Oxidative Transformation of Lactic Acid By Pyridiniumdichromate in Non-Aqueous Medium-Kinetic and Mechanistic Study
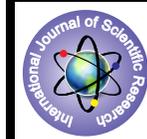
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ABSTRACT *The alpha-hydroxy acids (AHA) are naturally occurring organic acids.The oxidation of lactic acid by pyridiniumdichromate has been studied spectrophotometrically in the presence of p-toluenesulphonic acid (PTSA) in dimethylsulphooxide(DMSO) as solvent. The reaction is first order with respect to oxidant and [H+]. Michaelis–Menten type kinetics is observed.The rate of reaction decreases with an increase in the polarity of solvent indicating an ion–dipole interaction in the slow step. The reactions exhibit no primary kinetic isotope effect. The activation parameters have been evaluated.*

Introduction-
Hydorxy and carboxylic acids (in particular water soluble) play significant role in many biological processes as well as in organic synthesis. Oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry.[1-5] For this a number of different chromium(VI) derivatives have been reported.[6-9]

The oxidation of α-Hydroxy acids by Pyridinium Dichromate (PDC) has been studied by Ahmed S.Zaheer et.al[10]. The reaction is pseudo first order, with respect to hydroxy acid, [H+] and [PDC]. Hiran et.al.[11] studied the oxidation of lactic and mandelic acid by quinolinium dichromate in aqueous acetic acid medium. The reaction is first order in each reactant. The kinetics of oxidation of lactic acid[12] and oxalic acid[13] by pyridiniumdichromate in perchloric acid medium studied by Dangarh et al. Active oxidizing species involved is protonated PDC.

Materials and Method-
Pyridiniumdichromate was prepared by the method describe in the literature [14] and its purity was checked by iodometrically and by IR spectrum.

Lactic acid (A.R.grade) was used as supplied. DMSO was purified by distillation. All other reagents used were of "AnalaR" grade.

The pseudo-first order conditions were attained by keeping a large excess of the hydroxy acid over PDC. The temperature was kept constant to ± 0.1 K.The solvent was DMSO. The reactions progress was followed by monitoring the decrease in the concentration of PDC spectrophotometrically at 385 nm forup to 80% of the reaction.

RESULTS AND DISCUSSION:
Effect of Substrate-
At constant [PDC], the rate constants for oxidation calculated at different initial concentration of substrates found to increase linearly with the increase in concentration of substrates (2×10^{-2}M to 6×10^{-2}M). The results are summarized in (Table - 1). A plot of log k_1 against log [substrate] gives a straight line revealed that the rate of oxidation is first order with respect to the acid. It has been found that plot of [$1/k_1$] versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating Michaelis–Menten type kinetics.

Effect of H+ Ion-
To study effect of hydrogen ion p-toluenesulphonic acid was used. The rate of oxidation was studied from [H+] = 0.0 M to 1.6
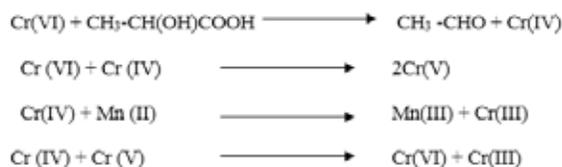
M. It was observed that rate increases with increase in hydrogen ion concentration. log k_1 v/s log [H+] is a stright line in all the cases and the slopes ar near to one. The results are summarized in Table-1.

Effect of Solvent composition-
Effect of solvent was studied by changing proportion of DMSO and water; varied from 10 to 50 % water v/v. The reaction rate decreases with an increase in the percentage of water, suggesting that a low dielectric medium favors the oxidation (Table-1). A plot of log k_1 against 1/D (dielectric constant) is linear with a positive slope for the acids under study. This indicates an ion–dipole type of interaction in the rate-determining step[15-17].

Effects of Mn (II) and Ce (III) Ion-
It has been observed that addition of low concentration of Mn (II) and Ce (III) ions retard the rate of oxidation of acids. The retardation of the rate by addition of Mn(II) ion can be explained by te dispropotion of Cr(VI), Cr(V) and Cr(III). The general scheme of oxidation of acids with PDC may be represented as:

$$Cr(VI) + CH_3\text{-}CH(OH)COOH \longrightarrow CH_3\text{-}CHO + Cr(IV)$$
$$Cr(VI) + Cr(IV) \longrightarrow 2Cr(V)$$
$$Cr(IV) + Mn(II) \longrightarrow Mn(III) + Cr(III)$$
$$Cr(IV) + Cr(V) \longrightarrow Cr(VI) + Cr(III)$$

This may be taken as evidence for formation of Cr (IV) species and hence PDC is acting as two-electron transfer oxidant[12].

Effect of Temperature-
Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (303 to 323 K). In all the cases, a plot of log k_{obs} versus 1/T (inverse of absolute temperature) is a straight line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation is 72.56 kJ mol^{-1}. The negative entropy suggests the formation of cyclic intermediate from acyclic species. (Table 2 &3)

Conclusion-
Oxidative transformation of lactic acid is first order with respect to oxidant and [H+].Glasston[18] has pointed out that if entropy of activation is negative, the reaction is slow. Kemp and Water[19] suggest that C-H fission must occur with Cr(VI). Littler[20] has shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr (VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus the overall mechanism is pro-

posed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product. The observed negative value of entropy of activation also supports a polar transition state.
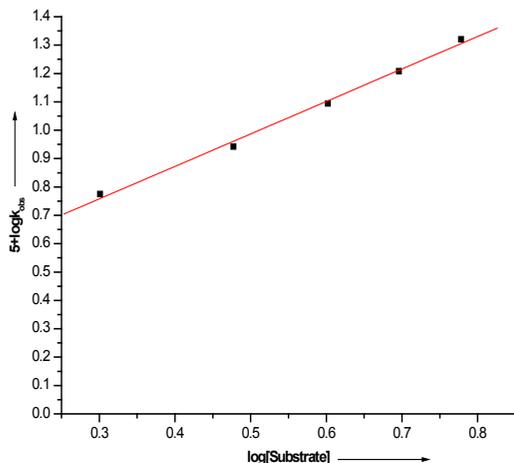
Fig—Variation of rate with [Lactic acid]

TABLE NO. 1
Effect of [Substrate], [H⁺] and Solvent
[PDC] = 2 x 10⁻³ M   T = 308 K

[Substrate] x 10² M	[PTSA] x 10³ M	Water in DMSO % v/v	k_1 x 10⁵ , sec⁻¹
2.0	3	0	17.84
3.0	3	0	23.07
4.0	3	0	29.09
5.0	3	0	34.78
6.0	3	0	40.68
2.0	3	0	17.84
2.0	3.5	0	20.07
2.0	4.0	0	22.3
2.0	4.5	0	25.57
2.0	5.0	0	28.85
2.0	5.5	0	31.74
2.0	6.0	0	34.63
2.0	3	10	16.08
2.0	3	20	11.77
2.0	3	30	9.78
2.0	3	40	8.67
2.0.	3	50	7.95

TABLE NO. 2 Effect of Temperature
[Substrate] = 2 x 10⁻² M   [PTSA] =3 x 10⁻³ M   [PDC] = 2 x 10⁻³ M

Temp (K)	k_1 x 10⁵ , sec⁻¹
303	5.97
308	8.98
313	15.13
318	24.2
323	33.89

TABLE NO. 3
THERMODYNAMIC PARAMETERS

Substrate	log A	Energy of activation $\Delta E^{\#}$ kJ mol⁻¹	Entropy of activation $\Delta S^{\#}$ Jmol⁻¹K⁻¹	Free energy of activation $\Delta G^{\#}$ kJ mol⁻¹	**Enthalpy of activation ΔH kJ mol⁻¹**
Lactic acid	12.50	72.56	-9.57	2.96	70.04

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