



## Kinetics and mechanism of electron transfer reaction between tetraoxiodate(VII) ion and 1,3-benzenediol

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### ABSTRACT

The stoichiometry, kinetics and mechanism of the electron transfer reaction between tetraoxiodate (VII) ion and 1,3-benzenediol have been investigated at 30±0.5°C. The reaction follows the rate law:

$$-\frac{d[\text{IO}_4^-]}{dt} = (k_1K' + k_3[\text{H}^+]) [\text{H}_2\text{R}] [\text{IO}_4^-] \text{ where } \text{H}_2\text{R} = 1,3\text{-benzenediol. The rate of the reaction is independent of change in ionic strength of the reaction medium in the range of } 0.05 \leq I \leq 0.4 \text{ mol dm}^{-3}.$$

On the basis of the result obtained from Michaelis-Menten plot, outersphere mechanistic pathway is proposed for this reaction.

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### INTRODUCTION

Several studies addressing the dynamics of the electron transfer reaction of benzenediols with a wide range of oxidants have been reported<sup>[1-13]</sup>. These reactions have shown a lot complexities both in terms of acid dependencies and the products<sup>[1,6,9]</sup>. For example, Iyun<sup>[6]</sup> reported acid dependence and acid independence in the oxidation of 1,2-benzenediol by  $\text{BrO}_3^-$  and  $\text{MnO}_4^-$  respectively in aqueous acidic medium and free radicals in both systems.

In addition, the desire to gain adequate knowledge on the redox pattern of  $\text{IO}_4^-$  also heightened our interest in investigating its reaction with 1,3-benzenediol. Most of its reactions with both organic and inorganic substrates are thought to occur by both inner- and outersphere mechanisms<sup>[14-19]</sup>. It is our hope that the data obtained in this investigation will assist in providing

more information on the complexities that attend the reaction of  $\text{IO}_4^-$ .

### EXPERIMENTAL

The purity of 1,3-benzenediol (Hopkins & Williams) hereafter referred to as  $\text{H}_2\text{R}$  was confirmed by its melting point (110°C). Fresh solutions of  $\text{NaIO}_4$  (BDH) and  $\text{H}_2\text{R}$  were prepared daily before use. Standard solution of HCl was prepared as described in the literature<sup>[20]</sup>. All other chemicals were of analytical reagent grade. All solutions were prepared with distilled water.

#### Stoichiometry

This was determined by spectrophotometric titration using condition identical to those described earlier<sup>[6-13]</sup>. Absorbances of the product were measured

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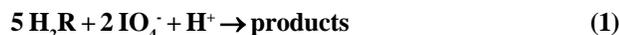
immediately after the reaction has gone to completion. The stoichiometry was then evaluated from the point of inflexion on a curve of absorbance ( $A_{\infty}$ ) versus [reductant].

### Kinetics

Kinetics measurements were conducted with Chroma Digital Colorimeter 254 at the  $\lambda_{\max}$  (470nm) of the reaction product as the reaction progressed after having confirmed that none of the reactants absorbed at this wavelength. All reactions were carried out under pseudo-first order condition with the [reductant] in at least 100-fold excess over that of the oxidant.

## RESULTS AND DISCUSSION

The stoichiometric studies indicated that for each mole of  $\text{IO}_4^-$  consumed, 2.5 moles of  $\text{H}_2\text{R}$  were oxidized according to eq. (1)



Similar stoichiometry was reported for the oxidation of  $\text{H}_2\text{R}$  by  $\text{IO}_3^-$  (10) and 1,2-isomer by  $\text{BrO}_3^-$  and  $\text{MnO}_4^-$  (6). Recently we also reported the same stoichiometry for the reaction between the 1,2-isomer and  $\text{IO}_3^-$  [13].

Some yellow crystals were obtained when 2,4-dinitrophenylhydrazine was reacted with some portion of the product solution suggesting that one of the products contained carbonyl functional group. Further test on the product solution confirmed quinone (ketone) to be the organic product [21]. The formation of  $\text{I}_2$  was inferred by its characteristic yellowish brown colour, formation of a blue-black color when the product solution was reacted with starch solution and the spectrum characteristic of the product solution ( $\lambda_{\max} = 470\text{nm}$ ). In the previous study, the concentration of molecular iodine has been determined spectrophotometrically at  $\lambda_{\max} = 469\text{nm}$ , where the measurements of optical density uniquely characterized the concentration of dissolved iodine which are independent of other species in the solution [22].

The linearity of the pseudo-first order plots of  $\log(A_{\infty} - A_t)$  versus time (where  $A_{\infty}$  and  $A_t$  are the absorbances at the end of the reaction and the reaction mixture at time,  $t$  respectively) indicates a first order dependence of the reaction on  $[\text{IO}_4^-]$ . A plot of  $\log k_{\text{obs}}$

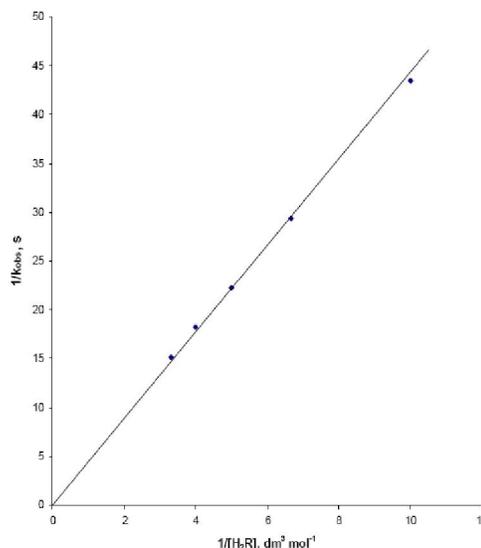


Figure 1: Michaelis-Menten plot of  $1/k_{\text{obs}}$  versus  $1/\text{H}_2\text{R}$

(where  $k_{\text{obs}}$  is the observed pseudo-first order rate constant obtained from the slope of the pseudo-first order plots) versus  $\log[\text{H}_2\text{Q}]$  gave a slope of 0.96, an indication that the reaction is first order in  $[\text{H}_2\text{R}]$ . This finding corroborates other observations on the oxidation of benzenediols by  $\text{IO}_3^-$  [10,13] and  $\text{MnO}_4^-$  [6]. The second order rate constants,  $k_2$ , were determined as ratios of  $k_{\text{obs}}$  to  $[\text{H}_2\text{R}]$ . The rate law of the reaction is according to equation [2].

$$-\frac{d[\text{IO}_4^-]}{dt} = k_2 [\text{H}_2\text{R}] [\text{IO}_4^-] \quad (2)$$

In the range  $5 \times 10^{-3} \leq [\text{H}^+] \leq 40 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $k_2$  increased from 0.231 to  $0.503 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  as indicated in TABLE 1. A plot of  $\log k_{\text{H}^+}$  versus  $\log[\text{H}^+]$  was linear with a slope of 0.86 (Figure 1) suggesting a first order dependence on  $[\text{H}^+]$ . Also, a plot of  $k_2$  versus  $[\text{H}^+]$  was linear and consistent with eq. (3).

$$k_2 = a + b[\text{H}^+] \quad (3)$$

This relationship is consistent with the kinetic pattern of the reaction of benzenediol with oxyanions [6,10,13]. Direct acid dependence has been explained in terms of the various equilibrium established by the oxyanions in aqueous acidic medium. The proton has also been reported to enhance the cleavage of the bond between the oxide ions and the central atom [23]. Various workers have indicated existence of  $\text{H}_5\text{IO}_6$ ,  $\text{H}_4\text{IO}_6^-$  and  $\text{H}_3\text{IO}_6^{2-}$  in the reduction of  $\text{IO}_4^-$  in aqueous acidic medium.

The above observation is at variance with that ob-

TABLE 1 : Pseudo-first order and second order rate constants for the reduction of  $\text{IO}_4^-$  by 1,3-benzenediol ( $\text{H}_2\text{R}$ ) at  $T=30\pm 1^\circ\text{C}$ ,  $\lambda_{\text{max}} = 470 \text{ nm}$  and  $[\text{IO}_4^-] = 1\times 10^{-3} \text{ mol dm}^{-3}$

| $10^2[\text{H}_2\text{R}], \text{mol dm}^{-3}$ | $10^3[\text{H}^+], \text{mol dm}^{-3}$ | $\text{I}(\text{NaCl}), \text{mol dm}^{-3}$ | $10^3 k_{\text{obs}}, \text{s}^{-1}$ | $10^2 k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|--|--|---|--------------------------------------|---|
| 10   | 10                                     | 0.10  | 23.0                                 | 23.0  |
| 15   | 10                                     | 0.10  | 34.0                                 | 22.9  |
| 20   | 10                                     | 0.10  | 45.0                                 | 22.7  |
| 25   | 10                                     | 0.10  | 55.0                                 | 22.0  |
| 30   | 10                                     | 0.10  | 66.0                                 | 22.0  |
| 20   | 10                                     | 0.05  | 45.4                                 | 22.7  |
| 20   | 10                                     | 0.10  | 46.8                                 | 23.4  |
| 20   | 10                                     | 0.15  | 46.8                                 | 23.4  |
| 20   | 10                                     | 0.20  | 46.8                                 | 23.4  |
| 20   | 10                                     | 0.30  | 46.8                                 | 23.4  |
| 20   | 10                                     | 0.40  | 46.8                                 | 23.4  |
| 20   | 5                                      | 0.10  | 46.0                                 | 23.1  |
| 20   | 10                                     | 0.10  | 49.0                                 | 24.6  |
| 20   | 15                                     | 0.10  | 58.0                                 | 24.0  |
| 20   | 20                                     | 0.10  | 68.0                                 | 34.2  |
| 20   | 30                                     | 0.10  | 94.0                                 | 47.2  |
| 20   | 40                                     | 0.10  | 106.0                                | 50.3  |

tained in the oxidation of  $\text{H}_2\text{R}$  by  $[(\text{bpy})_2 \text{H}_2\text{O Ru}^{\text{III}}]_2\text{O}^{4+}$ , oxobridged ruthenium dimer<sup>[9]</sup> where the rate of the reaction decreased as  $[\text{H}^+]$  increased. Although,  $\text{H}_2\text{R}$  has a very low dissociation constant ( $K_a = 3\times 10^{-3}$ )<sup>[24]</sup>, the observed acid dependence study in this reaction has been attributed to its possible deprotonation of the dimer prior to the electron transfer step.

Increasing the ionic strength of the reaction medium from 0.05 to 0.4  $\text{mol dm}^{-3}$  has no effect on the rate of the title reaction (TABLE 1). This observation is typical of reaction occurring between neutral and charged ion<sup>[25]</sup>.

Based on the results obtained, the scheme below is proposed for this reaction,

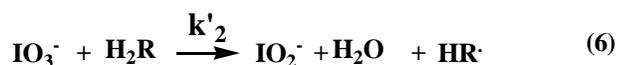
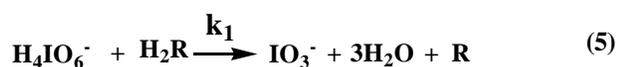


TABLE 2 : Effect of added methanoate ions on the pseudo-first order and second order rate constants for the reduction of  $\text{IO}_4^-$  by 1,3-benzenediol ( $\text{H}_2\text{R}$ ) at  $[\text{IO}_4^-] = 2\times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}_2\text{R}] = 20\times 10^{-2} \text{ mol dm}^{-3}$   $T=30\pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 470 \text{ nm}$

| $10^3[\text{HCOO}^-], \text{mol dm}^{-3}$ | $10^3 k_{\text{obs}}, \text{s}^{-1}$ | $10^2 k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|---|--------------------------------------|---|
| 1   | 46.1                                 | 23.1  |
| 15  | 42.1                                 | 21.1  |
| 20  | 41.2                                 | 20.6  |
| 40  | 36.4                                 | 18.2  |
| 60  | 34.5                                 | 17.3  |



$$\text{Rate} = k_1 [\text{H}_4\text{IO}_6^-] [\text{H}_2\text{R}] + k_3 [\text{H}^+] [\text{H}_2\text{R}] [\text{IO}_4^-] \quad (10)$$

But  $[\text{H}_4\text{IO}_6^-] = K' [\text{IO}_4^-]$  since  $[\text{H}_2\text{O}]^2$  is approximately unity.

Therefore,

$$\text{Rate} = k_1 K' [\text{IO}_4^-] [\text{H}_2\text{R}] + k_3 [\text{H}^+] [\text{H}_2\text{R}] [\text{IO}_4^-] \quad (11)$$

Eq. (11) is similar to eq. (2) where  $k_2 = k_1 K' + k_3 [\text{H}^+]$ .

The presence of free radicals was indicated by the positive polymerization test on adding acrylamide to the reaction mixture containing excess methanol. The monomer did not polymerize in solutions of  $\text{H}_2\text{R}$  and  $\text{IO}_4^-$  when taken separately. Thus free radicals are important intermediates in this reaction. Several studies have shown that free radicals intermediates are involved in the oxidation of benzenediols<sup>[7-11]</sup>.

Addition of methanoate ions retarded the rate of the reaction (TABLE 2). This shows that substitution of the  $\text{H}_2\text{R}$  into the inner coordination shell of  $\text{IO}_4^-$  did not precede the electron transfer step. The inhibition of the reaction by this anion could be due to coulombic effect as the intervention of the anion in between  $\text{H}_5\text{IO}_6^-$  or  $\text{IO}_4^-$  and  $\text{H}_2\text{R}$  in the activated complex would lead to the repulsion of these species and hence a decrease in reaction rate.

A further evidence for the operation of outersphere in this reaction is provided by the Michaelis-Menten plot<sup>[7,8,11,19]</sup> of  $1/k_{\text{obs}}$  versus  $1/[\text{H}_2\text{R}]$  which was linear without intercept (Figure 1).

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