Three-Electron Oxidations. 16. Chromic Acid Oxidation of Mandelic Acid[1,2]

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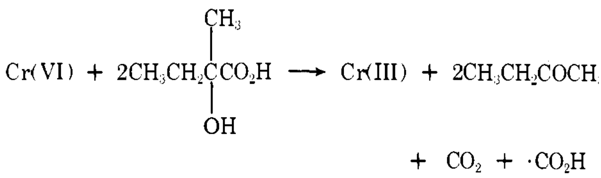
Abstract: The chromic acid oxidation of mandelic acid (MA) obeys the rate law $-d[Cr(VI)]/dt = [HCrO_4^-][MA](k_1 + k_2[H^+] + k_3[MA])$. The reactions corresponding to the two first-order kinetic terms (k_1 and k_2) yield benzaldehyde, benzoic acid, and carbon dioxide in a 1:1:2 ratio, while the second-order reaction (k_3) produces a benzaldehyde, phenylglyoxylic acid, and carbon dioxide in a 2:1:2 ratio. Neither benzaldehyde nor phenylglyoxylic acid is intermediate in the formation of benzoic acid. Both the first-order and the second-order reactions are three-electron oxidations. It is proposed that in the first-order reaction mandelic acid is oxidized to carbon dioxide and a benzoyl radical. This reaction represents the first example of an intramolecular three-electron oxidation in which a carbon hydrogen and a carbon–carbon bond to the same carbon atom are broken simultaneously in the rate-limiting step.

In previous communications in this series, we have examined a new class of oxidation–reduction processes between chromium(VI) and organic substrates in which chromium(VI) is reduced directly to chromium(III) in the rate-limiting step of the reaction. We found that these three-electron oxidations require the participation of an oxidizable bidentate ligand, e.g., oxalic acid or an α-hydroxy acid. In the examples studied so far, three-electron oxidations involved the oxidation on either four functional groups, as in the second-order oxidation of oxalic acid[3] (eq 1)

$$Cr(VI) + 2(CO_2H)_2 \rightarrow Cr(III) + 3CO_2 + \cdot CO_2H \quad (1)$$

or 2-hydroxy-2-methylbutyric acid[4] (eq 2)



$$Cr(VI) + 2CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CO_2H \rightarrow Cr(III) + 2CH_3CH_2COCH_3 + CO_2 + \cdot CO_2H \quad (2)$$

or on three functional groups as in the cooxidation of alcohols with oxalic acid[5] or hydroxy acids[6] (eq 3, 4)

$$Cr(VI) + R_2CHOH + (CO_2H)_2 \rightarrow Cr(III) + R_2CO + CO_2 + \cdot CO_2H \quad (3)$$

$$Cr(VI) + R_2CHOH + HOCH_2CO_2H \rightarrow Cr(III) + R_2CO + HO\dot{C}HCO_2H \quad (4)$$

A three-electron oxidation reaction has also been observed within a single organic substrate molecule with three functional groups placed at appropriate distances allowing the formation of a bicyclic intermediate chromium complex and a tricyclic transition state[7] (eq 5).

$$Cr(VI) + HOCH_2(CH_2)_4CH(OH)CO_2H \rightarrow Cr(III) + OCH(CH_2)_4\dot{C}H(OH) + CO_2 \quad (5)$$

In order to understand three-electron oxidations more fully, it was desirable to determine whether the presence of at least three functional groups in the activated complex is indeed required. In our search for a simpler system we noticed that earlier investigations of the chromic acid oxidation of mandelic acid[8-15] led to results which were difficult to reconcile with a one- or two-electron oxidation mechanism. Literature reports indicated, on the one hand, that mandelic acid undergoes carbon–carbon bond cleavage to give carbon dioxide[10,12] but, on the other hand, exhibits a large deuterium isotope effect,[9,15] suggesting carbon–hydrogen bond cleavage in the rate-limiting step; however, the corresponding oxidation product, phenylglyoxylic acid, had never been detected.[10,12,14,15] These results would seem to suggest a three-electron oxidation in which both a carbon–hydrogen and a carbon–carbon bond are broken. Unfortunately, previous studies did not provide sufficient data for a rigorous analysis of the mechanism since they were carried out only under single reaction conditions or over narrow concentration ranges and were usually restricted only to a qualitative, if any, analysis of products.

Experimental Section

Materials. The following materials were purified by crystallization: *dl*-mandelic acid (Aldrich) from water (2×), mp 118 °C (lit.[16] 118–119 °C); atrolactic acid hemihydrate from water (Aldrich, mp 85–86 °C), softening at 75 °C (lit.[17] 90–91 °C, softening at 75 °C); phenylglyoxylic acid (Aldrich from carbon tetrachloride, mp 67 °C (lit.[18] 65–66 °C). *dl*-Methyl mandelate (Aldrich) was dissolved in CH_2Cl_2, washed with sodium bicarbonate, and recrystallized from methylene chloride- hexane, mp 55–55.5 °C (lit.[19] 57 °C).

Commercially available benzyl alcohol (Fisher) and 1-phenylethanol (Aldrich) were found to contain noticeable amounts of the corresponding aldehyde or ketone, which were removed by treatment with 2,4-dinitrophenylhydrazine; subsequent vacuum distillation yielded pure products (>99% by LC).

Benzaldehyde (Fisher) and *m*-tolualdehyde (Aldrich) were purified by washing their etheral solutions with saturated sodium bicarbonate solution, followed by fractional distillation through a Vigreux-Claisen type distilling column in a stream of prepurified nitrogen.

Oxalic acid (Baker Analyzed Reagent), benzoic acid (Sublimed, Fisher), isopropyl alcohol (Fisher), ethyl acetate (Fisher), ethanol (200 proof, CSC), acrylonitrile (99%, Aldrich), acrylamide (99% Aldrich), 2,4-dinitrophenylhydrazine (97%, Aldrich), potassium iodide (Baker Analyzed Reagent), sodium dichromate (J. T. Baker Reagent), sodium perchlorate (Fisher), perchloric acid (Fisher, 70% Reagent), hydrochloric acid (Fisher), ceric ammonium sulfate (Baker Analyzed Reagent), ceric perchlorate (Hydrated, G. Frederick Smith Chemical Co.), potassium hydrogen phthalate (Merck & Co.), and sodium thiosulfate (Baker Analyzed Reagent) were used without purification.

Benzene (Mallinckrodt Analytical Reagent) and hexane (Mallinckrodt Analytical Reagent) were distilled before use as solvents for column chromatography.

m-Methylmandelic acid was prepared from *m*-tolualdehyde[20] via the bisulfite addition compound and *m*-methylmandelonitrile: mp 86–86.5 °C (lit.[21] 84 °C).

m-Toluic acid was prepared in 60% yield by permanganate oxidation of *m*-tolualdehyde in potassium carbonate solution,[22] mp 110 °C (lit.[23] 110.2 °C).

α-*d*-Mandelic acid was prepared by base-catalyzed deuterium exchange from sodium mandelate and D_2O following the procedure of Kemp and Waters.[9] The recrystallized product (ethyl acetate) showed the absence of an α proton in the δ 5.2–5.3 ppm region of ^1H NMR spectrum; deuterium content was determined by mass spectroscopy to be >99%.

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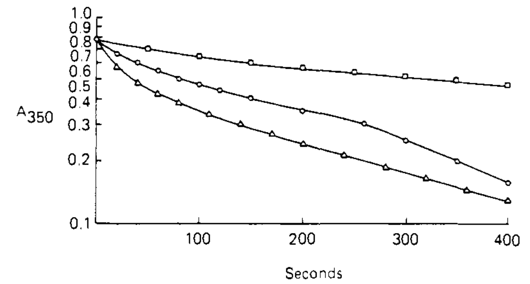


Figure 1. Log A_{350} vs. time plots for chromic acid oxidation of mandelic acid. Conditions: 25 °C, $[\mathrm{Cr(VI)}]_0 = 5 \times 10^{-4}$ M; (□) [MA] = 0.2 M; $[\mathrm{H^+}] = 0.1$ M; (⊙) [MA] = 0.5 M; $[\mathrm{H^+}] = 0.005$ M; (△) [MA] = 0.8 M; $[\mathrm{H^+}] = 0.03$ M.

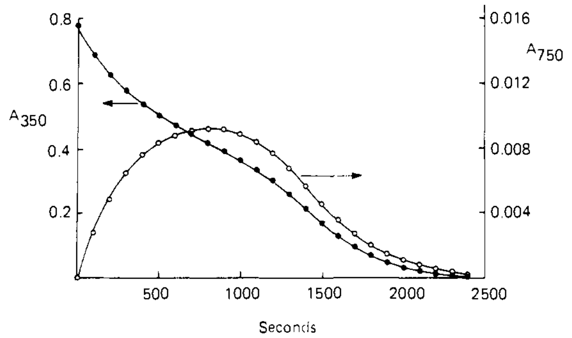


Figure 2. Absorbance vs. time plots at 350 nm (●) (1 cm cell) and 750 nm (⊙) (5 cm cell); only Cr(V) absorbs at 750 nm. Conditions: 25 °C; [MA] = 0.2 M; $[\mathrm{H^+}] = 0.01$ M; $[\mathrm{Cr(VI)}] = 5 \times 10^{-4}$ M.

Acetonitrile (Fisher), glacial acetic acid (Mallinckrodt Analytical Reagent), and distilled water were filtered through a 4–8-μm filter before preparing the solvent mixture for LC analysis.

Kinetic Measurements. Reaction rates of chromium(VI) oxidation of mandelic acid were determined spectrophotometrically on a Cary Model 15 recording spectrophotometer equipped with a thermostated cell holder. The initial chromium(VI) concentrations were 5×10^{-4} M in kinetic and 5×10^{-4} or 5×10^{-3} M in product studies. All oxidation experiments in these studies were carried out under pseudo-first-order conditions, with at least a tenfold excess of substrate over oxidant concentration.

Perchloric acid was used as source of hydrogen ions. The amount of acid added in order to achieve a desired concentration of hydrogen ions was determined from eq 6

$$[\mathrm{HClO_4}] = [\mathrm{H^+}] - \frac{K_a[\mathrm{MA}]}{K_a + [\mathrm{H^+}]} \qquad (6)$$

where [MA] is the total concentration of mandelic acid and $K_a = 1.4 \times 10^{-4}$, its dissociation constant.[24] Low acidity measurements were carried out by using mandelic acid–sodium mandelate buffers.

At high acidities and low concentrations of mandelic acid excellent straight-line plots of log A_{350} vs. time[25] were obtained; pseudo-first-order rate constants were calculated from the slopes of the plots. However, at lower perchloric acid concentrations and higher concentrations of mandelic acid the log A_{350} vs. time plots became nonlinear (Figures 1 and 2) due to the accumulation of significant quantities of chromium(V), a situation previously encountered in the oxidation of oxalic[5,26] and 2-hydroxy-2-methylbutyric[4] acids. Under these conditions, the reaction was monitored at two wavelengths (at 350 nm in 1-cm cells and at 750 nm in 5- or 10-cm cells) and A_{350}^{VI}, the absorbance of Cr(VI) at 350 nm, calculated[4] from eq 7

$$A_{350}^{\mathrm{VI}} = A_{350} - \frac{l_1 \epsilon_{350}^{\mathrm{V}}}{l_2 \epsilon_{750}^{\mathrm{V}}} A_{750} \qquad (7)$$

where A_{350} and A_{750} are the measured absorbances[26] at 350 and 750 nm in cells of lengths l_1 and l_2, respectively. The ratio of molar absorbitivities of chromium(V), $\epsilon_{350}^{\mathrm{V}}/\epsilon_{750}^{\mathrm{V}}$, was obtained by plotting l_2A_{350}/l_1A_{750} vs. time[4] for a number of reaction conditions (Figure 3) and determining the limiting value $\epsilon_{350}^{\mathrm{V}}/\epsilon_{750}^{\mathrm{V}} = 38.0$. Figure 3 shows data obtained at [MA] = 0.5 M; similar results were obtained for sets by using lower mandelic acid concentrations (0.2 M, 0.1 M).[27] Plots of log A_{350}^{VI} vs. time gave very good straight-line plots (Figure 4) which were used to calculate pseudo-first-order rate constants.

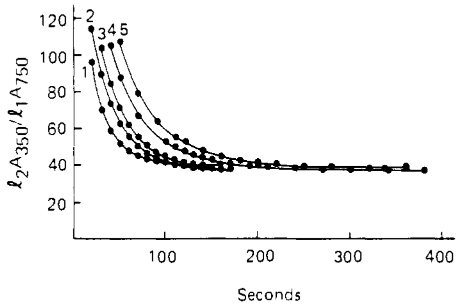


Figure 3. Determination of the ratio of molar extinction coefficients $\Sigma_{350}^{\mathrm{V}}/\Sigma_{750}^{\mathrm{V}}$. Conditions: 25 °C; $[\mathrm{Cr(VI)}]_0 = 5 \times 10^{-4}$ M; [MA] = 0.5 M; (1) $[\mathrm{H^+}] = 0.3$ M; (2) $[\mathrm{H^+}] = 0.1$ M; (3) $[\mathrm{H^+}] = 0.03$ M; (4) $[\mathrm{H^+}] = 0.01$ M; (5) $[\mathrm{H^+}] = 0.005$ M.

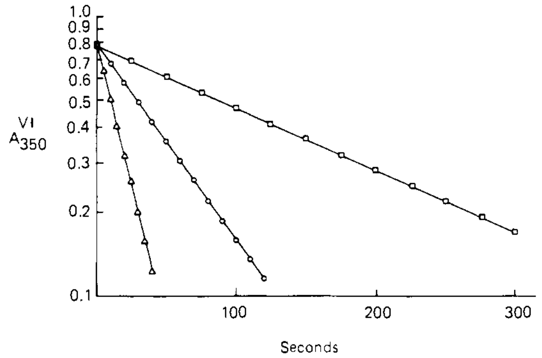


Figure 4. Log A_{350}^{VI} (from eq 7) vs. time plots; same data as in Figure 1.

Since the reaction was found to be insensitive to salt effects,[27] no effort to maintain ionic strength was made.

Product Analysis. Reaction products were analyzed by LC on a Waters Associates M-6000A liquid chromatograph equipped with a Model 440 254-nm absorbance detector and a μ-Bondapak C_{18} 4 mm i.d. × 30 m reverse phase column. The solvent mixture of acetonitrile–water–acetic acid (26:68:6, v/v) gave a good separation of all components with the following retention times (in minutes at a flow rate of 1.0 mL/min): $\mathrm{HClO_4}$, 2.7; phenylglyoxylic acid, 3.6; mandelic acid, 4.1; benzoic acid, 7.0; benzaldehyde, 9.0. Calibration curves were constructed by using authentic samples.

In a typical experiment, 2 mL of a solution containing mandelic acid (0.2 M) and perchloric acid (0.5 M) were equilibrated at 25 °C for 30 min, purged with nitrogen for 10 min, whereupon 5 μL of a 0.2 M chromium(VI) solution was injected. After the reaction was over (ca. 1 h), the solution was analyzed by LC, flow rate 1 mL/min, sensitivity 0.05 AUFS, ambient temperature. At least three runs were made for each analysis; results were reproducible to ±0.5%.

Some oxidation reactions were carried out under oxygen, either by bubbling O_2 for 10–60 min through the sample prior to the addition of chromium(VI), or in a closed system under oxygen by using a magnetic stirrer throughout the reaction. The results of all experiments were quite similar; only two are shown in Table XII.[27]

In the analysis of reaction products as a function of time, 2-mL samples of the reaction solution were quenched with 0.5 mL of a mixture of oxalic acid (0.3 M) and isopropyl alcohol (10 M).

In several experiments, benzaldehyde was also determined gravimetrically as the 2,4-dinitrophenylhydrazone; phenylglyoxylic acid was determined polarographically.[29] The results of the gravimetric and polarographic analyses agreed well with those obtained by LC.

Carbon dioxide was determined manometrically, employing the same procedure as in previous investigations.[5,7] Except where indicated otherwise, a standard amount of chromium(VI) (2×10^{-5} mol in 4 mL) was used; the amounts of mandelic acid and perchloric acid were varied as needed. No gas evolution was observed when a piece of filter paper moistened with a solution of sodium hydroxide was placed in the "well" of the Warburg flask, excluding thus formation of carbon monoxide.

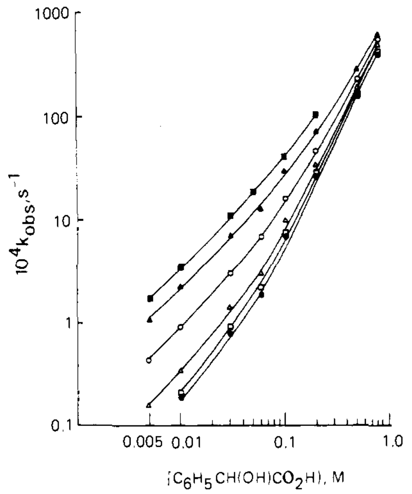


Figure 5. Effect of mandelic acid concentration on rates of chromic acid oxidations. Data of Table II. Conditions: 25 °C; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; (■) $[H^+] = 0.5$ M; (▲) $[H^+] = 0.3$ M; (◎) $[H^+] = 0.1$ M; (△) $[H^+] = 0.03$ M; (◻) $[H^+] = 0.01$ M; (●) $[H^+] = 0.005$ M.

Table I. Dependence of Oxidation Rates on Initial Concentration of Chromium(VI)[a]

10^4 [Cr(VI)], M	10^4k_{obsd}, s^{-1}
40	1.51[b,c]
20	1.57[b,c]
10	1.62[c]
5.0	1.74
1.0	1.71
0.5	1.71

[a] [MA] = 0.005 M; $[H^+] = 0.5$ M; 25 °C. [b] From second-order plots. [c] Measurements carried out by Dr. M. Krumpolc.

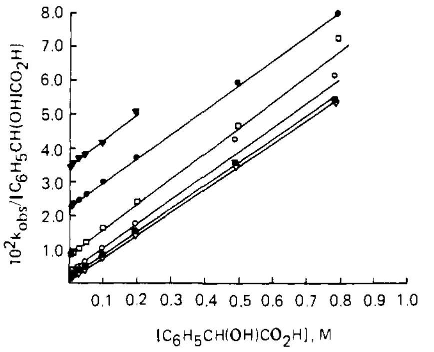


Figure 6. Determination of rate constants k' and k_3 (eq 8). Data of Table II. Conditions: 25 °C; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; (▲) $[H^+] = 0.5$ M; (●) $[H^+] = 0.3$ M; (◻) $[H^+] = 0.1$ M; (◎) $[H^+] = 0.03$ M; (■) $[H^+] = 0.01$ M; (△) $[H^+] = 0.005$ M.

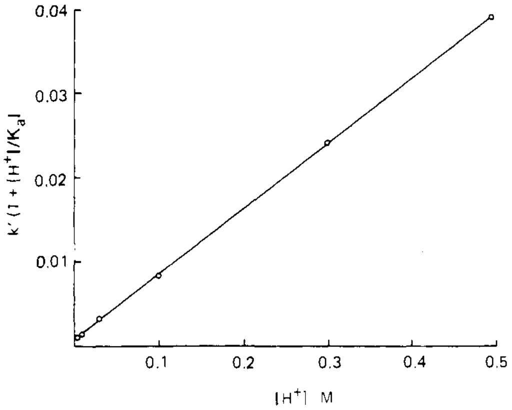


Figure 7. Plot of $k'(1 + [H^+]/K_a)$ vs. $[H^+]$ (eq 10). Data from Table III.

Results and Discussion

Rate Studies. The good straight line log [Cr(VI)] vs. time plots obtained throughout the study (Figure 4) indicate a first-order dependence in chromium(VI). This conclusion is supported by the data in Table I showing that the experimental pseudo-first-order rate constants are approximately independent of the initial chromium(VI) concentration; the slight trend toward lower values at high chromium(VI) concentration suggests that $HCrO_4^-$ is more reactive than $Cr_2O_7^{2-}$.

Table II and Figure 5 show the dependence of reaction rates on the concentration of mandelic acid at six different acidities. The reaction is first order in mandelic acid at low substrate concentrations and high acidities but changes to second order at high substrate concentrations and low acidities. The acidity dependence is first order in hydrogen ions at high acidities and low mandelic acid concentrations and approaches a zero-order dependency at low acidities and high substrate concentrations.

At any given acidity, the observed pseudo-first-order rate constant can be expressed as the sum of two terms (eq 8).

$$k_{obsd} = k'[MA] + k_3[MA]^2 \qquad (8)$$

Plots of k_{obsd}/[MA] vs. [MA] gave reasonably good straight lines (Figure 6). A linear least-square computer program was used to obtain the values of k' and k_3 at six different acidities (Table III).

While the second-order rate constants k_3 are practically independent of acidity over the entire range of hydrogen ion concentrations, the first-order rate constants k' show a clear dependence on acidity.

A plot of k' vs. $[H]^+$ showed some curvature at high acidities. A similar phenomenon has been observed in chromic acid oxidations of other organic compounds[3,4] and is due to the protonation of the monochromate anion $HCrO_4^-$ to chromic acid H_2CrO_4. A plot of corrected rate constants k'_{corr} vs. $[H^+]$

$$k'_{corr} = k'[Cr(VI)]/[HCrO_4^-] \qquad (9)$$
$$= k'(1 + [H^+]/K_a)$$
$$K_a = [H^+][HCrO_4^-]/[H_2CrO_4] = 4.2 \text{ M}^{28}$$

gave a good straight line (Figure 7). The acidity dependence of k' can therefore be expressed by eq 10

$$k'(1 + [H^+]/K_a) = k_1 + k_2[H^+] \qquad (10)$$

where $k_1 = (9.2 \pm 1.4) \times 10^{-4}\ M^{-1}\ s^{-1}$ and $k_2 = (7.6 \pm 0.6) \times 10^{-2}\ M^{-2}\ s^{-1}$ (from least-square calculations).

The complete rate law for the chromic acid oxidation of mandelic acid is thus given by

$$-\frac{d[Cr(VI)]}{dt} = k_{obsd}[Cr(VI)] \qquad (11)$$
$$= [HCrO_4^-][MA](k_1 + k_2[H^+] + k_3[MA]) \qquad (12)$$
$$= [Cr(VI)][MA](k_1 + k_2[H^+] + k_3[MA])/(1 + [H^+]/K_a) \qquad (13)$$

Hence

$$k_{obsd} = [MA](k_1 + k_2[H^+] + k_3[MA])/(1 + [H^+]/K_a) \qquad (14)$$

Rate constants calculated from eq 14 are compared with experimental data in Table II and give an excellent agreement over a wide range of concentrations.

Table II. Observed and Calculated (Equation 14) Pseudo-First-Order Rate Constants (10^2k_{obsd}, s^{-1}) for the Chromic Acid Oxidation of Mandelic Acid (MA)[a]

	$[H^+]$, M											
	0.5		0.3		0.1		0.03		0.01		0.005	
[MA], M	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
0.8			6.1	6.4	5.20	5.76	4.7	4.9	4.6	4.3	4.6	4.2
0.5			2.8	3.0	2.20	2.32	1.90	1.95	1.8	1.8	1.8	1.7
0.2	1.00	1.02	0.71	0.74	0.45	0.48	0.33	0.35	0.31	0.30	0.30	0.28
0.1	0.41	0.42	0.29	0.30	0.154	0.164	0.10	0.10	0.082	0.078	0.079	0.076
0.05	0.19	0.19	0.13	0.13	0.059	0.060	0.031	0.032	0.024	0.023	0.022	0.020
0.03	0.11	0.11	0.073	0.074	0.031	0.031	0.015	0.015	0.010	0.0093	0.0093	0.0080
0.01	0.036	0.035	0.023	0.024	0.0091	0.0093	0.0034	0.0035	0.0021	0.0021	0.0017	0.0019
0.005	0.0176	0.0174	0.0113	0.0113	0.0044	0.0044	0.0015	0.0016				

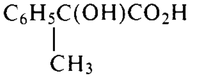
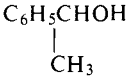
[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; 25 °C.

Table III. Determination of Rate Constants k' and k_3[a]

$[H^+]$, M	$10^3k'$, M^{-1} s^{-1}	10^3k_3, M^{-2} s^{-1}
0.5	34.7	69.6
0.3	22.6	73.1
0.1	8.2	78.8
0.03	3.4	73.7
0.01	1.6	69.2
0.005	1.2	68.2
av:		72

[a] From data in Table II.

Table IV. Cr(VI) Oxidation Rates of Mandelic Acid and Related Compounds[a]

[substrate]	10^5k_{obsd}, s^{-1}
$C_6H_5CH(OH)CO_2H$	17.4
$C_6H_5CH(OH)CO_2CH_3$	2.85[b]
 $C_6H_5C(CH_3)(OH)CO_2H$	1.60
 $C_6H_5CH(CH_3)OH$	6.06
$C_6H_5CH_2OH$	14.7
C_6H_5CHO	0.849
$C_6H_5COCO_2H$	56.1
m-$CH_3C_6H_4CH(OH)CO_2H$	18.2
m-$CH_3C_6H_4CHO$	0.810

[a] $[Substrate] = 5 \times 10^{-3}$ M; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; $[H^+] = 0.5$ M; 25 °C. [b] Hydrolysis of the ester during the reaction resulted in curved plots; rate constants were therefore determined from initial rates.

Table V. Relative Rates of Oxidation of Mandelic Acid and Phenylglyoxylic Acid (PGA)[a]

$[H^+]$, M	[substrate], M	10^4k_{MA}	10^4k_{PGA}	k_{PGA}/k_{MA}
0.5	0.02	7.06	26.2	3.71
0.5	0.01	3.53	12.8	3.63
0.5	0.005	1.74	5.61	3.22
0.1	0.01	0.932	2.07	2.22
0.1	0.005	0.441	0.984	2.23
0.01	0.01	0.21	0.0628	0.30

[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; 25 °C.

Table VI. Effect of Phenylglyoxylic Acid (PGA) on Oxidation Rates of Mandelic Acid (MA) and m-Methylmandelic Acid (MeMA)[a]

substrate, M	10^3[PGA], M	$10^4\Sigma k^b$, s^{-1}	10^4k_{obsd},[c] s^{-1}
MA, 0.01	8.76	14.4	14.3
0.7	8.76	471[d]	476[d]
MeMA, 0.005	2.50	4.54	6.50
	1.55	3.56	4.02
	0.50	2.29	2.37
	0.10	1.85	1.74
	0.067	1.81	1.73
0.01	0.50	4.09	4.34
	0.10	3.64	3.74

[a] $[H^+] = 0.5$ M; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; 25 °C. [b] Sum of individual oxidation rates of substrate and phenylglyoxylic acid; $\Sigma k = k_{PGA} + k_{MA}$(or k_{MeMA}). [c] Observed oxidation rate when both compounds were present. [d] $[H^+] = 0.1$ M; rates obtained after correcting for Cr(V) by using $\epsilon^{V}_{350}/\epsilon^{V}_{750} = 38.0$.

Table IV gives the chromic acid oxidation rates of mandelic acid and of related compounds. The results which are significant in the context of this study are:

(a) Benzaldehyde is about 20 times less reactive than mandelic acid and should therefore be easily isolated among the reaction products in virtually quantitative yields.

(b) Phenylglyoxylic acid is about three times as reactive as mandelic acid (Table V); it should therefore be easy to isolate it in a significant yield particularly when a fairly large excess of mandelic acid over chromic acid is being used.

(c) m-Methylmandelic acid and m-tolualdehyde exhibit rates which are very close to those of the parent compounds. This is consistent with the low value of the Hammett substituent constant[29] ($\sigma_m = -0.069$).

The presence of phenylglyoxylic acid has no significant rate-accelerating effect on the chromic acid oxidation of mandelic acid or m-methylmandelic acid (Table VI), thus ruling out the possibility of significant cooxidation of phenylglyoxylic acid and mandelic acid or m-methylmandelic acid.

Table VII gives the results of kinetic deuterium isotope effect measurements under various conditions ranging from almost entirely first order to 98% second order. Within the first-order terms, the conditions extend from those under which the reaction proceeds almost entirely by the acid-catalyzed route up to 26% by the acidity independent route. Although some variations in the magnitude of the kinetic isotope effect are observed, it is clear that all three processes exhibit a very significant isotope effect and must therefore involve the breaking of the carbon-hydrogen bond in the rate-limiting step.

The temperature dependence of the oxidation rates for mandelic (under first-order conditions), α-d-mandelic, and atrolactic acids is given in Table VIII; Table IX lists the activation parameters. The oxidation of atrolactic acid gives good straight-line plots for A^{VI}_{350} vs. time and shows a first-order dependence in atrolactic acid (Table X), making the comparison of activation parameters justified. The oxidation of

Table VII. Deuterium Isotope Effect in the Oxidation of $C_6H_5CD(OH)CO_2H$[a]

$[H^+]$, M	[MA], M	10^4k_H	10^4k_D	k_H/k_D	kinetic term, % k_1[b]	$k_2[H^+]$[c]	$k_3[MA]$[d]
0.5	0.005	1.74	0.193	9.0	2.3	96.7	0.9
0.3	0.005	1.13	0.135	8.4	3.8	94.7	1.5
0.1	0.005	0.44	0.056	7.9	10.4	85.6	4.1
0.03	0.005	0.16	0.021	7.6	25.9	64.0	10.1
0.3	0.03	7.4	0.80	9.2	3.6	88.1	8.4
0.01	0.2	30	4.6	6.5	5.7	4.7	89.6
0.005	0.8	420	55.3	7.6	1.6	0.7	97.8

[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; 25 °C. [b] $100k_1/\Sigma k$; $\Sigma k = k_1 + k_2[H^+] + k_3[MA]$. [c] $100k_2[H^+]/\Sigma k$. [d] $100k_3[MA]/\Sigma k$.

Table VIII. Temperature Dependence of Oxidation Rates for Mandelic Acid (k_2^H), α-*d*-Mandelic Acid (k_2^D), and Atrolactic Acid (k_2)[a]

[substrate]	$[H^+]$, M	*T*, K	k_2^H, M^{-1} s^{-1}	k_2^D, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}	k_2^H/k_2^D
mandelic acid (5×10^{-3} M)	0.5	353	0.526	0.148		3.55
	0.5	343	0.326	0.0820		3.98
	0.5	333	0.208	0.0430		4.84
	0.5	318	0.102	0.0169		6.02
	0.5	308	0.0582	0.00822		7.08
	0.5	298	0.0348	0.00386		9.02
mandelic acid (5×10^{-3} M)	0.3	353	0.342	0.0984		3.48
	0.3	343	0.220	0.0538		4.09
	0.3	333	0.136	0.0298		4.55
	0.3	298	0.0226	0.0027		8.37
atrolactic acid (0.1 M)	0.3	333			0.0839	
	0.3	318			0.0216	
	0.3	308			0.00820	
	0.3	298			0.00286	

[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M.

mandelic acid requires a considerably lower activation energy (10.3 vs. 19.0) but has a much more negative activation entropy (−33 vs. −8 eu) than atrolactic acid, indicating a much more highly ordered but energetically more favorable transition state. The difference between the activation parameters of α-*d*-mandelic acid and mandelic acid are fairly large ($E_a^D - E_a^H = 3.4$ kcal/mol, $A^D/A^H \approx 36$), suggesting the possibility of proton tunneling.[30,31]

While at 25 °C, mandelic acid is about ten times as reactive as atrolactic acid, the rate ratio becomes much smaller at higher temperatures (Table XI) resulting in a remarkably small difference in reactivity between a secondary and tertiary hydroxyl group.

Heckner et al.[15] reported that the oxidation rates are retarded to about 60% by the presence of cerium(III). Under our conditions ([MA] = 0.01 M; $[H^+] = 0.5$ M; [Cr(VI)] = 0.002 M; [Ce(III)] = 0–0.002 M), no significant effect on the reaction rate could be detected; however, our conditions differed from those used by previous investigators.

Reaction Products. The yields of products formed in the chromic acid oxidation of mandelic acid in the absence of oxygen at different acidities and substrate concentrations are shown in Table XII. Also indicated are the relative contributions of the kinetic terms of the rate law (eq 12). The total yield in all experiments is close to the theoretical value of 1.50 mol/mol of Cr(VI), providing proof that all major oxidation products have been accounted for.

The yield of carbon dioxide is practically constant; under all conditions about 1 mol of CO_2 per mol of chromium(VI) is formed. The yield of all other products depends on reaction conditions.

Figure 8 gives the graphic representation of the product plotted against the percentage of second-order pathway. The good straight-line plots indicate that the two first-order reactions, corresponding to rate constants k_1 and k_2, yield identical compositions of reaction products.

Under second order conditions, i.e., at low acidities and high mandelic acid concentrations, the principal products are benzaldehyde and phenylglyoxylic acid in a 2:1 ratio and the stoichiometry of the reaction corresponds to eq 15

$$3C_6H_5CH(OH)CO_2H + 2Cr(VI) \rightarrow C_6H_5COCO_2H + 2C_6H_5CHO + 2CO_2 + 2Cr(III) \quad (15)$$

First-order conditions in mandelic acid (high acidities, low mandelic acid concentrations) result in the formation of approximately equal amounts of benzaldehyde and benzoic acid and low yields of phenylglyoxylic acid (about 10%).

The formation of the two principal products corresponds to eq 16:

$$2C_6H_5CH(OH)CO_2H + 2Cr(VI) \rightarrow C_6H_5CO_2H + C_6H_5CHO + 2CO_2 + 2Cr(III) \quad (16)$$

α-*d*-Mandelic acid yields *d*-benzaldehyde (deuterium content >90% by mass spectroscopy), thus ruling out the possibility that benzaldehyde might be formed through phenylglyoxylic acid by decarboxylation.

When the reaction is carried out in oxygen, the yield of both benzoic acid and benzaldehyde increase, while the yield of

Table IX. Activation Parameters[a]

$[H^+]$, M	[substrate], M	log *A*	log A^D	A^D/A^H	$\Delta S^{\ddagger b}$	$\Delta S_D^{\ddagger b}$	E_a	E_a^D	$E_a^D - E_a^H$
0.5	mandelic acid (5×10^{-3} M)	6.09 ± 0.07	7.69 ± 0.06	39.8	−32.7 ± 0.3	−25.3 ± 0.3	10.3 ± 0.1	13.8 ± 0.1	3.48 ± 0.13
0.3	mandelic acid (5×10^{-3} M)	5.90 ± 0.06	7.41 ± 0.05	32.4	−33.5 ± 0.3	−26.6 ± 0.2	10.3 ± 0.1	13.6 ± 0.1	3.29 ± 0.11
0.3	atrolactic acid (0.1 M)	11.4 ± 0.02			−8.4 ± 0.1		19.0 ± 0.03		

[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M. [b] $\Delta S^{\ddagger} = 2.303R(\log A - \log T - 10.753) = 4.575(\log A - 13.227)$.

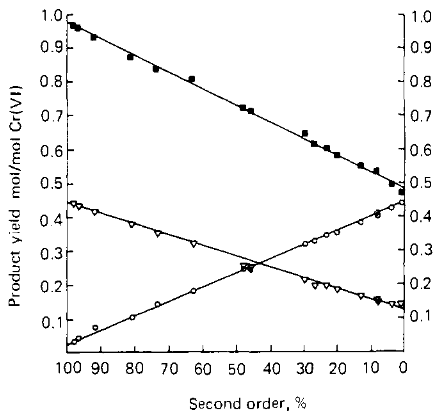


Figure 8. Product yields in chromic acid oxidation of mandelic acid plotted against percent of second-order kinetic term. Data from Table XII. (○) $C_6H_5CO_2H$; (▲) $C_6H_5COCO_2H$; (■) C_6H_5CHO.

Table X. Oxidation of Atrolactic Acid (AL)[a,b]

[AL], M	60 °C		45 °C	
	10^2k_{obsd}, s^{-1}	k_{obsd}/[AL], $M^{-1}\,s^{-1}$	10^3k_{obsd}, s^{-1}	k_{obsd}/[AL], $M^{-1}\,s^{-1}$
0.2	2.25	0.11	5.23	0.026
0.1	0.839	0.084	2.51	0.025
0.03	0.242	0.081	0.647	0.022
0.01	0.0789	0.079	0.199	0.020
0.005	0.0377	0.075	0.095	0.019
0.001[b]	0.0078	0.078	0.0221	0.022

[a] $[H^+] = 0.3$ M; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M. [b] $[Cr(VI)]_0 = 5 \times 10^{-5}$ M; rate obtained from initial slope.

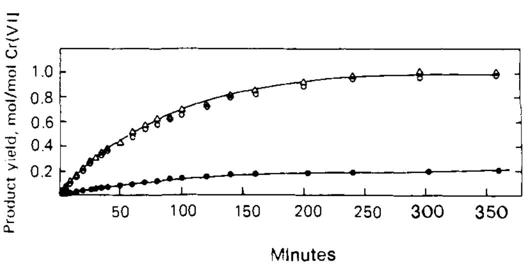


Figure 9. Time dependence of the formation of benzaldehyde (△), benzoic acid (○), and phenylglyoxylic acid (●). Conditions: $[Cr(VI)] = 5 \times 10^{-4}$ M; $[MA] = 0.005$ M; $[H^+] = 0.5$ M; 25 °C.

Table XI. Temperature Dependence of Relative Oxidation Rates of Mandelic Acid and Atrolactic Acid (AL)[a]

°C	k_{MA}/k_{AL}
25	10.5
35	6.72
45	3.92
60	1.73

[a] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; [MA] or [AL] = 0.1 M; $[H^+] = 0.3$ M.

phenylglyoxylic acid is sharply reduced. The total yield approaches an equivalent of four electrons per each chromium(VI), suggesting that one molecule of O_2 is reduced for every four Cr(VI) molecules.

In a formal sense, benzoic acid is a four-electron oxidation product of mandelic acid and its formation in an equimolar amount with benzaldehyde (eq 16) is thus entirely unexpected. Great care was therefore taken to test whether benzoic acid could be formed through one of the expected two-electron oxidation products, benzaldehyde or phenylglyoxylic acid. Chromium(VI) oxidation rates given in Table IV show that benzaldehyde is oxidized much less readily than mandelic acid. Although phenylglyoxylic acid is oxidized about three times faster (Table V), this rate difference is insufficient to account for the high yield of benzoic acid in the presence of a large excess of mandelic acid. Phenylglyoxylic acid does not undergo decarboxylation under the reaction conditions employed in this study.[27]

Figure 9 shows the product formation as a function of time under first-order conditions (99% first order). The ratio of benzaldehyde to benzoic acid remains constant throughout the reaction; little phenylglyoxylic acid is found and no induction period in the formation of benzoic acid is observed. These results make it very unlikely that benzoic acid could be formed through benzaldehyde or phenylglyoxylic acid as intermediates.

Further evidence was obtained from the oxidation of *m*-methylmandelic acid in the presence of benzaldehyde and phenylglyoxylic acid, respectively. If benzoic acid in the oxidation of mandelic acid were formed through either of these compounds by whatever mechanism (by induced oxidation by Cr(V) or Cr(IV), or by cooxidation), then significant yields of benzoic acid would be formed. Table XIII shows that this is not the case. In each experiment the amount of benzoic acid is about that expected from a simple competition of the aldehyde or keto acid for chromium(VI) as calculated from chromium(VI) oxidation rates (Table IV).

Table XIV shows the effect of free radical scavengers, acrylamide and acrylonitrile, on the yields of reaction products under first-order conditions. The yields of both benzaldehyde and benzoic acid are reduced significantly by either of the scavengers, but are still formed in an approximately equimolar ratio. The yield of carbon dioxide is unaffected, while that of phenylglyoxylic acid is unaffected by acrylonitrile and slightly increased by acrylamide. One thus can conclude that benzaldehyde and benzoic acid are formed through a common free radical intermediate, while carbon dioxide and phenylglyoxylic acid are formed directly.

In the presence of acrylamide (0.5 M), polymer formation can be observed (after dilution with methanol). Surprisingly enough, we were unable to observe polymer formation with acrylonitrile in spite of its equal effectiveness in reducing the yields of benzoic acid and benzaldehyde; a plausible explanation may be that the polymers formed were of too low a molecular weight to precipitate from the solution.

We were unable to observe polymer formation with either acrylamide or acrylonitrile under second-order conditions ($[H^+] = 0.005$ M; [MA] = 0.2-0.8 M); this is surprising as polymer formation is usually observed much more easily at low than at high acidities.[3,32] We are nevertheless convinced that free radicals must be formed. We suspect that at high mandelic acid concentrations a significant amount of chromium(VI) is converted into a highly reactive mandelic acid-chromium(VI) complex; this complex may be sufficiently reactive toward free radicals to suppress their capture by the trapping agent or interrupt the growth of a primary free radical-monomer adduct before it can reach a sufficiently high molecular weight needed for the formation of an insoluble polymer.

Mechanism. Since the rate law (eq 12) contains three terms, the oxidation of mandelic acid takes place through three different transition states at comparable rates.

The second-order kinetic term ($k_3[HCrO_4^-][MA]^2$) proceeds through a negatively charged activated complex formed from two molecules of mandelic acid and one molecule of $HCrO_4^-$. The magnitude of the kinetic deuterium isotope effect (Table VII) indicates that a carbon-hydrogen bond is broken in the rate-limiting step. The mechanism in Scheme

Table XII. Products in the Chromic Acid Oxidation of Mandelic Acid[a]

$[H^+]$, M	[MA], M	products, yields (mol/mol of Cr(VI))					kinetic term, %[d]		
		$C_6H_5COCO_2H$	$C_6H_5CO_2H$	C_6H_5CHO	CO_2[b]	total[c]	k_1	$k_2[H^+]$	k_3[MA]
0.5	0.5	0.256	0.248	0.724	0.98	1.48	1.2	50.7	48.0
	0.2	0.198	0.330	0.618	0.98	1.48	1.7	71.3	27.0
	0.05	0.150	0.410	0.535	0.98	1.51	2.2	89.4	8.5
	0.005	0.140	0.442	0.470	0.996[e]	1.49	2.3	96.7	0.9
	0.005[f]	0.020	0.440	0.640[g]		1.54			
	0.005[h]	0.014	0.641	0.581		1.88			
	0.005[i]	0.010	0.640	0.610		1.90			
0.3	0.1	0.196	0.348	0.606		1.50	3.0	73.7	23.3
	0.05	0.165	0.385	0.553		1.49	3.4	83.4	13.2
	0.03	0.142	0.404	0.532		1.43	3.6	88.1	8.3
0.1	0.5	0.380	0.105	0.875	1.01	1.47	2.1	17.1	80.8
	0.2	0.323	0.183	0.810		1.50	4.0	33.2	62.8
	0.1	0.252	0.248	0.715	1.02	1.46	5.9	48.3	45.8
	0.05	0.214	0.320	0.646	1.01	1.50	7.6	62.7	29.7
	0.03	0.186	0.355	0.581	1.01	1.48	8.6	71.2	20.2
	0.005	0.138	0.424	0.497		1.48	10.4	85.6	4.1
0.005	0.8	0.440	0.037	0.968	0.94	1.48	1.6	0.6	97.8
	0.5	0.433	0.046	0.961	0.94	1.49	2.5	1.0	96.5
	0.2	0.412	0.076	0.931	1.07	1.50	5.9	2.4	91.7
	0.05	0.350	0.145	0.842	1.06	1.48	18.8	7.8	73.5

[a] 25 °C; $[Cr(VI)]_0 = 5 \times 10^{-4}$ M; solutions purged with nitrogen for 10 min prior to the addition of chromium. [b] $[Cr(VI)]_0 = 5 \times 10^{-3}$ M in 4 mL. [c] Total yield = $C_6H_5COCO_2H + C_6H_5CHO + 2C_6H_5CO_2H$. [d] Cf. footnotes *b*-*d* in Table VII. [e] $[Cr(VI)]_0 = 5 \times 10^{-4}$ M in 25 mL. [f] α-*d*-Mandelic acid. [g] C_6H_5CDO; deuterium content > 90% by mass spectroscopy of the 2,4-dinitrophenylhydrazone. [h] Saturated with O_2 prior to oxidation. [i] In O_2; magnetic stirring during the reaction.

Table XIII. Effect of Benzaldehyde and Phenylglyoxylic Acid on Product Yields in the Chromic Acid Oxidation of *m*-Methylmandelic Acid (MeMA)[a]

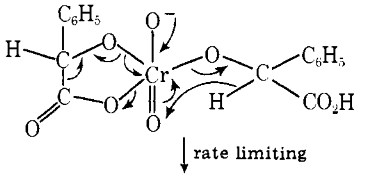
[MeMA], M	$[C_6H_5CHO]$, M	$[C_6H_5COCO_2H]$, M	$C_6H_5CO_2H$		yield, mol/mol of Cr(VI)		
			calcd[b]	found	*m*-$MeC_6H_4CO_2H$	*m*-MeC_6H_4CHO	*m*-$MeC_6H_4COCO_2H$[c]
0.005	0.0	0.0			0.445	0.464	0.114
0.05	0.0	0.0			0.424	0.556	0.122
0.005	0.0025	0.0	0.023	0.014	0.435	0.451	0.117
0.0	0.0025	0.0		0.012[d]			
0.005	0.0	0.00025	0.134	0.110	0.352	0.471	0.119
0.01	0.0	0.00025	0.072	0.055	0.389	0.509	0.127
0.02	0.0	0.00025	0.037	0.034	0.410	0.520	0.130
0.05	0.0	0.00025	0.015	0.018	0.406	0.535	0.143

[a] $[Cr(VI)] = 5 \times 10^{-4}$ M; $[H^+] = 0.5$ M; 25 °C. [b] Calculated from Cr(VI) oxidation rate constants for benzaldehyde, phenylglyoxylic acid, and *m*-methylmandelic acid (Table IV). [c] Estimated from LC analysis by using the phenylglyoxylic acid calibration curve. [d] Quenched with oxalic acid–isopropyl alcohol mixture at time required for the complete oxidation of the α-hydroxy acid.

I is consistent with all observations including the composition of reaction products and stoichiometry (eq 15). The mechanism closely resembles those earlier proposed for other chromic acid oxidations with activated complexes containing two substrate molecules.[3-6] The rate-limiting step is a three-electron oxidation–reduction reaction taking place in a termolecular complex formed from two molecules of mandelic acid and

Scheme I

$2C_6H_5CH(OH)CO_2H + HCrO_4^- \rightleftharpoons$


(17)

$\downarrow$ rate limiting

$C_6H_5COCO_2H + C_6H_5CHO + \cdot CO_2^- + Cr(III)$ (18)

or $C_6H_5\dot{C}HOH + CO_2$

C_6H_5CHOH (or $\cdot CO_2^-$) + Cr(VI)

$\longrightarrow C_6H_5CHO$ (or CO_2) + Cr(V) (19)

$C_6H_5CH(OH)CO_2H$ + Cr(V)

$\longrightarrow C_6H_5CHO + CO_2$ + Cr(III) (20)

Table XIV. Effect of Free Radical Scavengers on Product Yields in the Cr(VI) Oxidation of Mandelic Acid[a]

scavenger, M	yields, mol/mol Cr(VI)				
	C_6H_5-$COCO_2H$	C_6H_5-CO_2H	C_6H_5-CHO	CO_2[b]	total[c]
0.0	0.140	0.442	0.470	0.996	1.49
0.1[d]	0.150	0.370	0.380	*e*	1.27
0.5[d]	0.170	0.308	0.328	0.970	1.11
0.1[f]	0.140	0.360	0.385		1.25
0.5[f]	0.130	0.300	0.339	0.970	1.07

[a] [MA] = 5×10^{-3} M; $[H^+] = 0.5$ M; $[Cr(VI)] = 5 \times 10^{-4}$ M; 25 °C; purged with N_2 for 10 min prior to the addition of chromium. [b] Determined in 25-mL samples. [c] Total yield = $2 \times C_6H_5CO_2H + C_6H_5CHO + C_6H_5COCO_2H$. [d] Acrylamide. [e] Not determined. [f] Acrylonitrile.

an acid chromate ion. A simultaneous breaking of a carbon-hydrogen bond and a carbon-carbon bond is assumed; evidence for the simultaneous breaking of a C-H and C-C bond in a related reaction has recently been obtained from carbon-13 isotope effect studies.[33]

Our principal interest was directed at the reaction corresponding to the two first-order kinetic terms of eq 12, $k_1[HCrO_4^-][MA]$ and $k_2[HCrO_4^-][MA][H^+]$. We assume that the two transition states have similar structures differing only by the presence or absence of a proton. The mechanism for this oxidation must be consistent with the following results:

1. Benzaldehyde and benzoic acid are formed in about equimolar amounts of 0.5 mol/mol of Cr(VI) (Table XII, Figure 9).

2. Benzoic acid cannot be formed via benzaldehyde or phenylglyoxylic acid as intermediates (Table XIII, Figure 9).

3. One mole of carbon dioxide per mol of Cr(VI) is formed (Table XII).

4. $C_6H_5CD(OH)CO_2H$ is oxidized to C_6H_5CDO and benzoic acid (Table XII). The oxidation rate of α-*d*-mandelic acid is eight to nine times slower than that of mandelic acid (Tables VII, VIII).

5. Mandelic acid reacts about six times faster than its methyl ester (20 times faster than the ethyl ester[34]), indicating the importance of a free carboxyl group for the oxidation. This conclusion is further supported by the higher oxidation rate of mandelic acid as compared with benzyl alcohol (Table IV) in spite of the electronegativity of the carboxyl group.

6. Polymer formation occurs in the presence of acrylamide. Acrylamide or acrylonitrile does not affect the yield of carbon dioxide, but significantly reduces the yields of both benzaldehyde and benzoic acid (Table XIV).

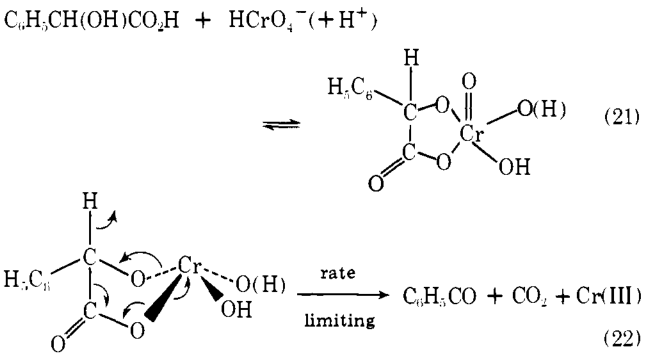
7. Activation parameters indicate that the oxidation of mandelic acid requires a considerably lower activation energy but has a much more negative activation entropy than atrolactic acid, suggesting thus a more highly ordered transition state (Table XI).

The most unusual feature of the reaction is the formation of benzoic acid. We have ruled out the possibility that it could be formed by subsequent oxidation of one of the expected two-electron oxidation products, benzaldehyde, or phenylglyoxylic acid. It could be formed by a direct four-electron oxidation in which chromium(VI) would be reduced to chromium(II), but we consider this unlikely, particularly in the light of the unfavorable potential of the Cr(VI)/Cr(II) couple (0.9 V) compared with that of the Cr(VI)/Cr(III) (1.33 V).[35] The most plausible origin of benzoic acid therefore is a free radical intermediate, $C_6H_5\dot{C}O$, formed from mandelic acid and chromium(VI) in a three-electron oxidation (Scheme II).

The formation of the benzoyl radical (eq 22) represents the first example of a three-electron oxidation in which a hydrogen and a carbon bond to the same carbon atom are broken simultaneously in a three-electron oxidation.

Reaction 22 results in the formation of chromium(V); evidence for chromium(V) formation and accumulation during the reaction has been obtained (Figure 4). It should be noted that mandelic acid is the first secondary alcohol sufficiently stable toward chromium(V) oxidation to allow a significant accumulation of a chromium(V) compound in aqueous solution.

Scheme II



$$C_6H_5\dot{C}O + Cr(VI) \longrightarrow C_6H_5CO_2H + Cr(V) \quad (23)$$

$$C_6H_5CH(OH)CO_2H + Cr(V) \longrightarrow C_6H_5CHO + CO_2 + Cr(III) \quad (20)$$

The last equation in Scheme II (and also in Scheme I) postulates that chromium(V) oxidation of mandelic acid occurs on the carbon-carbon bond and yields benzaldehyde and carbon dioxide. Evidence supporting this assumption has been obtained from a preliminary examination of the reaction of mandelic acid with sodium bis(2-hydroxy-2-methylbutyrato)oxochromate(V); the results[27] will be reported separately. At low mandelic acid concentrations prevailing under first-order conditions, the oxidation by chromium(V) does not occur directly, but involves disproportionation of chromium(V) to chromium(VI) and chromium(IV) and oxidation by chromium(IV). Under the first-order reaction conditions of the chromic acid oxidation of mandelic acid, the following sequence of reactions therefore may take place.

$$2Cr(V) \rightarrow Cr(VI) + Cr(IV) \quad (24)$$

$$C_6H_5CH(OH)CO_2H + Cr(IV) \rightarrow C_6H_5\dot{C}HOH + CO_2 + Cr(III) \quad (25)$$

$$C_6H_5\dot{C}HOH + Cr(VI) \rightarrow C_6H_5CHO + Cr(V) \quad (26)$$

The sum of reactions 24-26 equals eq 20.

The formation of the small amount of phenylglyoxylic acid under first-order conditions probably results from a slower two-electron oxidation by chromium(VI) or chromium(V) occurring in parallel with the principal reactions.

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Mechanism of Oxidative Addition. Reaction of Nickel(0) Complexes with Aromatic Halides

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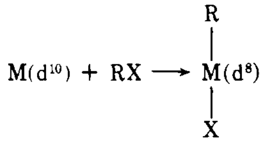
Abstract: The oxidative addition of aryl halides to triethylphosphinenickel(0) complexes affords *trans*-arylnickel(II) halides A, together with paramagnetic nickel(I) halides B as side products. The relative yields, A/B, are strongly dependent on the halide (I < Br < Cl), as well as the nuclear substituents and the solvent polarity. The second-order rate constants (log k_{obsd}) for various meta- and para-substituted iodobenzenes are linearly related to those of the corresponding bromo- and chloroarenes. However, the absence of a direct correlation between the reactivities of various aryl halides and the distribution between nickel(I,II) products demands that the rate-limiting activation process precedes, and is separate from, the product-forming step(s). Evidence for the paramagnetic ion pair [Ni(I)ArX$^{-}\cdot$] as the common intermediate which is partitioned between A and B is presented, and discussed in the light of electrochemical measurements of the one-electron oxidation of nickel(0) complexes and the reduction of aryl halides. According to the mechanistic Scheme III, the rate-limiting electron transfer from the nickel(0) donor to the aryl halide acceptor produces an ion pair which is subject to two competitive modes of decay, viz., (1) collapse to oxidative adduct and (2) fragmentation of the ArX$^{-}\cdot$ moiety, followed by diffusion of aryl radicals (observed by ESR spectroscopy) out of the solvent cage. The importance of electrostatic effects in the collapse of the ion pair to oxidative adduct is shown by the high sensitivity of A to the presence of charged nuclear substituents such as $\mathrm{Me_3N^+}$– and $^{-}\mathrm{O_2C}$– groups. The aryl-halogen bond strength is the most important factor in the spontaneous fragmentation of the anion radical of the aromatic halide as determined from lifetimes obtained from electrochemical studies. Finally, the coordinatively unsaturated $\mathrm{Ni(PEt_3)_3}$ is the kinetically active species and responsible for the inverse phosphine dependence on the rate of reaction. It is included in the preequilibrium formation of a π complex [$\mathrm{(Et_3P)_3NiArX}$] as a possible precursor to electron transfer. Scheme III for oxidative addition is discussed in relation to other mechanisms involving either a concerted or a radical-chain process.

Introduction

Oxidative addition represents one of the most basic transformations in organometallic chemistry.[1-7] Its importance also lies in its key role in the conversion of organic substrates to reactive intermediates in many metal-catalyzed processes.[8] Oxidative addition is a generic term used to designate, without mechanistic implication, a ubiquitous class of reactions in which the formal oxidation of a metal complex by an electrophile is accompanied by a concomitant increase in its coordination number.[2-4] As applied to organohalogen compounds (RX), oxidative addition converts a metal complex such as a zerovalent d^{10} complex (M) to an organometal adduct, i.e.



$$\mathrm{M(d^{10})} + \mathrm{RX} \longrightarrow \begin{array}{c}\mathrm{R}\\ |\\ \mathrm{M(d^{8})}\\ |\\ \mathrm{X}\end{array}$$

Two basic types of mechanisms have been proposed for this process, involving either (1) concerted 2-equiv transformations such as three-center additions[9] and S_N2 displacements[10] or (2) multistep successions of 1-equiv changes involving paramagnetic intermediates.[11] Our problem here is to reconcile these apparently diverse mechanisms, and to identify the basic interactions between metal complexes and organohalogen compounds which allow these 2- and 1-equiv pathways to evolve.

The system we chose for study is the reaction of nickel(0) complexes with aromatic halides. The latter was selected since meta and para substituents enable polar effects to be examined separately from steric effects (ortho) in the organic moiety. Furthermore, selectivities observed in the reactions of polyhaloarenes[12] suggest a mechanism analogous to the well-considered, nucleophilic aromatic substitution.[13,14] At the same time, paramagnetic nickel(I) complexes and products derived from radicals have been observed in the reactions of some aryl halides with nickel(0) complexes.[15] Importantly, the isolation and characterization of both the oxidative arylnickel(II) adducts as well as the paramagnetic nickel(I) complexes facilitate the direct observation and analysis of the primary products in this system.

Results

Oxidative additions with nickel(0) complexes were all carried out in this study with the triethylphosphine derivative. When crystalline, colorless tetrakis(triethylphosphine)nickel (for convenience, alternatively referred to as $\mathrm{NiL_4}$) is dissolved in either a hydrocarbon or ethereal solvent, it readily dissociates to the purple-red, coordinatively unsaturated species, i.e.[16]

$$\mathrm{Ni(PEt_3)_4} \overset{K_1}{\rightleftharpoons} \mathrm{Ni(PEt_3)_3} + \mathrm{PEt_3} \qquad (1)$$

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