

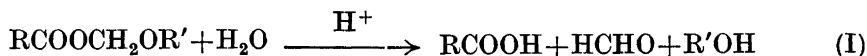
## The Acid-Catalysed Solvolysis of Alkoxyethyl Esters. Part I. The Relation between the Rate of Hydrolysis and the Acidity Function

PENTTI SALOMAA

*Department of Chemistry, University of Turku, Turku, Finland*

Kinetic measurements are made of the rate of hydrolysis of methoxymethyl acetate, ethoxymethyl acetate and methoxymethyl formate in different aqueous acids up to 5 N acid concentration. In all cases, the velocity of hydrolysis is more closely related to the acidity function  $H_0$  of the solution than to its acid concentration, thus indicating that the critical complex behaves like the conjugate acid of the ester and does not contain a water molecule. The plots of the logarithms of the first-order rate constants against  $-H_0$  give straight lines with slopes varying between 1.00 and 1.15. The results suggest that the reactions take place predominantly according to a mechanism, which in the rate-determining reaction stage involves the formation of an alkoxyethyl cation from the conjugate acid of the ester. This mechanism is identical with the unimolecular alkyl-oxygen fission mechanism of acid-catalysed ester hydrolysis, designated *AAL* by Ingold.

The acid-catalysed hydrolysis reaction of alkoxyethyl esters



provides an interesting problem for kinetic investigations. Owing to the fact that these compounds are as well esters as acetals, various reaction mechanisms may be expected to be involved. The hydrolysis by dilute aqueous hydrochloric acid has been previously investigated by Palomaa and co-workers<sup>1-3</sup> and by Salmi<sup>4</sup>. As the temperature dependence of the rate of hydrolysis was more closely related to that of dialkyl formals than to that of simple alkyl esters, the latter author suggested that the point of initial rupture was on the alkoxy side of the ester.

The acidity function  $H_0$ , first introduced by Hammett and co-workers<sup>5,6</sup>, has furnished a criterion which has been frequently used to obtain information about the mechanisms of acid-catalysed hydrolysis reactions<sup>e.g. 7-11</sup>. Its use

necessarily involves the extension of the rate measurements up to relatively high acid concentrations in which the difference between the values of  $H_0$  and pH becomes significant. The present paper describes the results obtained for the hydrolysis of some constitutionally simple alkoxyethyl esters in different aqueous acids.

### RESULTS AND DISCUSSION

The basic idea about the application of the acidity function  $H_0$  to acid-catalysed hydrolysis reactions originates from Zucker and Hammett<sup>7</sup>. The authors showed that if the critical complex contains only a proton in addition to the substrate molecule, there exist a linear relation between the logarithm of the first-order rate constant and  $-H_0$  with a slope of nearly unity. On the other hand, if the critical complex contains also a water molecule, such a dependence of the reaction rate on the acidity function is not to be expected. In the latter case, the reaction velocity is more closely related to the acid concentration of the solution. The former type of mechanism is to be termed unimolecular, because only one reacting species, the conjugate acid of the substrate, is undergoing a change of covalency in the rate-determining reaction stage, whereas the latter mechanism is bimolecular, two molecular species being involved in the rate-determining reaction<sup>12</sup>.

Our kinetic method to follow reactions (I) was based on the determination of formaldehyde produced at various reaction times. The experimental results are given in Tables 1, 2 and 3. In the tables,  $k$  denotes the first-order rate constant, and  $k_c$  the rate constant reduced to 1 N catalyst concentration by dividing  $k$  by the normality of the acid. The tables also include the values of the Hammett acidity function  $H_0$  for the solutions used. The latter values have been obtained by interpolation from the data given by Hammett and Deyrup<sup>5</sup> and by Bell, Dowling and Noble<sup>10</sup> for aqueous hydrochloric acid, and by Hammett and Paul<sup>6</sup> for aqueous sulphuric acid, and by Harbottle<sup>13</sup> for aqueous perchloric acid containing added sodium perchlorate, respectively. Since the values given by Hammett and co-workers refer to molal concentrations of the solute, the corresponding molar concentrations were calculated from the data given by Harned and Ehlers<sup>14</sup> and in the International Critical Tables<sup>15</sup>.

The values obtained for  $k_c$  at relatively low acid concentrations show but slight differences from the corresponding values determined earlier by Palomaa and co-workers<sup>2,3</sup>. These authors measured the velocity of reaction (I) by a titrimetric determination of the acid produced, and found for  $k_c$  at 25°C the values: 0.00247 l mole<sup>-1</sup>sec.<sup>-1</sup> for methoxymethyl acetate, 0.00875 l mole<sup>-1</sup>sec.<sup>-1</sup> for ethoxymethyl acetate, and 0.00918 l mole<sup>-1</sup>sec.<sup>-1</sup> for methoxymethyl formate, respectively. In the present case, the determination of the rate constants by an alkalimetric titration was not possible, because the concentration of the catalyst acid was usually relatively high in comparison to that of the acid formed during the reaction. In addition, the formaldehyde analysis allowed to bring the reactions to stop, and the end points of the titrations were sharp, whereas in the alkalimetric titration the rapidity of the alkaline hydrolysis of alkoxyethyl esters is a source of error in analysis. In the

Table 1. Hydrolysis of methoxymethyl acetate in various aqueous acid solutions at 25°C. Acid concentrations in moles/l of solution.

Solution	Acid concn.	$10^3 \times k$ sec. <sup>-1</sup>	$10^3 \times k_c$ l mole <sup>-1</sup> sec. <sup>-1</sup>	$H_0$
Hydrochloric acid	0.0998	0.237	2.37	+1.07
»	0.450	1.30	2.89	+0.33
»	0.632	2.09	3.31	+0.18
»	0.866	3.16	3.65	0.00
»	1.245	6.23	5.00	-0.24
»	1.549	9.14	5.90	-0.35
»	2.42	22.0	9.09	-0.71
»	2.62	25.6	9.77	-0.77
»	2.91	36.4	12.5	-0.89
»	3.42	62.8	18.4	-1.09
»	3.83	99.2	25.9	-1.22
»	4.29	170	39.6	-1.38
»	5.01	290	57.9	-1.64
Sulphuric acid	0.740	3.11	2.10	+0.08
»	1.166	6.16	2.64	-0.22
»	1.99	18.2	4.57	-0.66
»	2.41	28.7	5.95	-0.89
»	3.28	104	15.9	-1.33
{0.300 M perchloric acid	0.300	14.4	48.0	-0.74
{5.700 M sodium perchlorate				
{0.500 M perchloric acid	0.500	24.5	49.0	-1.00
{5.500 M sodium perchlorate				
{1.000 M perchloric acid	1.000	54.9	54.9	-1.35
{5.000 M sodium perchlorate				

Table 2. Hydrolysis of ethoxymethyl acetate in aqueous hydrochloric acid at 25°C. Acid concentrations in moles/l of solution.

Acid concn.	$10^3 \times k$ sec. <sup>-1</sup>	$10^3 \times k_c$ l mole <sup>-1</sup> sec. <sup>-1</sup>	$H_0$
0.1066	0.929	8.71	+1.05
0.632	8.04	12.7	+0.18
0.947	15.7	16.6	-0.03
1.245	24.4	19.6	-0.24
1.549	37.2	24.9	-0.35
1.851	50.0	27.0	-0.48
2.42	95.5	39.5	-0.71

Table 3. Hydrolysis of methoxymethyl formate in aqueous hydrochloric acid at 25°C. Acid concentrations in moles/l of solution.

Acid concn.	$10^3 \times k$ sec. <sup>-1</sup>	$10^3 \times k_c$ l mole <sup>-1</sup> sec. <sup>-1</sup>	$H_0$
0.1066	0.916	8.59	+1.05
0.632	6.77	10.7	+0.18
0.947	11.6	12.2	-0.03
1.245	16.9	13.6	-0.24
1.549	23.7	15.3	-0.35
1.851	28.6	15.5	-0.48
2.42	51.3	21.2	-0.71

case of methoxymethyl acetate, the present method allowed an accurate determination of rate constants up to nearly 5 N hydrochloric acid concentration, whereas the rapidity of the reactions of ethoxymethyl acetate and methoxymethyl formate limited the measurements to a narrower range of concentrations.

The values of  $k_c$  given in Tables 1, 2 and 3 show that the rate of hydrolysis increases much more rapidly than the acid concentration of the solution. For instance, in the case of methoxymethyl acetate, the value of  $k_c$  increases by a factor of about 25 when the hydrochloric acid concentration is increased from 0.1 N to 5 N. In the case of ethoxymethyl acetate, the relative increase in the values of  $k_c$  with hydrochloric acid concentration is nearly of the same order of magnitude, whereas the increase is less pronounced in the hydrolysis of methoxymethyl formate.

Like the hydrolysis reactions of methylal<sup>8</sup> and trioxan<sup>11</sup>, the hydrolysis of alkoxyethyl esters shows a close relation between the reaction velocity and the acidity function of the solution. This is seen from Figs. 1 and 2 in which the values of  $\log k$  are plotted against the Hammett acidity function. The plots follow an approximately linear course as shown by the straight lines drawn in the diagrams which have slopes of 1.15 in the cases of methoxymethyl acetate and ethoxymethyl acetate, and a slope of 1.00 in the case of methoxymethyl formate, respectively. In the hydrolysis of methoxymethyl acetate (Fig. 1), the points corresponding to hydrochloric and sulphuric acids lie approximately on the same straight line, whereas the points referring to perchloric acid solutions containing added sodium perchlorate show systematic deviations from the former solutions. This may be due to small systematic differences between the values of  $H_0$  determined by different authors, and to the limitations involved in assuming that the ratio of the activity coefficients of the substrate ester and the critical complex would vary with the solvent composition in an exactly similar way as the activity coefficient ratio of the indicator base and its conjugate acid, which have been used in the determination of  $H_0$ <sup>cf.8,13,16</sup>. Systematic deviations between the results for different acids were also observed in the hydrolysis of trioxan, investigated by Bell, Bascombe and McCoubrey<sup>11</sup>.

From the relationship between the hydrolysis rate of alkoxyethyl esters and the acidity function it may be concluded that the reactions take place by a mechanism, in which no water molecule is undergoing a change of covalency on the attainment of the transition state, *i.e.* the slow, rate-determining stage of the reaction is unimolecular and involves the formation of a carbonium ion from the conjugate acid of the ester. Similar conclusions were reached by McIntyre and Long<sup>8</sup> for the hydrolysis of methylal, and by Bell, Bascombe and McCoubrey<sup>11</sup> for the hydrolysis of trioxan. The plots corresponding to those of Figs. 1 and 2 gave a slope of 1.15 for methylal, and a slope of 1.2 for trioxan. In the case of acetal hydrolysis, the unimolecular mechanism has been also supported by other lines of experimental evidence<sup>17,18</sup>.

The similarity of alkoxyethyl ester hydrolysis to acetal hydrolysis is not confined to a similar dependence of the reaction rate on the acidity function of the solution. In addition, it is most probable that the carbonium ion produced in the rate-determining stage of the hydrolysis of alkoxyethyl esters is structurally similar to that postulated for the hydrolysis of acetals<sup>8,11,17,18</sup>,

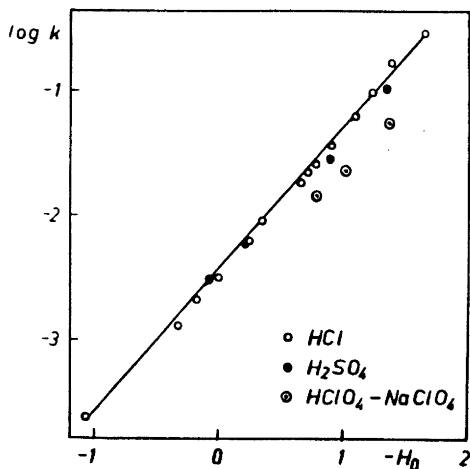


Fig. 1. Plot of  $\log k$  against  $-H_0$  for the hydrolysis of methoxymethyl acetate at 25°C.

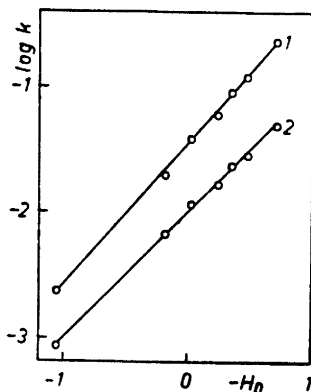
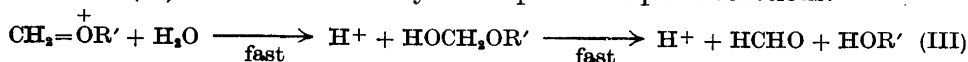


Fig. 2. 1. Plot of  $\log k + 0.40$  against  $-H_0$  for the hydrolysis of ethoxymethyl acetate. 2. Plot of  $\log k$  against  $-H_0$  for the hydrolysis of methoxymethyl formate. Hydrochloric acid solutions, 25°C.

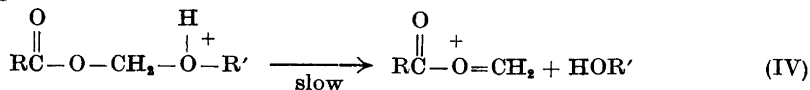
*i.e.* the intermediate ion is a mesomeric alkoxyethyl cation. For that case, the rate-determining reaction stage which follows the preliminary proton uptake can be represented as follows:



Reaction (II) is then followed by the rapid subsequent reactions:



which lead to the final products. In the present case, there are no structural factors to favour the formation of cations such as  $\text{R}^+$ ,  $\text{R}'^+$  or  $\text{RCO}^+$  in the rate-determining reaction stage, whereas the production of an alkoxyethyl cation according to eqn. (II) is greatly facilitated by its mesomeric structure<sup>19-21</sup>. The only alternative unimolecular mechanism, which were conceivable, would involve the formation of an acyloxyethyl cation in the rate-determining reaction stage:



Also in this case, the formation of the cation is facilitated, although to a minor extent, by its possibility to resonate between different valence bond structures. Owing to the influence of the carbonyl group which is directly attached to the

ether oxygen atom, the resonance energy of this cation is materially reduced, and the conditions for its formation are thus less favourable. This is clearly illustrated by the results obtained for the solvolysis of chlorine in alkoxyethyl chlorides<sup>19-21</sup>,  $\text{ROCH}_2\text{Cl}$ , when compared with those obtained for the corresponding reaction of acyloxyethyl chlorides,  $\text{RCOOCH}_2\text{Cl}$ , investigated by Euranto<sup>22</sup>. The former reaction takes place very rapidly with the unimolecular  $S_N1$  mechanism involving the production of the alkoxyethyl cation in the rate-determining reaction stage, whereas the latter reaction is relatively slow and does not produce an intermediate carbonium cation, the reaction mechanism being  $S_N2$ . We must therefore conclude that the unimolecular hydrolysis of alkoxyethyl esters by aqueous acids takes place by the mechanism represented by eqns. (II) and (III). Our results thus provide an illustration for an acid-catalysed ester hydrolysis involving unimolecular alkyl-oxygen fission, designated  $A_{AL}1$  by Ingold<sup>23</sup>.

The application of the Hammett acidity function to relatively complicated reactions, where different points for initial rupture are conceivable as in the present case, does not give an information about the possible side mechanisms. Suppose, for instance, that a reaction in dilute acid solutions occurs by two simultaneous mechanisms, a unimolecular mechanism the rate of which follows the acidity function, and a bimolecular mechanism the rate of which depends primarily on the acid concentration. When passing to relatively concentrated acid solutions, the contribution of the latter reaction from the total reaction rate falls gradually off, and its presence cannot be clearly shown by the plot of  $\log k$  against the acidity function. On view of the structural factors, discussed below, it is very probable that, at least in the case of methoxyethyl formate, the unimolecular reaction is at low acid concentrations accompanied to a certain extent by a bimolecular reaction, the mechanism of which is that of acid-catalysed ester hydrolysis involving bimolecular acyl-oxygen fission<sup>23</sup>. As shown by Bell, Dowling and Noble<sup>10</sup>, the velocity of the latter type of reaction is more closely related to the acid concentration than to the acidity function of the solution.

The value of  $k_c$  (Table 3) determined for methoxyethyl formate in 0.1 N hydrochloric acid at 25°C,  $0.00859 \text{ l mole}^{-1}\text{sec.}^{-1}$ , is only 3.5-fold in comparison to the corresponding value for methyl formate,  $0.00247 \text{ l mole}^{-1}\text{sec.}^{-1}$ , determined by Salmi<sup>4</sup>. Owing to the fact that the rate of bimolecular acid-catalysed ester hydrolysis taking place with acyl-oxygen fission is but slightly influenced by changes in the alkyl part of the ester<sup>23</sup>, it is reasonable to assume that the rate constant determined for methoxyethyl formate includes a contribution resulting from its hydrolysis by the acyl-oxygen fission mechanism, in addition to that which results from the unimolecular mechanism. Euranto<sup>22</sup> found that the rate constant for acid-catalysed ester hydrolysis at 25°C was reduced by a factor of about 3, when passing from methyl acetate to chloromethyl acetate, and a similar, although probably a smaller decrease is to be expected in the velocity of the bimolecular ester hydrolysis, when passing from methyl formate to methoxyethyl formate. On the contrary, in the cases of methoxyethyl acetate and ethoxyethyl acetate, the contribution from the bimolecular mechanism to the total hydrolysis rate is probably too small to be of practical importance. Tommila and Hella<sup>24</sup> determined for the rate constant

of methyl acetate in dilute aqueous acid at 25°C the value 0.000109 l mole<sup>-1</sup> sec.<sup>-1</sup>, whereas the corresponding values for methoxymethyl acetate and ethoxymethyl acetate (Tables 1 and 2) are considerably higher, 0.00237 l mole<sup>-1</sup> sec.<sup>-1</sup> and 0.00871 l mole<sup>-1</sup>sec.<sup>-1</sup>, respectively. The smaller slope, 1.00, obtained for methoxymethyl formate by the plot of log *k* against  $-H_0$ , as compared with the slopes of 1.15 obtained for methoxymethyl acetate and ethoxymethyl acetate, is readily understood if it is assumed that in the former case the reaction rate involves a contribution from an accompanying bimolecular mechanism.

### EXPERIMENTAL

**Materials.** Methoxymethyl acetate, CH<sub>3</sub>COOCH<sub>2</sub>OCH<sub>3</sub>, and ethoxymethyl acetate, CH<sub>3</sub>COOCH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>, were prepared from the corresponding alkoxymethyl chlorides and potassium acetate according to Palomaa<sup>1</sup>. After fractionation, the products were found to be free from chlorine. The boiling points were: 118.6–118.8°C/766 mm Hg for methoxymethyl acetate, and 132.5–133.0°C/762 mm Hg for ethoxymethyl acetate. The purity of the products was controlled by hydrolysing weighed samples in dilute acid solutions and determining both the acetic acid and formaldehyde produced at the end of hydrolysis, the former by titrating against a standard sodium hydroxide solution, the latter using the modified bisulphite method described earlier by the author<sup>19,25</sup>. In the analysis, 59.9 mg of methoxymethyl acetate was found to be equivalent to 11.21 ml of 0.0519 N sodium hydroxide (*calc.* 11.09 ml), and to 16.64 ml of 0.0688 N iodine (*calc.* 16.73 ml). Ethoxymethyl acetate (78.3 mg) was equivalent to 12.58 ml of 0.0519 N sodium hydroxide (*calc.* 12.77 ml), and to 19.12 ml of 0.0688 N iodine (*calc.* 19.27 ml). Methoxymethyl formate, HCOOCH<sub>2</sub>OCH<sub>3</sub>, was prepared from methoxymethyl chloride and lead formate as described by Palomaa and Herna<sup>2</sup>. The boiling point was 103.6°C/762 mm Hg. In the analysis, 51.7 mg of the compound was equivalent to 11.24 ml of 0.0519 N sodium hydroxide (*calc.* 11.06 ml), and to 16.58 ml of 0.0688 N iodine (*calc.* 16.68 ml).

The acidic reaction solutions were prepared by diluting the corresponding concentrated acids, and their concentrations were determined by titrating against standard alkali solutions. Commercial acids of highest grade of purity were employed.

**Kinetic measurements.** The thermostat used in kinetic measurements and the technique of sampling were the same as described earlier<sup>19,20</sup>. The samples withdrawn from the reaction mixture at different time intervals were run into conical flasks, which contained 10 ml of the phosphate buffer solution (pH 7.3) which was employed for the formaldehyde determinations<sup>19,25</sup>, and an amount of 0.5–5 N sodium hydroxide solution, which was calculated to neutralise the catalyst acid present in the sample. In the experiments, in which the concentration of the catalyst acid was relatively high, an amount of crushed ice was added, in order to avoid the considerable warming up of the mixture as a result of the heat of neutralisation. Particular experiments indicated that the velocities of alkaline hydrolysis of methoxymethyl acetate and ethoxymethyl acetate in the phosphate buffer were sufficiently small and did not cause an error in analysis. However, in the case of methoxymethyl formate it was established that an error in analysis resulted from a delayed analysis of the sample. The observed formaldehyde content increased slightly with time. The effect of this source of error was eliminated by performing the analysis immediately after taking the samples and by using a constant standing period (three minutes) for the bisulphite-formaldehyde addition reaction *cf.* 19. In this case the small error resulting from the additional formaldehyde (estimated to be less than 5 % of the amount of remaining ester) did not affect the values of the rate constants as they were calculated by the first-order equation.

Zero time was the time of taking of the first sample. In addition, 6–8 samples were taken during the reaction. The concentration of formaldehyde formed after infinite time (over ten-fold period of the half-life) was checked by several parallel determinations. The initial concentration of the ester varied between 0.03–0.06 M. The volumes of the samples withdrawn from the reaction mixtures were 5 ml or 10 ml, and the concentration of the standard iodine solution used in the formaldehyde determinations was 0.06–0.07 N. The details for some typical runs are given in Tables 4, 5 and 6. In the tables, *a* denotes the

concentration of the ester at zero time,  $x$  the concentration of formaldehyde produced during time  $t$ , and  $k$  the first-order rate constant. The values of the rate constants were calculated by the usual equation for first-order reactions.

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Table 4. Hydrolysis of methoxymethyl acetate in different acidic solutions at 25°C

A. 0.450 M hydrochloric acid.  $a = 0.0348$ .

$t$ (in min.)	2	4	6	8	10	12	14
$10^3 \times (a-x)$	2.99	2.52	2.20	1.88	1.59	1.38	1.14
$10^3 \times k$	1.26	1.34	1.27	1.28	1.31	1.28	1.33

average  $k = 0.00130 \text{ sec.}^{-1}$

B. 1.99 M sulphuric acid.  $a = 0.0278$ .

$t$ (in sec.)	15	30	45	60	75	90	105
$10^3 \times (a-x)$	2.09	1.60	1.23	0.92	0.72	0.54	0.46
$10^3 \times k$	1.90	1.84	1.81	1.84	1.80	1.82	1.71

average  $k = 0.0182 \text{ sec.}^{-1}$

C. 0.300 M perchloric acid, 5.700 M sodium perchlorate.  $a = 0.0297$ .

$t$ (in sec.)	15	30	45	60	75	90	105
$10^3 \times (a-x)$	2.39	1.93	1.55	1.26	1.01	0.85	0.65
$10^3 \times k$	1.45	1.44	1.45	1.43	1.44	1.39	1.45

average  $k = 0.0144 \text{ sec.}^{-1}$

Table 5. Hydrolysis of ethoxymethyl acetate in 1.245 M hydrochloric acid at 25°C.  
 $a = 0.0296$ .

$t$ (in sec.)	15	30	45	60	75	90
$10^3 \times (a-x)$	2.01	1.45	1.02	0.71	0.49	0.31
$10^3 \times k$	2.58	2.38	2.37	2.38	2.40	2.51

average  $k = 0.0244 \text{ sec.}^{-1}$

Table 6. Hydrolysis of methoxymethyl formate in 1.549 M hydrochloric acid at 25°C.  
 $a = 0.0397$ .

$t$ (in sec.)	10	20	30	40	50	60	70
$10^3 \times (a-x)$	3.08	2.52	1.96	1.50	1.20	1.00	0.79
$10^3 \times k$	2.54	2.27	2.35	2.43	2.39	2.30	2.31

average  $k = 0.0237 \text{ sec.}^{-1}$

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