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## Kinetics of the reduction of trioxiodate (V) ion by 1,4 – Benzenediol in aqueous acidic medium

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### ABSTRACT

*The kinetics of the reduction of trioxiodate (V) ion by 1,4–benzenediol under pseudo-first order condition of an excess 1,4-benzenediol has been investigated in aqueous hydrochloric acid medium. The reaction conforms to a rate law:*

$$\frac{-d[IO_3^-]}{dt} = k_1 K' [IO_3^-] [H_2Q] [H^+]$$

*The reaction rate was not affected by change in ionic strength and dielectric constant of the reaction medium. A mechanism consistent with the experimental findings has been proposed.*

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### INTRODUCTION

The most popular of the benzenediols is 1,4–benzenediol (hydroquinone), probably because of its industrial application and greater stability of the product of its oxidation over that of the other isomers [1]. Studies have identified it as essential in the preparation of styrene oxide [2]. The formation of ubiquinone (a 1,4–quinone with a lengthy hydrocarbon chain in the 3-position) in conjunction with a metal center as an electron acceptor in photosynthetic bacterial action has been reported [3]. Researches have also shown that unlike reactions of alkanediols for which there is a general agreement on their reaction pathways, there is no general consensus regarding the mechanisms of reaction of benzenediols [4]. We recently reported oxidation of 1,2–benzenediol by oxo–bridged binuclear complex of iron (III), in which we have suggested an outersphere mechanism via ion–pair formation for the reaction [5]. In the quest to throw more light on the complex pathways of reactions of benzenediols, we herein report the electron transfer reaction between 1,4-benzenediol and  $IO_3^-$ .

## MATERIALS AND METHODS

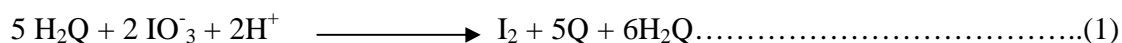
Standard solution of  $\text{KIO}_3$  (M&B) was prepared by dissolving accurately weighed amount of the previously dried and cooled salt in a known volume of distilled water. The purity of 1,4-benzenediol (BDH) hereafter referred to as  $\text{H}_2\text{Q}$  was ascertained by its melting point [6]. Fresh solutions of the reductant were made daily and were covered with aluminum foil [7]. Solution of hydrochloric acid was standardized titrimetrically with a standard solution of sodium carbonate. All other reagents were of analytical reagent grade and were used without further purification. All solutions were made with distilled water.

All kinetics studies were performed under pseudo-first order conditions with the  $[\text{H}_2\text{Q}]$  in at least 32-fold excess over  $[\text{IO}_3^-]$ . The rate of reaction was monitored by measuring the increase in absorbance of the product at 460 nm with Corning Colorimeter 253. Pseudo-first order rate constants ( $k_1$ ) were obtained from the slopes of the logarithmic plots of absorbance differences against time. The temperature was maintained constant at  $32 \pm 0.5^\circ\text{C}$  with  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (NaCl) unless otherwise stated.

The stoichiometry was determined by spectrophotometric titration [8]. Absorbance containing varying concentration of the reductant ( $1 \times 10^{-3} - 3.5 \times 10^{-3} \text{ mol dm}^{-3}$ ) at  $[\text{oxidant}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and ionic strength of the reaction medium =  $0.10 \text{ mol dm}^{-3}$  (NaCl) were measured at 460 nm when there were no further changes in absorbance.

## RESULTS AND DISCUSSION

It was found from the point of inflexion of plot of absorbance against [reductant] that 2.5 moles of  $\text{H}_2\text{Q}$  were consumed per mole of  $\text{IO}_3^-$ . Thus the overall reaction may be represented by equation (1).



Similar stoichiometry was reported for the oxidation of 1,2 – benzenediol by  $\text{MnO}_4^-$  and  $\text{BrO}_3^-$  [9]. However, it differs from the 2:1 stoichiometry (oxidant/reductant) established for the oxidation of  $\text{H}_2\text{Q}$  by oxo-bridged ruthenium dimeric ion [10] and trisoxalatocobaltate (III) ion [7].

Formation of aqueous iodine in the product was identified by its characteristic yellowish brown colour, formation of blue-black colour when product solution was reacted with starch solution and characteristic absorption peak at 460nm. Other workers [11] have determined the concentration of molecular iodine spectrophotometrically at  $\lambda_{\text{max}} = 469\text{nm}$ , at which measurement of optical density uniquely characterize the concentration of dissolved iodine, independent of the presence of other species in the solution.

Red crystals were obtained when some portion of the reaction product was reacted with 2,4-dinitrophenylhydrazine, suggesting the presence of carbonyl compound [12]. Further addition of Schiff's reagent to another portion of the reaction product did not show visible reaction, an indication that the organic product, Q is a ketone [13].

The linearity of pseudo-first order plots to more than 80% extent of reaction suggests first order dependence on the [oxidant]. This also shows that there is no product inhibition as the reaction progressed. On the other hand, the invariance of second order rate constants,  $k_2$  (obtained as ratio of  $k_1$  to  $[H_2Q]$ ) with the reductant over the concentration range in this study (Table 1), indicates that the reaction is first order in the [reductant], the rate equation for the title reaction can therefore be represented by equation (2) with  $k_2 = 0.32 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

$$\frac{-d[IO_3^-]}{dt} = k_2 [IO_3^-] [H_2Q] \dots\dots\dots (2)$$

Second order kinetics have also been observed for the oxidation of  $H_2Q$  [7,10] and other isomers of benzenediol [9,12].

The effect of  $[H^+]$  on the rate of the reaction was determined by keeping all other conditions constant while varying the acid concentration in the range  $0.6 - 12 \times 10^3 \text{ mol dm}^{-3}$ . The reaction rate increases with increase in  $[H^+]$ . A plot of  $k_2$  versus  $[H^+]$  was linear without intercept (Fig.1) indicating that  $k_2$  varies with  $[H^+]$  according to equation (3).

$$k_2 = a [H^+] \dots\dots\dots (3)$$

where  $a = 2.52 \times 10^2 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

Benzenediols have shown some complexities in terms of acid dependence in their electron transfer reactions. For example, increase in  $[H^+]$  has been reported for bromate oxidation of 1,2-benzenediol [9]. Similarly, rate of trioxodiodate (V) ion oxidation of 1,3-benzenediol increases with increase in hydrogen ion concentration [12]. These results are however at variance with oxidation of 1,3-benzenediol by oxo-bridged ruthenium dimeric ion where the rate of the reaction decreases as the  $[H^+]$  increases [14]. In other studies, the rate of oxidation of  $H_2Q$  by oxo-bridged ruthenium dimeric ion [10], trisoxalatocobaltate (III) ion [7] and 12-tungstocobaltate (III) ion [15] were insensitive to change in  $[H^+]$ . Therefore the dependence of benzenediol reactions depends on the nature of the oxidant. Hydrogen ion dependence of the rate of reaction in this study can be rationalized from the fact that protonated trioxodiodate (V) ion in acidic solution is more reactive than the native form of the oxidant.

Changes in ionic strength of the reaction medium had no effect on the rate of the reaction (Table 1). The observed zero Bronsted–Debye salt effect is consistent with reaction involving neutral molecule in the rate determining step [16]. It is therefore most probable that the native reductant or  $HIO_3$  is involved in the rate determining step. This view point is reinforced by the non-dependence of rate constant on dielectric constant,  $D$  of the reaction medium. The rate of the reaction was however inhibited by added  $HCOO^-$  and  $CH_3COO^-$  (Table 2). The inhibition in the reaction rate was in the order  $CH_3COO^- > HCOO^-$  in the range  $0.5 \times 10^{-3} \leq X \leq 3 \times 10^{-3} \text{ mol dm}^{-3}$  (where  $X = CH_3COO^-$  or  $HCOO^-$ ). A plot of the anion dependence second order rate constants,  $k_2$  fitted equation (4).

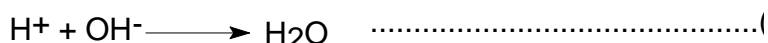
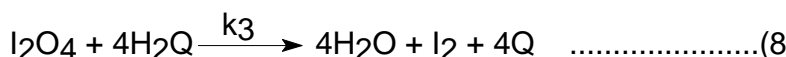
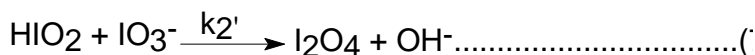
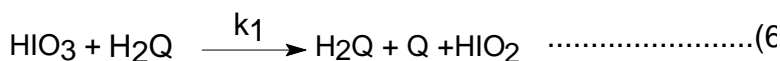
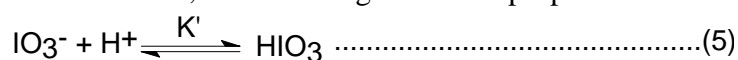
$$k_2 = b + c [X^-] \dots\dots\dots (4)$$

With  $b [CH_3COO^-] = 0.19 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $c [CH_3COO^-] = 0.05 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  and

b  $[\text{HCOO}^-] = 0.27 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , c  $[\text{HCOO}^-] = 0.09 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at  $[\text{H}^+] = 1 \times 10^3 \text{ mol dm}^{-3}$  and  $\text{I} = 0.01 \text{ mol dm}^{-3}$  (NaCl).

Addition of acrylamide, a radical scavenger to partially oxidized mixture did not lead to gel formation even on addition of large excess of methanol. This does not, however, rule out the possibility of formation of semiquinone radical in this reaction as earlier investigations on the reaction of  $\text{H}_2\text{Q}$  with  $\text{Fe}^{3+}$ ,  $\text{Ce}^{4+}$  and  $\text{Co}^{3+}$  have implicated free radicals formation [17]. Baxendale and Hardy [18] have indicated that such radical is so reactive in most systems that it is difficult to observe it experimentally. This may account for our inability to observe it in this study.

From the above results, the following scheme is proposed for the reaction under investigation:



with equation (6) as the rate determining step, the rate equation is given by equation (10).

$$\frac{-d[\text{IO}_3^-]}{dt} = k_1[\text{HIO}_3][\text{H}_2\text{Q}] \dots\dots\dots(10)$$

By steady state hypothesis  $[\text{HIO}_3] = K[\text{IO}_3^-][\text{H}^+]$ . Therefore, the rate of the reactions is

$$\frac{-d[\text{IO}_3^-]}{dt} = k_1 K' [\text{IO}_3^-][\text{H}_2\text{Q}][\text{H}^+] \dots\dots\dots(11)$$

Equation (11) is analogous to equation (2) where  $k_2 = k_1 K' [\text{H}^+]$

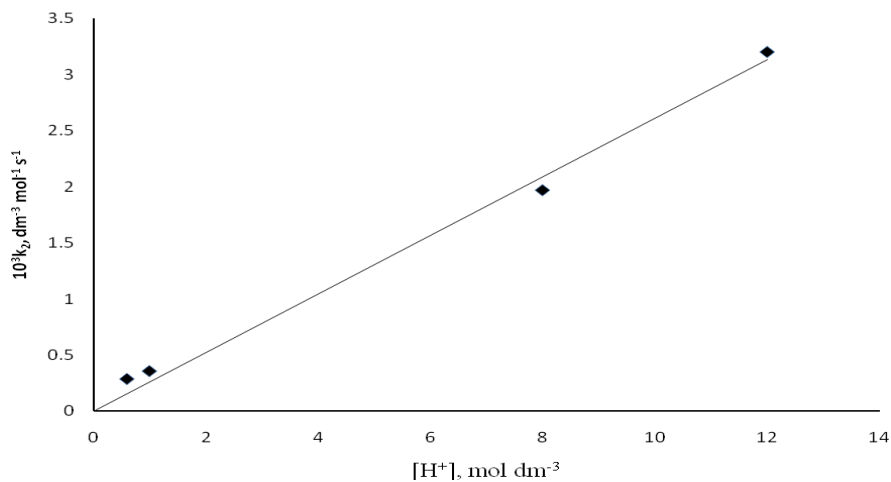
The above reaction steps point to an outersphere mechanistic pathway. This reasoning is supported by the lack of spectrophotometric evidence for formation of precursor complex prior to electron transfer step (equation 6) as there was no shift in  $\lambda_{\text{max}}$  when the reaction mixture was monitored as the reaction progressed. The diminution in reaction rate on addition various concentrations of  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  are explained in terms of outersphere mechanism. A further evidence for the operation of outersphere mechanism for this reaction is provided by the modified Michaelis-Menten plot [8] of  $k_1^{-1}$  versus  $[\text{H}_2\text{Q}]^{-1}$  which was linear and passed through the origin. This tends to suggest absence of innersphere complex formation. We therefore propose that trioxoiodate(V) ion oxidation of 1,4-benzenediol proceeds via outer sphere mechanism.

**Table 1: Second order rate constants for the reduction of trioxiodate(V) ion by 1,4-benzenediol at  $32 \pm 0.5$  °C,  $[\text{IO}_3^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $\lambda_{\text{max}} = 460 \text{ nm}$** 

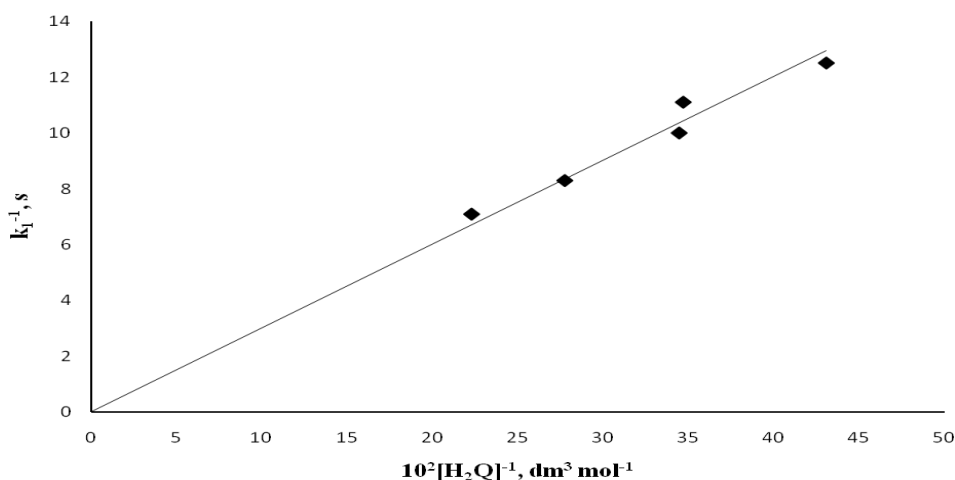
$10^2 [\text{H}_2\text{Q}], \text{mol dm}^{-3}$	$10^3 [\text{H}^+], \text{mol dm}^{-3}$	$10 \text{ I}, \text{mol dm}^{-3}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
8.0	1.0	1.0	0.29
9.0	1.0	1.0	0.32
10.0	1.0	1.0	0.29
11.0	1.0	1.0	0.34
12.0	1.0	1.0	0.30
13.0	1.0	1.0	0.35
14.0	1.0	1.0	0.32
10.0	0.6	1.0	0.29
10.0	1.0	1.0	0.36
10.0	8.0	1.0	1.97
10.0	12.0	1.0	3.20
10.0	1.0	0.5	0.29
10.0	1.0	1.0	0.30
10.0	1.0	1.5	0.30
10.0	1.0	2.0	0.29
10.0	1.0	3.0	0.30

**Table 2: Dependence of Second order rate constants for the oxidation of 1,4-benzenediol  $[\text{H}_2\text{Q}]$  by  $\text{IO}_3^-$  on anions at  $[\text{IO}_3^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{Q}] = 10 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 32 \pm 0.5^\circ\text{C}$ ,  $\lambda_{\text{max}} = 460 \text{ nm}$  and  $\text{I} = 0.1 \text{ mol dm}^{-3}$** 

$10^3 [\text{X}], \text{mol dm}^{-3}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
$\text{X} = \text{CH}_3\text{COO}^-$	0.8
	1.0
	1.5
	2.0
	3.0
$\text{X} = \text{HCOO}^-$	0.8
	1.0
	1.5
	2.0
	3.0



[1]

**Fig.1 : Plot of  $k_2$  versus  $[H^+]$** **Fig.2: Michaelis-Menten plot of  $k_1^{-1}$  versus  $[H_2Q]$** **REFERENCES**

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