

Alkyl Formate Esters Hydrolysis In Aqueous Medium. A comparative study of Acid-catalyzed Hydrolysis

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(Received 18th August, 1998, revised 16th July, 2001)

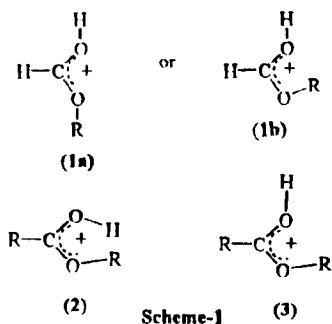
Summary: The hydrolysis of alkyl formates in neutral medium has been studied in the temperature range 293-343K. The reaction was autocatalytic. There was an increase in the rate of reaction with increasing hydrogen ion produced in the bulk of the solution. The rate constants, k_1 (L mol⁻¹ S⁻¹) proposed by A. Kirman for acid-catalyzed reactions in neutral medium have been evaluated by the method of sum of trapezoids and were compared with the values obtained by other workers in purely acidic media. The values obtained in the present investigation were in fairly good agreement with those reported in literature. The rate of hydrolysis increased in the order methyl formate < ethyl formate while the k_1 values estimated for isopropyl ester were approximately the same as that for ethyl formate. The $A_{AL}1$ mechanism was operative in neutral hydrolysis of esters.

The Arrhenius equation was applied to express the effect of temperature on the specific rates. The experimental observations concluded that the equation proposed by A. Kirman was a suitable working equation for the hydrolysis of esters in neutral medium.

Introduction

The hydrolysis of esters has been of primary interest to the research workers and many investigations have been made in this regard to elucidate the mechanism as well as energetic of the hydrolytic reactions [1 - 5]. Deno *et al* [6] were the first who studied the formation of acyl cations from protonated carboxylic acids and esters. Much work has been done on ester hydrolysis catalyzed by different acids as well as bases [7,8]. However, little attention has been paid to formate esters hydrolysis in neutral medium.

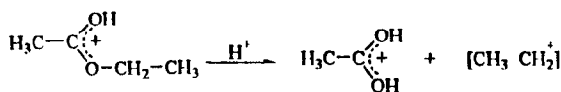
The carboxylic esters in general and the formate esters in particular can be protonated on either of its two oxygen atoms. The isomers of protonated formate esters [9] are given by the structure (1_a) or (1_b) as shown in scheme 1.



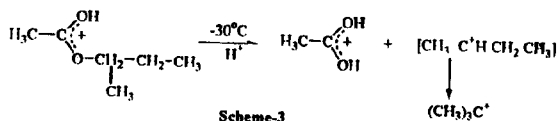
There is a controversy [10] about adopting either cisoid or transoid or mixture of both forms in case of the formates. Form [2] is ruled out on steric grounds. It seems, however, reasonable to suppose that the favored conformation of a protonated ester is represented by form [3].

In the present investigation, the reaction is auto catalytic. The H^+ produced acts as an acid and favors the alkyl-oxygen fission. Many of the esters, which are hydrolyzed by the $A_{AL}1$ mechanism in acid, are also hydrolyzed with alkyl-oxygen fission under neutral conditions [11,12].

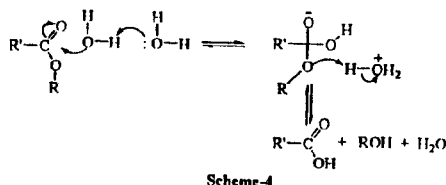
A change of mechanism to alkyl-oxygen fission [13] was observed in the case of ethyl esters (scheme-2).



The esters of secondary alcohols cleave exclusively by alkyl-oxygen fission and give protonated acids and stable tertiary carbonium ions (scheme-3).



A more elaborate explanation of the $A_{AC}I$ mechanism of neutral hydrolysis is given below scheme-4.



This mechanism elaborately explains the involvement of a molecule of water acting as a general base to assist the addition of a second molecule of water to the ester carbonyl group.

The aims of the present investigations were to follow a comprehensive study of the hydrolysis of alkyl formates in neutral medium and to verify the validity of the equation proposed by A. Kirmman [14] for the hydrolysis of esters in pure water.

Results and Discussion

As described in our previous work, the general rate expression for the hydrolysis of esters is,

$$[R'COOR](K_0 + K_H^+[H_3O^+] + K_{OH^-}[OH^-]) \quad (1)$$

Simple formates when hydrolyze in neutral water, do so sufficiently fast to make the concentration of H^+ , appreciable, so that the general expression for the hydrolysis of esters $[R'COOR]$ is reduced to

$$\frac{-d(R'COOR)}{dt} = [R'COOR] K_0 + K_H^+[H_3O^+] \quad (2)$$

Where K_H^+ represents the rate coefficient for the catalyzed reaction.

This expression is the same, which was proposed by A. Kirmman [14] for the neutral hydrolysis of esters.

The integral form of equation 2 is calculated as a sum of trapezoids by a method described by P.

Salomaa [15] in connection with a study of the alcoholysis of α -halogenoethers. For neutral hydrolysis we have modified the same equation as given below and has been described in detail in our previous work.

$$\frac{1}{t} \ln \frac{a}{(a-x)} = K_0 + K_1 \int_0^t CH^+ dt \quad (3)$$

Equation (3) on integration yielded

$$K_1^- = K_0 + K_1 C_t^- \quad (4)$$

The Kimman equation is expressed as

$$\frac{dx}{dt} = K_0(a-x) + K_1(a-x)C_H^+ \quad (5)$$

Where 'a' denotes the initial concentration of ester, 'x' the decrease in this concentration during time 't' CH^+ is the concentration of hydrogen ion, which is also a function of time in the present study k_0 (sec^{-1}) and k_1 ($\text{L mol}^{-1}\text{S}^{-1}$) are the rate constants for uncatalyzed and acid catalyzed reactions respectively.

The first term in this equation represents the uncatalyzed spontaneous hydrolysis considered to follow first order kinetics whereas the second term represents the superimposed acid catalyzed reaction due to the production of hydrogen ions by the spontaneous hydrolysis.

To evaluate k_0 (sec^{-1}) and k_1 ($\text{L mol}^{-1}\text{S}^{-1}$) in Kirmman's equation, k_1^- was plotted versus C_t^- for alkyl formates studied at 293-343 K as shown in Figure 1-3. The coefficients k_0 and k_1 were calculated by the method of least squares [16].

In the present investigation K_1 ($\text{L mol}^{-1}\text{sec}^{-1}$), the rate constant for acid catalyzed reaction in neutral medium has been evaluated in order to compare it with the values obtained by other workers in purely acidic media.

The results thus obtained for K_1 ($\text{L mol}^{-1}\text{sec}^{-1}$), are summarized in Table I. For comparison, Table 2 lists the values reported in literature obtained at a temperature of 298 K for the hydrolysis of alkyl formates in purely acidic medium.

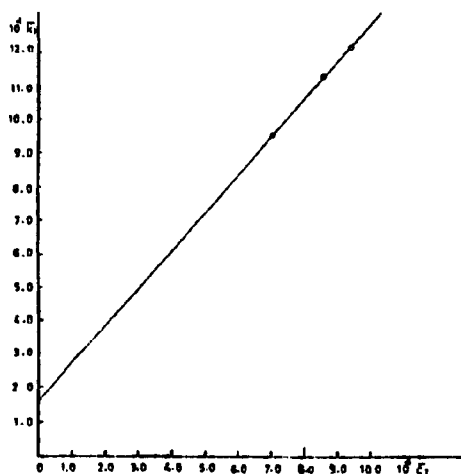
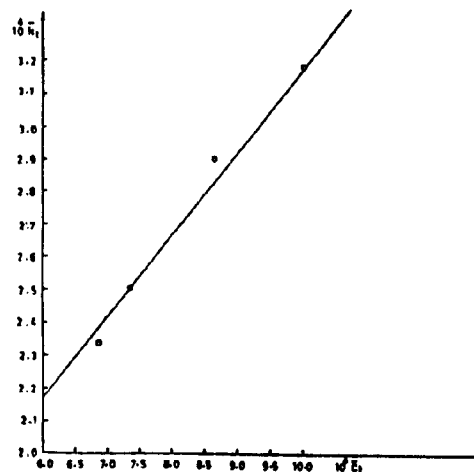
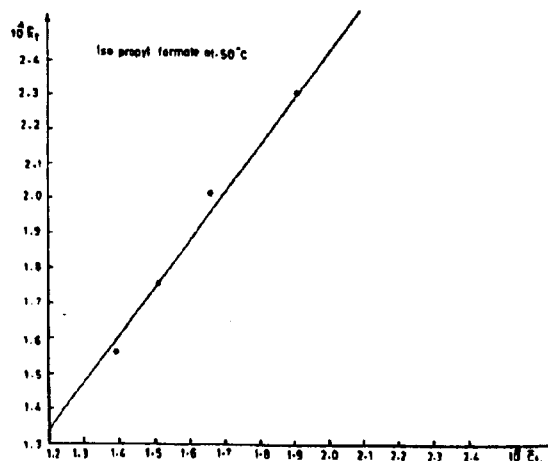
Table I The hydrolysis of alkyl formates, HCOOR, in neutral medium at different temperatures

R	Temp K	$10^3 k_1$ (L mol ⁻¹ sec ⁻¹)
CH ₃	293	1.23
	298	1.89
	303	3.49
	308	4.42
	313	5.22
C ₂ H ₅	298	2.52
	303	3.45
	308	4.47
	313	4.64
C ₃ H ₇	318	9.70
	298	2.24
	303	3.71
	313	6.89
	323	13.93
	333	27.61
	343	30.23

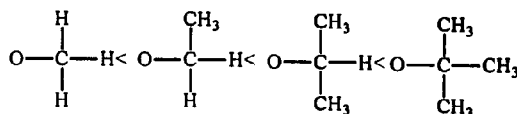
Table 2. Selected values of the rate constants at 298 K

Ester	$10^3 K_1$ (L mol ⁻¹ sec ⁻¹)	$\Psi 10^3 K_1$ (L mol ⁻¹ sec ⁻¹)	Reference Number
Methyl formate	1.89	2.40	(17)
		2.50	(18)
Ethyl formate	2.52	2.39	(19)
		3.10	(20)
		3.20	(18)
		3.10	(21)
		3.20	(15)
Iso Propyl formate	2.24	2.80	(17)
		2.93	(22)

*present work, Ψ , values obtained by other workers


 Fig. 1: The rate coefficients \bar{K}_1 for the hydrolysis of methyl formate at 25°C as functions of the mean hydrogen ion concentration \bar{C}_1 .

 Fig. 2: The rate coefficients \bar{K}_1 for the hydrolysis of ethyl formate at 35°C as functions of the mean hydrogen-ion concentration \bar{C}_1 .

 Fig. 3: The rate coefficient K_1 for the hydrolysis of iso propyl formate at 50°C as functions of the mean hydrogen-ion concentration C_1 .

It is expected that the alkyl group on successive substitution should increase the rate of hydrolysis as shown below,



This anticipation is borne out by the data given in Table I. However, the K_1 values obtained for iso propyl ester at 298 K are approximately the same as that for ethyl formate. The rate of hydrolysis

increases in the order methyl formate < ethyl formate, as ethyl group is more electropositive than the methyl group. For iso propyl formate, the conclusion can either be (a) steric hindrance is involved or (b) further substitution at α -C atom does not produce any further significant polarization. Table 2 lists the values for K_1 ($L \text{ mol}^{-1} \text{ sec}^{-1}$) obtained by other workers in purely acidic media. As can be seen, the values of K_1 given in the Table I at 298 K for the second order rate constant obtained indirectly in the neutral medium are slightly lower than those reported in literature (Table-2). The increase may be attributed to the fact that most workers have studied the reaction in acidic medium.

The relation between specific rate and temperature is given by the Arrhenius equation,

$$K = A.e^{-E/RT} \quad (6)$$

Where A is the frequency factor for the reaction and E is the energy of activation. Equation (6) may be written as

$$\text{Log } K = \text{Log } A - \frac{E}{2.303RT} \quad (7)$$

Thus $\log k_1$ obtained for catalyzed reactions were plotted against the reciprocal of the absolute temperature. The straight lines shown in figure 4 were the Arrhenius plots based on data obtained in the temperature range 293-343 K. The slopes of the straight lines gave activation energies and the corresponding intercepts provided the constants A. (Table 3) shows a comparative study of the activation parameters and frequency factors, obtained indirectly in the present investigation and directly by other workers.

TABLE 3: Comparison of the acid-catalyzed hydrolysis of HCOOR in water.

R	Log A*	E*	Log A Ψ	E Ψ	Reference Number
CH ₃	7.33	13.69	9.01	15.8	[18]
C ₂ H ₅	5.62	11.23	8.18	14.5	[18]
			9.04	15.77	[21]
			8.76	15.34	[15]
C ₂ H ₇	5.95	11.59	8.79	15.44	[15]

* Present work. Ψ , Values obtained by other workers.

It is seen that our values under report are in fairly good agreement with those obtained by other

workers although an indirect method for computing the values has been employed.

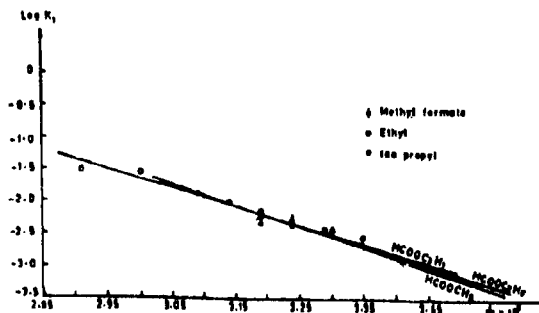
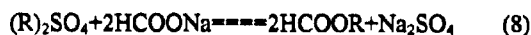


Fig. 4: Arrhenius plot for the hydrolysis of alkyl formates in neutral medium
Log K_1 as a function of $\frac{1}{T}$

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Experimental

The esters were prepared by the method of double decomposition between alkyl sulphates and sodium formate according to the equation [23].



The apparatus used in the present investigation shown in fig. (5) was an improved form of the one used by E.A.Molwyn Hughes for the kinetic studies of the ester hydrolysis. The modified form included a three-channeled tube with 15.24cm length and 7.62cm diameter. One side of this tube consisted of a single stem, which connected this tube with the vertical reservoir by means of a pressure tubing through stopcock S1. On the other side, this tube was divided into three channels each having a stopcock, which lead the channels into a separate reaction vessel. Each channel was marked A, B and C. When the stopcock was opened, the corresponding vessel was connected with the mercury reservoir. The tube was supported by a horizontal bar by means of two rubber-cushioned holders. The three-channeled tube remained filled with mercury throughout the work. The purpose of this tube was to connect the three reaction vessels with a single mercury reservoir

A high vacuum pump was used to support 25Kg mercury in the cylindrical mercury reservoir and to raise or lower the mercury level in the said reservoir for filling or emptying the reaction vessels.

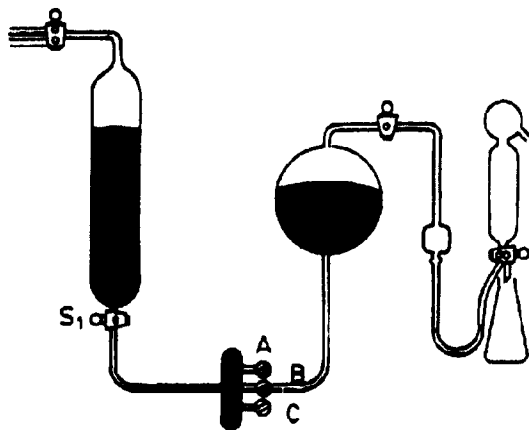


Fig. 5: Apparatus for Hydrolysis

The reaction vessels containing mercury were immersed in a constant temperature bath. Each reaction vessel was made airtight with a rubber bung, which carried a capillary tube and a delivery tube. The capillary tube connected the reaction vessel with the automatic pipette while the delivery tube helped to connect the reaction vessel with the atmosphere when the stopcock was opened. A small electrical stirrer was inserted in each reaction vessel through the rubber bung to stir the reaction mixture. At convenient intervals of time, measured amount of reaction mixture i.e. ester into conductivity water was withdrawn directly from the reaction vessel through automatic pipette into the titration flask containing powdered ice, which served to chill the reaction. The chilled samples were titrated against standard solution of NaOH using phenolphthalein as indicator.

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