Kinetics of uncatalysed and catalysed oxidation reactions of α-hydroxy acids by periodate

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Abstract. Kinetics of oxidation of mandelic acid by periodate in presence and absence of OsO_4 at pH 10 are reported. Second order dependence is observed in mandelic acid even in the uncatalysed reaction at pH 10 as against unit dependence in glycolic and lactic acids in the oxidations catalysed by OsO_4 in alkaline medium. The dependence on OsO_4 is unity for the oxidation of mandelic, glycolic and lactic acids. There is zero order dependence in periodate in all the OsO_4 catalysed reactions. The oxidation of mandelic acid has also been studied in acid medium. Unit dependence each in the substrate and periodate has been observed in acid medium. All these are rationalised and a suitable mechanism is postulated.

1. Introduction

Radhakrishnamurti *et al* (1976) have reported the oxidation of phenol and substituted phenols by periodate. The kinetics of oxidation of mandelic acid and bromo mandelate ion in alkaline media by $K_3Fe(CN)_6$, catalysed by OsO_4 has been reported by Soni and Meghani (1972) and Singh *et al* (1975). These workers postulated a rate determining decomposition of Os(VIII)-acid ion complex. In the present paper the kinetics of oxidation of α-hydroxy acids are reported i.e. mandelic acid, glycolic acid and lactic acid by periodate with a view to correlating structure and reactivity and to postulate a plausible mechanism for these oxidation processes. As the oxidation of mandelic acid is very fast in aqueous alkali, it was carried out at pH 8·9 to 11·7, in the presence and absence of OsO_4, so that measurable rates could be obtained. For the purpose of comparison the oxidation of mandelic acid has also been studied in acid medium. The investigation has been extended to the oxidation of glycolic and lactic acids in alkaline medium for a comparative study.

2. Materials and methods

All the chemicals used are of BDH(AR) grade. The estimation has been done at pH 7 by a standard iodometric method for computing the periodate consumption at any instant of time during a kinetic run.

2.1. *Product analysis*

In the oxidation of mandelic acid the product is benzaldehyde as identified by its 2:4 dinitro phenyl hydrazone. In the presence of Os (VIII) at pH 10 a separate run was carried out and it was found that the oxidation of benzaldehyde is extremely sluggish as compared to the oxidation of mandelic acid under the same conditions. Hence the main product is the benzaldehyde under the experimental conditions used.

3. Results and discussion

3.1. *Oxidation of mandelic acid at pH 10*

The oxidation of mandelic acid by periodate at pH 10 has been studied and it is found that the order with respect to oxidant is one as the plots of log $(a-x)$ vs time are perfectly linear and order with respect to substrate is two as the plots of log k vs log $[S]$ showed a slope of two. The first order rate constants at varying substrate concentrations are given in table 1.

The oxidation has been studied at various pH and the first order rate constants are given in table 2.

This indicates that the reaction has first order dependence on pH in the range studied, as seen by the unit slope of the log k vs pH plot, hence the equilibrium is

$$[OsO_4(OH)(H_2O)]^{1-} \cdot OH^- \quad \rightleftharpoons \quad [OsO_4(OH)_2]^{2-} + H_2O$$

3.2. *Oxidation of mandelic acid catalysed by OsO$_4$ at pH 10*

The oxidation of mandelic acid by periodate catalysed by OsO$_4$ has been studied and it is found that the orders with respect to oxidant is zero, to Os(VIII) is one and to substrate is two.

Table 1. Dependence on [substrate] in the oxidation of mandelic acid by periodate at pH 10.

[Periodate] $= 1 \cdot 5 \times 10^{-3}$M   Temp: 60°C

10^3 [substrate]	$10^2 k_1$ min^{-1}
2·53	0·30
5·51	2·72
10·14	9·14

Table 2. Dependence on pH in the oxidation of mandelic acid by periodate [Periodate] $= 1 \cdot 5 \times 10^{-3}$ M   [Substrate] $= 5 \cdot 0 \times 10^{-3}$M   Temp: 60°C

pH	$10^2 k_1$ min^{-1}
8·9	0·316
10·0	2·721
11·7	62·12

The plots of IO_4^- vs time are linear thereby showing the typical zero order rates for the oxidation of mandelic acid in the presence of OsO_4, the rate constants are computed from the initial percentages of the reactions. It is obvious from these plots that the deviations appear at 65–70% of the reaction. The data in table 3 show that the values of k_0 ($-dc/dt$) are fairly constant for different periodate concentrations. This confirms the zero order dependence of the reaction rate with respect to periodate. The values of $-dc/dt$ have been calculated from the initial slopes of the curves obtained by plotting the unreacted periodate against time to avoid possible errors involved due to intervention of the oxidation products.

Os(VIII) catalyses the reaction considerably, indicating that Os(VIII) has a remarkable influence in the oxidation of mandelic acid by periodate. It has been reported that in alkaline medium OsO_4 exists as the octahedral complexes (trans-form) of the types: (Mayell 1968; Griffith 1965; Cotton and Wilkinson 1966)

$$[OsO_4(OH)(H_2O)]^{1-} \text{ and } [OsO_4(OH)_2]^{2-}.$$
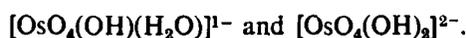
In high alkali conditions OsO_4 exists as $[OsO_4(OH)_2]^{2-}$. As stated earlier in low alkali conditions the equilibria between OH^- and $[OsO_4(OH)(H_2O)]^{1-}$ exist as follows

$$[OsO_4)(OH)(H_2O)]^{1-} + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} + H_2O.$$
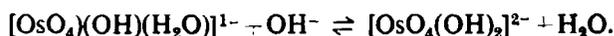
With increase in the amount of Os(VIII) the reaction rate is enhanced. The plot of log k_0 vs log $[OsO_4]$ is linear with unit slope indicating the first order dependence on the concentration of the catalyst. Such unit dependence on OsO_4 in the oxidation reactions has been earlier reported by Singh *et al* 1975 in their studies. The zero order rate constants are given in table 4.

Table 3. Dependence on [oxidant] in the oxidation of mandelic acid by periodate in presence of Os(VIII) at pH 10.

[Substrate] $= 5 \cdot 0 \times 10^{-3} M$ [Os(VIII)] $= 3 \cdot 9 \times 10^{-8}$ Temp: 60°C

10^3 [oxidant]	$10^5 k_0$ mole min^{-1}
1·42	4·7
2·58	4·75
4·43	4·00

Table 4. Dependence on $[OsO_4]$ in the catalysed oxidation reaction of mandelic acid by periodate at pH 10.

[Periodate] $= 1 \cdot 5 \times 10^{-3}$ M   [Substrate] $= 5 \times 10^{-3}$ M   Temp: 60° C

$[OsO_4] \ 10^8$	$10^5 k_0$ mole min^{-1}
1·91	2·45
3·90	4·68
5·85	5·45
7·80	6·64

The zero order rate constants at constant Os(VIII) concentration with varying substrate concentration are given in table 5.   The plot of log k_0 vs log [S] is linear with a slope two, indicating second order dependence on the substrate.

3.3. *Oxidation of mandelic acid in acid medium*

The oxidation of mandelic acid by periodate has been studied at (0·01, 0·02 and 0·03 M $HClO_4$) in aqueous and aqueous acetic acid medium. It is found that the order with respect to oxidant is one, with respect to substrate is one and independent with respect to H^+.

The first order rate constants obtained at different acidities in perchloric acid medium are given in table 6.   This indicates that this oxidation process is independent of acidity under our experimental conditions.

The effect of solvent composition on the reaction rate has been studied by varying the amount of acetic acid.   It is observed that the reaction is independent of the composition of the solvent.   Such independence of reaction rates to added acetic acid has been observed by other workers (Benerjee 1973).

Table 5. Dependence on [substrate] in presence of OsO_4 in the oxidation reaction of mandelic acid by periodate at pH 10.

[Periodate] = $1·5 \times 10^{-3}$ M   [Os(VIII)] = 3.9×10^{-6} M   Temp: 60° C

10^3 [substrate]	$10^6 \, k_0$ mole min^{-1}
1·61	2·53
2·63	6·45
5·02	46·86
7·53	57·50

Table 6. Effect of acid in the oxidation of mandelic acid by periodate.

[Periodate] = $1·5 \times 10^{-3}$ M   [Substrate] = $5·0 \times 10^{-3}$ M   Temp: 60° C

[$HClO_4$] M	$10^3 \, k_1$ min^{-1}	k_2 1. mole^{-1} min^{-1}
0·01	2·85	0·56
0·02	2·83	0·54
0·03	2·61	0·51

Table 7. Effect of solvent in the oxidation of mandelic acid by periodate.

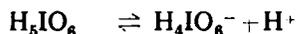[Periodate] = $1·5 \times 10^{-3}$ M   [substrate] = $5·0 \times 10^{-3}$M   [$HClO_4$] = 0.01 M
Aqueous HOAc   Temp: 60° C

%HOAc	$10^3 \, k_1$ min^{-1}	k_2 1. mole^{-1} min^{-1}
0	2·85	0·56
20	2·57	0·49
30	2·52	0·51

The effect of change of concentration of substrate in perchloric acid medium has been determined. The plot of log k_1 vs log $[S]$ is linear, with unit slope indicating a first order dependence on the substrate concentration.

3.4. *Nature of the periodate species*

Periodic acid exists in the following equilibria in alkaline medium:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{-2} + H^+$$

$$H_3IO_6^{-2} \rightleftharpoons H_2IO_6^{-3} + H^-$$

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^-$$
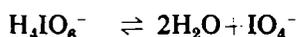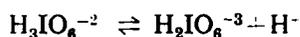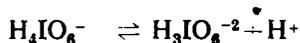
At pH 10 it is likely that the $H_3IO_6^{2-}$ and IO_4^- are both the active species. For convenience only IO_4^- is presented in the mechanism postulated (Dryhurst 1970).

3.5. *Comparative study of oxidation of glycolic and lactic acids in alkaline medium*

For the purpose of comparison the oxidation of glycolic and lactic acids by periodate in alkaline medium has been investigated. In case of glycolic and lactic acids, it was prudent to take the initial rates, as the aldehydes formed also get oxidised complicating the evaluation of the rate constants of each oxidation. Hence the initial rates computed represent the oxidation of the substrate to the aldehyde stage. The zero order rate constants with respect to oxidant, at various concentrations of oxidant at various concentrations of substrate, at various concentrations of alkali and at various concentrations of Os(VIII) are given in tables 9 to 12. This clearly shows that these oxidation processes are first order with respect to substrate, first order with respect to Os(VIII), zero order with respect to oxidant and independent with respect to the concentrations of alkali.

Table 8. Dependence on [substrate] in presence of perchloric acid in the oxidation of mandelic acid by periodate.
[Periodate] $=1.5 \times 10^{-3}$ M   [HClO$_4$] $=0.02$ M   Temp: 60° C

10^3 [substrate] M	$10^3 k_1$ min^{-1}	k_2 1. mole^{-1} min^{-1}
5·21	2·83	0·55
7·31	3·69	0·51
9·76	4·83	0·50
12·86	6·90	0·53

Table 9. Dependence on [OsO$_4$] in the oxidation of glycolic and lactic acids by periodate at constant alkali concentration.
[Periodate] $=1.5 \times 10^{-3}$M   [substrate] $=5.0 \times 10^{-3}$M   [NaOH] $=0.022$ M
Temp: 60°C

[Os(VIII)] $\times 10^6$	$10^6 k_0$ mole min^{-1}	
	Glycolic acid	Lactic acid
7·8	1·40	2·55
11·7	2·12	4·40
15·6	3·00	6·01

Table 10. Dependence on alkali concentration in presence of OsO_4 in the oxidation of glycolic and lactic acids by periodate.

[Periodate] $= 1 \cdot 5 \cdot 10^{-3}$ M   [substrate] $= 5 \cdot 0 \times 10^{-3}$ M
[Os(VIII)] $= 7 \cdot 8 \times 10^{-6}$ M   Temp: 60° C

10^2 [NaOH] M	$10^6 k_0$ mole min^{-1}	
	Glycolic acid	Lactic acid
2·20	1·39	2·55
3·40	—	2·75
4·50	1·22	2·82
5·88	1·30	—
8·00	1·72	—

Table 11. Dependence on [substrate] in absence and presence of OsO_4 in the oxidation of glycolic acid by periodate.

[Periodate] $= 1 \cdot 5 \times 10^{-3}$ M   [NaOH] $= 0 \cdot 022$ M   Temp: 60° C

10^3 [substrate]	[Os(VIII)] $=0$ $10^2 k_2$ l.mole^{-1} min^{-1}	[Os(VIII)] $=7.8 \times 10^{-6}$ M 10^3 [substrate]	$10^6 \times k_0$ mole min^{-1}
5·41	4·03	4·85	0·9
10·69	4·93	7·43	1·50
18·16	4·58	12·72	2·94

Table 12. Dependence on [oxidant] in the catalysed oxidation reaction of glycolic acid by periodate.

[Periodate] $= 1 \cdot 5 \times 10^{-3}$M [substrate] $= 5 \cdot 0 \times 10^{-3}$M   [Os(VIII)] $= 7 \cdot 8 \times 10^{-6}$

NaOH $= 0 \cdot 045$ M   Temp: 60° C

10^3 [oxidant]	$10^6 k_0$ mole min^{-1}
0·92	1·31
1·29	1·20
1·61	1·53
2·93	1·59
4·64	1·63

The values in table 10 show that the reaction is independent of the alkali concentration. Hence the species $[OsO_4(OH)_2]^{2-}$ is predominant in these reactions.

The order with respect to substrate in these oxidations is one as against two that is observed in the case of mandelic acid. Obviously the complex should be between acid anion and OsO_4, which breaks down in a rate determining step yielding an aldehyde in the first stage which rapidly yields the corresponding acid.

In the absence of catalyst the acid complexes with HIO_4 and the complex rapidly breaks down to the aldehyde which subsequently yields a corresponding acid.

3.6. *Structure and reactivity*

The reactivity order is mandelic acid > lactic acid > glycolic acid. In mandelic acid the conjugative ability of the phenyl group to stabilise the transition state leading to

oxidative decarboxylation is the maximum and hence highest reactivity is observed. The next in order of reactivity is lactic acid which also reacts faster compared to glycolic acid due to the methyl group participating in a hyperconjugative manner.

3.7. *Mechanism of oxidation of α-hydroxy acids in alkaline medium*

The rate expression of Os(VIII) catalysed reaction of mandelic acid at pH 10 is

$$V = k \text{ [Mandelic acid]}^2 \text{ [Os(VIII)]}^1 \text{ [HIO}_4]^0.$$

In conformity with the results the reaction envisages a complex with OsO_4 and 2 mols of mandelate anions formed reversibly from 2 mols of mandelic acid which breaks down in a slow step leading to benzaldehyde and Os(IV). The Os(IV) is rapidly converted to Os(VIII) and IO_2^-. The α C–H bond fission occurs in the rate determining step. The whole process is oxidative decarboxylation with a total 4 electron change leading to Os(IV) as simultaneously 2 mols of mandelic acid ions are involved (chart 1)
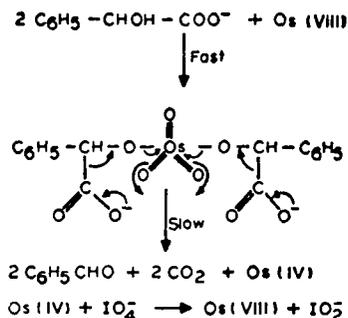

Chart 1

$$2 \text{ C}_6\text{H}_5 \text{ CHOH COOH} \rightleftharpoons 2 \text{ C}_6\text{H}_5 \text{ CHOH COO}^-$$

$$2 \text{ C}_6\text{H}_5 \text{ CHOH COO}^- + [\text{OsO}_4 \text{ (OH)}_2]^{2-} \xrightarrow{\text{fast}} \text{Complex}$$

$$\text{Complex} \xrightarrow{\text{slow}} 2 \text{ Benzaldehyde} + 2\text{CO}_2 + \text{Os(IV)}$$

$$\text{Os(IV)} + \text{IO}_4^- \longrightarrow \text{Os(VIII)} + \text{IO}_2^-.$$
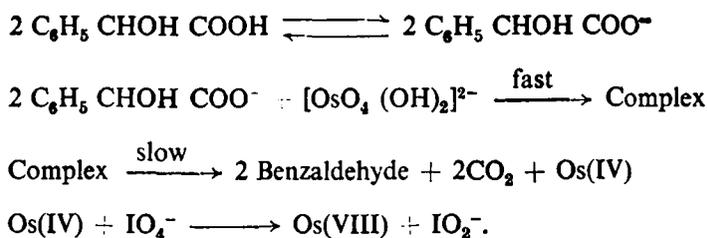
In the uncatalysed reactions the oxidative decarboxylation occurs during the breakdown of the complex between the IO_4^- and 2 mandelic acid ions, leading to the same products (chart 2).

In acid medium the sequence of the reaction envisages a molecule of mandelic acid and HIO_4 forming a complex which breaks down leading to benzaldehyde and IO_3^- (chart 3). Such a sequence of reactions for the oxidation of mandelic acid in H_2SO_4 has been postulated earlier (Paul and Pradhan 1973) and it appears that the same holds good in the present study in HClO medium also.

For glycolic and lactic acids the same mechanism holds good, except the fact, that one molecule is involved in the complexation step. The complex breaks down in a

$$2\ C_6H_5 CHOH - COO^- + IO_4^-$$

↓ Fast

$$C_6H_5 - CH - O - I - O - CH - C_6H_5$$

↓ Slow

$$2\ C_6H_5 CHO + 2CO_2 + IO_2^- + 2H_2O$$

Chart 2

$$C_6H_5 CHOH - COOH + IO_4^- \rightleftharpoons C_6H_5 - C - O - I$$

Chart 3

slow step giving the initial product aldehyde which is rapidly oxidised to the corresponding carboxylic acids.

Acknowledgement

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