

Kinetics and mechanism of the electron transfer reaction between tetraoxoiodate(VII) ion and indigo carmine in aqueous hydrochloric acid medium

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ABSTRACT

The stoichiometry, kinetics and mechanism of the electron transfer reaction between tetraoxoiodate(VII) ion and indigo carmine (IC) have been investigated at 27 ± 1 °C. The rate of the reaction is:

$$\text{Rate} = \left\{ k_4 + \left(\frac{k_6 K_3 [H^+]}{1 + K_3 [H^+]} \right) \right\} [IO_4^-]_t [IC].$$

The rate of the reaction is independent of changes in ionic strength of the reaction medium in the range of $0.1 \leq I \leq 0.8 \text{ mol dm}^{-3}$. Added cations catalyzed the reaction whereas added anions inhibited the rate of the reaction. On the basis of the result obtained the outersphere mechanistic pathway is proposed for this reaction.

Key words: Tetraoxoiodate(VII) ion, Indigo carmine, Mechanism, Kinetics, Ionic strength.

INTRODUCTION

Interest in tetraoxoiodate(VII) ion as an oxidant in electron transfer reaction has received much attention [1-5]. The use of periodate as an oxidant has been extended to organic compounds especially in the oxidation of phenols [6], glyoxylic and pyruvic acid [7], ethylamine [8], cyclohexanone [9], azide [10] and esters [11].

Indigo carmine (IC), here and thereafter referred to as IC, is one of the oldest dyes and still one of the important dyes in use. Its major applications are the dyeing of clothes (blue jeans) and other blue denim [12]. It is one cause of dermatitis because of positive patch test reaction to both commercial and purified sample of it. IC is harmful if swallowed, inhaled or absorbed through the skin [13]. Due to its sharp absorption peak, it has been used as indicator substance in a number of kinetic analytical methods [14] also for the measurement of kidney function and as a stain for Negro bodies in biology [15].

This present work is carried out to obtain relevant kinetic data which would give an idea on the best conditions suitable for studying the redox reaction between IC and tetraoxoiodate(VII) ion and to propose a suitable mechanism.

MATERIALS AND METHODS

Materials

A $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ stock solution of indigo carmine (BDH, AR) and 0.5 mol dm^{-3} of tetraoxoiodate(VII) ion were prepared by dissolving 4.66 g and 10.70 g of NaIO_4 in distilled water in 100 cm^3 volumetric flask respectively. The $\lambda_{\text{max}} = 610 \text{ nm}$ of IC was determined by running the electronic spectrum of solution of IC in the wavelength range of 400-700 nm. Sodium chloride (BDH, AR) was used to maintain the ionic strength of the medium constant and 1.0 mol dm^{-3} solution of hydrochloric acid (BDH) was also prepared (36%, specific gravity 1.18) to investigate the effect of hydrogen ion on the rate of the reaction. All other reagents used were of analar grade.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [16]. The concentration of indigo carmine (IC) was kept constant at $2.8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, and $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 610 \text{ nm}$ while that of tetraoxoiodate(VII) ion was varied in the range $(0.76 - 2.8) \times 10^{-5} \text{ mol dm}^{-3}$. The absorbance of the reacting mixtures was measured after the reaction had gone to completion as indicated by a steady absorbance value over a period of two days. A point of inflexion on the curve of the absorbance versus mole ratio corresponds to the stoichiometry of the reaction (Fig. 1).

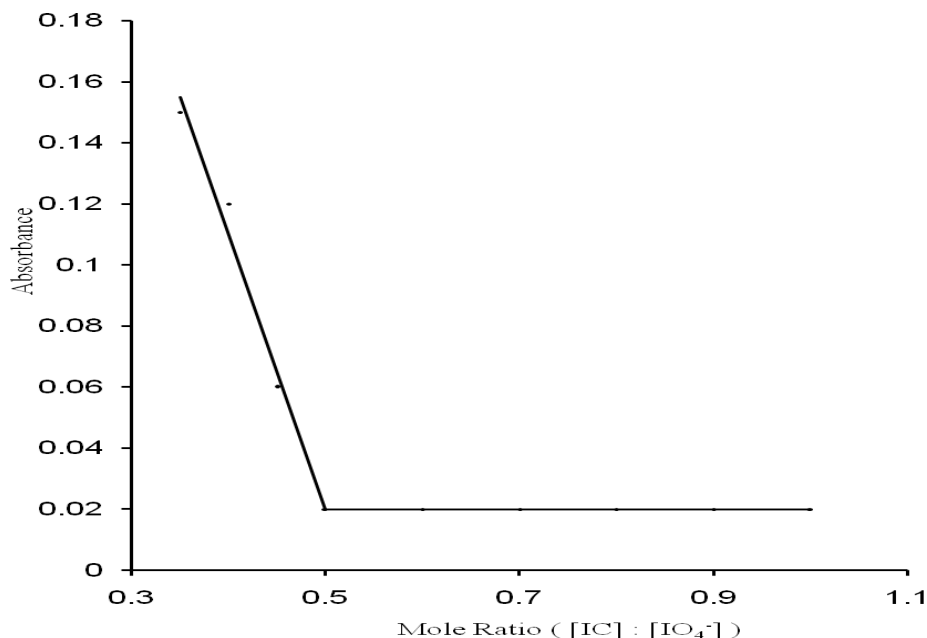


Figure 1: Plot of absorbance versus mole ratio for the redox reaction of indigo carmine with IO_4^- at $[\text{IC}] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{IO}_4^-] = (7.50 - 120) \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $\mu = 0.50 \text{ mol dm}^{-3}$, $\lambda = 610 \text{ nm}$ and $T = 27 \pm 1 \text{ }^\circ\text{C}$

Kinetic measurements

The kinetic of the reaction was monitored using a Corning Colorimeter Model 252 at $27 \pm 1 \text{ }^\circ\text{C}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaCl) and $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ (HCl). The progress of the reaction was

monitored by following the decrease in absorbance of the dye at 610 nm. All the kinetic measurements were carried out under pseudo-first order conditions with the concentration of tetraoxoiodate(VII) ion at least 700 folds greater than that of the dye. The pseudo-first order plots of $\log (A_t - A_\infty)$ versus time, were made (where A_∞ and A_t are the absorbance at the end of the reaction at time, t) and from the slope of the plots, the pseudo-first order rate constant (k_1) was determined. The second order rate constant (k_2) was obtained from k_1 as $k_2 / [\text{IO}_4^-]$. A typical pseudo- first order plot is presented in Fig. 2.

Effect of ionic strength of the reaction medium on the reaction rate

The effect of ionic strength of the rate of the reaction was investigated in the range of 0.2- 1.0 mol dm⁻³ (NaCl) while the concentration of other reactants was kept constant at 27 ± 1 °C. The result is presented in Table 1.

Effect of added cations and anions on the reaction rate

The effect of added cations and anions were investigated for $X = 1 \times 10^{-3}$ - 1.6×10^{-2} mol dm⁻³ ($X = \text{Ca}^{2+}$, Mg^{2+} , CH_3COO^- , HCOO^-) and the concentration of other reactants was kept constant at 27 ± 1 °C and ionic strength of 0.5 mol dm⁻³ (NaCl). The result is presented in Table 2.

Effect of changes of acid concentration on the reaction rate

The effect of acid on the rate of the reaction was studied in the range of $(0.1-4.0) \times 10^{-1}$ mol dm⁻³ while the concentration of the dye and periodate ion were kept constant ion at 27 ± 1 °C and $I = 0.50$ mol dm⁻³. The results are presented in Table 1.

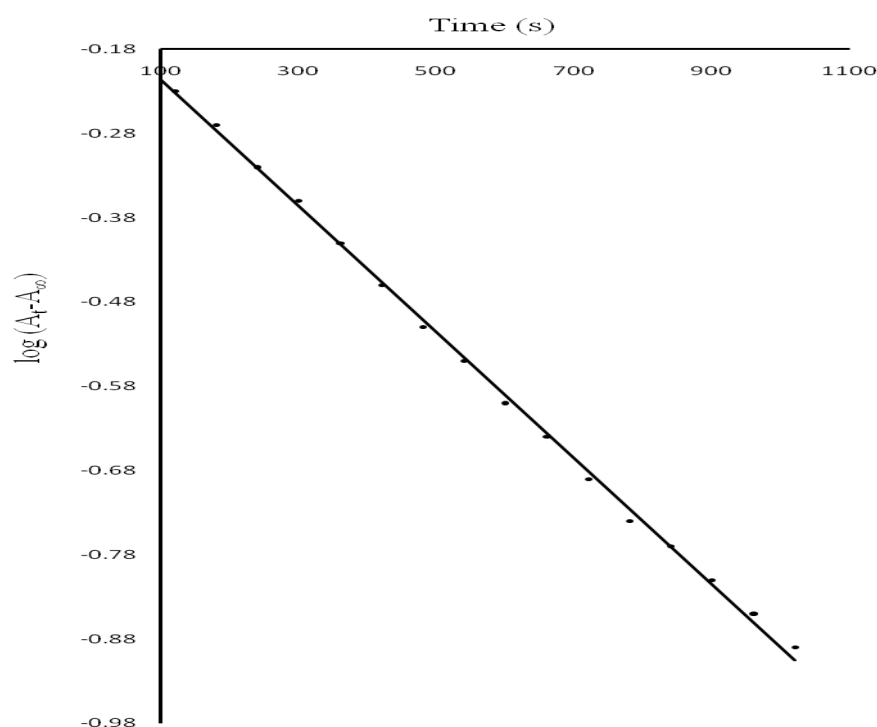


Figure 2: Typical pseudo-first order plot for the redox reaction of indigo carmine with IO_4^- at $\text{IC} = 2.8 \times 10^{-5}$ mol dm⁻³, $[\text{IO}_4^-] = 1.96 \times 10^{-2}$ mol dm⁻³, $[\text{H}^+] = 0.1$ mol dm⁻³, $I = 0.5$ mol dm⁻³, $\lambda = 610$ nm, $T = 27 \pm 1$ °C

Table 1: Pseudo-first order and second order rate constants for the IC – IO₄⁻ reaction [IC] = 2.8 × 10⁻⁵ mol dm⁻³, T = 27 ± 1⁰C.

10 ² [IO ₄ ⁻], mol dm ⁻³	10 ¹ [H ⁺], mol dm ⁻³	10 ¹ I, mol dm ⁻³	10 ³ k ₁ , s ⁻¹	10 ¹ k ₂ , dm ³ mol ⁻¹ s ⁻¹
1.66	1.0	5.0	2.25	1.36
1.82	1.0	5.0	2.42	1.36
1.96	1.0	5.0	2.69	1.38
2.10	1.0	5.0	2.86	1.36
2.24	1.0	5.0	3.11	1.39
2.38	1.0	5.0	3.29	1.38
2.52	1.0	5.0	3.38	1.34
1.96	0.1	5.0	0.77	0.39
1.96	0.5	5.0	1.81	0.93
1.96	1.0	5.0	2.69	1.38
1.96	1.5	5.0	2.90	1.48
1.96	2.0	5.0	3.27	1.68
1.96	2.5	5.0	3.36	1.71
1.96	3.0	5.0	3.59	1.83
1.96	4.0	5.0	3.94	2.01
1.96	1.0	2.0	2.66	1.36
1.96	1.0	3.0	2.68	1.37
1.96	1.0	4.0	2.72	1.39
1.96	1.0	5.0	2.69	1.38
1.96	1.0	6.0	2.69	1.38
1.96	1.0	7.0	2.66	1.36
1.96	1.0	10.0	2.67	1.36

Table 2: Rate data for the effect of added cations and anions on the redox reaction of indigo carmine with periodate ion, at I = 0.5 mol dm⁻³. λ_{max} = 610 nm, T = 27 ± 1⁰C, [IC] = 2.8 × 10⁻⁵ mol dm⁻³, [IO₄⁻] = 1.96 × 10⁻² mol dm⁻³, [H⁺] = 1.0 × 10⁻¹ mol dm⁻³

10 ³ [Mg ²⁺], mol dm ⁻³	10 ³ k ₁ , s ⁻¹	k ₂ , dm ³ mol ⁻¹ s ⁻¹
40	2.34	1.54
80	5.94	3.03
100	8.96	4.57
120	10.36	5.29
10 ³ [Ca ²⁺], mol dm ⁻³		
20	3.16	1.61
40	3.94	2.01
60	4.47	2.28
100	4.70	2.40
10 ³ [CH ₃ COO ⁻], mol dm ⁻³		
40	2.35	1.20
80	1.76	0.80
120	1.22	0.57
160	0.66	0.34
10 ³ [HCOO ⁻], mol dm ⁻³		
20	2.35	1.20
40	1.95	1.00
60	1.84	0.94
80	1.24	0.63

Test for intermediate complex formation

The spectra of the reaction mixture were obtained after one minute. The spectra of the dye alone were compared over a range of wavelength 420 nm and 700 nm to test for the possibility of any intermediate complex formation. Michaelis-Menten plots of $1/k_1$ versus $1/[IO_4^-]$ is shown in Fig.3.

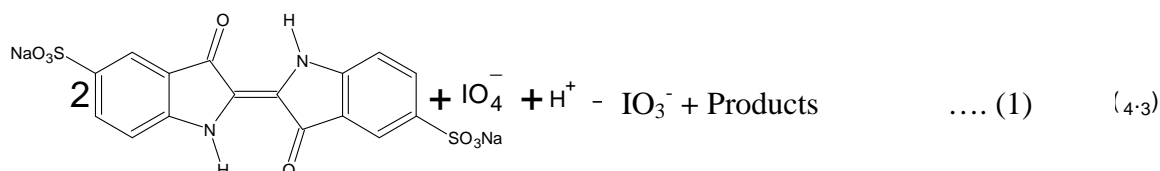
Test for free radicals

Acrylamide was added to test for the presence of any free radical under working conditions. There was no polymerization after the addition of excess methanol confirming that no free radical was detected.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

The stoichiometric studies showed that two moles of indigo carmine was consumed by one mole of IO_4^- . The overall stoichiometric equation is;



Similar stoichiometry has been reported for the reduction of tetraoxoiodate(VII) [10, 17-18]. Iodate, one of the products was confirmed qualitatively through the positive starch-indicator test for liberated I_2 when KI was added to the reaction mixture at the equivalent point.

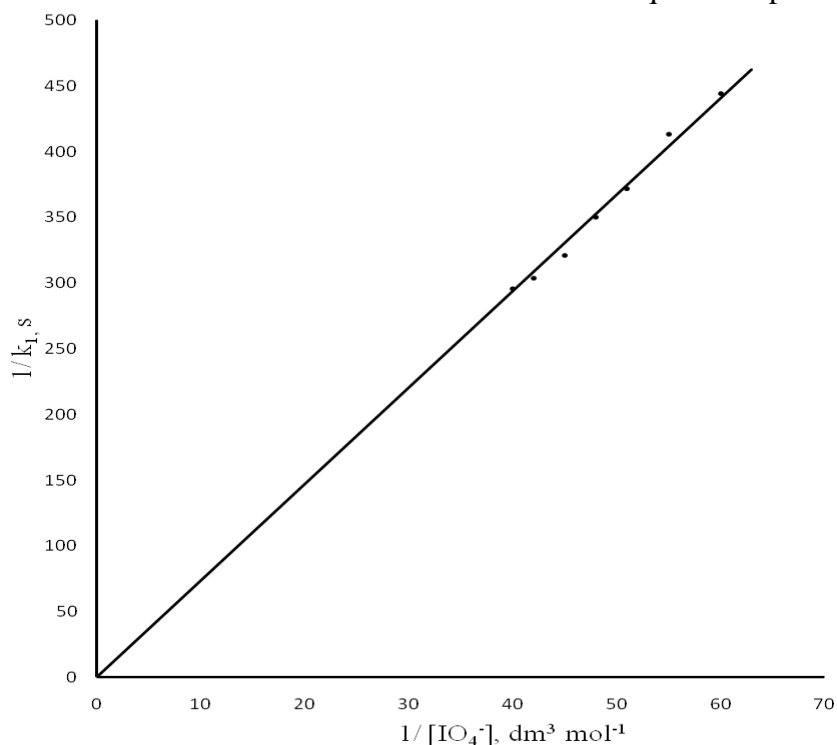


Figure 3: Michaelis - Menten plot for the redox reaction between indigo carmine and IO_4^- at $[IC] = 2.80 \times 10^{-5} \text{ mol dm}^{-3}$, $[IO_4^-] = (1.54 - 2.55) \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $\mu = 0.50 \text{ mol dm}^{-3}$, $\lambda = 610 \text{ nm}$ and $T = 27 \pm 1 \text{ }^\circ\text{C}$

The reaction of iodate by iodide ions in acidic medium liberates molecular iodine as given by the equation below [19];



This agrees with the findings of Abdel-Khalek that IO_4^- is known to be reduced to IO_3^- in most of its reactions [20].

Kinetics

The pseudo-first order plots of $\log (A_t - A_\infty)$ versus time for this reaction were linear for about 90% of the reactions (Fig. 2). The linearity of these plots indicates that this reaction is first order with respect to [IC]. A plot of $\log k_1$ versus $\log [\text{IO}_4^-]$ was linear with a slope of 1.0 showing that the reaction is also first order with respect to $[\text{IO}_4^-]$ and second order overall. This is also supported by the constancy of k_2 values (1.37 ± 0.03) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Similar order was reported for the oxidation of hexacyanoferrate(III) by IO_4^- [4] and the oxidation of amine - *N* - polycarboxylates of cobalt (II) by periodate ion [21].

Effect of changes in acid concentration on the reaction rate

The rate constants of this reaction increases with increase in hydrogen ion concentration, plot of $\log k_{\text{H}^+}$ versus $\log [\text{H}^+]$ showed an order of 0.45 with respect to $[\text{H}^+]$. Plot of k_2 versus $[\text{H}^+]$ was linear with a positive intercept. This kind of acid dependence shows that there is rapid pre-equilibrium between the protonated and deprotonated forms, and the value of the protonation equilibrium constant is great enough that at higher acidities, protonation is almost complete, leading to a limiting rate; both the protonated and unprotonated forms are reactive [22].

Effect of changes in ionic strength and added ions on the reaction rate

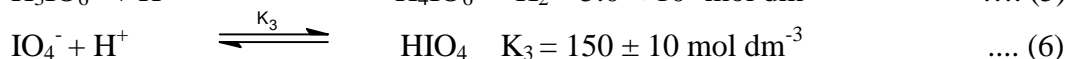
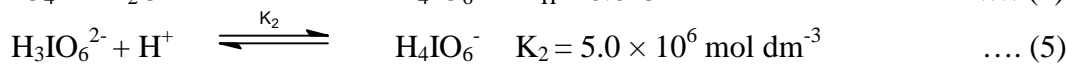
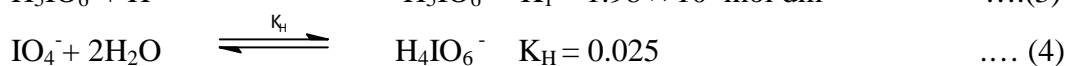
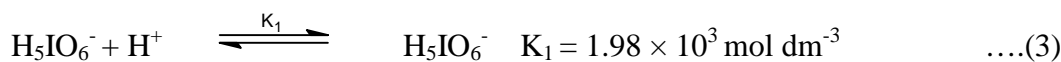
Changes in the ionic strength of the reaction medium had no effect on the oxidation of IC by IO_4^- . The observed independence on the rate of the reaction suggests that either charged and neutral species or two neutral species are reacting at the rate determining step [23].

Plots of $1/k_1$ versus $1/[\text{IO}_4^-]$ gave no intercept suggesting no detectable binuclear intermediate formation. Added ions had effect on the rate of the reaction. The inclusion of Mg^{2+} and Ca^{2+} to the reaction medium accelerated the rate of the reaction; this is expected as one of the reacting species at the rate determining step is an anion. Therefore, the ions will tend to attract each other thereby reducing the inter-ionic distance between them and consequently catalyze the rate of the reaction; also the inhibition of the rate of the reaction by added CH_3COO^- and HCOO^- is not unexpected due to the same reason. There is an interference caused by the electrostatic interactions between these ions in the transition state; this observation excludes the possible formation of a binuclear intermediate in the activated complex [24-25].

Spectroscopic studies and test for intermediate complex formation

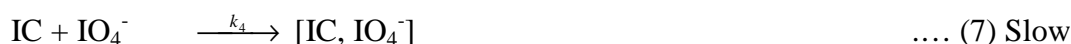
Acrylamide solution which did not polymerize either of the reactant alone was added to the partially oxidized reaction mixtures to initiate polymerization if free radicals were present in the reaction medium. No gel formation was observed even on the addition of excess methanol, indicating the probable absence of free radicals in the reaction mixture. The results of the spectroscopic studies indicated no significant shift from the absorption maxima of 610 nm characteristic of IC. This suggests that the formation of an intermediate complex during the reactions is very unlikely.

Based on the above results, it is evident that the reaction is operating through the outersphere mechanism. In aqueous medium, periodate has been shown to exist in different species [26]. These species include H_5IO_6^- , H_4IO_6^- , $\text{H}_3\text{IO}_6^{2-}$ and IO_4^- which are involved in the following equilibria;



However, H_4IO_6^- and IO_4^- are the dominant and reactive species in acid (pH 4.2) at $I = 1.0 \text{ mol dm}^{-3}$ [27].

From the results, the mechanism proposed below accommodates all the experimental findings for the reaction of IC with IO_4^- ;



From the acid dependence studies both the protonated form (HIO_4) and the unprotonated form (IO_4^-) of the oxidant is reacting at the rate determining step which imply that a two-termed rate law is expected. Therefore equations (7) and (9) are the rate determining steps

$$\text{Rate} = k_4[\text{IC}][\text{IO}_4^-] + k_6[\text{IC}][\text{HIO}_4] \quad \dots(11)$$

Since equation (6) is a fast rapid equilibrium, HIO_4 is in equilibrium with IO_4^- and H^+ and corresponds to the arrhenius concept;

$$K_3 = \frac{[\text{HIO}_4]}{[\text{IO}_4^-][\text{H}^+]} \quad \dots (12)$$

In this expression, $[\text{IO}_4^-]$ is not the total concentration of periodate ion but the equilibrium concentration. Therefore if $[\text{IO}_4^-]_t$ represent the total concentration of periodate ion, then

$$[\text{IO}_4^-]_t = [\text{IO}_4^-]_0 + [\text{HIO}_4] \quad \dots(13)$$

From equation 6

$$[\text{HIO}_4] = K_3[\text{IO}_4^-][\text{H}^+] \quad \dots(14)$$

$$[IO_4^-] = \frac{[HIO_4]}{K_3[H^+]} \quad \dots(15)$$

Substituting equation 15 into 13

$$[IO_4^-]_t = \frac{[HIO_4]}{K_3[H^+]} + [HIO_4] \quad \dots(16)$$

$$[IO_4^-]_t = \frac{[HIO_4] + K_3[H^+][HIO_4]}{K_4[H^+]} \quad \dots(17)$$

$$K_3[H^+][IO_4^-]_t = [HIO_4](1 + K_4[H^+]) \quad \dots(18)$$

$$[HIO_4] = \frac{K_3[H^+][IO_4^-]_t}{1 + K_4[H^+]} \quad \dots(19)$$

Substituting equation 19 into 11

$$Rate = k_4[IC][IO_4^-]_t + \left\{ \frac{k_6 K_3[H^+][IO_4^-]_t}{1 + K_4[H^+]} \right\} [IC] \quad \dots(20)$$

$$Rate = k_4[IC][IO_4^-]_t + \left\{ \frac{k_6 K_3[H^+]}{1 + K_4[H^+]} \right\} [IC][IO_4^-]_t \quad \dots(21)$$

$$Rate = \left\{ k_4 + \left(\frac{k_6 K_3[H^+]}{1 + K_4[H^+]} \right) \right\} [IO_4^-]_t [IC] \quad \dots(22)$$

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