

**The Acid-Catalysed Solvolysis of Alkoxyethyl Esters.**  
**Part IV. The Temperature Dependence**  
**of the Hydrolysis Rate**

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The kinetics of the hydrolysis of methoxymethyl acetate, ethoxymethyl acetate and methoxymethyl formate by dilute hydrochloric acid have been investigated over a temperature range from 0°C to 60°C. The reactions of the two former compounds show a linear relationship between the logarithm of the rate constant and  $1/T$ , in a satisfactory agreement with the Arrhenius equation, over the whole temperature range investigated. By methoxymethyl formate, on the contrary, an apparent deviation from the Arrhenius equation is notable especially at relatively low temperatures, the logarithm of the rate constant increasing more rapidly than as proportional to  $-1/T$ . This deviation can be interpreted in terms of the previous observations according to which the hydrolysis of this compound by dilute aqueous acid occurs by two simultaneous mechanisms, a unimolecular and a bimolecular mechanism, the unimolecular mechanism involving a considerably higher activation energy. By assuming the Arrhenius equation to be well obeyed by the two reactions involving the different mechanisms, the respective activation energies and frequency factors have been estimated from the experimental rate constants and found to be in agreement with the mechanisms suggested. The factors determining the mechanism of the acid-catalysed solvolysis of alkoxyethyl esters have been generally discussed.

In the previous kinetic study on the acid-catalysed solvolysis of alkoxyethyl esters in water<sup>1</sup> and in water-alcohol mixtures<sup>2,3</sup> it was established that these reactions can take place by two different mechanisms. The former mechanism involves a unimolecular formation of an alkoxyethyl cation in the rate-determining reaction stage, whereas the latter mechanism is bimolecular and consists of an acyl-oxygen bond fission. In the solvolysis by dilute aqueous acids at 25°C, it was found that the bimolecular mechanism is insignificant except the reaction of methoxymethyl formate.

In view of the relatively large differences between the activation energies involved in the two different reaction mechanisms, it was expected that these differences might be revealed by deviations from the Arrhenius equation, thus furnishing an additional criterion for the simultaneous occurrence of the two mechanisms. The present paper gives the results obtained for the hydrolysis of methoxymethyl acetate, ethoxymethyl acetate and methoxymethyl formate by dilute hydrochloric acid solutions over a wide temperature range. The kinetics of the hydrolysis of these compounds have been previously investigated by Palomaa and co-workers<sup>4,5</sup> at three temperatures from 15°C to 35°C, but this temperature range is too limited to allow a reliable experimental verification as to the validity of the Arrhenius equation for the reactions investigated.

### RESULTS AND DISCUSSION

At relatively low acid concentrations the first-order rate constants of the hydrolysis of alkoxyethyl esters are directly proportional to the concentration of the catalyst acid, the values of pH and the acidity function  $H_0$  becoming practically identical, *cf.* Refs.<sup>1,6</sup>. For these solutions the second-order rate constant which is obtained by dividing the experimental first-order constant by the catalyst concentration is thus independent of the latter. The concentration of the catalyst hydrochloric acid used in the present study was about 0.1 N, except in the measurements carried out at 45°C and at 60°C, at which temperatures, owing to the rapidity of the reactions, lower catalyst concentrations, *viz.* about 0.025 N, were chosen. The results obtained in the rate measurements are given in Table 1. In the table,  $k$  denotes the second-order rate constant.

Table 1. The values of the second-order rate constants (in  $l \text{ mole}^{-1} \text{ sec}^{-1}$ ) for the hydrolysis of alkoxyethyl esters in dilute aqueous hydrochloric acid at various temperatures.

°C	$10^4 \times k$		
	$\text{CH}_3\text{COOCH}_2\text{OCH}_3$	$\text{CH}_3\text{COOCH}_2\text{OC}_2\text{H}_5$	$\text{HCOOCH}_2\text{OCH}_3$
0	0.746	2.82	5.09
6			9.80
12	4.26	15.7	20.0
18			40.6
25	24.5	88.6	85.8
35	83.3	302	254
45	270	954	794
60	1 360	4 300	3 480

As shown by the values of Table 1, the effect of structure on the velocity of hydrolysis is notably dependent on the temperature. At relatively low temperatures methoxymethyl formate is hydrolysed more rapidly than methoxymethyl acetate and ethoxymethyl acetate, whereas at higher temperatures its hydrolysis rate is between those of the two latter compounds.

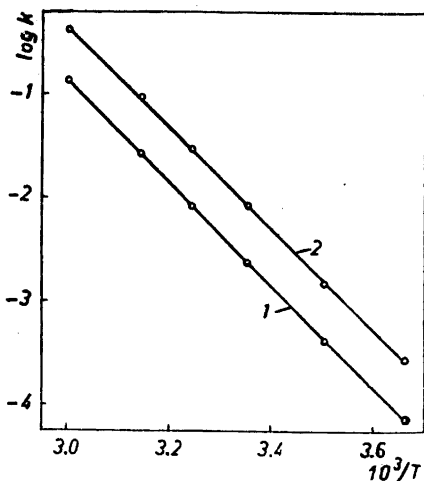


Fig. 1. The plot of  $\log k$  against  $1/T$  for the hydrolysis of methoxymethyl acetate (1) and ethoxymethyl acetate (2).

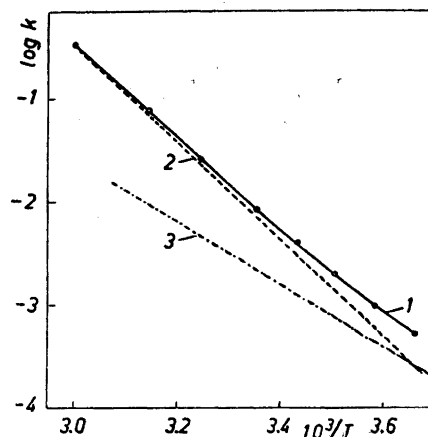


Fig. 2. The plot of  $\log k$  against  $1/T$  for the hydrolysis of methoxymethyl formate. 1. The experimental values. 2. The values calculated for the unimolecular mechanism. 3. The values calculated for the bimolecular mechanism.

In Figs. 1 and 2 the values of  $\log k$  are plotted against  $1/T$  for the hydrolysis of the different alkoxyethyl esters investigated. By methoxymethyl acetate and by ethoxymethyl acetate the plots show a linear course over the whole temperature range investigated, in accord with the Arrhenius equation. In the case of methoxymethyl formate, on the contrary, the logarithm of the rate constant decreases somewhat less rapidly than as directly proportional to  $1/T$ . This apparent deviation from the Arrhenius equation is most material at relatively low temperatures. The difference in the temperature dependence of the hydrolysis rates of the different alkoxyethyl esters is also seen, although to a more limited extent, from the values determined by Palomaa and co-workers<sup>4,5</sup>; the relative increases in the rate constants of methoxymethyl acetate and ethoxymethyl acetate are seen to be slightly higher, when passing from 15°C to 25°C, than when passing from 25°C to 35°C, in accordance with the Arrhenius equation, whereas the opposite situation is found to prevail in the hydrolysis of methoxymethyl formate.

From the plots of Fig. 1, the following values can be calculated for the parameters of the Arrhenius equation:  $\log A = 13.97$ ,  $E = 22\,600$  cal/mole for methoxymethyl acetate, and  $\log A = 14.19$ ,  $E = 22\,150$  cal/mole for ethoxymethyl acetate, respectively. Thus the frequency factor of the former compound is slightly lower than that of the latter, the activation energy of the former compound being somewhat higher. Both of these factors act in the same direction and increase the hydrolysis rate, when passing from the methoxymethyl ester to the corresponding ethoxymethyl ester.

In the case of methoxymethyl formate, a calculation of the parameters of the Arrhenius equation by a similar method is not possible over the whole temperature range. However, the satisfactory validity of the Arrhenius equation for the acetates, and the previous results<sup>1,2</sup>, allow it to be presumed that the apparent deviation is in the present case due to two simultaneously occurring reaction mechanisms. The Arrhenius parameters for both the reactions concerned can be, at least approximately, evaluated from the experimental data by the method described below.

Let  $A_1$  and  $E_1$  denote the frequency factor and the activation energy of the one reaction, and  $A_2$  and  $E_2$  the corresponding parameters of the other reaction, respectively. If the Arrhenius equation can be assumed to be obeyed by both the reactions separately, and if the respective rate constants are denoted by  $k_1$  and  $k_2$ , we have the following expression for the experimentally determined rate constant  $k$ :

$$k = k_1 + k_2 = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$$

The values of  $E_1$  and  $E_2$  must necessarily differ essentially, in order to give rise to such an apparent deviation from the Arrhenius equation, that can be experimentally detected at the temperatures investigated. Let the value of  $E_1$  be higher than that of  $E_2$ . That implies that the relative contribution of  $k_1$  to the experimentally measured rate constant  $k$  increases with temperature, and if the rate determinations have been extended up to sufficiently high temperatures the total reaction rate is practically determined by the values of  $k_1$ . In this case the plot of  $\log k$  against  $1/T$  at high temperatures gives the parameters  $A_1$  and  $E_1$  as a first approximation. From these values the values of  $k_1$  can be calculated for the lowest temperatures, and the values of  $k - k_1$  thus give the first approximations for the values of  $k_2$  at these temperatures. A plot of the values of  $\log k_2$  thus found against  $1/T$  gives approximations for the values of  $A_2$  and  $E_2$  from which, in turn, the values of  $k_2$  and  $k_1 = k - k_2$  can be calculated for the higher temperatures. From the values of  $\log k_1$  thus obtained, the second approximations for  $E_1$  and  $A_1$  can be determined. Similar successive approximations are reiterated until both the sets of values for the parameters of the Arrhenius equation remain practically constant over the whole temperature range investigated.

The application of the above method of successive approximations to the rate constants of the hydrolysis of methoxymethyl formate at various temperatures (Table 1) gave the following values for the parameters of the Arrhenius equation:  $\log A_1 = 13.82$ ,  $E_1 = 21\,790$  cal/mole, and  $\log A_2 = 7.6$ ,  $E_2 = 14\,000$  cal/mole, respectively. It is to be noted that the above values are influenced by experimental errors much more significantly than such, in which only one reaction is involved, because the errors are here absorbed into four parameters instead of two. In addition, small genuine deviations from the Arrhenius equation which are conceivable, will be included in the values calculated for the two sets of parameters. However, owing to the fact that the hydrolysis rates of methoxymethyl and ethoxymethyl acetates are satisfactorily expressed in terms of the Arrhenius equation, we have no reason to assume that this would not be the case for that reaction of methoxymethyl formate, the values of which have been denoted by the subscript 1, these values being similar to those determined for the acetates, and thus obviously referring to the same reaction mechanism. Because this reaction of methoxymethyl formate was the dominating over nearly the whole temperature range investigated, its Arrhenius parameters could be calculated relatively accurately, whereas the corresponding values for that reaction, the constants of which have been denoted by the subscript 2, were found to be relatively inaccurate (*e. g.* it could

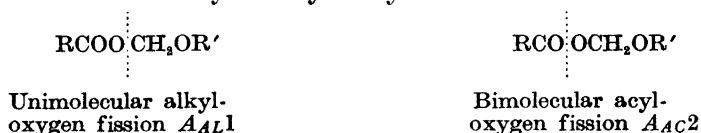
be estimated that the value of  $E_2$  is accurate only within  $\pm 2000$  cal/mole). Table 2 gives the values of  $k_1$  and  $k_2$  for the hydrolysis of methoxymethyl formate at various temperatures which have been calculated from the above values for the respective activation energies and frequency factors. It is seen that the contributions of both the reactions are nearly equal at  $0^\circ\text{C}$ , but at higher temperatures the contribution of  $k_2$  to the total hydrolysis rate is rapidly decreased with temperature. Thus a more accurate determination of the parameters of the Arrhenius equation for the latter reaction would necessarily involve an extension of the rate measurements down to very low temperatures. The contributions estimated for the two different reactions are also illustrated by the straight lines drawn in Fig. 2.

Table 2. The values of  $k_1$  and  $k_2$  (in  $\text{l mole}^{-1} \text{sec.}^{-1}$ ) for the hydrolysis of methoxymethyl formate at various temperatures.

$^\circ\text{C}$	0	6	12	18	25	35	45	60
$10^3 \cdot k_1$	0.238	0.564	1.29	2.85	6.90	22.8	69.7	329
$10^3 \cdot k_2$	0.25	0.43	0.73	1.2	2.1	4.6	9.5	26

The values of  $\log A_1$  and  $E_1$  calculated for methoxymethyl formate which are close to the corresponding values of  $\log A$  and  $E$  determined for methoxymethyl and ethoxymethyl acetates are in good agreement with the assumption that all of the respective reactions take place by the same mechanism, *i. e.* by the unimolecular mechanism involving an alkoxyethyl cation as a reaction intermediate<sup>1-3</sup>. On the other hand, those values for methoxymethyl formate which have been denoted by the subscript 2, show, in spite of the approximateness of their determination, a close similarity to the corresponding values of the acid-catalysed hydrolysis of simple alkyl formates. The value of  $k_2$  estimated for methoxymethyl formate at  $25^\circ\text{C}$ ,  $0.0021 \text{ l mole}^{-1} \text{sec.}^{-1}$ , is of the same order of magnitude as the corresponding values for methyl formate and ethyl formate,  $0.00247 \text{ l mole}^{-1} \text{sec.}^{-1}$  and  $0.00307 \text{ l mole}^{-1} \text{sec.}^{-1}$ , determined by Salmi<sup>7</sup> and by Tommila and Hella<sup>8</sup>, respectively. The activation energies calculated for the hydrolysis of methyl and ethyl formates are 14 500 and 15 770 cal/mole correspondingly, which are of that order of magnitude than the approximate value of  $E_2$ , 14 000 cal/mole, estimated for methoxymethyl formate.

Although the experimental material presented in this and in the three preceding papers<sup>1-3</sup> has so far been confined to the acid-catalysed solvolysis reactions of relatively few, constitutionally simple alkoxyethyl esters, some characteristic features of the different solvolysis mechanisms of these compounds may be presented, in accordance with the general theory on the acid-catalysed ester hydrolysis, extensively discussed by Ingold<sup>9</sup>. The two mechanisms established by alkoxyethyl esters are the following:



In the first place, the above mechanisms are differently influenced by the external conditions, the reaction medium and temperature. The unimolecular mechanism is much more dependent on the proton-availability of the reaction solution than is the bimolecular mechanism. Thus the contribution of the bimolecular mechanism becomes more significant in solutions of low proton-donating power, whereas the unimolecular mechanism is greatly favoured by solvents of high proton-availability, in particular by concentrated, strong aqueous acids. As to the effect of temperature, the bimolecular mechanism involving a lower activation energy is more favoured by low temperatures.

From the constitutional point, the bimolecular mechanism is more notably dependent on the structure of the acyl group of the ester than is the unimolecular mechanism. In the case of the latter mechanism, changes of the acyl part of the ester do not materially influence the reaction velocity, as shown by the rate constants of the solvolysis of methoxymethyl formate and methoxymethyl acetate, the values for the former compound being only about 1.5—3 times larger than those of the latter compound in the solvolysis in water and in methanol-water mixtures. In the case of the bimolecular mechanism, the effect of the structure of the acyl group is much more significant. Alkyl formates are hydrolysed much more rapidly than the corresponding acetates by the bimolecular acyl-oxygen fission mechanism. The same structural effect is clearly illustrated also by alkoxymethyl esters. In water-methanol mixtures, the solvolysis rate constants of methoxymethyl formate which referred to the bimolecular mechanism, were observed to be about 30 times higher than the corresponding values for methoxymethyl acetate<sup>2</sup>. The fact that in the hydrolysis in water, the bimolecular mechanism has a significant contribution only for methoxymethyl formate, but not for methoxymethyl and ethoxymethyl acetates, is also well understood in terms of these structural effects.

In addition, the polar effects in the alkoxy group of the ester are much more significant for the unimolecular mechanism which involves a production of an alkoxymethyl cation in the rate-determining reaction stage. Electron-releasing substituents are able greatly to stabilise the mesomeric cation, and thus favour the unimolecular mechanism, whereas electron-attracting substituents effect a material decrease of the velocity of the unimolecular reaction, thus favouring the bimolecular mechanism. The extent of this influence of a substituent depends primarily on the distance between the substituent and the point of the reaction, *i. e.* the carbon atom of the methylene group which acquires a positive charge on the attainment of the transition state. The retarding influence of an electron-attracting substituent on the velocity of the unimolecular reaction is clearly illustrated by the rate constants, determined by Palomaa and Herna<sup>4</sup> for the hydrolysis of 2-chloro-ethoxymethyl formate,  $\text{HCOOCH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ . The value of the rate constant at 25°C,  $0.00187 \text{ l mole}^{-1}\text{sec.}^{-1}$ , as well as the value for the activation energy, 15 200 cal/mole, which can be calculated from the rate constants given by these authors for different temperatures, show such a close similarity to the corresponding values for simple alkyl formates (see above) that one can rather safely presume that in this case, the rate of the unimolecular reaction is effectively suppressed by the negative chlorine as a substituent, and hence the bimolecular mechanism is the dominating. Palomaa and Herna also

suggested that the hydrolysis mechanism of this compound will resemble most closely that of simple alkyl formates, thus differing from the behaviour of the other alkoxyethyl esters investigated, although the actual nature of the different mechanisms could not be elucidated by the observations thus far made.

### EXPERIMENTAL

The preparation and purification of the materials used and the technique of kinetic measurements have been described in the first part of the present study<sup>1</sup>. The thermostat which was employed for measurements below room temperature, was situated in a room the temperature of which was refrigerated to  $-2^{\circ}\text{C}$ , and the thermostat was filled with sodium chloride solution to allow the measurements at  $0^{\circ}\text{C}$ . The electrical heating and controlling system of this thermostat was the same as that used for measurements at the higher temperatures.

The concentration of the catalyst hydrochloric acid in the reaction solutions was 0.1 N or 0.025 N, measured at  $20^{\circ}\text{C}$ . The corresponding concentrations at the temperatures of the rate measurements were calculated from the values of the density of water at different temperatures, using the data given in the *International Critical Tables*<sup>10</sup>. Tables 3, 4 and 5 give the details for three typical individual runs. In the tables,  $a$  denotes the ester concentration at zero time (at the time of taking of the first sample),  $a-x$  the ester concentration remaining after time  $t$ , and  $\bar{k}$  the first-order rate constant.

Table 3. The hydrolysis of methoxymethyl acetate at  $60^{\circ}\text{C}$ .  $[\text{HCl}] = 0.02464$ ,  $a = 0.0838$ .

$t$ (in minutes)	1	2	3	4	5	6	7	8
$10^2 \cdot (a-x)$	6.89	5.58	4.60	3.78	3.13	2.47	1.93	1.62
$10^3 \cdot \bar{k}$	3.26	3.39	3.33	3.32	3.28	3.39	3.49	3.42

$$\text{Average } \bar{k} = 0.00336 \text{ sec.}^{-1}$$

Table 4. The hydrolysis of ethoxymethyl acetate at  $12^{\circ}\text{C}$ .  $[\text{HCl}] = 0.1001$ ,  $a = 0.0601$ .

$t$ (in minutes)	20	40	60	80	100	120	140	160
$10^2 (a-x)$	4.96	4.15	3.42	2.76	2.41	1.93	1.59	1.36
$10^4 \cdot \bar{k}$	1.60	1.54	1.57	1.62	1.52	1.58	1.58	1.55

$$\text{Average } \bar{k} = 0.000157 \text{ sec.}^{-1}$$

Table 5. The hydrolysis of methoxymethyl formate at  $35^{\circ}\text{C}$ .  $[\text{HCl}] = 0.0996$ ,  $a = 0.0776$ .

$t$ (in minutes)	1	2	3	4	5	6	8	10
$10^2 (a-x)$	6.71	5.65	4.95	4.21	3.66	3.09	2.31	1.72
$10^3 \cdot \bar{k}$	2.42	2.65	2.50	2.55	2.50	2.56	2.52	2.51

$$\text{Average } \bar{k} = 0.00253 \text{ sec.}^{-1}$$

## REFERENCES

1. Salomaa, P. *Acta Chem. Scand.* **11** (1957) 132.
2. Salomaa, P. *Acta Chem. Scand.* **11** (1957) 141.
3. Salomaa, P. *Acta Chem. Scand.* **11** (1957) 235.
4. Palomaa, M. H. and Herna, T. O. *Ber.* **66** (1933) 305.
5. Palomaa, M. H. and Jaakkola, V. *Ber.* **67** (1934) 949.
6. Hammett, L. P. *Physical Organic Chemistry*, New York 1940, p. 269.
7. Salmi, E. J. *Ann. Univ. Turkuensis, Ser. A III* (1932), No. 3.
8. Tommila, E. and Hella, A. *Ann. Acad. Sci. Fennicae, Ser. A II* (1954), No. 53.
9. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, London 1953, pp. 767—782.
10. *International Critical Tables*, New York 1928, Vol. III, pp. 24—26.

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