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NOTES

Study of the Ion-pair and Triple- Ion Formation by Conductivity Measurement

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Conductance of lactyl lactic acid in acetic acid-sulphuric acid mixtures (80% acetic acid and different concentration of sulphuric acid) has been measured at 45°C. The equivalent conductance at infinite dilution and the association constants have been calculated using Fuoss and Kraus equation. Addition of sulphuric acid further lowers the rate and exhibits formation of ion-pairs, triple-ions and higher aggregates. Effect of ionic strength, Arrhenius parameters and other molecular concepts etc. have been studied to discuss the mechanistic implications.

In recent years, binary solvents have been utilised for several kinetic mechanism of hydrolysis of esters[1–3]. Sarkar and Rakshit[4] have studied the solvent effects on the base hydrolysis of some β-keto and γ-keto esters and shown a mixed mechanism. Hydrolysis of lactyl lactic acid in aqueous solutions earlier reported proceeds only via the conjugate acid form as neutral form is inert[5] and exhibits ionic acceleration in the presence of sulphuric acid. Mishra and Saxena[6] have studied the acid hydrolysis of lactyl lactic acid and the influence of solvent media on the rate constants and shown the conventional effects of dimer of the medium. In the present work the relevent experimental data of solvent effect on kinetics of acid hydrolysis of lactyl lactic acid in dimer acetic acid—sulphuric acid media is reported.

Lactyl lactic acid was prepared by reported methods[5,6] and all other reagents were of A.R. or B.D.H. grade. All the reactions were carried out at 45 ± 0.01°C.

The rate of hydrolysis of lactyl lactic acid was studied at its different concentrations. The reaction rate coefficient in lactyl lactic acid hydrolysis was found to be independent of its concentration. Kinetic runs for the hydrolysis of lactyl lactic acid in AcH-H_2SO_4 (v/v) aqueous mixtures were made in the range 0·05–4.0 M H_2SO_4 in 80% AcH at 45°C. Reaction rate was measured by following conductivity method[7,8]. Pseudo-first order rate coefficients with respect to lactyl lactic acid were obtained throughout (Table 1). Observed rates gradually decrease with rise in

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TABLE 1

HYDROLYSIS OF LACTYL LACTIC ACID IN AcH-H_2SO_4 MIXTURES
Lactyl lactic acid = 9.6×10^{-2}M, AcH = 80%, Temp. = 45°C

S. No.	H_2SO_4 [M]	$10^3\ k_1$ min^{-1}	$1/[H_2SO_4]^2$	7 + log f AcH$_2^+$HSO$_4^-$]	[Ion-pair] $K_2\times10^6$	[Triple-ions] $K_3\times10^7$
01	0.05	0.683	399.900	1.7782	005.916	00001.906
02	0.10	0.632	100.000	1.7061	011.830	00007.626
03	0.15	0.601	044.360	1.6415	017.750	00017.160
04	0.20	0.583	025.020	1.5889	023.670	00030.500
05	0.25	0.563	016.010	1.5394	029.590	00047.650
06	0.30	0.521	011.110	1.4967	035.500	00068.630
07	0.35	0.511	008.162	1.4573	041.370	00093.440
08	0.50	0.453	003.999	1.3564	059.190	00182.100
09	0.75	0.402	001.777	1.2277	088.780	00429.000
10	0.85	0.383	001.385	1.1850	100.600	00550.900
11	1.00	0.321	000.000	1.1284	118.300	00762.600
12	1.50	0.292	000.444	0.9799	177.500	01716.000
13	2.00	0.273	000.250	0.8687	236.700	03057.000
14	2.50	0.235	000.160	0.7807	295.900	04765.000
15	3.00	0.213	000.111	0.7075	355.000	06863.000
16	3.50	0.195	000.082	0.6447	413.700	09344.000
17	4.00	0.153	000.063	0.5900	473.500	12200.000

acidity in the medium due to sulphuric acid. The equilibrium in the presence of various ions can be represented as:

$$CH_3COOH + H_2SO_4 \rightleftharpoons CH_3COOH_2^+ + HSO_4^- \qquad (1)$$

$$CH_3COOH + H\ HSO_4 \rightleftharpoons \underset{\text{(solvent ion-pair)}}{CH_3COOH_2^+HSO_4^-} \qquad (2)$$

Since H_2SO_4 behaves as the strongest acid amongst others in the medium of AcH, therefore such formation of solvent ion-pairs is quite apparent in 80% AcH. Though experimentally the existence of such ion-pairs is not examined. In the absence of this knowledge, using dissociation constant of H_2SO_4 in 80% AcH i.e. 4.4×10^{-6}, the fraction of the solvent ion-pairs expected to be present at each concentration of H_2SO_4 was calculated:

$$K = \frac{[AcH_2^+HSO_4^-]}{[AcH][H_2SO_4]} \qquad (3)$$

fraction:

$$[\mathrm{AcH_2^+HSO_4^-}] = \frac{[\mathrm{AcH_2^+HSO_4^-}]}{[\mathrm{AcH_2^+HSO_4^-}] + [\mathrm{AcH}] + [\mathrm{H_2SO_4}]} \tag{4}$$

For the purpose of calculation the first term of the denominator $[\mathrm{AcH_2^+\ HSO_4^-}]$, eq. (4), is neglected. The magnitudes of the fractions present at each concentration of H_2SO_4 are shown in Table 1. It has been noticed that the presence of such solvent ion-pairs in the medium too has relevant influence on the rate of hydrolysis of lactyl lactic acid; the plot obtained between K_{obs} and $[\mathrm{AcH_2^+HSO_4^-}]$ shows a linear decrease in rate, with specific retardation rate. The intercept of the plot on rate axis also inevitably shows that the specific retardation rate due to dimer $(\mathrm{AcH})_2$ is 7.0×10^{-3} min^{-1}.

It is, therefore, assumed that the constituted medium also helps in the ion aggregation with the substrate molecules i.e. the formation of ion-pairs, triple-ions or still higher aggregates, since acetic acid has low dielectric constant. The degree of association depends on its concentration. Hydrolysis of acetamide in AcH is also explained on similar lines by considering the formation of acetamidium ion, acetamidium ion-pair and triple-ions by Martin and others[9, 10]. Following the procedure of Fuoss and Kraus[8], a plot obtained between log λ_c (equivalent conductance) vs log $[H_2SO_4]$ is well illustrative of the formation of such ion aggregates (Table 2). The behaviour of the curve obtained can be expressed by the following relation:

$$\lambda_c = A/\sqrt{c} + B\sqrt{c} \tag{5}$$

TABLE 2

CONDUCTANCE DATA FOR LACTYL LACTIC ACID IN AcH-H_2SO_4 MIXTURES

Lactyl lactic acid = 9.6×10^{-2}M, AcH = 80%, Temp. = 45°C

H_2SO_4 [M]	λ_c ohm^{-1}	H_2SO_4 [M]	λ_c ohm^{-1}
0.350	069.75	0.025	148.50
0.321	078.85	0.019	151.73
0.250	089.38	0.015	155.84
0.125	113.49	0.010	159.93
0.085	118.67	0.008	168.32
0.054	126.54	0.006	173.54
0.044	128.69	0.004	185.64
0.037	133.79	0.003	180.48
0.029	144.32	0.001	178.86

where λ_c is the equivalent conductance at some known concentration of H_2SO_4. A and B are constants for the medium and c is the total concentration of the acid. Since cm (concentration at minimum) $= A/B$ and $(\lambda_c)_m = 2AB$, association constants for ion-pairs and triple-ions were obtained, and are

$$K_1 = 12.33\times10^{-4} \text{ (Ion-pair)}$$

$$K_2 = 7.943\times10^{-4} \text{ (Triple-ions)}$$

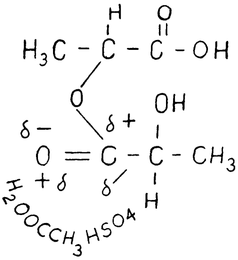
The possible ion-pairs, triple-ions or still higher aggregates may be formulated as:

$$[SH^+] + [HSO_4^-] \rightleftharpoons [SH^+HSO_4^-] \qquad (6)$$

$$[SH^+] + 2[HSO_4^-] \rightleftharpoons [HSO_4^-SH^+HSO_4^-] \qquad (7)$$

$$[SH^+] + [CH_3COOH_2^+HSO_4^-] \rightleftharpoons [CH_3COOH_2^+HSO_4^-SH^+] \qquad (8)$$

where SH^+ is the conjugate acid form of the substrate. Such an aggregation involving substrate ions is expected to lower its reactivity on one side and at the same time also responsible to hinder sterically attack by the water molecule. Possibility of attack by a nucleophile (water) can also be lowered due to cage type blockade by the existing ions in the medium even over a neutral molecule of lactyl lactic acid. As changes of protonation of substrate moles by H_2SO_4 are lowered much due to the presence of AcH in the medium[11, 12],



Therefore, considering the various equilibria for the formation of ion associations and using association constants $K_1 = 12.33\times10^{-4}$ and $K_2 = 7.943\times10^{-4}$, the concentrations of existing ion-pairs and triple ions were calculated (Table 1). Thus the retardation caused in the observed rate of hydrolysis of ester acid due to these ion-pairs and triple-ions was calculated by using the following relations:

$$4 + \log K_1 = 2.113\times10^{-3} - 0.4(6 + \log K_2)\,\frac{[H_2SO_4]}{[\text{Lactyl lactic acid}]} \qquad (9)$$

$$4 + \log K_1 = 1.122\times10^{-3} - 0.17(7 + \log K_3)\,\frac{[H_2SO_4]^2}{[\text{Lactyl lactic acid}]} \qquad (10)$$

Since contribution in the observed rates at various acidities of H_2SO_4 due to both ion-pairs and triple-ions is almost constant and is of the similar order and also as there is not much difference between the two computed association constants (K_1 and K_2), thus the overall rate of hydrolysis of lactyl lactic acid in AcH-H_2SO_4 mixtures could be calculated from the relation:

$$10^3 \text{ kcal} = KS_1[(AcH)] - KS_2[CH_3COOH_2^+HSO_4]$$
$$-KS_3[SH^+HSO_4^-][HSO_4^-SH^+HSO_4^-][H_2SO_4] \times a^*_{H_2O} \quad (11)$$

where KS_1, KS_2 and KS_3 are the specific retardation rates due to dimer, solvent ion-pair, and ionic associations (both ion-pairs and triple-ions), respectively. The concentrations of the species $(AcH)_2$ is kept *ca.* 80% throughout [$CH_3COOH_2^+HSO_4^-$], [$SH^+HSO_4^-$] and [$HSO_4^-SH^+HSO_4^+$] are directly dependent on H_2SO_4 values of $a^*_{H_2O}$ used above 1.0 M are those of H_2SO_4 in aqueous solutions.

Few kinetic runs were also carried out by taking small volumes of water in order to judge its effect on the rate of hydrolysis of lactyl lactic acid keeping concentration of various other ionic species in the system constant. The rate data obtained reveals that the increase in concentration of water molecules helps in accelerating the rate of hydrolysis. Water molecule is, therefore, included in the rate determining step.

In order to investigate the cause of decrease in rates in acid media, it was thought necessary to examine the effect of ionic strength on the rate of hydrolysis of the lactyl lactic acid. Kinetic runs were carried out at a series of ionic strength which were maintained by using appropriate mixtures of sodium sulphate and sulphuric acid. The rate coefficients for all the kinetic runs have been summarised in Table 3.

The graph plotted between rate coefficients and acid molarity, the curves do not show that lactyl lactic acid does not undergo acid catalysis. Since the three linear curves meet at a point on the rate axis making some intercept, the contribution of neutral hydrolysis to the overall rate of the reaction is said to be constant. The negative slopes of the linear curves show the absence of acid catalysed hydrolysis and as the value of negative slopes decreases with the increase in ionic strength and since the slopes of the linear plots increase with the increase in ionic strength, the hydrolysis of lactyl lactic acid exhibits positive salt effect. Since the contribution of the neutral rate, to the overall rate of hydrolysis, is constant, this indicates the non-variation of neutral rate with the changes in ionic strength.

Kinetics of hydrolysis is also studied at four different temperatures i.e. 35°, 45°, 55° and 65°C, which permits the determination of Arrhenius parameters: $E = 2.6$ kcal. mole^{-1}, $A = 9.3$ min^{-1} and $-S = 71.0$ e.u. Three values of energy of activation (E) in AcH, AcH-$HClO_4$ and AcH-H_2SO_4 media are contradictory to the observed facts; however, the large magnitude of S in AcH-H_2SO_4 mixture may be due to high solvation and increased alkylation of the substrate[13, 14].

TABLE 3

HYDROLYSIS OF LACTYL LACTIC ACID AT DIFFERENT CONSTANT IONIC STRENGTH

Lactyl lactic acid = 9.6×10^{-2}M, AcH = 80%, Temp. = 45°C

H_2SO_4 (N)	Na_2SO_4 (N)	$10^3 k_1$ min^{-1}	Intercept		Slope
$\mu = 0.05$					
0.0050	0.0150	0.6050			
0.0075	0.0125	0.5430			
0.0100	0.0100	0.4340	7.0×10^{-3} min^{-1}	k_1	−20.0
0.0125	0.0075	0.4210			
0.0150	0.0050	0.4040			
$\mu = 0.25$					
0.0100	0.0900	0.6483			
0.0250	0.0750	0.5234			
0.0500	0.0500	0.3012	7.0×10^{-3} min^{-1}	k_1	−07.5
0.0750	0.0250	0.1282			
0.0900	0.0100	0.0184			
$\mu = 0.50$					
0.0100	0.1900	0.6821			
0.0500	0.1500	0.5642			
0.0750	0.1250	0.4832	7.0×10^{-3} min^{-1}	k_1	−02.5
0.1000	0.1000	0.4135			
0.1500	0.0500	0.2734			

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