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Kinetics And Mechanism Of The Redox Reaction Between Catechol And Trisoxalatocobaltate (Iii) Ion In Aqueous Acid Medium.

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ABSTRACT

The kinetics of the reduction of $[\text{Co}(\text{Ox})_3]^{3-}$ with catechol has been studied in aqueous acid (HClO_4) medium at $I = 1.00\text{mol dm}^{-3}$ (NaClO_4) and $T = 26.3 \pm 0.1^\circ\text{C}$. Two moles of oxidant were consumed by one mole of reductant. The reaction is second order overall, first order in both oxidant and reductant and shows a first order direct acid dependence. Polymerisation test suggested the presence of free radicals as intermediates in the reaction. The kinetic data are consistent with the following equation:

$$-d/2dt[\text{Co}(\text{Ox})_3^{3-}] = k_2[\text{Co}(\text{Ox})_3^{3-}][\text{H}_2\text{Q}]. \quad \text{Where } k_2 = k_a[\text{H}^+].$$

The experimental results are in favour of the outer-sphere mechanism.

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INTRODUCTION

Very few kinetic studies have been reported^{1, 2, 3} on $[\text{Co}(\text{Ox})_3]^{3-}$ when compared to cobalt (III) complexes involving other ligands. Redox investigations between $[\text{Co}(\text{Ox})_3]^{3-}$ and some dihydroxylbenzene have been reported^{2,3}. These exclude catechol. However, some redox studies have been reported^{4,5,6} on catechol with other oxidants. Kaiser and Weidman⁷ have reported that there is no generalized behavioural pattern in the kinetics and mechanism of redox reactions of aromatic dihydroxylbenzene.

We are therefore, in this paper, interested in the Kinetics and mechanism of the redox reaction between Catechol and $[\text{Co}(\text{Ox})_3]^{3-}$ in aqueous acid medium.

EXPERIMENTAL

Reagents

The trisoxalatocobaltate(III) complex, $[\text{Co}(\text{Ox})_3]^{3-}$ was prepared, characterized and stored according to the methods outlined by Bailer and Jones⁸. The complex was characterized by a typical peak at $\lambda_{\text{max}} = 605\text{nm}$. Solution of the complex was usually freshly prepared

before use and its concentration determined spectrophotometrically.

Catechol (1,2-dihydroxybenzene) and other reagents used were of B.D.H, analar grade and were used as supplied.

Stoichiometry

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method. This was accomplished by measuring the absorbance of solutions containing varying concentrations of catechol in the range $(0.5 - 40.00) \times 10^{-2} \text{mol dm}^{-3}$, $[\text{Co}(\text{Ox})_3^{3-}] = 3.50 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 0.30 \text{mol dm}^{-3}$ and $I = 1.00 \text{mol dm}^{-3} (\text{NaClO}_4)$ at 605nm, after the reaction had gone to completion.

Kinetics

All kinetics measurements were made under pseudo-first order conditions with the catechol in at least 100-fold excess at 605nm and constant ionic strength adjusted to 1.00mol dm^{-3} by NaClO_4 . The progress of each reaction was followed by monitoring absorbance changes due to $[\text{Co}(\text{Ox})_3^{3-}]$ using a corning 253 colorimeter. Observed rate constants were evaluated from pseudo-first order plots, which were linear to about 85%.

Absorption spectra

The absorption spectra of solutions, containing oxidant alone and solution of the reaction mixture, under similar

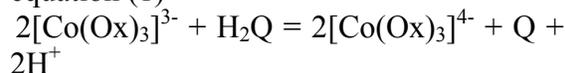
conditions, were compared between 400nm and 700nm, to test for the possibility of an intermediate complex formation. There was no observable difference in both spectra with respect to the λ_{max} .

Product Analysis

The product of the reaction was identified as in the case of the reaction of Resorcinol with trioxiodate(v) ion⁹. The product had a melting point of $119.0 \pm 1.0^\circ\text{C}$ and its derivative (a hydrazone) had a melting point of $187.0 \pm 1.0^\circ\text{C}$.

RESULTS AND DISCUSSION

Two moles of oxidant were consumed per mole of catechol, suggesting the overall stoichiometry shown in equation (1)



.....(1). Where $\text{H}_2\text{Q} = \text{Catechol}$.

Q, identified as quinone in this work, was also established by other workers^{4,9,10,11} in the redox studies of dihydroxybenzene.

The linearity of the pseudo-first order plots suggested that there is no inhibition by the product of the reaction and that the order with respect to the oxidant is unity. Values of the rate constants obtained by varying the concentrations of the reductant and hydrogen ion are presented in Table 1.

Table 1: Pseudo-first order and second order rate constants for the $[\text{Co}(\text{Ox})_3^{3-}]$ -catechol reaction. $[\text{Co}(\text{Ox})_3^{3-}] = 3.50 \times 10^{-3} \text{mol dm}^{-3}$, $I = 1.00 (\text{NaClO}_4) \text{mol dm}^{-3}$, $T = 26.3 \pm 0.1^\circ\text{C}$.

| $10^2 [\text{H}_2\text{Q}] \text{mol dm}^{-3}$ | $10^1 [\text{H}^+] \text{mol dm}^{-3}$ | $10^2 k_{\text{os}}^{-1}$ | $10^1 k_2 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ |
|--|--|---------------------------|--|
| 30.0 | 3.0 | 5.73 | 1.91 |
| 35.0 | 3.0 | 6.65 | 1.90 |
| 40.0 | 3.0 | 7.73 | 1.93 |
| 45.0 | 3.0 | 8.67 | 1.93 |

| | | | |
|------|-----|-------|------|
| 50.0 | 3.0 | 9.62 | 1.93 |
| 55.0 | 3.0 | 10.67 | 1.94 |
| 60.0 | 3.0 | 11.57 | 1.93 |
| 40.0 | 1.0 | 3.60 | 0.90 |
| 40.0 | 1.5 | 4.68 | 1.17 |
| 40.0 | 2.0 | 5.70 | 1.43 |
| 40.0 | 3.0 | 7.71 | 1.93 |
| 40.0 | 3.5 | 8.76 | 2.19 |
| 40.0 | 4.0 | 9.75 | 2.44 |

A plot of $\log k_o$ vs $\log[\text{Reductant}]$ displays a first order dependence on reductant concentration (Slope = 1.02 ± 0.03). The intercept obtained was insignificant, showing a lack of appreciable kinetic evidence for other oxidation pathways.

A plot of the acid dependent rate constant, k_o versus $[\text{H}^+]$ was linear passing through the origin and the dependence on $[\text{H}^+]$ can be represented by equation (2)

$$k_2 = k_a [\text{H}^+] \dots \dots \dots (2)$$

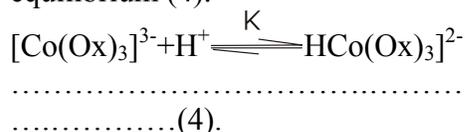
Hence, the reaction may be represented by the rate equation (3).

$$-1/2 \frac{d}{dt} [\text{Co}(\text{Ox})_3^{3-}] = k_a [\text{H}^+] [\text{Co}(\text{Ox})_3^{3-}] [\text{H}_2\text{Q}] \dots \dots \dots (3)$$

The average value of the second order rate constants, k_2 is $(3.21 \pm 0.01) \times 10^{-3} \text{mol dm}^{-3}$ at

$$[\text{H}^+] = 0.30 \text{mol dm}^{-3}$$

The observed acid dependence, similar to some previous reports on benzendiols^{3,4,9} and $[\text{Co}(\text{Ox})_3^{3-}]^1$ suggested that the reactive species of the oxidant is the protonated form as shown by equilibrium (4).



The suggestion of $[\text{HCo}(\text{Ox})_3]^{2-}$ as the reactive species of $[\text{Co}(\text{Ox})_3]^{3-}$ is supported by lack of dependence of the rate of this reaction on ionic strength (Table 2) which suggests a reaction between undissociated H_2Q and $[\text{HCo}(\text{Ox})_3]^{2-}$ in the rate determining step^{7,12,13}. This is corroborated by a non-dependence of rate on the dielectric constant (Table 2) of the reaction medium.

Table 2: Effect of ionic strength and dielectric constant (Dm) on the second order rate constants for the $[\text{Co}(\text{Ox})_3]^{3-}$ -catechol reaction. $[\text{Co}(\text{Ox})_3^{3-}] = 3.50 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{H}_2\text{Q}] = 40.0 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 0.30 \text{mol dm}^{-3}$, $T = 26.3 \pm 0.1^\circ\text{C}$.

| I (NaClO ₄) | $10^1 k_2 \text{mol}^{-1} \text{s}^{-1}$ | Dm (Acetone) | $10^1 k_2 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ |
|-------------------------|--|--------------|--|
| 0.30 | 1.95 | 79.80 | 1.93 |
| 0.50 | 1.93 | 78.60 | 1.92 |
| 0.70 | 1.93 | 77.40 | 1.93 |
| 1.00 | 1.93 | 76.20 | 1.93 |
| 1.20 | 1.95 | 75.00 | 1.93 |
| 1.50 | 1.93 | 73.80 | 1.93 |

When acrylamide was added to a partially oxidized reaction mixture, under our working conditions, followed by addition of a large excess of methanol, a suspension of polyacrylamide was formed. The

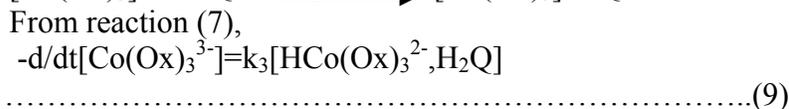
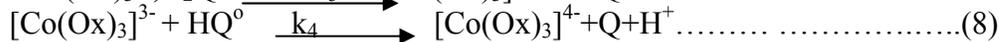
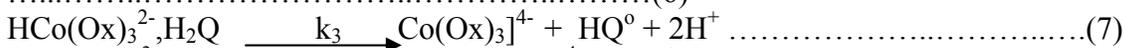
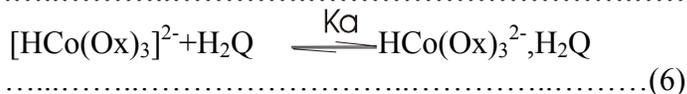
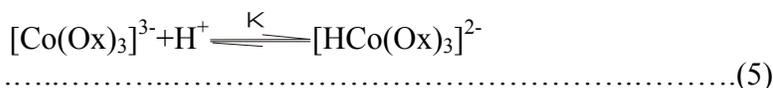
monomer did not polymerise in solutions of $[\text{Co}(\text{Ox})_3]^{3-}$ and catechol when taken separately. Thus free radicals are important intermediates in the title reaction. Other workers^{3,9,11} pointed out that in the

oxidation of benzenediols, free radicals are produced as intermediates.

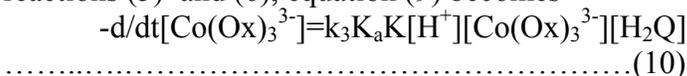
From the above results, the overall picture of the redox reaction can be formulated in terms of reactions 5-8.

Table 3: Effect of added electrolyte on the second order rate constants for the $[\text{Co}(\text{Ox})_3]^{3-}$ - catechol reaction. $T = 26.3 + 0.1^\circ\text{C}$, $[\text{Co}(\text{Ox})_3]^{3-} = 3.50 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{H}_2\text{Q}] = 40.0 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{H}^+] = 0.30 \text{mol dm}^{-3}$, $I = 1.00 \text{mol dm}^{-3}$ (NaClO_4).

| Electrolyte | $10^2[\text{Electrolyte}] \text{ mol dm}^{-3}$ | $10^1 k_2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ |
|-------------------|--|---|
| NaCl | 0.50 | 1.92 |
| | 1.00 | 1.94 |
| | 2.50 | 1.93 |
| NaNO ₃ | 0.50 | 1.93 |
| | 1.00 | 1.93 |
| | 2.50 | 1.93 |
| LiCl | 0.50 | 1.91 |
| | 1.00 | 1.93 |
| | 2.50 | 1.93 |



When substitutions are made for $[\text{HCo}(\text{Ox})_3]^{2-}, \text{H}_2\text{Q}$ and $[\text{HCo}(\text{Ox})_3]^{2-}$ from reactions (5) and (6), equation (9) becomes



Equation (10) compares with equation (3)

Where $k_3 K_a K = 2k_a$

i.e. $k_2 = k_3 K_a K [\text{H}^+]$.

Table 3 shows that both anions and cations have no effect on the rate of reaction. Although, this observation implies inner-sphere character, there is no kinetic or spectrophotometric evidence for

stable inner-sphere complex formation in the present study. For instance, Michealis Menten's plot of $1/k_o$ versus $1/[\text{H}_2\text{Q}]$ was linear with zero intercept. And the comparison of the initial absorbances of

reaction medium with those of $[\text{Co}(\text{Ox})_3]^{3-}$ in the absence of reductant showed no significant difference suggesting the absence of intermediates.

In line with earlier^{1-4,10,14,15} trends in Co(III) redox reactions, the rate-determining step in this reaction probably involves simple electron transfer from the reductant to the oxidant.

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