Kinetics and mechanism of oxidation of 1,3-dihydroxybenzene by trioxoiodate(V) ion in aqueous perchloric acid medium

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The kinetics of oxidation of 1, 3-dihydroxybenzene by trioxoiodate(V) ion in aqueous perchloric acid medium has been studied at 0.20≤[H⁺]≤2.0 mol dm⁻³ under pseudo-first order conditions of an excess [benzenediol] at T=1.10 mol dm⁻³ (NaClO₄). The reaction obeys the rate expression.

\[ \frac{d[IO₃]}{dt} = \left( k_1 + k_2[H^+] \right) [IO₃] [H₂Q] \]

The reaction has been rationalised on the basis of the outer-sphere electron transfer mechanism.

Oxidation of phenols by metal complexes leading to the production of quinones has generated great interest of recent. Most of these studies have focussed on the 1, 2- and 1', 4-dihydroxybenzenes. These reactions have from investigations shown a lot of complexities both in terms of acid dependencies and the products. For example the tetravalent rhodium (VII) and trioxotungstate(V) ions oxidation of catechol (1, 2-dihydroxybenzene) was studied by Iyun, where various acid dependencies as well as free radical intermediates were reported.

Oxidation of 1, 3-dihydroxybenzene has not received much attention when compared to the 1, 2- and 1', 4-isomers. However, its reaction with oxobridged ruthenium dimer \([\text{bpy}_2\text{Ru}^\text{II}]=\text{O}^\text{v}^\text{•}\) has been studied. Here a 2:1 stoichiometry and an inverse acid dependence were reported. The rate of reaction increased with increase in the ionic strength of the medium.

We hereby report the kinetics and mechanism of oxidation of 1, 3-dihydroxybenzene by trioxoiodate (V) ion. This is with a view to throwing more light on the mechanistic pathway of 1, 3-benzenediol electron transfer reactions. Choice of trioxoiodate(V) ion as the oxidant derives from our desire to gain indepth knowledge of the reactions of oxyhalogen anions and the various complexities that attend them. Also since polyphenols are the major components of tannins (a major component of several plants), we hope this study will complement the much needed kinetic information relating to the processes of oxidation of vegetable tannins.²

Experimental

The purity of resorcinol (1, 3-dihydroxybenzene, BDH Analar grade) hereafter designated as H₂Q was ascertained by its m.p. (109-110°C), Potassium iodate (BDH, Analar grade) was standardised iodimetrically before use. NaClO₄ was standardised gravimetrically and was used to maintain a constant ionic strength. All other reagents were of Analar grade and were used without further purification unless otherwise stated. Stock solutions of reagents were prepared with doubly distilled water.

Changes in absorbances of solutions were monitored on Milton Roy Spectronic 21 spectrophotometer. Having ascertained that neither resorcinol nor IO₃⁻ or any of the products of the reaction absorb significantly at 480 nm, kinetic measurements were conducted at this wavelength which is the λₘₐₓ of aqueous iodine. Kinetic measurements reflected increase in absorbance of the reaction mixture as iodine is being generated in the course of the reaction. All kinetic runs were carried out under pseudo-first order conditions with [H₂Q] in at least 20-fold excess over [IO₃⁻] while ionic strength was maintained constant for each particular set of reactions using NaClO₄ unless otherwise stated. Reported rate constants are the mean of replicate runs.

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. [IO₃⁻] was kept constant at 2.5×10⁻⁴ mol dm⁻³ and [H₂Q] varied from 0.5×10⁻⁴ to 1.0×10⁻¹ mol dm⁻³ at [H⁺]=1.0 mol dm⁻³, I=1.10 mol dm⁻³ (NaClO₄) and T=30.0±0.1°C. A point of inflexion on a curve of absorbance (A) versus mole ratio plot gave the mole ratio corresponding to the stoichiometry.
Plots of log \((A_o-A_t)/A_t\) against time, \(t\), (where \(A_o\) and \(A_t\) are the absorbances at the end of the reaction and at time, \(t\) respectively) were linear for about 90% of reaction. Pseudo-first order rate constants, \(k_{obs}\), were determined as the slopes of above plots as given by Eq. (1).

\[
(A_o-A_t)/A_t = \left(\frac{A_o-A_0}{A_0}\right) e^{k_{obs} t}
\]

\(A_0\) is the absorbance at the beginning of the reaction. Second order rate constants, \(k_2\), were obtained as ratios of \(k_{obs}\) to \([H_2Q]\). Rate constants of replicate runs agreed with in \(\pm 1.3\%\).

**Results and discussion**

**Stoichiometry**

Stoichiometric studies indicated that for every 2.5 moles of \([H_2Q]\) oxidised, one mole of \([IO_3^-]\) is consumed. This gives the overall equation of the reaction to be

\[
5H_2Q + 2IO_3^- + 2H^+ \rightarrow 5Q + H_2O + 6H_2O
\]

This is consistent with what has been reported for similar reactions\(^{11}\). In the reaction of 1, 2-dihydroxybenzene with \(BrO_3^-\), a 5:2 stoichiometry was established.

**Product analysis**

Resorcinol (0.5 mol) and \(KIO_3\) (0.2 mol) were mixed together in a conical flask and the reaction mixture maintained at \([H^+] = 1.0\) mol dm\(^{-3}\) and \(I = 1.10\) mol dm\(^{-3}\) (NaClO\(_4\)) was left in a dark cupboard overnight. A dirty yellow solid separated which was filtered, washed, recrystallized in glacial acetic acid and dried. The product had a melting point of 120-121°C. On reacting a little quantity of the product with 2, 4-dinitrophenylhydrazine, red crystals were formed which indicated the formation of hydrazone and confirmed the presence of carbonyl group in the other reactant. The hydrazone was recrystallized from glacial acetic acid and dried. It gave a melting point of 185-187°C. The formation of hydrazone when reacted with 2,4-dinitrophenylhydrazine,\(^{2-6}\) showed the product to be a quinone. Other workers\(^{3-4}\) also identified \(Q\) [cf Eq. (2)] to be a quinone in the oxidation of 1, 3-dihydroxybenzene by metal ions.

**Test for free radicals**

Addition of acrylamide to the partially oxidised reaction mixtures of \(IO_3^-\) and \(H_2Q\) at \([H^+] = 1.0\) mol dm\(^{-3}\) and \(I = 1.10\) mol dm\(^{-3}\) showed little gel formation on addition of excess methanol to the reaction mixture.

| Table 1—Second order rate constants for the reaction of 1, 3-dihydroxybenzene, \((H_2Q)\) and trioxoiodate \((V)\) \((IO_3^-)\) at
| \[T=30.0 \pm 0.1\degree C\] and \([IO_3^-] = 1 \times 10^{-5} \text{ mol dm}^{-3}\] at \(\lambda_{max}=480\) nm
| \(|10^6[H_2Q]|, M| 10^6[H^+], M| M(\text{NaClO}_4)| k_2 \text{ M}^{-1}\text{s}^{-1}\)
| 5.0 | 100 | 1.10 | 0.25 |
| 1.0 | 100 | 1.10 | 0.25 |
| 7.0 | 100 | 1.10 | 0.27 |
| 8.0 | 100 | 1.10 | 0.25 |
| 9.0 | 100 | 1.10 | 0.24 |
| 10.0 | 100 | 1.10 | 0.26 |
| 8.0 | 20 | 1.10 | 0.15 |
| 8.0 | 50 | 1.10 | 0.19 |
| 8.0 | 100 | 2.0 | 0.21 |
| 8.0 | 150 | 2.0 | 0.26 |
| 8.0 | 200 | 3.0 | 0.39 |
| 8.0 | 100 | 0.99 | 0.23 |
| 8.0 | 100 | 1.19 | 0.24 |
| 8.0 | 100 | 1.29 | 0.25 |
| 8.0 | 100 | 1.59 | 0.25 |

Therefore, free radicals may be produced as intermediates in the reaction Lyun\(^{11}\), and other workers\(^{18-19}\) pointed out that in the reaction of benzenediol with \(BrO_3^-\) and \(MnO_4^-\), and other metal ions, free radicals are produced as intermediates.

**Kinetics**

Plots of log \((A_o-A_t)/A_t\) versus time were linear to about 90% of reaction. This suggests that there is no product inhibition and that the reaction is first order in \([IO_3^-]\). Plot of log \(k_{obs}\) versus \([H_2Q]\) was linear with a gradient of 1.15 which is indicative of first order in \([H_2Q]\).

In the range \(0.20\leq[H^+]\leq 2.0 \text{ mol dm}^{-3}\), \(k_2\) increased from 0.15-0.39 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) as shown in Table 1. A plot of \(k_2\) versus \([H^+]\) was linear with a slope of 0.15 and an intercept of 0.13 dm\(^3\) mol\(^{-1}\) s\(^{-1}\). Hence the acid dependence of the rate constant for the reaction is given by

\[
k_2 = 0.13 + 0.15[H^+]\]

and the rate of reaction as

\[
d[IO_3^-]/dt = (0.13 + 0.15[H^+])[IO_3^-][H_2Q]\]

Increase in rate with increase in \([H^+]\) has been reported for bromation of oxidation of 1, 2-dihydroxybenzene\(^{11}\) and 1, 4-dihydroxybenzene\(^{8}\) but is at variance with oxidation of 1, 3-dihydroxybenzene by \([RuO_2]\)\(^{16}\) where the rate of reaction decreases as \([H^+]\) increases\(^{8}\). Hydrogen ion dependence of the rate of reaction in this study can be rationalised from the fact that iodate ion established an equilibrium in aqueous and acidic solutions as follows\(^{16}\).
\[ H^+ + IO_3^- \rightarrow HIQ_3 \]  

---(5)---

The preprotonated species is more reactive than \( IO_3^- \).

Table 1 shows that the ionic strength of the medium has no effect on the rate of reaction. This is likely to suggest the absence of anion-cation, cation-cation or anion-anion interaction. It supports our suggestion of the main reaction being between undissociated \( HIQ_3 \) and \( IO_3^- \). This is corroborated by the non-dependence of the rate of reaction on dielectric constant, \( D \), of the reaction medium. Also the rate of reaction was unaffected by the addition of any ions. Although the absence of catalysis could be pointing to an inner-sphere mechanism, this might be due to the absence of charge on the reactants in Eq. (7) (refs 15, 16).

From the above data we propose Scheme 1 for this reaction.

\[ IO_3^- + H^+ \xrightarrow{k_1} HIQ_3 \]  

---(6)---

\[ HIO_3 + H_2Q \xrightarrow{k_2} HQ^+ + H_2O + IO_2 \]  

---(7)---

\[ IO_2 + 4H_2Q \xrightarrow{k_4} 4HQ^+ + 2H_2O + I^+ \]  

---(8)---

\[ IO_3^- + H_2Q \xrightarrow{k_5} HQ^+ + IO_2 + OH^- \]  

---(9)---

\[ IO_2 + 4H_2Q \xrightarrow{k_6} 4HQ^+ + 2H_2O + I^+ \]  

---(10)---

\[ OH^- + H_2Q \xrightarrow{k_7} H_2O \]  

---(11)---

\[ H^+ + 5HQ^+ + IO_3^- \xrightarrow{k_8} 5Q + I^+ + 3H_2O \]  

---(12)---

\[ I^+ + I^- \xrightarrow{k_9} I_2 \]  

---(13)---

Scheme 1

Rate = \( k_1[HIO_3][H_2Q] + k_4[IO_3^-][H_2Q] \)  

---(14)---

but \( [HIO_3] = k_1[IO_3^-][H^+] \)  

---(15)---

Substituting Eq. (15) into (14) gives

\[ \text{Rate} = k_2k_1[IO_3^-][H^+][H_2Q] + k_4[IO_3^-][H_2Q] \]

\[ = (k_2k_1[H^+]+k_4)[IO_3^-][H_2Q] \]  

---(16)---

Equation (16) is similar to Eq. (4) with \( k_5k_9 = 0.15M^{-2}s^{-1} \) and \( k_9 = 0.13 M^1s^{-1} \).

As to whether the reaction occurs by inner or outer sphere mechanism, the following points have to be considered: Michaelis-Menten plot \( 1/k_{obs} \) of \( 1/[H_2Q] \) was linear and gave a small negative intercept which is not enough to implicate inner-sphere mechanism. This suggests that intermediate complex formation prior to electron transfer step is very unlikely in this reaction. The absence of catalysis on addition of \( CH_3COO^- \) and \( NO_3^- \) is not likely to be the result of formation of intermediate complex since the rate determining step in the reaction involves neutral molecules or anion-neutral molecule interaction. Also scanning of the reaction mixture did not show any shift in absorbance pointing to the absence of intermediate complex in the reaction. The above reasons suggest that the reaction proceeds via outer-sphere path 15, 16.

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References