ChemClass Journal, 2004 (27-30)

Kinetics and mechanism of the oxidation of catechol by $Fe_2(bipy)_4O^{4+}$ in aqueous hydrochloric acid medium

S. O. Idris*, J.F. Iyun and E.B. Agbaji
Chemistry Department, Ahmadu Bello University,
Zaria, Nigeria.

ABSTRACT

The kinetics of the oxidation of catechol, an orthodihydroxybenzene by $Fe_2(bipy)_4O^{4+}$ (bipy = $2,2^1$-bipyridine) has been studied in aqueous hydrochloric acid medium. In the acid range $[H^+] = 1 \times 10^{-5}$-12×10^{-5} mol dm^{-3}. The kinetic data are consistent with the rate law:

Rate = $k_{obs}[Fe_2O^{4+}]$

where $k_{obs} = 0.022 \pm 0.002$ s^{-1} at 29^{0}C and 0.01 mol dm^{-3} ionic strength.
The reaction rate was not affected by change in the dielectric constant of the reaction medium and added anions. An outersphere via ion pair pathway is proposed for the reaction.

* Author for correspondence

INTRODUCTION

Oxygen-bridged binuclear complexes of iron (III) have continued to evoke interest probably because these complexes have the potential of showing similar characteristics to metalloenzymes [1-4]. The binuclear oxobridged complexes of iron (III) with $2,2^1$-bipyridine are high spin complexes with a linear Fe-O-Fe bridge [5]. Most of the studies on these complexes have centred on their synthesis, characterization [6] and stability in aqueous and acidic medium [5]. However, literature on the redox reaction of this class of complexes is scanty. Adequate knowledge of the redox parameters of the oxobridge, $Fe_2(bipy)_4O^{4+}$ is essential since oxobridged binuclear complexes of iron (III) have been reported to have characteristics similar to some haem proteins [1-4]. This investigation is an attempt in this direction.

Catechol, 1,2–dihydroxybenzene was first isolated from acacia catechu tree. It has pharmaceutical and industrial applications. It is used in the synthesis of adrenaline – a valuable hormone drug, as photographic developer and in the manufacture of alizarin dye. The ethers of catechol like guaiacol are used as antioxidant and as expectorant for cough remedies (7). However, definite knowledge on the details of its redox kinetics is surprisingly scanty as most chemical literature on benzenediols weigh more on the side of quinol, 1,4-dihydroxybenzene [8-10]. In this paper we report the kinetics and mechanism of the oxidation of catechol by $Fe_2(bipy)_4O^{4+}$ with the objective of obtaining relevant information on the electron transfer parameters of this reaction.

EXPERIMENTAL

Material

Catechol (BDH) hereafter represented as H_2Q was used as supplied. The binuclear complex of iron (III), $[Fe_2(bipy)_4O]C1_4$ hereafter represented by Fe_2O^{4+} was prepared and characterized as described elsewhere [6]. This complex was unstable in the acid concentration greater than 10^{-4} mol dm^{-3} hence kinetic studies was limited to 1×10^{-5} mol dm$^{-3} \leq [H^+] \leq 12 \times 10^{-5}$ mol dm^{-3}. Stock solutions of the complex and catechol were prepared freshly prior to kinetic and stoichiometric studies. HCl (M&B) was used to investigate the effect of $[H^+]$ on the reaction rate after it has been standardized titrimetically while NaCl (Analar) was used to maintain the ionic strength of the reaction medium at 0.01moldm^{-3}. $NaNO_3$ (BDH) and $NaClO_4$ (BDH) were used to probe the effect of anions on the reaction rate.

Kinetic Measurement

The rate of the reaction was followed by monitoring absorbance increase at520 nm using Chroma Colorimeter model 254. Plots of log $(A_\infty - A_t)$ against time (where A_∞ is the final absorbance at completion of the reaction and A_t is the absorbance at time, t.) were linear at about 80% extent of reaction and first order rate constants (k_{obs}) were calculated from the slope.

Stoichiometry

The stoichiometry was determined by spectrophotometric titrations under the condition $[H^+] = 4 \times 10^{-5}$ mol dm^{-3}, I = 0.01mol dm^{-3}, $[Fe_2O^{4+}] = 4 \times 10^{-5}$ mol dm^{-3} and $[H_2Q] = 0.6 – 16 \times 10^{-5}$ mol dm^{-3}.

Polymerization Studies

The presence of free radicals was not detected by addition of acrylamide to a partially oxidized reaction mixture in the presence of excess methanol as described earlier [3,4,11,12].

RESULTS AND DISCUSSION

The result of stoichiometry studies indicated 1:1.2 ratio according to the following equation:

$$Fe_2O^{4+} + H_2Q \rightarrow 2Fe^{2+} + Q + H_2O \;.....(1)$$

The appearance of an absorption maximum at 520 nm confirmed the formation of $[Fe(bipy)_3^{3+}]$ [11]. Also the absence of an absorption peak at 620 nm indicates the absence of mononuclear complex of iron (III), $[Fe(bipy)_3^{3+}]$ [11,12]. The presence of ketone (orthobenzoquinone) was confirmed as the organic product of the oxidation by qualitative test using 2,4-dinitrophenylhydrazine and Schiff's reagent [13].

The linearity of pseudo-first order plots indicates first order dependence on the oxidant. On the other hand, the invariance of observed first order rate constant with $[H_2Q]$ over the concentration range shown in Table 1 suggests zero order dependence on the reductant. At $[H^+] = 4 \times 10^{-5}$ mol dm^{-3}, the experimental rate law can therefore be represented by equation (2):

$$\frac{1}{2} d[Fe(bipy)_3^{2+}]/dt = k_{obs}[Fe_2O^{4+}]........(12)$$

where $k_{obs} = 0.022 \pm 0.002$ s^{-1} at 29^{0}C and I = 0.01 mol dm^{-3} (NaCl)

In the acid range investigated, the reaction rate was unaffected by change in acid concentration (Table 1). This observation supports earlier studies on benzenediols [9, 14]. The invariance of k_{obs} with increase in $[H^+]$ in this investigation is attributed to the very low dissociation constant of catechol (Ka = 1×10^{-10}) [14]. It is therefore most likely that the native form of catechol predominates in the acid range investigated.

Increasing the ionic strength of the reaction medium from 0.005 to 0.05 mol dm^{-3} (NaCl) had no effect on the reaction rate (Table 2). Similar observation has been made in some reactions of benzenediol [9]. The zero Debye [15] salt effect is consistent with the native reductant molecule as the principal reactant species. It also agrees with the observed acid independence. The addition of acrylamide to a partially oxidized mixture in the presence of excess methanol did not gel. This suggests absence of free radical. However, earlier studies on the redox reaction of benzenediols especially with one electron oxidizing agent like Fe^{3+} reveal the participation of radical in the reaction [9]. Change in dielectric constant between 77.4 and 81 using propan-2-one-water mixture did not affect the rate (Table 2). This indicates that rate determining step may not involve participation of two charged reacting species.

Based on the result of the stoichiometric and kinetic studies, the following mechanism is proposed for the reaction:

$$H_2Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + HQ^- \;.......(3)$$

$$Fe_2O^{4+} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe_2OH^{5+} \;.........(4)$$

$$Fe_2O^{4+} + HQ^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe_2OH^{5+},Q^{2-}] + H^+ \;......(5)$$

$$[Fe_2OH^{5+},Q^{2-}] \xrightarrow{k_4} Fe_2OH^{4+} + Q^- \;....(6)$$

$$Fe_2OH^{4+} + Q^- \xrightarrow{k_5} Fe_2OH^{3+} + Q \;....(7)$$

Rate = $k_4 [Fe_2OH^{5+}, Q^{2-}]$ -----(9)

Applying steady state approximation to $[Fe_2OH^{5+},Q^{2-}]$ gives

$$[Fe_2OH^{5+},Q^{2-}] = \frac{k_3[Fe_2OH^{5+}][HQ^-]}{k_{-3}[H^+]+k_4} \text{.......(10)}$$

Application of steady state approximation to $[Fe_2OH^{5+}]$ gives

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2OH^{4+}][H^+]}{k_{-2}+k_3[HQ^-]} \text{........(11)}$$

If $k_{-3}[H^+] > k_4$, equation (10) reduces to:

$$[Fe_2OH^{5+},Q^{2-}] = \frac{k_3[Fe_2OH^{5+}][HQ^-]}{k_{-3}[H^+]} \text{........(12)}$$

In equation (11), if $k_{-2} << k_3$ $[HQ^-]$ then the equation reduces to:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2OH^{4+}][H^+]}{k_3[HQ^-]} \text{.......(13)}$$

$$Fe_2OH^{3+} + H^+ \xrightarrow{k_6} 2Fe^{2+} + H_2O \text{.....(8)}$$

Table 1 :The observed first order rate constants (k_{obs}) for the oxidation of catechol (H_2Q) by Fe_2O^{4+} at $[Fe_2O^{4+}]$ = $3.33x10^{-5}$ mol $dm^{-3,}$ T= 29^0C and λ_{max} = 520 nm

$10^4[H_2Q]$,mol dm^{-3}	$10^5[H^+]$, mol dm^{-3}	10^2 I, mol dm^{-3}	$10k_{obs}$, s^{-1}
16.65	4	1	0.21
19.98	4	1	0.23
23.31	4	1	0.25
26.64	4	1	0.20
29.97	4	1	0.23
33.30	4	1	0.20
39.96	4	1	0.22
29.97	1	1	0.20
29.97	4	1	0.22
29.97	10	1	0.20
29.97	12	1	0.20
29.97	4	0.5	0.21
29.97	4	1	0.23
29.97	4	2	0.22
29.97	4	3	0.21
29.97	4	5	0.23

Table 2 : Dependence of observed first order rate constants for the oxidation of catechol (H_2Q) by Fe_2O^{4+}on anions and on dielectric constant (D) at Fe_2O^{4+}= 3.33 x 10^{-5} mol dm^{-3}, $[H_2Q]$ = $29.97x10^{-4}$ mol dm^{-3}, $[H^+]$ = 4 $x10^{-5}$ mol dm^{-3}, I= 0.01mol dm^{-3}, T=29^0C and λ_{max} = 520 nm

	10^4 [X], mol dm^{-3}	$10k_{obs}$, s^{-1}
X = NO_3^-	12	0.21
	16	0.22
	20	0.20
	30	0.20
	40	0.20
X=ClO_4^-	12	0.20
	16	0.19
	20	0.19
	30	0.19
	40	0.19
	D	
	75	0.28
	77.4	0.25
	78.6	0.20
	79.8	0.23
	80.6	0.25
	81	0.22

Substituting equation (13) into (12) gives:

$$[Fe_2OH^{5+}, Q^{2-}] = \frac{k_3\, k_2 [Fe_2O^{4+}][H^+]\,[HQ^-]}{k_{-3}[H^+]\, k_3\,[HQ^-]}$$

$$= \frac{k_3\, k_2}{k_{-3}\, k_3}[Fe_2O^{4+}]$$

$$= K_3 k_2 k_3^{-1}[Fe_2O^{4+}] \text{ ....(14)}$$

Substituting equation (14) into (9) gives:

$$Rate = K_3 k_4 k_2 k_3^{-1}[Fe_2O^{4+}] \quad \text{....(15)}$$

Equation (15) is similar to equation (9) where

$$K_3 k_4 k_2 k_3^{-1} = k$$

Variation of anions concentration using $NaNO_3$ and $NaClO_4$ between 0.0012 and 0.004 moldm^{-3} had no effect on the reaction rate (Table 2). This observation agrees with an earlier work on benzenediol with oxobridge ruthenium dimmer [10]. Independence of anions effect on the rate of reaction is a common feature of reactions proceeding by innersphere pathway [4,9,10]. However, an innersphere mechanism proceeding through formation of intermediate in the title reaction is remote. This is because the chances of H_2Q displacing bipyridine in Fe_2O^{4+} to form an intermediate is very unlikely due to the relative position of H_2Q and bipyridine in the spectrochemical series. The formation of ion pair (cf equation 5) as proposed in our mechanism is very probable because of the high charge density of the oxidant. This may be the reason why variation of anions concentration and change in dielectric constant of the reaction medium had no effect on the reaction rate. It is therefore suggested that this reaction proceeds by outersphere via ion pair pathway.

REFERENCES

1. H.J. Schugar, J. Hubbard, C. Walling, R. B. Jones and H.B. Gray. (1967). *J. Am. Chem. Soc.*, **89**, 3712.
2. H.J. Schugar, G.R. Rossman, G.C. Barraclongh and H.B. Gray (1972). *J. Am. Chem. Soc.*, **94**, 2683.
3. P.O. Ukoha and J.F Iyun (2002). *J. Chem. Soc. Nigeria*, **27** (2), 119.
4. P.O. Ukoha and J.F Iyun (2001). *J. Chem. Soc. Nigeria*, **26** (2), 163.
5. P.G. David and P.C.. de Mello (1973). *Inorganic Chemistry,* **112** (9), 2188.
6. P.G. David (1973). *J. Inorg. Nucl. Chem.* **35**, 1463.
7. K.S. Tewari, N.K.. Vishnoi and S.N. Mehirotra (1998). *A Text book of Organic Chemistry*. Second Revised Edition. Viskas Publishing House PVT Ltd. 468.

8 P.O. Ukoha (1999). Ph.D Thesis, A.B.U., Zaria.

9 J.F. Iyun, H.M. Lawal and O.T. Olagbemiro (1995). *Indian J. Chem*. **34A**, 446 (and the references therein).

10 J.F. Iyun, K.Y. Musa and G. Adefikayo Ayoko (1996). *Science in New Guinea*, **22** (1) 9

11. J. F. Iyun, U. Faruk and G. A Ayoko (1996) *International Journal of BioChemPhysics*. **5** (1&2), 25 – 28
12. G.A. Ayoko, F.J. Iyun and S. Mamman (1994). *Transition Metal Chemistry*, **19**, 151 – 153.
13. H.T. Clarke (1975). A Handbook of Organic Analysis Qualitative and Quantitative. 5th Edition, Edward Arnold Publishers Ltd London.

14 R.T. Morrison and R.N. Boyd (1983). Organic Chemistry. 4th Edition. Allyn and Bacon Inc., 958.

15. J.N. Bronsted (1922) *Z. Phys. Chem.* **102**, 160.