

# KINETICS AND MECHANISM OF THE OXIDATION OF SUBSTITUTED MANDELIC ACIDS BY ACID PERMANGANATE

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**Abstract**—The oxidation of mandelic acid and nine monosubstituted mandelic acids by acid permanganate, in the presence of fluoride ions, have been studied. The reaction is of first order with respect to each the oxidant, the substrate and hydrogen ions. The kinetic isotope effect,  $k_H/k_D = 3.76$  at 25°. The oxidation exhibits a reaction constant  $\rho = -2.23 \pm 0.07$  at 25°. The oxidation does not induce polymerisation of acrylonitrile and does not show any solvent isotope effect. The activation enthalpies entropies are linearly related ( $r = 0.979$ ). A mechanism involving transfer of a hydride ion to the oxidant is proposed.

## INTRODUCTION

The oxidation of  $\alpha$ -hydroxy acids by acid permanganate has not received much attention except for some reports by Bakore *et al.*,<sup>1,2</sup> who studied the reaction under the conditions where the oxidising species are intermediate valency states of manganese instead of permanganate itself. The mechanism suggested by them is similar to that postulated for the oxidation of  $\alpha$ -hydroxy acids by Mn(III).<sup>3,4</sup> Evidently the oxidation by permanganate needs further study. This communication reports the oxidation of mandelic acid and monosubstituted mandelic acids by acid permanganate and evaluates the reaction constant. The mechanistic conclusions are also discussed. The reaction conditions are so chosen as to minimise the participation of intermediate valency states of manganese in the oxidation process.

## RESULTS

The oxidation of all the acids are autocatalytic. Such a phenomenon is well known in permanganate oxidations and is attributed to the reactions of Mn(III)/Mn(IV). To suppress these reactions a large excess of sodium fluoride was added to each reaction mixture.<sup>5</sup> Addition of fluoride ions suppresses the autocatalysis and good first order plots were obtained for at least two half lives.

Mandelic acid (0.02 M) reacts with potassium permanganate (0.002 M) in the presence of perchloric acid (1.0 M) and sodium fluoride (0.02 M) to give benzaldehyde, which is isolable in 94% yield. The rate constant for the oxidation of mandelic acid (M.A.) under these conditions, at 25°, is  $0.0111^2 \text{ mol}^{-2} \text{ s}^{-1}$ , whereas the rate constant for

the oxidation of benzaldehyde under similar conditions is  $0.0131^2 \text{ mol}^{-2} \text{ s}^{-1}$ . Although the rate constant for the oxidation of benzaldehyde is slightly more than that of mandelic acid, the kinetic importance of the same may be reduced to an acceptable level by using a concentration of hydroxy acid many times that of permanganate.

The oxidation of *p*-fluoro- and *m*-nitro- mandelic acids also give corresponding benzaldehydes in >90% yield.

*Rate laws.* When the concentration of the hydroxy acid is in excess the rate of disappearance of permanganate follows first order rate laws. The order with respect to the hydroxy acid is also one (Table 1). The rate constant varies linearly with acidity at constant ionic strength (Table 2).

The rate constants for the oxidation of mandelic acid and  $\alpha$ -deuteriomandelic acid, at 25°, are  $10^3 k =$

Table 1. Dependence of the reaction rate on the substrate concentration

[KMnO <sub>4</sub> ] 0.001 M	[H <sup>+</sup> ] 1.0 M		Temp. 25°C		
10 <sup>2</sup> [M.A.] M	1.0	2.0	4.0	6.0	8.0
10 <sup>4</sup> k <sub>1</sub> s <sup>-1</sup>	1.10	2.23	4.50	6.60	8.72

Table 2. Dependence of the reaction rate on acidity

[KMnO <sub>4</sub> ] 0.001 M	[M.A.] 0.02 M		Temp 25°			
			$\mu = 2.0$			
[H <sup>+</sup> ] M	0.2	0.5	1.0	1.3	1.7	2.0
10 <sup>4</sup> k <sub>1</sub> s <sup>-1</sup>	0.48	1.25	2.41	3.08	4.10	4.75

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11.0 and  $2.93 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , respectively. The kinetic isotope effect,  $k_{\text{H}}/k_{\text{D}} = 3.76$  at  $25^\circ$ .

Mandelic acid was oxidised in 95% deuterium oxide and the rate constant was  $0.012 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , at  $25^\circ$ . The rate constant under similar conditions in ordinary water is  $0.011 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . The solvent isotope effect,  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 0.92$ .

The oxidation of mandelic acid, under an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Thus formation of free radicals in this reaction is unlikely. In control experiments, with the hydroxy acid absent, the concentration of permanganate does not show any change during the period, it is reduced to one-fourth in the presence of mandelic acid.

The rate of oxidation of  $\alpha$ -methoxyphenylacetic acid (0.02 M), which is also of first order with respect to the substrate, the oxidant and hydrogen ions, is  $9.0 \times 10^{-3} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , at  $25^\circ\text{C}$ .

The rate of the oxidation of mandelic acid and nine monosubstituted mandelic acids were determined at different temperatures (Table 3) and activation parameters were evaluated.

Table 3. Effect of temperature on the reaction rate and the activation parameters

Substituents	$10^5 \text{ k l}^2 \text{ mol}^{-2} \text{ s}^{-1}$				$\Delta H^*$ kcal/mol	$-\Delta S^*$ cal/mol/K
	$15^\circ$	$25^\circ$	$30^\circ$	$35^\circ\text{C}$		
H	560	1100	1510	2050	11.3	30.3
<i>p</i> -F	851	1580	2140	2850	10.8	31.3
<i>p</i> -Cl	302	603	840	1160	11.8	29.8
<i>p</i> -Br	240	500	710	990	12.3	28.5
<i>p</i> -Et	2450	4360	5760	7500	9.8	31.9
<i>p</i> -Pr <sup>t</sup>	2240	4000	5290	6920	10.0	32.1
<i>p</i> -OMe	42700	66000	82100	99700	7.5	34.9
<i>m</i> -Br	54.3	121	178	259	13.7	26.6
<i>m</i> -NO <sub>2</sub>	15.5	34.7	53.1	80.0	15.1	24.4
<i>p</i> -NO <sub>2</sub>	6.25	18.5	28.6	43.6	15.5	24.3

The error limits in the values of  $\Delta H^*$  and  $\Delta S^*$  are  $\pm 1.0 \text{ kcal mol}^{-1}$  and  $\pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$  respectively.

#### DISCUSSION

The linear dependence of the reaction rate on acidity may be attributed to the protonation of permanganate anion to give permanganic acid, a more powerful oxidant.<sup>6</sup>

The kinetic isotope effect,  $k_{\text{H}}/k_{\text{D}} = 3.76$ , is very close to the value reported by Littler in the oxidation of cyclohexanol.<sup>7</sup> This confirms that the rate-determining step involves cleavage of C—H bond from the carbon bearing the functional groups. Bakore *et al.*,<sup>2</sup> on the other hand suggested that the rate-determining step in the oxidation of mandelic acid by acid permanganate involves decarboxylation producing a free radical. The absence of induced polymerisation of acrylonitrile makes this proposition highly unlikely. Under their reaction conditions, the reactive species is likely

to be Mn(III), which is known to attack  $\alpha$ -hydroxy acids at the carboxyl group.<sup>3,4</sup>

The activation enthalpies and entropies of the ten compounds are linearly related ( $r = 0.979$ ). The correlation was tested and found genuine by applying Exner's criterion.<sup>8</sup> The isokinetic temperature, obtained from the slope of  $\Delta H^*$  and  $\Delta S^*$  plot is  $710 \pm 54 \text{ K}$ . Current views do not attach much physical significance to isokinetic temperature,<sup>9</sup> though a linear correlation is usually a necessary condition for the validity of the Hammett equation.

No systematic study on the effect of substituents on the oxidation of  $\alpha$ -hydroxy acids by acid permanganate has been reported. The rates of the oxidation of the ten mandelic acids correlate well with the  $\sigma^+$  values ( $r = 0.996$ ). The correlation with  $\sigma$  values was poor. The reaction constant  $\rho^+ = -2.23 \pm 0.07$  at  $25^\circ\text{C}$ . The magnitude of the reaction constant decreases with temperature as is expected (Table 4). The negative value of reaction constant points to an electron-deficient carbon centre in the transition state.

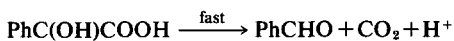
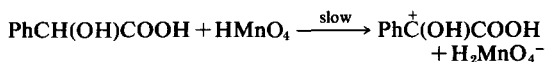
Table 4. Reaction constants at different temperatures and the correlation coefficient

Temp K	288	298	308
$-\rho^+$	$2.40 \pm 0.10$	$2.23 \pm 0.07$	$2.12 \pm 0.05$
$r$	0.989	0.996	0.998

Wiberg and Stewart<sup>10</sup> have suggested an initial formation of a permanganate ester in the permanganate oxidation of aromatic aldehydes, under basic conditions. However, ester formation is unlikely in the present reaction because of the almost equal ease of the oxidation of mandelic acid and its methyl ether. In chromic acid oxidation, where a chromate ester is initially formed, diisopropyl ether is oxidised at only one fifteenth-hundredth the rate of isopropyl alcohol.<sup>11</sup> The large negative reaction constant can thus arise only out of the differential effects of the substituents

in the rate-determining step. The correlation with  $\sigma^+$  values together with the substantial deuterium isotope effect suggest a considerable carbonium ion character in the transition state.

The above results supports a mechanism involving transfer of a hydride ion from the hydroxy acid to the oxidant. The synchronous removal of the hydroxylic proton is unlikely in view of the absence of any solvent isotope effect. The following mechanism may then be proposed.



#### EXPERIMENTAL

**Materials.** Halogeno-, alkyl, and *p*-methoxy-mandelic acids were prepared from the corresponding benzaldehydes by cyanohydrin formation followed by acid hydrolysis.<sup>12</sup> Mandelic and nitromandelic acids were commercial products. The acids were purified by repeated crystallisation and their m.p. checked with the reported values.<sup>13</sup>

$\alpha$ -Deuteriomandelic acid was prepared by the method of Kemp and Waters.<sup>3</sup> The isotopic purity, as ascertained by its NMR spectrum, was 96.7%.

$\alpha$ -Methoxyphenylacetic acid was prepared by the method of Reeve and Christoffel.<sup>14</sup>

All reagents were of analytical grade.

**Kinetic measurements.** The reactions were carried out under pseudo-first-order conditions by keeping a large excess of the hydroxy acid ( $\times 10$ ) over permanganate. The reactions were followed spectrophotometrically at 532 nm and the first order rate constant,  $k_1$ , were evaluated from the plots of  $\log[\text{Oxidant}]$  against time. The

specific rate constant,  $k$ , is obtained from the relation  $k = k_1/[\text{H}^+]$  [Hydroxy Acid]. The rates were obtained from at least duplicate runs and their reproducibility was within  $\pm 5\%$ .

The usual concentration of the reactants in the reaction mixtures were hydroxy acid, 0.01–0.08 M, permanganate ca. 0.001 M, sodium fluoride 0.02 M and perchloric acid 0.2–1.0 M.

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#### REFERENCES

- <sup>1</sup>G. V. Bakore and R. Shanker, *Indian J. Chem.* **1**, 108, 286 (1963)
- <sup>2</sup>G. V. Bakore, R. Shanker and U. Goyal, *Ibid.*, **1**, 331 (1963)
- <sup>3</sup>T. J. Kemp and W. A. Waters, *J. Chem. Soc.* 1194 (1964)
- <sup>4</sup>A. Y. Drummond and W. A. Waters, *Ibid.*, 2836 (1953)
- <sup>5</sup>R. N. Barter and J. S. Littler, *Ibid.* (B), 205 (1967)
- <sup>6</sup>P. Nath and K. K. Banerji, *Bull. Chem. Soc. Japan* **42**, 2038 (1969)
- <sup>7</sup>J. S. Littler, *J. Chem. Soc.* 2190 (1962)
- <sup>8</sup>O. Exner, *Coll. Czech. Chem. Comm.* **29**, 1094 (1964)
- <sup>9</sup>J. E. Leffler, *J. Org. Chem.* **31**, 533 (1966)
- <sup>10</sup>K. B. Wiberg and R. Stewart, *J. Am. Chem. Soc.* **77**, 1786 (1955)
- <sup>11</sup>R. Brownell, A. Leo, Y. W. Chang and F. H. Westheimer, *Ibid.*, **82**, 406 (1960)
- <sup>12</sup>A. I. Vogel, *A Test Book of Practical Organic Chemistry* p. 774. Longmans Green, London (1956)
- <sup>13</sup>J. J. Klingenberg, J. P. Thole and R. D. Lingg, *J. Chem. Eng. Data* **11**, 94 (1966), and refs cited
- <sup>14</sup>W. Reeve and I. Christoffel, *J. Am. Chem. Soc.* **72**, 1480 (1950)