

The Acid-Catalysed Solvolysis of Alkoxyethyl Esters.
Part III. Reaction Rates and Products in the Solvolysis of
Ethoxymethyl Acetate in Ethanol-Water Mixtures

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The kinetics of the acid-catalysed solvolysis of ethoxymethyl acetate have been investigated in six ethanol-water mixtures containing 35–78 moles per cent of ethanol. By the composition of the solvolysis product it has been established that the reaction takes place in these media by two simultaneously occurring mechanisms: a unimolecular mechanism which involves an intermediate formation of ethoxymethyl cation, and a bimolecular mechanism which is identical with the acyl-oxygen fission mechanism of the acid-catalysed solvolysis of simple alkyl esters. The contribution of the unimolecular mechanism has been found to be more marked than that of the bimolecular mechanism in the solvents investigated. The results have been discussed and compared to earlier observations made on the hydrolysis of ethoxymethyl acetate in water solution.

In extension of the earlier study on the mechanisms of acid-catalysed solvolysis reactions of alkoxyethyl esters^{1,2}, the present paper deals with results obtained for the solvolysis of ethoxymethyl acetate in ethanol-water mixtures of a sufficiently low proton-availability, in which an experimental distinction could be made between the two different mechanisms of the solvolysis.

Table 1. The first-order rate constants (in sec.⁻¹) for the formation of formaldehyde (k') and ethylal (k'') from ethoxymethyl acetate in ethanol-water mixtures at 25° C at 0.1 N hydrogen chloride concentration.

Moles % of EtOH	0	34.9	43.8	51.2	60.9	69.3	78.1
H_0	+ 1.01	+ 2.07	+ 2.19	+ 2.23	+ 2.24	+ 2.23	+ 2.16
$10^5 \times k'$	87.1	8.38	6.57	6.05	5.29	4.78	4.48
$10^5 \times k''$	—	4.12	3.43	3.30	3.54	4.70	6.12

Table 2. The molar ratios of formaldehyde and ethylal formed by the solvolysis of ethoxymethyl chloride in ethanol-water mixtures at 25° C at 0.1 N initial hydrogen chloride concentration.

Moles % of EtOH	34.9	43.8	51.2	60.9	69.3	78.1
$[\text{HCHO}] / [\text{CH}_2(\text{OEt})_2]$	1.430	1.008	0.766	0.534	0.394	0.280

Table 3. The values of first-order rate constants (in sec.⁻¹) calculated for the unimolecular (k_1) and bimolecular (k_2) solvolysis of ethoxymethyl acetate in ethanol-water mixtures at 25° C at 0.1 N hydrogen chloride concentration.

Moles % of EtOH	34.9	43.8	51.2	60.9	69.3	78.1
$10^6 \times k_1$	10.0	6.9	5.8	5.4	6.6	7.8
$10^6 \times k_2$	2.5	3.1	3.5	3.4	2.9	2.8
$\log k_1 + H_0$	-1.93	-1.97	-2.01	-2.03	-1.95	-1.95

The method of measuring the rates of the solvolysis reactions and that of estimating the rate constants referring to the different mechanisms were those described in the second part of the present study². The results are given in Tables 1, 2 and 3, the meaning of the symbols being the same as before. Table 1 also includes the value of k' in water solution which has been taken from the results of the previous measurements¹, and the values of the Hammett acidity function H_0 for the reaction solutions employed. The latter values have been obtained by interpolation from the data given by Braude and Stern³ for ethanol-water mixtures. The rate constants of the slow, subsequent reactions, the hydrolysis of ethylal and its reverse reaction, which were used for the calculation of the values of k' and k'' are given in the experimental part.

The results of the present study show a close similarity to the corresponding values determined for the solvolysis of methoxymethyl acetate in methanol-water mixtures². As indicated by the values of Table 3, the contribution of the unimolecular mechanism is about 60—80 % of the total rate of solvolysis in the media investigated. Although the resolution of the solvolysis rate into the two parts which correspond to the different mechanisms is remarkably susceptible to the influence of experimental errors, the values of k_1 are seen, as expected by the theory, to pass through a minimum at approximately the same alcohol contents of the solvent at which the solutions have their lowest proton-availabilities, as measured by the Hammett acidity function.

The value of H_0 decreases by about one unit, when passing from a solution containing 34.9 moles per cent of ethanol to water solution. The theory suggests that the rate constant of the unimolecular reaction will be increased by a factor of about 10 by this change of medium, whereas a decrease of the value of k_2 is to be expected, *cf.* Ref.² Thus the fact that in 34.9 moles per cent ethanol approximately 80 % of the total solvolysis reaction does occur by the unimolecular mechanism furnishes an additional evidence for the suggestion made¹, according to which the hydrolysis of ethoxymethyl acetate by aqueous acid takes place almost exclusively by the unimolecular mechanism.

Table 4. The values of k_a and k_h (in sec.^{-1}) determined for the reversible acetalisation of formaldehyde in ethanol-water mixtures at 25°C at 0.1 N hydrogen chloride concentration.

Moles % of EtOH	34.9	43.8	51.2	60.9	69.3	78.1
$10^4 \cdot (k_a + k_h)$	4.38	3.53	3.50	3.69	4.40	6.20
$k_h / (k_a + k_h)$	0.301	0.244	0.200	0.160	0.125	0.087

Table 5. The determination of the constants k_a and k_h for the reversible acetalisation of formaldehyde in 69.3 moles per cent ethanol at 25°C at 0.1 N hydrogen chloride concentration.

t (in minutes)	0	600	900	1 200	1 525	1 900	2 100	2 400	7 250	∞
$10^4 \cdot [\text{HCHO}]$	9.25	8.10	7.51	7.05	6.54	6.03	5.80	5.49	2.36	1.16
$10^4 \cdot (k_a + k_h)$		4.26	4.48	4.40	4.46	4.46	4.42	4.34	4.38	

$$\text{Average } k_a + k_h = 0.00000440 \text{ sec.}^{-1}; k_h / (k_a + k_h) = 0.125$$

Table 6. The determination of the first-order rate constants for the formation of formaldehyde (k') and ethylal (k'') by the solvolysis of ethoxymethyl acetate in 60.9 moles per cent ethanol at 25°C at 0.1 N hydrogen chloride concentration. Eqns. 3, 4 and 5 (Ref.²) have been used for the calculations. $k_a + k_h = 0.00000369 \text{ sec.}^{-1}$,
 $k_h / (k_a + k_h) = 0.160$, $\alpha = 0.0613$.

$t-t_0$ in minutes	[HCHO]	t in minutes	α	$k' + k''$ in sec.^{-1}
0	0.0002			
1	0.0004			
2	0.0007			
30	0.0057	31		0.0000908
50	0.0085	51		0.0000865
70	0.0116	71		0.0000897
90	0.0141	91		0.0000896
125	0.0177	126		0.0000884
155	0.0202	156		0.0000873
275	0.0271	276		0.0000860
1 505	0.0296	1 506	0.611	
2 030	0.0279	2 031	0.623	
2 210	0.0271	2 211	0.620	

$$\text{Averages: } \alpha = 0.618, k' + k'' = 0.0000883 \text{ sec.}^{-1}$$

$$k' = 0.0000529 \text{ sec.}^{-1}, k'' = 0.0000354 \text{ sec.}^{-1}$$

The values of k_1 determined in ethanol-water mixtures (Table 3) are nearly of that order of magnitude which is to be expected for the unimolecular mechanism. From the first-order rate constant of the hydrolysis of ethoxymethyl acetate in water at 25°C at 0.1 N hydrogen chloride concentration, $0.000871 \text{ sec.}^{-1}$, and from the corresponding value of the acidity function, $+1.01$, it is obtained: $\log k + H_0 = -2.05$. This value shows a satisfactory agreement with the values calculated for $\log k_1 + H_0$ for ethanol-water mixtures (Table 3), in view of the difficulties encountered in revealing the actual dependence of $\log k_1$ on the acidity function in ethanol-water mixtures, cf. Ref.²

EXPERIMENTAL

The methods of preparing and purifying the materials used were those described earlier^{1,4}. The technique of the kinetic measurements and the methods of calculation were the same as those applied to the solvolysis of methoxymethyl esters in methanol-water mixtures². Table 4 gives the rate constants measured for the hydrolysis of ethylal and its reverse reaction, the acetalisation of formaldehyde, Table 5 illustrating one of the individual measurements. Table 6 gives the details for a typical example of the experimental runs in which the solvolysis of ethoxymethyl acetate was investigated. The meaning of the symbols is the same as previously².

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