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The Kinetics of 1-Chloroether Alcoholysis

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The exceptional reactivity of 1-chloroethers has called the attention of numerous investigators and several explanations for this have been offered[1]. Whereas a number of theoretical approaches to the mechanisms of the reactions of the 1-chloroethers may be found in the literature[2], in only a few instances have these compounds been subjected to kinetic investigation. Clarke's[3] attempts to follow the reaction of methyl chloromethyl ether in alcoholic pyridine failed due to the rapid rate of reaction. Conant, Kirner and Hussey[4], however, were able to appraise the rate of reaction between methyl chloromethyl ether and potassium iodide in acetone solution. More interesting are the results of Böhme[2c], who followed the rate of hydrolysis of ethyl chloromethyl ether in aqueous dioxane solution. He noted that the hydrogen chloride produced catalyzed the reaction but did not take into account the concentration of the hydrogen chloride in calculating the rate constants. On the contrary, he attempted to show that, except for a short initial period, the reaction follows the first order law.

A conflicting view of the reaction in this respect is given by the results of Leimu[5] for the rates of alcoholysis of 1-chloroethers in dioxane solution containing one and two moles per liter of *n*-propyl alcohol. Catalysis by hydrogen chloride was also observed in these reactions and to such an extent that constants calculated from the first order equation, neglecting autocatalysis, increased toward the end of the reaction. Reactions carried out in solutions initially containing hydrogen chloride indicated that the rate is proportional to the concentration of this substance. The data obtained were found to fit the integrated form (2) of the differential equation (1):

$$\frac{dx}{dt} = k_s a \; (b - x) \; (c + x) \qquad (1)$$

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$$k_s = \frac{1}{a(b+c)t} \ln \frac{b(c+x)}{c(b-x)} \text{*} \qquad (2)$$

In these equations the relatively small change in the alcohol concentration a is disregarded; b and c are the initial concentrations of chloroether and hydrogen chloride, respectively, and x the amount of chloroether reacted at time t.

Certain observations led us to suspect that the reaction is reversible in this medium and this has been confirmed in the present work. In order to ascertain the nature of the reaction, it was followed in solvents containing various amounts of the lower aliphatic alcohols in dioxane and in the pure alcohols. The results reveal that the alcoholysis of 1-chloroethers is very susceptible to changes in medium.

THE RATE EQUATIONS

The method of analysis used to follow the reaction

$$ROCH_2Cl + HOR' \longrightarrow ROCH_2OR' + HCl \qquad (I)$$

was the same as that used in the previous work[5]. Samples were withdrawn from the reaction solution with an automatic pipette and run into aqueous sodium hydroxide solution. The liberated formaldehyde was determined iodometrically following the method originally developed by Ripper[6].

In dioxane solutions containing small amounts of alcohol, reaction (I) was found to be catalyzed. The rate is approximately directly proportional to the hydrogen chloride concentration. The reaction did not proceed to completion in these solvents but attained a state of equilibrium. The existence and nature of the reverse reaction was confirmed by experiments in which the corresponding formal was substituted for the chloroether. The numerical data obtained in these experiments were found to fit satisfactorily the rate equation derived on the assumption that the rate of the reverse reaction was proportional to the first power of the formal concentration and to the square of the concentration of the hydrogen chloride.

Following these considerations, the differential equation for the reaction in dioxane solutions containing small amounts of alcohol and added hydrogen chloride, but no initial formal, may be written

$$\frac{dx}{dt} = k_1(a-x)\ (b-x)\ (c+x) - k_2x(c+x)^2 \qquad (3)$$

where a, b and c are the initial concentrations of alcohol, chloroether and hydrogen chloride, respectively, x the amount of chloroether reacted at time t, k_1 and k_2 the rate constants for the alcoholysis and the reverse reaction.

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* An error appearing in this equation in the previous paper[5] is here corrected.

Experiments carried out with different initial concentrations of chloroether and hydrogen chloride gave values of the equilibrium constant conforming with equation (3). The equilibrium constant K is in this case given by

$$\frac{k_1}{k_2} = \frac{\xi\ (c + \xi)}{(a - \xi)\ (b - \xi)} = K \tag{4}$$

where ξ is the value of x at equilibrium $(dx/dt = 0)$.

The integrated form of equation (3) suitable for the application of the numerical results may be derived as follows[7]:

If $k_1 \neq k_2$, equation (3) may be written

$$\frac{dx}{dt} = (k_1 - k_2)\ (c + x)\ (x^2 + px + q), \text{ where}$$

$$p = -\frac{k_1(a + b) + k_2c}{k_1 - k_2} = -\frac{K(a + b) + c}{K - 1} \text{ and}$$

$$q = \frac{k_1ab}{k_1 - k_2} = \frac{Kab}{K - 1}$$

$(\xi - x)$ is one factor of the expression $x^2 + px + q$. If the other factor is designated by $(\zeta - x)$, the value of ζ is given by

$$\zeta = \frac{Kab}{(K - 1)\,\xi} \tag{5}$$

The differential equation now takes the form

$$\frac{dx}{dt} = (k_1 - k_2)\ (c + x)\ (\xi - x)\ (\zeta - x) \tag{3'}$$

which is easily integrated by the method of partial fractions.

With the condition $t = 0$, $x = x_0$, we have then

$$(k_1 - k_2)t = \frac{1}{(c + \xi)(c + \zeta)} \ln \frac{c + x}{c + x_0} + \frac{1}{(c + \xi)\ (\zeta - \xi)} \ln \frac{\xi - x_0}{\xi - x} + \frac{1}{(c + \zeta)\,(\xi - \zeta)} \ln \frac{\zeta - x_0}{\zeta - x} \tag{6}$$

The individual constants k_1 and k_2 are calculated from the difference and the value of K from (4). In certain cases, where the absolute value of ζ is found to be relatively large, the last term of (6) is of a much smaller magnitude than the others and may be disregarded in the calculations. In particular, when K is approximately unity, the absolute value of ζ is so high that the following approximation holds:

$$\zeta \sim c + \zeta \sim \zeta - \xi$$

The equation (6) may then be replaced by the approximate equation

$$k_1 t = \frac{\xi}{ab(c+\xi)} \ln \frac{(\xi - x_0)\ (c + x)}{(c + x_0)\ (\xi - x)} \tag{7}$$

This equation is easily shown to be the solution of equation (3) in the special case of $k_1 = k_2$ $(K = 1)$.

Equations for the reverse reaction between the formal and hydrogen chloride may be derived in a similar manner. Following the considerations outlined above, the differential equation corresponding to (3) is

$$\frac{dx}{dt} = k_2 (d - x)\ (c - x)^2 - k_1 x (a + x)\ (c - x) \tag{8}$$

in which a, c, k_1 and k_2 have the same significance as above, d is the initial concentration of the formal and x the amount of formal reacted at time t. If the equilibrium value of x is again denoted by ξ, the equilibrium constant is obtained from

$$\frac{k_1}{k_2} = \frac{(d - \xi)\ (c - \xi)}{\xi (a + \xi)} = K \tag{9}$$

For the condition $k_1 \neq k_2$, (8) may be transformed into

$$\frac{dx}{dt} = (k_2 - k_1)\ (c - x)\ (\xi - x)\ (\zeta - x) \tag{8}$$

where ζ is calculated from

$$\zeta = \frac{cd}{(1 - K)\xi} \tag{10}$$

On substituting the limit $x = x_0$, when $t = 0$, the integrated form of (8′) is

$$(k_2 - k_1)t = \frac{1}{(c - \xi)\ (c - \zeta)} \ln \frac{c - x_0}{c - x} + \frac{1}{(c - \xi)\ (\zeta - \xi)} \ln \frac{\xi - x_0}{\xi - x} + \frac{1}{(c - \zeta)\ (\xi - \zeta)} \ln \frac{\zeta - x_0}{\zeta - x} \tag{11}$$

When K is approximately unity, the following approximate equation corresponding to (7) is obtained

$$k_2 t = \frac{\xi}{cd(c - \xi)} \ln \frac{(\xi - x_0)\ (c - x)}{(c - x_0)\ (\xi - x)} \tag{12}$$

This is the exact solution of (8) when k_1 is equal to k_2 $(K = 1)$.

These equations were found to agree fairly well with the numerical values obtained in following the reactions in the dioxane solutions containing one mole of alcohol per liter. Since the agreement was not so satisfactory for the values obtained for the higher concentrations of alcohol, experiments were extended to include the pure alcohols as reaction media. Under these conditions the reactions were found to exhibit no catalysis by hydrogen chloride, and no reverse reaction was detected. The rate constants were calculated from the simple first order equation

$$kt = \ln \frac{b}{b - x} \tag{13}$$

DISCUSSION

A survey of the experimental data obtained is presented in the following tables. As above, the letters a, b, c and d denote the concentrations in moles per liter of the various components of the reaction mixtures: a alcohol, b chloroether, c hydrogen chloride and d formal. k_1 is the alcoholysis rate constant in $1^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$ and $K = k_1/k_2$ the equilibrium constant. k is the first order rate constant of the uncatalyzed reaction in pure alcohol, in min^{-1}.

The values of the equilibrium constant given in the tables reveal that the state of equilibrium is adequately defined by equations (4) and (9) in that experiments conducted with various initial concentrations give identical values of this constant. Worth notice in this respect is the fact that the same state of equilibrium is attained in both directions starting from ethyl chloromethyl ether and from ethylal, giving 1.22 for the average of the equilibrium constant for the former reaction and 1.28 for the latter in 1 M ethanol solution at 15° C (table 4). In 2 M alcohol solution the alcoholysis reaction proceeds almost to completion, due to which the values of the equilibrium constants of table 1 are relatively inaccurate *. This pertains particularly to the data for the reaction of methyl chloromethyl ether as the reverse reaction in 2 M solution is very slight. In these cases the error in the value of the equilibrium constant does not, however, noticeably affect the value of the alcoholysis rate constant when this is calculated from the equations given above. The equilibrium constant is, contrary to that observed in the esterification of carboxylic acids [8], very sensitive to changes in temperature, the temperature coefficients being much larger for the reverse reaction than for the alcoholysis. This is observed as a sometimes steep fall in the values of the equilibrium constant as the temperature is increased.

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* In comparing the values of the equilibrium constant it must be noted that the state of equilibrium is not so simple for those reactions in which the alkyl components of the chloroether and alcohol are different and the final equilibrium mixture may be composed of two chloroethers and three formals.

Table 1. Alcoholysis in 2 M ethanol in dioxane ($a = 2$). Rate constants calc. from (6) and (7).

$ROCH_2Cl$	t° C	b	c	K	k_1
CH_3OCH_2Cl	15	0.119	0.125	5.1	0.089
—»—	»	0.121	0.229	6.7	0.083
—»—	»	0.119	0.377	6.3	0.079
—»—	25	0.117	0.125	4.2	0.139
—»—	»	0.110	0.229	4.6	0.135
—»—	»	0.117	0.377	4.7	0.127
—»—	35	0.0473	0.125	2.7	0.216
—»—	»	0.127	0.125	3.5	0.209
—»—	»	0.105	0.229	3.3	0.202
—»—	»	0.0724	0.377	3.7	0.186
$C_2H_5OCH_2Cl$	15	0.099	0.0663	0.96	0.228
—»—	»	0.120	0.0663	1.05	0.219
—»—	»	0.156	0.114	1.04	0.226
—»—	»	0.163	0.244	0.98	0.207
—»—	25	0.135	0.114	0.71	0.365
—»—	»	0.101	0.133	0.73	0.357
—»—	35	0.153	0.114	0.46	0.576
—»—	»	0.121	0.114	0.42	0.543
—»—	»	0.096	0.311	0.50	0.527
n-$C_3H_7OCH_2Cl$	15	0.135	0.098	1.22	0.232
—»—	»	0.112	0.243	1.23	0.213
—»—	25	0.118	0.098	1.00	0.392
—»—	»	0.111	0.243	1.09	0.334
—»—	35	0.129	0.098	0.87	0.587
—»—	»	0.094	0.243	0.88	0.510
i-$C_3H_7OCH_2Cl$	15	0.111	0.0596	0.43	1.13
—»—	»	0.156	0.0596	0.46	1.03
—»—	25	0.109	0.0596	0.38	1.68
—»—	»	0.160	0.0596	0.42	1.56
—»—	35	0.101	0.0596	0.39	2.34
—»—	»	0.140	0.0596	0.38	2.21

Table 2. Alcoholysis in dioxane solutions containing different alcohols. The alcoholysis of methyl chloromethyl ether in 1 M solutions of alcohol in dioxane ($a = 1$) at 15° C. Constants calc. from (6) and (7).

ROH	b	c	K	k_1
CH_3OH	0.130	0.164	2.42	0.0375
C_2H_5OH	0.131	0.492	1.13	0.0296
$ClCH_2CH_2OH$	0.128	0.241	0.45	0.0047

Table 3. Alcoholysis in dioxane solutions containing different concentrations of ethyl alcohol. The alcoholysis of methyl chloromethyl ether at 15° C. Constants calc. from (6) and (7).

a	b	c	K	k_1
2	0.121	0.229	6.7	0.083
1	0.131	0.492	1.13	0.0296
1	0.184	0.607	1.17	0.0300
0.5	0.120	0.169	1.26	0.0154
0.25	0.191	0.219	0.94	0.0055
0.125	0.202	0.349	0.205	0.0014

Table 4. Equilibrium constant determination. A. The alcoholysis of ethyl chloromethyl ether in 1 M solutions of ethanol in dioxane at 15° C. ($a = 1$). Constants calc. from (6) and (7).

b	c	K	k_1
0.177	0.209	1.29	0.086
0.181	0.325	1.15	0.092
0.193	0.410	1.26	0.101
0.214	0.567	1.17	0.103

B. The reaction between ethylal and hydrogen chloride in 1 M solutions of ethanol in dioxane ($a = 1$). Constants calc. from (11) and (12).

t° C	d	c	K	k_1
15	0.166	0.144	1.33	0.100
»	0.193	0.210	1.32	0.114
»	0.204	0.255	1.30	0.105
»	0.197	0.410	1.27	0.107
»	0.192	0.567	1.17	0.119
25	0.213	0.431	1.08	0.166
35	0.212	0.431	0.96	0.257

The proportionality between the reaction rate and the hydrogen chloride concentration is not explicit and due to this the equations used in the calculations of the results obtained in the experiments in dioxane solutions containing higher concentrations of alcohol are only approximate. It may be seen from table 1 that the rate constants calculated from the results of experiments in 2 *M* alcohol solutions increase slightly with decreasing hydrogen chloride concentration; this is also evident in the results of the previous investigation [5]. This is paralleled by the increase in the values of the rate constants when the initial concentration of the chloroether is decreased. In 1 *M* solutions of alcohol the state of affairs is the opposite, the decrease in the rate of alcoholysis being less than the decrease in catalyst concentration, as shown by the data of table 4.

Table 5. Alcoholysis in pure alcohol. Equation (13).

Solvent	$ROCH_2Cl$	k_5	k_{15}	k_{25}	k_{35}	k_{15}/k_5	k_{25}/k_{15}	k_{35}/k_{25}
CH_3OH	CH_3OCH_2Cl	10.2	22.3			2.19		
—»—	$C_2H_5OCH_2Cl$	19.4						
C_2H_5OH	CH_3OCH_2Cl	1.53	3.86	9.0	19.7	2.52	2.33	2.19
—»—	$C_2H_5OCH_2Cl$	5.05	10.4			2.06		
$(CH_3)_2CHOH$	CH_3OCH_2Cl	0.520	1.29	3.08	6.88	2.48	2.39	2.23
—»—	$C_2H_5OCH_2Cl$		4.03					
$CH_3O(CH_2)_2OH$	CH_3OCH_2Cl		3.12	6.96			2.23	
—»—	$C_2H_5OCH_2Cl$	4.84	10.4			2.15		
$Cl(CH_2)_2OH$	CH_3OCH_2Cl	7.83	15.9			2.03		

The rate constants of the different chloroethers given in table 1 show the same sequence for the effect of structure on the velocity of reaction as that found in the acid catalyzed hydrolysis of dialkylformals [6b], namely, that the rate increases in the following order respecting the alkyl groups:

$$CH_3 \lesssim C_2H_5 < n\text{-}C_3H_7 < i\text{-}C_3H_7.$$

A remarkable fact is revealed by the small values of the temperature coefficients of the alcoholysis in dioxane solution, which vary from 1.4 to 1.7 and are of the same magnitude as those observed in the alcoholysis of acid chlorides in similar media [9].

Table 2 shows that the rates in dioxane containing the same concentration of various alcohols vary in the following order:

$$ClCH_2CH_2OH < C_2H_5OH \leq CH_3OH$$

This order is the same as that observed in other reactions of alcohols involving an electrophilic attack on oxygen [10]. The same order has been observed in the alcoholysis of acid chlorides in alcohol-dioxane solutions *.

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* Unpublished work carried out in this aboratory.

Table 3, giving the results of experiments in solutions containing various amounts of alcohol, shows that as the smaller alcohol concentrations are approached the rate continues to decrease steeply with no indication of attaining a limiting rate as is the case in the bimolecular alcoholysis of acid chlorides [9a].

In pure alcohol no catalysis by hydrogen chloride was detected up to concentrations of one mole per liter. Table 5 contains the first order rate constants of the alcoholysis in the various alcohols at four temperatures and the temperature coefficients calculated from them. The effect of the alkyl group shows the same order as that observed in the dioxane solutions. When the alcoholysis rates are high, as in methyl alcohol, the relative differences are smaller. The temperature coefficients are much higher for the reaction in the pure alcohols than in the dioxane solutions although the rates are of a much higher order of magnitude. The temperature coefficients of the more reactive ethyl chloromethyl ether are much smaller than those of the lower homolog, whereas in the dioxane solutions they are approximately the same. The rate of alcoholysis in 2-chloroethanol is considerably higher than in ethanol, which is the opposite of that observed in the dioxane solutions (table 2).

On the basis of these results, an approach to the mechanisms of the alcoholysis in the various media may be attempted. Although we are of the opinion that the alcoholysis and hydrolysis of 1-chloroethers in all probability follow a similar course, it is difficult to apply to the alcoholysis reaction in dioxane-alcohol solution the hydrion catalyzed mechanism proposed by Böhme [2c] for the hydrolysis in aqueous dioxane solution, as it would not lead to the production of formal. Böhme's mechanism does not conform with his views of the independence of the rate on the catalyst concentration since it requires that the rate be proportional to this concentration. The mechanism for the hydrolysis of 1-chloroethers given by Farren, Fife, Clark and Garland [2a] on the basis of their observations of the reverse reaction, the formation of 1-chloroethers, can neither be applied to the alcoholysis reaction as it would lead to alkyl exchange instead of the formation of the formal.

The results of our experiments in pure alcohol offer many points of comparison with those numerous kinetic investigations which deal with the reactions of certain organic halides [11]. It seems that some of the theoretical views based on the observations of these investigations may be advantageously considered in an effort to elucidate the mechanism of 1-chloroether alcoholysis. For the uncatalyzed reaction in pure alcohol the following two mechanisms are possible:

A. A nucleophilic attack of alcohol on carbon:

$$\begin{array}{ll} \mathrm{ROCH_2Cl} \longrightarrow \mathrm{ROCH_2OR} + \mathrm{HCl}\ \text{bimolecular.} & \text{(II)} \\ \nearrow & \\ \mathrm{ROH} & \end{array}$$

B. Ionization of chloroether promoted by solvolysis of the chloride ion by alcohol:

$$\mathrm{ROCH_2Cl} \longrightarrow \mathrm{ROCH_2^+} + \mathrm{Cl^-}\ \text{unimolecular,} \qquad \text{(III)}$$

followed by the fast reaction

$$\mathrm{ROCH_2^+} + \mathrm{ROH} \longrightarrow \mathrm{ROCH_2OR} + \mathrm{H^+}$$

The results of our investigation seem to favour the latter of these two mechanisms, which are identical with those designated by Ingold and Hughes[11a] as S_N2 and S_N1, although very little conclusive evidence can be adduced to allow a final decision. The bimolecular mechanism is not supported by the fact that the rate of alcoholysis in 2-chloroethanol is faster than in ethanol since previous work has confirmed that the reactivity of the former alcohol in electrophilic displacements on oxygen is much weaker than that of the latter. Explanations based on the dielectric constants of the solvents can neither be adduced to support the bimolecular mechanism in this case since the dielectric constants of both alcohols have approximately the same value. We may then consider the alcoholysis reaction as a unimolecular solvolysis (III). It has been observed in other reactions which are classified under this name that solvents having a great tendency to solvate halide ion bring about a marked increase in the rate of reaction[11], and, in addition, that certain metal halides, which favour the ionization of triphenylmethyl chloride[12] by their ability to form complex halides, also accelerate this type of reaction[13]. This is paralleled by our observations of the effect of the different alcohols on the rate of chloroether alcoholysis and, especially, by the effect of addition of mercuric chloride, the rate of alcoholysis in ethanol at 15°C increasing from 3.86 (table 5) to 10.6 on addition of this salt to give a concentration of 0.017 *M*. The S_N1-mechanism is also given support by the observation that comparatively small additions of sodium alcoholate do not materially increase the rate. With larger additions of alcoholate, however, the reaction was bimolecular, being proportional to both the concentration of the chloroether and that of the alcoholate *. Similar changes in mechanism from the S_N1 to S_N2 as the concentration of the more active nucleophilic reagent is in-

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* Experiments performed in ethanol solution containing 0.0733 moles per liter of sodium ethylate at 15°C gave with methyl chloromethyl ether a rate constant of 4.6 (3.86 in pure alcohol). With the larger additions the rate was too fast for accurate measurement but approximate results indicated the reaction to be bimolecular.

creased have been observed in the reactions of halogen acids[14]. The proposed unimolecular mechanism is in accord with the effect of the structure on the velocity. The change in electron releasing character of the group $ROCH_2$- when ethyl is introduced in place of methyl facilitates the ionization and causes an increase in velocity.

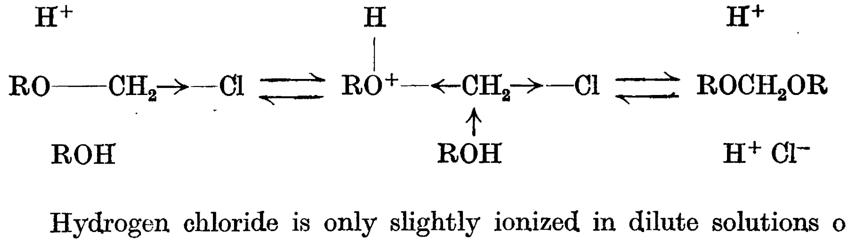
Ingold and Hughes[2b] have expressed the opinion that the S_N1-mechanism is a very plausible one for the hydrolysis of 1-chloroethers, but for obvious reasons it has not been possible to investigate the reaction in highly ionizing media. The mechanism is also in accord with the views of Cocker, Lapworth and Walton[1a].

The solvolysis by alcohol proposed above for the alcoholysis of chloroethers in pure alcohols may also be extended to alcohol-dioxane solutions, provided that the alcohol concentration is large. As this concentration decreases the part played by this reaction becomes negligible and the rate becomes very slow unless the solution contains hydrogen chloride. The acceleration effected by hydrogen chloride may also be of a solvolytic nature but there is an alternate possibility that a change in mechanism from S_N1 to S_N2 occurs as is the case in some reactions of alkyl chlorides as the ionizing power of the solvent decreases[11a]. The S_N2-mechanism as given by (II) is no longer valid, but if the reaction is formulated as following a mechanism analogous to that ascribed to the hydrolysis of acetals[15], the catalytic effect of the hydrogen chloride may be also accounted for.

For the hydrogen chloride catalyzed reaction in alcohol-dioxane solution, the following two mechanisms are thus left for consideration:

A A first order solvolysis by the undissociated hydrogen chloride, similar to (III).

B. A catalyzed reaction resembling the hydrolysis of acetals:



$$\underset{\mathrm{ROH}}{\overset{\mathrm{H^+}}{\mathrm{RO}}}\text{——}\mathrm{CH_2}{\rightarrow}\text{—}\mathrm{Cl} \rightleftharpoons \overset{\mathrm{H}}{\overset{|}{\mathrm{RO^+}}}\text{—}{\leftarrow}\underset{\underset{\mathrm{ROH}}{\uparrow}}{\mathrm{CH_2}}{\rightarrow}\text{—}\mathrm{Cl} \rightleftharpoons \underset{\mathrm{H^+\,Cl^-}}{\overset{\mathrm{H^+}}{\mathrm{ROCH_2OR}}} \qquad \text{(IV)}$$

Hydrogen chloride is only slightly ionized in dilute solutions of alcohols in dioxane[16] and undissociated hydrogen chloride has been found to induce the ionization of triphenylmethyl chloride and related compounds[17]. In pure alcohol solution hydrogen chloride is maintained to be fully ionized[18], which may account for the fact that it does not catalyze the alcoholysis reaction in this medium.

In the light of the solvolytic mechanism, it is easily understood that the effect of structure is the same in both the pure alcohol and the alcohol-dioxane solutions. This mechanism also conforms with the observations that the values of the rate constants continue to decrease as the molarity of the alcohol and the ionizing power of the solvent decreases. This mechanism is also able to account for the variations of the rate observed with varying hydrogen chloride and alcohol concentrations.

On the other hand, the solvolytic mechanism does not explain the slow rate of alcoholysis in 2-chloroethanol solution and the regularity shown by the equilibrium constants. These observations are, however, easily understood on the basis of mechanism (IV), which also accounts for the effect of structure on the rate. Here, as in acetal hydrolysis, the reaction is favored by increasing electron releasing character of the alkyl substituent. The gradual decrease in the rate as the alcohol concentration is decreased may also be explained according to this mechanism, but not the dependence of the rate on the concentration of hydrogen chloride when the proportion of alcohol in the solvent is varied. It should be noted, however, that these variations are very slight and may also be due to other complications [11b].

In view of these considerations it is quite possible that in the alcohol-dioxane solutions both the unimolecular solvolysis by undissociated hydrogen chloride and the solvated hydrion catalyzed reaction proceed concurrently, but it is not possible to bring forth at present quantitative, conclusive evidence in this respect.

EXPERIMENTAL

Materials. The 1-chloroethers were prepared according to Karvonen [19] and Farren, Fife, Clark and Garland [2a]. The boiling points were:

Methyl chloromethyl ether, b. p.$_{762}$59.0 — 59.6°;
Ethyl chloromethyl ether, b. p.$_{765}$82.4°;
Propyl chloromethyl ether, b. p.$_{752}$108.5 — 109.0°;
Isopropyl chloromethyl ether, b. p.$_{764}$96.8 — 97.6°.

Diethyl formal was obtained by Ghysels' [20] method. Its boiling point was 84 — 85° at 763 mm. pressure.

Methyl, ethyl and isopropyl alcohols were pure technical products and were purified with magnesium according to the methods described by Bjerrum and Zechmeister [21] and Lund and Bjerrum [22]. The 2-methoxyethanol and 2-chloroethanol were technical products and were purified by fractionation. The boiling points were:

2-Methoxyethanol, b. p.$_{762}$124.5°;
2-Chloroethanol, b. p.$_{760}$128.5°.

1,4-Dioxane of technical grade was purified by the method previously used [23,9].

Kinetic Measurements. The reactions were carried out in glass-stoppered flasks, from which samples were transferred with a five ml. automatic pipette into an erlenmeyer flask containing sodium hydroxide solution. The liberated formaldehyde was titrated as described earlier [6].

In the experiments with dioxane solutions, dry hydrogen chloride was led into the solvent and its concentration was determined by titration with standard sodium hydroxide solution.

The rate constants were calculated from equations (6), (7), (11), (12) and (13) with time in minutes and concentrations in moles per liter. In the calculations 4-figure logarithms were used.

Zero time was the time of taking of the first sample. In the alcoholysis determinations carried out in dioxane solutions the amount of chloroether x_0 reacted at zero time was determined by extrapolation, the time between the addition of chloroether and zero time being known. In the fast reactions the initial sample was taken as soon as possible, while in the slower reactions it was taken after the reaction had proceeded for some time. The difference between the iodine consumption corresponding to the bisulphite solution added and the end value gave $b—\xi$.

In the reaction between ethylal and hydrogen chloride it was not necessary to determine x_0 by extrapolation but it was calculated from the difference between the amount of iodine solution corresponding to the added amount of sodium bisulphite and the initial value. The initial formal concentration d was determined by hydrolysing samples taken from the reaction mixture with approximately 2 M hydrochloric acid and titrating the liberated formaldehyde in the usual manner.

The procedure used in the fast reactions is the same as that used in the determination of the rates of alkaline hydrolysis of formic esters [24].

In the following are given examples of the rate determinations. The significance of the letters is the same as above. Time t' is in minutes, t'' in seconds; the rate constants have been calculated with time in minutes.

I. Alcoholysis in 2 *M* ethanol in dioxane ($a = 2$)

1. *Methyl chloromethyl ether*

15° C

$b = 0.1190,\ c = 0.1250,\ \xi = 0.1160\ (= 11.85\ *).\ K = 5.1$

t'	0	10	20	30	40	50	60	80
$\xi - x$ *	11.57	8.79	6.50	4.93	3.34	2.20	1.69	0.87
$c + x$ *	13.05	15.83	18.12	19.69	21.28	22.42	22.93	23.75
k_1		0.095	93	87	89	91	86	83 av. 0.089

25° C

$b = 0.1171,\ c = 0.1250,\ \xi = 0.1137\ (= 11.61).\ K = 4.2$

t'	0	6	12	18	24	30	37	45
$\xi - x$	11.22	8.84	6.65	4.98	3.59	2.51	1.54	1.04
$c + x$	13.16	15.54	17.73	19.40	20.79	21.87	22.84	23.34
k_1		0.138	141	138	138	139	143	137 av. 0.139

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* Expressed in ml of standard iodine solution.

35° C

$b = 0.1265$, $c = 0.1250$, $\xi = 0.1219$ ($= 12.45$). $K = 3.5$

t'	0	3	7	11	14	19	23	27	
$\xi - x$	11.75	9.65	7.32	5.34	4.28	2.60	2.12	1.38	
$c + x$	13.47	15.57	17.90	19.88	20.94	22.62	23.10	23.84	
k_1		0.224	214	212	206	213	196	201	av. 0.209

2. *Ethyl chloromethyl ether*

15° C

$b = 0.1560$, $c = 0.1135$, $\xi = 0.1380$ ($= 14.64$). $K = 1.04$

t'	0	1.75	3.5	5.0	6.5	8.0	9.5	11.5	13.0	15.0	17.0	
$\xi - x$	13.14	11.72	10.22	8.87	7.95	6.66	5.62	4.92	4.12	3.53	2.83	
$c + x$	13.54	14.96	16.46	17.81	18.73	20.02	21.06	21.76	22.56	23.15	23.85	
k_1		0.215	224	235	224	235	239	222	226	217	217	av. 0.226

II. Alcoholysis in dioxane solutions of different alcohols

The alcoholysis of methyl chloromethyl ether in 1 *M* solutions of alcohol in dioxane ($a = 1$) at 15° C.

Methyl alcohol

$b = 0.1303$, $c = 0.1636$, $\xi = 0.1153$ ($= 12.69$). $K = 2.42$

t'	0	15	30	46	60	75	90	105	120	135	150	
$\xi - x$	12.61	11.38	9.99	8.71	7.87	6.94	6.03	5.28	4.68	4.12	3.53	
$c + x$	18.09	19.32	20.71	21.99	22.83	23.76	24.67	25.42	26.02	26.58	27.17	
k_1		0.0360	394	396	379	375	378	375	367	363	366	av. 0.0375

Ethyl alcohol

$b = 0.1306$, $c = 0.4918$, $\xi = 0.0839$ ($= 9.23$). $K = 1.13$

t'	0	5	15	20	25	35	45	
$\xi - x$	9.00	8.01	6.21	5.57	5.03	4.01	3.21	
$c + x$	54.37	55.36	57.16	57.80	58.34	59.36	60.16	
k_1		0.0300	313	302	291	286	281	av. 0.0296

III. Alcoholysis in dioxane solutions containing different concentrations of ethyl alcohol

The alcoholysis of methyl chloromethyl ether at 15° C

$a = 0.5$, $b = 0.1202$, $c = 0.1694$, $\xi = 0.0815$ ($= 8.97$). $K = 1.26$

t'	0	30	60	90	148	206	268	356	459	588	
$\xi - x$	8.97	8.47	7.93	7.42	6.57	5.75	5.17	4.24	3.36	2.53	
$c + x$	18.65	19.15	19.69	20.20	21.05	21.87	22.45	23.38	24.26	25.09	
k_1		0.0152	160	163	159	159	149	149	148	145	av. 0.0154

IV. Equilibrium constant determination

A. The alcoholysis of ethyl chloromethyl ether in 1 M solutions of ethanol in dioxane at 15° C ($a = 1$).

$b = 0.1805$, $c = 0.3246$, $\xi = 0.1247$ ($= 14.22$). $K = 1.15$

t'	0	7	12	18	24	30	38	45	
$\xi - x$	11.63	8.40	6.35	4.68	3.31	2.40	1.59	1.04	
$c + x$	39.59	42.82	44.87	46.54	47.91	48.82	49.63	50.18	
k_1		0.089	94	92	93	92	90	91	av. 0.092

B. The reaction between ethylal and hydrogen chloride in 1 M solution of ethanol in dioxane at 15° C ($a = 1$).

$d = 0.2044$, $c = 0.2547$, $\xi = 0.02938$ ($=3.35$). $K = 1.30$

t'	0	12	18	24	30	
$\xi - x$	2.94	1.94	1.56	1.26	1.01	
$c - x$	28.62	27.62	27.24	26.94	26.69	
k_2		0.079	81	82	83	av. 0.081

$d = 0.1969$, $c = 0.4101$, $\xi = 0.0481$ ($= 4.88$). $K = 1.27$

t'	0	10	15	20	25	30	35.5	
$\xi - x$	4.24	2.27	1.70	1.22	0.92	0.70	0.44	
$c - x$	46.11	44.14	43.57	43.09	42.79	42.57	42.31	
k_2		0.084	82	85	84	82	88	av. 0.084

V. Alcoholysis in pure alcohol

1. *Alcoholysis in methyl alcohol*

Methyl chloromethyl ether

5° C

0.0833 N iodine as standard solution.

t''	0	3.3	6.3	9.5	12.8	16.5	
$b - x$	4.77	2.70	1.62	0.98	0.54	0.35	
k		10.3	10.3	10.0	10.2	9.5	av. 10.1 Parallel values: 10.1, 10.1 and 10.3

15° C

0.0833 N iodine.

t''	0	3.7	7.0	
$b - x$	1.39	0.36	0.11	
k		21.9	21.7	av. 21.8 Parallel values: 23.1, 21.6, 21.7, 23.1 and 22.7

2. *Alcoholysis in ethyl alcohol*

Methyl chloromethyl ether

5° C

0.0862 *N* iodine.

t''	0	6.7	13.2	21.8	32.8	54.9	80.5	
$b - x$	6.97	5.84	4.97	3.99	2.99	1.79	0.90	
k		1.58	1.54	1.54	1.55	1.49	1.53	av. 1.54 Parallel values: 1.53, 1.49 and 1.54

15° C

0.0829 *N* iodine.

t''	0	4.4	8.9	14.4	20.5	26.5	33.3	43.1	
$b - x$	6.95	5.48	3.91	2.90	1.92	1.38	0.86	0.41	
k		(3.24)	3.88	3.64	3.77	3.66	3.77	3.94	av. 3.78 Parallel values: 3.83, 3.92, 3.90, 3.87, 3.88, 3.93, 3.85 and 3.75

25° C

0.0833 *N* iodine.

t''	0	3.0	6.1	9.6	13.3	17.8	
$b - x$	6.73	4.42	2.72	1.62	0.98	0.50	
k		(8.4)	8.9	8.9	8.7	8.8	av. 8.8 Duplicate value: 9.2

35° C

0.0833 *N* iodine.

t''	0	2.8	5.7	
$b - x$	5.48	2.15	0.84	
k		20.1	19.7	av. 19.9 Duplicate value: 19.4

3. *Alcoholysis with mercuric chloride as catalyst*

The alcoholysis of methyl chloromethyl ether in ethyl alcohol solution containing 0.0170 moles/l mercuric chloride.

15° C

0.0862 *N* iodine.

t''	0	3.5	6.4	9.6	13.2	17.8	
$b - x$	5.54	2.95	1.71	0.96	0.63	0.27	
k		10.8	11.0	11.0	9.9	10.2	av. 10.6

SUMMARY

1. The rates of alcoholysis of several 1-chloroethers $ROCH_2Cl$ (R = methyl, ethyl, propyl and isopropyl) have been measured in alcohol and alcohol-dioxane solutions.

2. In pure alcohol the alcoholysis is rapid and follows the first order law.

3. In dilute solutions of alcohol in dioxane the reaction is reversible, slow and catalyzed by the hydrogen chloride formed. The rate of the alcoholysis is approximately directly proportional to the hydrogen chloride concentration. The reverse reaction is catalyzed by hydrogen chloride and the rate is proportional to the square of the hydrogen chloride concentration.

4. The rates of reaction of the 1-chloroethers in all the media investigated vary with the alkyl component R in the following order: methyl $<$ ethyl $<$ propyl $<$ isopropyl.

5. In dioxane solutions of the different alcohols the rate decreases in the following order: methanol $>$ ethanol $>$ 2-chloroethanol. In the pure alcohols the order is: methanol $>$ 2-chloroethanol $>$ ethanol.

6. The activation energy of the reaction in dioxane solution is much smaller than that of the reaction in pure alcohol.

7. The results obtained indicate that the reaction in pure alcohol is a unimolecular solvolysis. In dilute solutions of alcohols in dioxane in which the reaction is catalyzed by hydrogen chloride the reaction is considered to follow, at least partly, a bimolecular mechanism.

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