

Activation parameters in the Elucidation of Reaction Mechanism: Oxidation of Mandelic Acid by Lead Tetra-acetate

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Recent work on the decomposition of lead tetra-carboxylates in benzene has provided convincing evidence for the mediation of free radicals¹. It is also well known that bases like pyridine catalyse the oxidation of alcohols, α -hydroxy acids and formic acid² by lead tetra-acetate, Pb(IV). Here it is assumed that role of pyridine in a non-polar solvent like benzene is one of diverting the homolytic path to that involving the heterolytic cleavage of the Pb-O bond³. Since hydroxy acids are reported to undergo C-C bond cleavage with Pb(IV)⁴, it was considered fruitful to investigate the oxidation of mandelic acid in benzene and in benzene containing pyridine with particular reference to the evaluation of activation parameters in the two media. Since our findings were unusual, it prompted us to make a preliminary report on the reaction.

Solvents and reagents used were purified and dried in a conventional manner. Pb(OAc)₄, prepared by the method of BAILAR⁵ (purity 98% after recrystallisation twice from AcOH) was washed several times with

benzene and then used to prepare its solution in benzene. The reaction was carried out in a thermostat ($\pm 0.02^\circ\text{C}$) and was followed by the method of CORDNER and PAUSACKER⁶. In every case 1% AcOH (v/v) was added to avoid phase separation and to keep Pb(OAc)₂ in solution. A parallel blank was always run to account for the decomposition, if any, of Pb(IV). Oxidation of mandelic acid in both media gave mainly benzaldehyde ($85 \pm 5\%$) identified and estimated as its 2 : 4 dinitrophenylhydrazone.

Mandelic acid (α -D; 98% deuterated) was prepared by the method of KEMP and WATERS⁷. Ph.Ch(OD)COOD and Ph.CD(OD)COOD (both 95% deuterated) were prepared by refluxing their protiated analogues with D₂O (>98%; supplied by B.A.R.C., Trombay, Bombay, India) for four hours three times; each time fresh D₂O was used after vacuum distilling the solvent. Reaction with these two compounds were carried out in presence of AcOD(1% (v/v)) prepared by refluxing redistilled acetic anhydride with a desired amount of D₂O.

As the reaction was too fast to be measured under pseudo first order conditions it was studied under second order conditions. Solubility of mandelic acid and Pb(IV) limited the choice of measurement.

Second order rate constants k_2 ($= 3.87 \pm 0.15 \times 10^{-1} \text{ l mole}^{-1}\text{sec}^{-1}$) do not vary significantly with variation of initial [mandelic acid] (1.2 to $2.6 \times 10^{-3}\text{M}$, [Pb(IV)]: $1.0 \times 10^{-3}\text{M}$; t 35°C). The fair constancy of k_2 values for individual runs indicated a first order dependence on [Pb(IV)] and mandelic acid. The order with respect to these reagents remains unchanged in presence of pyridine. The order in pyridine is one (cf. Table I) Tables II and III record the data on the effect of

Table I. Variation of k_2 ($\pm 5\%$) with initial pyridine.

[Pb(IV)] : = [Mandelic acid] : $1.0 \times 10^{-3}\text{M}$ t : 25°C					
[Pyridine] $\times 10^3\text{M}$:	0.0	0.05	1.0	2.0	4.0
$k_2 \times 10 \text{ l mole}^{-1}\text{sec}^{-1}$:	2.84	7.00	10.8	18.9	35.7
$k_2 \times 10 \text{ l mole}^{-1}\text{sec}^{-1}$:	—	4.16	7.96	16.1	32.8
$(k_2/[\text{Py}]) \times 10^{-2} \text{ l}^2 \text{mole}^{-2}\text{sec}^{-1}$	—	8.32	7.96	8.05	8.20

$$k'_2 = k_2 - 2.84$$

Table II. Temperature dependence of rate in benzene.

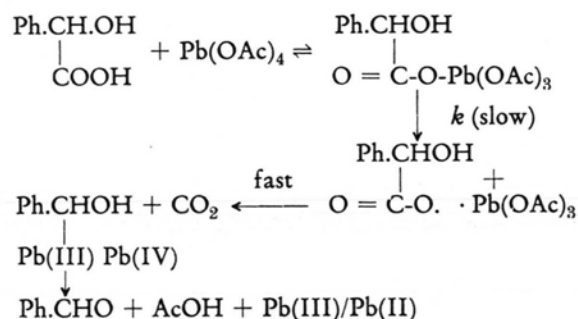
[Pb(IV)] : = [Mandelic acid] : $2.5 \times 10^{-3}\text{M}$						
t :	25	30	35	40	ΔH^*	ΔS^*
$k_2 \times 10$	2.12	2.61	3.34	4.48	kcls/mole	e.u.
($\text{l mole}^{-1}\text{sec}^{-1}$)					8.4 ± 1.5	-34 ± 5.0

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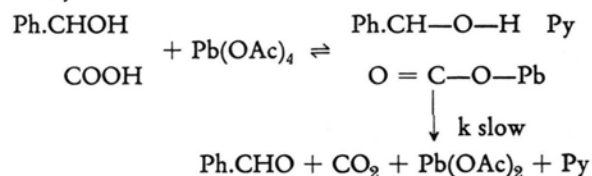
Table III. Temperature dependence of rate in benzene containing pyridine.

[Pb(IV)]: = [Mandelic acid]: $1.0 \times 10^{-3}M$ [Py]: $5.0 \times 10^{-4}M$						
t :	25	30	35	40	ΔH^*	ΔS^*
$k_2 \times 10$ (l/mole. sec.)	4.88	9.39	15.1	27.0	20.9 ± 1.5	$+24 \pm 5.0$
Corrected for the rate in absence of pyridine; ΔS^* calcd. using $k_3 = (k_2/[Py])$						

temperature on the rate of uncatalysed and catalysed reactions respectively. It is interesting to note that activation parameters in both media are quite different whereas the oxidation product is the same *i.e.* benzaldehyde. This indicates that the mechanism of oxidation of mandelic acid is different in these media. Since carboxylic acids are known to undergo rapid anion exchange reaction with Pb(IV), reaction in a non-polar medium can be assumed to resemble the oxidation of carboxylic acids by Pb(IV).



The mechanism is also consistent with the results on the study of kinetic isotope effect (*cf.* Table IV) in benzene. On the basis of data of Table IV it seems plausible to suggest following mechanism for pyridine catalysed reaction:



It appears that entropy of activation has a compensatory effect on the catalysed rate of oxidation of mandelic acid by Pb(IV). A low kinetic isotope effect (k_H/k_D) suggests an asymmetric transition stage. The reaction does not seem to be typical of mandelic acid, as α -hydroxy isobutyric acid also behaves likewise. (*cf.* Table V).

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Table IV. Kinetic isotope effect studies.

[Pb(IV)]: = [Mandelic acid]: $1.0 \times 10^{-3}M$; t : 25°		
Substrate	$k_2 \times 10$ (l mole ⁻¹ sec ⁻¹)	
	In benzene	In benzene-pyridine*
Ph.CH(OH)COOH	2.20	3.82
Ph.CD(OH)COOH	2.12	3.78
Ph.CH(OD)COOH	2.18	3.20
Ph.CD(OD)COOH	2.15	3.15

Table V. Activation parameters of the reaction of α -hydroxy isobutyric acid with Pb(IV).

$\Delta H^* = 10 \pm 1.5$ kcal.mole ⁻¹ ;	$\Delta S^* = -45 \pm 5.0$ e.u. in benzene.
$= 29 \pm 1.5$ kcal.mole ⁻¹	$= +30 \pm 5.0$ e.u. in benzene-pyridine

* [Py]: $5.0 \times 10^{-4}M$

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