

**The Acid-Catalysed Solvolysis of Alkoxyethyl Esters.  
Part II. Reaction Rates and Products in the Solvolysis of  
Methoxymethyl Esters in Methanol-Water Mixtures**

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The acid-catalysed solvolysis reactions of methoxymethyl formate and methoxymethyl acetate have been investigated kinetically in methanol-water mixtures containing 30–65 moles per cent of methanol. A method has been developed to determine the reaction mechanisms which takes advantage of analysis of the different solvolysis products. The results indicate that the reactions of the esters take place involving two simultaneous mechanisms in the solvents under study. One mechanism is unimolecular and leads to the formation of methoxymethyl cation in the rate-determining stage. The second mechanism is bimolecular and takes place with an acyl-oxygen fission. The contribution of the bimolecular mechanism to the total solvolysis rate is more notable with methoxymethyl formate than with methoxymethyl acetate. Approximate calculations are made by Hammett's acidity function to elucidate the reaction mechanisms in pure water solution, the results suggesting that methoxymethyl acetate hydrolyses in this medium almost exclusively by the unimolecular mechanism, whereas in the case of methoxymethyl formate the unimolecular reaction is accompanied by a contribution from the bimolecular reaction.

In the first part of the present study<sup>1</sup> it was established that the acid-catalysed solvolysis of simple alkoxyethyl esters in water solution takes place predominantly according to a unimolecular mechanism involving the production of an intermediate alkoxyethyl cation. However, it was considered as being probable that, at least in the case of methoxymethyl formate, an alternative reaction mechanism of a normal type of acid-catalysed ester hydrolysis might play some role in the hydrolysis by dilute aqueous acids. The purpose of the present work is to furnish additional evidence for the reaction mechanisms suggested for the solvolysis of alkoxyethyl esters in hydroxylic media.

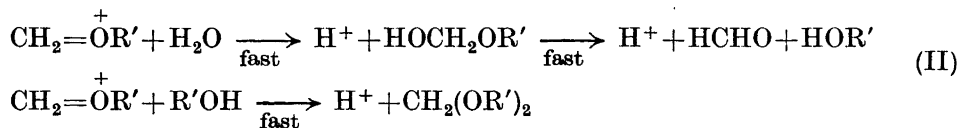
## METHOD OF DETECTING THE MECHANISMS

In an earlier study <sup>2</sup> the author determined the values of Hammett's acidity function  $H_0$  for solutions of hydrogen chloride in methanol-water mixtures and found the values to increase by 0.7—0.8 units when passing from water to media containing 30—65 moles per cent of methanol. The theory suggested <sup>cf. 1</sup> that the logarithm of the rate constant for the unimolecular mechanism should decrease by an amount of nearly this order of magnitude when passing from water to the water-methanol mixtures, whereas such a decrease would not be probable for the postulated bimolecular mechanism. The change in solvent composition was thus expected to facilitate the detection of the possible bimolecular mechanism.

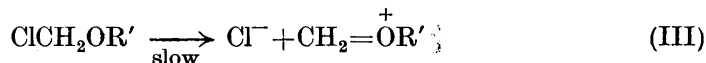
The investigation of reaction mechanisms in alcohol-water mixtures may be based on the following considerations. Let us assume that the alkoxy group of the alkoxyethyl ester is the same as that of the alcohol in the water-alcohol mixture under study. Let it be at first presupposed that the reaction mechanism is unimolecular. The rate-determining stage which follows the initial proton uptake leads to the formation of an alkoxyethyl cation:



The fast, product-forming reactions of the unstable cation are those given by eqns. (II):

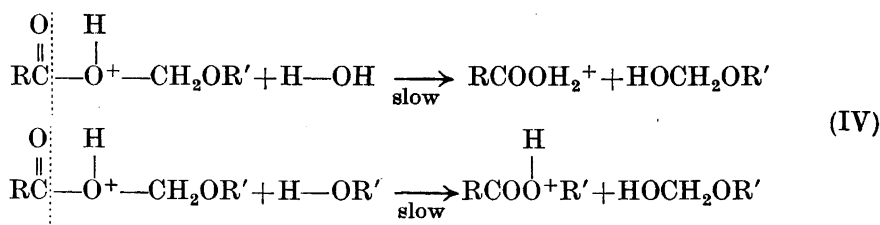


The intermediate mesomeric ion is exactly the same, which is formed in the solvolysis reaction of the corresponding alkoxyethyl chloride. The latter reaction has been shown to take place by the  $S_N1$  mechanism involving the ionisation reaction (III) as the rate-determining stage<sup>3</sup>:



When the solvolysis of an alkoxyethyl ester in an alcohol-water mixture takes place exclusively by the mechanism represented by eqns. (I) and (II), that implies that the relative amounts of formaldehyde and formic acid produced at the end of reaction are the same as in the solvolysis reaction of the corresponding alkoxyethyl chloride under the same external conditions, because the product-forming reactions are identical in both cases.

Let us now suppose that the solvolysis occurs by a bimolecular mechanism, which involves an acyl-oxygen fission. In that case, the rate-determining, slow reactions which follow the preliminary proton uptake are those given by eqns. (IV)<sup>cf. 4</sup>:



Both of the possible reactions, the reaction with water and that with alcohol, give no formal, formaldehyde being one of the reaction products in both cases. Actually, the formaldehyde formed in the alcoholic media may be present, at least partly, in the form of semiacetal, but that is of no importance from the analytical viewpoint.

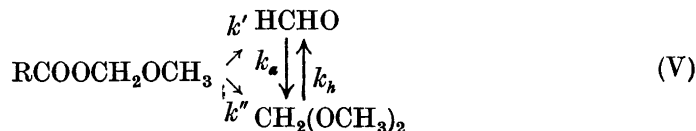
It thus appears that the relative amount of formaldehyde formed furnishes a criterion for the reaction mechanism. The unimolecular mechanism yields both formaldehyde and formal in a molar ratio, which is equal to that by the solvolysis of the corresponding alkoxyethyl chloride under the same conditions, whereas the bimolecular mechanism gives an amount of formaldehyde, which is equivalent to the amount of the ester initially present. It is seen that an assumption of alternative, less probable reaction mechanisms *cf.* 1 would not essentially alter the method of revealing the different mechanisms by the reaction products. If the mechanism (IV) were replaced by a unimolecular acyl-oxygen fission mechanism 4, the reaction would similarly produce quantitatively formaldehyde. The same situation prevails when the solvolysis would occur on the alkoxy side of the ester molecule, the reaction with water giving formaldehyde and that with alcohol regenerating the ester, the observed net change thus being formaldehyde formation. Hence the contributions of these less probable mechanisms would be included in the observed net rate of formaldehyde production. The only alternative mechanism, which could produce formal in addition to formaldehyde, were bimolecular nucleophilic substitution at the carbon atom of the methylene group. This carbon atom is, however, much less electrophilic than that present in the carbonyl group, and actually, a bimolecular alkyl-oxygen fission mechanism has never been established in acid-catalysed ester hydrolysis 4.

The subsequent reactions, the esterification of the carboxylic acid formed and its reverse reaction, which followed the solvolysis of alkoxyethyl esters in methanol-water mixtures, did not affect our method as it took advantage only of the amounts of formaldehyde and methylal produced by the reactions. On the contrary, the rates of the subsequent acetalisation of formaldehyde and its reverse methylal hydrolysis were of such an order of magnitude, that these reactions must be taken into account in order to obtain reliable results.

#### METHOD OF CALCULATION

As shown experimentally, the acid-catalysed solvolysis of methoxymethyl esters in methanol-water mixtures under study proceeds to completion and yields both formaldehyde and methylal. The sum of the concentrations of

formaldehyde and methylal formed is equivalent to the amount of methoxy-methyl ester reacted. Formaldehyde and methylal are converted to each other in a slow, subsequent equilibrium reaction. At a given acid concentration, all of these reactions are of the first order. Let the respective first-order rate constants be denoted as follows:  $k'$  for the formation of formaldehyde from the ester,  $k''$  for the formation of methylal from the ester,  $k_a$  for the acetalisation of formaldehyde, and  $k_h$  for the hydrolysis of methylal. Independently of the reaction mechanisms involved, we thus have the following simplified reaction-scheme:



Making use of the known values of  $k_a$  and  $k_h$  which can be measured separately, we wish to calculate the values of  $k'$  and  $k''$  from the experimental data.

If  $a$  denotes the initial ester concentration, and  $x$  and  $y$  are the concentrations of formaldehyde and methylal present at time  $t$ , respectively, we obtain eqns. (1) which express the rates of increase in formaldehyde and methylal concentrations:

$$\begin{aligned} \frac{dx}{dt} &= k'(a-x-y) - k_ax + k_hy \\ \frac{dy}{dt} &= k''(a-x-y) + k_ax - k_hy \end{aligned} \quad (1)$$

By applying the initial conditions,  $x = 0$  and  $y = 0$ , when  $t = 0$ , eqns. (1) may be integrated to give

$$\frac{x}{a} = \frac{k_h}{k_a + k_h} \left( 1 - e^{-(k_a + k_h)t} \right) + \alpha \left( e^{-(k_a + k_h)t} - e^{-(k' + k'')t} \right) \quad (2)$$

in which

$$\alpha = \frac{k' - k_h}{(k' + k'') - (k_a + k_h)} \quad (3)$$

Taking advantage of the fact that the value of  $(k' + k'')$  is large in comparison to that of  $(k_a + k_h)$ , the last exponential of eqn. (2) can be neglected for large values of  $t$ , i.e. when practically all of the ester present initially has been converted to the final products, formaldehyde and methylal. We thus obtain from eqn. (2) the following expression which is valid for sufficiently long reaction times:

$$\alpha = \frac{x}{a} e^{(k_a + k_h)t} - \frac{k_h}{k_a + k_h} \left( e^{(k_a + k_h)t} - 1 \right) \quad (4)$$

By this equation, the value of  $\alpha$  can be calculated, and using the value found, values of  $(k' + k'')$  can be calculated from the data referring to the earlier stages of the reaction by the following equation which is readily obtained from eqn. (2):

$$k' + k'' = \frac{1}{t} \ln \frac{\alpha a}{\alpha a e^{-(k_a + k_h)t} - x + \frac{k_h a}{k_a + k_h} (1 - e^{-(k_a + k_h)t})} \quad (5)$$

From the known values of  $\alpha$ ,  $(k' + k'')$ ,  $k_a$  and  $k_h$ , the values for  $k'$  and  $k''$  can be calculated separately by eqn. (3).

The above calculation implies that the zero time is to be chosen at that time when no reaction has occurred. In actual measurements, some formaldehyde had been already formed at the time of taking of the first sample. The real zero time was hence determined by taking several samples with short time intervals at the initial phase of the reaction and by extrapolating to zero formaldehyde concentration. Table 1 shows a typical example of the individual experimental runs. Eqns. (3), (4) and (5) have been used in the calculations. The time interval passed from the time of taking of the first sample has been denoted by  $(t - t_0)$ ,  $t$  being the actual reaction time which is found by a short extrapolation. As shown by the last column of the table, the values of  $(k' + k'')$  remain practically constant at the different time intervals when the subsequent reactions have been taken into account. The effect of the subsequent reactions is clearly illustrated by the fact that the formaldehyde concentration which increases at first, reaches a maximum value, and then begins slowly to decrease, as shown by the values given in the second column of the table.

The solvolysis of methoxymethyl formate in methanol-water mixtures was so rapid in comparison to the subsequent reactions that their influence could be neglected, except in order to correct the final concentration of formaldehyde formed. In this case, the exponentials in eqn. (5) were practically unity, and the equation could be replaced by

$$k' + k'' = \frac{1}{t - t_0} \ln \frac{\alpha a - x_0}{\alpha a - x} \quad (5 a)$$

Table 1. The calculation of the constants  $k'$  and  $k''$  for the solvolysis of methoxymethyl acetate in 47.2 moles per cent methanol at 25°C at 0.1182 N hydrogen chloride concentration.  $\alpha = 0.0658$ .  $k_a + k_h = 2.92 \times 10^{-6}$  sec.<sup>-1</sup>,  $k_h/(k_a + k_h) = 0.155$ .

$t - t_0$ in min.	$10^2 \times x$	$t$ in min.	$\alpha$	$10^4 \times (k' + k'')$ in sec. <sup>-1</sup>
0	0.03			
2	0.08			
4	0.11			
20	0.53	21.5		1.19
40	0.91	41.5		1.13
60	1.25	61.5		1.11
80	1.58	81.5		1.14
100	1.83	101.5		1.12
120	2.12	121.5		1.15
150	2.37	151.5		1.13
180	2.59	181.5		1.11
210	2.80	211.5		1.13
720	3.53	721.5	0.588	
1440	3.17	1 441.5	0.576	
1800	3.08	1 801.5	0.582	
2880	2.68	2 881.5	0.566	

Averages:  $\alpha = 0.578$ ,  $k' + k'' = 0.000113$  sec.<sup>-1</sup>

$k' = 0.000064$  sec.<sup>-1</sup>

$k'' = 0.000049$  sec.<sup>-1</sup>

Table 2. The calculation of the constants  $k'$  and  $k''$  for the solvolysis of methoxymethyl formate in 64.2 moles per cent methanol at 25°C at 0.1182 N hydrogen chloride concentration.  $a=0.0686$ .  $k_a+k_h = 3.32 \times 10^{-6}\text{sec.}^{-1}$ ,  $k_h/(k_a+k_h) = 0.086$ . The times are given in minutes, the rate constants in  $\text{sec.}^{-1}$ .

$t-t_0$	0	3	6	9	12	15	18	21	24	120	240	360	480
$10^3 \times x$	0.83	1.87	2.68	3.39	3.89	4.30	4.67	4.82	5.13	6.08	5.99	5.77	5.66
$\alpha$										0.906	0.912	0.897	0.899
$10^3 \times (k'+k'')$		1.20	1.17	1.20	1.17	1.15	1.16	1.08	1.12				
Averages: $\alpha = 0.904$ , $k'+k'' = 0.00116$													
$k' = 0.00105$ , $k'' = 0.00011$													

in which  $x_0$  denotes the formaldehyde concentration present at the time ( $t_0$ ) of taking of the first sample. Table 2 shows an example of experimental runs illustrating this case. The value of  $\alpha$  has been calculated as above from the data referring to long reaction times, taking into account that for these times ( $t-t_0$ ) becomes practically equal to  $t$ .

## RESULTS AND DISCUSSION

Table 3 gives the experimental results for the solvolysis of methoxymethyl formate and methoxymethyl acetate in methanol-water mixtures. The rate constants for the subsequent reactions which were necessary for the calculation of the values of  $k'$  and  $k''$  were estimated simultaneously by determining both the rate of formation of methylal from formaldehyde and the rate of methylal hydrolysis, as described in the experimental part which also contains the values observed. Although it was verified that the values of  $k'$  and  $k''$  were proportional to the acid concentration when it was varied but slightly, all of the values included in Table 3 were determined at the same concentration, 0.1182 N, of hydrogen chloride.

Table 4 gives the average values determined for the molar ratios of formaldehyde and methylal formed in the solvolysis of methoxymethyl chloride in the methanol-water mixtures. Also in this case it was established that the

Table 3. The solvolysis of methoxymethyl esters in methanol-water mixtures at 25°C at 0.1182 N hydrogen chloride concentration. The values of  $k'$  and  $k''$  are given in  $\text{sec.}^{-1}$ .

		Moles per cent of methanol		
		30.9	47.2	64.2
HCOOCH <sub>2</sub> OCH <sub>3</sub>	$\left\{ \begin{array}{l} k' \\ k'' \end{array} \right.$	0.000965	0.000919	0.00105
		0.000065	0.000081	0.00011
CH <sub>3</sub> COOCH <sub>2</sub> OCH <sub>3</sub>	$\left\{ \begin{array}{l} k' \\ k'' \end{array} \right.$	0.000098	0.000064	0.000054
		0.000043	0.000049	0.000057

Table 4. The molar ratios of formaldehyde and methylal formed in the solvolysis of methoxymethyl chloride in methanol-water mixtures at 25°C at 0.1182 N initial hydrogen chloride concentration.

		Moles per cent of methanol		
		30.9	47.2	64.2
[HCHO]/[CH <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> ]		1.538	0.681	0.348

product ratio was not affected by small variations in the initial hydrogen chloride concentration. The solvolysis of methoxymethyl chloride in these solvents took place much too rapidly to permit of kinetic measurements; still the composition of the final product could be easily determined. In this case, the slow, subsequent reactions of formaldehyde and methylal did not affect the results, the product analysis being performed almost immediately after mixing the components.

As shown above, the bimolecular solvolysis mechanism (IV) could produce no methylal, *i.e.* the value of  $k''$  would be zero. This is not the case here, as indicated by the values determined for  $k''$  (Table 3). On the other hand, the unimolecular mechanism which is presented by eqns. (I) and (II) would give formaldehyde and methylal in a molar ratio, which were exactly the same as in the solvolysis of methoxymethyl chloride under the same conditions, *i.e.* the value of the ratio  $k'/k''$  would be identical with the molar ratio of formaldehyde and methylal, which is given in Table 4 for the solvent in question. A comparison between the values of Tables 3 and 4 shows that in all cases the values of  $k'/k''$  are higher than the respective molar ratios of formaldehyde and methylal produced in the unimolecular solvolysis of methoxymethyl chloride. This indicates that the both reaction mechanisms occur simultaneously. The respective contributions of the mechanisms to the total rate of solvolysis may be evaluated as shown below.

Let  $k_1$  denote the first-order rate constant for the solvolysis by the unimolecular mechanism. The first-order rate constants for the formation of formaldehyde and methylal by this mechanism are then given by  $^c$   $r k_1/(1+r)$  and  $k_1/(1+r)$ , respectively, in which  $r$  denotes the molar ratio of formaldehyde and methylal formed in the rapid, product-forming reactions (II) of the intermediate methoxymethyl cation. The values of  $r$  are identical with the ratios of formaldehyde and methylal concentrations, which are determined for the solvolysis of methoxymethyl chloride (Table 4). Let  $k_2$  denote the first-order rate constant for the production of formaldehyde by the bimolecular mechanism (IV), the rate of methylal formation by this mechanism being zero. It is to be noted that in the case of bimolecular mechanism there are two different reactions, hydrolysis and alcoholysis, which both lead to the formation of formaldehyde, and  $k_2$  thus represents the sum of the rate constants of these two reactions. Altogether, we obtain for the first-order rate constants of the formation of formaldehyde ( $k'$ ) and methylal ( $k''$ ) the following expressions:

$$\begin{aligned}k' &= r k_1/(1+r) + k_2 \\k'' &= k_1/(1+r)\end{aligned}\tag{6}$$

by which, using the known values of  $k'$ ,  $k''$  and  $r$  (Tables 3 and 4), the values of  $k_1$  and  $k_2$  can be readily calculated. The results of such calculations are given in Table 5 which also includes the values of the Hammett acidity function  $H_0$  for the solutions under study<sup>2</sup>.

A comparison between the values of  $k_1$  and  $k_2$  indicates that in the case of methoxymethyl formate, the contribution of the bimolecular mechanism is more pronounced than that of the unimolecular mechanism in the media under study, whereas the opposite situation prevails in the solvolysis of methoxy-

Table 5. The first-order rate constants (in sec.<sup>-1</sup>) for the unimolecular ( $k_1$ ) and bimolecular ( $k_2$ ) solvolysis of methoxymethyl esters in methanol-water mixtures at 25°C at 0.1182 N hydrogen chloride concentration.

Moles % of MeOH $H_0$	0 +0.91	30.9 +1.62	47.2 +1.69	64.2 +1.69
HCOOCH <sub>2</sub> OCH <sub>3</sub>	$k_1$		0.00016	0.00014
	$k_2$		0.00087	0.00086
	$\log k_1 + H_0$		-2.18	-2.16
CH <sub>3</sub> COOCH <sub>2</sub> OCH <sub>3</sub>	$k_1$		0.000109	0.000082
	$k_2$		0.000032	0.000031
	$\log k_1 + H_0$		-2.34	-2.40

methyl acetate. This is in good accord with the previous results<sup>1</sup>. In addition, the values of the rate constants  $k_1$  and  $k_2$  are approximately of those orders of magnitude, which are to be expected in view of the reaction mechanisms involved (see below).

The unimolecular mechanism presupposes a linear relation between the logarithm of the first-order rate constant and  $-H_0$  with a slope of close to unity. If the slope would be exactly unity,  $\log k_1 + H_0$  would be constant for different media. In this case, the values of  $\log k + H_0$  ( $k$ , the first-order rate constant in water solution) determined in water solution would be equal or higher in comparison to the respective values of  $\log k_1 + H_0$  in methanol-water mixtures depending as the reaction mechanism in water solution were purely unimolecular or, if the unimolecular mechanism were accompanied by a contribution from the bimolecular mechanism. According to the previously determined values<sup>1</sup>, the first-order rate constants for 0.1182 N aqueous hydrochloric acid at 25°C are: 0.00102 sec.<sup>-1</sup> for methoxymethyl formate, and 0.000281 sec.<sup>-1</sup> for methoxymethyl acetate; from these we obtain for the respective values of  $\log k + H_0$  in water solution: -2.08 for methoxymethyl formate, and -2.64 for methoxymethyl acetate. The value for methoxymethyl formate is somewhat higher than the corresponding values of  $\log k_1 + H_0$  determined in methanol-water mixtures (Table 5), whereas the opposite situation prevails in the case of methoxymethyl acetate. In view of the limitations involved in the calculation, this is in accord with the difference in mechanisms assumed for the hydrolysis of these compounds by aqueous acids<sup>1</sup>. The actual dependence of  $\log k_1$  on  $H_0$  in methanol-water mixtures remains obscure owing to the difficulties encountered in the determination of the values for  $k_1$  in solvents of lower methanol content in which the changes in  $H_0$  were more significant than in the present solvents<sup>2</sup>. In solvents of relatively low methanol content the determination of  $k_1$  was found to be very inaccurate. This is also seen from the latter of eqns. (6) according to which the value of  $k_1$  in water solution takes the indefinite form  $0 \cdot \infty$ .

The values of  $k_2$  determined for methoxymethyl formate and methoxymethyl acetate in methanol-water mixtures (Table 5) are approximately threefold as compared with the respective rate constants for the hydrolysis of methyl formate and methyl acetate in aqueous acid (see *ref.* 1). This is in accord with the relatively small constitutional effect of the alkyl group of an ester,



which undergoes acid-catalysed solvolysis by the bimolecular acyl-oxygen fission mechanism<sup>4</sup>, and to the relatively slight solvent influence. A comparison between the values determined by Salmi<sup>5</sup> and by Tommila and Hella<sup>6</sup> for the rate constants of acid-catalysed hydrolysis of methyl formate and methyl acetate in water, and the respective values for the hydrolysis in 50 moles per cent methanol, determined by Palomaa and Siitonen<sup>7</sup>, shows the rate constants to decrease by 30—40 % when passing from water to the methanol solution. However, in the reactions of simple alkyl esters in alcoholic media, in which the alkyl group of the alcohol is the same as that present in the esters in question, the hydrolysis reactions of the esters and their reverse reactions are the only measurable processes, the reactions with alcohol molecules remaining obscure because they regenerate the esters present initially. Such a situation does not prevail in the solvolysis of methoxymethyl esters in methanol-water mixtures, the sum of the rates of the hydrolysis and alcoholysis reactions (IV) being that which is measured, and the somewhat higher values of  $k_2$  as compared with the corresponding rate constants of the hydrolysis of alkyl esters may be primarily ascribed to the competing alcoholysis reactions.

## EXPERIMENTAL

*Materials.* The methoxymethyl esters were prepared as described in the first part of the present study<sup>1</sup>. Methylal, which was used in the determination of the rates of its reversible hydrolysis reaction, was prepared from paraformaldehyde and methanol with hydrogen chloride as the catalyst. The raw product was refluxed over sodium and fractionated, b.p. 44°C/755 mm Hg. The degree of purity of the product was found to be over 99 % by formaldehyde analysis which followed the hydrolysis of a weighed sample by 2 N hydrochloric acid. Methanol, *pro analysi* from E. Merck, Darmstadt, was purified as described earlier<sup>2</sup>. The methanol-water mixtures employed for the kinetic measurements were prepared by weighing, after which carefully dried hydrogen chloride gas was passed in, and the solutions were diluted to give the hydrogen chloride concentration desired. All of the solutions were made up freshly before the experiments.

*Kinetic measurements.* The method of analysis used in following the solvolysis of methoxymethyl esters in methanol-water mixtures was essentially the same as in the first part of the present study<sup>1</sup>. In the kinetic experiments, a weighed sample of the ester which was sealed in a small glass bulb was brought into a measured volume of the reaction solvent, and after attainment of the thermostat temperature, the bulb was broken and the components were mixed by vigorous shaking to start the reaction. The value of the initial ester concentration was calculated from the amount of ester weighed, taking into account a small correction which was due to the deviation of the degree of purity of the ester from 100 %<sup>1</sup>. Particular experiments indicated that the solvolysis of the esters which produced both formaldehyde and methylal proceeded to completion, no methoxymethyl ester being present in the reaction mixture after sufficiently long reaction time. This was seen by running the samples into a large excess of 1 N sodium hydroxide solution, and after a standing period of 1 h, analysing the samples for formaldehyde. No increase in the formaldehyde content was observed during this time, which is sufficient to the quantitative hydrolysis of the methoxymethyl esters by the alkaline solution.

The method of determining the product composition for the solvolysis of methoxymethyl chloride in methanol-water mixtures was that described earlier by the author<sup>3</sup>. In all solvents investigated, several parallel determinations were conducted. In the solvolysis in 64.2 moles per cent methanol at 25°C, for instance, the following values were found for the molar percentage of formaldehyde in the product: 25.8, 26.6, 25.8, 25.4 and 25.6 (average 25.8). From the average value, the value 0.348 is obtained for the molar ratio of formaldehyde and methylal.

*Table 6.* The values of  $k_a$  and  $k_h$  (in  $\text{sec}^{-1}$ ) for the reversible acetalisation of formaldehyde in methanol-water mixtures at  $25^\circ\text{C}$  at 0.1182 N hydrogen chloride concentration. A. Measured by following the acetalisation of formaldehyde. B. Measured by following the hydrolysis of methylal.

Moles % of methanol		30.9	47.2	64.2
A	$\{10^6 \cdot (k_h + k_a)$	3.12	2.94	3.35
	$\{k_h/(k_h + k_a)$	0.264	0.155	0.084
B	$\{10^6 \cdot (k_h + k_a)$	3.16	2.91	3.28
	$\{k_h/(k_h + k_a)$	0.276	0.156	0.088

*Table 7.* The determination of  $k_a$  and  $k_h$  by measuring the rate of the reversible acetalisation of formaldehyde in 30.9 moles per cent methanol at  $25^\circ\text{C}$  at 0.1182 N hydrogen chloride concentration.

$t$ (in hours)	0	18	24	42	48	72	96	120	148	$\infty$
$10^3 \cdot [\text{HCHO}]$	5.34	4.61	4.38	3.86	3.64	3.22	2.75	2.44	2.21	1.41
$10^6 \cdot (k_h + k_a)$		3.17	3.24	3.12	3.28	2.99	3.11	3.10	2.99	
$\text{average } k_h + k_a = 0.00000312 \text{ sec}^{-1}$ $k_h/(k_h + k_a) = 1.41/5.34 = 0.264$										

The determination of the rate constants for the hydrolysis of methylal ( $k_h$ ) and the acetalisation of formaldehyde ( $k_a$ ) took place by two different ways. In the first method, the acetalisation of formaldehyde was followed until the attainment of the equilibrium, in the second method the initial reactant was methylal. Both methods gave nearly identical results, as indicated by the values given in Table 6. Formaldehyde analysis was used for the rate measurements. In the second method, weighed samples of methylal were dissolved in measured volumes of the solvent, in order to calculate the initial concentration of methylal. In both methods, the first samples were taken almost immediately after mixing the components. Zero time was the time of taking of the first sample. Owing to the slowness of the reactions, practically no reaction had occurred at the zero time. The rate constants were calculated by the usual formulas for reversible first-order reactions<sup>8</sup>. Table 7 gives the details for one of the individual runs.

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