Oxidative Cleavage by Lead(IV). I. The Mechanism of Decarboxylation of 2-Hydroxycarboxylic Acids[1]

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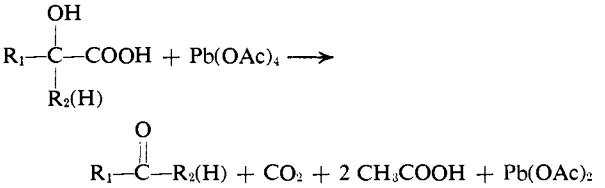
Abstract: The oxidative decarboxylations of 2-hydroxycarboxylic acids by lead tetraacetate (LTA) in anhydrous acetic acid solvent clearly follow second-order kinetics, $V = k_{\text{obsd}}[\text{LTA}][\text{hydroxy acid}]$. Rates of Pb$^{\text{IV}}$ disappearance measured spectrophotometrically, titrimetrically, and polarimetrically are identical. The kinetic data coupled with vpc and nmr product studies establish unambiguously the stoichiometry of these reactions and demonstrate that these cleavages are relatively free from side reactions. The inverse linear dependence of these oxidation rates on acetic acid concentration ($V = k[\text{LTA}][\text{hydroxy acid}][\text{HOAc}]^{-1}$) and solvent deuterium isotope effects ($k_{\text{H}}/k_{\text{D}} = 0.63$) both suggest that a cyclic intermediate with both hydroxy acid oxygens bonded to lead is formed prior to the rate determining ring opening. Activation parameters (*e.g.*, mandelic acid: $E_{\text{a}} = 20.1$, $\Delta S^{\ddagger} = +1.7$), determined for these oxidations, were also consistent with the proposed mechanism. Lack of sensitivity to solvent polarity, to general salt effects, and to substituent effects all strongly indicate that the formation of ions, prior to or during the rate-determining step, is quite unlikely. Similarly, use of free radical trapping agents indicates that radical intermediates are not produced in detectable quantities during the course of these oxidative cleavages, except under certain extreme conditions. Parallel studies, indicating the usefulness of this system for the investigation of base catalysis in LTA oxidation, are reported.

Lead tetraacetate (LTA), originally introduced by Dimroth and coworkers[4] as a powerful oxidizing agent, has subsequently found wide application because of its strength, selectivity, and versatility. In spite of the usefulness of this reagent, the mechanisms of its oxidative cleavages are in many cases still not fully understood.[5] Nonetheless, extensive mechanistic studies of glycol cleavage reactions, especially by Criegee and coworkers,[6] have provided much insight into the understanding of their reaction pathways. Mechanistic investigations of related LTA oxidative cleavages have been fewer in number and generally much more limited in scope.[7] The timing and mode of oxidative fission in relationship to the various intermediate species constitute the central areas of our concern in understanding the mechanisms of these cleavages. We describe here a kinetic, stereochemical, and mechanistic study of the oxidative decarboxylation of 2-hydroxycarboxylic acids by LTA.

The oxidative cleavage of 2-hydroxycarboxylic acids by LTA, first performed by Oeda,[8] reportedly followed the stoichiometry shown in eq 1.



$$\text{R}_1\text{—}\underset{\text{R}_2(\text{H})}{\overset{\text{OH}}{\text{C}}}\text{—COOH} + \text{Pb(OAc)}_4 \longrightarrow \text{R}_1\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—R}_2(\text{H}) + \text{CO}_2 + 2\,\text{CH}_3\text{COOH} + \text{Pb(OAc)}_2 \quad (1)$$

Criegee and Büchner[9] followed titrimetrically the kinetics of cleavage of four 2-hydroxycarboxylic acids but were unable to observe kinetics of integral order. However, by a careful exclusion of adventitious moisture which accompanies 2-hydroxy acids, we were able to demonstrate that the overall rate expression for these reactions is strictly second order, first order in both hydroxy acid and LTA.

Mechanisms proposed for the oxidation of simple alcohols,[10] the cleavage of 1,2-diols,[6,11] the decomposition of lead tetracarboxylates,[12] and the decarboxylation of monofunctional acids[13] by LTA suggest three main possibilities for the course of LTA decarboxylations of 2-hydroxy acids, Scheme I, eq 2–4.

Intermediates analogous to 2 are proposed almost universally for LTA oxidations of compounds containing -O-H and >N-H groups.[5,14] Aside from kinetic evidence for such intermediates, the Pb(IV) compound, $\text{Pb(OAc)}_2\text{(OH)(OMe)}$, has actually been isolated from a solution of LTA in wet methanol.[6b] This paper also explores the possibility of mechanistic pathways involving a cyclic intermediate 3, analogous to the cyclic intermediates often postulated in the cleavage of *cis*-1,2-diols,[6,11a] and allows a comparison of the oxidations of the same hydroxy acids by other

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[3] (a) National Science Foundation predoctoral fellow; (b) taken in part from the Ph.D. dissertation of B. C. Davis, University of Washington, 1972.

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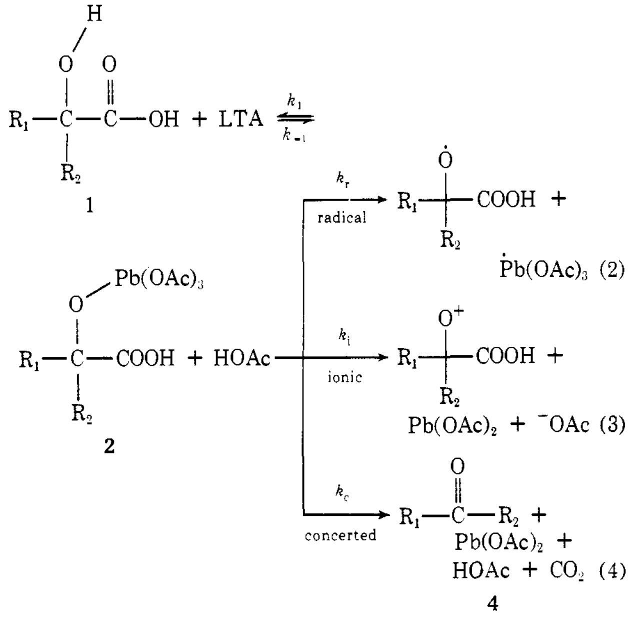
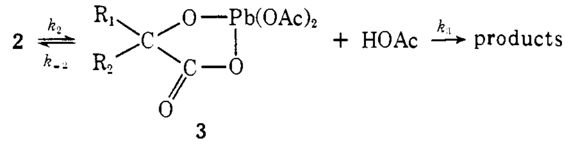
Scheme I



Scheme II



oxidants, *e.g.*, permanganate,[15] Cr(VI),[16] V(V),[17] Ce(IV),[18] and Mn(III).[19]

Experimental Section

Materials. Purification of solvent acetic acid followed standard methods;[20,21] in all cases only acetic acid with a minimum melting point of 16.58° was used for kinetic studies. Acetic acid-d_1 (CH_3-COOD) was prepared by adding freshly distilled acetic anhydride to an equivalent amount of Bio-Rad D_2O (99.85%). After reaction and fractional distillation analysis by nmr and vpc showed less than 1% CH_3COOH with kinetically negligible amounts of acetic anhydride.

Reagent grade benzene, carbon tetrachloride, ethyl acetate, and acrylonitrile were dried then distilled just before use. Acetonitrile was refluxed with triphenylmethyl tetrafluoroborate and fractionally distilled through a column packed with glass helices.

Lead tetraacetate (Alfa Inorganics) was recrystallized from anhydrous acetic acid, washed with hexane without allowing the precipitated LTA to dry completely, and dried under vacuum for 25 hr at room temperature. The purified material was stored over P_2O_5 in a desiccator taped to exclude the light.[22]

D,L-Mandelic acid (Eastman Organic Chemicals), benzilic acid (Matheson Coleman and Bell), D,L-α-methylmandelic acid (J. T. Baker Chemical Co.), D-mandelic acid, *p*-chloromandelic acid, *p*-bromomandelic acid, *p*-fluoromandelic acid, 2-hydroxyisobutyric acid (all Aldrich Chemical Co.), benzopinacol (synthesized by the method of Pocker and Ronald[21]), and D,L-*p*-methylmandelic acid (synthesized by the method of Corson, *et al.*,[23]) were recrystallized two to four times from hot benzene. Benzil and benzoin were recrystallized from hot methanol. Mandelic acetate was prepared from mandelic acid and acetyl chloride. The product was recrystallized twice from heptane, as were benzoylformic acid and DL-methyl mandelate. After vacuum drying at room temperature for 24 hr, melting points of all the above solids matched literature values. Citric acid monohydrate was heated for 3 hr at 80°. Enough acetic anhydride to react with the water of crystallization originally present was added to an acetic acid solution of the hydroxy acid. After standing overnight and heating for 2 hr, the rate constants for the oxidative cleavage of citric acid were reproducible over a wide concentration range of hydroxy acid. *p*-Toluenesulfonic acid monohydrate was purified in the same way. Malic acid (J. T. Baker Chemical Co.) was dried at 80° for 24 hr and used without further purification. The concentration of aqueous lactic acid solutions (J. T. Baker Chemical Co.) was determined by titration with standard base to a phenolphthalein end point. Acetic anhydride was added in slightly greater molar amounts than the water present. After standing overnight the solution was heated for 3 hr. Good second-order rate constants were obtained with lactic acid varying between 0.05 and 0.5 *M*.

Lithium perchlorate (G. Frederick Smith Chemical Co.) was purified by the method of Pocker and Buchholz.[24] Anhydrous lithium acetate, sodium acetate, and potassium acetate were dried under vacuum for 8 hr at 80° and were stored in a desiccator over P_2O_5. Hydrated lead acetate, $Pb(OAc)_2 \cdot 3H_2O$, was recrystallized twice from methanol, then vacuum dried. Catalysis by lead diacetate, added in concentrations produced during these oxidations, was negligible. Perchloric acid in acetic acid solution was prepared by adding dropwise, with ice cooling, a slight excess of acetic anhydride (dissolved in an equal volume of acetic acid) to a previously analyzed sample of 71% aqueous perchloric acid (Mallinkrodt).

Absolute methanol was prepared by the method of Vogel.[25] *N,N*-Dimethylformamide was dried overnight over $MgSO_4$ and carefully fractionated. The constant boiling portion was refractionated (bp 152.5–153°). 1,4-Dioxane was purified by the method of Pocker and Hill.[26] Ethylene glycol was fractionated under reduced pressure, the middle fraction dried 24 hr over anhydrous sodium sulfate, then refractionated under reduced pressure (bp 197–197.3°). For all solvents described above the refractive indices also matched literature values.[27]

Kinetic Measurements. Spectrophotometric rates were followed using a Beckman Model D.U. spectrophotometer or a high speed Gilford multiple sample recording spectrophotometer, Model 2000, each fitted with a constant temperature sample compartment. Rates were determined by monitoring the disappearance of the lead tetraacetate absorption at various wavelengths between 290 and 320 nm. It was experimentally confirmed that the change in absorption was directly proportional to the change in Pb(IV) concentration. Other workers have followed lead tetraacetate oxidation rates in a similar fashion.[12b,28]

Oxidation rates were monitored titrimetrically, using the method of Criegee,[6] by quenching an aliquot of solution at a given time with excess iodide and titrating the iodine produced with standard thiosulfate solution using a starch indicator. A thermostated Model 965 Bendix digital polarimeter was used to follow the loss of optical activity of D-mandelic acid solutions. All of the above rates were followed from 2 to 5 half-lives or the equivalent time. Infinities were taken after at least 10 half-lives.

Product studies were carried out in three ways. (1) 2,4-Dinitrophenylhydrazone derivatives were isolated. (2) Nmr spectra of acetic acid solutions of ~0.4 *M* 2-hydroxycarboxylic acids with an equivalent amount of added LTA were taken after CO_2 evolution was no longer evident. This procedure was repeated using acetic acid-d_1 (CH_3COOD) as solvent, to check for deuterium incorporation. A Varian Associates A-60 instrument was used. (3) Samples of the raw reaction mixtures from adding 0.4 *M* 2-hydroxy acid in HOAc to an equivalent amount of LTA were injected into a Mod e 5750 Hewlett-Packard research gas chromatograph with a flame ionization detector, chart recorder, and an integrator, using a 6-ft

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Table I. Oxidative Cleavage of Mandelic Acid by Lead Tetraacetate at 25.0° [a]

$[MA]_0 \times 10^2$, M[b]	$[LTA]_0 \times 10^3$, M[b]	Solvent	Method[c]	$k_{obsd} \times 10^3$, M^{-1} sec^{-1}	$k^{av}_{obsd} \times 10^3$,[a] M^{-1} sec^{-1}
0.500	2.62	HOAc	S	9.33[e]	9.4 ± 0.6 (av of 20 runs)
0.563[d]	43.3	HOAc	S	9.43[f]	
1.06[d]	0.77	HOAc	S	9.33[f]	
1.33	4.73	HOAc	S	8.82[e]	
8.00	0.59	HOAc	S	9.55[f]	
0.294[d]	45.9	HOAc	P	8.94[f]	9.4 ± 0.6 (av of 15 runs)
0.563[d]	43.3	HOAc	P	9.42[e]	
1.08[d]	36.1	HOAc	P	9.72[e]	
1.85	10.1	HOAc	T	10.2[e]	9.5 ± 0.6 (av of 10 runs)
7.65	4.99	HOAc	T	9.03[f]	
5.72	0.81	DOAc	S	15.2[f]	14.6 ± 0.6 (av of 10 runs)
6.32[g]	0.35	DOAc	S	14.2[f]	

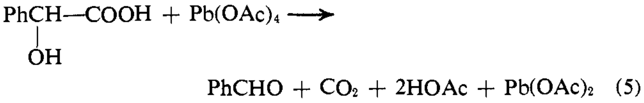
[a] Only a selection of runs is shown; however, k^{av}_{obsd} refers to the average of all runs monitored by the method shown; MA refers to mandelic acid and LTA refers to lead tetraacetate. [b] Initial stoichiometric concentrations. [c] S refers to changes in $[Pb(IV)]_{total}$ monitored spectrophotometrically; P refers to changes in [D-mandelic acid] monitored polarimetrically; T refers to changes in $[Pb(IV)]_{total}$ monitored titrimetrically. [d] Runs with D-mandelic acid. [e] Calculated from second-order rate plots. [f] Calculated from pseudo-first-order plots and the corresponding hydroxy acid concentrations. [g] Mandelic acid-d_2, PhCH(OD)COOD, initially added to DOAc.

column packed with 10% U.C. W98 on 80–100 sieve firebrick. A 14 ml/sec flow rate, programmed temperature rise from 70 to 212°, and an injection port temperature of 240° produced the best results.

The kinetic order for the lead tetraacetate oxidation of each hydroxy acid studied was independently determined. Runs at several concentrations of 2-hyroxy acid (in large excess) were monitored, and changes in hydroxy acid concentration were shown to be linear with changes in the pseudo-first-order rate constants for all substrates studied. Benzilic, mandelic, and p-methylmandelic acid oxidations gave linear second-order plots when oxidant and substrate were present in similar concentrations.

Results

The spectroscopically monitored rate of disappearance of lead tetraacetate during the oxidation of mandelic acid in anhydrous acetic acid solvent, eq 5,



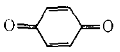
$$\underset{\displaystyle OH}{PhCH}\text{—}COOH + Pb(OAc)_4 \longrightarrow PhCHO + CO_2 + 2HOAc + Pb(OAc)_2 \quad (5)$$

is second order, first order in lead tetraacetate, and first order in mandelic acid, Table I. Also, the second-order rate constant calculated from pseudo-first-order runs was identical with that determined directly from rates of oxidation run under second-order contions. Identical results were obtained from a parallel study using titrimetric methods. Further, the rate of loss of optical activity as D-mandelic acid is converted into benzaldehyde was found, within experimental error, to be identical with the rate of Pb(IV) consumption, Table I. Using polarimetric methods, rates were followed both under conditions giving second-order kinetics and pseudo-first-order kinetics for several concentrations of lead tetraacetate (in large excess). In fact, the polarimetric method allowed an excellent check on the stoichiometry of the reaction. Thus, when 0.0125 M lead tetraacetate was mixed with 0.0127 M D-mandelic acid ($\alpha_0 = 0.167°$) and the reaction allowed to proceed until no more Pb(IV) was present, it was found that the rotation dropped to nearly zero ($\alpha_\infty = 0.006°$). Furthermore, when half as much LTA was used, the final rotation was exactly half that of the original. These experiments show that equimolar amounts of hydroxy acid and oxidant are consumed in the reaction, confirming the stoichiometry given in eq 5; see also Figure 1.

A comparison of the integration of the nmr peak area representing the benzyl proton of mandelic acid and the aldehyde proton of benzaldehyde throughout the reaction showed that the loss in moles of reactant corresponds, within experimental error, to moles of product formed. After the oxidation was performed in acetic acid-d_1 (CH_3COOD), 97% of the original benzyl hydrogen was accounted for both in the product benzaldehyde and in the starting material. Thus, within experimental error, there was no detectable deuterium incorporation, and hence no observable equilibrium of benzyl protons with the solvent, either in a preequilibrium step or after the rate-determining step. Solvent deuterium isotope effects were also investigated using acetic acid-d_1, Table I. For mandelic acid oxidation, $k_H/k_D = 0.63$, whether PhCH(OD)COOD or PhCH(OH)COOH was initially added to CH_3COOD.

For vpc product studies excess hydroxy acid was added to a saturated solution of lead tetraacetate in acetic acid (0.072 M). Immediate evolution of CO_2 was discernible. After the evolution stopped, samples of reaction mixture were injected into the vpc. Using conditions for optimum separation, the area of benzaldehyde product peak accounted for 95% of the total integrations for all product peaks. Peaks for starting material, solvent, and major product were identified by comparing retention times with those of authentic samples of mandelic acid, acetic acid, and benzaldehyde and also by spiking the reaction mixture in turn with each of the three samples and observing the relative increase in the area of a given peak. When the amplitude of the spectrum was increased, nine minor peaks representing compounds other than those above were discernible from the raw reaction mixture. None of the minor peaks alone accounted for more than 3% of the total products. It was interesting, though certainly not conclusive, that on spiking the reaction mixture with benzyl acetate and benzyl alcohol, the relative areas of the two largest of the minor peaks increased in size. Thus the oxidation of mandelic acid by LTA gives

Table II. Medium Effects

Addend	Concn, M	[HOAc], M	$k_{\text{obsd}} \times 10^2$,[a] M^{-1} sec^{-1}
A. Rate Enhancement by Dilution Mandelic Acid Oxidation			
		17.5	0.942
Benzene	0.77	16.3	1.49
	1.86	14.6	1.79
	2.78	13.1	2.06
	4.66	10.2	2.54
	6.00	8.1	3.76
	6.22	6.9	4.08
$(CH_3CO)_2O$	0.623	16.5	1.49
	3.21	12.0	2.12
	3.97	10.9	2.95
	4.86	9.47	4.72
	6.52	6.56	7.60
CH_3CN	1.68	16.0	1.26
	2.78	14.9	1.41
	4.45	13.4	2.10
	5.56	12.4	2.58
	6.02	12.0	2.72
	8.33	9.86	4.07
	11.1	7.36	9.09
CCl_4	1.73	14.6	2.12
$CH_3COOC_2H_5$	1.71	14.6	1.98
Dioxane	1.89	14.6	1.38
	3.77	11.8	2.14
	5.64	9.04	3.77
2-Hydroxyisobutyric Acid Oxidation			
		17.5	0.051
Benzene	1.65	14.7	0.104
	3.16	12.0	0.114
	4.74	9.3	0.173
	6.33	6.56	0.474
Benzopinacol Oxidation			
		17.5	16.7
Benzene	0.704	16.4	17.5
	1.41	15.3	18.7
	2.11	14.2	20.9
	3.52	12.0	24.0
	6.34	7.65	30.8
B. Rate Enhancement by Dilution and Addend Catalysis			
CH_3OH	1.98	16.1	3.1
	3.35	12.0	7.1
H_2O	2.38	16.8	3.7
	4.91	15.9	11.5
$(CH_3)_2NCHO$	1.21	15.9	17.3[b]
	1.92	14.9	103[b]
$HOCH_2CH_2OH$	0.515	17.0	3.7[b]
	1.68	15.8	17.1[b]
p-$CH_3C_6H_4SO_3H$	0.033	17.5	1.77
	0.067	17.5	2.49
$HClO_4$	0.4	17.4	3.06
$LiClO_4$	2.52	17.1	1.21
KOAc	0.0167	17.5	27.6
$(CH_3CH_2)_3N$	0.0123	17.5	31.3[b]
	0.004	17.5	1.48

[a] At 25.0°; k_{obsd} are average values of the spectrophotometric second-order rate constants obtained under the specified conditions; k_X/[2-hydroxy acid] where k_X is the rate coefficient monitored under pseudo-first-order conditions. [b] Values corrected for the oxidation of the addend by LTA.

more than 95% benzaldehyde product. The 2,4-dinitrophenylhydrazone of benzaldehyde was also isolated, further confirming the identity of the product.

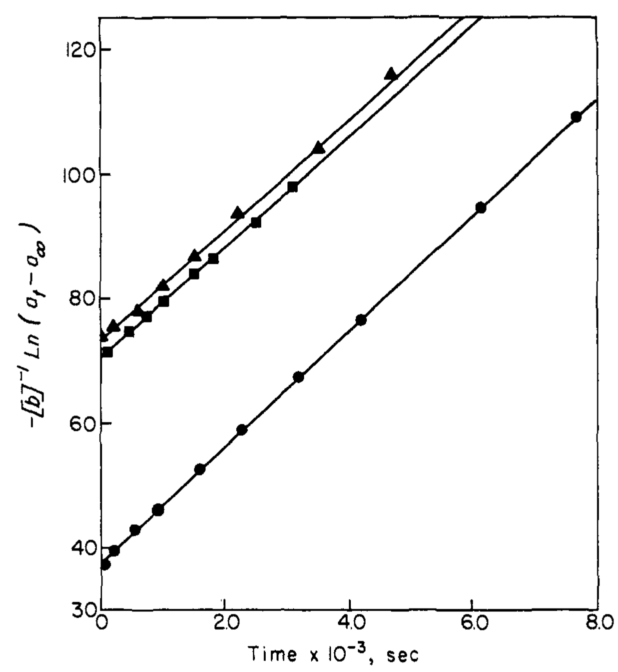


Figure 1. Rate of mandelic acid cleavage by lead tetraacetate in anhydrous acetic acid at 25°: (▲) monitored polarimetrically, a = rotation of D-mandelic acid, b = [LTA]; (■) monitored titrimetrically, a = [Pb(IV)], b = [mandelic acid]; (●) monitored spectrophotometrically, a = absorbance of Pb(IV), b = [mandelic acid].

To examine the possibility of charge development in the transition state, the oxidation of mandelic acid was carried out in the presence of lithium perchlorate. However the addition of 0.13 M salt produced only a 1.2-fold increase in rate; even with 0.252 M salt only a 1.3-fold increase was observed. These increases are very small when contrasted with those caused by the addition of acetate salts, Table II.

To investigate the dependence of oxidation rate on acetic acid concentration, various amounts of benzene were added to the reaction medium for the oxidative decarboxylation of mandelic acid, Table II. Plots of log k_{obsd} *vs.* log [HOAc] gave straight lines with slopes of about −1.1 for acetic acid concentrations varying from 17.0 to 6.90 M. Plots of k_{obsd} *vs.* 1/[HOAc] and k_{obsd} *vs.* $1/[(HOAc)_2]$ were both linear and the correlation coefficient for both lines was 0.98 (Figure 2). The rate of cleavage of 2-hydroxyisobutyric acid was also inversely proportional to the acetic acid concentration when low to moderate amounts of benzene were added. At higher concentrations of added benzene, a more pronounced rate increase was noted, similar to the one observed by Criegee and Büchner[9] in the oxidation of *cis*-cyclohexanediol. Parallel studies were conducted with added acetic anhydride and acetonitrile. For the oxidation of mandelic acid, only the lower concentrations of added solvents gave a linear plot of k_{obsd} *vs.* 1/[HOAc], Figure 2. When the oxidation of benzopinacol was carried out in acetic acid, to which various amounts of benzene were added, the same result was obtained as with mandelic acid; *i.e.*, the rate constant was found to be inversely proportional to the acetic acid concentration. To characterize more fully the transition state, the rate of mandelic acid cleavage by lead tetraacetate was studied in several solvent mixtures. When solvents not normally thought to catalyze lead tetraacetate reactions were added to acetic acid

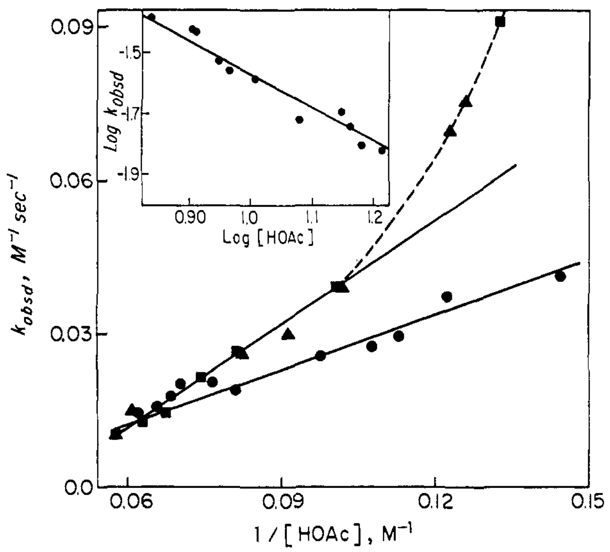


Figure 2. Effect of changing acetic acid concentration on the rate of mandelic acid cleavage by lead tetraacetate at 25°. [HOAc] varied by adding: (●) benzene; (▲) acetic anhydride; (■) acetonitrile. Insert: a plot of log k_{obsd} *vs.* log [HOAc] for mandelic acid oxidation by LTA at 25° with added benzene; slope = -1.1.

solvent, small rate increases were noted. These small increases in rate were nearly all of the same magnitude, Table II. Control experiments indicated that with addends, carbon tetrachloride, ethyl acetate, acetic anhydride, benzene, and *p*-dioxane, no loss of Pb(OAc)$_4$ is spectrophotometrically detectable under the conditions employed in these rate studies in the absence of hydroxy acid substrate. Parallel studies were also carried out with added compounds known to catalyze lead tetraacetate oxidations, possibly by forming complexes which are more active than LTA itself. We hope to more fully report on these in a subsequent publication in this series.

Several means were used to investigate the possibility of a free radical mechanism. The lack of significant amounts of side products in lead tetraacetate oxidations of 2-hydroxycarboxylic acids contrasts sharply with the LTA oxidations of monofunctional carboxylic acids, where the major products apparently come from several different radicals.[29,30] When the oxidation rates of two samples were monitored under identical conditions, save that one was illuminated with a low-pressure uv Westinghouse Sterilamp G15-T8, no differences in rate or in amounts of side products could be detected, even though uv decomposition of LTA has been reported.[31] Thus, it seems clear that rate increases, similar to those reported by Kochi in the LTA decomposition of monofunctional acids,[30] do not occur in the respective oxidative decarboxylation of mandelic acid.

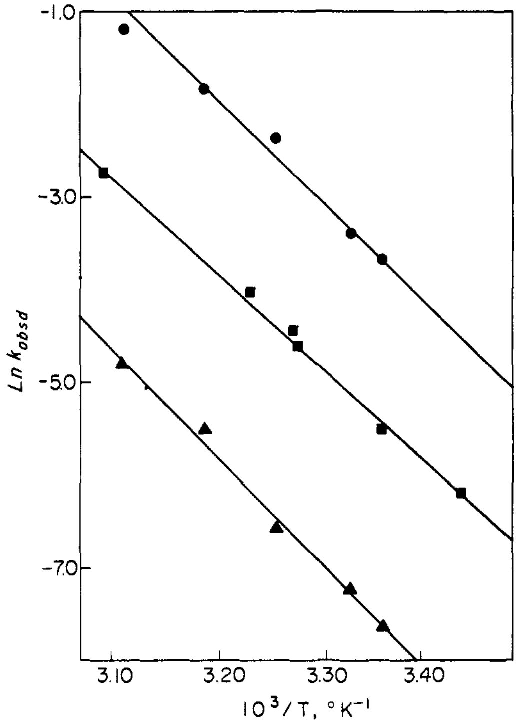


Figure 3. Arrhenius plots for the lead tetraacetate cleavage of 2-hydroxycarboxylic acids in anhydrous acetic acid: (●) benzilic acid; (■) mandelic acid; (▲) 2-hydroxyisobutyric acid.

Several attempts were made to capture free radical intermediates by using suitable trapping agents. (i) *p*-Benzoquinone, a useful radical scavenger,[32] not only did not slow down the rate but actually increased it, Table II. (ii) Mercuric chloride, which has been used as a free radical trap in similar systems,[33] gave no visible precipitate of Hg^0 during the LTA oxidations of lactic, 2-hydroxyisobutyric, mandelic, and benzilic acids. (iii) Observable precipitation of acrylonitrile polymer[19a] or reduced rates of oxidation with added acrylonitrile[34] have been cited as evidence for free radical reactions. However, no polymerization of acrylonitrile[35] could be detected under any of the reaction conditions used in our kinetic studies.[36] In fact, with 4.7 *M* added acrylonitrile, the rate of mandelic acid oxidation by LTA is markedly increased, $k_{obsd}/k_0 = 9.2$. This rate increase can be attributed in part to the dilution of acetic acid and in part to direct catalysis by the addend.

The correlation of rates with structural alterations and with substituent effects often provides additional mechanistic characterization. The most obvious observations from Table III are that substituent effects are negligibly small and that even significant structural changes give rise to relatively small rate differences. Thus, there is only a 240-fold increase in the LTA oxidation rate between lactic and benzilic acids. Citric

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[29] M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, 14, 19 (1949).

[30] Reference 13a,b.

[31] V. Franzen and R. Edens, *Justus Liebigs Ann. Chem.*, **735**, 47 (1970).

[32] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 323-324.

[33] (a) The oxidation of mandelic acid by Mn(OAc)$_3$ in acetic acid solvent: R. N. Mehrota, *Z. Phys. Chem.*, **43**, 140 (1964); (b) the oxidation of lactic acid by V(V) in aqueous HClO$_4$: U. S. Mahnot, R. Shanker, and S. N. Swami, *Z. Phys. Chem.*, **222**, 240 (1963); (c) the oxidation of ethylene glycol with acidic permanganate: P. Nath, K. K. Banerje, and G. V. Bakore, *Indian J. Chem.*, **8**, 1113 (1970).

[34] L. N. Patnaik, G. Behera, and G. V. Bakore, *Indian J. Chem.*, 9, 432 (1971).

[35] Our control experiments indicate that polymerization of acrylonitrile constitutes a more sensitive test for the presence of free radicals than the mercuric chloride reduction.

[36] The polymerization of acrylonitrile could only be detected under extreme conditions, *i.e.*, when a saturated solution of LTA, with excess solid oxidant, was mixed with a large excess of certain hydroxy acids (mandelic, *p*-fluoromandelic, and lactic acids). These results indicate that some minor free radical reactions, detectable under rather extreme conditions, may nevertheless accompany the major mode of oxidative cleavage of 2-hydroxy acids by LTA.

Table III. Substituent and Structural Effects on the Reactivity of $R_1R_2C(OH)COOH$[a] and of Some Related Compounds

R_1	R_2	$k_{obsd} \times 10^3$,[b] $M^{-1}\ sec^{-1}$	k_{obsd}/k_{MA}[c]
CH_3	H	0.109 ± 0.009	0.0116
CH_3	CH_3	0.485 ± 0.013	0.0515
$HOOCCH_2$	H	0.475 ± 0.02	0.0485
$HOOCCH_2$	$HOOCCH_2$	2.75 ± 0.0	0.291
C_6H_5	CH_3	8.40 ± 0.06	0.892
p-FC_6H_4	H	8.61 ± 0.06	0.915
C_6H_5	H	9.42 ± 0.06	[1.00]
p-BrC_6H_4	H	10.4 ± 0.05	1.10
p-ClC_6H_4	H	10.9 ± 0.06	1.16
p-$CH_3C_6H_4$	H	12.0 ± 0.05	1.27
C_6H_5	C_6H_5	26.0 ± 1.2	2.77
		Related Compd[d]	
$C_6H_5CH(OH)COOCH_3$[e]		0.18 ± 0.01	0.019
$C_6H_5CH(OH)COC_6H_5$[f]		1.87 ± 0.06	0.20
$(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$[h]		167 ± 7	18
$C_6H_5CH(OAc)COOH$		*g*	
$C_6H_5COCOC_6H_5$		*g*	
$C_6H_5COCOOH$		*g*	

[a] The oxidative cleavage of 2-hydroxycarboxylic acids by lead tetraacetate in acetic acid solvent at 25.0°. [b] k_{obsd} is the average second-order rate constant. [c] k_{MA} is the average second-order rate constant for the oxidative cleavage of mandelic acid; the ratio, k_{obsd}/k_{MA}, is unitless. [d] Oxidation by lead tetraacetate in acetic acid solvent at 25°. [e] Cleavage yields benzaldehyde. [f] The product of benzoin oxidation is benzil, not benzaldehyde. [g] No observable reaction in 24 hr at 25°. [h] Cleavage yields benzophenone.

Table IV. Activation Parameters for the Oxidations of 2-Hydroxycarboxylic Acids

Hydroxy acid	Oxidant	Solvent	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Temp, °C	Proposed rds
PhCHOHCOOH	$Pb(OAc)_4$	HOAc(anhyd)	20.1[f]	+1.7	25	RO[a]
$(CH_3)_2COHCOOH$	$Pb(OAc)_4$	HOAc(anhyd)	22.6[f]	+9	25	RO[a]
$Ph_2COHCOOH$	$Pb(OAc)_4$	HOAc(anhyd)	21.6[f]	+12	25	RO[a]
p-$ClC_6H_4CHOHCOOH$	Cr(VI)	H_2O-HOAc 50:50	13.6[g]	−25.7	45	Cycl[b]
$PhCCH_3(OH)COOH$	Cr(VI)	H_2O-$HClO_4$	11.6[h]	−40.0	40	Cycl[c]
HOOCCHOHCHOHCOOH	Cr(VI)	H_2O-$HClO_4$	16.3[i]	−13	35	Cycl[c]
PhCHOHCOOH	Cr(VI)	H_2O-$HClO_4$	7.9[j]	−39.5	25	Cycl[b]
$CH_3CHOHCOOH$	Cr(VI)	H_2O-$HClO_4$	9.04[j]	−37.3	25	Cycl[b]
$CH_3CHOHCOOH$	Mn(III)	HOAc(anhyd)	14[k]	−26.9	30	RO[d]
$(CH_3)_2COHCOOH$	Mn(III)	H_2O-H_2SO_4	20[l]	+5.3	24.4	RO[a]
PhCHOHCOOH	Ce(IV)	H_2O-H_2SO_4	18.9[m]	+0.3	25	RO[d]
$CH_3CH_2CHOHCOOH$	Ce(IV)	H_2O-H_2SO_4	22.8[m]	+4.8	25	RO[d]
$CH_3CHOHCOOH$	Ce(IV)	H_2O-H_2SO_4	19.4[n]	+5.6	25	I[e]
$CH_3CHOHCOOH$	Ce(IV)	H_2O-H_2SO_4	17.5[o]	−17.2	30	I[e]
$(CH_3)_2COHCOOH$	Ce(IV)	H_2O-H_2SO_4	20.6[n]	−0.85	25	I[e]
$(CH_3)_2COHCOOH$	V(V)	H_2O-H_2SO_4	21.8[p]	−2.8	26.6	RO[a]
PhCHOHCOOH	V(V)	H_2O-H_2SO_4	14.0[q]	−19.86	20	I[e]
$CH_3CHOHCOOH$	V(V)	H_2O-$HClO_4$	16.5[r]	−24	30	I[e]

[a] The proposed rate-determining step (rds) is the ring opening (RO) of a cyclic complex with no concurrent proton transfer(s). In the complex one or more of the hydroxy acid oxygens are directly bonded to the oxidant, *e.g.*, Scheme II above. [b] Formation of a cyclic (cycl) transition state has been proposed during which a proton is removed from the α carbon, eq 7. [c] Suggested rds involves the cyclic transfer of one of the oxygen-bound hydroxy acid protons to the oxidant portion of the preformed complex, *e.g.*, eq 8. [d] The ring opening of a preformed cyclic complex is postulated as the rds. An important difference from (*a*) above is that a proton is transferred in the rds. [e] The nature of the preformed complex (cyclic or open) was left indeterminate, I. [f] Activation parameters in the present work were calculated from $\Delta S^{\ddagger}_{25} = (\Delta H^{\ddagger}_{25} - \Delta F^{\ddagger}_{25})/298\,°K$, where $\Delta H^{\ddagger} = E_a - RT$ and $\Delta F^{\ddagger} = -2.303RT(\log k_{obsd} - \log kT/h)$. [g] S. Sundaran and N. Venkatasubramanian, *Indian J. Chem.*, **8**, 1104 (1970). [h] Reference 47. [i] G. V. Bakore and S. Narain, *Z. Phys. Chem.*, **227**, 8 (1964). [j] Reference 38a. [k] Reference 33a. [l] Reference 19b. [m] A. McAuley and C. H. Brubaker, Jr., *J. Chem. Soc. A*, 960 (1966). [n] R. Dayal, K. K. Banerji, and G. V. Bakore, *Indian J. Chem.*, **8**, 1017 (1971). [o] K. K. Sengupta, *ibid.*, **2**, 267 (1964). [p] G. V. Bakore, R. Shanker, and S. S. Dua, *Z. Phys. Chem.*, **236**, 129 (1967). [q] R. Shanker and S. N. Swami, *J. Indian Chem. Soc.*, **40**, 105 (1963). [r] Reference 33b.

and malic acid oxidations consitute something of a special case. In general the 2-hydroxy acids which are better able to stabilize the development of some sp^2 character at the α carbon appear to have larger oxidation rate constants. *A priori*, then, one might have anticipated malic acid to be cleaved at a slower rate than lactic acid and citric slower than 2-hydroxyisobutyric. Perhaps the multidentate nature of malic and citric acids accounts for faster oxidation rates than might have been predicted from inductive effects alone. Here one might also note that the rapid oxidation of the products of these latter cleavages makes it imperative to determine initial rate constants.

Activation parameters were also obtained for mandelic, 2-hydroxyisobutyric, and benzilic acids by plotting ln k_{obsd} *vs.* T^{-1}(°K) and using the slope to calculate the Arrhenius energy of activation, Figure 3. It is interesting to note that the entropies of activation, $\Delta S^{\ddagger}$, vary from +1 to +12 eu for the oxidations of these three acids, Table IV.

Strong acids mildly catalyze the oxidative cleavage of mandelic acid by lead tetraacetate. Perchloric acid, 0.4 *M*, was only 30% more efficient than 0.07 *M* *p*-toluenesulfonic acid. Additionally, in the presence of 0.4 *M* acid, 3% of the overall rate of LTA disappearance is due to a side reaction between acid and oxidant.

Discussion

A detailed study of the lead tetraacetate oxidation of mandelic acid in glacial acetic acid, undertaken in part because of the earlier reported difficulties in obtaining kinetics of constant order,[9] indicated that the rate of Pb(IV) disappearance, measured titrimetrically or spectrophotometrically, was, within experimenta error, the same as the loss of optical activity of D-mandelic acid. Parallel product analyses showed that these cleavages proceed quite cleanly with the stoichiometry indicated by eq 5.[37]

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(37) Recently, in a short exploratory note, the same stoichiometry has been considered for similar oxidations: K. Swaminathan, S. Sundaram, and N. Venkatasubramanian, *Curr. Sci.*, 394 (1970).

While the above kinetics and stoichiometry would support pathways 2–4 above, 2-keto acid intermediates, like those found in 2-hydroxy acid oxidation by Cr(VI),[38] MnO_4^-,[39] and concentrated sulfuric acid,[40] are definitely precluded. The possibility of a keto acid intermediate is further eliminated by the lack of deuterium incorporation at the α carbon during oxidation in acetic acid-d_1 (CH_3COOD). Perhaps even more significant was the fact that lead tetraacetate oxidation rates in CH_3COOD were actually faster for mandelic acid cleavage than rates in CH_3COOH, $k_{AcOD}/k_{AcOH} = 1.6$, possibly indicating the formation of intermediates like **2** and **3**.[41] Cyclic intermediates, analogous to **3**, formed in the oxidations of diols by osmium tetroxide[42a] and $Na[Sb(OAc)_6]$[42b] have actually been isolated and characterized. To investigate the possible existence and nature of such intermediates in hydroxy acid cleavages, the effect on oxidation of changing the concentration of acetic acid was delineated in some detail.

For benzene ($D = 2.3$)–acetic acid ($D = 6.2$) mixtures the second-order rate constants for oxidation of mandelic and 2-hydroxyisobutyric acids were inversely proportional to acetic acid concentration over an unexpectedly wide range of concentrations, considering the drastic change in the nature of the solvent. Plots of k_{obsd} *vs.* $[HOAc]^{-1}$ for 2-hydroxyisobutyric acid were linear up to at least a mole fraction of 0.34, *i.e.*, nearly 45% by volume in added benzene; for mandelic acid such a plot is linear up to a mole fraction of 0.48, *i.e.*, about 60% by volume in added benzene. Further, for the LTA oxidation of mandelic acid similar plots remain linear up to a mole fraction of 0.27 (about 40% by volume) in added acetic anhydride ($D = 20.7$) and 0.46 (nearly 40% by volume) in added acetonitrile ($D = 37.5$). Not only does this show an inverse dependence of the rate constant on acetic acid concentration but also a great insensitivity to changing solvent composition. This same inverse dependence on acetic acid concentration and first-order dependence on substrate and on oxidant were shown for the LTA oxidation of benzopinacol up to a mole fraction of 0.45, *i.e.*, to more than 60% by volume in added benzene. Thus benzopinacol cleavage seems mechanistically similar to the mandelic acid cleavage. Clearly, these oxidative cleavages do not seem to be sensitive to changes in solvent polarity as would be expected for a reaction where charge separation occurs in the rate-determining step (*e.g.*, eq 3). This insensitivity is further shown by Table II where reactions with similar molarities of added solvents have similar second-order rate constants and by the minor effect produced by added lithium perchlorate. All of the above is consistent with a basically concerted pathway, eq 4, in which intermediates like **2** (Scheme I) and/or **3** (Scheme II) are formed in a preequilibrium step.

At first glance the inverse dependence on acetic acid concentration, rather than a dependence on $[HOAc]^{-2}$, might seem good evidence for the noncyclic intermediate **2** rather than **3**, *i.e.*, assuming **2** and/or **3** to be present in very small, relatively constant amounts; for Scheme I

$$\text{rate} = \frac{k_2k_1[\text{hydroxy acid}][\text{LTA}]}{k_{-1}[\text{HOAc}]}$$

and for Scheme II

$$\text{rate} = \frac{k_3k_2k_1[\text{hydroxy acid}][\text{LTA}]}{k_{-2}k_{-1}[\text{HOAc}]^2}$$

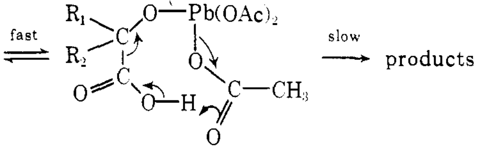
However, glacial acetic acid is more than 85% dimeric[43] and becomes more so as inert solvents like benzene are added.[44] Taking this into account, a rate dependence on $[HOAc]^{-1/2}$ would have suggested a modified Scheme I, *i.e.*

$$\text{hydroxy acid} + \text{LTA} \rightleftharpoons \mathbf{2} + {}^1\!/_2(\text{HOAc})_2 \xrightarrow{\text{rds}} \text{products}$$

while the actually observed dependence on $[HOAc]^{-1}$ suggests a modified Scheme II with the formation of the cyclic intermediate **3**.

$$\text{hydroxy acid} + \text{LTA} \rightleftharpoons \mathbf{2} + {}^1\!/_2(\text{HOAc})_2 \rightleftharpoons$$
$$\mathbf{3} + (\text{HOAc})_2 \xrightarrow[k_3]{\text{rds}} \text{products}$$

The solvent deuterium isotope effects seem in better agreement with the above scheme in which k_3 is rate determining. In contrast, the concerted conversion of **2** directly to products, eq 6, would involve a rate-determining proton transfer in HOAc and deuteron transfer in DOAc. Generally, such a transfer could be expected to result in a slower rate in the deuterated solvent.[45]



(6)

The entropies of activation for 2-hydroxyisobutyric acid, mandelic acid, and benzilic acid are also consistent with a cyclic intermediate **3**. Such small entropies might be expected in a system where the negative entropy of activation resulting from ring closure of the two initial reactants would be offset by that from ring opening in the rate-determining step to three products. Cyclic intermediates similar to **3** have also been proposed for the oxidation of 2-hydroxycarboxylic acids by a variety of oxidants. In most cases where these hydroxy acid oxidations were found to have $\Delta S^{\ddagger}$ values near zero, the proposed rate-determining step involved the opening of a preformed cyclic intermediate, Table IV. In contrast, the Cr(VI) oxidations of alcohols and hydroxy acids, where concerted proton removal leads to either keto acid intermediates (eq 7) or ketones (eq 8, similar to Scheme II), have large negative entropies of activation, Table IV.[19b,46,47]

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[38] (a) G. V. Bakore and S. Narain, *J. Chem. Soc.*, 3419 (1963); (b) N. Venkatasubramanian, S. Sundaram, and G. Srinivasan, *Indian J. Chem.*, 6, 708 (1968).

[39] S. Senet-Perez and L. Ramos-Garcia, *An. Real Soc. Espan. Fis. Quim., Ser. B*, 53, 673 (1957); *Chem. Abstr.*, 54, 1992 (1960).

[40] P. Hunacus and Th. Zincke, *Ber.*, 10, 1486 (1877).

[41] Although for acetic acid solvent not enough information is available to claim that this result strongly indicates a preequilibrium proton transfer, it is instructive to note that the formation of such an intermediate, with a preequilibrium proton transfer (Scheme I), is consistent with these data.

[42] (a) R. Criegee, B. Marchard, and H. Wannowius, *Justus Liebigs Ann. Chem.*, 550, 99 (1942); (b) F. Nerdel, J. Buddrus, and K. Hoher, *Ber.*, 97, 124 (1964).

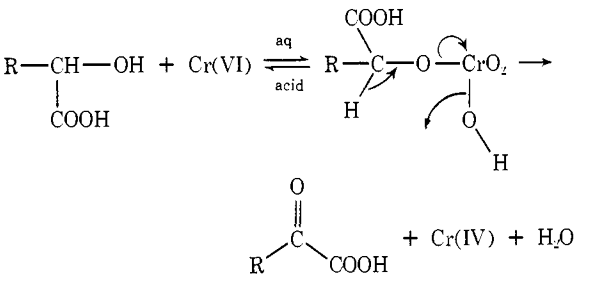
[43] P. Waldstein and L. A. Blatz, *J. Phys. Chem.*, 71, 2271 (1967).

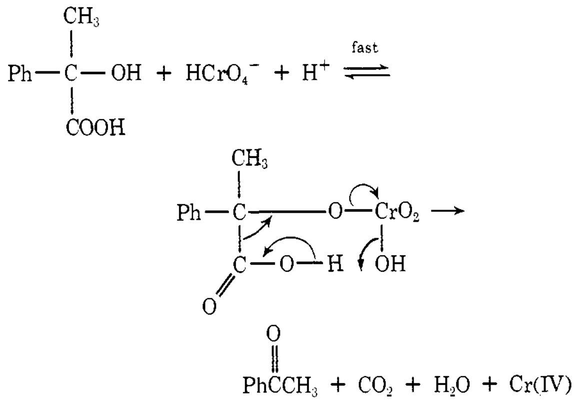
[44] D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 61, 1199 (1965); G. Allen and E. F. Caldin, *Quart. Rev.*, 7, 255 (1953).

[45] B. C. Challis, F. A. Long, and Y. Pocker, *J. Chem. Soc.*, 4679 (1957); Y. Pocker, *Proc. Chem. Soc., London*, 17 (1960); Y. W. Chang and F. H. Westheimer, *J. Amer. Chem. Soc.*, 82, 1401 (1960).

[46] (a) F. H. Westheimer and N. Nicholaides, *J. Amer. Chem. Soc.*, 71, 25 (1949); (b) U. Kwart and P. S. Francis, *ibid.*, 81, 2116 (1959); (c) F. B. Beckwith and W. A. Waters, *J. Chem. Soc. B*, 929 (1969).

[47] K. K. Sengupta, A. K. Chatterjee, B. B. Pal, and N. Sasmal, *Z. Phys. Chem.*, 72, 330 (1970).

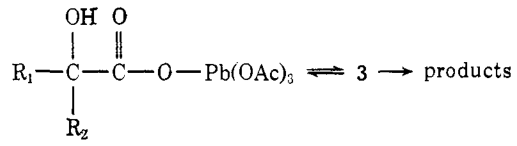

(7)


(8)

The effects of para substitutents on the rate of mandelic acid oxidation by $Pb(OAc)_4$ are found to be very minor. However, with greater structural changes in the 2-hydroxy acids, somewhat larger differences in oxidation rate are observed. These structural effects may reflect differences in the stabilization of developing sp^2 character or may indicate that such cleavages, though concerted, are not strictly synchronous.

All the evidence so far cited strongly indicates that 2-hydroxycarboxylic acid oxidations occur *via* a more or less concerted mechanism in which the rate-determining step involves the decomposition of a Pb(IV)–hydroxy acid intermediate. On the basis of the present study it seems more probable that the cyclic intermediate **3** is involved in the rate-determining step. However, none of the facts so far reported would preclude the formation of **3** from **2′**, Scheme III. The importance of the hydroxyl group is made apparent in Table III. Thus, whereas 1,2-diols, 2-hydroxy acids, hydrobenzoin, and 2-hydroxy esters are oxidized by LTA, 2-keto acids, mandelic acetate, and benzil are not. At present, Scheme II is preferred, although Scheme III is certainly not excluded.

Scheme III


2′

The Production of Singlet Oxygen in Electrogenerated Radical Ion Electron Transfer Reactions

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Abstract: The electrochemical reduction of oxygen generated superoxide ion and the electrochemical oxidation of ferrocene yielded the ferricenium ion. Both of these ion radicals were produced alternately in the same solution by pulsing the electrode potential between the reduction potential of oxygen and the oxidation potential of ferrocene. The homogeneous electron transfer reaction between superoxide ion and the ferricenium ion then produced ferrocene and singlet oxygen. The intermediacy of singlet oxygen was demonstrated by chemical quenching with 1,3-diphenylisobenzofuran (DPBF) which produced *o*-dibenzoylbenzene (DBB). The electron transfer reaction between superoxide and DPBF cation radical also produced singlet oxygen.

The annihilation reaction between ion radicals has recently been an area of intense study. It has been well documented that the mechanism of these reactions is an electron transfer reaction between a cation radical and an anion radical producing an electronically excited species and a neutral ground state molecule.[1-3] The effect of these reactions is the ultimate emission of radiation characteristic of the fluorescence of either R_1 or R_2. When the ion radicals are generated electrochemically, this phenomenon is called electrogenerated chemiluminescence (ecl). In ecl, both ion radicals are generated in the same solution by alternately pulsing the electrode potential from that where the reduction of R_1 occurs to that for the oxidation of R_2. In this manner a very high concentration of ion radicals can be produced in a small volume near the electrode.

$$\left.\begin{array}{l} R_1 \xrightarrow{-e} R_1\cdot^+ \\ \\ R_2 \xrightarrow{+e} R_2\cdot^- \end{array}\right] \longrightarrow \begin{array}{ll} R_1 + R_2^* \longrightarrow R_2 + h\nu & (1) \\ \text{or} & \\ R_2 + R_1^* \longrightarrow R_1 + h\nu & (2) \end{array}$$

Luminescence was not, however, the desired product in this investigation. Since electronically excited species are generated in ecl when the enthalpy of the

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[1] D. M. Hercules, *Accounts Chem. Res.*, 2, 301 (1969); A. Wessberger and B. Rossiter, Ed., "Physical Methods of Organic Chemistry," 4th ed, Part IIA, Academic Press, New York, N. Y., 1971.

[2] A. J. Bard, K. S. V. Santhanam, S. A. Cruser, and L. R. Faulkner, "Fluorescence," G. G. Guilbault, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 14.

[3] T. Kuwana, "Electroanalytical Chemistry," Vol. 1, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1966, Chapter 3.