Kinetics & Mechanism of Oxidation of Benzyl Alcohol & 1-Phenylethanol by Lead Tetraacetate

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Oxidation of benzyl alcohol (BnOH) and 1-phenylethanol by lead tetraacetate is first order with respect to the oxidant and second order with respect to the alcohol. Addition of pyridine increases the reaction rate; the catalysed reaction being first order in pyridine. In the presence of pyridine, the reaction shows a first order dependence on each of the oxidant and the alcohol. The oxidation of benzhydrol (α-H and α-D) exhibits a kinetic isotope effect. A mechanism involving a slow decomposition of the Pb(IV)-alkoxide derivative with heterolysis of the Pb-O bond has been suggested.

OXIDATION of alcohols by lead tetraacetate (LTA) is postulated[1] to involve the initial formation of a complex of the type RO-Pb (OAc)$_3$. However, Pocker and Davis[2] suggested the possibility of higher complexes of the type (RO)$_n$ Pb(OAc)$_{4-n}$ in the oxidation of methanol. Partch and Monthony[3] also postulated complexes of the type [(RO)$_n$Pb(OAc)$_{4-n}$ pyridine] in the oxidation of butanol in pyridine. With a view to verifying the above possibilities we undertook studies on the kinetics of oxidation of benzyl alcohol (BnOH) and 1-phenylethanol by LTA in benzene, both uncatalysed by pyridine, and suggested a probable mechanism. The kinetic isotope effect on the LTA oxidation of benzhydrol was studied.

Materials and Methods

BnOH (Rhodia) and 1-phenylethanol (L. Light) were distilled under reduced pressure, before use. Solvents and others reagents used were purified and dried as usual. α-Deuteriobenzhydrol was prepared by the method of Shanker and Suresh[4], and the isotopic purity was determined to be $85 \pm 3\%$ by its NMR spectrum. LTA was prepared by the method of Blair[5], and recrystallized twice from AcOH (purity = 98%).

Kinetic measurements — Since benzene was used as the solvent, AcOH (1%, v/v) was added in every case to avoid phase separation and to keep Pb(OAc)$_2$ in solution. Conductivity measurements showed that there was no appreciable interaction between pyridine and acetic acid in this medium, and hence no correction was applied for the initial [pyridine]. The reactions were conducted under psuedo-first order conditions by keeping a large excess of the alcohol over LTA, and were followed by the method of Cordner and Pausacker[6]. The temperature was maintained within $\pm 0.1°$. A parallel blank was always run to account for the decomposition, if any,

of LTA. The observed oxidation rates of pyridine-catalysed reactions were corrected for the rate of the uncatalysed reaction. Similarly the oxidation rate of α-deuteriobenzhydrol was corrected for its proton content. The rates were computed from the plots of log [LTA] against time and were reproducible within $\pm 4\%$.

Results and Discussion

The kinetic and other experimental data were obtained for the oxidation of both BnOH and 1-phenylethanol. Since the results are similar, only those of BnOH are reported here.

Stoichiometry and product analysis — The main oxidation products of BnOH and 1-phenylethanol (both catalysed and uncatalysed), were benzaldehyde and acetophenone, respectively and these were characterized and estimated as their 2,4-dinitrophenylhydrazones.

Excess of LTA was allowed to react with BnOH ($2.5 \times 10^{-3}M$) in the presence of varying amounts of pyridine and the unreacted oxidant estimated. In those cases where the carbonyl product was estimated, the reactions were conducted with an excess of the alcohol. The values of LTA and alcohol consumed and the carbonyl product formed corresponded to the reaction shown in Eq. (1).

$$Ph.CHOH.R + Pb(OAc)_4 \rightarrow Ph.CO.R + Pb(OAc)_2 + 2AcOH \quad ...(1)$$
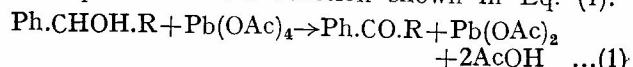
Rate laws — The reaction was found to be first-order with respect to the oxidant and was independent of the initial [LTA]. At [BnOH] = $4.37 \times 10^{-2}M$ and 308 K, the values of the rate constant (k_1) were 4.18, 5.02, 4.85 and 4.99×10^{-5} sec^{-1} at [LTA] = 5.00, 6.20, 8.30 and $10.0 \times 10^{-3}M$ respectively. For the uncatalysed reaction, the order with respect to BnOH was two (Table 1) whereas for the pyridine-catalysed reaction, the order with

TABLE 1 — EFFECT OF VARYING [SUBSTRATE] ON THE REACTION RATE, IN THE ABSENCE OF PYRIDINE

$\{[LTA] = 5\cdot0 \times 10^{-3}M$; temp. $= 308$ K$\}$

| [BnOH] $\times 10^2$ M	$k_1 \times 10^5$ sec^{-1}	$k_1 \times 10^2/[BnOH]^2$
4·37	5·18	2·71
6·25	8·83	2·26
8·75	16·1	2·10
11·2	29·2	2·33

respect to LTA remained unchanged and was one with respect to the substrate. At $[LTA] = 5 \times 10^{-3}M$ [pyridine] $= 0\cdot20M$ and temp. $= 308$ K, the values of the rate constant (k_1) were 4·50, 8·20, 14·5 and $20\cdot2 \times 10^{-5}$ sec^{-1}, respectively at [BnOH] $= 2\cdot5$, 4·37, 8·75 and $11\cdot2 \times 10^{-2}M$. The reaction showed a first-order dependence in pyridine. At $[LTA] = 5\cdot0 \times 10^{-3}M$, [BnOH] $= 4\cdot37 \times 10^{-2}M$ and temp. $=$ 308 K, the values of k_1 were 3·75, 8·20, 12·2 and $15\cdot7 \times 10^{-5}$ sec^{-1} at [pyridine] $= 0\cdot10$, 0·20, 0·30 and 0·40M respectively.

An attempt was made to detect the formation of free radicals during the oxidation in benzene using acrylonitrile under nitrogen atmosphere. No free radicals could be detected.

The oxidation of alcohols by LTA is considered to occur via Pb(IV)-alkoxide. In fact, Criegee[7] has reported the precipitation of a complex Pb(OAc)$_2$ (OMe)(OH) from LTA and moist methanol. The strict second order dependence on [alcohol] suggests that the reaction proceeds through the disproportionation of the dialkoxide derivative, the mono-alkoxide derivative being kinetically insignificant.

Disproportionation of the dialkoxide derivative may either involve a heterolysis of Pb-O bond with the rupture of a C-H bond, or a rapid sequential two successive one-electron process. The presence of the kinetic isotope effect in the oxidation of benzhydrol and the failure to induce polymerization of acrylonitrile suggest that the disproportionation involves a 2-electron process. It may be mentioned here that the homolytic oxidation of alcohols in non-polar solvents produces fragmentation products, tetrahydrofurans and tetrahydropyrons[8,9]. Absence of such products indicates a heterolytic disproportionation. Thus, the mode of the oxidation may be represented as shown in Eqs 2 and 3.

The observed negative entropies of activation (Table 2) also favour this mechanism over the homolysis of Pb-O bond.
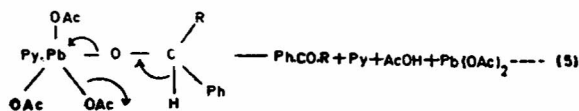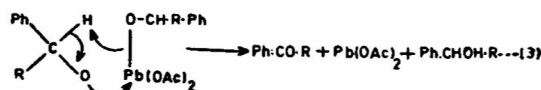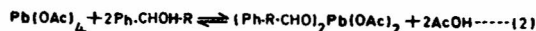
The reaction in the presence of pyridine is smooth and involves heterolysis of Pb-O bond[3]. The first order dependence on [alcohol] shows that pyridine coordinates with Pb(IV) to form a complex of the type [Pb(OAc)$_4$(C$_5$H$_5$N)]. Such a complex has been isolated from benzene by Partch and Monthony[3]. The LTA-pyridine complex reacts with the alcohol to give an intermediate (Eq. 4) which then disproportionates via the heterolysis of Pb-O bond to give the products (Eq. 5).

The increased polarization interaction in Pb-N bond as compared to Pb-O bond renders the complex more labile and electrophilic. When [pyridine]$\gg$[Pb(IV)] the effective concentration of the species like LTA-Py will be fairly constant and catalysis due to pyridine seems to be more profound. Further, in the presence of pyridine a high kinetic isotope effect ($\simeq$4·9) (Table 3) in the oxidation of benzhydrol is probably due to catalysis by pyridine. Partch and Monthony[3], however, indicated against pyridine catalysis in the oxidation of butanol. Their results differ from those of ours because in the oxidation of butanol in benzene, variation in [pyridine] does not alter the rate of oxidation.

TABLE 3 — KINETIC ISOTOPE EFFECT IN THE OXIDATION OF BENZHYDROL

$\{[LTA]=5\cdot0 \times 10^{-3}M$; [Alcohol]$=0\cdot05M$; temp.$=308$ K$\}$

[Pyridine] M	10^5k, sec^{-1}		k_H/k_D
	α-H	α-D	
0·00	2·33	1·10	2·01
0·20	18·5	3·80	4·87

TABLE 2 — TEMPERATURE DEPENDENCE AND ACTIVATION PARAMETERS

Alcohol	10^3k litre^2 mole^{-2} sec^{-1}				$\Delta H\ddagger$ kJ mole^{-1}	$-\Delta S\ddagger$ J mole^{-1} K^{-1}
	303 K	308 K	313 K	318 K		
	IN THE ABSENCE OF PYRIDINE					
BnOH	16·7	22·6	26·4	32·8	37·4	160
1-Phenylethanol	2·88	3·45	4·41	5·18	31·5	194
	IN THE PRESENCE OF PYRIDINE					
BnOH	8·95	9·41	12·9	33·6	33·6	178
1-Phenylethanol	4·18	5·66	7·51	9·28	44·1	149

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