suspended in 20 mL of degassed methanol containing 100 mg of sodium hydroxide at 0 °C and was reduced with 50 mg of sodium borohydride. 1,1-Dimethylallene (0.8 mmol) was added, followed by the dropwise addition of glacial acetic acid until the solution turned orange-red. Ice water (100 mL) was added, resulting in the formation of orange-red crystals. The crystals were collected by filtration and were recrystallized from methanol–water. ^{1}H NMR ($CDCl_3$): δ 1.15 (br, s, 3 H), 1.25 (br s, 3 H), 2.10 (s, 12 H), 2.43 (d, J = 9.43 Hz, 2 H), 5.00 (br t, J = 9.43 Hz, 1 H), 7.29 (m, 2 H), 7.69 (m, 1 H), 8.55 (m, 2 H).

Anal. Calcd for $C_{18}H_{28}CoN_5O_4$: C, 49.42; H, 6.46; N, 16.01. Found: C, 49.11; H, 6.48; N, 15.86.

Preparation of 5-Hexen-1-ylcobaloxime (14). To a solution of 0.1 g of sodium hydroxide in 25 mL of methanol under an argon atmosphere was added 0.5 g (1.3 mmol) of bis(dimethylglyoximato)(pyridine)cobalt(III) chloride, followed by the addition of 60 mg (1.6 mmol) of sodium borohydride. The dark blue reaction mixture was stirred for 5 min and cooled to −20 °C, and 215 mg of 1-bromo-5-hexene was added. The reaction mixture was allowed to come to room temperature and was stirred for 1 h. Ice water (200 mL) was then added, and the mixture was allowed to stand overnight in the refrigerator. The orange-brown crystals (30%) were collected and recrystallized from methanol–water; mp >170 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.93 (m, 2 H), 1.28 (m, 2 H), 1.62 (m, 2 H), 1.97 (m, 2 H), 2.15 (s, 12 H), 4.87 (dd, J = 10.16, 1.66 Hz, 1 H), 4.92 (dd, J = 13.50, 1.66 Hz, 1 H), 5.73 (ddt, J = 10.16, 13.50, 6.74 Hz, 1 H), 7.32 (dd, J = 4.86, 7.50 Hz, 2 H), 7.73 (t, J = 7.50 Hz, 1 H), 8.59 (d, J = 4.86 Hz, 2 H).

Anal. Calcd for $C_{19}H_{30}CoN_5O_4$: C, 50.55; H, 6.70; N, 15.51. Found: C, 50.37; H, 6.47; N, 15.26.

Sodium Borohydride Reduction of 14. To a solution of 20 mg of sodium hydroxide and 216 mg (0.5 mmol) of **14** in 20 mL of methanol at 25 °C under an argon atmosphere was added 120 mg (3.2 mmol) of sodium borohydride. The reaction mixture was stirred for 30 min, and the volatiles were then removed on a vacuum line. The volatile fraction was analyzed by GC using a 24-ft DEGS column at 80 °C showing the presence of 1-hexene and methylcyclopentane (by comparison of retention times with authentic samples) in a 0.80:1.00 ratio.

An identical reduction was carried out, and the organic phase was diluted with ice water and extracted with a small volume of deuteriochloroform. The deuteriochloroform extract was repeatedly washed with cold water and was dried over $MgSO_4$. The ^{1}H NMR spectrum of the extract displayed a triplet at δ 0.88 for 1-hexene (Sadtler No. 3427, δ 0.89) and a doublet at δ 0.96 for methylcyclopentane (Sadtler No. 3436, δ 0.97).

Reduction of Bis(dimethylglyoximato)(3,3-dimethylallen-1-yl)(pyridine)cobalt (8b, R = R′ = CH_3) with Sodium Borodeuteride in Methanol. To a solution of 300 mg of **8b** (R = R′ = CH_3) and 0.15 g of sodium hydroxide in 10 mL of methanol under an argon atmosphere was slowly added an excess (100%) of sodium borodeuteride. A stream of argon was slowly bubbled through the reaction mixture and passed through 1 mL of deuteriochloroform cooled in a dry ice–carbon tetrachloride bath. The NMR spectrum of the deuteriochloroform solution contained only a triplet methyl resonance for 1,1-dimethylallene and a doublet methyl resonance for 3-methyl-1-butyne. The methynyl CH resonance of 3-methyl-1-butyne was clearly evident.

Reduction of Bis(dimethylglyoximato)(3,3-dimethylallen-1-yl)(pyridine)cobalt (8b, R = R′ = CH_3) with Sodium Borohydride in Methanol-*d*. In a solution of sodium methoxide (prepared by the addition of 50 mg of sodium to the methanol-*d*) in 8 mL of methanol-*d* 200 mg of **8b** (R = R′ = CH_3) was reduced with an excess (50%) of sodium borohydride under an argon atmosphere. A stream of argon was bubbled through the reaction solution and passed through 1 mL of deuteriochloroform in a dry ice–carbon tetrachloride cooling bath. The NMR spectrum of the deuteriochloroform solution showed a methyl doublet for 1,1-dimethylallene, and a methyl doublet (C–H coupling) and methyl triplet (C–D coupling) for 3-methyl-1-butyne in a 0.11:0.89 ratio.

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Registry No. 1 (R = H), 42568-33-2; **7**, 42568-31-0; **8a**, 42568-34-3; **8b**, 42568-35-4; **9a**, 42568-38-7; **9b**, 92490-51-2; **10**, 513-35-9; **11**, 563-45-1; **14**, 42568-40-1; $ClCH_2C{\equiv}CH$, 624-65-7; $ClCH_2C{\equiv}CCH_3$, 3355-17-7; $ClCH(CH_3)C{\equiv}CH$, 21020-24-6; $ClC(CH_3)_2C{\equiv}CH$, 1111-97-3; $ClC(CH_3)_2C{\equiv}CCH_3$, 999-79-1; $NaBH_4$, 16940-66-2; bis(dimethylglyoximato)(pyridine)cobalt chloride, 23295-32-1; 1-hexene, 592-41-6; methylcyclopentane, 96-37-7; 1,1-dimethylallene, 598-25-4; 3-methyl-1-butyne, 598-23-2; 1-methylallene, 590-19-2; 1,1,3-trimethylallene, 3043-33-2; 1-butyne, 107-00-6; 2-butyne, 503-17-3; 4-methyl-2-pentyne, 21020-27-9; 1-bromo-5-hexene, 2695-47-8.

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Mechanism of Oxidation of Mandelic Acid by Fenton's Reagent

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The oxidation of organic substrates by Fenton's reagent (Fe^{2+}–H_2O_2, Fe^{2+}–$S_2O_8^{2-}$, Cu^{2+}–$S_2O_8^{2-}$, and related systems) presents unusual complexity at the molecular level.[1] The role of the hydroxyl radical and sulfate radical anion as primary oxidants has been recognized. The ferryl radical (FeO^{2+} or $Fe(OH)^{3+}$) has been implicated in biological oxidations.[2] The mechanistic conflict boils down to one of oxidation due to OH· and SO_4^{-}·, vis-a-vis oxidation by an Fe^{IV} intermediate.

The intermediacy of an Fe^{IV} species was postulated in the oxidative decarboxylation of phenylglyoxylic acid (PGA).[3] Recently Walling and co-workers addressed this problem in the oxidation of mandelic acid.[4] The choice of mandelic acid was unique in the sense that it formed a stable 1:1 complex with Fe^{2+} offering an opportunity to detect intramolecular oxidation by higher valent Fe^{IV} species. In addition to the usual hydroxyl radical reaction, Walling proposed a cage reaction of the OH· radical that could not be eliminated by hydroxyl radical traps. Shinra[5] has proposed the intermediacy of PGA to account for the formation of benzoic acid in the oxidation of mandelic acid by the Cu^{2+}/Ag^{+}–$S_2O_8^{2-}$ system. Walling considered PGA an unlikely intermediate. Benzoic acid was thought to arise due to oxidation of benzaldehyde. Mandelic acid seemed important to us in another respect. One-electron oxidants cleave the C–C bond, giving exclusively benzaldehyde.[6] Two-electron oxidation involving C–H cleavage should give the keto acid, i.e. PGA.

In Walling's work, benzaldehyde was the major product (the highest reported yield being 66%). Benzoic acid (5%) and ring-hydroxylated mandelic acids (3.5%) were the other products in the oxidation. Strangely enough, 25% of the material balance was still missing. We were intrigued by the

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Table I. Product Yields in Fenton's Reaction of Mandelic Acid (MA)[a,b]

no.	$[H^+]$, M	[MA], M	reaction conditions concn, M	yield, mol/mol of oxidant C_6H_5CHO	$C_6H_5COCOOH$
1	0.1	0.1	$[Fe^{2+}] = 0.02$ $[H_2O_2] = 0.01$	0.53	0.17
2	0.1	0.5	$[Fe^{2+}] = 0.02$ $[H_2O_2] = 0.01$	0.7	0.25
3	0.01	0.5	$[Fe^{2+}] = 0.02$ $[H_2O_2] = 0.01$	0.63	0.10
4	0.01	0.1	$[Fe^{2+}] = 0.02$ $[S_2O_8^{2-}] = 0.01$	0.7	0.2
5	0.1	0.1	$[Fe^{2+}] = 0.02$ $[S_2O_8^{2-}] = 0.01$	0.75	0.16
6	0.1	0.1	$[Fe^{2+}] = 0.02$ $[H_2O_2] = 0.01$ [acetone] = 0.10		0.152[c]

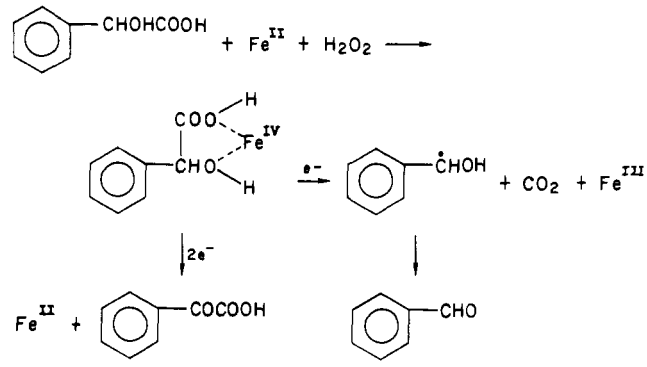
[a] Reaction carried out at 35 °C in a total volume of 100 mL in the presence of atmospheric oxygen. [b] Control experiments under identical conditions without hydrogen peroxide in the presence of oxygen (saturation solubility of oxygen at 35 °C $\sim 1 \times 10^{-3}$ M) showed that solutions of mandelic acid (0.1–0.5 M) and ferrous mandelate ($[Fe^{2+}] = 0.02$ M) are stable in acidic pH and the product of slow autooxidation is benzaldehyde (<1% over a period of 24 h) but *not* phenylglyoxylicacid. [c] In the presence of acetone, the 2,4-dinitrophenylhydrazones of benzaldehyde and acetone were mixed up. The benzaldehyde yield was not determined.

total absence of PGA and decided to reinvestigate the oxidation of mandelic acid.

Product analysis in our hands showed that phenylglyoxylic acid is indeed a major product under all the conditions. We have been able to characterize and quantitate it as its 2,4-dinitrophenylhydrazone derivative. The 2,4-dinitrophenylhydrazone of PGA is incompletely precipitated because of the –COOH group. Repeated bicarbonate extraction completely separated it from the unreacted 2,4-dinitrophenylhydrazine and 2,4-dinitrophenylhydrazone of benzaldehyde.

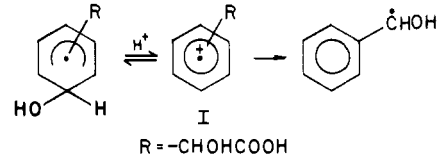
In a typical experiment the reaction was initiated by adding 50 mL of peroxide solution (0.02 M) slowly to a solution of Fe^{2+}–mandelic acid (50 mL, [mandelic acid] = 1 M, $[Fe^{2+}]$ = 0.04 M) over a period of 1 h. The reaction mixture was left for an additional period of 2 h. The completion of the reaction was tested by iodometry in the presence of ammonium molybdate. It was then treated with 200 mL of a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl and left overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone was filtered with a G-3 crucible, washed with 2 N HCl and distilled water, and dried. The residue (R_1) was extracted with a saturated solution of $NaHCO_3$ and filtered. The residue (R_2) was washed with 2 N HCl and distilled water, dried in a vacuum desiccator, identified as 2,4-DNPH of benzaldehyde, mp 235 °C, and weighed. The original filtrate was continuously extracted with ether; the ether extract was dried ($MgSO_4$) and evaporated to yield a residue (R_3) that was again extracted with $NaHCO_3$. The bicarbonate extracts were combined and filtered to remove unreacted 2,4-dinitrophenylhydrazine, and the residue was rejected. The filtrate was acidified and allowed to stand. Sometimes the yellow 2,4-dinitrophenylhydrazone of PGA precipitated. Ether extraction, drying, and evaporation yielded 2,4-DNPH of PGA, mp 195 °C, mmp 195 °C. The ^1H NMR was identical with that of an authentic sample.

Scheme I



Product yields in the oxidation of mandelic acid are given in Table I. The yield of PGA has been found to be in the range 0.10–0.25 mol/mol of the oxidant. We have not characterized benzoic acid or the ring-hydroxylated products. In the presence of Cu^{2+}, mandelic acid–Cu^{2+} complex precipitated out in the acidity range 0.1–0.02 M $HClO_4$ and hence product analysis could not be carried out. Our finding of significant amounts of PGA has a bearing on the nature of the intermediate formed in Fenton's reaction of mandelic acid. This points to a species that could react by two-electron transfer. This may well be the Fe^{IV} species. The major product benzaldehyde could be accounted for by a one-electron pathway from the same intermediate. The yield of PGA remained essentially the same, in the presence of a radical trap like acetone, pointing to the presence of a two-electron pathway (Scheme I).

In Walling's work the $C_6H_5CHOH\cdot$ radical was obtained from the radical cation I, which was produced from the acid-catalyzed dehydration of the hydroxycyclohexadienyl radical.



The small amounts of ring-hydroxylated products (<5%, ref 4) show that there is a small contribution of the OH· hydroxylation (addition to the aromatic ring) to give the hydroxycyclohexadienyl radical. Hydroxylation of the aromatic ring is an important step in the oxidation of benzene and toluene by Fenton's reagent.[7] In phenylacetic acid the yield of ring-hydroxylated product is markedly decreased, as the side chain is activated by the carboxyl. The C–H and C–C bonds in mandelic acid are sufficiently activated to be directly oxidized by any higher valent Fe^{IV} species without any obligation to go through the cyclohexadienyl and/or the cation radical intermediates. The activation of C–H bonds toward direct oxidation by Fenton's reagent by an α-OH group has been noticed earlier.[8] Our experimental results clearly show that there is indeed direct oxidation of the C–H bond in Fenton's oxidation of mandelic acid.

Registry No. Mandelic acid, 90-64-2.

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