple equation, however, seems to be justified. Further, because of the variable ionic strength, the rate coefficients k^H include the contribution of the negative salt effects of added perchloric acid on the neutral B_{AC}3 reactions. Fortunately, these salt effects seem to be somewhat reduced in aqueous organic binary systems compared with the effects in water.[7]

The total reactions of chloromethyl chloroacetate in aqueous methanol are the sums of the simultaneous ester hydrolysis and methanolysis. Thus, the rate coefficients k_h for the hydrolysis of the ester in each methanol–water solution can be evaluated from equation (3).

$$k_h = k_T - k_m \quad (3)$$

The experimental data for the neutral and acid-catalysed reactions of chloromethyl chloroacetate in aqueous and anhydrous methanol at 25 °C are shown in Tables 1 and 2 and Figures 1 and 2, respectively. The data obtained for the neutral hydrolysis and methanolysis at 15 and 35 °C are included in Figure 1. At these temperatures, the effects of the consecutive reactions on the k_m and thus on the k_h values were not taken into account. These uncertainties are also included in the values of the activation enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$), obtained from the Arrhenius equation for the neutral methanolysis of chloromethyl chloroacetate at x_w 0.907, 0.790, and 0.553 (Table 3).

Discussion

Neutral Reactions.—It is generally known that organic

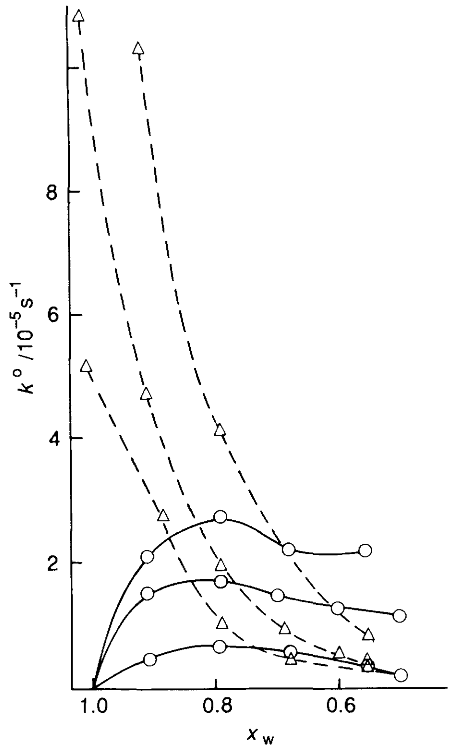


Figure 1. Rate coefficients k_m^o (○) and k_h^o (△) for the neutral methanolysis and hydrolysis of chloromethyl chloroacetate at 15, 25, and 35 °C in aqueous methanol *vs.* mole fraction of water (x_w).

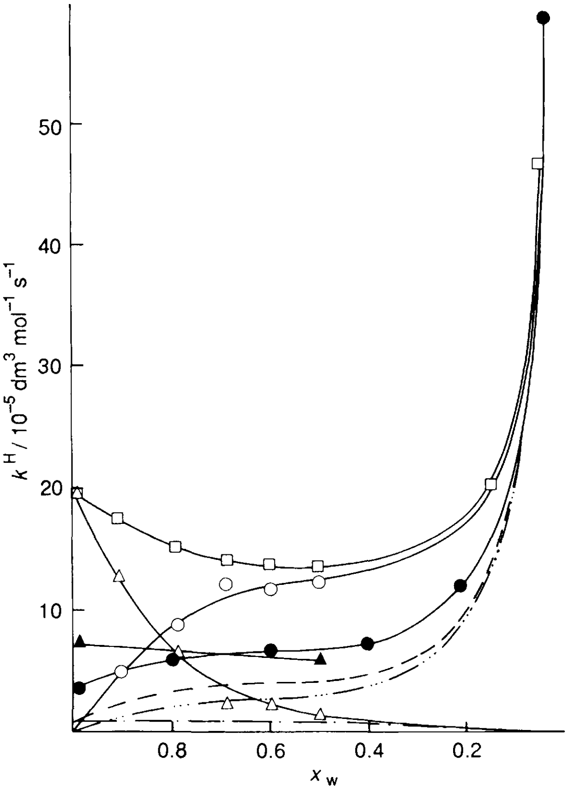


Figure 2. Rate coefficients k^H for the acid-catalysed total reaction (□), methanolysis (○), and hydrolysis (△) of chloromethyl chloroacetate observed and (– – –), (– · · · ·), and (– · · –), respectively, approximated for its $A_{AC}2$ reactions in aqueous methanol *vs.* x_w; (●) and (▲) the plots for the total reaction of chloromethyl acetate[23] and for the hydrolysis of methyl chloroacetate[10] by the $A_{AC}2$ mechanism, respectively.

Table 4. Rate ratios k_m^o/k_h^o, k_m^H/k_h^H, k_m^H/k_m^o, and k_h^H/k_h^o for the neutral (o) and acid-catalysed (H) hydrolyses and methanolyses of chloromethyl chloroacetate at 25 °C in aqueous methanol. x_w = mole fraction x_w of water.

x_w	k_m^o/k_h^o	k_m^H/k_h^H	k_m^H/k_m^o	k_h^H/k_h^o
1.000[a]				1.8
0.907	0.32	0.37	3.1	2.7
0.790	0.88	1.4	5.1	3.2
0.690	1.6	6.0	7.9	2.1
0.600	2.6	6.5	9.1	3.0
0.500	6.4	11	11	6.1

[a] Reference 6.

cosolvents added to water decrease the rates of the neutral hydrolysis of esters.[1,2] In accord with this, the first-order rate coefficients k_T^o for the reaction of chloromethyl chloroacetate in aqueous methanol at 25 °C decrease by a factor of 8.1 when x_w decreases from 1.00 to 0.50 (Table 1). In the case of the more hydrophobic chloromethyl dichloroacetate (according to Rekker's *f*-values[12] log P = 1.49 and 2.06 for chloromethyl chloro- and dichloro-acetates, respectively) the respective rate retardation is of the order of 12.9.[2] The gas-chromatographic product analysis for the both reactions, however, clearly reveals that the rate coefficients k_T^o include contributions from the simultaneous hydrolysis and methanolysis of the esters. Thus, a proper insight into any effects involved in these reactions demands the consideration of the separate effects on each of the simultaneous reactions.

Hydrolysis.—The rate coefficients k_h^o for the neutral hydrolysis of chloromethyl chloroacetate in aqueous methanol decrease continuously with the decrease in the water content of the system (Table 1, Figure 1). In aqueous alcohol solutions, the temperature and solvent effects on the rate coefficients for the neutral ester hydrolysis have been thoroughly studied and the data presented here are in full agreement with the previous results.[2,13]

Methanolysis.—The kinetics of the methanolysis of α-halo-alkyl acetates in aqueous methanol can be followed by gas chromatography as described in the Experimental section. The low values of activation enthalpy and entropy for the methanolysis of chloromethyl chloroacetate in the present work (Table 3) are in accord with the $B_{AC}3$ mechanism.

The first-order rate coefficients k_m^o for the methanolysis of chloromethyl chloroacetate in aqueous methanol go through a maximum at x_w close to 0.8 (Table 1, Figure 1), the rate increase caused by the initial additions of methanol being more pronounced at higher temperatures. This behaviour is in accord with the data for the alcoholyses of acetic anhydride[14] and benzoyl chloride[15] in aqueous methanol and isopropyl alcohol, respectively. Further, the rate of the neutral methanolysis of chloromethyl chloroacetate exceeds that of its simultaneous hydrolysis at x_w between 0.7 and 0.8 (Figure 1). This, together with the increase of the rate ratio k_m^o/k_h^o with the decrease of x_w (Table 4) leads one to assume that the reactivity of methanol exceeds that of water. This can be understood by the fact that methanol is a stronger acid than water over the whole composition profile from 100% water to 100% methanol.[16] The difference between the acid strengths becomes even more pronounced with increased methanol content, the value of $pK_a = pK_a(H_2O) - pK_a(MeOH)$ being 0.191 in water and 0.275 in aqueous methanol at x_w 0.5425 at 25 °C. Thus, the nucleophilic addition of methanol to the carbonyl group of the ester in the rate-limiting step is evidently favoured compared with that of water; the water molecule is acting as a general-base catalyst :B. However, the maximum in the plots of k_m^o *vs.* x_w cannot solely be explained on this basis.

It seems that the maximum in the plots of k_m^o *vs.* x_w for the methanolysis of chloromethyl chloroacetate in aqueous methanol solutions is connected with the changes in the solvent structure. There are many kinds of evidence for the enhancement of hydrogen bonds between water molecules when small amounts of a monohydric alcohol are added to water; larger amounts break the structure.[17,18] In the case of aqueous methanol, the solvent ordering increases until x_{ROH} values of 0.2 to 0.3 are reached. In these water-rich solutions, methanol molecules evidently accommodate in the cavities within the water structure thereby participating in strong hydrogen-bonding with water, *i.e.*, methanol–water interactions increase. In accordance with this, the rates of the neutral methanolysis of chloromethyl chloroacetate increase (Table 1, Figure 1) because the concentration of the more reactive methanol increases. When the water structure collapses, not only water–water but also methanol–water interactions begin to decrease while methanol–methanol interactions increase.[18] When methanol loses its extraordinary position as a hydrogen-bonded participant in the water structure, other effects generally responsible for the rate retardations of the $B_{AC}3$ reactions evidently retain their importance. Thus, *e.g.*, the dielectric properties of the medium decrease when methanol is added into water.[19] It is also possible that with the decreasing water content the more acidic methanol molecule more often replaces a water molecule as a general-base catalyst.

The minimum values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ observed for the methanolysis of chloromethyl chloroacetate at x_w = *ca.* 0.8 (Table 3) are in accordance with the changes in the solvent structure.

Acid Catalysis.—The acid-catalysed hydrolysis or alcoholysis of an ester by the $A_{AC}2$ mechanism is generally thought to proceed by a pre-equilibrium protonation followed by the rate-limiting nucleophilic addition of water or alcohol to the carbonyl group of the ester.[6,8,11] In the case of ordinary esters steric effects on reaction rates are of most importance. If one or several hydrogen atoms in an ordinary ester is replaced by chlorine the negative inductive effect of a halogen atom on the protonation step is largely responsible for the rate retardation observed.[5,6] Thus the rate coefficients $k_h^H/10^{-4}$ dm^3 mol^{-1} s^{-1} for the $A_{AC}2$ hydrolyses of methyl,[20] ethyl,[20] and chloromethyl[11] acetates and of chloromethyl chloroacetate[21] in water at 25 °C are 1.09, 1.07, 0.354, and 0.11, respectively. The rate coefficients for the acid-catalysed methanolyses of the same esters, are 50.5 (30 °C), 13.7 and 13.4 (Table 2), respectively.[22,23] Thus, the observed rate coefficient 19.5×10^{-5} dm^3 mol^{-1} s^{-1} for the acid-catalysed hydrolysis of chloromethyl chloroacetate in water is much greater than the above value approximated according to its $A_{AC}2$ reaction.[21] It is obvious that the exceptionally high rate of acid hydrolysis observed is caused by the intervention of the exceptional $A\text{–}B_{AC}3$ mechanism: it has previously been proposed that the proportions of the $A_{AC}2$ and $A\text{–}B_{AC}3$ mechanisms are *ca.* 10 and 90%, respectively.[5,6,21] On the other hand, for the acid-catalysed methanolysis of chloromethyl chloroacetate in methanol, the observed rate coefficient, 13.4×10^{-4} dm^3 mol^{-1} s^{-1} (Table 2) is of the order expected for the $A_{AC}2$ mechanism. As support for this, the acid-catalysed alcoholyses of alkyl trichloroacetates in methanol have previously been shown to proceed by the pure $A_{AC}2$ mechanism, although their hydrolyses in water take place by the pure $A\text{–}B_{AC}3$ mechanism.[5,6,24]

Although there are some common features in the plots of k_m^o and k_m^H and k_h^o and k_h^H *vs.* x_w in Figures 1 and 2, respectively, the mechanistic interpretation on the basis of the kinetic data for the acid-catalysed methanolysis of chloromethyl chloroacetate in aqueous methanol is not straightforward. It should also be born in mind that the experimental difficulties described in the Experimental section may affect the values of k_m^H and k_h^H. Further, the $A\text{–}B_{AC}3$ and $A_{AC}2$ reactions of chloromethyl chloroacetate cannot be examined experimentally as they take place simultaneously. Some approximations are, however, possible. Let us assume that the kinetic solvent effects on the total decomposition and on the hydrolysis of chloromethyl chloroacetate by the $A_{AC}2$ mechanism behave uniformly with those on the total reaction of chloromethyl acetate[23] (Figure 2) and on the hydrolysis of methyl chloroacetate[10] in aqueous methanol. On this basis, the plots of k_T^H and k_h^H *vs.* x_w for the $A_{AC}2$ reactions of chloromethyl chloroacetate are shown in Figure 2, the difference of the curves representing the plot for its $A_{AC}2$ methanolysis in aqueous methanol.

Contrary to the neutral $B_{AC}3$ hydrolysis and to the acid-catalysed $A\text{–}B_{AC}3$ mechanisms, organic cosolvents seem to cause almost negligible rate retardations for the $A_{AC}2$ hydrolysis of halogen-substituted esters.[5,610] This behaviour accords with the reduced polarity brought about by the organic cosolvents in water and with the proposal that the rate-limiting addition of water to the carbonyl group of the ester takes place to the protonated ester in the case of the $A_{AC}2$ mechanism, while it in the case of the $A\text{–}B_{AC}3$ mechanism takes place to the neutral ester molecule. Thus, for the $A_{AC}2$ hydrolysis of methyl chloroacetate the value 7.43×10^{-5} dm^3 mol^{-1} s^{-1} observed for k_h^H in water decreases to the value 5.93×10^{-5} dm^3 mol^{-1} s^{-1} in aqueous methanol at x_w 0.50 at 25 °C;[10] in the present work (Table 2) there is eighteen-fold rate retardation under the same conditions. This observation supports the proposal that the acid-catalysed hydrolysis of chloromethyl chloroacetate in aqueous methanol at $x_w > 0.5$ takes place simultaneously by the $A\text{–}B_{AC}3$ and $A_{AC}2$ mechanisms, the proportion of the latter mechanism increasing with increasing methanol content. In accord with this proposal, the value 1.1×10^{-5} dm^3 mol^{-1} s^{-1} of k_h^H at x_w 0.500 (Table 2) nearly equals to the value approximated for the $A_{AC}2$ hydrolysis of chloromethyl chloroacetate in water (Figure 2). Thus, although it is not experimentally possible to separate the acid-catalysed hydrolysis of chloromethyl chloroacetate from the total reaction when $w_w < 0.5$ (the difference $k_h^H = k_T^H - k_m^H$ is negligible; Figure 2), it seems that the $A\text{–}B_{AC}3$ hydrolysis is practically slown down when x_w is approximately 0.5.

In the water-rich methanol solutions the observed second-order rate coefficients k_m^H for the acid-catalysed methanolysis of chloromethyl chloroacetate first increase considerably with increasing methanol content of the system, then staying on a level higher than that approximated for its $A_{AC}2$ reaction (Table 2, Figure 2). The different behaviour of the plots of k_m^H *vs.* x_w for the observed acid-catalysed and $A_{AC}2$ methanolyses of chloromethyl chloroacetate in Figure 2 are obvious. On this basis, the involvement of the $A\text{–}B_{AC}3$ mechanism in the case of its acid-catalysed methanolysis is obvious and agrees with the proposal that water acts as an effective general-base catalyst in the rate-limiting nucleophilic addition of methanol to the carbonyl group of halogen-substituted esters.[4] On the other hand, the rate coefficients k_m^H for the acid-catalysed methanolysis of chloromethyl chloroacetate decrease sharply when minor amounts of water are added to methanol (Table 2). This behaviour is consistent with the $A_{AC}2$ mechanism. Thus, *e.g.*, the rate coefficients for the acid-catalysed methanolysis of ethyl acetate at 30 °C decrease by a factor of 2.2 when 0.536% water is added into methanol.[22]

Because the $B_{AC}3$ and $A\text{–}B_{AC}3$ mechanisms go through the same rate-limiting step, the existence of the latter mechanism demands the existence of a measurable $B_{AC}3$ reaction as well. In accordance with the prevailing A–$B_{AC}3$ mechanism for the acid-catalysed methanolysis of chloromethyl chloroacetate in water-rich aqueous solutions, the ratio k_m^H/k_m^o is of the order found for k_h^H/k_h^o (Table 4). The increase in k_m^H/k_m^o with decreasing x_w seems to indicate an increasing contribution of the $A_{AC}2$ mechanism until in the alcohol-rich solutions only the $A_{AC}2$ mechanism is observed.

Conclusions

In aqueous methanol, chloromethyl chloroacetate reacts with both the components of the solvent. Kinetic data for the neutral $B_{AC}3$ hydrolysis of the ester follow the lines generally observed for halogen-substituted esters.[1,2,5,7] Both the neutral and the acid-catalysed methanolyses of the ester behave anomalously: the rate of methanolysis first increases with methanol concentration (Figures 1 and 2) and, in the case of the $B_{AC}3$ reaction, goes through the maximum at x_w close to 0.8. The rate maximum is proposed to be connected with the changes in the water–water, methanol–water, and methanol–methanol interactions in the solvent system.[17,18] The rate of the acid-catalysed methanolysis is found to decrease sharply if minor amounts of water are added into methanol (Figure 2).

In dilute acid solution, the acid-catalysed hydrolysis and methanolysis of chloromethyl chloroacetate in water-rich methanol solutions take place simultaneously by the $A_{AC}2$ and A–$B_{AC}3$ mechanisms. The proportion of the former mechanism seems to increase with increased methanol content of the system. In the case of hydrolysis, the A–$B_{AC}3$ mechanism evidently is slowed down when x_w reaches a value of *ca.* 0.5; in the case of methanolysis, highly alcohol-rich methanol solutions are needed for the pure $A_{AC}2$ mechanism.

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