Kinetics and Mechanisms of the Acid Hydrolysis of Chloromethyl Chloroacetate in Moderately Concentrated Electrolyte Solutions in Aqueous Dioxane

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The hydrolysis of acyl activated and α-haloalkyl acetates is known to take place as the neutral ester hydrolysis ($B_{AC}3$);[1-3] for the latter esters also solvolysis of the α-halogen is possible.[2-4] The uncatalysed reaction is accompanied by acid-catalysed hydrolysis, which in dilute acid solution is an $A_{AC}2$ reaction for esters with only one chloro-substituent,[2-5] a simultaneous $A_{AC}2$ and $A-B_{AC}3$ for those with two chlorine atoms[5,6] and $A-B_{AC}3$ for alkyl trichloroacetates and chloromethyl dichloroacetate.[5] The observed fact that the rates of the acid-catalysed hydrolyses of polyhalogen-substituted esters in water[2,5-12] increase non-linearly with increasing hydrogen-ion concentration has been previously[5,11,12] explained on the basis of an unsymmetrically catalysed partition of the tetrahedral intermediate which is common for the neutral $B_{AC}3$ and acid-catalysed $A-B_{AC}3$ mechanisms. Thus, the rate for the hydrolysis of chloromethyl chloroace-

tate in water at 25 °C is known to go through a flat maximum in about 2 M perchloric acid solution followed by a minimum in ca. 4 M acid and a rapid rate increase in more concentrated acid solutions.[6,9]

The aim of the present work was to study the acid-catalysed hydrolysis of chloromethyl chloroacetate in 40 wt. % aqueous dioxane containing sodium perchlorate or perchloric acid to obtain more information about the $A-B_{AC}3$ mechanism and solvent effects on it.

Experimental. Chloromethyl chloroacetate[8] and the reaction solutions[4,8] were prepared as described earlier. 1,4-Dioxane (E. Merck AG) was purified before use by the method of Hess and Frahm.[13] The reactions were followed by an argentometric method[6,8] by adding about 0.8 ml of the ester into 160 ml of the reaction mixture and pouring samples from there into cold acetone. In the most concentrated perchloric acid solutions ice was added to the arresting solution before titration.

The time-dependent first-order rate coefficients k_t and the time-average c_t of the hydrogen-ion concentration were calculated as described earlier.[4,5] The experimental results are given in Table 1.

Discussion. The mean value $\bar{k}_t$ of k_t for the hydrolysis of chloromethyl chloroacetate in perchloric acid solutions in 40 wt. % aqueous dioxane increases non-linearly with increasing hydrogen-ion concentration (Table 1, Fig. 1). The initial slope 8.94×10^{-5} s^{-1} M^{-1} for the plot of $\bar{k}_t$ vs. $\bar{c}_t$, calculated by fitting a parabolic equation

$$\bar{k}_t = k_o + k_{HX}\bar{c}_t + k_s\bar{c}_t^2$$

Table 1. Kinetic data for the hydrolysis of chloromethyl chloroacetate in sodium perchlorate or perchloric acid solutions of 40 wt. % aqueous dioxane at 25 °C.

[NaClO$_4$]/M	[HClO$_4$]/M	$\bar{c}_t$/M	$\bar{k}_t/10^{-5}$ s^{-1}	$k_\psi^a/10^{-5}$ s^{-1}	$k_H^b/10^{-5}$ s^{-1} M^{-1}
0.197	0	0.0170	1.092		
0.477	0	0.0168	0.908		
1.125	0	0.0146	0.597		
0	0	0.0205	1.318		8.7^c
0	0.197	0.2190	2.96	1.81	8.26
0	0.477	0.4986	4.98	4.03	8.08
0	1.018	1.042	7.76	7.08	6.79
0	1.462	1.482	9.69	9.19	6.20
0	1.954	1.972	11.24	10.9	5.53
0	2.764	2.782	12.56	12.4	4.46
0	3.530	3.547	12.72	12.6	3.55
0	4.015	4.033	13.67	13.6	3.37
0	4.54	4.556	14.97	14.9	3.27

^{a} $k_\psi = \bar{k}_t$ (HClO$_4$)$-\bar{k}_t$ (NaClO$_4$); ^{b} $k_H = k_\psi/\bar{c}_t$; ^{c} the initial slope for the plot of k_ψ vs. $\bar{c}_t$.
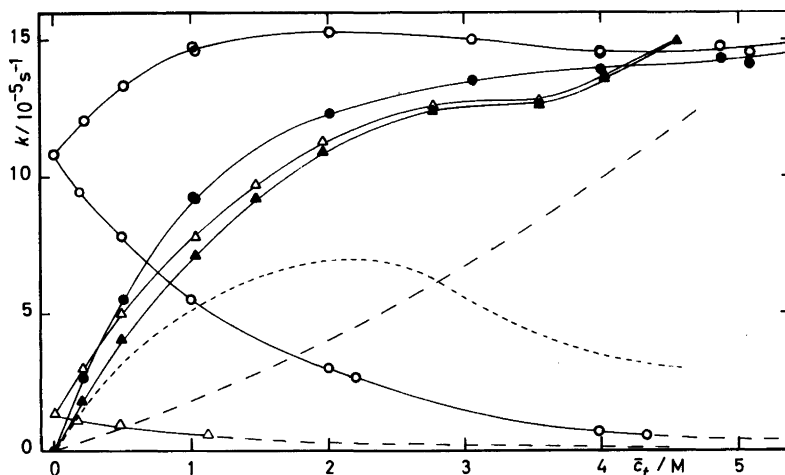
Fig. 1. Plots of the first-order rate coefficients $\bar{k}_t(HClO_4)$ and $\bar{k}(NaClO_4)$ for the hydrolysis of chloromethyl chloroacetate in water[6] (O) and in 40 wt. % aqueous dioxane ($\triangle$) and $k_y = \bar{k}_t(HClO_4) - \bar{k}_t(NaClO_4)$ in water[6] (●) and aqueous dioxane (▲), respectively, *vs.* hydrogen-ion concentration $\bar{c}_t$ at 25 °C. The broken curve is a calculated plot for the $A_{AC}2$ mechanism with the Bunnett-Olsen ϕ value 0.92 and 20 % proportion for this mechanism in dilute acid solutions; the dotted curve is the respective plot for the $A-B_{AC}3$ mechanism.

to the data by the method of least squares, is higher than the value 6.7×10^{-5} s^{-1} M^{-1} found for the acid hydrolysis of the same ester in water at 25 °C.[8] This unexpected solvent effect of dioxane is explained by the reduced salt effect of the added acid on the neutral ester hydrolysis when compared to that in water (Fig. 1, Refs. 8 and 9). Thus the dependence of rate on the perchloric acid concentration for the hydrolysis of chloromethyl chloroacetate in 40 wt. % aqueous dioxane, obtained by the difference $k_w = k(HClO_4) - k(NaClO_4)$, is only slightly smaller and very similar to that on the hydrolysis in water[9] (Table 1, Fig. 1). On this basis it can be concluded that also the reaction mechanisms in the two solvents are similar.

The rate coefficients for the hydrolysis of chloromethyl chloroacetate in dilute acid solutions is known to include the contributions of the mechanisms $A_{AC}2$ and $A-B_{AC}3$.[5,6] Thus, for the reaction in water at 25 °C it has been estimated that the rate coefficient is 1.2×10^{-5} s^{-1} M^{-1} for the $A_{AC}2$ hydrolysis[6] when the observed rate coefficient k_H is 12.7×10^{-5} s^{-1} M^{-1} for the acid-catalysed hydrolysis.[8,9] In more concentrated acid solutions the reaction is shown to take place by the $A_{AC}2$ mechanism.[6]

It is known that the solvent effects on reaction rates for the $A_{AC}2$ mechanism in dilute acid solutions are much smaller for the esters with one

chloro-substituent than for unsubstituted esters such as methyl acetate.[4,5,14,15] On this basis it might be expected that addition of acetone or dioxane should increase the hydrolysis rate of chloromethyl chloroacetate by the normal $A_{AC}2$ mechanism. However, for the neutral ester hydrolysis of chloromethyl chloroacetate at 25 °C the rate coefficient k_o 10.8×10^{-5} s^{-1} in water[8] is reduced to the values 1.13×10^{-5} and 0.50×10^{-5} s^{-1} in 40 wt. % aqueous dioxane and acetone,[5] respectively; for the hydrolysis in dilute perchloric acid solutions the rate retardation is from the value 12.7×10^{-5} s^{-1} M^{-1} of k_H in water[8,9] to the values 8.7×10^{-5} and 5.6×10^{-5} s^{-1} M^{-1} in 40 wt. % aqueous dioxane and acetone,[5] respectively. These results indicate that the prevailing mechanism for the hydrolysis of chloromethyl chloroacetate in dilute acid solutions of aqueous organic cosolvents is $A-B_{AC}3$ rather than $A_{AC}2$. This is also in accord with the model that the same tetrahedral intermediate is formed in the rate-determining step of both the neutral $B_{AC}3$ and acid-catalysed $A-B_{AC}3$ mechanisms.[5,11,12] This result does not support the proposal made by Paleta *et al.*[10] that the acid hydrolysis of many highly acyl-halogenated methyl propionates in 0.5 M solution of hydrochloric acid in 80 vol. % aqueous methanol take place by the $A_{AC}2$ mechanism. However, on the basis of their results, there seems to be no reasons why the

$A_{AC}2$ mechanism could be a better explanation than the $A-B_{AC}3$ mechanism, proposed for the hydrolyses of alkyl trichloroacetates in dilute acid solutions in water.[5,11]

Various linear free energy relationships have been employed to the present data using the Hammett acidity function H_o for perchloric acid solutions in 40 wt. % aqueous dioxane measured by Bunton et al.[16] In accord with the acid-catalysed hydrolysis of chloromethyl chloroacetate in water[6] the most useful of these relationships seems to be the plot of $(H_o+\log k_\psi)$ vs. $(H_o+\log \bar{c}_t)$ with the slope ϕ, proposed by Bunnett and Olsen.[17] For the reactions which take place by the $A_{AC}2$ mechanism the value of ϕ has been found to range from 0.74 to 1.0.[2] Thus, ϕ is 0.9 for the $A_{AC}2$ hydrolysis of chloromethyl acetate and chloroacetate in water[6] and 0.87 and 0.92 in the case of ethyl acetate in water[18] and 60 wt. % aqueous dioxane,[16] respectively. Various rate coefficients for the $A_{AC}2$ hydrolysis of chloromethyl chloroacetate in 40 wt. % aqueous dioxane have been calculated using ϕ values from 0.85 to 1.0 and assuming that in dilute acid solutions 5 to 30 % of the reaction takes place by this mechanism. The respective rate coefficients for the $A-B_{AC}3$ hydrolysis then result from the differences between the observed and calculated rate coefficients. On the other hand, as in the case of the reaction in water,[6] in moderately concentrated acid solutions the $A-B_{AC}3$ hydrolysis should gradually slow down with the increasing proportion of the $A_{AC}2$ mechanism (Fig. 1). Taking this into account it seems that in the present case a good agreement is obtained using the ϕ value 0.92, found for the hydrolysis of ethyl acetate in 60 wt. % aqueous dioxane,[16] and assuming that in dilute acid solutions about 20 % of the reaction takes place by the $A_{AC}2$ mechanism. By these assumptions the second-order rate coefficient for the $A_{AC}2$ hydrolysis at 25 °C is 1.7×10^{-5} s^{-1} M^{-1} which is in agreement with the above-mentioned expectation about solvent effects on the $A_{AC}2$ hydrolyses of halogen-substituted esters. For the $A-B_{AC}3$ hydrolysis, the Bunnett-Olsen plot is then upward curved in the most concentrated acid solutions and the slope for the linear part of the plot is 1.3. This ϕ value compares satisfactorily with the value 1.4, found for the reaction in water,[6] and is in accord with the higher number of water molecules associated with the rate-limiting step in this mechanism. However, it should be remembered that mechanistic interpretation of ϕ values for weakly basic substrates may be fraught with uncertainty.[17] Also the low experimental accuracy of the kinetic measurements must be taken into account when the proportions of the two mechanisms are discussed.

On the basis of the above consideration it may be concluded that, for the acid-catalysed hydrolysis of chloromethyl chloroacetate, dioxane slightly increases the ratio of the $A_{AC}2$ and $A-B_{AC}3$ mechanisms when compared to that in water.[6] This result supports the proposal made for the acid-catalysed hydrolysis of the same ester in aqueous acetone solutions at the constant ionic strength of 0.2.[5]

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