

## Hydrolysis of Methyl Formate in Aqueous Solutions And The Evaluation of Rate Constants

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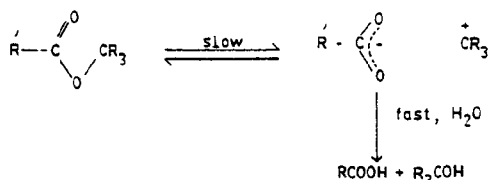
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**Summary:** Emphasis has been placed on the data for the hydrolysis of methyl formate in neutral medium over the temperature range 293-343 K to illustrate the method, employing numerical integration and the criteria of least squares for the evaluation of the first and second order rate constants in Kirmman's equation by sum of trapezoids. The values obtained for second order rate constant  $K_1$  ( $L \text{ mol}^{-1} \text{ sec}^{-1}$ ) contrast the values reported in literature. The hydrolysis of methyl 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.

### Introduction

Hydrolysis of esters has been studied by several investigators in acidic and basic medium [1-5]. 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 [6-8]. These reactions have the high enthalpies 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 the 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 Kirmman's equation [9] and to evaluate the first and second order rate constants by the method of sum of trapezoids described by

penttisaloma [10] and modified for the hydrolysis of esters in neutral medium in the present investigation.

### Results And Discussion

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

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

Where  $K_0$  ( $\text{sec}^{-1}$ ) is the rate constant for uncatalysed reactions. In dilute aqueous solutions in which pH control is maintained, hydrolysis follows first-order kinetics, and the observed rate-coefficient is given by the equation

$$K_{\text{obs}} = K_0 + K_H[H_3O^+] + K_{OH^-}[OH^-] \quad (2)$$

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.

If simple formates such as Methyl formates are hydrolyzed in neutral water, they hydrolyze sufficiently fast to make the concentration of  $H^+$  sufficiently large so that even in the initial stages the concentration of  $[OH^-]$  can be neglected. Therefore in (eq. 1)  $K_{OH^-}[OH^-]$  can be neglected in the study of

the neutral hydrolysis of simple formates. The remaining equation e.i.

is the same which was proposed by A. Kirmman [9] for the neutral hydrolysis of esters.

#### Kinetic Measurements:

Auto catalytic hydrolysis of esters is believed to obey the rate expression,

$$\frac{dx}{dt} = K_0(a-x) + K_1(a-x)C_{H^+} \quad (4)$$

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,  $K_1$  ( $L \text{ mol}^{-1} \text{ sec}^{-1}$ ) is the rate constant for acid-catalyzed reactions.

The solution of differential equation(4) may also be written as,

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

which on integration yields(11)

$$\frac{1}{t} \ln \frac{a}{(a-x)} = K_0 + K_1 \frac{1}{t} \int_0^t C_{H^+} dt \quad (6)$$

or

$$K_t = K_0 + K_1 C_t \quad (7)$$

Where  $K_t$  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,

$$C_t = \frac{1}{t} \int_0^t C_{H^+} dt \quad (8)$$

is the time average of hydron concentration over the interval (0,t). The value of the integral in Eqn. (8) 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 penttisaloma(10). Thus the integral (8) is evaluated on the basis of experimental data as a sum of the trapezoids.

$$C_t = \frac{1}{t} \int_0^t C_{H^+} dt = \frac{1}{2} \sum_{v=1}^t (C_{H^+_{v-1}} + C_{H^+_v})(\tau_v - \tau_{v-1}) \quad (9)$$

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

In equation (9)  $T_1=T$ ,  $T_0=0$ , 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

$$C_{H^+} = \frac{-K + \sqrt{K^2 + 4KC_f}}{2} \quad (10)$$

Where  $K$  is the acid dissociation constant of formic acid at the temperature in question,  $C_f$  is  $g.\text{moles L}^{-1}$  produced.

For the temperature dependence of this dissociation constant, Harned and Embree [11] have given the following equation

$$\text{Log}K = -(173.624/T) + 17.88348 \log T - 0.0280387T - 39.06123 \quad (11)$$

The values of  $K_t$  and  $C_t$  are calculated from the data of each run and both sets of values are averaged [12]. 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 7 becomes,

$$K_t^- = K_0 + K_1 C_t^- \quad (12)$$

To illustrate the method  $K_t^-$  was plotted verses  $C_t^-$  for methyl formate studied at 298 K. The

coefficients  $K_0$  and  $K_1$  were calculated by the method of least squares [13]. Each value pair ( $K_1$ ,  $C_1$ ) thus gave a point on the plot which represented the over all first order specific rate as a function of hydrogen ion concentration.

A "BASIC" computer program reproduced below performed the above calculations. The program 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.

## Computer Program

```

5      REM rate constants for hydrolysis of esters.
10     FDIM %MM(25), %HH(25), %LL(25), %KK(25)
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 =" %T
25     GOS.r; %E = VAL A; FP. "ESTER =" %E
26     GOS.r; %B = VAL A; FP. "BASE =" %B
27     GOS.r; %V = VAL A; FP. "VOLUME =" %V
32     GOS.r; %K = VAL A; FP. "DISS. CONST. =" %K
34     GOS.a : GOTO x
35a    P, $10
36     P, "PRESS SHIFT TO CONTINUE"
37     DO T = T + 1; WAIT
38     UNTIL ? ≠ BOOI <> ≠ FF
39     P, $10, RETURN
45x   P, "TIME ML "
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 = 7 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 = Q7R
270   UNTIL A7R = CH " " OR A7R = ≠D
280   IF A7R = ≠D Q = Q + 3
290   Q = Q + 1; A7R = ≠D; RETURN
300w  P, " G.MOLES /T LN A/(A-X) "
301   %J = O
302   FOR I = 1 TO N
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(I) * %TT (I)
337   %KK(I) = %Z * .5 / %TT(I)
340   FOR I = 2 TO N
342   %Z = %Z + (%HH(I-1) + %HH(I)) * (%TT(I) - %TT (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 = O; %B = O; %C = O; N = O
392   %D = O; %E = O; %F = O
393   FOR I = 1 TO N; %WW(I) = 1, NEXT
394   FOR I = 1 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 * %X
408   %F = %F + %W * %U * %U
410   NEXT I
412   %S = %A * %E - %B * %B
414   %R = (%A * %D - %B * %C) / %S
416   %Q = (%E * %C - %C - %B * %D) / %S
418   %V = O

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420 FOR I = 1 TO N
421 %P = %LL(I) - %Q - %R * %KK(I)
422 %V = %V + %P * %P
424 NEXT I
426 %Z = %V / (N - 2)
428 %L = SQR (%Z)
430 %J = SQR (%Z * %A / %S)
432 %K = SQR ((%Z / %A) * (1 + ((%B * %B) / %S)))
434 GOSUB a
435 P. $ 12
436 P. "LINEAR LEAST SQUARES FIT "
438 FP. "SLOPE = " %R '
440 FP. "SIGMA SQUARE = " %J '
442 FP. "INTERCEPT = " %Q '
444 FP. "SIGMA SQUARE = " %K '
446 FP. "ST. DEVIATION = " %L '
450 END
9000t (data)

```

To show the accuracy of the kinetic equations and the program, the results of calculations for methyl formate are shown in Table 1-3.

The values obtained for ( $K_t$ ,  $C_t^{-1}$ ) and the corresponding coefficients  $K_0 \text{ sec}^{-1}$  and  $K_1 \text{ L mol}^{-1} \text{ sec}^{-1}$  are shown in Table 4.

Table 1

t(min)	$C_t(10^3 \text{ g mol L}^{-1})$	$10^4 C_{H^+}$	$10^4 C_t$	$10^3 K_t$
774	1.05	3.52	1.76	2.81
1142	2.36	5.64	2.67	4.35
1468	3.94	7.51	3.54	5.74
2064	7.08	10.35	5.09	7.62
2476	9.18	11.90	6.09	8.44
2837	12.33	13.92	6.96	10.29
3522	14.43	15.13	8.43	9.98
3956	18.89	17.43	9.29	12.41
4310	21.25	18.54	10.01	13.30
5076	25.98	20.59	11.45	15.02
5510	27.55	21.23	12.19	15.14

**Experimental Conditions:**HCOOCH<sub>3</sub>, 0.05M; Temp., 298 K

Table 2

t(min)	$C_t(10^3 \text{ g mol L}^{-1})$	$10^4 C_{H^+}$	$10^4 C_t$	$10^3 K_t$
761	1.57	4.46	2.23	3.58
1128	3.40	6.93	3.36	5.32
1454	5.50	9.02	4.39	6.80
2050	10.21	12.59	6.26	9.37
2462	11.25	13.26	7.37	8.69
2824	17.80	16.89	8.36	12.87
3508	21.99	18.87	10.22	13.46
3942	25.13	20.23	11.25	14.27
4296	30.10	22.23	12.07	16.86
5062	32.45	23.11	13.67	16.03
5495	35.33	24.15	14.46	16.90

**Experimental Conditions:**HCOOCH<sub>3</sub>, 0.06M; Temp., 298 K

Table 3

t(min)	$C_t(10^3 \text{ g mol L}^{-1})$	$10^4 C_{H^+}$	$10^4 C_t$	$10^3 K_t$
731	2.11	5.29	2.65	4.20
1102	4.49	8.08	4.01	6.03
1429	7.13	10.39	5.20	7.54
2021	13.99	14.89	7.38	11.07
2435	17.96	16.98	8.83	12.22
2798	24.83	20.11	10.09	15.71
3481	27.99	21.40	12.19	14.73
3915	31.16	22.63	13.28	15.11
4269	35.65	24.26	14.12	16.75
4967	41.46	26.23	15.68	18.15

**Experimental Conditions:**HCOOCH<sub>3</sub>, 0.07M; Temp., 298 K

Table 4

Temp K	$10^4 C_t$ mol.L <sup>-1</sup>	$10^4 K_t$ min <sup>-1</sup>	$10^7 K_0$ Sec <sup>-1</sup>	$10^3 K_1$ L.mol <sup>-1</sup> Sec <sup>-1</sup>	* $10^3 K_1$ L.mol <sup>-1</sup> Sec <sup>-1</sup>
298	7.05	0.96	2.61	1.89	2.4 (14)
	8.51	1.13			2.47 (15)
	9.34	1.22			2.39 (16)

\*, values reported in literature

As can be seen, the values of  $K_1$  for the second order rate constant obtained indirectly in the neutral medium are slightly lower than those reported in the literature. In the neutral medium the reactions are pseudo first order and autocatalytic, which are superimposed by a second order reaction. The  $H^+$  produced during the reaction in the neutral medium acts as an acid while in the acidic medium acid is added to follow the reaction. So, the increase may be attributed to the fact that most workers have studied the reaction in acidic medium.

**Experimental**

The ester was prepared by the method of double decomposition between methyl sulphate and sodium formate according to the equation,



The hydrolysis of methyl formate was performed by using the same apparatus as designed by E. A. Moelwyn Hughe [17] shown in Fig. 1. 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 vessel. The reaction vessel containing mercury is immersed in a constant temperature bath. The reaction vessel was made airtight with a rubber bung which carried a capillary tube and a delivery tube. The capillary tube

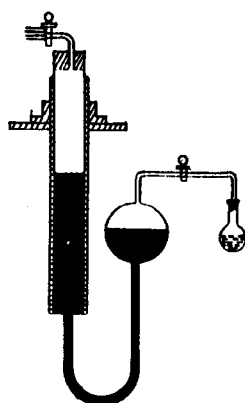


Fig. 1: Apparatus for the hydrolysis of esters designed by E.A. Moelwayn Hughes.

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, measure amount of reaction mixture e.i 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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