Oxidation of Mandelic Acid by Os(VIII)

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Mandelic Acid, Osmium(VIII)

In the reaction between mandelic acid and Os(VIII), the rate of Os(VIII) disappearance was found to be proportional to the concentration of mandelate ion and Os(VIII). At low and high hydroxyl ion concentration the rate shows second and zero order dependence respectively. The reaction was studied at different temperatures and various activation parameters ΔE , PZ , ΔS^* etc. were evaluated.

Kinetic studies on the oxidation of a variety of substances both organic and inorganic [1, 4–7] reveal extensive use of Os(VIII) as catalyst. Little evidence, however, is available on the vigour of Os(VIII) as an independent oxidant [3, 8, 9]. Therefore, oxidation of glycolic, lactic, mandelic, malic acids by Os(VIII) was investigated and the present report deals with the oxidation of mandelic acid by Os(VIII).

Experimental

OsO₄ (Johnson & Mathey) and mandelic acid Riedle A. R. were used. All other reagents were of A. R. grade. The reaction was started by mixing the alkaline solution of OsO₄ and mandelic acid, maintained at constant temperature in a thermostat, regulated by electronic relay with an accuracy of ± 0.1 °C. The kinetics of the reactions were followed colorimetrically using Klett-Summerson photoelectric colorimeter and employing a blue light filter No. 42.

Results

The results summarised in Table I–III show dependence of the rate on [mandelate], [Os(VIII)], [OH[−]]. Increase in ionic strength as a result of addition of KNO₃ or K₂SO₄ increases the rate of oxidation (Table IV). Addition of sulphuric acid at constant [SO₄^{2−}] decreases the rate of oxidation, but further addition of acid does not change the rate significantly.

Stoichiometry

Number of reaction mixtures containing excess of Os(VIII) were thermostated at 35 °C for 1–4 h. A known volume was withdrawn from each reaction

Table I. Effect of varying the oxidant concentration.

[mandelate] = 5.0×10^{-3} M temp. 35 °C [OH [−]] = .012 M	
[OsO ₄] $\times 10^4$ M	K ₁ $\times 10^4$ sec ^{−1}
5.0	7.1
4.0	7.0
3.0	6.9
2.0	6.8
1.0	6.8

Table II. Effect of varying the reductant concentration.

[OsO ₄] = 5.0×10^{-4} M temp. 35 °C. [OH [−]] = .012 M		
[mandelate] $\times 10^3$ M	K ₁ $\times 10^4$ sec ^{−1}	$\frac{K_1}{[\text{mandelate}]}$ l · mole ^{−1} sec ^{−1}
5.0	7.1	0.14
4.0	5.2	0.13
3.0	4.5	0.15
2.0	2.8	0.14
1.0	1.5	0.15

Table III. Effect of varying the alkali concentration.

[OsO ₄] = 5.0×10^{-4} M [mandelate] = 5.0×10^{-3} temp. 35 °C. $\mu = 1.5$	
[OH [−]] $\times 10^2$ M	K ₁ $\times 10^3$ sec ^{−1}
1.2	0.71
1.6	1.20
2.0	2.0
3.0	4.30
4.0	4.28
6.0	4.31
20.0	4.30

mixture and analysed colorimetrically for un-consumed Os(VIII). Two moles of Os(VIII) are required for each mole of reductant. Benzoic acid

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Table IV. Effect of varying the ionic strength.

[mandelate] = 5.0×10^{-3} M [OsO ₄] = 5.0×10^{-4} M temp. 35 °C [OH ⁻] = .012 M		
μ M	$K_1 \times 10^4 \text{ sec}^{-1}$ KNO ₃	$K_2 \text{SO}_4$
1.23	—	8.30
1.14	—	8.11
1.05	—	7.86
0.96	—	7.63
0.86	7.70	—
0.83	7.42	—
0.80	7.28	—
0.77	7.12	—
0.74	6.89	—
0.71	6.78	—

Table V. Effect of varying H⁺ concentration.

[mandelate] = 5.0×10^{-3} M [OsO ₄] = 5.0×10^{-4} M [OH ⁻] = .012 M [SO ₄ ²⁻] = .5 M temp. 35 °C		
[H ⁺] × M	$K_1 \times 10^4 \text{ sec}^{-1}$	
0.1	7.3	
0.08	7.4	
0.06	7.6	
0.04	7.9	
0.02	8.0	

was identified to be the main reaction product in the samples after complete reduction of Os(VIII).

Discussion

The possibility of a free radical mechanism is excluded on the grounds that the reaction involves a two electron change, does not show an induction period and the rate of reaction is unaffected by addition of acrylonitrile. The alkali dependence of rate of reaction indicates that mandelate ions are the entities oxidised. In view of the fact that OsO₄ in alkaline solution coordinates with OH⁻ and occurs as osmate ion [2], it is suggested that oxidation of mandelic acid involves formation of ester intermediate and its subsequent rapid cleavage into products. The [OsO₄OH]³⁻ species is hydrated to

[OsO₂(OH)₄]²⁻, this is fully supported by the fact [2] that Os(VIII) conclusively exists as [OsO₂(OH)₄]²⁻ species.

Applying steady state approximation, the rate of disappearance of Os(VIII) is given by:

$$-\frac{d[\text{Os(VIII)}]}{dt} = K_2 [\text{mandelate}] [\text{Os(VIII)}]$$

This explains first order dependence of rate on mandelate and [Os(VIII)]. According to equation (1) the concentration of active oxidant species [OsO₄(OH)₂]²⁻ would depend on [OH⁻]² upto a limit, beyond that whole of OsO₄ will exist as [OsO₄(OH)₂]²⁻, this explains second and zero-order dependence of the rate on [OH⁻] at low and high hydroxyl ion concentration respectively.

The activation parameters ΔE , PZ , ΔS^* were evaluated and found to be 5.6 kcal, $2.6 \times 10^3 \text{ sec}^{-1}$ and -43.7 E. U. respectively. More negative value of ΔS^* and positive salt effect lend further support to the rate determining step.

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