Oxidative Cleavage by Lead(IV). II. The Role of Oxidant Modification in the Mechanism of the Base-Catalyzed Decarboxylation of Mandelic Acid by Lead Tetraacetate[1]

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The oxidative decarboxylation of mandelic acid by lead tetraacetate (LTA) in acetic acid solvent is strongly catalyzed by a variety of Lewis bases, such as water, methanol, DMF, and acetate ion. The rate of cleavage, v_{obsd}, consists of two terms, one representing the uncatalyzed reaction, v_0, and the second the base-catalyzed reaction, v_{b}. The dependence of v_{b} on [MeOH] suggests that reaction pathways involving both one and two molecules of methanol in the transition state are important. Below 3 *M* addend the dependence of v_{b} on [MeOH] is most important, whereas in the region 3–8 *M*, $[\mathrm{MeOH}]^2$ dependence predominates. With added water v_{b} is similarly dependent on $[\mathrm{H_2O}]$ and $[\mathrm{H_2O}]^2$, with the term involving $[\mathrm{H_2O}]^2$ making the greatest contribution over the concentration range studied. Catalysis by alkali metal acetates is more effective than that afforded by methanol or water, and follows the order KOAc > NaOAc > LiOAc. The kinetic order in the above acetates is close to, but less than, one, suggesting that both free and ion-paired acetate ions are involved in catalysis. Rate enhancement with added amines appears to arise from oxidant modification, not only through the generated acetate, but also through the free amine. For all cases studied oxidant modification seems to provide a more important channel for base catalysis than proton removal.

The oxidative cleavages of 2-hydroxycarboxylic acids by lead tetraacetate (LTA) are rapid, clean, and relatively free from side reactions. The reaction kinetics are well defined and indicate a concerted reaction pathway.[3] Thus general salt and substituent effects are minor, and with inert cosolvents there is little rate dependence on solvent composition save for an inverse dependence on acetic acid concentration, due to the preequilibrium displacement of two acetate moieties as the dimer $(\mathrm{HOAc})_2$.[3] Free radicals cannot be detected by the usual trapping reagents, except under quite extreme conditions.[3] Consequently, these cleavage reactions seemed particularly appropriate for an investigation of Lewis base catalysis in Pb(IV) oxidations. Not only is the kinetic behavior of these reactions in mixed solvents well characterized, but their concerted nature precludes an array of accompanying homolytic or heterolytic side reactions.[4]

Lead tetraacetate is claimed to be octacoordinate in its ground state.[6,7] Certainly all eight acetate oxygens appear to be bonded to the lead, as indicated by the absence of a carbonyl band in the ir spectrum of LTA.[6,8] Further, low molar conductivity shows that LTA has little salt character, whether in acetic acid,[9] dimethyl sulfoxide,[7b] or pyridine.[7b] The most often postulated preequilibrium intermediates for LTA oxidations are Pb(IV) complexes with electron-donating substrates, where displacement of one or more of the acetate ligands is complete. Certainly the isolation and characterization of $\mathrm{Pb(OAc)_2(OMe)(OH)}$ from wet methanol[10] tends to confirm this hypothesis, as do the kinetic results of Pocker and Davis.[3] Furthermore, Partch and Monthony[7b] have isolated $\mathrm{Pb(OAc)_4(C_5H_5N)}$ from a solution of LTA in benzene and pyridine, showing that in certain cases coordination may take place without the complete displacement of an acetate. We have found that formation of Lewis base–LTA complexes of some kind is indicated by color development when $\mathrm{Pb(OAc)_4}$ is added to neat methanol, acetone, acetonitrile, nitrobenzene, nitromethane, DMSO, DMF, pyridine, 2,4- and 2,6-lutidine, and triethylamine. This color disappears in methanol on addition of as little as 5% acetic acid without loss of titratable oxidant.

Two possible mechanisms for base catalysis of LTA oxidations have received the greatest attention. In one, the base is assumed to coordinate with the Pb(IV), transforming it into a much more powerful oxidant; in the other, the base is cast in the role of a proton acceptor in the rate-determining step. The oxidant modification pathway has been postulated by Partch[7b,11] for the acceleration of alcohol oxidation by LTA, by Criegee and Buchner[12] in cyclohexanediol cleavages, by Starnes[13] in the formation of hemiketal acetates from triarylmethanols, by Kochi[14a,b] for lead tetracarboxylate decompositions, and by Benson et al. in the LTA oxidations of Co(II),[15a] Ce(III),[15b] and *tert*-butyl hydroperoxide.[15c] On the other hand, that bases function as proton acceptors has been suggested by Norman[16] for the decomposition of LTA in acetic acid, and by Grob[17] for the Pb(IV) decarboxylation of dicarboxylic acids.

The present study examines in some detail the Lewis base catalysis of mandelic acid cleavage by lead tetraacetate. This is a particularly appropriate system for elucidating the relative importance of oxidant modification and proton removal because the amount and stoichiometry of catalysis can be easily determined without being obscured by accompanying side reactions.

Experimental Section

Materials. All kinetic studies were performed with solvent acetic acid of minimum melting point 16.58°.[3,18] Reagent-grade benzene was shaken with Drierite, stored over sodium wire, and distilled just before use. Freshly opened acrylonitrile was distilled immediately before use, as was reagent-grade acetic anhydride (bp 139–140°). Ethyl lactate was carefully fractionated. The middle cut (about ⅓ of the total volume) was again fractionated just before use, keeping only the constant-boiling fraction, bp 153–154° (lit. bp 154.5°).[19] *N,N*-Dimethylformamide (DMF) was purified in the same manner after drying overnight over anhydrous $\mathrm{MgSO_4}$ (bp 152.5–153°). 1,4-Dioxane was purified as described by Vogel.[20] 2,6-Lutidine, 2,4-lutidine, and triethylamine were each dried overnight over anhydrous potassium carbonate and then carefully fractionated. Absolute methanol was prepared by the method of Vogel.[21] Reagent-grade ethylene glycol was fractionated and the middle third of the distillate dried for 24 hr over anhydrous sodium sulfate. This cut was then carefully refractionated just before use (bp 197–198°).[22] The refractive indices and boiling points of all the solvents used matched literature values.

Lead tetraacetate was purified as in the previous study.[23,3] Real concentrations of LTA in solution were determined either spectrophotometrically or titrimetrically rather than by weight of solid oxidant added. Anhydrous reagent-grade sodium and potassium acetate were dried under reduced pressure at 80° for 24 hr. Reagent grade $\mathrm{LiOAc \cdot 2H_2O}$ was heated in acetic acid with 2 equiv of

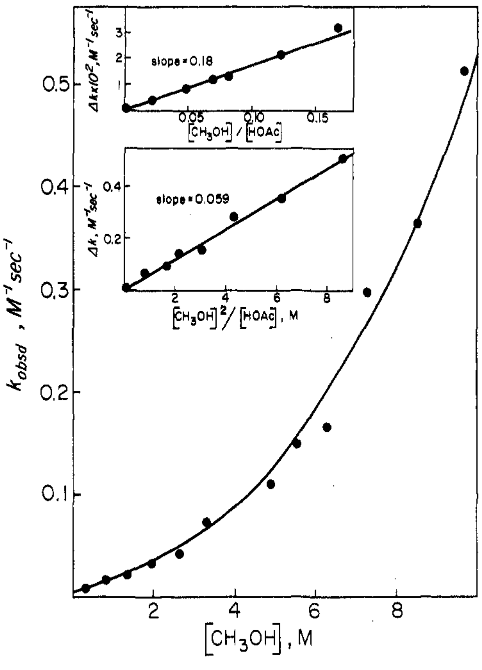


Figure 1. Effect of added methanol on mandelic acid cleavage by lead tetraacetate in acetic acid at 25.0°. Points are experimental and the solid line is calculated from $k_{obsd} = k_0 + k_A[MeOH]/[HOAc] + k_B[MeOH]^2/[HOAc]$, where $k_0 = 9.8 \times 10^{-3}$ M^{-1} sec^{-1}, $k_A^{MeOH} = 0.13$ M^{-1} sec^{-1}, and $k_B^{MeOH} = 0.043$ M^{-2} sec^{-1}. Upper insert: a plot of Δk vs. $[CH_3OH]/[HOAc]$ where $\Delta k = k_{obsd} - k_0$. Lower insert: a plot of Δk vs. $[CH_3OH]^2/[HOAc]$ at higher methanol concentrations.

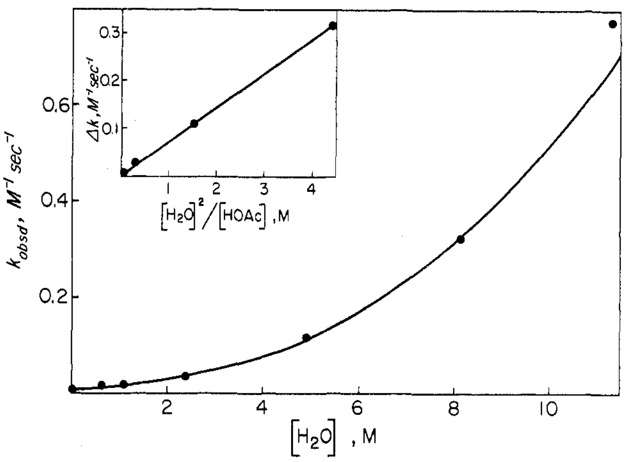


Figure 2. Effect of added water on mandelic acid cleavage by lead tetraacetate in acetic acid at 25.0°. Points are experimental and the solid line is calculated from $k_{obsd} = k_0 + k_A[H_2O]/[HOAc] + k_B[H_2O]^2/[HOAc]$, where $k_0 = 9.8 \times 10^{-3}$ M^{-1} sec^{-1}, $k_A^{H_2O} = 0.065$ M^{-1} sec^{-1}, and $k_B^{H_2O} = 0.060$ M^{-2} sec^{-1}. Insert: a plot of Δk vs. $[H_2O]^2/[HOAc]$, where $\Delta k = k_{obsd} - k_0$.

acetic anhydride. Control runs indicated that rate contributions from the acetic anhydride added were negligible. Benzoin was recrystallized several times from hot methanol (mp 136–137°), as was methyl mandelate (mp 54–55°) from hot heptane. Benzopinacol was synthesized by the method of Pocker and Ronald[18] and recrystallized four times from benzene–ligroin.[24]

Kinetic Measurements. All rates were monitored from 2 to 5 half-lives. Infinities were taken after 10 half-lives. Spectrophotometric rates were determined by following the disappearance of Pb(IV) absorption at various wavelengths between 300 and 330 nm,[3] using a high-speed Gilford multiple sample recording spectrophotometer, Model 2000, fitted with a thermostatted immersion sample compartment. Control runs indicated that no significant loss of Pb(IV) absorbance occurred due to possible thermal or photochemical decompositions of LTA under the conditions employed in this study. In any given run, independent of the Lewis base used, the kinetics of oxidation were first order in mandelic acid and first order in Pb(IV) oxidant; i.e., base catalysis does not change dependence on oxidant or substrate.

Further, control experiments were carried out to determine absorbance changes due to addend oxidation and catalysis of LTA decomposition. Also as indicated, solutions of LTA in triethylamine, 2,4- and 2,6-lutidine, methanol, ethanol, acetonitrile, dimethyl sulfoxide, DMF, nitrobenzene, and nitromethane are highly colored, but decolorize with added acetic acid. Consequently, with none of the added compounds was the absorbance of the LTA–acetic acid–addend solution any higher than would have been expected for LTA alone. However, significant rates of Pb(IV) absorbance loss were noted with added *N,N*-dimethylformamide (DMF) and ethylene glycol. Corrections were made for these side effects in the rate constants reported here for these two cosolvents.

To better understand the interaction of LTA and methanol catalyst, a parallel study of methanol oxidation by LTA in methanol solvent was undertaken.[25] Using Criegee's titration method for [Pb(IV)] determination,[6,10,12] changes in the absorptions of the highly colored LTA–methanol solutions were found to be linear with [Pb(IV)]. Rates of methanol oxidation were followed both titrimetrically and spectrophotometrically. The effect of added acetic acid on this oxidation was also examined. In mixed MeOH–HOAc solvents no color formation was noted with 5% or more acetic acid, and the decrease in Pb(IV) absorbance could be monitored directly. To investigate product catalysis, formaldehyde, produced by warming paraldehyde, was bubbled through methanol and subjected to LTA oxidation. The concentration of formaldehyde was titrimetrically assayed by the method of Buchi.[26]

Product identification for the methanol oxidation was made by injecting samples of the raw reaction mixture directly into a Carbowax column mounted in a Model 5750 Hewlett-Packard research gas chromatograph with a flame ionization detector. Retention times for the reaction mixture were compared with those for a mixture of acetic acid, methanol, formaldehyde, methyl acetate, and methyl formate. Additionally each of these compounds was used in turn to spike the reaction mixture. Identification could then be confirmed by the relative increase in corresponding peak areas. An isothermal oven temperature of 53° was maintained for all VPC product studies.

Results

The base-catalyzed cleavage of mandelic acid (MA) by lead tetraacetate in anhydrous acetic acid was investigated in the presence of several Lewis bases (Table I). When the cleavage is carried out in the presence of methanol, water, DMF, ethylene glycol, and acrylonitrile, a far greater rate enhancement occurs than could be explained by the dilution of acetic acid solvent; e.g., in solvent mixtures containing 25% (v/v) acetic acid the oxidative fission of mandelic acid with added water occurs 63 times faster than that with added benzene (Table I). A detailed examination of MA oxidation with different acetic acid–methanol solvent mixtures reveals that catalysis rates are dependent on both [MeOH] and $[MeOH]^2$. As can be seen from Figure 1, an expression of the type $k_{obsd} = k_0 + k_A[MeOH]/[HOAc] + k_B[MeOH]^2/[HOAc]$ fits the experimental data well for $k_A^{MeOH} = 0.13$ M^{-1} sec^{-1} and $k_B^{MeOH} = 0.043$ M^{-2} sec^{-1}. It is interesting that plots of Δk vs. [MeOH]/[HOAc] and log Δk vs. log ([MeOH]/[HOAc]) are very nearly linear up to 3 *M* addend with slopes of 0.18 M^{-1} sec^{-1} and 0.99, respectively.[27] Further, Δk vs. $[MeOH]^2/[HOAc]$ and log Δk vs. log ($[MeOH]^2[HOAc]$) plots are also linear with respective slopes 0.059 M^{-1} sec^{-1} and 1.0 with 3 $M <$ [MeOH] $<$ 8 *M*.[25] Catalysis by added water follows a similar pattern with the calculated curve for $k_{obsd} = k_0 + k_A^{H_2O}[H_2O]/[HOAc] + k_B^{H_2O}[H_2O]^2/[HOAc]$ closely fitting the experimental points with $k_A^{H_2O} = 0.065$ M^{-1} sec^{-1} and $k_B^{H_2O} = 0.060$ M^{-2} sec^{-1} (Figure 2). However, water catalysis is predominantly dependent on the $[H_2O]^2$ term for most of the concentration range studied. A plot of log Δk vs. log ($[H_2O]^2/[HOAc]$) is linear for 1 $M < [H_2O] < 11$ M with slope 0.92. The slope of the Δk vs. $[H_2O]^2/[HOAc]$ plot shown in Figure 2 is 0.070 M^{-2} sec^{-1}.

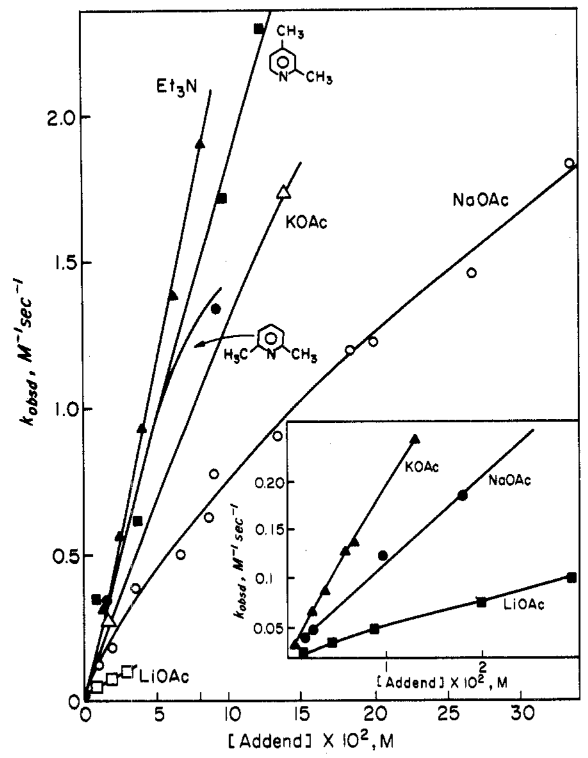


Figure 3. The effect of added acetates and amines on the rate of mandelic acid oxidation by lead tetraacetate in acetic acid at 25°. Addends: ▲, triethylamine; ■, 2,4-lutidine; ●, 2,6-lutidine; △, potassium acetate; ○, sodium acetate; □, lithium acetate. Insert: an expansion of the smaller [addend], lower rate constant portion of the figure. Addend: ▲, potassium acetate; ●, sodium acetate; ■, lithium acetate.

The rate increases observed in water–acetic acid and methanol–acetic acid mixtures are much greater than those observed with cosolvent benzene or dioxane. Even acetonitrile (up to 6 M) and acetic anhydride (up to 4 M) lead to about the same amount of rate enhancement as does added benzene,[3] each exhibiting an inverse dependence on [HOAc]. With such cosolvent catalysis, which is directly attributable to the dilution of acetic acid, the quantity k_{obsd}[HOAc] should remain small and relatively constant. Considering the drastic change in the composition of the solvent, the mandelic acid oxidation with added benzene approximates this condition quite well (Table I). However, addition of either acrylonitrile or DMF leads to a much larger rate enhancement than could be explained by solvent dilution. Only nonlinear kinetics were observed with added DMF.

Catalysis by acetate salts is dramatic (Table II), especially in comparison to the minor effects noted with added $LiClO_4$.[4] However, the amount of catalysis observed with a given molarity of added salt was greater for potassium acetate than for sodium acetate; similarly, sodium acetate was catalytically more efficient than lithium acetate (Figure 3). The initial slopes of Δk vs. [acetate], taken from Figure 3, are as follows: KOAc, 15 M^{-2} sec^{-1}; NaOAc, 11 M^{-2} sec^{-1}; LiOAc, 4.2 M^{-2} sec^{-1}. Plots of log Δk vs. log [salt] were straight for all of the above acetates and had slopes between 0.5 and 1.0: KOAc, 0.85; NaOAc, 0.70; LiOAc, 0.92 (Figure 4).

Plots of log Δk vs. log [amine] were also straight with slopes of 0.88, 1.0, and 0.97 for added 2,6-lutidine, 2,4-lutidine, and triethylamine, respectively (Figure 4). With amine-generated acetate catalysis, plots of addend concentrations vs. observed rates were more nearly linear (Figure 3), with added amines catalytically more efficient than acetate salts. Initial slopes: added Et_3N, 22.7 M^{-2} sec^{-1}; added lutidines, 18.5 M^{-2} sec^{-1}.

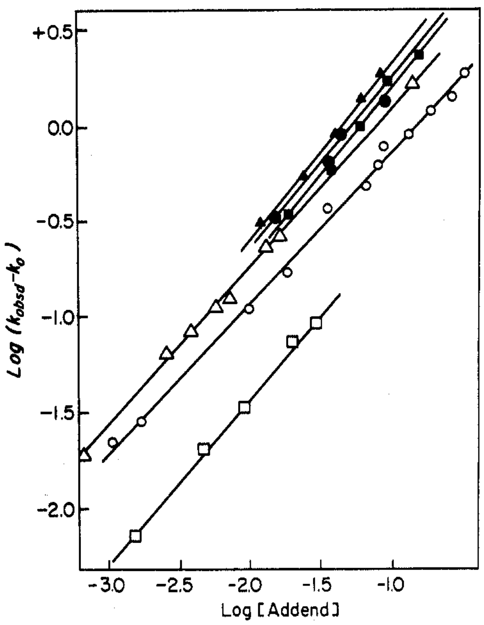


Figure 4. Determination of reaction order in addend for acetate catalysis of mandelic acid cleavage by lead tetraacetate in acetic acid at 25°. Addend: □, lithium acetate; ○, sodium acetate; △, potassium acetate; ■, acetate generated by adding 2,6-lutidine; ▲, acetate generated by adding 2,4-lutidine; ●, acetate generated by adding triethylamine.

The effect of adding both methanol and water to the same run was very interesting. The k_{obsd} for mandelic acid oxidation with 2.25 M added methanol is 0.0379 M^{-1} sec^{-1} and that for 3.30 M added water is 0.0645 M^{-1} sec^{-1}. The sum of these extrapolated[28] rate constants is 0.102 M^{-1} sec^{-1}, while k_{obsd} for the above amounts of methanol and water added simultaneously is 0.105 M^{-1} sec^{-1}. In contrast, added simultaneously, methanol and sodium acetate lead to an observed rate increase which is much more than additive. Thus, with 7.28 M MeOH in acetic acid, k_{obsd} = 0.299 M^{-1} sec^{-1}, and with 0.184 M NaOAc, k_{obsd} = 1.19 M^{-1} sec^{-1}; however, when both of the above addends were present together in the same amounts, k_{obsd} = 20.7 M^{-1} sec^{-1}.

Addition of ethylene glycol, a bidentate reagent, is especially interesting, allowing the investigation of possible autocatalysis in glycol cleavage. The second-order rate constant for ethylene glycol oxidation in acetic acid at 25° (k_{obsd} = 2.49 × 10^{-3} M^{-1} sec^{-1}) agrees well with that reported by Cordner and Pausacker.[29] To avoid the necessity for corrections due to changes in acetic acid concentration, only small amounts of ethylene glycol were added. Under these conditions the sum of pseudo-first-order rate constants for uncatalyzed mandelic acid oxidation and the uncatalyzed ethylene glycol cleavage is nearly the same as the overall pseudo-first-order rate constant for the mixture (Table I).

A parallel study was also conducted to more fully understand the LTA oxidation of methanol, the addend most extensively employed in this study.[25] Addition of LTA to pure methanol gave highly colored brown-red solutions, whose absorbances were proportional to the concentration of lead tetraacetate (determined titrimetrically). The rate of methanol oxidation, i.e., Pb(IV) disappearance, is the same whether the absorption of the LTA–methanol complex is spectrophotometrically monitored or the concentration of Pb(IV) is titrimetrically followed. However, in pure methanol solvent these rates appeared constant only to

Table I
Cosolvent Rate Enhancement of Lead Tetraacetate Oxidations in Acetic Acid

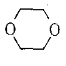
Cosolvent	M	[HOAc], M	$k_{obsd} \times 10^2$, M^{-1} sec^{-1} [a]	k_{obsd}/k_0 [c]	k_{obsd}[HOAc], [c] sec^{-1}
		Mandelic Acid Cleavage			
CH_3OH	0.357	17.2	1.35	1.38	0.232
	0.820	16.9	1.78	1.82	0.301
	1.06	16.7	2.14	2.18	0.357
	1.34	16.5	2.27	2.32	0.375
	1.98	16.1	3.10[d]	3.16	0.499
	2.64	15.6	4.21	4.29	0.656
	3.35	14.9	7.13[d]	7.28	1.08
	4.87	14.1	10.1	10.3	1.42
	5.40	13.6	15.0	15.3	2.04
	6.30	13.1	16.5	16.9	2.16
	7.28	12.3	29.9	30.5	3.68
	8.48	11.5	36.6	37.4	4.21
	9.60	10.7	52.5	53.6	5.62
	10.8	9.87	90.4	92.2	8.92
	13.8	7.75	242	247	18.8
	14.3	7.35	410	418	30.1
	16.8	5.66	1160	1180	65.7
$HOCH_2CH_2OH$	0.160	17.4	2.88	2.94	0.501
	0.209	17.3	3.50	3.57	0.605
	0.286	17.2	3.76	3.84	0.646
	0.388	17.1	5.37	5.48	0.918
	0.515	17.0	7.13	7.28	1.21
	0.771	16.7	10.7	10.9	1.79
	1.68	15.8	47.6	48.6	7.51
C_6H_6	1.86	14.6	1.79[d]	1.82	0.266
	2.78	13.1	2.06[d]	2.10	0.270
	4.66	10.2	2.54[d]	2.59	0.259
	6.00	8.1	3.76[d]	3.84	0.296
	6.22	6.9	4.08[d]	4.17	0.282
CCl_4	1.73	14.6	2.12[d]	2.16	0.310
CH_3OH and H_2O	2.25 3.30	14.9	10.5	10.7	1.56
H_2O	0.638	17.3	1.66	1.69	0.287
	1.09	17.1	1.83	1.87	0.313
	2.38	16.8	3.66[d]	3.73	0.615
	4.91	15.9	11.5[d]	11.6	1.81
	8.13	14.9	32.2	32.9	4.80
	11.3	13.9	77.5	79.1	10.8
	16.1	12.4	248	254	30.8
$(CH_3)_2NCHO$	0.369	17.0	3.56	3.63	0.605
(DMF)	0.727	16.5	12.1[b]	12.4	2.00
	1.21	15.8	17.3[b]	7.7	2.80
	1.92	14.9	103[b,d]	105	15.6
	1.89	12.6	1.38	1.41	0.174
	3.77	11.8	2.14	2.18	0.252
	5.64	9.04	3.77	3.85	0.341
$CH_2{=}CHCN$	4.78	12.0	8.95	9.13	1.07
CH_3CN	1.68	16.0	1.26[d]	1.29	0.202
	2.78	14.9	1.41[d]	1.44	0.210
	4.45	13.4	2.10[d]	2.14	0.281
	5.56	12.4	2.58[d]	2.63	0.320
	6.02	12.0	2.72[d]	2.78	0.326
	8.33	9.86	4.07[d]	4.16	0.401
	11.1	7.36	9.09[d]	9.28	0.670
$(CH_3CO)_2O$	3.21	12.0	2.12[d]	2.16	0.254
	3.97	10.9	2.95[d]	3.01	0.322
	4.86	9.47	4.72[d]	4.82	0.447
	6.52	6.56	7.60[d]	7.75	0.499
$CH_3COOC_2H_5$	1.71	14.6	1.98	2.02	0.289

Table I
(Continued)

Cosolvent	M	[HOAc], M	$k_{obsd} \times 10^2$, M^{-1} sec^{-1} [a]	k_{obsd}/k_0 [c]	k_{obsd}[HOAc], [c] sec^{-1}
Benzopinacol Cleavage[e]					
		17.5	16.7	1.0	2.89
C_6H_6	1.41	15.3	18.7	1.12	2.86
	3.52	12.0	24.0	1.44	2.87
	6.34	7.65	30.8	1.84	2.36
Benzoin Oxidation[f]					
		17.5	1.87	1.0	0.327
CH_3OH	6.70	12.7	12.3	6.58	1.56
Methyl Mandelate Cleavage[g]					
		17.5	0.018	1.0	0.00315
CH_3OH	7.65	12.0	0.377	2.10	0.00452
	15.4	6.57	0.402	22.3	0.00264
	20.8	2.92	0.195	108	0.0569
Methanol Oxidation[h]					
CH_3OH	7.60	13.5	0.000110		0.00148
	15.2	6.73	0.000420		0.00282
	19.0	4.04	0.000973		0.00762
	24.7	0.00	0.00185		0.00
CH_3OD	(solvent, >99% d_1)	0.00	0.0012		0.00
CH_3OD	(solvent, >99% d_4)	0.00	0.00048		0.00
Ethyl Lactate Oxidation[i]					
		17.5	0.0181	1.0	0.00317
C_6H_6	1.79	11.9	0.0287	1.59	0.00342
	3.58	9.15	0.0346	1.91	0.00317
	5.37	6.40	0.0495	2.73	0.00317
$CH_2{=}CHCN$	2.40	12.0	0.0260	1.44	0.00312
	7.20	6.39	0.0301	1.66	0.00192
CH_3OH	1.58	13.6	0.0274	1.51	0.00372
	3.16	12.5	0.0466	2.58	0.00582
	4.74	4.74	0.0596	3.30	0.0283
	6.32	6.32	0.0892	4.93	0.0564
H_2O	1.72	14.2	0.0283	1.56	0.00400
	3.44	13.6	0.0443	2.45	0.00646
	6.88	12.5	0.0962	5.31	0.0120

[a] At 25.0°; k_{obsd} are average values of the spectrophotometric second-order rate constants obtained under the specified conditions; $k_{obsd} = k_x$/[mandelic acid] where k_x is the rate coefficient monitored under pseudo-first-order conditions. [b] Corrected for addend oxidation by lead tetraacetate. Such oxidation is negligible in undesignated cases. [c] In pure acetic acid ([HOAc] = 17.5 M), the rate constant for mandelic acid oxidation, k_0, is 9.80×10^{-3} M^{-1} sec^{-1} and k_0[HOAc] = 0.173 sec^{-1}. Rate enhancements are caused not only by acetic acid dilution (ref 3) but also, in some cases, by direct addend catalysis: $\Delta k = k_{obsd} - k_0 = k_A[\text{addend}]/[\text{HOAc}] + k_B[\text{addend}]^2/[\text{HOAc}]$. [d] Data taken from ref 3. [e] Cleavage product benzophenone; $k_{obsd} = k_x$/[benzopinacol]. [f] Product benzil (i.e., no cleavage); $k_{obsd} = k_x$/[benzoin]. [g] Cleavage product benzaldehyde; $k_{obsd} = k_x$/[methyl mandelate]. [h] Oxidation products formaldehyde and methyl formate; $k_{obsd} = k_x/[CH_3OH]$. [i] Cleavage product acetaldehyde; $k_{obsd} = k_x$/[ethyl lactate].

25% reaction, with rate increase occurring thereafter. Addition of acetic acid leads to more linear kinetics. Under these conditions methanol oxidation rates appear to be inversely proportional to acetic acid concentrations. Addition of even small amounts (5–10%) of acetic acid results in rapid loss of Pb(IV)–methanol absorbance at 370 nm ($\epsilon_{complex}$ = 1830), and the resultant spectrum is virtually that of LTA in pure acetic acid.

Solvent deuterium isotope effects were also determined. With methanol-d_1, k_{CH_3OH}/k_{CH_3OD} = 1.5, but with methanol-d_4, k_{CH_3OH}/k_{CD_3OD} = 3.8 (Table I). When methanolic solutions containing formaldehyde (the expected product of methanol oxidation) are oxidized by LTA, both the spectrophotometric and the titrimetric rates are faster than expected. However, the rapid rate of absorbance change is even greater than that which could be explained by increased oxidation rates. Product studies using VPC show that both formaldehyde and methyl formate are produced. Traces of methyl acetate were also detected.

Discussion

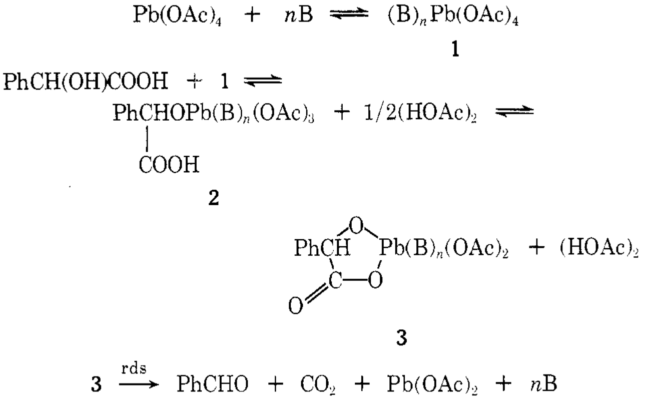
Two fundamental base- (B) catalyzed pathways can be envisaged for the concerted cleavage of mandelic acid by lead tetraacetate. Scheme I visualizes that this oxidative decarboxylation is channeled through certain Pb(IV) complexes, **1**, which are more reactive than $Pb(OAc)_4$ itself. Such carriers of Pb(IV) arise from the complexation of certain Lewis bases with LTA. The second pathway, Scheme II, consists of a proton removal which could be synchronous as below, or stepwise with the formation of carboxylate anion. The inverse dependence of the base-catalyzed reactions studied on acetic acid concentration, $v_b \propto [(CH_3COOH)_2]^{-1}$, favors Scheme I over either case of Scheme II.[30]

Table II
Amine and Acetate Salts Rate Enhancement of Lead Tetraacetate Oxidations in Acetic Acid

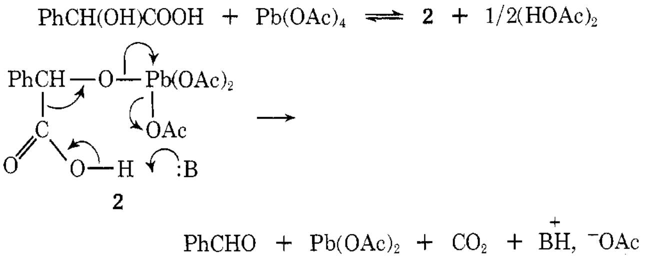
Addend	$M \times 10^2$	$k_{obsd} \times 10^2$, $M^{-1}\ sec^{-1}$ [a]	k_{obsd}/k_0 [b]	Addend	$M \times 10^2$	$k_{obsd} \times 10^2$, $M^{-1}\ sec^{-1}$ [a]	k_{obsd}/k_0 [b]
			Mandelic Acid Cleavage				
LiOAc	0.156	1.96	2.00	2,6-Lutidine	1.56	34.3	35.0
	0.472	3.26	3.33		3.71	63.0	64.3
	0.893	4.61	4.71		4.30	92.0	94.0
	2.00	7.13	7.28		9.22	133	136
	2.94	9.87	10.1				
NaOAc	0.105	3.50	3.57	2,4-Lutidine	1.85	35.0	35.7
	0.167	4.07	4.15		3.70	61.7	63.0
	0.973	12.0	12.2		6.17	103	105
	1.80	17.8	18.2		9.25	172	175
	3.59	38.6	39.4		12.3	229	234
	6.65	49.2	50.2				
	8.50	62.5	63.8				
	8.90	77.7	79.3	Triethylamine	1.23	31.3[c]	31.9
	13.3	90.0	91.8		2.46	56.6	57.8
	18.4	119	121		4.11	92.7	94.6
	19.9	122	124		6.17	138	141
	26.8	142	145		8.23	190	194
	33.5	183	187				
KOAc	0.0658	3.10	3.16	NaOAc and	18.2		
	0.249	6.39	6.52	MeOH	728	2070	2110
	0.385	8.68	8.85	([HOAc] = 12.3 M)			
	0.576	12.6	12.9				
	0.676	13.5	13.8				
	1.33	24.1	24.6				
	1.67	27.6[c]	28.2				
	13.9	176	180				

[a] At 25.0°, average second-order rate constants; individual $k_{obsd} = k_x/[\text{mandelic acid}]$, where k_x is the slope of $-\ln(A_t - A_\infty)$ vs. time for rates monitored spectrophotometrically under pseudo-first-order conditions. [b] $k_0 = 9.80 \times 10^{-3}\ M^{-1}\ sec^{-1}$; k_0 is the rate constant for mandelic acid oxidation in pure acetic acid with no added catalyst. [c] Data taken from ref 3.

Scheme I



Scheme II



Rate enhancement by addition of either water or methanol clearly involves moieties containing both one and two molecules of addend. Indeed, catalysis involving two molecules of water seems to make the major contribution for most of the concentration range studied (insert, Figure 2). With added methanol the transition state in which one molecule of addend is involved makes the major contribution at low concentration ([MeOH] < 3 M); the primary catalytic contributor at higher concentration (3 M < [MeOH] < 8 M) appears to be a species in which two molecules of addend are important (see insert, Figure 1). It is instructive to compare the rate constants calculated to give the best curve fit for methanol and water catalysis, respectively.

	k_A, M^{-1} sec^{-1}	k_B, M^{-2} sec^{-1}
Methanol	0.13	0.043
Water	0.065	0.060

Further, there is good agreement between these constants and the slopes of the inserts in Figures 1 and 2. As expected, each slope is somewhat higher than the corresponding catalytic rate constant, because it contains contributions from other order terms.

It should also be noted that the inverse dependence on acetic acid concentration is identical for catalyzed and uncatalyzed cleavage of mandelic acid. This is exactly as would be expected if the catalytic species were a complex between base and Pb(IV) without complete displacement of an acetate moiety. Actual reaction would then involve displacement of acetate by substrate, giving the same rate dependence as in the uncatalyzed case ($v \propto [(HOAc)_2]^{-1}$). When ethylene glycol is present during the mandelic acid cleavage, both compounds are oxidized at the rate expected for the concentration employed, independent of the presence of the other. Apparently both of these bidentate reagents coordinate to the Pb(IV) such that they displace an acetate moiety and are then cleaved so efficiently that they fail to act as oxidation catalysts for each other.

This bidentate nature may also be important in the oxidation of formaldehyde methyl hemiacetal in methanol solvent. When $Pb(OAc)_4$ is added to methanol, complex formation is indicated by a dark brown-red color. Changes in absorbance corresponded to changes in [LTA] during the oxidation of methanol to formaldehyde. However, after about 30% reaction the rate of apparent oxidation, spectrophotometrically measured, accelerated. Thereafter, it was found that the addition of a methanol solution of formaldehyde, mainly present as the hemiacetal, caused rapid decolorization of a freshly prepared solution of LTA in methanol, which did not correspond, titrimetrically, to loss of Pb(IV). Thus it seems that bidentate CH_3OCH_2OH can successfully compete with a much larger concentration of methanol for Pb(IV). With this addition the real oxidation rate, measured titrimetrically, also increases, with oxidation in the new complex giving methyl formate.[25] That oxidant modification takes place during methanol oxidation is indicated by the intense color of CH_3OH–LTA solutions, which disappears with even 5% acetic acid without loss of oxidant, and by the $Pb(OAc)_2(OCH_3)(OH)$ isolated by Criegee et al.[10] from wet methanol.

Further indications of oxidant modification by alcohols include the observations that log k_{obsd} vs. vol % methanol plots were parallel for LTA cleavage of several glycols[12] and that k_{obsd} is linearly dependent on ethanol concentration in the alcohol catalysis of *tert*-butyl hydroperoxide decomposition by LTA.[15] Similarly, in mandelic acid cleavage the total rate is the sum of uncatalyzed and catalyzed hydroxy acid cleavage, i.e., $k_{obsd} = k_0 + \Delta k$.

All of the above evidence seems to imply that only a small percentage of catalytically effective modified oxidant is produced. The independence of catalyzed and uncatalyzed rates is also observed in acetate catalysis, both with respect to added salts and with those generated by the addition of amines. In this connection, Criegee has shown by solubility measurements that added acetate ion modifies LTA to produce new complexes in acetic acid.[6] Further, Benson and Sutcliffe[15] found that lead migrates to the anode in acetic acid solutions containing both sodium acetate and LTA, whereas no such migration was seen in the absence of acetate salt.

Initially all k_{obsd} vs. [acetate salt] plots are nearly linear (Figure 3). A comparison of the $k_{obsd}[HOAc]_0$/[acetate salt] with k_A for water and methanol, respectively, emphasizes the greater catalytic efficiency of acetate catalysis: water, 0.065 M^{-1} sec^{-1}; methanol, 0.13 M^{-1} sec^{-1}; LiOAc, 73.5 M^{-1} sec^{-1}; NaOAc, 193 M^{-1} sec^{-1}; KOAc, 263 M^{-1} sec^{-1}. However, as [addend] increases, catalytic efficiency decreases for all acetate-producing catalysts except 2,4-lutidine and triethylamine. The log $(k_{obsd} - k_0)$ vs. log [salt] plots for mandelic acid cleavage are straight but with slopes slightly less than one for added LiOAc, NaOAc, KOAc, and 2,6-lutidine; however, slopes of one are observed with added 2,4-lutidine and triethylamine. The key to the understanding of this acetate catalysis in acetic acid is the great range of electrostatic forces in this solvent.[31] Thus, it is known that salts do exist in acetic acid essentially as ion pairs, in equilibrium with small proportions of free ions, triplet ions, and perhaps also quadruplets.[32] If only free acetate were the catalytic agent, a dependence of k_{obsd} on $[salt]^{1/2}$ would have been observed; however, if acetate salt ion pairs were responsible for the catalysis, the log–log plots would have yielded a slope of unity. Clearly, the concurrent catalytic action of the prevalent ion pairs and the more efficient, but less abundant, free ions would result in the observed fractional order. Indeed, the relative catalytic efficiency, KOAc > NaOAc > LiOAc, parallels the order of dissociation of ion pairs into free ions found by Kolthoff and Bruckenstein,[32] $K^+OAc^- > Na^+OAc^- > Li^+OAc^-$.[33] However, amine catalysis is more difficult to analyze. Thus in addition to free acetate and amine-H^+, OAc^- ion pairs one has to consider catalytically significant concentrations of remaining free amine (e.g., pyridine + HOAc $\rightleftharpoons$ pyridine-H^+OAc^-, $K_B{}^{Py} = 5.4^{32b}$). Such contributing catalysis by free amine has been shown by other workers, who actually isolated a pyridine · $Pb(OAc)_4$ complex.[7b]

It is interesting that when mandelic acid was cleaved in a solvent containing 7.28 *M* methanol, 0.182 *M* NaOAc, and 12.3 *M* HOAc, the observed rate constant was 14 times greater than the sum of rate constants for identical quantities of each catalyst independently added. A similar instance was reported by Criegee[12] where mixed water–potassium acetate catalysis of *cis*-cyclohexanediol cleavage was 2.7 times faster than the sum of rate constants for independent addition.

The addition of DMF to the reaction mixture results in rate increases, $H_2O < DMF < CH_3CO_2^-$. However, neither k_{obsd} vs. [DMF] nor log k_{obsd} vs. log [DMF] plots were linear for this addend. Nevertheless, it is interesting to note that DMF exerts a profound effect on LTA oxidations either by virtue of its bidentate nature or possibly because small but catalytically significant amounts of $DMFH^+OAc^-$ are formed in these solutions.[34] Acrylonitrile causes a ninefold increase in rate, when added in the same concentration that only produces a two- to three-fold rate increase with added acetonitrile. This effect might also arise via a bidentate interaction with Pb(IV).

It is attractive to attribute most of the observed catalysis to the production of a more reactive oxidant. Certainly oxidant modification does take place. Further, this study has shown that the catalytic portion of the observed rate is inversely proportional to $[(HOAc)_2]$, as would be expected from Scheme I, not $[(HOAc)_2]^{1/2}$, as Scheme II would have predicted. Analogously, Criegee[12] has shown that the relative amounts of Lewis base catalysis in glycol cleavage reactions are independent of the nature of the diol, as would accord with a catalytic mechanism involving oxidant modification. Similar conclusions have been reached by Benson and Sutcliffe[15] for a variety of Pb(IV) oxidations of metal ions and hydroperoxides. Finally, the apparent order of catalytic efficiency parallels the ability of the various addends to donate an electron pair to Pb(IV).

Registry No.—LTA, 546-67-8; mandelic acid, 90-64-2; methanol, 67-56-1; 1,2-ethanediol, 107-21-1; benzene, 71-43-2; carbon tetrachloride, 56-23-5; water, 7732-18-5; dimethylformamide, 68-12-2; *p*-dioxane, 123-91-1; acrylonitrile, 107-13-1; acetonitrile, 75-05-8; acetic anhydride, 108-24-7; ethyl acetate, 141-78-6; benzopinacol, 464-72-2; benzoin, 119-53-9; methyl mandelate, 771-90-4; ethyl lactate, 97-64-3; methanol-*d*, 1455-13-6; methanol-d_4, 811-98-3; lithium acetate, 546-89-4; sodium acetate, 127-09-3; potassium acetate, 127-08-2; 2,6-lutidine, 108-48-5; 2,4-lutidine, 108-47-4; triethylamine, 121-44-8.

References and Notes

(1) This work was supported in part by a Public Health Service Grant from the National Institute of Arthritis and Metabolic Diseases. Taken in part from the Ph.D. Dissertation of B. C. Davis, University of Washington, 1972.

(2) National Science Foundation Predoctoral Fellow, 1968–1971.

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(4) Extensive controls (ref 3 and subsequent experiments) exclude both ionic and free-radical mechanisms. Minor salt effects (with 2.5 *M* added

LiClO$_4$, k_{salt}/k_0 = 1.2), small substituent effects ($k_{C_6H_5C(Me)OHCO_2H}$:$k_{C_6H_5CHOHCO_2H}$:$k_{p\text{-}CH_3C_6H_4CHOHCO_2H}$ = 0.91:1.0:1.2), and relative insensitivity to solvent polarity (small and parallel rate changes with cosolvents, acetic anhydride, acetonitrile, and benzene) argue against pathways involving rate-determining ionization.[3] Furthermore, none of the observations indicating a free-radical pathway for the decarboxylation of monofunctional carboxylic acids, (1) induction times and sigmoidal rate profile with time, (2) very strong inhibition by oxygen in every case, (3) increased rates with uv illumination, and (4) radical trapping, were observed during mandelic acid cleavage by Pb(OAc)$_4$ in acetic acid solvent. Parallel runs using degassed samples in an oxygen-free atmosphere had virtually identical rates with those exposed to the atmosphere; also, bubbling air through a degassed sample did not change the rate of oxidative cleavage. Decarboxylations of pivalic, phenylacetic, and acetic acids all yielded free radicals which were trapped by acrylonitrile. In contrast, no radicals could be detected during the cleavage of mandelic acid under identical conditions. Similarly, Trahanovsky[5] differentiated between free-radical and non-free-radical mechanisms for glycol cleavage by Ce^{IV} and Pb(OAc)$_4$, respectively, by trapping radicals with acrylamide during the cerium(IV) oxidation. None could be detected during the lead tetraacetate cleavage.

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(27) Rate constant for the catalytic portion, $\Delta k = k_{obsd} - k_0$, where k_{obsd} is the experimentally determined second-order rate constant and k_0 is the constant for mandelic acid cleavage in the absence of catalyst; $k_0 = 9.80 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

(28) These rate constants were extrapolated from the data in Table I and Figures 1 and 2, correcting to the solvent dilution found when both addends are present, i.e., [HOAc] = 14.9 *M*.

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(30) All the evidence so far cited indicates that the oxidative cleavage of mandelic acid by (B)$_n$Pb(OAc)$_4$ occurs via a more or less concerted pathway in which the rate-determining step apparently involves the decomposition of the cyclic intermediate **3.** In Scheme I, we depicted intermediate **3** as being formed from **2** ≡ PhCH(COOH)OPb(OAc)$_3$(B)$_n$; however, none of the above observations would preclude its formation from **2′** ≡ PhCH(OH)COOPb(OAc)$_3$(B)$_n$. Similarly, in the reaction pathway depicted in Scheme II, intermediate **2** ≡ PhCH(COOH)OPb(OAc)$_3$ could be replaced by **2′** ≡ PhCH(OH)COOPb(OAc)$_3$. At the same time, the importance of a free hydroxyl group in the substrate is made apparent by the fact that whereas 1,2-diols, 2-hydroxy acids, 2-hydroxy esters, and benzoin are oxidized by LTA, 2-keto acids, mandelic acetate, and benzil are not.[3]

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(33) Clearly, it should be recognized that even more complex equilibria may play a significant part in catalysis; e.g., efficiency among acetate salts may also be related to the relative abilities of $(M^+)^n[Pb(OAc)_{4+n}{}^{-n}]$ ion pairs to form Pb(IV)–mandelic acid intermediates. Further, changing Δk/[addend] with greater catalyst concentration could be related not only to the number of addend molecules in the activated complex, but also to the amount of aggregation into even larger species. Norman[16] has isolated a salt from a mixture of NaOAc and LTA in pyridine and acetic acid containing two lead and ten acetate moieties, and Kolthoff and Bruckenstein[32a] have reported that KOAc and pyridine in HOAc begin to form ionic aggregates above 0.04–0.05 *M* addend.

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A Reexamination of the Equilibrium Addition of Bisulfite and Sulfite Ions to Benzaldehyde

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The equilibrium constants for the addition of "bisulfite ion" to benzaldehyde were determined at 21° and μ = 1.0 *M* over the pH range 3.55–12.62. A spectrophotometric method was employed. The pH dependence of these observed constants was used to obtain values for the equilibrium constants for the reaction of benzaldehyde with HSO_3^- and SO_3^{2-}, and for the acidity constant of the benzaldehyde–HSO_3^- adduct. A comparison of our results with the earlier reports of Stewart and Donnally suggests that the titration method used by these workers yielded inaccurate equilibrium constants at pH's >8. The effect of our equilibrium results on the kinetic scheme and parameters for the reaction of benzaldehyde and bisulfite ion is also discussed.

Some time ago Stewart and Donnally[1] reported a study of the equilibria for the reaction of bisulfite ion[2] and benzaldehyde over the pH range 0–13 in which they determined the extent of reaction by titration of unreacted bisulfite ion with iodine. We became interested in reexamining this reaction because in the above study the observed dependence of the equilibrium constant vs. pH led to the claim that at the more basic pH's hydroxide ion was adding to a measurable extent to the carbonyl group of benzaldehyde. Using Stewart and Donnally's value for the equilibrium constant for the addition of hydroxide ion to benzaldehyde, $10^{1.4}$ M^{-1},[1c,3] together with an estimate of the pK_a of benzaldehyde hydrate of $10^{-12.7}$ *M*,[4] one can calculate that in aqueous solution the ratio of hydrated to unhydrated benzaldehyde should be about 1.0, which is contrary to the known lack of hydration of this compound.[5] Recently, Greenzaid[5] and Zuman[6] have determined that the equilibrium constant for the addition of hydroxide ion to benzaldehyde is in fact only $10^{-0.9}$ M^{-1}. Thus either Stewart and Donnally's determination of the observed equilibrium constant[1b] for the addition of bisulfite ion to benzaldehyde at high pH is in error, or their interpretation of the observed behavior is in error.

Similarly, the work of Stewart and Donnally[1c] led to a value for the pK_a of PhCH(OH)SO$_3^-$ of 9.5, while Taft[7] and "σ^I"[10] correlations lead to estimates of this pK_a as 11.7