

NOTE

Comments on the Pyridine Catalysed Reaction of Alcohols with Lead Tetraacetate in Benzene Containing 1% Acetic Acid (v/v)

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The role of pyridine in catalysis, as ligand or proton abstracting base, in the lead tetra-acetate oxidation of alcohols has been evaluated using a novel molecular geometry (and kinetics) approach.

Key words: Pyridine, catalysed, reaction, alcohol, lead tetraacetate

Oxidation of some alcohols by lead tetra-acetate (LTA) in benzene containing 1% acetic acid (v/v) proceeds through the formation of dialkoxy Pb(IV) derivative $(RO)_2Pb(OAc)_2$,^{1,2} as evidenced by a second order rate dependence on $[R(OH)]$. Interestingly in such cases, there is little or no contribution of the rate of disproportionation of monoalkoxy derivative of Pb(IV), $(RO)Pb(OAc)_3$, to the observed overall rate. This follows from a linear plot² of k_0 and $[R(OH)]$, which passes through the origin. Normally $Pb(OAc)_4$ is a flattened dodecahedron (triangulated dodecahedron)³. However, the most probable geometry of the dialkoxy Pb(IV) derivative in solution is expected to be a tetrahedron. Thus, due to the release of lattice constraints, $Pb(OAc)_4$ in solution may also be tetrahedral. The fact that $Pb(OAc)_4$ undergoes a fast exchange reaction with carboxylic acids⁴ also favours tetrahedral structure in solution over the flattened dodecahedral structure.

If so, the role of pyridine in these reactions needs a re-examination. In presence of pyridine $Pb(OAc)_4$ py adduct is supposed to be formed⁵, and the dependence on $[R(OH)]$ changes from second order to first order† rate dependence^{1,2,7}. Now if the penta-coordinated adduct is the reactive species, then it is expected to be trigonal bipyramidal with pyridine in the trigonal plane. Such a reactive species $Pb(OAc)_4$ ·py is bound to form $(RO)_2Pb(OAc)_2$ ·py in a much more facile manner than $(RO)_2Pb(OAc)_2$ in the same medium in absence of pyridine. Experiments do not however support this, and the formation of $(RO)Pb(OAc)_3$ ·py is indicated,

†This implies that one of the coordination positions of Pb(IV) is fully occupied by pyridine and the contribution of dialkoxy complex is insignificant compared to mono-alkoxy complex in the overall reaction rate. Sterically also, dialkoxy complex formation can be precluded as incompatible with pyridine catalysis (cf. ref. 7 For similar catalysis with 2,6-lutidine.)

which disproportionates because of the labilising influence of Pb-N bond on the Pb-O bond of $(RO)Pb(OAc)_3 \cdot Py$. An increase in the concentration of pyridine should limit the rate when $[Py] \gg [Pb(IV)]$ by limiting the concentration of $Pb(OAc)_4 \cdot py$. This too is not borne out by experiments¹ and a steady increase in rate is observed which has a first order dependence on $[py]$. We feel that the role of pyridine, here, is one of removal of $-C-H$ as proton. This is supported by primary kinetic isotope effect (cf. Table-1) and the fact that 2,6-lutidine, which cannot complex with Pb(IV), also catalyses these reactions. At $[LTA] = 5.0 \times 10^{-3} M$, $[benzyl\ alcohol] = 4.37 \times 10^{-2} M$ and temperature = 308 K, the values of k_t were 3.75, 8.20, 12.2 and $15.7 \times 10^{-5} sec^{-1}$ at $[pyridine] = 0.10, 0.20, 0.30, 0.40 M$ respectively¹, while k_t were 5.01 and $9.15 \times 10^{-5} sec^{-1}$ at $[2,6-lutidine] = 0.10$ and $0.20 M$ respectively⁶. (Similar results were obtained with 1-phenyl ethanol.) This certainly rules out the formation of $Pb(OAc)_4 \cdot py$ species as the precursor to the rate limiting step. We felt that these bases not only assist the rate limiting step by removing the H of $\alpha-C-H$ as proton but also assist the formation of the mono-alkoxy derivative $(RO)Pb(OAc)_3$ by removing the H of R(OH), again as proton, thereby increasing the concentration of $(RO)Pb(OAc)_3$.

Thus the catalysis due to pyridine and 2,6-lutidine can be summed up as:

- (i) Assisting the formation of $(RO)Pb(OAc)_3$, and
- (ii) Acting as a base in removing the H of $\alpha-C-H$ as proton:

TABLE-1
KINETIC ISOTOPE EFFECT IN THE OXIDATION OF BENZHYDROL¹
(cf. Ref 2 also)

$[LTA] = 5.0 \times 10^{-3} M$; $[Alcohol] = 0.05 M$; temp. = 308 K

[Pyridine] M	$\alpha-H$	$\alpha-D$ ($10^5 k_1 sec^{-1}$)	kH/kD
0.00	2.33	1.10	2.01
0.20	18.50	3.80	4.87

TABLE 2
TEMPERATURE DEPENDENCE AND ACTIVATION PARAMETERS¹

Alcohol	$10^3 L^2 mole^{-2} sec^{-1}$				ΔH^* (kJ mol ⁻¹)	$-\Delta S^*$ (J mol ⁻¹ K ⁻¹)
	303 K	308 K	313 K	318 K		
In the absence of pyridine						
Benzyl alcohol	16.7	22.6	26.4	32.8	37.4	160
1-Phenyl ethanol	2.88	3.45	4.41	5.18	31.5	194
In the presence of pyridine						
Benzyl alcohol	8.95	9.41	12.9	33.6	33.6	178
1-Phenyl ethanol	4.18	5.66	7.51	9.28	44.1	149

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