# Kinetics and Mechanisms of the Hydrolysis of 1-Chloroalkyl Esters in Dilute and Moderately Concentrated Aqueous Acid Solutions

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The hydrolysis rates of chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate have been measured in 0 to 9 M perchloric acid and 0 to 5 M lithium perchlorate solutions at 25 °C. The rate of the former ester is a maximum at a $\sim$2 M and a minimum at a $\sim$5 M acid and that of the latter ester is a minimum at a $\sim$6 M acid solution, whereas in salt solutions, the rates decrease continuously. This is explained assuming that, in addition to a neutral $B_{AC}3$ hydrolysis, there is a normal $A_{AC}2$ type acid catalysis at high acid concentrations whereas in less concentrated acid solutions, an $A-B_{AC}3$ reaction prevails.

It is now well known[1a] that 1-haloalkyl esters undergo a neutral hydrolysis which takes place as a solvolysis of the halogen when the ester has no other electronegative substituents. When there are several halogen atoms in the $\alpha$ positions of the ester, the reaction usually is a neutral $B_{AC}3$ hydrolysis. These reactions are accompanied by acid-catalysed hydrolyses. For the former esters, it is the normal $A_{AC}2$ hydrolysis[1b,2] in dilute and moderately concentrated acid solutions. A change to a unimolecular mechanism has been observed in more concentrated acid solutions.[2,3] For chloromethyl acetate, the change only begins at about 10 to 12 M acid,[2] but is clearer at 10 M acid for chloromethyl pivalate[3] which for steric reasons has a slower $A_{AC}2$ reaction. The unimolecular acid-catalysed hydrolysis of these esters was concluded as taking place by the $A_{AC}1$ mechanism.[2,3]

Esters with several electronegative substituents, such as chloromethyl chloroacetate[2] and ethyl trichloroacetate, also hydrolyse at high acid concentrations by the $A_{AC}2$ mechanism, but in less concentrated acid solutions the mechanism is assumed to include an unsymmetrically acid-catalysed partition of the intermediate formed in the neutral $B_{AC}3$ hydrolysis.[4,5] Therefore, it is called

an $A-B_{AC}3$ mechanism.[6-8] A detailed consideration of this mechanism was recently given by two of us.[9] According to that report, the assymmetry in the catalysis is mainly a consequence of the decomposition of the neutral intermediate formed via the $B_{AC}3$ path, by a concerted reaction catalysed by the oxonium ion and water as a general acid and a general base, respectively. Because the structural and other factors influencing this assymmetrical catalysis are still inadequately known, we now report the results obtained for the two esters not studied previously, chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate.

## Experimental

*Materials.* Chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate were previous preparations.[10] Perchloric acid solutions[11] and a 5 M stock solution of lithium perchlorate[3] were prepared as described earlier.

*Kinetic measurements* were performed[3] and the time-dependent first order rate coefficients $k_t$ and the time averages $c_t$ of the oxonium ion concentration were calculated[8] as described previously. The standard deviations of the mean $\bar{k}_t$ for ex-

*Table 1.* Kinetic data for the hydrolyses of chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate in initially neutral aqueous solutions containing lithium perchlorate at 25 °C

| | CH$_2$FCOOCH$_2$Cl | | CH$_2$ClCOOCHClCH$_2$Cl | |
| --- | --- | --- | --- | --- |
| $c$(LiClO$_4$)/M | $\bar{c}$/10$^{-3}$ M | $\bar{k}$/10$^{-4}$ s$^{-1}$ | $\bar{c}$/10$^{-3}$ M | $\bar{k}$/10$^{-4}$ s$^{-1}$ |
| 0.0 | 1.9 | 1.44(1) | 2.3 | 3.85(2) |
| 0.1 | 2.6 | 1.41(1) | 2.8 | 3.64(5) |
| 0.2 | 2.8 | 1.32(1) | 1.3 | 3.63(1) |
| 0.5 | 2.1 | 1.26(1) | 1.9 | 3.43(7) |
| 1.0 | 2.6 | 1.16(2) | 2.3 | 2.59(2) |
| 2.0 | 1.9 | 0.92(6) | 1.6 | 1.91(2) |
| 5.0 | 2.9 | 0.41(4) | 2.1 | 0.87(1) |

perimental runs in dilute and moderately concentrated electrolyte solutions were in general of the order of 1 %, the deviations for parallel runs being somewhat greater (up to 2.7 %). However, in the most concentrated acid solutions the standard deviations increased rapidly, evidently because of the evaporation of hydrogen chloride from these solutions when the samples were pipetted from the reaction mixtures into the chilling solution.

*Acidity functions.* The values of the Hammett acidity function $H_0$ and the function $X_0 = H_0 + \log c_{H^+}$ for the perchloric acid solutions were calculated according to Cox and Yates.[12] The densities of the solutions at 25 °C, required to convert the molar concentrations into weight percentages, were calculated by the interpolation equation given by Markham[13] for the range from 0 to 65 weight per cent and estimated from the density data[14] for 20 °C and the average value of 0.9975 for the temperature coefficient $d_4^{25}/d_4^{20}$ for higher concentrations.

## Results and discussion

*Neutral hydrolysis.* Owing to the halogen atoms in both the acyl and alkyl components of the esters, the hydrolyses of chloromethyl chloroacetate and fluoroacetate and 1,2-dichloroethyl chloroacetate in water at 25 °C take place by the neutral ester hydrolysis mechanism, $B_{AC}3$,[1c,9,15] although at higher temperatures, the solvolysis of the 1-halogen is possible, too.[16] In accordance with the higher electronegativity and the smaller size of fluorine, the rate coefficient $k_0$ for the $B_{AC}3$ hydrolysis of chloromethyl fluoroacetate (1.44×10$^{-4}$ s$^{-1}$, Table 1) is higher than that of chloromethyl chloroacetate[11] (1.082×10$^{-4}$ s$^{-1}$).

The chloromethyl group in 1,2-dichloroethyl chloroacetate increases the hydrolysis rate ($k_0 = 3.85×10^{-4}$ s$^{-1}$, Table 1) compared to that of the latter ester.

As shown in Fig. 1, the added electrolytes decrease the rate of the neutral ester hydrolysis.[11,15] This effect seems to be quite similar for sodium and lithium perchlorates at least up to 1 M solution.[5,8] The retarding effect of the added salts increases in the order of chloromethyl fluoroace-
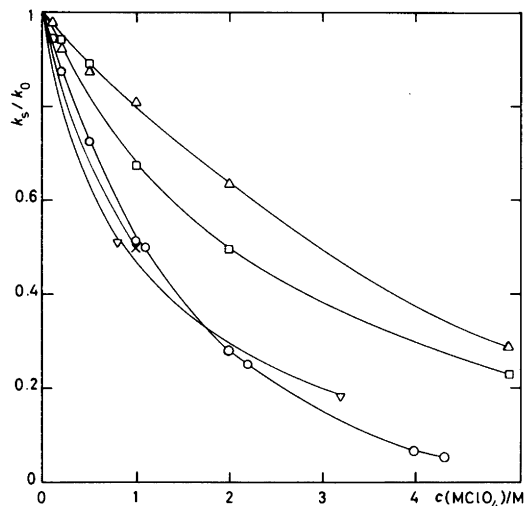


*Fig. 1.* Plots of the ratio $k_s/k_0$ of the rate coefficients in aqueous solutions with or without added salts at 25 °C versus the molar concentration $c$ of MClO$_4$ for the hydrolyses of chloromethyl fluoroacetate ($\triangle$, M = Li), 1,2-dichloroethyl chloroacetate ($\square$, M = Li), chloromethyl chloroacetate[2] ($\bigcirc$, M = Na), ethyl difluoroacetate[15] ($\triangledown$, M = Na) and ethyltrichloroacetate[5] ($\times$, M = Li).

*Table 2.* Kinetic data for the acid-catalysed hydrolyses of chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate in aqueous perchloric acid solutions at 25 °C

| | | $CH_2FCOOCH_2Cl$ | | | | $CH_2ClCOOCHClCH_2Cl$ | |
|---|---|---|---|---|---|---|---|
| $\bar{c}/M$ | $H_0$ | $\bar{k}/10^{-4}\,s^{-1}$ | $K_\psi^*/10^{-4}\,s^{-1}$ | $\bar{c}/M$ | $H_0$ | $\bar{k}/10^{-4}\,s^{-1}$ | $k_\psi^*/10^{-4}\,s^{-1}$ |
| 0.002 | 2.72 | 1.44(1) | 0 | 0.002 | 2.64 | 3.85(2) | 0 |
| 0.102 | 0.96 | 1.51(1) | 0.14 | 0.101 | 0.96 | 3.67(2) | – |
| 0.195 | 0.65 | 1.56(3) | 0.23 | 0.195 | 0.65 | 3.81(4) | 0.15 |
| 0.502 | 0.15 | 1.64(1) | 0.37 | 0.501 | 0.15 | 3.82(2) | 0.54 |
| 1.000 | −0.27 | 1.74(3) | 0.58 | 1.000 | −0.27 | 3.30(2) | 0.60 |
| 2.024 | −0.81 | 1.84(2) | 0.93 | 2.022 | −0.81 | 2.99(1) | 1.12 |
| 4.059 | −1.72 | 1.78(8) | 1.25 | | | | |
| 4.908 | −2.16 | 1.75(1) | 1.33 | 4.922 | −2.17 | 1.81(1) | 0.93 |
| 5.987 | −2.80 | 1.79(4) | 1.47 | | | | |
| 6.785 | −3.33 | 1.87(3) | 1.62 | | | | |
| 8.879 | −4.93 | 2.55(1) | 2.42 | 8.879 | −4.93 | 2.10(2) | 1.69 |
| 9.246 | −5.24 | 3.02(8) | 2.91 | | | | |

tate, 1,2-dichloroethyl chloroacetate and chloromethyl chloroacetate (Fig. 1), but, taking into account the quite similar effect for chloromethyl



*Fig. 2.* Plots of the rate coefficients $k$ versus the molar concentration $c_{H^+}$ of perchloric acid at 25 °C for the hydrolyses of chloromethyl fluoroacetate ($\triangle$), 1,2-dichloroethyl chloroacetate ($\square$) and chloromethyl chloroacetate[2] ($\bigcirc$). Full lines: observed rate coefficients $\bar{k}_t$. Broken lines: $k_\psi^* = k(HClO_4) - k(MClO_4)$.

chloroacetate, ethyl trichloroacetate and ethyl difluoroacetate, it seems that no single structural factor can explain the observations or the effects of the perchlorates on the structure of water.
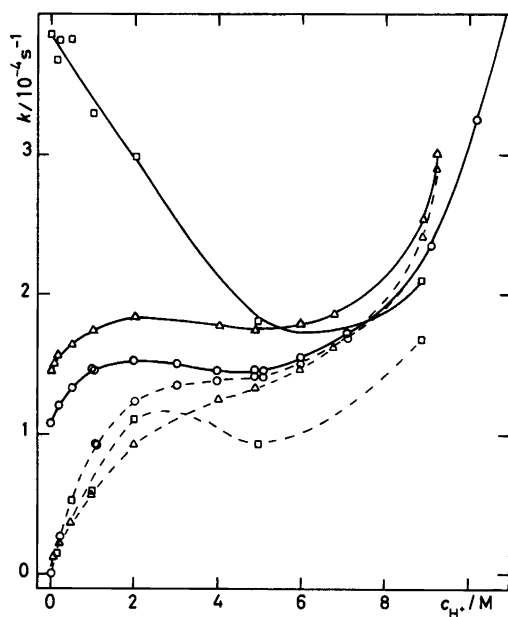
*Acid catalysis.* As mentioned above, esters which show a measurable neutral ester hydrolysis ($B_{Ac}3$), such as chloromethyl chloroacetate, also have an acid-catalysed $A−B_{Ac}3$ reaction for which it is typical that the rate does not increase linearly with the oxonium ion concentration.[7,17] Thus, the values of $\bar{k}_t$ for the hydrolyses of chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate change non linearly with increasing oxonium ion concentration at least up to 9 M perchloric acid solution (Table 2, Fig. 2). As shown in Fig. 2, the behaviour of the former ester is similar to that found for the hydrolysis of chloromethyl chloroacetate,[2] the plot of $\bar{k}_t$ versus $c_{H^+}$ going through a maximum at ~2 M acid and a minimum at ~5 M acid solution. In the case of 1,2-dichloroethyl chloroacetate the respective curve decreases to a minimum at 6 M acid.

In acid solutions, the measured rates include, in addition to the acid-catalysed hydrolysis, neutral $B_{Ac}3$ hydrolysis also, upon which, perchloric acid evidently has a negative electrolyte effect. It seems quite safe to assume that this effect of acids does not differ much from that of alkali metal salts with the same anion, at least not in relatively dilute solutions.[2] Thus, the rate for the perchloric acid-catalysed reaction can be calculated from eqn. (1) where the $k(HClO_4)$ and the

339

*Fig. 3.* The Bunnett-Olsen plots of $(H_0 + \log k_\psi^*)$ versus $(H_0 + \log c_{H^+})$ for the acid-catalysed hydrolyses of chloromethyl fluoroacetate ($\triangle$), 1,2-dichloroethyl chloroacetate ($\square$) and chloromethyl chloroacetate[2] ($\bigcirc$). The straight line represents the estimated $A_{AC}2$ reaction of chloromethyl chloroacetate.
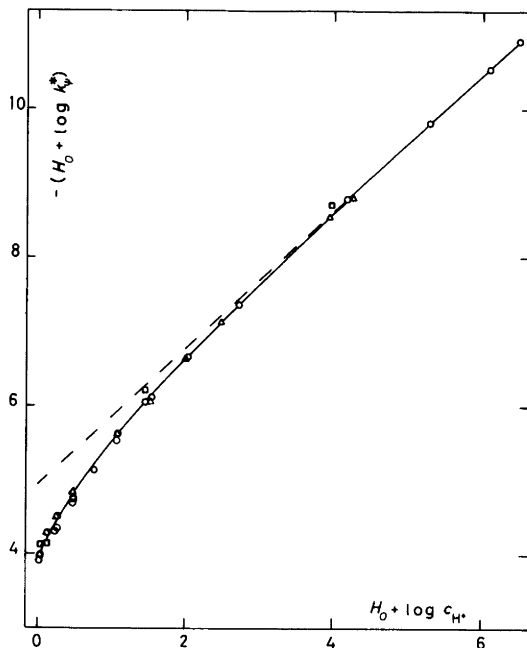


$k(\text{LiClO}_4)$ are the observed rate coefficients for hydrolyses in acid and salt solutions, respectively.

$$k_\psi^* = k(\text{HClO}_4) - k(\text{LiClO}_4). \qquad (1)$$

Because of experimental scatter and the limited solubility of lithium perchlorate the rate coefficients for neutral hydrolysis in salt solutions were fitted to eq. (2) by the method of least-squares to obtain the values of $k(\text{LiClO}_4)$ above the solubility limit, $\sim 5$ M.

$$k(\text{LiClO}_4) = a_0 + a_1y + a_2y^2, \text{ and}$$
$$y = 1/[1+c(\text{LiClO}_4)]. \qquad (2)$$

Fig. 2 shows that the rate coefficient $k_\psi^*$ for the perchloric acid-catalysed reaction first increases quite similarly for the hydrolyses of chloromethyl chloroacetate, chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate, the increase being fastest for chloromethyl chloroacetate. Thus, the hydrolysis mechanism is evidently the same in this range. Further conclusions can be drawn by considering the Bunnett-Olsen plot[18] (Fig. 3). As mentioned above, the hydrolysis of chloromethyl chloroacetate in relatively dilute acid solutions takes place simultaneously by the $A-B_{AC}3$ and $A_{AC}2$ mechanisms, but in moderately concentrated acid solutions, the normal $A_{AC}2$ mechanism becomes dominant. On the basis of the similarity of the plots, this is evidently also true for the hydrolyses of chloromethyl fluoroacetate and 1,2-dichloroethyl chloroacetate. The kinetic data for chloromethyl chloroacetate were decreased using the new values[12] of $H_0$. The four points at the highest acid concentrations (Fig. 3) were fitted to the equation of a straight line by the method of least-squares, yielding for the slope the value of 0.916(13), which is typical for the $A_{AC}2$ reaction,[18] and for the intercept, $-\log k_\psi$ the value of 4.94(7). The last mentioned value, corresponding to the rate coefficient of $1.1 \times 10^{-5}$ $\text{M}^{-1}$ $\text{s}^{-1}$ for the $A_{AC}2$ hydrolysis in dilute acid solutions, is in good agreement with the earlier[2] estimate $1.2 \times 10^{-5}$ $\text{M}^{-1}$ $\text{s}^{-1}$. In the case of other esters considered, the hydrolysis reactions were not studied in sufficiently concentrated acid solutions to make any estimations about the rate coefficients for the $A_{AC}2$ hydrolysis, but on the basis of Fig. 2, it can be concluded that the rate for the $A_{AC}2$ hydrolysis of 1,2-dichloroethyl chloroacetate is slower than that for the other esters. This is also in accord with the steric effects which are important in the $A_{AC}2$ mechanism. The points of the Bunnett-Olsen plot for the three esters (Fig. 3) fall on the same curve, the slope of which approaches the exceptionally high value of 2, possibly reflecting the high degree of ordering in the water structure associated with the $A-B$ and $B_{AC}3$ reactions.

Kurz and Farrar[5] proposed that the dependence of the observed pseudo-first-order rate coefficient $k_\psi$ on $c_{H^+}$ at constant ionic strength for

340

*Table 3.* Rate parameters $k_a$, $k_b$ and $k_c$ [eqn. (3)] and derived parameters $k_1$ and $\alpha$ for the acid-catalysed hydrolysis at variable ionic strength in water at 25 °C from 0 to 2 M perchloric acid

| Ester | Data points | $k_a/10^{-4}\,s^{-1}$ | $k_b/M^{-1}$ | $k_c/10^{-4}\,s^{-1}$ | $k_1/10^{-4}\,s^{-1}$ | $\alpha$ |
|---|---|---|---|---|---|---|
| CH₂ClCOOCH₂Cl[a] | 6 | 1.07(2) | 0.78(10) | 2.4(2) | 3.1(5) | 1.9(5) |
| CH₂FCOOCH₂Cl | 6 | 1.47(3) | 0.67(20) | 1.9(4) | 3(1) | 1.0(7) |
| CH₂ClCOOCHClCH₂Cl | 6 | 3.85(7) | 0.3(3) | 1.9(13) | 7(9) | 1(2) |

[a]Experimental data from Ref. 2.

the exceptionally acid-catalysed hydrolysis follows eq. (3). In the case of variable ionic strength, all of the rate parameters represent data at a hypothetical zero electrolyte concentration and the values of $k\psi$ are obtained from eq. (4), in which $k_O$ is the rate coefficient for the neutral hydrolysis at zero electrolyte concentration.

$$k_\psi = (k_a+k_c[H^+])/(1+k_b[H^+]) \qquad (3)$$

$$k_\psi = k_O+k_\psi^*. \qquad (4)$$

The kinetic data were treated by eq. (3) as described previously.[9] From the parameters of eq. (3), one can calculate the rate constant $k_1 = k_c/k_b$ for the general base-catalysed addition of water to the carbonyl group of the ester and the partition coefficient $\alpha = (k_c/k_a k_b) - 1$ for the tetrahedral intermediate formed. The esters studied here also obey eq. (3) satisfactorily.The calculated values are given in Table 3. Because $k_a$, in accord with eqs. (3) and (4), is the rate coefficient of the neutral hydrolysis, it follows the trends discussed above. The value 1.9 now obtained for the partition coefficient $\alpha$ of the hydrolysis of chloromethyl chloroacetate for the concentration range from 0 to 2 M is in relatively good agreement with the previous values,[9] 2.4 and 1.7, for the ranges from 0 to 1 and from 0 to 4 M, respectively.

When considering the parameters of eq. (3), one should take into account that $k_b$ and $k_c$ are highly correlated (correlation coefficients in general > 0.99). Therefore, the unavoidable experimental errors may have an appreciable effect on these parameters. In addition, the extrapolation in Fig. 3 indicates that the measured rates include about a 10 % contribution of the $A_{AC}2$ reaction, requiring a term $k_d[H^+]$ to be added to eq. (3). However, as shown in the case of constant ionic strength,[9] the calculations regarding the $A_{AC}2$ reaction also led to a negative value for $k_d$, probably owing to the high correlations between $k_b$, $k_c$ and $k_d$ which make the addition of the fourth parameter to eq. (3) unreliable. Also, specific salt effects evidently are important at high electrolyte concentrations. Model calculations indicate that the omission of the term $k_d[H^+]$, when it really exists, leads to definite trends in the other parameters, which were not found in the actual regression analysis. Thus, one may conclude that the contribution of the $A_{AC}2$ mechanism is at least not markedly higher than the above estimation.

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