Kinetics and Mechanism of the Oxidation of the Esters of Mandelic Acid by Lead Tetraacetate

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The oxidation of eight esters of mandelic acid by lead tetraacetate in benzene solution has been studied. The product of the oxidation is the corresponding phenylglyoxylic ester. The oxidation is of first order with respect to the oxidant and second order to the ester. The reaction is catalysed by pyridine, the catalysed reaction being first order in pyridine. In the presence of pyridine, the reaction is first order with respect to each the oxidant and the ester. The oxidation of ethyl α-deuteriomandelate indicated a kinetic isotope effect. The activation parameters have been determined. The results have been interpreted in terms of a slow decomposition of lead tetraalkoxide derivative involving heterolysis of Pb–O bond.

Oxidation of organic compounds by lead tetraacetate (LTA) is known to involve both homolytic and heterolytic reactions.[1)] The mechanism depends mainly on the nature of the compound and the reaction conditions. Baer and Kates[2)] observed that the yield of pyruvic ester in the oxidation of methyl lactate varies with the solvent used. The oxidation of methyl mandelate in boiling benzene by LTA yields 70% methyl phenylglyoxylate.[2)] Little kinetic data are available on the oxidation of mandelic esters by LTA. Oxidation of mandelic acid has earlier been reported from this laboratory.[3)] However, hydroxy acids and their esters are known to react by different mechanisms.[4,5)] The present communication reports the oxidation of some esters of mandelic acid by LTA, both uncatalysed and pyridine-catalysed.

Results

The rate laws and other experimental data were obtained for the oxidation of eight esters of mandelic acid. Since results are similar, only those of methyl mandelate (MM) are reproduced here.

The oxidation of mandelic esters by LTA, both uncatalysed and catalysed, yields carbonyl products as evidenced by the isolation of their 2,4-dinitrophenylhydrazones (2,4-DNP). However, no data were available on the 2,4-DNP of phenylglyoxylic esters. The esters of phenylglyoxylic acid were therefore, prepared by the reported mehtods.[6)] Then the esters were converted into their 2,4-DNP. The 2,4-DNP of phenylglyoxylic esters and those of the oxidation products had identical mp. Mixed mp and mixed TLC confirmed that 2,4-DNP obtained by both the methods are identical. 2,4-DNP of the oxidation products of butyl and isopropyl mandelates showed correct analysis for C, H, and N. The mp of 2,4-DNP of the phenylglyoxylic esters are recorded in Table 1, along with the results of elemental analysis.

Stoichiometry. Excess of LTA was allowed to react with 0.0025 M of isopropyl mandelate in the presence of varying amounts of pyridine and the unreacted oxidant estimated. The ester and LTA react in 1 : 1 ratio. For some runs, the carbonyl product was estimated as its 2,4-DNP, using an excess of the ester. The carbonyl product is isolable in 80±3% yield. The overall reaction is as follows:

$$\mathrm{PhCH(OH)COOR} + \mathrm{Pb(OAc)_4} \rightarrow \mathrm{PhCOCOOR} + \mathrm{Pb(OAc)_2} + 2\,\mathrm{AcOH}. \qquad (1)$$

Rate Laws. When the ester is in excess, the rate of disappearence of LTA follows first order rate laws. The rate constant is independent of the initial concentration of LTA (Table 2) confirming that the order with respect to LTA is one. In uncatalysed reactions the order with respect to the ester is two (Table 3), In the presence of pyridine, the order with respect to LTA remains unchanged but the reaction becomes first order with respect to the substrate also (Table 4). The catalysed reaction is of first order in pyridine (Table 5).

An attempt was made to detect the formation of free radicals, during these oxidation in benzene, using acrylonitrile in an atmosphere of nitrogen. No free

TABLE 1. ANALYTICAL DATA FOR THE 2,4-DINITROPHENYLHYDRAZONES OF ALKYL PHENYLGLYOXYLATE

Alkyl group	Formula	Mp °C	Found (%)			Calcd (%)		
			C	H	N	C	H	N
Me	$C_{15}H_{12}N_4O_6$	169	—	—	—	—	—	—
Et	$C_{16}H_{14}N_4O_6$	152	—	—	—	—	—	—
n-Pr	$C_{17}H_{16}N_4O_6$	162	—	—	—	—	—	—
i-Pr	$C_{17}H_{16}N_4O_6$	171	50.04	4.35	14.99	54.83	4.30	15.05
n-Bu	$C_{18}H_{18}N_4O_6$	120	55.89	4.80	15.16	55.95	4.66	14.50
i-Bu	$C_{18}H_{18}N_4O_6$	138	—	—	—	—	—	—
s-Bu	$C_{18}H_{18}N_4O_6$	134	—	—	—	—	—	—
Benzyl	$C_{21}H_{16}N_4O_6$	189	—	—	—	—	—	—

radicals could be detected.

To ascertain the importance of α-C–H bond rupture in the rate-determining step, the oxidation of ethyl α-deuteriomandelate (PhCD(OH)COOEt) was investigated. The results are summarised in Table 6.

Tables 7 and 8 record the data on the effect of temperature on the uncatalysed and the catalysed oxidation respectively. The average error limits in the values of ΔH^*, ΔS^*, and ΔF^* are ±5 kJ mol^{-1}, ±10 J mol$^{-1}\cdot$K^{-1}, and ±7 kJ mol^{-1}, respectively.

TABLE 2. OXADATION OF METHYL MANDELATE: OXIDANT DEPENDENCE OF THE REACTION RATE

[MM] 0.05 M, Temp 318 K.

10^2[Pb(IV)]M	0.50	0.61	1.00	1.25	2.00
$10^5 k_1$ s^{-1}	3.17	3.30	3.30	3.00	3.17

TABLE 3. OXIDATION OF METHYL MANDELATE: SUBSTRATE DEPENDENCE OF THE REACTION RATE

[PV(IV)] 0.005 M, Temp 318 K.

10^2[MM]M	3.12	5.00	7.50	10.0	12.5
$10^5 k_1$ s^{-1}	1.27	3.17	7.87	13.0	20.3
$10^2 k_1$/[MM]^2	1.31	1.27	1.39	1.30	1.31

TABLE 4. DEPENDENCE OF THE REACTION RATE ON THE CONCENTRATION OF METHYL MANDELATE, IN THE PRESENCE OF PYRIDINE

[Pb(IV)] 0.005 M, [Pyridine] 0.20 M, Temp 298 K.

10^2[MM]M	1.87	3.12	5.00	6.25	10.0
$10^5 k_1$ s^{-1}	5.18	8.74	14.2	17.5	28.0

Discussion

The constancy of ΔF^* values indicates that the esters are oxidised by the same mechanism. Data in Tables 7 and 8 indicate the rate of oxidation of various esters do not differ markedly and a random variation becomes apparent when these rates are compared at different temperatures. This suggests that the structural changes in the alcohol moiety of the ester fail to affect the reaction rate. This is not surprising considering that at least four sigma bonds intervene between the reaction site and the substituent. Similar effects have been observed in many Ce(IV) oxidations.[7] Another possibility is that the reaction has been studied

TABLE 5. DEPENDENCE OF THE REACTION RATE ON PYRIDINE CONCENTRATION

[Pb(IV)] 0.005 M, [MM] 0.05 M, Temp 293 K.

[Pyridine] M	0.10	0.20	0.30	0.40	0.50
$10^5 k_1$ s^{-1}	4.60	9.98	13.9	20.0	25.2

TABLE 6. KINETIC ISOTOPE EFFECT IN THE OXIDATION OF ETHYL MANDELATE

[Pb(IV)] 0.005 M, [Ester] 0.05 M, Temp 308 K.

[Pyridine] M	$10^5 k_1$ s^{-1}		k_H/k_D
	α-H	α-D	
0.00	7.40	3.10	2.39
0.20	25.3	5.00	5.60

TABLE 7. RATE CONSTANTS AT DIFEERENT TEMPERATURES AND THE ACTIVATION PARAMETERS FOR THE UNCATALYSED OXIDATION OF ALKYL MANDELATES BY Pb(IV)

Alkyl group	$10^3 k$ l^2 mol^{-2} s^{-1}				ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔF^* kJ mol^{-1}
	308	313	318	323 K			
Me	5.18	7.26	13.0	22.9	74.7	50.3	91.6
Et	7.40	9.60	18.0	25.4	68.7	66.7	91.1
n-Pr	8.44	12.7	15.4	21.5	50.8	124	91.6
i-Pr	7.29	11.5	13.4	16.9	50.0	127	92.4
n-Bu	9.21	11.9	21.1	27.6	61.2	89.0	90.7
s-Bu	6.52	8.83	18.0	23.8	72.6	55.0	91.6
i-Bu	8.44	11.9	19.9	29.2	68.9	65.0	90.7
Benzyl	3.72	6.14	8.80	11.7	64.3	86.7	93.2

TABLE 8. RATE CONSTANTS AT DIFFERENT TEMPERATURES AND THE ACTIVATION PARAMETERS FOR THE PYRIDINE-CATALYSED OXIDATION OF ALKYL MANDELATES BY Pb(IV)

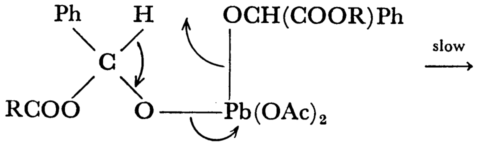
Alkyl group	$10^3 k$ l^2 mol^{-2} s^{-1}				ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔF^* kJ mol^{-1}
	293	298	303	308 K			
Me	9.98	14.2	21.1	27.3	48.7	121	85.7
Et	11.5	13.4	19.6	25.3	51.2	147	86.1
n-Pr	10.7	11.1	18.4	23.0	36.4	163	86.5
i-Pr	11.9	15.0	18.8	24.9	37.3	159	86.1
n-Bu	11.5	15.4	19.6	24.9	38.3	155	86.1
s-Bu	11.1	14.2	19.8	25.1	41.2	146	86.1
i-Bu	9.98	13.0	17.3	24.9	44.9	134	86.1
Benzyl	12.3	16.1	21.5	30.7	44.1	135	85.7

at or very near the isokinetic temperature. A plot of ΔH^* and ΔS^* (r=0.986) of the uncatalysed reaction gives an isokeintic temperature 312 K. Since the rates were determined close to the isokeintic temperature, consideration of rates alone could lead to erroneous conclusion about the nature of the reaction.

The formation of the keto ester in good yield and a second order dependence on substrate concentration indicate that the oxidation takes place through the decomposition of dialkoxylead(IV) derivative, the monoalkoxylead(IV) derivative being kinetically insignificant. The oxidation of alcohols is known to proceed through the disproportionation of such derivatives.[8,9]

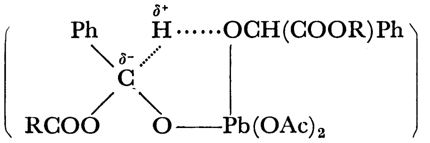
The disproportionation of the dialkoxy derivative may either involve a heterolysis of Pb–O bond (and a C–H bond rupture) or a rapid sequential two successive one electron processes. The presence of kinetic isotope effect and failure to induce polymerisation of acrylonitrile suggest that the disproportionation is a two-electron process. It may be mentioned here that homolytic oxidation of alcohols by LTA in nonpolar solvents results in cyclisation and fragmentation products—tetrahydrofurans and tetrahydropyrans.[1,10] Absence of such products also indicate a two-electron process.

$$\mathrm{Pb(OAc)_4 + 2\,PhCH(OH)COOR \rightleftharpoons 2\,AcOH + (PhCH(COOR)O)_2Pb(OAc)_2} \qquad (2)$$



$$\mathrm{PhCOCOOR + PhCOCOOR + Pb(OAc)_2 + PhCHOH\cdot COOR} \qquad (3)$$

The observed negative entropies of activation also favour this mechanism over homolysis of Pb–O bond. The following transition state could be envisaged.



Due to partial positive charge created in the transition state in a nonpolar solvent like benzene, the solvent molecules will acquire induced dipoles and ion-dipole forces will restrict the movements of many benzene molecules. Further, since the dielectric constant is small, the lines of force will go far out into the solvent and a great many solvent molecules will be involved. The immobilisation of a large number of benzene molecules reduces the partition function of the transition state as compared to the reactant states. This would result in a large negative entropy of activation.

The reaction in the presence of pyridine is a neat one involving heterolysis of Pb–O bond.[8] The first order dependence on the ester concentration shows that pyridine coordinates with LTA to form a complex. Such a complex has been isolated from benzene by Partch and Monthony.[8] The increased polarisation interaction in Pb–N as compared to Pb–O bond renders the complex more labile and electrophilic. When [pyridine]$\gg$[Pb(IV)] the effective concentration of species like LTA-Py will be fairly constant and catalysis due to bases like pyridine seems to be quite profound. Further, a high kinetic isotope effect in pyridine-catalysed oxidation also requires a catalysis by pyridine. It therefore, appears that pyridine also acts as a base in facilitating the rupture of α-C–H bond. Lowering of ΔF^* in all cases in going from the uncatalysed to catalysed reaction is expected.

Experimental

Esters of mandelic acid, prepared by the reported methods,[11] were purified by distillation under reduced pressure and crystallization. Their mp and bp agreed with the literature values.[12] Solvents and other reagents were purified and dried in the usual manner. Ethyl mandelate (α-D, 90±5% deuterated) was prepared by the esterification of α-deuteriomandelic acid, which itself was prepared by the method of Kemp and Waters.[13] LTA was prepared by the reported method[14] (purity=98%).

Kinetic Measurements. The solvent used was benzene. AcOH (1% v/v) was added to each reaction mixture to avoid phase separation and to keep $\mathrm{Pb(OAc)_2}$ in solution. Conductivity measurements showed that there was no appreciable interaction between pyridine and AcOH in this medium, hence no correction was applied to the initial concentration of pyridine. The reaction was studied under pseudo-first-order conditions by keeping a large excess the ester over LTA and were followed by the method of Cordner and Pausacker.[15] A parallel blank was always run to account for the decomposition of LTA, if any. The observed rates of pyridine-catalysed reactions were corrected for the rate of uncatalysed reaction. Similarly the rate of oxidation of the deuterated ester was corrected for the ordinary ester present. The first order rate constant, k_1, was evaluated from the plots of log[LTA] against time by a least square method and were reproducible within ±4%.

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