Kinetics of Orthoperiodate Dimerisation studied by Temperature-jump Spectrophotometry

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Relaxation spectra have been obtained for the formation and decomposition of $H_2I_2O_{10}^{4-}$ at 25.0 ± 0.2 °C and I = 0.25 ± 0.01 mol dm^{-3} ($Na_2[SO_4]$) in the pH range 9.1—9.6 by the temperature-jump method. The observed relaxation times (in the range 50—200 μs, depending on concentration and pH) could be fitted to a scheme involving dimerisation reactions of $H_3IO_6^{2-}$ with itself (k_f), and with $H_2IO_6^{3-}$ (k_f'). The values (dm^3 mol^{-1} s^{-1}) determined by least-squares analysis of the pH dependence are: for $2H_3IO_6^{2-}$, $k_f = (1.54 \pm 0.04) \times 10^5$; and for $H_3IO_6^{2-} + H_2IO_6^{3-}$, $k_f' \leqslant (6.94 \pm 0.50) \times 10^6$. The value of k_f' is close to the diffusion-control limit. The results are interpreted in terms of a nucleophilic mechanism in which there is attack on the iodine by $-O^-$ followed by elimination.

THE existence of a dimeric periodate species in solution postulated by Buist and Lewis[1] in 1965 was confirmed in the same year when the crystal structure of $K_4I_2O_9$ was reported.[2] Although equilibria in periodate solutions have subsequently been extensively investigated, few kinetics studies on these systems have appeared, and none on the formation of the dimer. We have therefore undertaken this study in order to understand more about the periodate dimer in terms of its formation from monomeric species.

Interest in periodate solutions had been prompted by the realisation that IO_4^- hydrates to form $H_4IO_6^-$, which then acts as a polyprotic acid. Early studies on periodate solutions, involving extensive use of u.v. spectroscopy, showed that the species and equilibria in equations (1)—(4) were a necessary minimum to explain the protolytic and hydrolytic behaviour of aqueous periodate.[3] No deviations from the Lambert–Beer law were observed in these studies by Crouthamel *et al.* because they were not carried out in alkaline media. Dimerisation occurs in the pH range 8.8—11.0, where the predominant species are $H_3IO_6^{2-}$, $H_2IO_6^{3-}$, and the dimer.[4,5] It was suggested[4] that $H_3IO_6^{2-}$ dimerises to form $H_2I_2O_{10}^{4-}$.

$$H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^- \quad (1)$$

$$H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^{2-} \quad (2)$$

$$H_3IO_6^{2-} \rightleftharpoons H^+ + H_2IO_6^{3-} \quad (3)$$

$$H_4IO_6^- \overset{K_H}{\rightleftharpoons} IO_4^- + 2H_2O \quad (4)$$

From the structural studies, it has been inferred that the dimer is a double octahedron. The two iodines occupy octahedral centres, with two oxygens acting as bridges to hold them together. Three types of I–O bonds were identified on the basis of position and bond length: terminal I–O, bridging I–O, and I–OH.

The kinetics of IO_4^- hydration have been studied by temperature-jump[6,7] and ^{17}O n.m.r. spectroscopy.[8] The interconversion of IO_4^- and $H_4IO_6^-$ (meta- and ortho-periodate, respectively) is a rapid reaction, which may be explained by hydrogen-bonding effects between periodate and the waters of hydration.[6] These iodine-containing species may be compared with other oxo-anions such as vanadate and molybdate, which are also known to polymerise and form complexes.

The kinetics of dimerisation of chromate[9] and vanadate[10] have been reported, as well as the formation of molybdate heptamer and octamer.[11] These studies show that protonation of the monomer plays an important role in the dimerisation, especially if a tetrahedral-to-octahedral expansion of co-ordination is involved.[11] Likewise, the complexation of an oxo-anion is usually faster for protonated than for unprotonated monomer.[12,13] The periodates are especially interesting in this regard, since the reacting species are clearly octahedral, and further polymerisation is not a complicating factor as it is for many other oxo-anions, *viz.* borate,[14] molybdate, and tungstate.

EXPERIMENTAL

The temperature-jump apparatus used for this study has been previously described.[6] The temperature bath was adjusted such that the final temperature of the reactants was 25.0 ± 0.2 °C.

The pH of buffered solutions was measured by means of an Orion Research model 801a Digital Ionalyser. The Davies equation[15] was used to convert the hydrogen-ion activity into hydrogen-ion concentration using a mean activity coefficient of $\gamma_\pm = 0.710$. The standardisation of the indicators was done with the aid of a Beckman model 25 spectrophotometer. The traces indicating the changes in percentage transmittance with respect to time were recorded on an oscilloscope and subsequently photographed.

The periodate ions were derived from reagent-grade sodium metaperiodate (Fisher Scientific Co.) which was used without further purification. The solubility of the sodium metaperiodate is so low, requiring prolonged and vigorous shaking, that a fresh solution had to be prepared for each run. Sodium sulphate was used as the inert electrolyte that kept the ionic strength constant at 0.25 ± 0.01 mol dm^{-3}. Experiments were carried out in the presence of Li^+ and K^+. Use of these counter ions decreased the amplitude of the response. In the case of lithium the decrease was due to the insolubility of lithium periodate, which decreased the concentration of reactive species in solution. For potassium, the observed responses were small, but detectable, and appeared to result in the same relaxation times as in comparable sodium-containing solutions, so all experiments were then carried out in the presence of sodium ions.

A number of buffers were tried (*e.g.* phosphates and carbonate–bicarbonate), and were found inadequate because the polyprotic species $H_4IO_6^-$ neutralised the basic species contained in these buffers, resulting in unpredictable final pH values. Most of these buffers too made the periodate solution prematurely precipitate the dimer. In an effort then to eliminate the extraneous anions coming from these buffers, we decided to adjust the pH by the more difficult method of adding sodium hydroxide until the desired pH is reached. Using this method it was discovered that it needed about a 1 : 1 mol ratio of metaperiodate to sodium hydroxide to make the pH rise above 7.00, suggesting the availability of at least one ionisable proton among the periodate species in solution.

We can also infer that, at our final pH values of *ca.* 9.0, we have virtually no IO_4^- and $H_4IO_6^-$ in solution and appreciable amounts of $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$.

The establishment of the chemical equilibria in solution after the perturbation produced by the rapid increase in the temperature was followed by an accompanying shift in hydrogen-ion concentration. This shift was observed spectrophotometrically by adding an acid–base indicator (phenolphthalein) to the solution. A volume of 1.2 cm^3 of stock 2.0×10^{-3} mol dm^{-3} phenolphthalein per 100 cm^3 of periodate solution was used. The indicator was monitored at $\lambda = 550$ nm where the RCA IP28 photomultiplier is most sensitive.† The pK_a[16] value of this indicator is of comparable magnitude to the pH of the reactants, and is affected maximally by the change in hydrogen-ion concentration in the medium.

Buffered periodate solutions usually gave white precipitates on prolonged standing, and so all solutions were 'temperature-jumped' within 5 min of their preparation. We assume the white precipitate to be the dimer, for this method was the one used by *X*-ray crystallographers to prepare the dimer.[2] No appreciable temperature-jump effect was observed in the pH range 8.0—8.8. From pH 8.8—9.0 a small effect was clearly seen, but not large enough to analyse. Many other acid-base indicators were tried for higher pH values, where phenolphthalein could no longer respond. Most, like Nile Blue, Alkali Blue 6B, and Alizarin interacted with the periodate (probably in a reductive manner), for after standing for a while they lost colour.

RESULTS AND TREATMENT OF DATA

To evaluate the relaxation data it was necessary to calculate concentrations of each of the periodate species at any pH value and total sodium metaperiodate concentration. The equilibrium quotients in Table 1 were used for this purpose.

Substitution of the relevant equilibrium concentrations into the iodine mass-balance relation leads to an equation quadratic in $[H_3IO_6^{2-}]$. This equation was solved for the positive root by means of a computerised program. All other species were then calculated by employing the equilibria in Table 1.

TABLE 1

Equilibrium quotients used [a]

$K_2 = [H_3IO_6^{2-}]_e[H^+]_e/[H_4IO_6^-]_e = 8.93 \times 10^{-9}$ mol dm^{-3}

$K_3 = [H_2IO_6^{3-}]_e[H^+]_e/[H_3IO_6^{2-}]_e = 2.50 \times 10^{-12}$ mol dm^{-3}

$K_H = [IO_4^-]_e/[H_4IO_6^-]_e = 40.0$

$K_D = [H_2I_2O_{10}^{4-}]_e/[H_3IO_6^{2-}]_e^2 = 141.0$ dm^3 mol^{-1}

$K_W = [H^+]_e[OH^-]_e = 1.98 \times 10^{-14}$ mol^2 dm^{-6} [b]

$K_I = [in^-]_e[H^+]_e/[Hin] = 2.513 \times 10^{-9}$ mol dm^{-3} [b,c]

[a] At 25 °C and $I = 0.1$ mol dm^{-3} (KCl). Data from ref. 4 unless stated otherwise. [b] From ref. 16. [c] The acid–base indicator, which in this case was phenolphthalein, is represented as Hin.

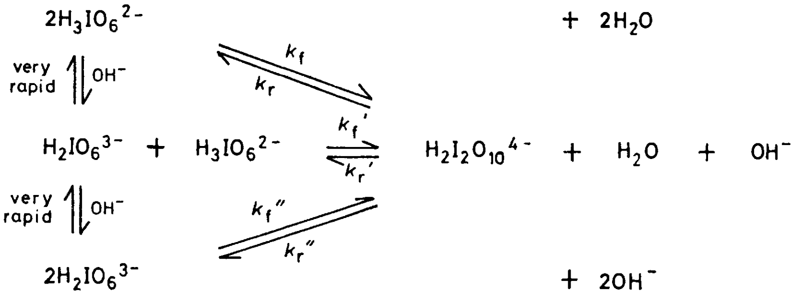
In deriving the expression for the reciprocal of the relaxation time τ, simple mechanisms (5a, b, c) were first postulated in which formation of the dimer was a consequence of a single reaction between two reactive species. The reciprocal of the relaxation time for each of

$$2H_3IO_6^{2-} \rightleftharpoons H_2I_2O_{10}^{4-} + 2H_2O \quad (5a)$$

$$H_3IO_6^{2-} + H_2IO_6^{3-} \rightleftharpoons H_2I_2O_{10}^{4-} + H_2O + OH^- \quad (5b)$$

$$2H_2IO_6^{3-} \rightleftharpoons H_2I_2O_{10}^{4-} + 2OH^- \quad (5c)$$

the reactions (5a, b, c) is of the form $1/\tau = 4k_f^*[H_3IO_6^{2-}]_e + k_r^*$ where subscript e denotes equilibrium concentrations, and k_f^* and k_r^* are composite rate constants containing concentrations and the equilibrium quotients of the protolytic reactions, (1)—(3), which are so fast that they are in equilibrium during the adjustment of reaction (5).[17] At our pH values there is very little $H_4IO_6^-$, so that the hydrolysis reaction (4) does not interfere.[6] The values of k_f^* and k_r^* determined by this treatment were inconsistent with the dimerisation equilibrium constant K_D.



$$\begin{tikzcd}[column sep=small] 2H_3IO_6^{2-} \arrow[d, shift left, "OH^-"] \arrow[rrd, shift left, "k_f"] & & & & + 2H_2O \\ H_2IO_6^{3-} \arrow[u, shift left, "\text{very rapid}"] \arrow[d, shift left, "OH^-"] + H_3IO_6^{2-} \arrow[rr, shift left, "k_f'"] & & H_2I_2O_{10}^{4-} \arrow[ll, shift left, "k_r'"] \arrow[llu, shift left, "k_r"] \arrow[lld, shift left, "k_r''"] & + H_2O & + OH^- \\ 2H_2IO_6^{3-} \arrow[u, shift left, "\text{very rapid}"] \arrow[rru, shift left, "k_f''"] & & & & + 2OH^- \end{tikzcd} \quad (6)$$

A more complete mechanism (6) was next postulated in which there are two dimerising species, namely $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. In deriving the $1/\tau$ expression for reaction (6), we have used the approach taken by Cavasino[18] in his analysis of metal–dibasic acid ligand-complexation reactions. A detailed derivation is given in the Appendix. The rate equation for dimer formation according to mechan-

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† Phenolphthalein was most ideal for this experiment because in basic medium it has a $\lambda_{max.}$ of 553 nm. The indicator absorbance was about 0.35 in the temperature-jump experiments.

ism (6) is as in (7). After applying mass-balance and electroneutrality relations, and expanding the instantaneous

$$d[H_2I_2O_{10}{}^{4-}]/dt = k_f[H_3IO_6{}^{2-}]^2 + k_f'[H_3IO_6{}^{2-}][H_2IO_6{}^{3-}] + k_f''[H_2IO_6{}^{3-}]^2 - k_r[H_2I_2O_{10}{}^{4-}] - k_r'[H_2I_2O_{10}{}^{4-}][OH^-] - k_r''[H_2I_2O_{10}{}^{4-}][OH^-]^2 \quad (7)$$

concentrations around equilibrium, this approach leads to expression (8) for $1/\tau$. The concentration and hydrogen-ion

$$1/\tau = k_fA + k_f'([OH^-]_e/K_B)(A + N) + k_f''([OH^-]_e{}^2/K_B{}^2)(A + 2N) \quad (8)$$

dependent terms A and N are given in the Appendix, and $K_B = [H_3IO_6{}^{2-}]_e[OH^-]_e/[H_2IO_6{}^{3-}]_e = K_w/K_3$.

The ratio N/A = constant = 0.4, so that, at constant pH, $1/\tau = k^{app.}A$, where $k^{app.}$ is given by equation (9). A

$$k^{app.} = k_f + 1.4\{k_f'([OH^-]_e/K_B) + 1.28\ k_f''([OH^-]_e{}^2/K_B{}^2)\} \quad (9)$$

plot of $1/\tau$ against A should give a straight line, of slope $k^{app.}$, and pass through the origin.

The results of the different concentration dependences taken at pH values 9.11, 9.21, and 9.56 are shown in Tables 2, 3, and 4 respectively. In the limit that $k_f'' = 0$, the data should fit a plot of $k^{app.}$ against $[OH^-]_e/K_B$; similarly, if k_f' is neglected, the plot follows $k^{app.}$ against $[OH^-]_e{}^2/K_B{}^2$. Assumption of $k_f' = 0$ yields a value of $k_f'' = 8 \times 10^8$ dm^3 mol^{-1} s^{-1} which exceeds the diffusion-controlled limit by about three orders of magnitude.[19] Thus, this pathway leading to the dimer was found to be unimportant under these experimental conditions.

TABLE 2

Concentration-dependence runs at pH 9.11

10^2[NaIO$_4$] / mol dm^{-3}	10^2A / mol dm^{-3}	$10^{-3}(1/\tau)$ * / s^{-1}
5.0	3.77	6.86
6.0	4.05	7.52
7.0	4.43	8.25
8.0	4.80	8.83
9.0	5.21	9.48
10.0	5.73	10.7
11.0	6.07	11.2
12.0	6.41	12.8

Average $k^{app.}$ = (1.84 ± 0.04) × 10^5 dm^3 mol^{-1} s^{-1}

* An average value from at least four different temperature jumps at each concentration. Indicator used is phenolphthalein.

TABLE 3

Concentration-dependence runs at pH 9.21

10^2[NaIO$_4$] / mol dm^{-3}	10^2A / mol dm^{-3}	$10^{-3}(1/\tau)$ * / s^{-1}
5.0	4.03	7.71
6.0	4.49	7.98
7.0	4.91	8.95
8.0	5.31	10.6
9.0	5.69	10.7
10.0	6.06	11.2
11.0	6.40	11.8
12.0	6.73	13.9

Average $k^{app.}$ = (1.96 ± 0.04) × 10^5 dm^3 mol^{-1} s^{-1}

* An average value from at least four different temperature jumps at each concentration. Indicator used is phenolphthalein.

Plots of $1/\tau$ against A and calculation of relative errors were done with the aid of a weighted linear least-squares computer program. In each of the plots of concentration dependence the only points weighted were the origins.

TABLE 4

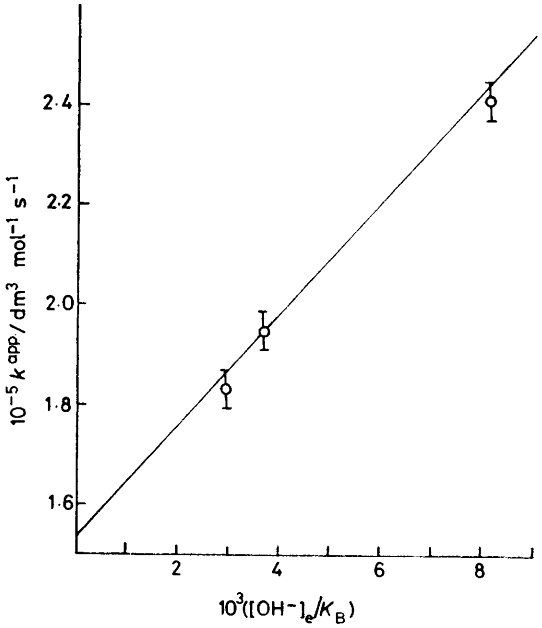
Concentration-dependence runs at pH 9.56

10^2[NaIO$_4$] / mol dm^{-3}	10^2A / mol dm^{-3}	$10^{-3}(1/\tau)$ * / s^{-1}
5.0	4.71	11.2
6.0	5.20	12.7
7.0	5.61	13.6
8.0	6.06	15.4
9.0	6.45	15.3
10.0	6.82	16.7
11.0	7.18	18.2
12.0	7.55	18.5

Average $k^{app.}$ = (2.42 ± 0.04) × 10^5 dm^3 mol^{-1} s^{-1}

* An average value from at least four different temperature jumps at each concentration. Indicator used is phenolphthalein.

From the plot of $k^{app.}$ *vs.* $[OH^-]_e/K_B$ (Figure) the following values (dm^3 mol^{-1} s^{-1}) were obtained: $k_f = (1.54 \pm 0.04) \times 10^5$ and $k_f' = (6.94 \pm 0.50) \times 10^6$.



Variation of $k^{app.}$ with [OH$^-$]. The vertical bars denote the relative error reported in Tables 2—4

DISCUSSION

Condensation of certain oxo-anions, especially those containing heavy central atoms, is well known.[20] Experimental descriptions of monomer–polymer equilibria and crystal structures have been fairly well documented, but the kinetics and mechanism of the condensation process are far from being adequately described. It is recognised that the size of the central ion, the structures of monomer and polymer, the degree of protonation, and the type of counter ion present are important factors to consider.[21] However, the relative importance of each factor is difficult to assess.

The dimerisation of periodate in aqueous solution allows us to concentrate on one of these effects, the degree of monomer protonation, since the structure around the central iodine remains octahedral, and counter-ion variation does not affect the kinetics. Dimerisation occurs only for protonated periodate ions; however, our results show that there appears to be an optimal degree of protonation.

The most protonated monomeric species, $H_4IO_6^-$, tends to dimerise slowly, or not at all. Since the rate of dimerisation of this species does not appear to interfere with its dehydration,[6-8] the rate constant for $H_4IO_6^-$ dimerisation should be $<5 \times 10^3$ dm^3 mol^{-1} s^{-1}. The species $H_3IO_6^{2-}$ has a dimerisation rate constant of 1.54×10^5 dm^3 mol^{-1} s^{-1}, which is well below the diffusional limit of about 10^8 dm^3 mol^{-1} s^{-1} for reactants of this charge type. The upper limit of the rate constant for $H_3IO_6^{2-} + H_2IO_6^{3-}$, 6.94×10^6 dm^3 mol^{-1} s^{-1}, is very close to the estimated diffusional limit of about 10^7 dm^3 mol^{-1} s^{-1} for a reaction between similarly charged 2—, 3— ions at a finite ionic strength.[19] The diffusional limit of a reaction between two periodate species with charge 3— on each would be about 10^4 dm^3 mol^{-1} s^{-1}.

The ion HIO_6^{4-}, should it prove to exist, would be expected to be an exceedingly weak acid; for example, by applying Pauling's rules to successive dissociation for the acids $H_iIO_6^{(5-i)-}$, $i = 4, 3, 2,$ or 1.[22] The diffusion-controlled rate constant for reaction partners bearing charges of 4— each would be many orders of magnitude less than the limit for a 3—, 3— reaction due to the exponential nature of the coulombic term in the Debye equation.[19] Thus, in the pH range of this study, dimerisation by HIO_6^{4-} could not be detected, as a result of its very low concentration and low rate constant for dimerisation relative to k_f and k_f'.

Both $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ are pseudo-octahedral in structure,* with the dimer being a double octahedron. For these ions, $k_f < k_f'$ in analogy with the formation of a bis(catecholato)molybdate complex,[12] where the reactant mono complex and the product bis complex are pseudo-octahedral.

The reactivity pattern $k_f < k_f'$ can be explained by a nucleophilic mechanism: $H_2IO_6^{3-}$ is a better nucleophile than $H_3IO_6^{2-}$. Initial attack on the iodine is by nucleophilic $^-O^-$ followed by elimination. The two oxygen bridges that hold the dimer together would be formed rapidly, but not necessarily simultaneously. After one bridge is made the chances are statistically enhanced for the second bridge being formed. Thus, the nucleophilic factor would be more important than ease of elimination, since hydroxide is not as good a leaving group as water.

The parameters for the reverse reaction can be calculated as follows: $k_r = k_f/K_D = 1.52 \times 10^3$ s^{-1}, and $k_r' = k_f'/K_DK_B = 1.23 \times 10^7$ dm^3 mol^{-1} s^{-1}. These reactions appear to be relatively rapid compared with the decomposition of dichromate[9] and decavanadate,[23] but of similar magnitude to the decomposition of heptamolybdate.[11,24] This more rapid dissociation into monomer may reflect the larger size of the central iodine and molybdenum ions compared with vanadium and chromium, which allows the attacking hydroxide or water molecules easier access to the bridging bonds.

APPENDIX

After a small perturbation, but still close to equilibrium, the relation (A1) holds for all the species in solution, where

$$[H_2I_2O_{10}^{4-}] = [H_2I_2O_{10}^{4-}]_e + \Delta[H_2I_2O_{10}^{4-}], \textit{ etc.} \qquad (A1)$$

Δ denotes a small increment. Substituting (A1) into (7), expanding, neglecting terms quadratic in Δ, and utilising the equilibrium relation $d[H_2I_2O_{10}^{4-}]_e/dt = d[H_3IO_6^{2-}]_e/dt = d[H_2IO_6^{3-}]_e/dt = 0$ yields (A2).

$$\begin{aligned} d(\Delta[H_2I_2O_{10}^{4-}])/dt = -\Delta[H_2I_2O_{10}^{4-}]/\tau = 2k_f[H_3IO_6^{2-}]_e\Delta[H_3IO_6^{2-}] + k_f'([H_3IO_6^{2-}]_e\Delta[H_2IO_6^{3-}] + \\ [H_2IO_6^{3-}]_e\Delta[H_3IO_6^{2-}]) + 2k_f''[H_2IO_6^{3-}]_e\Delta[H_2IO_6^{3-}] - k_r\Delta[H_2I_2O_{10}^{4-}] - k_r'([OH^-]_e\Delta[H_2I_2O_{10}^{4-}] + \\ [H_2I_2O_{10}^{4-}]_e\Delta[OH^-]) - k_r''[OH^-]_e(2[H_2I_2O_{10}^{4-}]_e\Delta[OH^-] + [OH^-]_e\Delta[H_2I_2O_{10}^{4-}]) \end{aligned} \qquad (A2)$$

$$K_D = k_f/k_r \qquad (A3a)$$

$$K_DK_B = k_f'/k_r' \qquad (A3b)$$

$$K_DK_B^2 = k_f''/k_r'' \qquad (A3c)$$

$$\Delta[H_2I_2O_{10}^{4-}] = -(\Delta[H_3IO_6^{2-}] + \Delta[H_2IO_6^{3-}])/2 \qquad (A4)$$

$$\Delta[Hin] = -\Delta[in^-] = \frac{[in^-]_e\Delta[H^+]}{K_I + [H^+]} = \beta \qquad (A5)$$

Using the mass-action relations (A3) and mass-balance relations (A4), and (A5), where we assume the concentration of $H_4IO_6^-$ is negligible, equation (A2) becomes (A6). By rearranging the terms, we obtain (A7). By substituting (A8) and (A9) in (A7), expression (A10) results which is equation (8).

$$\begin{aligned} \frac{1}{\tau} = \frac{4k_f[H_3IO_6^{2-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])} + \frac{4k_f''[H_2IO_6^{3-}]_e}{1 + (\Delta[H_3IO_6^{2-}]/\Delta[H_2IO_6^{3-}])} + \\ 2k_f'\left\{\frac{[H_3IO_6^{2-}]_e}{1 + (\Delta[H_3IO_6^{2-}]/\Delta[H_2IO_6^{3-}])} + \frac{[H_2IO_6^{3-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])}\right\} \\ + k_r + k_r'[OH^-]_e + k_r''[OH^-]_e^2 - \frac{2k_r'[H_2I_2O_{10}^{4-}]_e}{(\Delta[H_3IO_6^{2-}] + \Delta[H_2IO_6^{3-}])/\Delta[OH^-]} - \frac{4k_r''[H_2I_2O_{10}^{4-}]_e[OH^-]_e}{(\Delta[H_3IO_6^{2-}]\Delta[H_2IO_6^{3-}])/\Delta[OH^-]} \end{aligned} \qquad (A6)$$

From the mass-balance and equilibrium relations, the ratio $\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}]$ can be calculated as in (A11). The ratio $\Delta[OH^-]/\Delta[H_3IO_6^{2-}]$ is calculated using the electroneutrality relation (A12) (where the Na^+ ions arise from both the $Na[IO_4]$ and $Na[OH]$) and from (A13) (from

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* The periodate di- and tri-anions may be dehydrated, as inferred from a comparison of acid strengths with cyclic periodate esters (G. J. Buist, C. A. Bunton, and W. C. P. Hipperson, *J. Chem. Soc.* (*B*), 1971, 2128), in which case the central iodine would be five-co-ordinated.

$$\frac{1}{\tau} = k_f \left\{\frac{4[H_3IO_6^{2-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])} + \frac{1}{K_D}\right\} + k_f' \left(\frac{2[H_3IO_6^{2-}]_e\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}]}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])} + \right.$$
$$\frac{[OH^-]}{K_B}\left\{\frac{2[H_3IO_6^{2-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])}\right\} + \left.\frac{1}{K_D} - \frac{2[H_3IO_6^{2-}]_e{}^2}{(\Delta[H_3IO_6^{2-}] + \Delta[H_2IO_6^{3-}])/\Delta[OH^-]}\right) +$$
$$k_f''\left(\frac{4[H_2IO_6^{3-}]_e}{1 + (\Delta[H_3IO_6^{2-}]/\Delta[H_2IO_6^{3-}])} + \frac{[OH^-]_e^2}{K_B^2}\left\{\frac{1}{K_D} - \frac{4[H_3IO_6^{2-}]_e^2}{(\Delta[H_3IO_6^{2-}] + \Delta[H_2IO_6^{3-}])/\Delta[OH^-]}\right\}\right) \quad \text{(A7)}$$

$$A = \frac{4[H_3IO_6^{2-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])} + \frac{1}{K_D} \quad \text{(A8)}$$

$$N = \frac{2[H_3IO_6^{2-}]_e}{1 + (\Delta[H_2IO_6^{3-}]/\Delta[H_3IO_6^{2-}])}\left(\frac{K_B}{[OH^-]_e}\frac{\Delta[H_2IO_6^{3-}]}{\Delta[H_3IO_6^{2-}]} - \frac{[H_3IO_6^{2-}]_e\Delta[OH^-]}{[OH^-]_e\Delta[H_3IO_6^{2-}]} - 1\right) \quad \text{(A9)}$$

$$1/\tau = k_fA + k_f'([OH^-]_e/K_B)(A + N) + k_f''([OH^-]_e^2/K_B^2)(A + 2N) \quad \text{(A10)}$$

$$\frac{\Delta[H_2IO_6^{3-}]}{\Delta[H_3IO_6^{2-}]} = \frac{[H_2IO_6^{3-}]_e}{[H_3IO_6^{2-}]_e}\left\{1 - \frac{[H_2IO_6^{3-}]_e - (1 + K_H)[H_4IO_6^-]_e}{(1 + \beta)[H^+] + 2[H_2IO_6^{3-}]_e + (1 + K_H)[H_4IO_6^-]_e - [H_2IO_6^{3-}]_e}\right\} \quad \text{(A11)}$$

$$[H^+] + [Na^+] = [OH^-] + 2[H_3IO_6^{2-}] + 3[H_2IO_6^{3-}] + 4[H_2I_2O_{10}^{4-}] \quad \text{(A12)}$$

$$\Delta[OH^-] = -([OH^-]_e/[H^+])_e\Delta[H^+] \quad \text{(A13)}$$

$$\frac{\Delta[OH^-]}{\Delta[H_3IO_6^{2-}]} = \frac{[OH^-]_e}{[H^+]_e}$$
$$\left\{\frac{([H_2IO_6^{3-}]_e/[H_3IO_6^{2-}]_e) - (1 + K_H)[H_4IO_6^-]_e/[H_3IO_6^{2-}]_e}{1 + ([OH^-]_e/[H^+]_e) + \beta + 2([H_2IO_6^{3-}]_e/[H^+]) + (1 + K_H)([H_4IO_6^-]_e/[H^+]) - ([H_2IO_6^{3-}]/[H^+]_e)}\right\} \quad \text{(A14)}$$

$[H^+]_e[OH^-]_e = K_w$). Whereupon, we obtain (A14). In our case, $N/A = 0.4$ = constant, thus expression (A15) results which has the same form as equation (9).

$$1/\tau = \{k_f + 1.4\,k_f'([OH^-]_e/K_B) + 1.8k_f''([OH^-]_e^2/K_B^2)\}A \quad \text{(A15)}$$

The authors gratefully acknowledge partial support from the Institute of General Medical Sciences, U.S. Public Health Service, and from the African-American Institute for financial assistance (to R. H. S.).

[9/1903 *Received*, 30*th November*, 1979]

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