The stoichiometry and kinetics of oxidation of 1,4-benzenediol by diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) cation in perchlorate medium

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Received 30 December 1991; revised 2 June 1992; accepted 5 August 1992

The stoichiometry and kinetics of oxidation of 1,4-benzenediol (hydroquinone, H2O) by the oxo-bridged dimer, diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) cation ([RuO4]4+) has been investigated in aqueous perchloric acid. At [H+] = 0.05 mol dm−3, I = 1.0 mol dm−3 (NaClO4) and T = 25.0 ± 0.1°C, the reaction conforms to an overall equation,

2[RuO4]4+ + H2O → 2[RuO4]3+ + O2 + 2H+

The experimental result is consistent with a second-order rate law,

\[-\frac{d[RuO4^{4+}]}{dt} = k_2[RuO4^{4+}][H_2O]\]

with \(k_2 = (12.4 ± 1.1) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{s}^{-1}\). Added Li+, Na+, Pb2+, Mg2+ and Mn2+ have no effect on the rate of the reaction while Cl−, Br− and NO3− catalyze the reaction. Rate of the reaction is independent of change in [acid] of the reaction medium in the range 0.05 ≤ I ≤ 1.0 mol dm−3 and is not affected by changes in ionic strength in the range 0.25 ≤ I ≤ 2.0 mol dm−3. On the basis of the results of this investigation, the absence of both spectroscopic and kinetic evidence of complex formation prior to electron-transfer and the non-conformity of our results with the Michaelis-Menten equation, it is suggested that the oxidation of hydroquinone by [RuO4]4+ most probably proceed by an outer-sphere mechanism.

Meyer et al.1 reported that the μ-oxobridged complexes of ruthenium(III) displayed some properties quite different from analogous monomeric ruthenium(II) and ruthenium(III) complexes and attributed them to an extensive metal-metal electronic interaction across the oxide linkage. Such properties as displayed by these ruthenium(III) oxobridged dimers1, like their relatively high energy transfer ability, has provided a basis for the design of artificial systems used in the splitting of water with solar energy2 and for the use of their higher oxidation state forms as oxidative catalysts3. We have recently shown some interest4-7 in the substitution and electron-transfer reactions of some of these μ-oxobridged complexes. In this paper, we report the stoichiometry and kinetics of the oxidation of 1,4-benzenediol by diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) cation in acidic medium. It is our hope that these series of studies will highlight the effect of the cross-bridge electronic interaction of the ruthenium centres on the wet chemistry of the μ-oxobridged dimers.

Materials and Methods
Diaquotetrakis(2,2'-bipyridine)-μ-oxo-diruthenium(III) perchlorate, [(bipy)2H2ORuORuH2O(bipy)](ClO4)4 was prepared and characterized as reported by Meyer et al.1 (ε_{max} = 25,000). The solution of the dimer in aqueous media was very stable and was kept in the freezer when not being used. The dimer showed enhanced absorbance in aqueous acidic solutions when compared to aqueous solutions of the same concentration, although it
was equally stable. The enhancement in absorbance, which was independent of the acid concentration in the range, 0.05 < [H+] < 1.0 mol dm\(^{-3}\) suggested a possible protonation of the oxo-bridged dimer. The concentrations of the dimer solutions were determined spectrophotometrically before kinetic runs. Hydroquinone (M & B) was recrystallized from ethanol, washed with ether\(^8\) and its purity confirmed by its melting point\(^9\). All other reagents (analar grade) were used as supplied. All solutions were prepared with doubly distilled water.

The stoichiometry was determined by spectrophotometric titration using the mole ratio method. The concentration of [Ru\(_2\)O\(^{4+}\)] was kept constant at 1.87 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\) and that of H\(_2\)O varied from 10 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\) to 1.0 \(\times\) 10\(^{-2}\) mol dm\(^{-3}\) at [H\(^+\)] = 0.05 mol dm\(^{-3}\), \(f = 1.0\) mol dm\(^{-3}\) (NaClO\(_4\)) and \(T = 25.0 \pm 0.1^\circ\)C.

The rate of the reaction was monitored on a Corning colorimeter 253 with a Perkin-Elmer 56 recorder attached, by following the decrease in absorbance of the oxobridged dimer at \(\lambda = 658\) nm. The rates were monitored under pseudo-first order conditions with [H\(_2\)Q] at least 100-fold in excess over the [dimer]. The ionic strength was maintained constant at 1.0 mol dm\(^{-3}\) (NaClO\(_4\)). Temperature was kept constant at 25.0 \(\pm\) 0.1\(^\circ\)C for all runs.

**Results and Discussion**

The stoichiometry of the reaction was found to be in the ratio 2:1. The overall equation for the reaction of [Ru\(_2\)O\(^{4+}\)] by H\(_2\)O can therefore be written as,

\[
2[\text{Ru}_2\text{O}^{4+}] + \text{H}_2\text{O} \rightarrow 2[\text{Ru}_2\text{O}^{3+}] + \text{Q} + 2\text{H}^+ \quad (1)
\]

This suggests that [Ru\(_2\)O\(^{4+}\)] undergoes a one-electron reduction. A similar stoichiometry was reported for the oxidation of hydroquinone\(^{10,11}\) by Ce(IV), Fe\(^{3+}\) and Co\(^{3+}\).

Acrylamide (0.001-0.015 mol dm\(^{-3}\)) was added to partially oxidized reaction mixtures of the dimer and hydroquinone at [H\(^+\)] = 0.05 mol dm\(^{-3}\) and at 1.0 mol dm\(^{-3}\). We did not observe any gel formation even on addition of a large excess of methanol. This does not however rule out the possibility of the formation of the semiquinone radical in this reaction. Earlier reports on the reaction of hydroquinone with Fe\(^{3+}\), Ce(IV) and Co(III) which are one-electron oxidizing agents showed that the rate-determining step in these reactions\(^{12}\) is the formation of the semiquinone radical. However, Baxendale and Hardy\(^{13}\) have suggested that the semiquinone radical is so reactive in most systems that it is difficult to observe it experimentally. This may be one reason why we did not observe it in this investigation. The oxidation of hydroquinone by multi-electron oxidants like Cr(IV) usually takes place in a single two-electron step to form \(p\)-quinone\(^{12}\) although such oxidations can also pass through the semiquinone radical\(^{14}\).

The UV spectrum of the product of this reaction had a maximum at \(\lambda = 485\) nm. This is the same as the \(\lambda_{\text{max}}\) we observed in the reaction of [Ru\(_2\)O\(^{4+}\)] with Fe\(^{3+}\) and ascorbic acid\(^5\) and with \(I^-\) (ref. 6). We suspect that this is due to the [Ru\(_2\)O\(^{3+}\)] product of these reactions.

The electronic spectra of the reaction mixture containing [Ru\(_2\)O\(^{4+}\)] = 1.87 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\), [H\(_2\)Q] = 0.01 mol dm\(^{-3}\), [H\(^+\)] = 0.05 mol dm\(^{-3}\) and \(f = 1.0\) mol dm\(^{-3}\) (NaClO\(_4\)) was run after one and two minutes respectively and compared with that of the same concentration of the dimer alone at the same [H\(^+\)] and ionic strength. There was no shift in the \(\lambda_{\text{max}}\) of 658 nm characteristic of the oxobridged dimer\(^1\). The addition of H\(_2\)O to a solution of [Ru\(_2\)O\(^{4+}\)] also did not result in any enhancement of the absorbance of the oxobridged dimer. Although this does not completely negate the formation of an intermediate complex, it suggests that if any intermediate complex is formed at all, it must have a very small formation constant.

The linearity of the pseudo-first order plots of ln(A\(_0\) - A\(_t\)) versus time (A\(_0\) and A\(_t\) are the absorbances of the reaction mixture at time t and at the end of the reaction respectively) up to more than 80% reaction suggests a first order dependence of the reaction rate on [Ru\(_2\)O\(^{4+}\)]. A plot of log\(k_1\) (\(k_1\) is the pseudo-first order rate constant obtained from the slope of the pseudo-first order plots) versus log[H\(_2\)O] at [H\(^+\)] = 0.05 mol dm\(^{-3}\), \(f = 1.0\) mol dm\(^{-3}\) gave a slope of 0.98 \(\pm\) 0.06 indicating that the reaction is first order in [H\(_2\)Q]. At [H\(^+\)] = 0.05 mol dm\(^{-3}\), the reaction is overall second order and can be represented as in Eq. (2).

\[
-\frac{1}{2}\frac{d[\text{Ru}_2\text{O}^{4+}]}{dt} = k_2[\text{Ru}_2\text{O}^{4+}][\text{H}_2\text{O}] \quad (2)
\]

The second order rate constants, \(k_2\), determined as \(k_2/[\text{H}_2\text{O}]\) are presented in Table 1. A\(_1\) [H\(^+\)] = 0.05 mol dm\(^{-3}\) the average value of \(k_2\) was obtained as \((12.4 \pm 1.1) \times 10^{-2}\) mol\(^{-1}\) dm\(^3\) s\(^{-1}\). The second order kinetics observed in this investigation is similar to that observed in the reaction of hydroquinone with Mn\(^{3+}\) and Fe\(^{3+}\) (ref. 10),
The second order rate constant was determined as a function of [acid] in the range 0.05 ≤ [H⁺] ≤ 1.0 mol dm⁻³ and the results are presented in Table 1. The rate constant was insensitive to the changes in [H⁺] in the acid range investigated. This result correlates some earlier acid-dependence studies involving hydroquinone. For example, no hydrogen ion dependence was observed in the reaction of hydroquinone with 12-tungstocobaltate(III) ion and with Ce(IV). The lack of acid dependence of this reaction might not be unconnected with the very low acid dissociation constant of hydroquinone. The pKᵦ for the formation of the hydroquinone anion is 10.35 in the acid range investigated at 25°C. It is therefore most probable that the native form of the hydroquinone predominates over the acid range investigated. In some earlier reactions, the dependences of hydroquinone reactions on [H⁺] have been attributed to either the hydrolysis or the protonation capabilities of the metal ions involved.

On the basis of our results and the results of earlier investigations, we are proposing the mechanism in Scheme 1 for the oxidation of H₂O by [Ru₂O]⁺⁺⁺⁺.

\[ \text{[Ru₂O]⁺⁺⁺⁺ + H₂O} \rightarrow \text{[Ru₂O]⁺⁺⁺⁺H₂O} \quad \ldots \quad (3) \]

\[ \text{[Ru₂O]⁺⁺⁺⁺H₂O} \rightarrow \text{[Ru₂O]⁺⁺⁺⁺H⁺ + HQ} \quad \ldots \quad (4) \]

Equation (7) is similar to Eq. (2) with \( k₂ = k₃ k₄ \).

\[ k₂ = k₄ k₃ \quad \ldots \quad (8) \]

Hence the proposed mechanism agrees with experimental results.

The results in Table 1 show that changes in ionic strength has no effect on the oxidation of H₂O by [Ru₂O]⁺⁺⁺⁺. Similar results have been reported for some reactions of hydroquinone. The observed zero Bronsted-Debye salt effect is consistent with the undissociated or unprotonated hydroquinone as the reactant.

As the results of Table 2 show, the addition of different concentrations of Li⁺, Na⁺, Pb²⁺ and Mn²⁺ had no effect on the reaction rate. The rate of the reaction was however enhanced by added Cl⁻, Br⁻ and NO₃⁻. The enhancement in rate was in the order Br⁻ > Cl⁻ > NO₃⁻ in the range 0.01 ≤ (X⁻) ≤ 0.1 M (where X = Br, Cl, NO₃). The plot of the anion-dependent second order rate constant \( k₂ \) versus \[X⁻\] fitted an equation,

\[ k₂ = p + q[X⁻] \quad \ldots \quad (9) \]

with \( p(\text{Br}⁻) = (12.1 ± 0.2) \times 10⁻² \text{ mol}⁻¹ \text{ dm}³ \text{ s}⁻¹ \), q(\text{Br}⁻) = 1.67 ± 0.20 mol⁻² dm⁶ s⁻¹, p(\text{Cl}⁻) = (12.4 ± 0.1) \times 10⁻² mol⁻¹ dm³ s⁻¹, q(\text{Cl}⁻) = 1.50 ± 0.1 mol⁻² dm⁶ s⁻¹.
The effect of anions and cations on the second order rate constants for the [RuO₄]⁺ + H₂Q reaction. 

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The table shows the effect of various anions and cations on the rates of the reaction. The rate constants are given in terms of order of magnitude. The reaction follows the outer sphere mechanism.

References

   (c) Creutz C & Sutin N, Proc Natl Acad Sci, USA, 72 (1975) 2858.