

The Acid-Catalysed Solvolysis of Alkoxyethyl Esters

Part V. Hydrolysis of β -Chloroethoxymethyl Esters

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The acid-catalysed hydrolysis reactions of the β -chloroethoxymethyl esters of formic and acetic acids have been studied kinetically. Evidence has been collected which shows that the formic ester hydrolyses in dilute acid solution at low temperatures predominantly by the bimolecular $A_{AC}2$ mechanism with a minor contribution by the unimolecular $A_{AL}1$ mechanism. The existence of the two reaction paths is indicated, firstly, by the actual magnitudes of the rate coefficients in comparison to the values estimated from the linear free energy relations, secondly, by the deviation from linearity of the plot of the logarithm of the rate coefficient against reciprocal temperature, and, thirdly, by the variation of the rate coefficient in moderately acid solutions. The relative contributions of the two mechanisms to the over-all rates have been estimated.

The kinetic data for β -chloroethoxymethyl acetate, on the other hand, are consistent with the assumption that this ester hydrolyses predominantly by the unimolecular $A_{AL}1$ mechanism, although there is definite indication of a simultaneous, minor contribution by the $A_{AC}2$ mechanism.

In a recent study of the hydrolysis of alkoxyethyl esters of acetic and formic acids¹, evidence based on kinetic data obtained by different experimental methods was presented which suggested that methoxymethyl and ethoxymethyl esters of acetic acid hydrolyse in aqueous acid solutions by the unimolecular $A_{AL}1$ mechanism whereas a contribution of the bimolecular $A_{AC}2$ mechanism to the over-all rate was established in the hydrolysis of methoxymethyl formate. The magnitudes of the rate coefficients of the hydrolysis of β -chloroethoxymethyl formate* at different temperatures and the computed value of the activation energy indicated as highly probable that the electron-attracting substituent chlorine retards the unimolecular mecha-

* An error was made when the rate constants for this compound reported by Palomaa and Herna² were cited in Ref.¹. The correct value at 25°C is 0.00368 l mole⁻¹s⁻¹ and the correct value of the activation energy 15 300 cal/mole. These values are, however, close to those obtained for alkyl formates and do not therefore alter the conclusions drawn.

nism to such an extent that the bimolecular mechanism dominates this reaction. The present study was undertaken to obtain a more detailed picture of the nature of this reaction and also to determine the effect of the halogen on the reaction of the corresponding ester of acetic acid. The acid components of the esters were selected in order to effect a real change in the rate by the bimolecular mechanism (*cf.*, *e.g.*, *Ref.*³).

HYDROLYSIS OF β -CHLOROETHOXYMETHYL FORMATE

In dilute hydrochloric acid solutions, the rate of hydrolysis of β -chloroethoxymethyl formate was found to be proportional to the molar concentration of the acid and hence the values of the second-order rate coefficients k_c , obtained by dividing the directly computed first-order rate coefficients by the acid concentration, were essentially independent of the latter. Table 1 contains the values determined for k_c in these solutions at different temperatures. The values referring to the temperatures 15°, 25° and 35°C are from 4 to 9 % lower than the values obtained earlier by Palomaa and Herna² who used a slightly different method of following the reaction.

Table 1. Hydrolysis of β -chloroethoxymethyl formate in dilute (0.05–0.1 M) hydrochloric acid solutions. Values of k_c (in $l \text{ mole}^{-1}\text{s}^{-1}$) at different temperatures.

°C	0.88	9.00	15.00	25.00	35.00	46.00	55.83	67.60
$10^3 k_c$	0.318	0.775	1.40	3.33	7.72	22.6	[51.2	134

Although the rate coefficients at low temperatures are of the magnitude generally observed for formic esters that react by the normal type of acid-catalysed ester hydrolysis involving a bimolecular acyl-oxygen fission, certain observations suggest that the over-all rate coefficients include a minor contribution of another mechanism, the unimolecular alkyl-oxygen fission. In a recent study⁴ it was shown that the solvolytic reactions of alkoxyethyl compounds that can be assumed to involve a unimolecular formation of an unstable alkoxyethyl cation in the rate-determining stage exhibit approximately linear free energy correlations when the structure of the alkoxy group is varied. On the basis of the values of the rate coefficients, polar substituent constants and reaction constants given, it is possible to obtain an estimate, $k_c = 9 \times 10^{-4} l \text{ mole}^{-1}\text{s}^{-1}$, for the rate coefficient of the hydrolysis of β -chloroethoxymethyl formate at 25°C by the unimolecular mechanism; this amounts to one-fourth of the measured over-all rate coefficient. Although the estimated value cannot be very accurate, its magnitude shows that a concurrent reaction mechanism is highly probable.

The existence of two independent reaction paths is indicated also by the observed temperature dependence of the rate coefficients. The plot of $\log k_c$ for β -chloroethoxymethyl formate against reciprocal temperature shown in Fig. 1 reveals a satisfactory linearity in the low temperature range but increases in slope at the higher temperatures. Such a behaviour is in accord with the occurrence of two concurrent reactions with different activation energies;

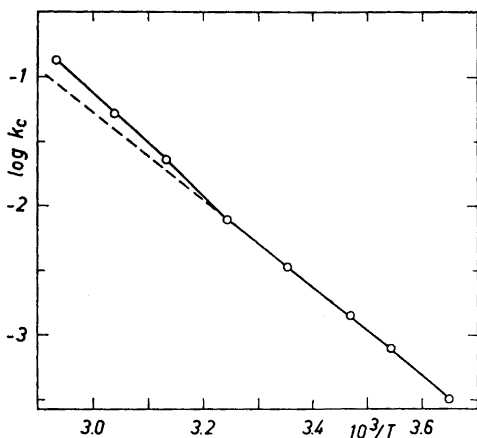


Fig. 1. Hydrolysis of β -chloroethoxy-methyl formate at different temperatures. Plot of $\log k_c$ against $1/T$.

the reaction with the lower activation energy dominates in the low temperature range but the contribution of the second reaction with the higher activation energy gradually becomes more significant as the temperature rises. The situation is in principle similar to that observed with methoxymethyl formate¹.

Calculations made by the iteration method¹ assuming that the over-all rate coefficient is the sum of two rate coefficients which both vary with temperature in accordance with the Arrhenius equation, $k_c = k_1 + k_2 = A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT)$, revealed that the following values of the four Arrhenius parameters, $E_1 = 22$ kcal/mole, $\log A_1 = 13$, $E_2 = 14.4$ kcal/mole and $\log A_2 = 8.0$, yield a plot which reasonably closely approximates the experimental plot. Although the above values of the constants include in addition to experimental errors any errors due to genuine deviations from the Arrhenius equation (the values for the reaction indicated by subscript 2 can be more reliably calculated than those for reaction 1 because the former reaction which has the lower activation energy dominates over the greater part of the temperature range), they are of the magnitudes expected for the postulated mechanisms (cf. Ref.¹). From the values of the parameters it can be estimated that the contribution of the unimolecular mechanism is about one-fourth of the over-all rate at 25°C. This estimate is in good agreement with the estimate obtained above on the basis of polar substituent effects.

The third item of evidence for the simultaneous operation of two mechanisms is obtained from the kinetic data for the reaction in moderately acid solutions when the data are considered in relation to the acidity function H_o of Hammett⁵. Although the general applicability of the Zucker-Hammett hypothesis^{5,6} for a basis of criterion of reaction mechanism has recently been questioned⁷⁻¹⁰, the hypothesis seems to be in satisfactory accord with the kinetic data for the hydrolysis reactions of aliphatic esters of different types in hydrochloric acid solutions^{1,11-13}. In this connection it may be pointed out that there hardly exists any single, unequivocal experimental criterion for the determination of the molecularity of a solvolytic reaction.

In a preliminary communication¹⁴ the authors drew attention to the fact that if the Zucker-Hammett hypothesis is valid for the types of reaction under study and these reactions involve concurrent unimolecular and bimolecular

Table 2. First-order rate coefficients k (in s^{-1}) for the hydrolysis of β -chloroethoxymethyl formate in hydrochloric acid solutions. The acid concentrations, given in moles per liter, refer to 25°C .

0.88°C		25.00°C	
c_{HCl}	10^4k	c_{HCl}	10^3k
0.1534	0.490	0.1534	0.511
0.590	2.06	0.590	2.15
0.944	3.44	0.944	3.98
1.534	5.40	1.534	8.20
2.36	11.6	2.36	14.0
3.07	19.2	3.06	21.5
3.78	28.9	3.77	38.5
4.72	63.7	4.72	67.8
6.93	421		

mechanisms, the latter mechanism will not become clearly evident when the reactions take place in hydrochloric acid solutions of moderate concentration unless its contribution happens to be the dominating one. This is because the unimolecular mechanism becomes more significant with increasing acidity and finally overweighs the bimolecular mechanism so that the latter can no longer be experimentally detected. If, however, the contribution of the bimolecular mechanism is large enough in dilute acid solution, the plot of $\log k$ against $-H_0$ will have a special form characterized by a point of inflexion. This follows from the fact that the rate increases less rapidly at low acidities where the contribution of the bimolecular mechanism is significant than at high acidities where the unimolecular mechanism assumes control.

The above behaviour expected in the case of two concurrent mechanisms was actually observed in the hydrolysis of β -chloroethoxymethyl formate¹⁴. The data relating to 25°C on the basis of which the plot of *Ref.*¹⁴ was made are given in Table 2. As the bimolecular mechanism could be assumed to become even more significant at lower temperatures because of its lower activation energy, the variation of the over-all rate with increasing acidity was investigated also at 0.88°C . These results are given in Table 2 in addition to those referring to 25°C . The curve plotting the logarithm of the observed first-order rate coefficient at 0.88°C against the value of the acidity function at 25°C (Fig. 2) is similar in form to that referring to the rate measurements at 25°C , but the unusual form of the curve is more clearly evident.

The contributions of the unimolecular mechanism to the over-all rate of hydrolysis of β -chloroethoxymethyl formate in dilute hydrochloric acid at 25°C as estimated by the three different methods are given below:

Method	Fraction of over-all rate
Effect of structure	0.3
» » temperature	0.3
» » acidity	0.2–0.5

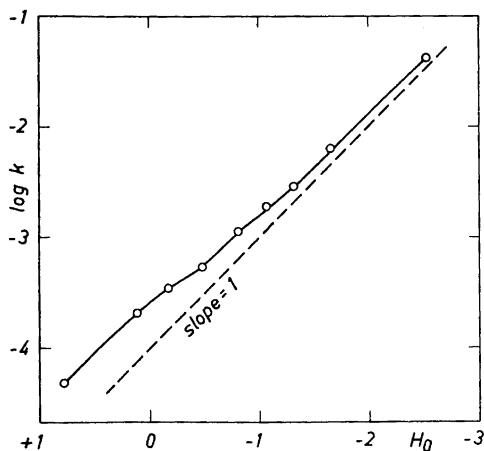


Fig. 2. Hydrolysis of β -chloroethoxymethyl formate at 0.88°C. Plot of $\log k$ against the values of the H_0 acidity function¹⁵ at 25°C.

The estimate based on the last method¹⁴ is the most uncertain because a more accurate result would require that the Zucker-Hammett hypothesis in its ultimate form⁵ would be accurately true and not a satisfactory approximation. In view of this limitation, the above estimates are consistent.

HYDROLYSIS OF β -CHLORETHOXYMETHYL ACETATE

The second-order rate coefficients k_c of the hydrolysis of β -chloroethoxymethyl acetate at the temperatures 15°, 25° and 35°C were reported in a recent paper in connection with a study of polar effects on the reactions of alkoxy-methyl compounds (Ref.⁴, Table 3). Although the estimated substituent effect of the β -chloroethyl group conformed well with the effect of this group in other reactions of alkoxy-methyl compounds which are assumed to involve the unimolecular formation of an alkoxy-methyl cation, and although the values of the activation energy and frequency factor of β -chloroethoxymethyl acetate were of approximately the same magnitude as the values of other alkoxy-methyl acetates studied, there is reason to suspect that the hydrolysis of β -chloroethoxymethyl acetate is a composite reaction with a minor contribution due to the normal type of acid-catalysed ester hydrolysis. In other reactions of alkoxy-methyl compounds the retarding effect of the β -chloroethyl group on the rate was associated with an elevated activation energy, whereas the opposite situation prevailed in the case of β -chloroethoxymethyl acetate. This exceptional observation can be explained by assuming that the over-all reaction includes a contribution of the bimolecular acyl-oxygen fission reaction with a lower activation energy that is not large enough to cause the Arrhe-

Table 3. Hydrolysis of β -chloroethoxymethyl acetate in dilute (0.05–0.1 M) hydrochloric acid solutions. Values of k_c (in $l \text{ mole}^{-1} \text{ s}^{-1}$) at different temperatures.

°C	0.88	6.56	15.00	25.00	35.00	49.90	64.70
$10^4 k_c$	0.119	0.251	0.711	2.41	7.56	40.4	188

Table 4. First-order rate coefficients k (in s^{-1}) for the hydrolysis of β -chloroethoxymethyl acetate in hydrochloric acid solutions. The acid concentrations, given in moles per liter, refer to 25°C .

0.88°C		25°C	
c_{HCl}	$10^5 k$	c_{HCl}	$10^4 k$
0.1534	0.182	0.1534	0.370
0.590	0.840	0.590	1.78
0.944	1.55	0.944	3.20
1.534	3.27	1.534	7.21
2.36	7.62	2.36	17.2
3.07	14.7	3.07	34.4
3.78	30.1	3.78	64.7
4.72	77.2	4.72	155
6.93	797		

nius plot to deviate from linearity when the temperature range is narrow. The participation of the normal type of acid-catalysed ester hydrolysis is also plausible in view of the actual magnitudes of the rate coefficients. The value ($0.000241 \text{ l mole}^{-1}\text{s}^{-1}$) of the rate coefficient k_c at 25°C is only 2.2 times the value reported by Tommila and Hella¹⁶ for methyl acetate and 6.8 times the value obtained by Euranto¹⁷ for chloromethyl acetate under the same conditions.

The simultaneous operation of the two mechanisms is indicated by the kinetic data relating to a wide range of temperature that are shown in Table 3. The plot of $\log k_c$ against reciprocal temperature drawn in Fig. 3

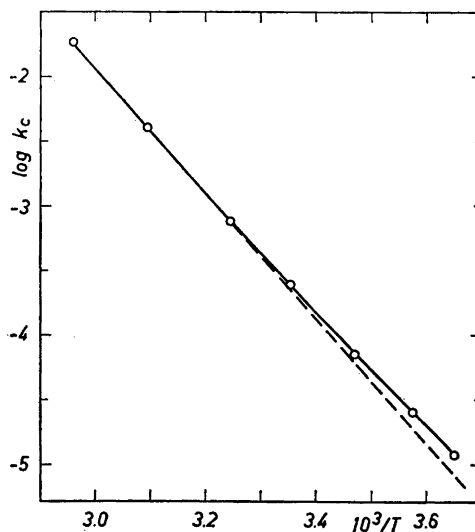


Fig. 3. Hydrolysis of β -chloroethoxymethyl acetate at different temperatures. Plot of $\log k_c$ against $1/T$.

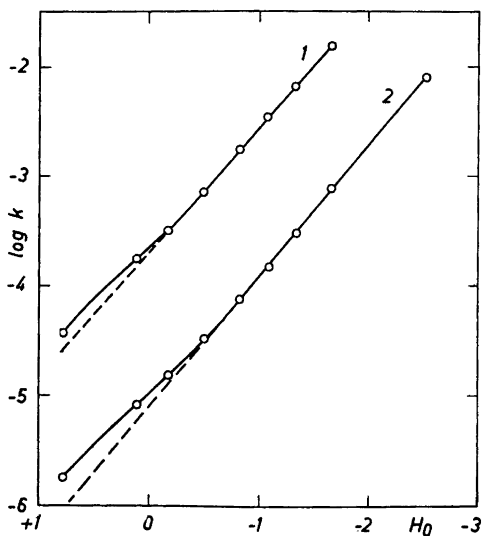


Fig. 4. Plot of $\log k$ against the values of the H_0 acidity function¹⁵ at 25°C for the hydrolysis of β -chloroethoxymethyl acetate in hydrochloric acid solutions. 1. 25°C. 2. 0.88°C.

shows that the Arrhenius equation is not satisfactorily obeyed. Although the departure from linearity is less than in the case of methoxymethyl formate¹ and β -chloroethoxymethyl formate (see above), it is larger than could be ascribed to experimental errors or genuine deviations from the Arrhenius equation that could occur in the present type of reaction. In order to obtain a satisfactory estimate of the contribution of the bimolecular mechanism to the rate, it would be necessary to study the reaction at much lower temperatures where, owing to its lower activation energy, the mechanism would contribute more to the over-all rate.

To permit a better comparison with other alkoxyethyl esters, the hydrolysis of β -chloroethoxymethyl acetate was also studied over a wider range of hydrogen chloride concentration. The first-order rate coefficients at different acid concentrations are given in Table 4 and their logarithms are plotted as a function of the value of the acidity function H_0 in Fig. 4. The plot of the data referring to 25°C is approximately linear with a slope close to unity, the deviation from linearity being hardly greater than can be ascribed to experimental error, whereas the data referring to 0.88°C yield a plot that clearly has a smaller slope at low acidities than at high acidities. This is the expected result¹⁴ if the Zucker-Hammett hypothesis can be assumed to be at least approximately valid for the reaction in question and if there are two concurrent reaction mechanisms which differ in their dependence on the acidity of the solution. Here the bimolecular acyl-oxygen fission with its lower activation energy can be expected to contribute more to the over-all rate at the lower temperatures.

EXPERIMENTAL

The preparation and purification of the compounds studied except β -chloroethoxymethyl formate have been described earlier^{1,4}. β -Chloroethoxymethyl formate was synthesized from α -chloromethyl- β -chloroethyl ether and lead formate. It was found advantageous to use a large excess of lead formate (about 140 % of the calculated amount) to effect complete conversion of the chloroether. After the components were mixed, the mixture was heated on a water bath. The crude product was extracted with ether, the lead chloride and unreacted lead formate removed by centrifugation and the residue remaining after the ether was distilled off distilled under reduced pressure. The main ester fraction boiled at 82.5°C under a pressure of 17 mm Hg. When the purity was checked by titration of the formaldehyde formed from the ester (*cf.* Ref.¹), 191.7 mg of the ester was equivalent to 41.16 ml of 0.0676 N iodine solution (calc. 40.93 ml).

The method of following the reactions was that used in earlier studies of alkoxyethyl esters¹. In all cases the first-order rate equation was satisfactorily obeyed.

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