

## The Kinetics of the Acid-Catalysed Solvolysis of Ethylal in Water-Ethanol Mixtures

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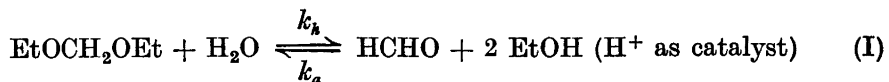
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The kinetics of the reversible, acid-catalysed hydrolysis of ethylal have been investigated in water-ethanol mixtures. By the stationary state principle, it has been shown that the results are in accord with a unimolecular solvolysis mechanism. The velocity of the overall solvolysis of ethylal can be measured by a refined kinetic method which makes use of determining the relative rates of the fast, product-forming hydrolysis and alcoholysis reactions of the unstable ethoxy-methyl cation which is formed in the rate-determining, unimolecular reaction stage. The solvolysis rate constants are found to be closely related to the Hammett acidity function of the reaction solution, in accord with the unimolecular mechanism suggested.

The dependence of the solvolysis rate on the acidity function and on the dielectric properties of the medium have been discussed. By electrostatic theories on solvent influence on relative base strengths, an equation has been derived for the effect of medium on the velocity of a unimolecular, acid-catalysed reaction.

In several recent publications<sup>1-4</sup> evidence has been furnished to support the assumption that the hydrolysis of acetals takes place by a unimolecular mechanism, which in the rate-determining stage of reaction involves a formation of a positively charged carbonium ion from the conjugate acid of the acetal. In two cases, in the hydrolysis reactions of methylal<sup>3</sup> and trioxan<sup>4</sup> in concentrated aqueous acids, Hammett's acidity function was applied as a criterion of molecularity of the rate-determining reaction step.

In connection with the earlier study on the mechanisms of solvolytic reactions of ethoxymethyl acetate<sup>5</sup>, the author also determined the rate constants for the reversible hydrolysis of ethylal



in a number of water-ethanol mixtures. As the main applications hitherto made of the Hammett acidity function are to hydrolysis reactions in concentrated acids, it seemed of interest to study whether the general theory could also

be applied to the solvolysis of ethylal by dilute acid solutions, if the solvent is varied. In the present work, the earlier data on the reaction of ethylal have been extended by complementary experimental measurements, which were necessary for the kinetic applications.

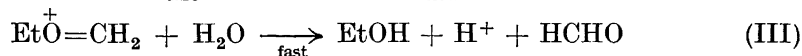
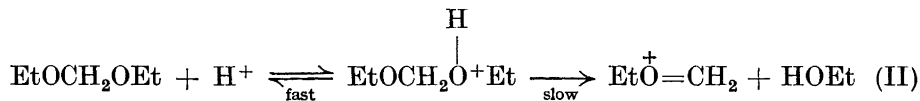
### RESULTS AND THEORY

Table I contains the values of the first-order rate constants  $k_h$ , determined for the hydrolysis of ethylal in water and in various water-ethanol mixtures at 25°C at 0.1 N hydrogen chloride concentration. The table also includes the values of the Hammett acidity function  $H_0$  for the reaction solutions employed. These have been obtained by interpolation from the data given by Braude and Stern<sup>6</sup>. It is seen from the table that the values of  $k_h$  decrease continuously with increasing alcohol content of the solvent, whereas the values of  $H_0$  pass through a maximum, *i. e.* the proton-availability of the solutions reaches a minimum, in solutions containing 50—70 moles per cent of ethanol. According to the theory (*cf.* Ref.<sup>7</sup>), the velocity of a mechanistically unimolecular, acid-catalysed solvolysis reaction should depend primarily on the acidity function of the reaction solution. As shown below, the requirements of the theory are satisfactorily fulfilled here, in spite of the continuously decreasing values of  $k_h$  with increasing alcohol content, depending on the fact that the values of  $k_h$  do not directly measure the velocity of a solvolysis reaction, which is assumed to be unimolecular.

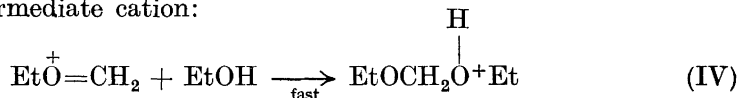
*Table I.* The solvolysis of ethylal in ethanol-water mixtures at 25°C at 0.1 N hydrogen chloride concentration.  $k_h$  = the first-order rate constant (in sec.<sup>-1</sup>) for the formation of formaldehyde from ethylal.  $r$  = the molar ratio of formaldehyde and ethylal formed by the solvolysis of ethoxymethyl chloride.  $k_1$  = the first-order rate constant (in sec.<sup>-1</sup>) calculated for the overall solvolysis reaction of ethylal.

Mols. % EtOH	$H_0$	$10^6 \cdot k_h$	$r$	$10^6 \cdot k_1$
0	+ 1.01	16.4	$\infty$	16.4
7.5	+ 1.20	10.3	89.0	10.4
18.2	+ 1.69	4.21	32.9	4.34
26.6	+ 1.91	2.64	20.6	2.77
34.9	+ 2.07	1.32	1.430	2.24
43.8	+ 2.19	0.861	1.008	1.72
51.2	+ 2.23	0.700	0.766	1.61
60.9	+ 2.24	0.590	0.534	1.69
69.3	+ 2.23	0.550	0.394	1.95
78.1	+ 2.16	0.539	0.280	2.46

For the sake of simplicity, let us neglect the reverse reaction, the acetalisation of formaldehyde, because this reaction does not affect the values of  $k_h$  (quite similar considerations apply to the case, in which the reverse reaction is taken into account). The unimolecular mechanism of acetal hydrolysis<sup>2</sup>, as particularised to the hydrolysis of ethylal, is the following:



The intermediate, unstable cation which is formed in the slow, rate-determining stage has a mesomeric structure, which is a hybridised form of the carbonium ion and oxonium ion structures. Supposing that the rate measurements are made at a fixed acid concentration, and denoting by  $1/K$  the ratio of the concentration of ethylal to its conjugate acid at this acid concentration, and by  $k$  the rate constant of the unimolecular rate-determining reaction stage, respectively, it is found that the product  $kK = k_1$  represents the experimental first-order rate constant of the reaction taking place at the acid concentration in question. Supposing that the reaction occurs in water, the value of  $k_1$  is identical with the value of  $k_h$ , because only minute quantities of ethanol, formed by the hydrolysis, are present, and therefore practically all of the mesomeric cations, once having been formed, react with water molecules to give formaldehyde. Such a situation does not prevail in solvents of a moderate ethanol content. In these solvents, reaction (IV) which is the reversal of the rate-determining reaction stage competes significantly with reaction (III) for the unstable, intermediate cation:



The relative contribution of this competing reaction increases with the alcohol content of the solvent, and thus the values of  $k_h$  which measure the rate of formaldehyde formation no longer represent the rate constants of the overall solvolysis reaction,  $k_1$ , which depend partly on the velocity of the rate-determining stage, partly on the pre-equilibrium of the proton uptake. In solutions containing ethanol, the other of the two rapid, product-forming reactions remains obscure, because it leads back to the initial reactant, ethylal. However, in this particular case, the relative contributions of the product-forming reactions are adapted to permit of measurements, and the values of  $k_1$  can be determined, as shown below.

In view that both the substituting agents, water and alcohol, are the main constituents of the reaction solutions, the reactions of ethoxymethyl cation with water and alcohol molecules can be considered as first-order reactions, irrespective of their actual molecularities. Let  $k_{\text{H}_2\text{O}}$  and  $k_{\text{EtOH}}$  denote the first-order rate constants for these reactions, respectively. By the stationary state principle, it is found that

$$\frac{d[\text{Et}\overset{\oplus}{\text{O}}=\text{CH}_2]}{dt} = k_1[\text{EtOCH}_2\text{OEt}] - (k_{\text{H}_2\text{O}} + k_{\text{EtOH}})[\text{Et}\overset{\oplus}{\text{O}}=\text{CH}_2] = 0 \quad (1)$$

From eqn. (1) it follows that the rate of formaldehyde formation is given by

$$\frac{d[\text{HCHO}]}{dt} = k_{\text{H}_2\text{O}}[\text{Et}\overset{\oplus}{\text{O}}=\text{CH}_2] = \frac{rk_1}{1+r}[\text{EtOCH}_2\text{OEt}] \quad (2)$$

in which the relative rates of the hydrolysis and alcoholysis reactions of the intermediate cation have been denoted by  $r$ :

$$r = k_{\text{H}_2\text{O}} / k_{\text{EtOH}} \quad (3)$$

On the other hand, the rate of formation of formaldehyde is given by

$$\frac{d[\text{HCHO}]}{dt} = k_h[\text{EtOCH}_2\text{OEt}] \quad (4)$$

in which  $k_h$  is the experimental rate constant for the hydrolysis reaction (I). A comparison of eqns. (2) and (4) shows that

$$k_1 = \frac{1+r}{r} k_h \quad (5)$$

Eqn. (5), derived above, is consistent with the typical kinetic form of a unimolecular nucleophilic substitution <sup>8</sup>.

From eqn. (5) it follows that, once we know the ratio of the rates of the rapid, product-forming reactions of the intermediate cation, the values of  $k_1$  for the overall solvolysis reaction can be readily calculated from the values of  $k_h$ . In the present case, the values of  $r$  can be easily determined from the solvolysis products of ethoxymethyl chloride,  $\text{EtOCH}_2\text{Cl}$ , in the same media <sup>5, 9, 10</sup>. As the product-forming reactions involved in the unimolecular solvolysis of this compound are identical with those of the unimolecular mechanism suggested for the solvolysis of ethylal, the relative amounts of formaldehyde and ethylal formed by the solvolysis of ethoxymethyl chloride directly measure the values of  $r$  which can be also applied to the solvolysis of ethylal under the same conditions. Table 1 includes the values thus determined for  $r$  which have been taken partly from the data given in connection with the solvolysis of ethoxymethyl acetate <sup>5</sup>, partly from the results of complementary measurements. Table 1 also gives the values calculated for  $k_1$  by eqn. (5). It is seen from the table that the rate constants of the overall solvolysis reaction are closely related to the acidity function of the reaction solution, and pass through a minimum at approximately the same alcohol contents of the solvent, at which the proton-donating power of the acid solutions is least pronounced. This is in excellent agreement with the unimolecular mechanism suggested.

As the present method allowed the determination of the rate constants  $k_1$  in alcohol-water mixtures of relatively widely varying values of the acidity function, thus differing from measurements on the solvolysis of alkoxymethyl esters <sup>5, 9</sup>, the dependence of  $\log k_1$  on the acidity function may be discussed in more detail. The theory in its original form suggests that a plot of  $\log k_1$  against  $-H_0$  should give a straight line with a slope of unity (for references, see Ref. 7). This relation has been found to be satisfactorily obeyed by several unimolecular hydrolysis reactions in concentrated aqueous acids. Table 2 which gives the values of  $\log k_1 + H_0$  for the solvolysis of ethylal in water-ethanol mixtures shows that the values increase with the alcohol content of the solvent. When the values of  $\log k_1$  are plotted against  $-H_0$ , it is found that the slope is somewhat less than unity, and decreases slightly, when passing to solutions of higher ethanol content. As shown below, these deviations

Table 2. The dependence of  $\log k_1$  on the acidity function and on the dielectric constant of the medium in the solvolysis of ethylal in water-ethanol mixtures at 25° C at 0.1 N hydrogen chloride concentration.

Mols. % EtOH	$D$	$\log k_1 + H_0$	$\log k_1 + H_0 - \frac{14.8}{D}$
0	78.5	- 3.78	- 3.97
7.5	68.6	- 3.78	- 4.00
18.2	57.3	- 3.67	- 3.93
26.6	50.0	- 3.65	- 3.95
34.9	44.5	- 3.58	- 3.91
43.8	39.8	- 3.57	- 3.94
51.2	36.5	- 3.56	- 3.97
60.9	32.8	- 3.53	- 3.98
69.3	30.5	- 3.48	- 3.97
78.1	28.0	- 3.45	- 3.98

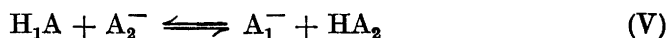
from the slope of unity can be interpreted in terms of changes in the relation between the solvolysis rate and the acidity function, which may be expected to occur, when passing from water to solvents of lower dielectric constants.

Supposing the reaction mechanism to be unimolecular, the dependence of  $\log k_1$  on the acidity function is given by the equation:

$$\log k_1 = \text{constant} - H_0 + \log \frac{f_S f_{IH^+}}{f_X + f_I} \quad (6)$$

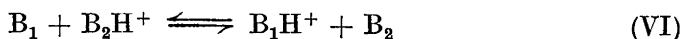
which is derived from the definition of  $H_0$  by the Brönsted rate equation. In this equation,  $f$ 's are the respective activity coefficients of the substrate S, the critical complex  $X^+$ , and the uncharged indicator base I and its conjugate acid  $IH^+$ , which have been used for the colorimetric determination of the values of  $H_0$ . As the critical complex contains only a proton, in addition to the substrate molecule, its activity coefficient is similarly affected by changes in medium as that of the conjugate acid of the substrate. Therefore, a slope of unity in the plot of  $\log k_1$  against  $-H_0$  implies merely that the activity coefficient ratios of different bases to their conjugate acids are influenced by medium in a similar way, *i. e.* the relative base strengths of the different bases remain unchanged. However, such a relation is not to be expected to be valid when passing from water to solvents of lower dielectric constants.

Minnick and Kilpatrick<sup>11</sup> measured the relative acid strengths of a number of organic acids in water, methanol, ethanol and in water-dioxan mixtures, by determining the equilibrium constants for reactions:



Here,  $HA_1$  and  $HA_2$  are the acids, and  $A_1^-$  and  $A_2^-$  their anions, respectively. It was found that the values of the logarithms of the equilibrium constants were in all cases satisfactorily represented by functions of the form:  $a + b/D$ ;  $a$  and  $b$  are constants for a given pair of acids, and  $D$  denotes the dielectric constant of the medium. This form of relation between the equilibrium constant and the dielectric constant is that expected by electrostatics (*cf.* Ref.<sup>12</sup>).

In this particular case, the success of the electrostatic theory, which has been found to fail for many other applications to solvent effects, is presumably due to the circumstance that the influence of solvent effects other than electrostatic becomes effectively masked, when changes of relative acid strengths are measured. As the electrostatic relation holds for reactions of type (V), it can be assumed that a similar relationship is valid for equilibria



which measure the relative strengths of a pair of uncharged bases,  $B_1$  and  $B_2$ . It may be written

$$\log \frac{[B_1H^+][B_2]}{[B_1][B_2H^+]} = a + \frac{b}{D} \quad (7)$$

in which  $a$  and  $b$  are constants. Taking into account that

$$\frac{[B_1H^+][B_2]}{[B_1][B_2H^+]} = \frac{f_{B_1}f_{B_2H^+}}{f_{B_1H^+}f_{B_2}} K_0 \quad (8)$$

in which  $K_0$  is the thermodynamic equilibrium constant, and  $f$ 's are the activity coefficients, eqn. (7) implies that

$$\log \frac{f_{B_1}f_{B_2H^+}}{f_{B_1H^+}f_{B_2}} = a' + \frac{b}{D} \quad (9)$$

in which  $a'$  is a constant, which is obtained by subtracting  $\log K_0$  from  $a$ . Let  $B_2$  denote the indicator base, which is used for the determination of the values of  $H_0$ , and let  $B_1$  mean the basic substrate, which is undergoing an acid-catalysed, unimolecular solvolysis reaction the critical complex of which resembles closely the conjugate acid of the substrate. From eqns. (6) and (9), it then follows that

$$\log k_1 = \text{constant} - H_0 + \frac{b}{D} \quad (10)$$

which equation represents the dependence of the velocity of the unimolecular reaction on the acidity function and on the dielectric constant of the reaction solution.

Table 2 contains the values of the dielectric constants for the water-ethanol mixtures employed. These values have been interpolated from the data of Åkerlöf<sup>13</sup>. A plot of  $\log k_1 + H_0$  against  $1/D$  for the solvolysis of ethylal in ethanol-water mixtures is found to give, within the limits of experimental accuracy, a straight line with a slope of 14.8. From the last column of Table 2, it is seen that the deviations from eqn. (10) are not larger than those, which may be ascribed to the sum of experimental errors involved in the determination of the values of  $\log k_1$  and  $H_0$ .

The electrostatic theory suggests that the value of  $b$ , 14.8, found for ethylal solvolysis should be roughly of a similar order of magnitude as the values obtained by Minnick and Kilpatrick<sup>11</sup>, when comparing the relative acid strengths of organic acids. Actually, the corresponding slopes measured for

different acid pairs varied between 5.5 and 21.0, when their signs were not taken into account. Moreover, the positive sign of  $b$  which indicates that the activity coefficient ratio of eqn. (6) decreases with increasing dielectric constant of the medium is not unexpected here. As the changes of activity coefficients of charged species with the dielectric constant are generally more significant than those of uncharged species, the decrease of the value of the activity coefficient ratio of eqn. (6) with increasing dielectric constant may be ascribed as being primarily due to a decrease in the value of  $f_{\text{IH}^+} / f_{\text{X}^+}$ . Here,  $\text{IH}^+$  is the conjugate acid of *p*-nitroaniline or *m*-nitroaniline, which were used by Braude and Stern<sup>6</sup> for the determination of the values of  $H_0$ . These protonated bases have probably a more intensive charge distribution than that in the critical complex of the solvolysis of ethylal. According to eqn. (II), the rate-determining stage of the ethylal solvolysis involves a relatively large dispersal of charge. On the attainment of the transition state, the positive charge is being partly removed from the oxygen atom to a nascent mesomeric system, in which the charge is shared between a carbon atom and another oxygen atom. In addition, that carbon-oxygen bond which is broken in the rate-determining reaction step, is lengthened. In view of the less intensive electrical field around the critical complex of the ethylal solvolysis, in comparison to the fields of the conjugate acids of the nitroanilines, the activity coefficient of the critical complex is less reduced by increases in the dielectric constant of medium, as a result of which the value of  $f_{\text{IH}^+} / f_{\text{X}^+}$  decreases, when passing over to solvents of higher water content.

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