

KINETICS OF HYDROLYSIS OF ESTERS Part I.

MOHAMMAD ZAHEERUDDIN AND H. A. KAZMI

Department of Chemistry, University of Peshawar, Peshawar

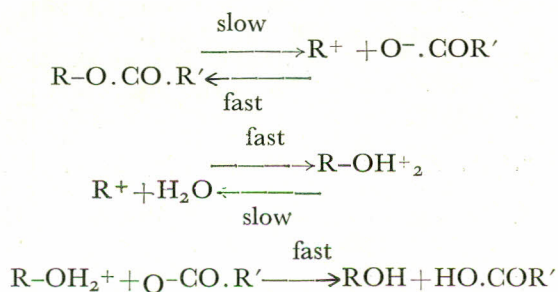
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The neutral hydrolysis of methyl and ethyl formate was studied and the reaction was found to follow first order kinetics.

It is shown that the non-exponential factor of the Arrhenius equation as well as the activation energy decreases upon passing from methyl to ethyl formate.

Introduction

It is fairly well established that the hydrolysis of esters in neutral medium follows a mechanism involving a Unimolecular alkyl fission.¹ The mechanism may be formulated as follows:



It is actually, apart from the final proton transfer, a typical unimolecular nucleophilic substitution. The alkyl-oxygen fission has been established by the usual methods: if the α -carbon atom of R is asymmetric, an optically active ester gives a racemised alcohol owing to the liberation of cationic form R^+ during the reaction;² considering the polar effects on rate, electropositive, especially +E, groups, if suitably situated in R accelerate the reaction, and so also do the electronegative groups if suitably located in R'.³ The kinetics of conversion of triphenyl methyl benzoate in a solvent of mixed ethyl alcohol and methyl ethyl ketone has been studied by Hammond and Rudesill⁴ and they have confirmed its first order rate. Graham, Hughes and Quayle,¹ similarly, have studied the hydrolysis of tert. butyl 2:4:6 triphenyl benzoate and have found the hydrolysis to be faster and obeying first order kinetics. The alkyl-oxygen fission in this reaction has also been proved by ^{18}O method.

In 1934, A. Kirmann⁵ studied the hydrolysis of allyl pyruvate in neutral medium and put forward the view that the hydrolysis in neutral medium is a unimolecular spontaneous reaction on which is superimposed an autocatalytic reaction due to the liberation of hydrogen ions. Following A. Kirmann's suggestion the rate of hydrolysis of an

ester in the initially neutral medium may be expressed as

$$dx/dt = k_0(a-x) + k_1(a-x)C_{\text{H}^+} \dots (i)$$

where k_0 and k_1 are the rate constants of unimolecular spontaneous hydrolysis and acid hydrolysis respectively, 'a' is the initial concentration of the ester, x is the concentration of the acid produced at any time, t, and C_{H^+} is the concentration of the hydrogen ions produced as a result of the dissociation of the weak acid. Thus the rate of hydrolysis of an ester is supposed to be made of two parts: $k_0(a-x)$, accounting for the unimolecular spontaneous reaction in the initial stages and $k_1(a-x)C_{\text{H}^+}$, accounting for the superimposed autocatalytic reaction, virtually eclipsing the contribution by the spontaneous unimolecular hydrolysis, in the later stages.

The present work was undertaken to study the kinetics of hydrolysis of simple esters like methyl and ethyl formates in neutral medium and to test the validity of the idea of Kirmann. Methyl and ethyl formates have been selected for study because their rates of hydrolysis in neutral medium are neither too slow like that of methyl acetate nor too fast like that of tert. butyl 2:4:6 triphenyl benzoate.

Experimental

To ensure the purity of esters, they were prepared in this laboratory fresh before every set of experiments. The method suggested by A. I. Vogel⁶ was employed for the preparation of esters.

Conductivity water was used in all the experiments for preparing solutions of esters.

The hydrolysis of esters was studied in an apparatus which was designed and assembled for the purpose, is shown in Fig. 1. The idea was borrowed from E. A. Moelwyn-Hughes.⁷ The objective was to avoid the loss of volatile reactant and to exclude the vapour phase entirely. The bulb B, 500 ml., is immersed in the thermostat, except for the capillary delivery tube C from which the samples of the reaction mixture are delivered at requisite times into the conical flask F contain-

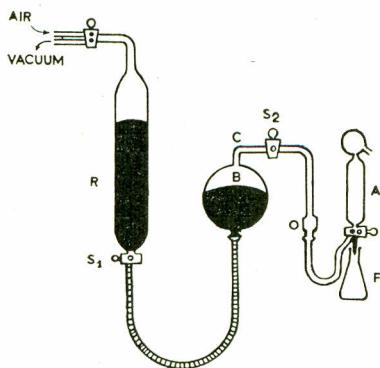


Fig. 1.—Apparatus for hydrolysis.

ing crushed ice to chill the reaction. The samples are automatically measured by means of an automatic pipette, A, before being delivered in the conical flask. Before the experiment is started, the whole apparatus is filled with clean mercury by applying suction. The mercury level in the reservoir, R, is then further raised in order to suck the solution of ester in bulb, B, from the opening, O, which is temporarily created by removing the automatic pipette. The stopcock, S₁, is then closed and the vacuum in the reservoir R is released. By manipulating the stopcock S₁, samples of the reaction mixture (volume 25 ml.) can be delivered in the conical flask at the requisite times. The reaction was followed by titrating the chilled samples of the reaction mixture with N/40 sodium hydroxide solution using phenolphthalein as the indicator. The concentration of the esters in the solution varied from 0.1 to 0.9M. The temperature range for the methyl formate was from 23.77°C. to 43.80°C. and for ethyl formate, it was from 20.18°C. to 58.57°C. The temperatures were measured with the help of a Beckmann thermometer.

The temperature of the thermostat could be maintained constant within $\pm 0.01^\circ\text{C}$. A "Colora" ultra thermostat manufactured by Papst, Germany was used.

Calculations and Results

Equation (i) cannot be integrated easily because $C_{\text{H}^+} = x\alpha$ where α is the degree of dissociation of the weak acid and it is a function of x . However, another method has been used by the present authors to find out the values of k_0 .

The hydrolysis of esters was followed over a period of six to seven hours and the number of g. moles of formic acid produced was plotted against time, t . The rate of reaction, dx/dt , was calculated

from the slopes drawn at various values of t in the initial stages and the values of dx/dt , thus obtained, were plotted against time t . These smooth curves were extrapolated to zero time and the initial rate of reaction $\left(\frac{dx}{dt}\right)_0$ obtained. At first the order of reaction was calculated by means of Van't Hoff's differential method, using the value of $\left(\frac{dx}{dt}\right)_0$ at two concentrations of esters *i.e.*, the order of reaction,

$$n = \frac{\log(dx_1/dt)_0 - \log(dx_2/dt)_0}{\log C_1 - \log C_2}$$

where C_1 and C_2 are the concentrations of the ester in two sets of experiments.

Having confirmed the order of reaction to be one, $\left(\frac{dx}{dt}\right)_0$ was equated to $k_0 a$ and thus k_0 was calculated. The data are shown in Tables 1 and 2.

TABLE 1.—METHYL FORMATE.

Temperature $^\circ\text{A}$	$k_0 \times 10^6 \text{ min}^{-1}$
296.78	0.55
302.17	1.20
308.26	2.61
313.82	5.42

Energy of Activation, $E=24900$ cal.

TABLE 2.—ETHYL FORMATE.

Temperature $^\circ\text{A}$	$k_0 \times 10^6 \text{ min}^{-1}$
293.19	1.19
304.22	3.03
312.76	7.43
323.64	7.20

Energy of Activation, $E=16800$ cal.

Each value of k_0 is a mean of five determinations, carried out at ca. 0.1, 0.3, 0.5, 0.7, and 0.9M concentrations of esters. The mean value of k_0 differs at the most by $\pm 0.05 \times 10^{-6}$ units from the individual values of k_0 . The plot of $\log k_0$ vs. $1/T$ is shown in Fig. 2. The values of energy of activation, E , were calculated in the usual manner.

Discussion

In the hydrolysis of esters a number of distinct mechanisms can be recognised. The esters may be hydrolysed by alkalis or by acids and a less

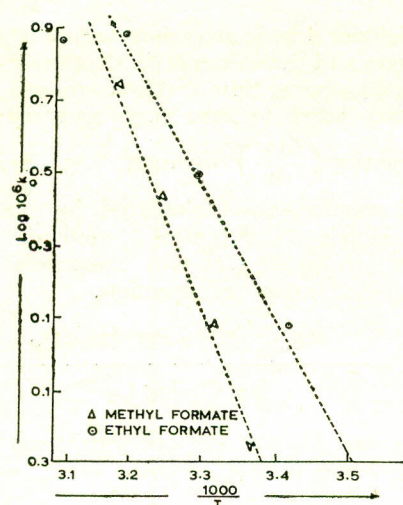


Fig. 2.—Arrhenius plot.

well known form of hydrolysis occurs in neutral solution. It appears there are three main groups of mechanisms, but two of these groups are related more closely to each other than to the third. In both alkaline and neutral hydrolysis, the carboxyl form which undergoes reaction is the neutral ester molecule $R'.CO_2.R$, while in acid hydrolysis it is the ionic conjugate acid $R'.CO_2HR^+$. The classification of mechanisms has further been inferred by the position of the rupture of the carboxyl compound. For hydrolysis, the possible modes of rupture are:



It is found that for alkaline hydrolysis, acyl-oxygen fission is usual and for neutral hydrolysis alkyl-oxygen fission is common. But these are by no means the exclusive features. So within a particular mechanism, there are two subgroups, distinguished by the position of the rupture of the ester group. It has also been found that in acid-catalysed hydrolysis, where the attacked entity is the conjugate acidic ion $R'.CO_2HR^+$, either acyl-oxygen or alkyl-oxygen fission may take place according to the structure and conditions. Thus the original two-fold classification of mechanisms becomes four-fold. The general result of the work on reaction kinetics of the hydrolysis of esters has been to show that just like the 'bimolecular' and 'unimolecular' mechanisms of nucleophilic substitution or elimination, two mechanisms exist—*i.e.*, 'bimolecular' and 'unimolecular'. These criteria allow for eight mechanisms, out of which

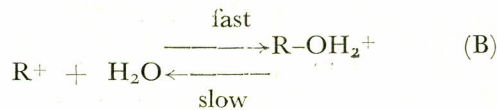
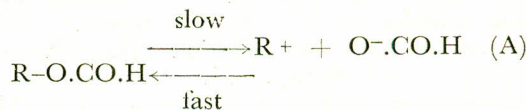
six have been reported by various workers. They are as follows:—

Basic hydrolysis: Bimolecular acyl-oxygen fission, Unimolecular alkyl-oxygen fission, bimolecular alkyl-oxygen fission.

Acidic hydrolysis: Unimolecular acyl-oxygen fission, Bimolecular acyl-oxygen fission, Unimolecular alkyl-oxygen fission.

"Many more than six mechanisms of hydrolysis and esterification have been suggested at various times, but some of these suggestions are elaborations of the others. Almost any hypothetical mechanism can be elaborated by the introduction of additional rapid proton movements, and in other ways; but unless such occurrences affect the observable chemistry of the reaction, one has no basis for discussing them. It is preferable to discuss each mechanism in its simplest conceivable form."¹

The neutral hydrolysis of methyl and ethyl formate like that of complicated esters previously referred to was expected to follow the first order kinetics according to the unimolecular alkyl-oxygen fission mechanism given below:



where $R=CH_3$ or C_2H_5 .

Obviously the rate controlling step according to this mechanism is the forward reaction in equation (A). In order to test this assumption in the neutral hydrolysis of methyl and ethyl formate, the kinetic investigation described under the experimental part was undertaken. The results clearly show that the order of reaction is one. The aim of the present work is not to prove or disprove any mechanism of the neutral hydrolysis of esters but to find out if the spontaneous hydrolysis of esters in pure water does follow the first order kinetics in order to justify the inclusion of the

term $k_0(a-x)$ on the right hand side of the equation (i). The first order kinetics have been observed and therefore the inclusion of the term $k_0(a-x)$, the contribution by the spontaneous neutral hydrolysis to the overall rate is justified.

It is interesting to note that the values of the energy of activation found for the neutral hydrolysis are 24,900 and 16,800 calories per g. mole. for the methyl and ethyl formate respectively. The values fall in their proper order as the ethyl group, being more electropositive than the methyl group, facilitates the neutral hydrolysis, supposedly involving a unimolecular alkyl-oxygen fission.

It is important to point out that the Arrhenius frequency factor A, which is related to the entropy of activation differs considerably in the two hydrolyses. Apparently the factor A increases simultaneously with the energy of activation, E. Such a result is understandable because the entropy of activation becomes modified by interference with the assembly and articulation of the reactants, and of components of the solvation shell of the transition state. As the reaction site involves $\text{CH}_3\delta^+$ and $\text{C}_2\text{H}_5\delta^+$ in the two esters, the composition of the solvation shell is bound to be different in the two cases and hence a difference in the entropy of activation. An increase in both

factors of the Arrhenius equation has been found by other workers also.⁸

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