A mixture of 6 mg of 18 and 0.5 g of zinc dust in 20 ml of glacial acetic acid was refluxed for 1.5 hr. During this time 1.5 g of more zinc dust was added in portions. Work-up as above gave 5 mg of a liquid identified by gpc and ir as diketone 3.

Disproportionation of Diketone 17a.—A solution of 25 mg of 17a and 30 mg of potassium hydroxide in 28 ml of methanol was kept at 0° under nitrogen for 1 hr. It was neutralized with 6.5 N hydrochloric acid, diluted with 30 ml of water, and extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue, 23 mg, on silica gel and elution with 6:1 petroleum ether–ether yielded 8 mg of a solid identified by gpc and ir as diketone 2a, while elution with 3:1 petroleum

ether–ether gave 7 mg of a liquid identified as dione 3 by gpc and ir.

Permanganate Oxidations. V. Kinetics and Mechanisms of the Oxidation of Mandelate Anions[1,2]
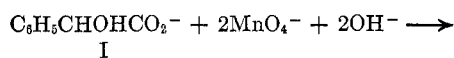
FILLMORE FREEMAN AND MARGARET ANN HOHLY SCOTT

Department of Chemistry, California State College, Long Beach, California 90801
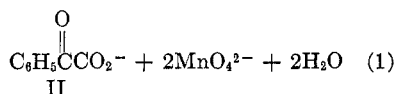
Received February 20, 1970

The kinetics of the permanganate oxidation of mandelic acid were examined over the pH range of 7.3 to 13.65 *via* spectrophotometric stopped-flow techniques. The reaction appears to proceed through three different paths. Presumably oxidative decarboxylation, to give benzaldehyde and carbon dioxide, and a reaction independent of hydroxide ion concentration occur between pH 7.3 and 12.7. Above pH 12.7, where phenylglyoxylic acid is formed, the reaction shows a first-order dependence on hydroxyl ion concentration and the rate expression is $v = k[\text{mandelate anion}][\text{OH}^-][\text{MnO}_4^-]$. The mandelate anion exhibits a kinetic isotope effect of 3.15 and 5.45 at pH 13.3 and 13.6, respectively. A positive salt effect is observed at pH 13.3. Correlation of the second-order rate constants with σ^n and σ^0 substituent constants gives ρ values of 1.0 and 0.97, respectively. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for four different mandelate anions varied from 6.6 to 7.7 kcal/mol and -33.3 to -38.2 eu. The kinetic data, at pH greater than 12.7, is consistent with either a hydride transfer from the mandelate dianion to permanganate or a hydrogen atom abstraction from the mandelate dianion by permanganate in the rate-determining step.

Although the kinetics and mechanisms of the permanganate oxidation of malic acid,[3] tartaric acid,[4,5] citric acid,[6] mandelic acid,[7] and lactic acid[8,9] have been investigated in neutral and acid media, no mechanistic studies have been reported concerning the permanganate oxidation of hydroxy acids in alkaline media. Permanganate oxidizes the mandelate anion (I) to phenylglyoxylic acid (II) under basic conditions (eq 1).[10] In contrast, when mandelic acid is oxidized
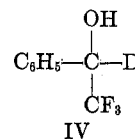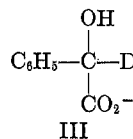
$$C_6H_5CHOHCO_2^- + 2MnO_4^- + 2OH^- \longrightarrow$$

$$\text{I}$$

$$\underset{\text{II}}{C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CO_2^-} + 2MnO_4^{2-} + 2H_2O \quad (1)$$

in acid solution, oxidative decarboxylation occurs to give benzaldehyde and carbon dioxide.[7] In order to obtain a more detailed mechanistic picture of the permanganate oxidation of the mandelate anion (I), we have examined the kinetics of the reaction from pH 7.3 to 13.65 *via* spectrophotometric stopped-flow techniques.

The permanganate oxidation of α-deuteriomandelate anion (III) is also of interest because of its close structural similarity to IV which gives a remarkably

$$\underset{\text{III}}{\overset{\displaystyle OH}{\underset{\displaystyle CO_2^-}{C_6H_5-C-D}}} \qquad \underset{\text{IV}}{\overset{\displaystyle OH}{\underset{\displaystyle CF_3}{C_6H_5-C-D}}}$$

large k_H/k_D of 16.1 in alkaline permanganate oxidations.[11–13]

Experimental Section

Reagents.—Distilled water was purified by passing through two type R-2 ion-exchange columns.[14] Standard volumetric (Acculute) sodium hydroxide (CO$_2$ free) concentrate was diluted to the specified volume for the desired pH. Potassium permanganate stock solutions were also prepared from standard volumetric solutions (Acculute). The stock solution was stored under nitrogen, and the absorbancy index was checked before each set of kinetic runs. Reagent grade sodium chloride (Mallinckrodt), potassium nitrate (Mallinckrodt), and potassium sulfate (Mallinckrodt) were used without further purification to adjust ionic strength. All solutions were prepared immediately before use, and the pH was measured potentiometrically.

Mandelic Acid (Matheson Coleman and Bell) was recrystallized from benzene before use, mp 118–119° (lit.[15] mp 119.5–120.5°).

Substituted Mandelic Acids.—Mandelic acid derivatives were prepared *via* the imido ester (eq 2),[16] the cyanohydrin (eq 3),[17]

(1) Part IV: F. Freeman and A. Yeramyan, *J. Org. Chem.*, **35**, 2061 (1970).

(2) Presented in part before the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 8, 1969.

(3) Y. K. Gupta and R. Dutta, *Proc. Nat. Acad. Sci., India, Sect. A*, **28**, 236 (1959).

(4) G. V. Bakore and R. Shanker, *Indian J. Chem.*, **1**, 108 (1963).

(5) G. V. Bakore and R. Shanker, *Curr. Sci.*, **28**, 279 (1959).

(6) G. V. Bakore and R. Shanker, *Indian J. Chem.*, **1**, 286 (1963).

(7) G. V. Bakore, R. Shanker, and U. Goyal, *ibid.*, **1**, 331 (1963).

(8) S. Senent-Perez, L. Ramos, and H. Sanz-Garcia, *An. Real Soc. Espan. Fis. Quim., Ser. B*, **53**, 573, 583 (1957); *Chem. Abstr.*, **54**, 1992 (1960).

(9) G. V. Bakore and B. P. Rishi, *Indian J. Chem.*, **4**, 4 (1966).

(10) C. D. Hurd and R. W. McNamee, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1941, p 244.

(11) R. Stewart and R. Van der Linden, *Tetrahedron Lett.*, **2**, 28 (1960).

(12) R. Stewart and R. Van der Linden, *Discuss. Farday Soc.*, 211 (1960).

(13) J. L. Kurz, *J. Amer. Chem. Soc.*, **86**, 2229 (1964).

(14) Illinois Water Treatment Co., Rockford, Ill.

(15) C. R. Zanesco, *Helv. Chim. Acta*, **49**, 1002 (1966).

(16) G. Barger and A. J. Ewins, *J. Chem. Soc.*, **95**, 552 (1908).

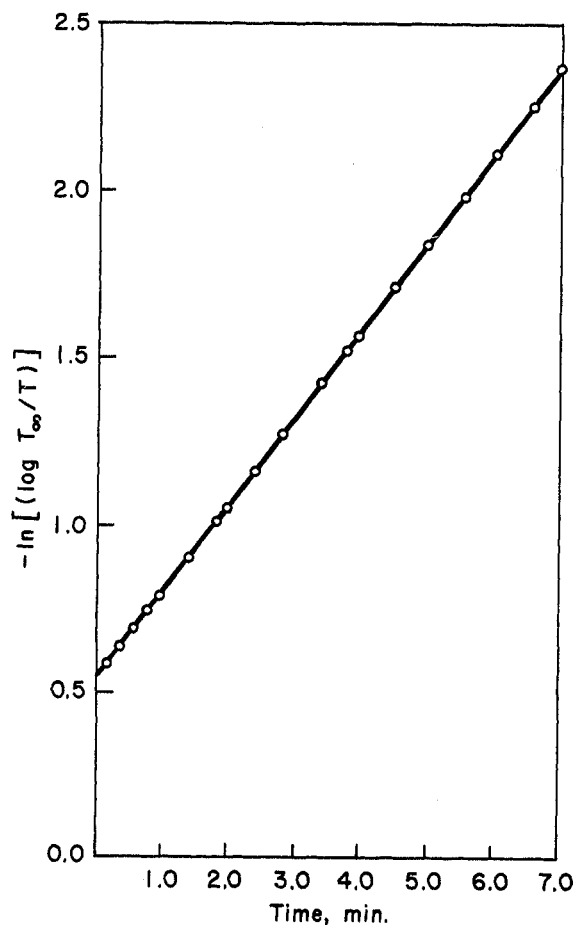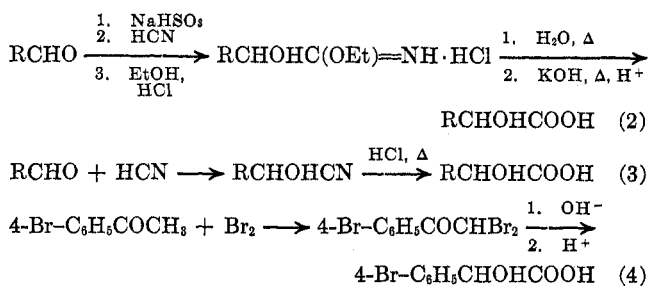(17) S. S. Jenkins, *J. Amer. Chem. Soc.*, **53**, 2341 (1931).

Figure 1.—A typical pseudo-first-order kinetic plot. The conditions are [mandelate anion] = 4.0 × 10⁻² M, [OH⁻] = 0.20 M, [MnO₄⁻] = 4.0 × 10⁻⁴ M, μ = 0.5 M, λ = 510 mμ, temp 25.0°.

$$
\text{RCHO} \xrightarrow[\substack{3.\ \text{EtOH,}\\ \text{HCl}}]{\substack{1.\ \text{NaHSO}_3\\ 2.\ \text{HCN}}} \text{RCHOHC(OEt)=NH·HCl} \xrightarrow[2.\ \text{KOH, }\Delta,\ \text{H}^+]{1.\ \text{H}_2\text{O, }\Delta}
$$

$$\text{RCHOHCOOH} \quad (2)$$

$$\text{RCHO} + \text{HCN} \longrightarrow \text{RCHOHCN} \xrightarrow{\text{HCl, }\Delta} \text{RCHOHCOOH} \quad (3)$$

$$4\text{-Br-C}_6\text{H}_5\text{COCH}_3 + \text{Br}_2 \longrightarrow 4\text{-Br-C}_6\text{H}_5\text{COCHBr}_2 \xrightarrow[2.\ \text{H}^+]{1.\ \text{OH}^-}$$

$$4\text{-Br-C}_6\text{H}_5\text{CHOHCOOH} \quad (4)$$

and the dibromo ketone (eq 4).[18] The deuterated acids were prepared according to the exchange procedure of Kemp and Waters.[19] Examination of the pmr spectra showed the complete disappearance (98–99%) (to within the limitations of the technique) of the α-proton signal. Table I summarizes the synthetic data.[18-23]

Apparatus and Kinetic Method.—The rate of disappearance of permanganate was followed spectrophotometrically, at 510 and 522 mμ, in a stopped-flow reactor.[24] The Beckman DU spectrometer was coupled to a Bristol strip chart recorder (0.2 sec for full-scale deflection and chart speeds to 120 in./min) or

(18) J. J. Klingenberg, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., p 110.

(19) T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1192 (1964).

(20) Aldrich Chemical Co.

(21) J. L. Riebsomer, J. Irvine, and R. Andrews, *J. Amer. Chem. Soc.*, **60**, 1015 (1938).

(22) J. J. Klingenberg, J. P. Thole, and R. D. Lingg, *J. Chem. Eng. Data*, **11**, 94 (1966).

(23) S. I. Vogel, "A Textbook of Practical Organic Chemistry," Wiley, New York, N. Y., 1966, p 715.

(24) F. Freeman, A. Yeramyan, and F. Young, *J. Org. Chem.*, **34**, 2438 (1969).

TABLE I

METHODS OF PREPARATION OF MANDELIC ACID DERIVATIVES

Substituent	Method of preparation[a]	Mp, °C Obsd	Mp, °C Lit.
2-Cl	Imido ester[b]	84–85	85.0–85.5[c]
4-Cl	Cyanohydrin[c]	120.5–121	120.5–121[c]
4-Br	Dibromo ketone[d]	118.5–120	117–119[d]
4-F[a,e]		135–136.5	138.5[d]
4-CH₃	Cyanohydrin[c]	144.5–145.5	145–145.5[f]
4-OCH₃	Imido ester[b]	105.5–107.5	108[g]
3,4-OCH₂O–	Imido ester[b]	158–158.5	162[h]
α-C₆H₆	Benzylic acid rearrangement[i]	149–150	149–150[i]
α-D	Exchange[j]	118.5–120	
4-Cl-α-D	Exchange[j]	115–117	

[a] Benzene was used as recrystallizing solvent. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 20. [f] Reference 21. [g] Reference 22. [h] Reference 10. [i] Reference 23. [j] Reference 19.

a Sargent Model SRLG recorder *via* an energy recording adapter.

The kinetics were studied under pseudo-first-order conditions, and the rate constants were obtained from the slopes of plots of $-\ln[\log(T_\infty/T)]$ against time where T_∞ is the per cent transmission at a point just before colloidal manganese dioxide begins to form (Figure 1). An IBM 1620 computer was used for all calculations,[25] and all rate constants given in the tables are the average of two or more determinations.

Results

Order of Reaction.—The rate law was determined by measuring the effect of varying the concentrations of the reactants on the rate constants. The effects of mandelate anion (I) and permanganate concentrations are summarized in Table II. A first-order dependence

TABLE II

RATE DATA FOR THE OXIDATION OF MANDELATE ANION AT pH 13.3[a]

[Mandelate anion] × 10² M	[MnO₄⁻] × 10⁴ M	k_ψ[b] × 10² sec⁻¹	k_2[c] × 10¹ M^{-1} sec⁻¹
2.0	4.0	0.65	3.25
4.0	4.0	1.28	3.20
8.0	4.0	2.57	3.20
10.0	4.0	3.05	3.05
12.0	4.0	3.55	2.96
20.0	4.0	5.85	2.93
4.0[d]	4.0	1.28	3.20
4.0[d]	8.0	1.25	3.13
4.0[d]	12.0	1.28	3.20
4.0[e]	4.0	1.35	3.38
4.0[e]	6.0	1.25	3.13
4.0[e]	7.0	1.22	3.04

[a] λ = 510 mμ, μ = 0.5, [OH⁻] = 0.20 M, 10-mm cell. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[mandelate anion]. [d] 4-mm cell. [e] λ = 522 mμ.

on the concentration of mandelate anion (I) is observed over a tenfold range of concentration at constant hydroxide and constant permanganate ion concentrations. A plot of the pseudo-first-order rate constant (k_ψ) *vs.* the concentration of I gives a straight line passing through the origin (Figure 2) which also indicates a first-order dependence on the concentration of I. The first-order dependence on permanganate concentration is demonstrated by the constancy of the

(25) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York,N. Y., 1965, p 168 ff.

pseudo-first-order rate constant (k_ψ) at 510 and 522 mμ over a 4 to 12 $\times$ 10^{-4} M permanganate concentration range.

The effect of hydroxide ion concentration on the rate of reaction (Figure 3) was determined giving the data in Table III. It is seen that the rate does not increase

TABLE III
EFFECT OF HYDROXIDE ION CONCENTRATION
ON THE RATE OF OXIDATION OF MANDELATE ANION[a]

pH	[OH$^-$], M	$k_\psi{}^b \times 10^3$ sec^{-1}	$k_2{}^c \times$ 10^2 M^{-1} sec^{-1}	$k_2 - k_0{}^d$ $\times$ 10^2 M^{-1} sec^{-1}	$k_3,{}^e$ 1.^{2} mol^{-2} sec^{-1}
7.31^f	2.19 $\times$ 10^{-7}	3.67	9.18		
8.60^f	3.98 $\times$ 10^{-6}	3.83	9.58		
9.64^f	4.37 $\times$ 10^{-5}	4.83	12.1		
11.0^f	10^{-3}	3.17	7.93		
12.7	0.05	4.33	10.8	6.5	1.30
13.0	0.10	7.00	17.5	13.2	1.32
13.3	0.20	12.8	32.0	27.7	1.38
13.4	0.25	15.7	39.3	34.8	1.39
13.6	0.40	23.5	58.8	54.3	1.36
13.65	0.45	26.0	65.0	60.7	1.35

[a] [C$_6$H$_5$CHOHCOO$^-$Na$^+$] = 4.0 $\times$ 10^{-2} M, [MnO$_4{}^-$] = 4.0 $\times$ 10^{-4} M, μ = 0.5 M, λ = 510 mμ, temp 25.0°, 10-mm cell. [b] Pseudo-first-order rate constant. [c] Second-order rate constant = k_ψ/[C$_6$H$_5$CHOHCOO$^-$Na$^+$]. [d] Intercept of a plot of k_2 vs. [OH$^-$] gives k_0. [e] Third-order rate constant, $(k_2 - k_0)$/[OH$^-$]. [f] Influenced by disproportionation of manganate [Mn^{VI}] and/or hypomanganate [Mn^V].[26]

appreciably from pH 7.3 to 12.7 which is consistent with a zero-order dependence on hydroxide ion concentration for this pH range. Indeed, a plot of the second-order rate constant $(k_2 = k_\psi/[\text{I}])$ vs. hydroxide ion concentration between pH 12.7 and 13.65 gives a straight line that does not go through the origin. This is also consistent with both zero-order and first-order terms describing the effect of hydroxyl ion concentration on the rate of oxidation. The rate law then appears to be

$$\frac{-d[\text{MnO}_4{}^-]}{dt} = k_0[\text{mandelate anion}][\text{MnO}_4{}^-] +$$

$$k[\text{mandelate anion}][\text{OH}^-][\text{MnO}_4{}^-] \quad (5)$$

where k_0 = 4.37 $\times$ 10^{-2} 1. mol^{-1} sec^{-1} and k = 1.36 1.^{2} mol^{-2} sec^{-1}. However, the intercept (k_0) is smaller than the average k_2 value (9.92 $\times$ 10^{-2} 1. mol sec^{-1}) observed over the pH range of 7.3–12.7. If one assumes that oxidative decarboxylation (eq 6) is also operative in

$$\text{C}_6\text{H}_5\text{CHOHCO}_2\text{H} \xrightarrow{\text{MnO}_4{}^-} \text{C}_6\text{H}_5\text{CHO} + \text{CO}_2 \quad (6)$$
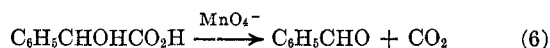
slightly basic solution,[7] then it would appear that the observed rate constant is composed of k_0, k, and a rate constant for eq 6.[26] The rate would then appear to be

$$\frac{-d[\text{MnO}_4{}^-]}{dt} = k_n[\text{mandelic acid}][\text{MnO}_4{}^-] +$$

$$k_0[\text{mandelate anion}][\text{MnO}_4{}^-] +$$

$$k[\text{mandelate anion}][\text{OH}^-][\text{MnO}_4{}^-] \quad (7)$$

(26) (a) It is difficult to attempt to elucidate the full significance of the rate constants over the unbuffered pH range of 7.3–12.7 owing to the number of possible reactions that can occur in the permanganate oxidation of I. Further complications are caused in the permanganate oxidation of I. Further complications are caused in the spectrophotometric studies by the precipitation of colloidal manganese dioxide and the disproportionation of manganate [Mn^{VI}] and hypomanganate [Mn^V]. Anomalous kinetic behavior has been observed, via titrimetric techniques, around pH 11 for the permanganate oxidation of formate anion[26b,c] and piperonal.[26d] (b) K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.,* **78**, 1214 (1955). (c) R. P. Bell and D. P. Onwood, *J. Chem. Soc. B,* **150** (1967). (d) K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.,* **77**, 1768 (1955).
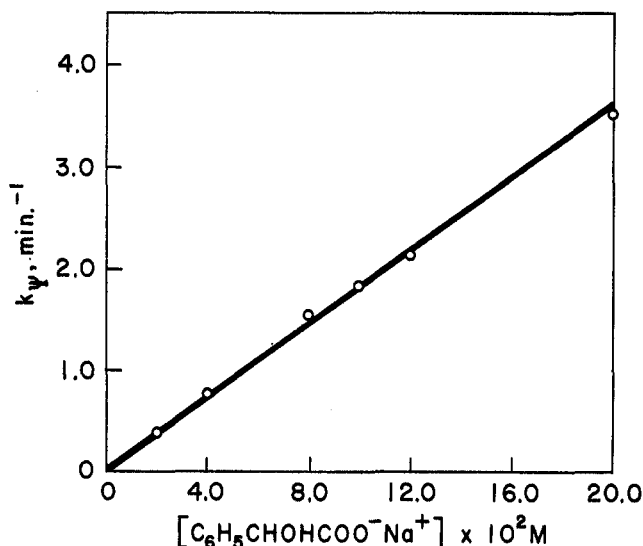
Figure 2.—Effect of mandelate anion concentration on the pseudo-first-order rate constants for the permanganate oxidation at 25.0°.
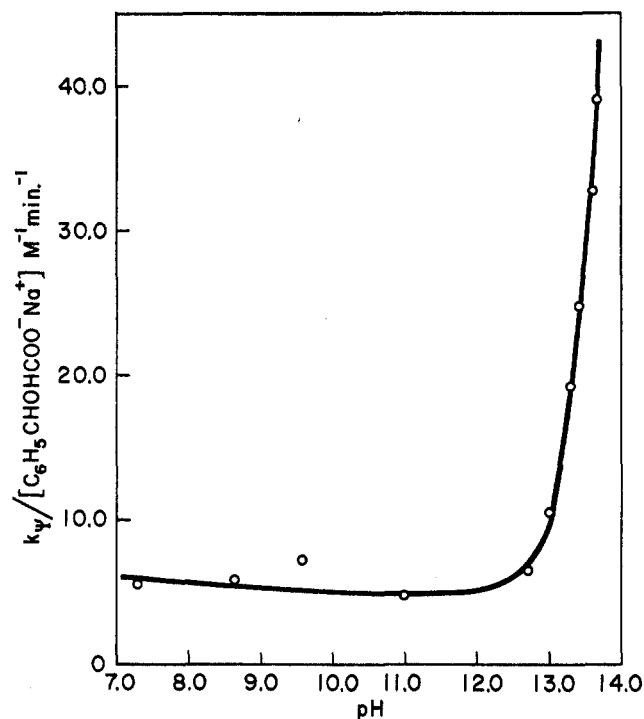
Figure 3.—Effect of pH on the rate of the permanganate oxidation of mandelate anion.

where k_n is presumably the constant for oxidative decarboxylation, k_0 is the rate constant for the uncatalyzed reaction, and k is the rate constant for the base-catalyzed reaction.

A plot of $k_2 - k_0$ against [OH$^-$] gives a straight line passing through the origin (Figure 4) which further supports the first-order dependence on hydroxide ion concentration above pH 12.7. The rate law above pH 12.7 then appears to be

$$\frac{-d[\text{MnO}_4{}^-]}{dt} = k[\text{mandelate anion}][\text{OH}^-][\text{MnO}_4{}^-] \quad (8)$$

Activation Parameters.—Table IV gives the thermodynamic data for the permanganate oxidation of I and its 4-bromo (V), 4-chloro (VI), and 4-methyl (VII) derivatives.
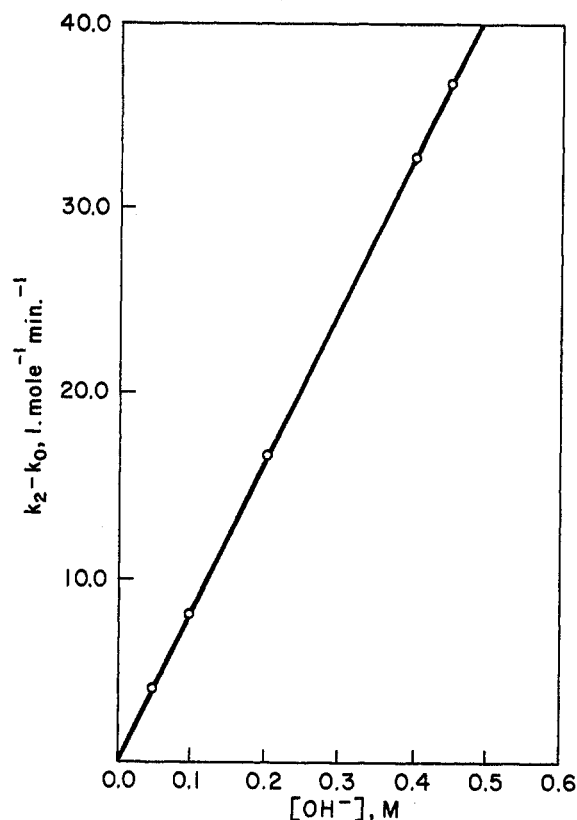
Figure 4.—Effect of hydroxide ion concentration on the rate of permanganate oxidation of mandelate anion. The conditions are [mandelate anion] = 4.0×10^{-2} M, [MnO_4^-] = $4.0 \times 10^{-4} M$, temp 25.0°.

TABLE IV
ACTIVATION PARAMETERS FOR THE
PERMANGANATE OXIDATION OF MANDELATE ANIONS[a]

Mandelate anion derivative	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
4-H	7.5	35.5
4-Br	7.7	33.3
4-Cl	6.6	37.2
4-CH₃	6.8	38.2

[a] [Anion] = 4.0×10^{-2} M, [MnO_4^-] = 4.0×10^{-4} M, [OH⁻] = 0.20 M, μ = 0.5 M, λ = 510 mμ, temp 25.0°.

Effects of Ionic Strengths.—Table V shows that there is a positive salt effect in the permanganate oxidation of I with sodium chloride, potassium nitrate, and potassium sulfate.

TABLE V
RATE DEPENDENCE ON IONIC STRENGTH[a]

μ	$k_2^b \times 10^1$ l. mol⁻¹ sec⁻¹		
	NaCl	KNO₃	K₂SO₄
0.25	2.13	1.98	1 98
0.50	3.22	3.25	2.80
0.75	4.35	4.60	3.68
1.00	5.60	5.10	4.70

[a] [$C_6H_5CHOHCOO^-Na^+$] = 4.0×10^{-2} M, [MnO_4^-] 4.0×10^{-4} M, [OH⁻] = 0.20 M, λ = 510 mμ, temp 25.0°. [b] k_2 = k_ψ/[$C_6H_5CHOHCOO^-Na^+$].

Kinetic Isotope Effects.—The isotope effects for the permanganate oxidation of α-deuteriomandelate anion (III) and 4-chloro-α-deuteriomandelic anion (VIII) are given in Table VI.

TABLE VI
KINETIC ISOTOPE EFFECTS IN THE PERMANGANATE
OXIDATION OF α-DEUTERIOMANDELATE ANIONS AT 25.0°

Mandelate anion	pH	$k_H/k_D{}^a$
III	13.3	3.15
III	13.6	5.45
VIII	13.3	2.79

[a] k_2 = k_ψ/[mandelate anion].

Linear Free-Energy Relationships.—Correlation of log k_2 with σ *normal* values[27,28] gave a ρ value of 0.996 with a correlation coefficient (r) of 0.970 and a standard deviation (s) of 0.047. A slightly better correlation was obtained with σ° values[27,29] giving a ρ of 0.97 with r = 0.975 and s = 0.043. The data are summarized in Table VII.

TABLE VII
EFFECTS OF SUBSTITUENTS ON THE RATE OF
PERMANGANATE OXIDATION OF MANDELATE ANIONS[a]

| Substituent	$k_2^b \times 10^1$ M^{-1} sec⁻¹	Log k_2
4-CH₃	2.92	0.4654
4-H	3.22	0.5079
4-F	4.70	0.6721
4-Cl	6.52	0.8143
4-Br	6.82	0.8338
2-Cl[c]	2.80	0.4472
OCH₃[c]	3.85	0.5855
3,4-OCH₂O–[c]	13.5	1.130

[a] λ = 510 mμ, pH = 13.3, [OH⁻] = 0.20 M, μ = 0.5 M, temp 25.0°. [b] k_2 = k_ψ/[mandelate anion]. [c] Not used in correlation.

Attempted Oxidation of Benzilic Acid.—At 25.0° benzilic acid (4.0×10^{-2} M) is essentially inert to permanganate ($4.0 \times 10^{-4} M$) at a pH of 13.3.

Discussion

It is clear from the kinetic data described above that at least three mechanisms are operative in the permanganate oxidation of I over the pH range of 7.3 to 13.65. The reactions from pH 7.3 to 12.7 are independent of hydroxyl ion concentration and the reaction pathway above pH 12.7 is dependent on the first power of hydroxide ion concentration. Since the hydroxy group of I is only partly ionized under the reaction conditions, the kinetic data suggest a scheme in which the mandelate dianion (IX) is formed in an equilibrium step and is oxidized by permanganate in the rate-determining step. A reasonable mechanism conforming to the observed kinetics between pH 12.7 and 13.65 is shown in Scheme I. The rate equation derived from this mechanism is

$$\nu = k[IX][MnO_4^-] = kK_{eq} \frac{[I][OH^-][MnO_4^-]}{[H_2O]} = \frac{kK_{eq}}{k_{eq'}}[I][OH^-][MnO_4^-] \quad (9)$$

where K_{eq} is the equilibrium constant for the formation of IX. Thus, it can be seen that the mechanism

(27) H. van Belkkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim Pays-Bas*, **78**, 815 (1959).
(28) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
(29) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

SCHEME I

$$C_6H_5-\underset{\underset{CO_2^-}{|}}{\overset{\overset{OH}{|}}{C}}-H + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_5-\underset{\underset{CO_2^-}{|}}{\overset{\overset{O^-}{|}}{C}}-H + H_2O$$

$$\text{I} \qquad\qquad\qquad\qquad \text{IX}$$

$$C_6H_5-\underset{\underset{CO_2^-}{|}}{\overset{\overset{O^-}{|}}{C}}-H + MnO_4^- \underset{slow}{\overset{k_3}{\longrightarrow}}$$

$$\text{IX}$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-CO_2^- + HMnO_4^{2-}$$

$$\text{II}$$

$$HMO_4^{2-} + MnO_4^- + OH^- \underset{fast}{\overset{k_4}{\longrightarrow}} 2MnO_4^{2-} + H_2O$$
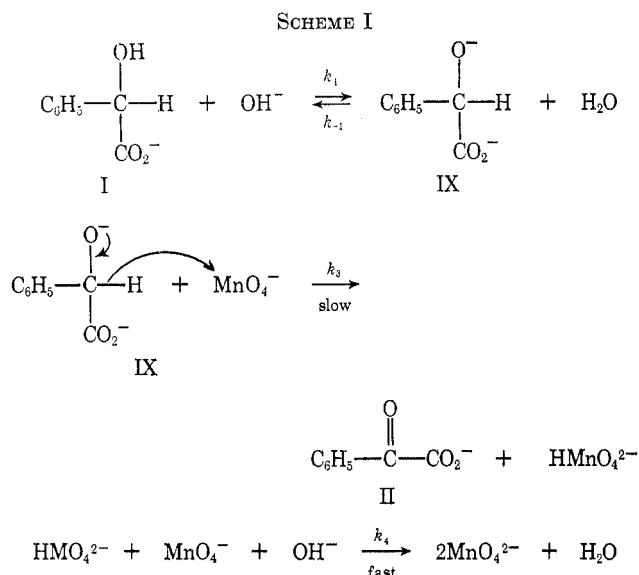
postulated in Scheme I can account for the observed rate law (eq 8).[30]

Although Scheme I depicts a reasonable mechanistic pathway for the permanganate oxidation of I, the anion-radical mechanism shown in Scheme II also merits consideration.

SCHEME II

$$\text{I} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{IX} + H_2O$$

$$\text{IX} + MnO_4^- \underset{slow}{\overset{k_3}{\longrightarrow}} C_6H_5-\underset{\underset{CO_2^-}{|}}{\overset{\overset{O^-}{|}}{C}}\cdot + HMnO_4^-$$

$$\text{X}$$

$$\text{X} + Mn^{VI} \text{ or } Mn^{VII} \underset{fast}{\overset{k_4}{\longrightarrow}} C_6H_5-\overset{\overset{O}{\|}}{C}-CO_2^-$$

$$\text{II}$$

The observed kinetic isotope effects of 3.15 and 5.45 for the oxidation of I at pH 13.3 and 13.6, respectively, and the k_H/k_D value of 2.79 for VIII at pH 13.3 clearly demonstrates that the rate-limiting step must involve the cleavage of the carbon–hydrogen bond. These observations may be accounted for by either a two-electron oxidation (Scheme I) or a one-electron oxidation (Scheme II). It might appear that the observed isotope effects are more consistent with a two-electron oxidation (Scheme I) since it is known that very large kinetic isotope effects are generally obtained for reactions involving a hydrogen atom abstraction from the α position of alcohols and alkoxides anions.[31] For example, the permanganate oxidation of IV,[11,12] XI,[12] and XII[13,32] have k_H/k_D values of 16.1, 19.1, and 14,

(CF₃)₂CHO⁻   CF₃CHOHO⁻   (HCO₂⁻)Coᴵᴵᴵ(NH₃)₅

$$(CF_3)_2CHO^- \qquad CF_3CHOHO^- \qquad (HCO_2^-)Co^{III}(NH_3)_5$$
$$\text{XI} \qquad\qquad \text{XII} \qquad\qquad \text{XIII}$$

respectively. The suggestion by Stewart that these oxidations may involve hydrogen atom abstraction

rather than hydride anion has appeared recently.[33,34] Furthermore, the k_H/k_D for the hydrogen abstraction in eq 10 is 17,[35] and the k_H/k_D for the one-electron per-

$$CH_3CH_2OH + H\cdot \longrightarrow CH_3\dot{C}HOH + H_2 \qquad (10)$$

manganate oxidation of XIII is 10.1.[36] However, this is not the complete picture since I is not completely ionized (to IX) at pH 13.3 and 13.6. Therefore, the observed k_H/k_D is probably not the maximum value for the oxidation of IX. Indeed, at pH 13.3 one is probably observing a secondary isotope effect of the *second kind*[37] for the ionization of I as well as a primary isotope effect for the oxidation of IX. At pH 13.6, the equilibrium lies farther toward IX and the k_H/k_D value of 5.45 is probably closer to the actual value for the permanganate oxidation of IX. Similar variations in the deuterium isotope effects, as a function of pH, have been reported for the permanganate oxidation of IV[12] and fluoral hydrate.[32]

The observed rate of oxidation is expected to be sensitive to the effect of ring substitution on the pre-equilibrium ionization step. It should be noted that two opposing substituent effects are operative in the permanganate oxidation of 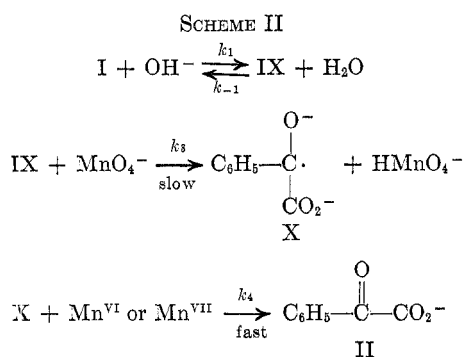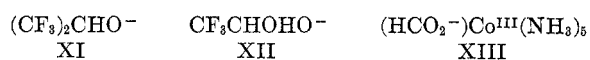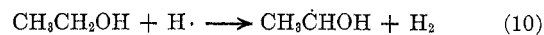IX. Electron-attracting groups should facilitate the ionization of I ($\rho = +$) and retard hydride transfer from IX to permanganate.

$$\log\left(\frac{k}{k_0}\right)_{obsd} = \log\left(\frac{K}{K_0}\right)_{eq} + \log\left(\frac{k}{k_0}\right)_{rate} = \sigma(\rho_{eq} + \rho_{rate})$$

The good correlations with σ^n and σ^0 substituent constants show that the ρ value of approximately 1.0 arises only from direct electrostatic and polar effects. Although free-radical reactions may be correlated by σ^n and σ^0 parameters,[38] the observed ρ ($\rho \cong 1.0$) probably results from ρ_{eq} being of opposite sign and larger size than ρ_{rate}.

A mechanism involving species of the same charge in the rate-determining step is consistent with the positive salt effects observed with sodium chloride, potassium nitrate, and potassium sulfate (Table V).

The thermodynamic parameters for the oxidation of mandelate anions (Table IV), which are characterized by low enthalpies of activation ($\Delta H^{\ddagger} = 6.6$ to 7.7 kcal/mol) and large negative entropies of activation ($\Delta S^{\ddagger} = -33.3$ to -38.2 eu), are consistent with other permanganate reactions involving anions and di-anions.[13,32,39,40] It has been postulated that the observed activation parameters also include the enthalpy and entropy of activation of the preequilibrium step.[40,41]

(33) Reference 31, p 67.

(34) In an attempt to differentiate between a hydrogen atom abstraction mechanism and a hydride transfer mechanism in the permanganate oxidation of fluoral hydrate, Kurz[13] estimated the acidity of the activated complex (from transition state theory) and concluded that the reaction proceeded *via* a hydride anion transfer. However, the validity of this conclusion depends on the accuracy of the estimated acidities.

(35) C. Lifshitz and G. Stein, *J. Chem. Soc.*, 3706 (1962).

(36) V. Halpern and J. P. Candlin, *J. Amer. Chem. Soc.*, **85**, 2518 (1963).

(37) E. A. Halevi in "Progress in Physical Organic Chemistry," Vol. I., S. G. Cohen, A. Streitiveiser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1963, p 109 ff.

(38) P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 35.

(39) F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. G. McLaughlin, and E. W. Paull, *J. Org. Chem.*, **35**, 982 (1970).

(40) R. Stewart, *J. Amer. Chem. Soc.*, **79**, 3057 (1957).

(41) More reliable[25a] rate coefficients for the hydroxide independent terms in eq 7 would enable one to calculate their contributions to the salt effects, the substituent effects, and the activation parameters.

(30) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1963, p 216.

(31) R. Stewart, "Oxidation Mechanisms: Applications to Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, pp 16, 63.

(32) R. Stewart and M. Mocek, *Can. J. Chem.*, **41**, 1160 (1963).

Although the kinetic data presented are consistent with both Scheme I and II, the activated complex in Scheme I could be represented by XIV and the acti-

vated complex for Scheme II could be represented by XV. In view of the close analogy between Scheme I

and II, the available data for the permanganate oxidation of alkoxide ions and the anions of aldehyde hydrates, it is not possible to differentiate between the hydride transfer mechanism and the hydrogen atom mechanism.

A Novel Single-Step Sulfone Synthesis

HARRY W. GIBSON AND DALE A. MCKENZIE

Chemicals and Plastics Division, Union Carbide Corporation, Tarrytown, New York 10591

A recently reported synthesis of sulfones from olefins and sulfur dioxide in the presence of formic acid–tertiary amine "adducts" has been investigated. The reaction appears to be limited to monosubstituted olefins bearing an electron-withdrawing group. The sulfones are usually accompanied by the corresponding disulfides, which can be the major products under certain conditions. Disubstituted terminal olefins do yield disulfides. The solvent "adducts" were found to be azeotropes; in fact formic acid *per se* is not required, only formate ion. Mechanistically the intermediacy of sulfoxylic acid (H_2SO_2, formed by reduction of sulfur dioxide) in the generation of a sulfinic acid from the olefin is confirmed. The sulfone is formed by addition of the sulfinic acid to a second mole of olefin. Deuterium tracer work indicates that exchange of the protons α to the sulfinyl group occurs in the intermediate sulfinic acid. The deuterium tracer work also militates against a termolecular reaction of olefin, sulfur dioxide, and formate ion leading in one step to sulfinic acid and thus supports stepwise generation of sulfoxylic and sulfinic acids. There are several feasible mechanistic pathways for disulfide formation. The most likely route consists of reaction of elemental sulfur (formed by formate reduction of sulfur dioxide) and a mercaptan (probably arising *via* disproportionation of the corresponding sulfinic acid).

A recent patent reported that reaction of certain terminal olefins with sulfur dioxide in the presence of "adducts" of formic acid and trimethyl- or triethylamine affords sulfones in 13–63% yield with evolution of carbon dioxide.[1a] The report states that "adducts"[1b]

a, R₁ = H; R₂ = CONH₂
b, R₁ = H; R₂ = COOH
c, R₁ = H; R₂ = CN
d, R₁ = H; R₂ = COOCH₃
e, R₁ = CH₃; R₂ = COOCH₃
f, R₁ = CH₃; R₂ = CONH₂

of formic acid and a variety of other tertiary amines are not as effective. Formic acid and formamides were also utilized.

In view of the intriguing nature of this transformation, the lack of evidence for mechanistic speculations and our interest in the chemistry of formic acid,[2] we have examined the scope and mechanism of the reaction.

The Reaction.—"Adducts" of formic acid and tertiary amines have been used as reducing media in other processes.[3] They have also seen use in other

applications.[4] Examination of the "adducts" of formic acid with trimethyl- and tributylamine by vpc, ir, and pmr revealed that no new covalent compounds were present. The only compounds present were formic acid and the tertiary amine. The molar ratio of the two components varied from amine to amine. Moreover, for a given amine the composition varied with distillation pressure. These data are interpreted as indicating that the "adducts" are really azeotropes. This is substantiated by the fact that synthetic mixtures of the two components are as effective in the reaction as the distilled materials.

Using acrylamide (**1a**) as starting material and the formic acid–trimethylamine azeotrope (3.0:1.0), the optimum temperature under our reaction conditions was found to be 100° at which a 61% yield of bis(2-carboxamidoethyl) sulfone (**2a**) was obtained. Variation of the formic acid–trimethylamine ratio appeared to have little effect on yield. The tertiary amines were not unique as cosolvents with the formic acid. Pyridine, secondary and primary amines, formamides, and ammonium and sodium formates were also satisfactory. These results suggested that the active species in the solvent was formate ion. This view was supported by the lack of reaction with neat formic acid, neat fromamide, and acetic acid–trimethylamine (3.0:1.0). Indeed solutions of sodium or ammonium formate in acetic acid were suitable (55% yield under conditions

(1) (a) Farbenfabriken Bayer A.-G., German Patent 1,222,048 (1966); *Chem. Abstr.*, **65**, 13545e (1966). (b) A referee states that in German "adduct" means "loose addition product without forming covalent bonds" and in this context is correct (*vide infra*).

(2) H. W. Gibson, *Chem. Rev.*, **69**, 673 (1969).

(3) (a) M. Sekiya and K. Ito, *Chem. Pharm. Bull.*, **12**, 677 (1964); (b) M. Sekiya, Y. Harada, and K. Tanaka, *ibid.*, **15**, 833 (1967). See ref 2 for discussion of these and other uses of formic acid media as reducing agents.

(4) M. Sekiya, M. Tomic, and N. J. Leonard, *J. Org. Chem.*, **33**, 318 (1968). See also ref 2.