

## Pseudo-first Order Rate Constants and Thermodynamic Parameters for Esters Hydrolysis in Neutral Medium

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(Received 4th November, 1998, revised 30th November, 2000)

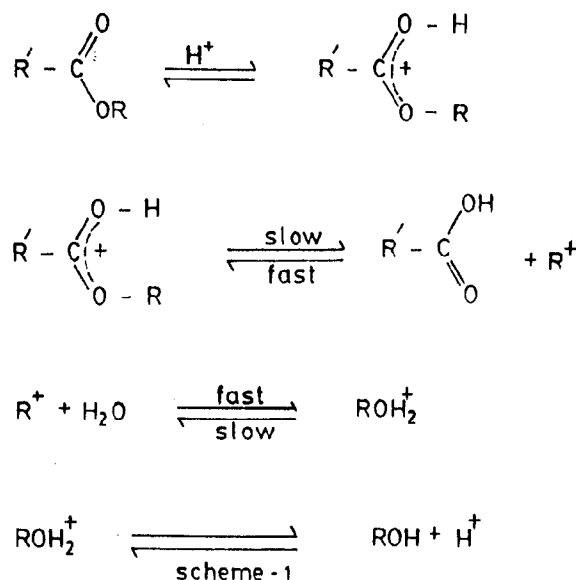
**Summary:** A comprehensive study of the Pseudo-first order rate constants  $k_0$  ( $\text{sec}^{-1}$ ) for uncatalysed reaction and the thermodynamic parameters for alkyl formates HCOOR in neutral medium in the temperature range (293-343 K) has been undertaken. The free energies, enthalpies and entropies of activation were measured according to the theory of absolute reaction rates. The enthalpies and entropies of activation decreased from methyl to ethyl formates whereas the  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  values obtained for isopropyl formate were approximately the same as that for ethyl formate indicating that further substitution at the  $\alpha$ -C atom did not produce any further significant intramolecular polarization. The  $A_{AL1}$  mechanism was operative in neutral hydrolysis of esters.

### Introduction

The hydrolysis of formate esters has been carried out in Acidic, Basic and neutral medium [1-4]. Many authors [5-8] have mentioned the activation parameters of formate esters in strongly acidic and basic media and their approach to the experimental work gives a clear and consistent picture of the mechanism. A large number of investigators have studied the ester hydrolysis involving alkyl-oxygen cleavage, usually using much less concentrated solutions of the strong acids than those required for significant rates of reaction by the  $A_{AC1}$  mechanism. Indeed some esters undergo alkyl-oxygen cleavage even in the absence of strong acids or under neutral conditions. The hydrolysis of t-butyl acetate was carried out in 20-30%  $\text{H}_2\text{SO}_4$  [9, 10], where only a very small proportion of the protonated species was present. However, the proton transfer step was rate-determining and the mechanism of  $A_{AL1}$  hydrolysis followed was that shown in scheme-1. Many of the esters which are hydrolyzed by the  $A_{AL1}$  mechanism in acids are also hydrolyzed with alkyl-oxygen fission under neutral conditions [11-13].

The hydrolysis of the formate esters in neutral medium has not been given so much attention in the past. Therefore, the present investigation was undertaken to study the hydrolysis of formate esters in neutral medium which has not been previously reported in literature. In the present study,  $k_0$  ( $\text{sec}^{-1}$ ), the rate constant in Kirmman's equation for uncatalysed reactions in neutral medium has been evaluated and the thermodynamic parameters are

determined in order to compare them with the values obtained by other workers in purely acidic media.



### Results And Discussion

#### Rate Constants:

As described in our previous work for the hydrolysis of Methyl formate in neutral medium [14] in detail, the general rate expression for the hydrolysis of esters is,

$$\frac{-d(\text{R}'\text{COOR})}{dt} = [\text{R}'\text{COOR}](k_0 + k_{\text{H}^+}[\text{H}_3\text{O}^+] + k_{\text{OH}^-}[\text{OH}^-]) \quad (1)$$

Where  $k_0$  ( $\text{sec}^{-1}$ ) is the rate constant for uncatalysed reactions. If simple formates such as alkyl formates are hydrolyzed in neutral water, they hydrolyze sufficiently fast to make the concentration of  $\text{H}^+$  sufficiently large so that the general expression for the hydrolysis of esters  $[\text{R}'\text{COOR}]$  is reduced to

$$\frac{-d(\text{R}'\text{COOR})}{dt} = [\text{R}'\text{COOR}]k_0 + k_{\text{H}^+} [\text{H}_3\text{O}^+] \quad (2)$$

Where  $k_{\text{H}^+}$  represents the rate coefficient for the catalyzed reaction.

This expression is the same which was proposed by A. Kirmann [15] 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 [16] in connection with a study of the alcoholysis of  $\alpha$  - halogenoethers [17]. For neutral hydrolysis we have modified the same equation as given below and has been discussed more elaborately in our previous work [14].

$$\frac{1}{t} \ln \frac{a}{(a-x)} = k_0 + k_1 \frac{1}{t} \int_0^t C_{\text{H}^+} dt \quad (3)$$

Where  $k_1$  ( $\text{L mol}^{-1} \text{sec}^{-1}$ ) is the rate constant for acid catalyzed reactions respectively.

Equation (3) on integration yielded

$$k_t = k_0 + k_1 C_t \quad (4)$$

The kirmann equation is expressed as

$$\frac{dx}{dt} = k_0(a-x) + k_1(a-x)C_{\text{H}^+} \quad (5)$$

Where 'a' denotes the initial concentration of ester, 'x' the decrease in this concentration during time 't'.  $C_{\text{H}^+}$  is the concentration of hydrogen ion which is also a function of time in the present study.

The first term in this equation represents the uncatalysed spontaneous hydrolysis considered to follow first order kinetics where as the second term

represents the superimposed acid-catalyzed reaction due to the production of hydrogen ions by the spontaneous hydrolysis.

To evaluate  $k_0$  ( $\text{sec}^{-1}$ ) and  $k_1$  ( $\text{L mol}^{-1} \text{sec}^{-1}$ ) in kirmann's equation,  $k_t$  was plotted versus  $C_t$  for alkyl formates studied at 293 - 343 K. The coefficients  $k_0$  and  $k_1$  were calculated by the method of least squares [18]. The results thus obtained for  $k_0$  ( $\text{sec}^{-1}$ ) are summarized in Table I.

Table 1: The Hydrolysis Of Alkyl Formates HCOOR In Neutral Medium At Different Temperatures

R	Temperature K	$10^7 k_0$ $\text{sec}^{-1}$
CH <sub>3</sub>	293	1.63
	298	2.61
	303	4.87
	308	7.85
	313	12.41
C <sub>2</sub> H <sub>5</sub>	298	2.95
	303	6.01
	308	9.02
	313	13.54
	318	19.28
C <sub>3</sub> H <sub>7</sub>	303	21.01
	313	35.78
	323	88.29
	333	241.85
	343	462.83

Arrhenius Parameters:

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

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

where A is a constant which is usually known as the frequency factor for the reaction and E is the energy of activation

Equation (6) may be written as,

$$\ln k = \ln A - \frac{E}{RT} \quad (7)$$

or

$$\log k = \log A - \frac{E}{2.303R} \cdot \frac{1}{T} \quad (8)$$

The  $\log k_0$  for uncatalysed reactions were plotted against the reciprocal of the absolute

temperature for the hydrolysis reactions of alkyl formates. The straight lines shown in figure 1 for uncatalysed reactions were the Arrhenius plotts 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 constant A (Table 2).

Table-2: Values Of Log A And E For The Hydrolysis Of Un-catalysed HCOOR In Neutral Medium

R	Log A	E k cal mol <sup>-1</sup> .
CH <sub>3</sub>	7.23	18.80
C <sub>2</sub> H <sub>5</sub>	6.16	17.24
C <sub>3</sub> H <sub>7</sub>	6.29	16.69

Free energies, enthalpies and entropies of activation:

According to the theory of absolute reaction rates developed by Eyring,

$$k = \frac{KT}{h} e^{-\Delta G^\ddagger / RT} \quad (9)$$

where k is the specific rate, K is Boltzmann's constant, h is Plank's constant and  $\Delta G^\ddagger$  is the standard free energy of activation.

or

$$k = \frac{KT}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT} \quad (10)$$

where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the enthalpies and entropies of activation.

$$\ln \frac{k}{T} = \ln \frac{K}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (11)$$

$\ln \frac{k}{T}$  was plotted versus  $\frac{1}{T}$

$$\Delta H^\ddagger = (-slope \times R) \quad (12)$$

$$\Delta S^\ddagger = (Intercept - \ln \frac{K}{h})R \quad (13)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (14)$$

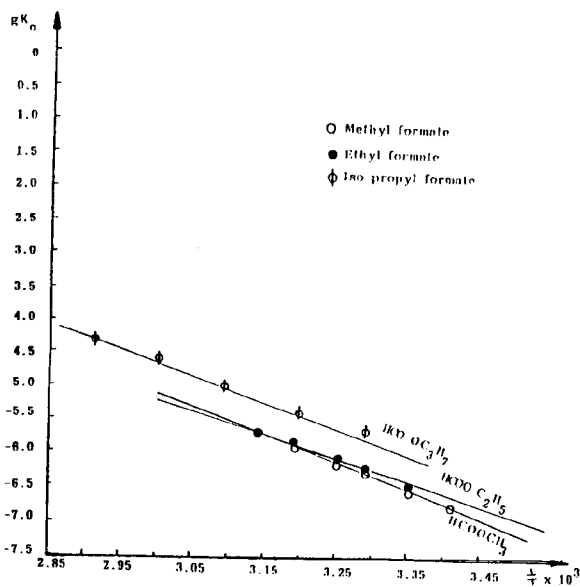
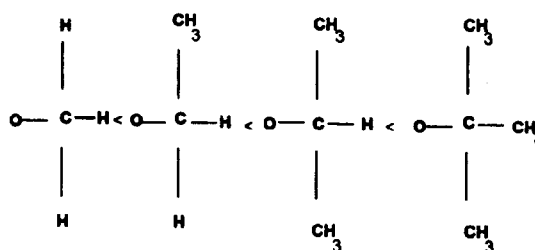


Fig. 1: The hydrolysis of alkyl formates in neutral medium. Log K<sub>o</sub> as a function of  $\frac{1}{T}$

The free energies, enthalpies and entropies of activation were measured according to the theory of absolute reaction rates developed by Eyring [19]. The values obtained for k<sub>o</sub> (sec<sup>-1</sup>) are given in table 3.

the alkyl group on successive substitution should increase the rate of hydrolysis as shown below.



This anticipation is clearly borne out by the data in table 3. It is seen that the values of  $\Delta H^\ddagger$  decrease or the rates of hydrolysis increase in order methyl formate < ethyl formate < iso-propyl formate with the respective  $\Delta H^\ddagger$  values as 18.20, 16.63, and 16.05 K cal mol<sup>-1</sup> and the respective k<sub>o</sub> (sec<sup>-1</sup>) values given in table 1 at 303 K as 4.87 × 10<sup>-7</sup>, 6.01 × 10<sup>-7</sup> and 21.01 × 10<sup>-7</sup>.

Table 3: The free energies, enthalpies and entropies of activation for the hydrolysis of uncatalysed HCOOR in neutral medium

R	Temperature K	$\Delta G^\ddagger$ (K cal mol <sup>-1</sup> )	$\Delta H^\ddagger$ (K cal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (e.u.)
CH <sub>3</sub>	293	26.25	18.20	-27.46
	298	26.38		
	303	26.52		
	308	26.66		
	313	26.80		
C <sub>2</sub> H <sub>5</sub>	298	26.18	16.63	-32.36
	303	26.44		
	308	26.60		
	313	26.76		
	318	26.92		
C <sub>3</sub> H <sub>7</sub>	303	25.70	16.05	-31.88
	313	26.03		
	323	26.35		
	333	26.67		
	343	26.99		

Table 4: Rate Coefficient And Activation Parameters For The Neutral Hydrolysis Of Esters In Water At 298 K

S.No	Esters	$k_{\text{hyd}}$ (sec <sup>-1</sup> )	$\Delta H^\ddagger$ (K cal mol <sup>-1</sup> )	$\Delta S^\ddagger$ (e.u.)	Ref.
1.	HCOOCH <sub>2</sub> Cl	$8.5 \times 10^{-5}$	11.4	-39.0	21
2.	HCOOCHClCH <sub>2</sub> Cl	$8.5 \times 10^{-5}$	11.4	-38.8	21
3.	CF <sub>3</sub> COO(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	$5.67 \times 10^{-6}$	9.21	-51.7	22
4.	CF <sub>3</sub> COO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	$3.50 \times 10^{-6}$	10.19	-49.1	22
5.	CF <sub>3</sub> COO(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	$2.56 \times 10^{-6}$	9.20	-51.7	22
6.	CF <sub>3</sub> COO(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	$2.59 \times 10^{-6}$	9.87	-51.1	22
7.	CF <sub>3</sub> COOC <sub>6</sub> H <sub>5</sub>	$1.67 \times 10^{-2}$	6.26	-45.9	22
8.	CF <sub>3</sub> COOC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> -p	$8.39 \times 10^{-3}$	6.23	-47.2	22

When substitution is made at  $\alpha$ -Carbon atom, maximum intramolecular electronic charge displacement is expected. With this the change in  $\Delta S^\ddagger$  values also becomes apparent due to the orientation of the solvent molecules. This is also borne out by the respective  $\Delta S^\ddagger$  values of methyl formate and ethyl formate. The values of  $\Delta S^\ddagger$  changes from -27.46 to -32.36 e.u. in passing from methyl to ethyl formate (table 3).

The same effect should have been displayed when further substitution was done at  $\alpha$ -carbon atom. But the  $\Delta S^\ddagger$  value obtained for isopropyl ester is approximately the same as that for ethyl formate i.e. -31.88 as compared with -32.36 e.u. The conclusion can be (a) either steric hindrance is involved or (b) further substitution at the  $\alpha$ -carbon atom does not produce any further significant

intramolecular polarization; and hence no significant change in  $\Delta S^\ddagger$  value.

Table 4 contained most of the data available in literature. The important generalization which could be drawn from the data in table 4 was that the entropy of activation was typically in or close to the region -40 to -50 e.u., and that changes in reactivity due to substituents appeared primarily in the enthalpy term.  $\Delta S^\ddagger$  was particularly low for alkyl and aryl trifluoroacetates and partially compensated, as so often, for particularly low values of  $\Delta H^\ddagger$ .

It is interesting to note that so far as the comparison of the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  of the present work (table 3) and those of the work reported by others (Table 4) is concerned, a very close parallelism exists. In table 4 esters at serial number

1 and 2 are constitution wise liable to hydrolyze slower compared to those given at serial number 3,4,5,6,7 and 8. This is found to be the case as the enthalpies of activation of former are higher in order of magnitude than those of the later. On inspection, it is found that  $\Delta S^\ddagger$  values of the former are also higher than those of the later. Exactly similar results have been obtained in the present work (Table 3). The enthalpies of activation decrease from methyl to ethyl formates and so do the entropies of activation.

This discussion leads to the conclusion that from Kirmans equation the kinetic parameters of the neutral hydrolysis have been obtained and can be considered fairly reliable.

### Experimental

All the reagents were of A.R. grade and were used without further purification. Conductivity water was used through out the experimental measurements for making all the solutions. The experimental setup used was the same as described in our previous work [14] for alkyl formate esters hydrolysis in aqueous medium.

The apparatus used was an improved form of the one used by E. A. Molwyn Hughes [20] for the kinetic studies of the ester hydrolysis. The modified form included a three channeled tube. One side of this tube consisted of a single stem which connected this tube with the vertical reservoir. On the other side, this tube was divided into three channels each having a stopcock which lead the channels into a separate reaction vessel. When the stopcock was opened, the corresponding vessel was connected with the 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. 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. A small electrical stirrer was inserted in each reaction vessel through the rubber bung to stir the reaction mixture.

At convenient intervals of time, the chilled samples were titrated against standard solution of NaOH using phenolphthalein as indicator.

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