

ISO-PROPYL FORMATE HYDROLYSIS IN WATER AND THE EVALUATION OF RATE CONSTANTS

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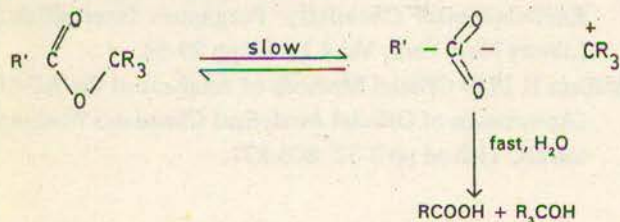
(Received 9 August 1998; accepted 22 July 1999)

Emphasis has been placed on the data for the hydrolysis of *Iso*-propyl formate in neutral medium over the temperature range 303-343 K to illustrate the method, employing numerical integration and the criteria of least squares, for the evaluation of the first and the second order rate constants in Kirmann's equation by the sum of trapezoids. The values obtained for the second order rate constant k_1 ($l\ mol^{-1}\ sec^{-1}$) are compared with the values reported in the literature. The hydrolysis of *iso*-propyl formate involves alkyl-oxygen cleavage. A mini computer program on a 6502 12K, Acorn Atom computer has been designed for the evaluation of rate constants.

Key words: Esters, Hydrolysis, Rate constant, *Iso*-propyl formate.

Introduction

Hydrolysis of esters has been studied by several investigators in acidic and basic medium (Pradhan 1988; Dash 1989; Kellogg 1996; Yamanoto 1996; Moeller 1997). However, little attention has been paid to the esters hydrolysis in neutral medium. Many of the esters which are hydrolyzed by the $A_{AL}1$ mechanism in acid i.e. involving alkyl-oxygen cleavage are also hydrolyzed with alkyl-oxygen fission under neutral conditions (Bunton 1957; Swain 1960; Bunton 1961). These reaction have the high enthalpie and entropies of activations characteristics of unimolecular reactions and involve the ionization of (usually) tertiary alkyl esters, to the carbonium ion and a carboxylate anion in the rate determining step as shown in Scheme 1.



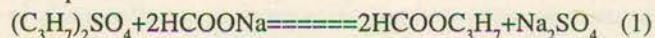
Scheme 1. Alkyl - oxygen cleavage.

These are best regarded as SN_1 reactions in which the leaving group is the carboxylate anion. The aims of the present study were to experimentally verify Kirmann's equation (Kirmann 1934) and to evaluate the first and the second order rate constants by the method of sum of trapezoids described by Salomaa (1960) and modified for the hydrolysis of esters in neutral medium in the present investigation.

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Experimental

Ester was prepared by the method of double decomposition from *iso*-propyl sulphate and sodium formate according to the equation.



The hydrolysis of *iso*-propyl formate was performed by using the same apparatus as designed by Moelwyn-Hughes (1941) and shown in Fig 1. A high vacuum pump was used to support 25 kg mercury in the cylindrical mercury reservoir and to raise or lower the mercury level in the said reservoir for filling or emptying the reaction vessel. The reaction vessel containing mercury is immersed in a constant temperature bath. The reaction vessel was made air tight 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 stop cock was opened. A small electrical stirrer was inserted in the reaction vessel through the rubber bung to stir the reaction mixture.

At convenient intervals of time, a specific amount of reaction mixture i.e. ester in conductivity water was with drawn 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.

Results and Discussion

The general rate expression for the hydrolysis of esters and of many other species is:

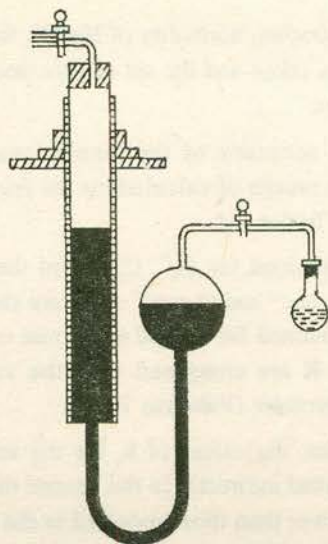


Fig 1. Apparatus for the hydrolysis of esters designed by E. A. Moelway Hughes.

$$-\frac{d[R^1\text{COOR}]}{dt} = [R^1\text{COOR}]k_0 + k_{H^+}[H_3O^+] + k_{OH^-}[OH^-] \quad (2)$$

In dilute aqueous solutions in which pH control is maintained, hydrolysis follows the first order kinetics and the observed rate-coefficient is given by the following equation:

$$k_{\text{obs}} = k_0 + k_{H^+}[H_3O^+] + k_{OH^-}[OH^-] \quad (3)$$

Usually k_{H^+} and k_{OH^-} can be determined at low and high pH respectively, where only one form of catalysis is significant. For unreactive esters k_0 is small and can be neglected.

Simple formates such as *iso*-propyl formates are hydrolyzed in neutral water sufficiently fast making the concentration of H^+ so large that even in the initial stages the concentration of $[OH^-]$ can be neglected. Therefore in equation 2 $k_{OH^-}[OH^-]$ can be neglected in the study of the neutral hydrolysis of simple formates. The following equation.

$$-\frac{d[R^1\text{COOR}]}{dt} = [R^1\text{COOR}]k_0 + k_{H^+}[H_3O^+] \quad (4)$$

is the same which was proposed by Kirmann (1934) for the neutral hydrolysis of esters.

Kinetic measurements. Auto catalytic hydrolysis of esters is believed to obey the rate expression (Kirmann 1934),

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

where a denotes the initial concentration of ester, x the decrease in this concentration during time t , C_{H^+} is the concentration of hydrogen ion which is also a function of time

in the experiments, k_1 ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) and k_0 (sec^{-1}) are the rate constants for acid-catalyzed and uncatalysed reactions, respectively.

The solution of differential equation 5 may also be written as,

$$\frac{dx}{(a-x)} = k_0 dt + k_1 C_{H^+} dt \quad (6)$$

which on integration yields (Salomaa 1953).

$$\frac{1}{t} \ln \frac{a}{(a-x)} = k_0 + k_1 \frac{1}{t} \int_0^t C_{H^+} dt \quad (7)$$

or

$$k_1 = k_0 + k_1 C_1 \quad (8)$$

Where k_1 is the value of the rate coefficient computed from the usual first-order rate equation. This first-order coefficient has different values at different times during the course of the reaction and the corresponding hydron concentration,

$$C_1 = \frac{1}{t} \int_0^t C_{H^+} dt \quad (9)$$

is the time average of hydron concentration over the interval $(0,t)$. The value of the integral in equation 9 can be determined when the variation of the hydron concentration with time is known. The integral is calculated as a sum of trapezoid by a method described by Saloma (1960). Thus the integral in equation 9 is evaluated on the basis of experimental data as a sum of the trapezoids:

$$C_1 = \frac{1}{t} \int_0^t C_{H^+} dt = \frac{1}{t} \left[\frac{1}{2} \sum_{v=1}^i (C_{H^+v-1} + C_{H^+v})(T_v - T_{v-1}) \right] \quad (10)$$

The error involved in the approximation is of a smaller order of magnitude than the experimental errors in determining concentrations.

In equation 10 $T_i = T$, $T_0 = 0$ and C_{H^+v} denotes the hydrogen ion concentration at the time T_v of taking of the sample. The hydron concentration in the reaction mixture at the time of sampling can be computed from

$$C_{H^+} = \frac{-k + \sqrt{k^2 + 4kC_f}}{2} \quad (11)$$

where k is the acid dissociation constant of formic acid at the temperature in question, C_f is g moles l^{-1} produced.

For the temperature dependence of this dissociation constant, Harned and Embree (1934) have given the following equation:

$$\log K = -(173.624/T) + 17.88348 \log T - 0.0280387T - 39.06123 \quad (12)$$

The values of k_t and C_t^- are calculated from the data of each run and both sets of values are averaged (Salomaa 1953). In this way an average value for the overall first order specific rate k_t^- and the corresponding hydrogen ion concentration C_t^- are obtained. Although a slight increase is noted in both sets of values, k_t and C_t^- the method of averaging is quite correct since the relation between the overall first order specific rate k_t^- and the corresponding hydrogen ion concentration can be taken to be linear over each run. Thus equation 8 becomes,

$$k_t^- = k_0 + k_1 C_t^- \quad (13)$$

To illustrate the method kt^- was plotted versus ct^- for iso-propyl formate studied at various temperatures. The coefficients k_0 and k_1 were calculated by the method of least squares (Sokolnikoff 1948). Each value pair (k_t^- , C_t^-) thus gave a point on the plot which represented the over all first order specific rate as a function of hydrogen ion concentration. Figure 2 depicts a plot of k_t^- vs C_t^- at 323K. The value for k_1 ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) at 298 K was evaluated by extrapolation.

A "BASIC" computer programme reproduced below performed the above calculations. The programme requires as input the

initial concentration, normality of NaOH, the volume of reaction mixture taken and the set of time and ml of titration for a given run.

To show the accuracy of the kinetic equations and the programme, the results of calculations for *Iso*-propyl formate are shown in Tables 1-4.

The values obtained for (k_t^- , C_t^-) and the corresponding coefficients $k_0 \text{ sec}^{-1}$ and ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) are shown in Table 5. The values obtained for second order rate constant ($1 \text{ mol}^{-1} \text{ sec}^{-1}$) at 298 K are compared with the values (Table 5) reported in literature (Palomaa 1935).

As can be seen, the values of k_1 for the second order rate constant obtained indirectly in the neutral medium at 298 K are slightly lower than those reported in the literature. This increase may be attributed to the fact that most workers have studied the reaction in acidic medium.

Computer Program

5 REM rate constants for hydrolysis of esters
10 FDIM %MM (25), %HH (25), %LL (25), %KK (25)

Table 3

Calculation for iso propyl formate at HCOOC_3H_7 ,
0.010M; Temp 303 K

t (min)	10^3 g mol^{-1}	$10^4 C_{H^+}$	$10^4 C_t^-$	$10^4 k_t^-$
110	2.99	6.44	3.22	2.79
244	7.28	10.49	6.10	3.13
305	9.36	12.01	7.13	3.25
391	12.73	14.15	8.44	3.52
488	1403	1489	9.65	3.13
575	18.97	1745	10.63	3.70
667	23.39	19.47	11.71	4.04
742	25.73	20.46	12.55	4.06
1429	48.60	28.44	18.27	4.72
1657	30.71	30.71	19.83	5.09
1889	31.99	31.99	21.24	5.08

Table 4

Calculation for iso propyl formate at HCOOC_3H_7 ,
0.15M; Temp 303 K

t (min)	10^3 g mol^{-1}	$10^4 C_{H^+}$	$10^4 C_t^-$	$10^4 k_t^-$
44	1.82	4.85	2.43	2.76
99	7.02	10.29	5.29	4.82
167	13.25	14.45	8.17	5.52
226	14.29	15.04	9.89	4.41
324	25.99	20.57	12.28	5.85
486	32.49	23.09	15.46	4.99
536	36.90	24.67	16.25	5.24
638	45.22	27.41	17.82	5.59
770	55.88	30.56	19.73	6.02
1543	87.07	38.36	27.11	5.59
2491	495.12	40.13	31.73	4.01
2613	97.46	40.64	32.13	3.99

Table 1

Calculation for *iso* propyl formate at HCOOC_3H_7 ,
0.08M; Temp 303 K

t (min)	10^3 g mol^{-1}	$10^4 C_{H^+}$	$10^4 C_t^-$	$10^4 k_t^-$
90	1.54	4.41	2.20	2.18
140	2.46	5.78	3.24	2.26
260	4.88	8.45	5.02	2.44
320	6.24	9.81	5.79	2.64
3.72	8.22	11.20	6.45	2.94
462	10.27	12.62	7.52	3.01
564	13.87	14.79	8.64	3.41
636	12.58	14.86	9.29	2.72
741	17.20	16.58	10.14	3.33
1395	32.61	23.14	14.70	3.80
1729	40.32	25.83	16.59	4.11
1937	44.42	27.16	17.65	4.25

Table 2

Calculation for *iso* propyl formate at HCOOC_3H_7 ,
0.09M; Temp 303 K

t (min)	10^3 g mol^{-1}	$10^4 C_{H^+}$	$10^4 C_t^-$	$10^4 k_t^-$
150	3.94	7.51	3.75	3.01
340	9.58	12.16	7.15	3.35
361	10.50	12.77	7.46	3.47
441	12.60	14.07	8.54	3.46
542	18.38	17.16	9.86	4.26
612	18.37	17.16	10.69	3.77
720	21.26	18.52	11.77	3.79
1404	41.74	26.29	16.95	4.50
1706	49.87	28.82	18.83	4.81

Table 5
The values obtained for k_t^- and C_t^-

Temp K	$10^4 C_t^-$ mol l ⁻¹	$10^4 k_t^-$ min ⁻¹	$10^7 k_o$ Sec ⁻¹	$10^3 k_1$ l mol ⁻¹ Sec ⁻¹	$*10^3 K_1$ l mol ⁻¹ Sec ⁻¹
303	8.94	3.09	21.01	3.71	--
	10.56	3.82	--	--	--
	11.71	3.86	--	--	--
	16.52	4.90	--	--	--
298	--	--	--	--	--
	--	--	--	2.24	2.80(15)
	--	--	--	(By extrapolation)	2.93(16)

*, values reported in literature

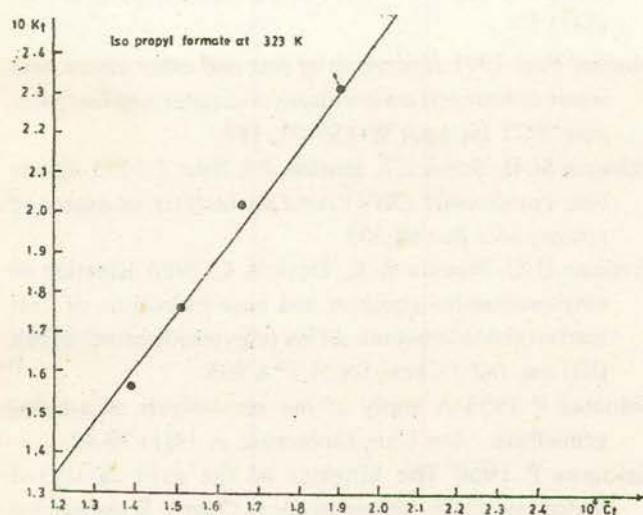


Fig 2. The rate coefficients k_t^- for the hydrolysis of iso propyl formate at 323 K as function of the mean hydrogen ion concentration C_t^-

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15.   FDIM % TT(25), %WW(25), %XX(25), %YY(25)
16.   DIM A(50). L= CH "t"; O = 1; P.$ 12
19.   INPUT "NO. OF SETS" S
20.   P.$ 12 "PLEASE WAIT"
21.   GOS. f
23g  GOS.r; N= Val A
24.   GOS.r; % T= VAL A; FP. "TEMP = % E'
25.   GOS.r; % E= VAL A; FP "ESTER = "%E'
26.   GOS.r; %B=VAL A; FP. "BASE = " %V'
27.   GOS.r, % V/=VAL A; FP. "VOLUME = "%K'
32.   GOS.r, %K = VAL A; FP. "DISS. CONST = "%K'
34.   GOS. a, GOTOx
35a  P. $S10
36.   P."PRESS SHIFT TO CONTINUE"
37.   DO T = T + 1; WAIT
38.   Until ? ≠ BOOL <> ≠ FF
39.   P. $ 10, RETURN
45x  P. "TIME      ML ""
    
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50.   FOR J = TO N
60.   GOS.r; %TT (J) =Val A
70.   GOS.r; %MM(J) = Val A
75.   FP.% TT (J), ""%MM (J)'
80.   NEXT J
82.   GOS.a
90.   GO TO w
200f Q = ? 18 * 256
210.   DO Q=Q+1
220.   UNTIL? Q==D and Q, 3 = L
230.   Q=Q+ 4 ; Return
250r  R=-1
260.   DO R=R+1 ; A,R=Q?R
270.   UNTIL A? R=CH"." or A?R==D
280.   IF A?R==DQ=Q+3
290.   Q=Q+R+1; A?R==D; RETURN
300w  P."G.MOLES 1/T LN A/(A-X)".
301.   % J=O
302.   FOR K=1 TON
305.   %G=%MM(I) * %B/%V
310.   %C=%E - %G
315.   %LL(I) = LOG (%E/ %C) / %TT (I)
320.   %HH(I) = (-%K + SQR (%K+@* %K * %G)/2
322.   %J = %J + %LL(I)
325.   FP,%G, "", %LL(I)
330.   NEXT
332.   %J=%J/N
333.   %YY (O) = %J
335.   %Z=%HH (1)* %TT(1)
337.   %KK(1)=%Z* .5/%TT(1)
340.   For I=2 To N
342.   %Z = %Z + (%HH(I-1)+)* (%TT(I) - %YY (I-1)
344.   %KK(I) = %Z* .5/%TT(I)
348.   NEXT
349.   GOS.a
350.   P."H-IONS  INTEGRAL ""
351.   %Q = O
352.   FOR I = 1 to N
353.   FP.%HH(I), "", %KK(I)'
354.   %Q=%Q + %KK(I)
355.   NEXT
356.   %Q = %Q/N
357.   %XX (O)=%Q
358.   FP." AVERAGE K = "%J'
359.   FP." AVERAGE C = "%Q'
382.   IF O=S THEN GOTO Y
383.   GOS.a; O=O+1, GOTO g
384y  P."AVR. C(T) AVR.K(T)"
385.   FOR I=1 To O
    
```


386 FP.%XX(I), "", %YY(I)
 387 NEXT
 388 GOS.a
 390 %A=0; %B=0; %C=0;N=0
 392 %D=0;%E=0; %F=0
 393 FOR I=1 To N; %WW(I) = 1, NEXT
 394 FOR I = To N
 396 %W=%WW (I), %X = %XX(I)
 398 %U = %YY (I)
 400 %A=%A+%W; %B+%W* %X
 402 %C= %C + %W * %U
 404 %D= %D+%W* %X* %U
 406 %E= %E + %W* %X* %U
 408 %F= %F + %W* %U* %U
 410 NEXT
 412 %S = %A* %E - %B* %B
 414 %R = (%A* %D - %B* %C) / %S
 416 %Q = (%E* %C - %C* %B* %D) / %S
 418 %V=0
 420 FOR I = 1 To N
 421 %P = %LL (I) - %Q - %R* %KK(I)
 422 %V = %V + %P* %P

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