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Determination of the nature of the diperiodatocuprate(III) species in aqueous alkaline medium through a kinetic and mechanistic study on the oxidation of iodide ion

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Abstract

The nature of the diperiodatocuprate(III) (DPC) species present in aqueous alkaline medium has been investigated by a kinetic and mechanistic study on the oxidation of iodide by DPC. The reaction kinetics were studied over the 1.0×10^{-3}–0.1 mol dm^{-3} alkali range. The reaction order with respect to DPC, as well as iodide, was found to be unity when $[\mathrm{DPC}] \ll [\mathrm{I}^-]$. In the 1.0×10^{-3}–1.0×10^{-2} mol dm^{-3} alkali region, the rate decreased with increase in the alkali concentration and a plot of the pseudo-first order rate constant, k *versus* $1/[\mathrm{OH}^-]$ was linear. Above 5.0×10^{-2} mol dm^{-3}, a plot of k *versus* $[\mathrm{OH}^-]$ was also linear with a non-zero intercept. An increase in ionic strength of the reaction mixtures showed no effect on k at low alkali concentrations, whereas at high concentrations an increase in ionic strength leads to an increase in k. A plot of $1/k$ *versus* [periodate] was linear with an intercept in both alkali ranges. Iodine was found to accelerate the reaction at the three different alkali concentrations employed. The observed results indicated the following equilibria for DPC.

$$[\mathrm{Cu(H_2IO_6)_2}]^{3-} \rightleftharpoons [\mathrm{Cu(H_2IO_6)}] + \mathrm{H_2IO_6^{3-}}$$
$$[\mathrm{Cu(H_2IO_6)}] + \mathrm{OH^-} \rightleftharpoons [\mathrm{Cu(HIO_6)}]^- + \mathrm{H_2O}$$

A suitable mechanism has been proposed on the basis of these equilibria to account for the kinetic results.

Introduction

Diperiodatocuprate(III) was first synthesized by Malatesta [1] more than half a century ago. A considerable amount of research has been reported since on the synthesis, structural determination and analytical applications of this complex [2–5]. However, some of the results are mutually contradictory regarding the extent of protonation of the DPC species in alkaline solutions, and the various equilibria existing between them. Furthermore, except for a few literature reports [6–10] little work has been devoted to kinetic and mechanistic studies on DPC oxidations. We have recently studied the kinetics of oxidation of sulfite ion by DPC (N. Sridevi, *et al.* unpublished), which resulted in the conclusion that the equilibria assumed earlier for the DPC species could well be in error. In order to obtain further insight, we have carried out a kinetic study on the oxidation of iodide by DPC. As a result we obtained firm evidence for the extent of protonation of the DPC species existing over a wide range of alkali concentrations. We now propose a set of new equilibria for the various DPC species in alkaline solutions, which may explain the results of the present mechanistic investigation as well as those reported earlier.

Experimental

All the chemicals employed were of analytical grade purity. Solutions of diperiodatocuprate(III) were prepared weekly and estimated according to the literature procedures [9]. Solutions of iodide and periodate were prepared and estimated daily. All kinetic runs were carried out at 30 °C unless stated otherwise. The reaction mixtures were initiated with DPC and were monitored spectrophotometrically by measuring the absorbance of DPC at 445 nm against suitable blanks, on a Shimadzu 160A UV-visible spectrophotometer. Except for iodine variation studies, time *versus* concentration data obtained was analyzed by integral methods. For iodine variations, the initial rate method was employed. A software, "AXUM", (2.0, Trimetrix) was used for the data analysis and for plotting the graphs.

Results and discussion

The oxidation of iodide by diperiodatocuprate(III) was studied over a wide range of alkali concentrations, from 1.0×10^{-3} to 0.1 mol dm^{-3}. All kinetic runs were performed employing iodide in at least ten-fold excess over DPC. Under these conditions, plots of log[DPC] *versus* time were linear for at least two half-lives,

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indicating pseudo-first order behaviour with respect to DPC. The values of the pseudo-first order rate constant, *k*, obtained from slopes of such plots for various kinetic runs carried out are presented in Table 1.

A plot of the pseudo-first order rate constant, *k*, obtained at different initial iodide concentrations against the corresponding iodide concentration, was linear passing through the origin, as shown in Figure 1, indicating the order with respect iodide also to be unity.

The observed first order with respect to iodide and DPC indicates that both are involved in the rate-determining step. It is well known that iodide exists as a uninegative species in aqueous solutions, but the DPC species could not be determined unambiguously. Diperiodatocuprate(III) has been prepared by oxidation of copper(II) in an alkaline medium in the presence of periodate, employing different oxidizing agents [2]. All authors who prepared this complex have agreed that it contains copper and periodate in a 1:2 ratio. However, there appears to be a controversy regarding the extent of protonation of the complex. Malatesta [1] was the first to synthesize DPC in solid form, and proposed it to be a six coordinated complex, $Na_5H_2Cu(IO_6)_2$. This formula indicates that two periodate entities are coordinated to copper, making it a diperiodato complex. However, it is not clear whether the protons are utilized to satisfy the primary valency of the complex ion, in which case the complex ion bears an overall charge of 7^-, or whether the protons exist within the coordination sphere bound to the oxygen atoms of the periodate ions, in which case the overall charge on the complex ion is 5^-. Later, Balikungeri [3] made further studies on this complex through chemical analysis, i.r. spectroscopy and conductivity measurements, in order to establish the structure as $[Cu(HIO_6)_2]^{5-}$. This structure confirms that the hydrogen atoms exist within the coordination sphere. An extensive study on this complex was made by Lister [4] who reported that two different periodato complexes are formed when uncomplexed copper ion $[Cu(OH)_4]^-$ reacts with periodate. In one of these, the metal-to-periodate ratio is 1:1, while in the other it is 1:2. Lister further suggested that the 1:1 complex is less stable than the 1:2 complex and that the latter exists independently of the alkali concentration. Rozovskii [5] studied the formation and decomposition of the copper(III) periodate complex in alkaline medium. He proposed that the rate of reduction of DPC is inversely proportional to [periodate]. The results obtained by Lister and Rozovskii indicate the existence of different diperiodatocuprate(III) species in equilibria with alkali and periodate, which thus cannot be explained by the single formulation, $[Cu(HIO_6)_2]^{5-}$ assumed by Balikungeri *et al.* [3]

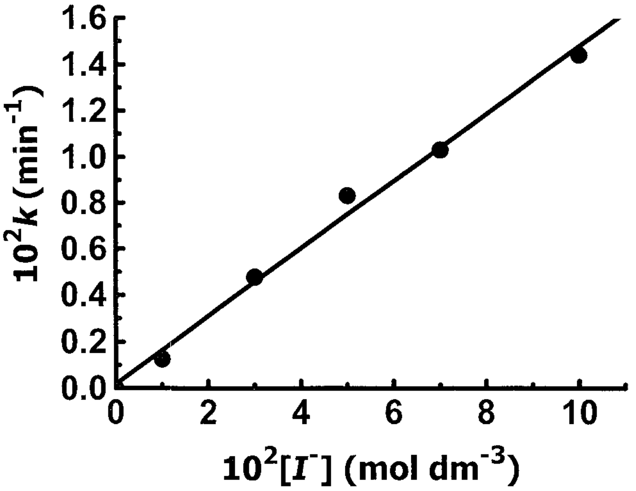

Fig. 1. Plot of *k versus* $[I^-]$.

Table 1. Effect of iodide, periodate, alkali and ionic-strength, μ on the pseudo-first order rate constant, *k*. [DPC] = 5.0×10^{-5} mol dm^{-3} and temperature = 303 K

10^2 [iodide] (mol dm^{-3})	10^4 [periodate] (mol dm^{-3})	10^2 [alkali] (mol dm^{-3})	10 [μ]	10^3 *k* (min^{-1})
1.0	1.0	1.0	1.1	1.3
3.0	1.0	1.0	1.1	4.8
5.0	1.0	1.0	1.1	8.3
7.0	1.0	1.0	1.1	10.3
10.0	1.0	1.0	1.1	14.4
10.0	1.0	1.0	1.1	13.8
10.0	4.0	1.0	1.1	7.4
10.0	6.0	1.0	1.1	5.4
10.0	8.0	1.0	1.1	4.6
10.0	1.0	10.0	2.0	7.7
10.0	6.0	10.0	2.0	3.9
10.0	8.0	10.0	2.0	3.2
10.0	10.0	10.0	2.0	2.9
10.0	1.0	0.1	2.0	55.4
10.0	1.0	0.3	2.0	26.8
10.0	1.0	0.5	2.0	17.9
10.0	1.0	0.7	2.0	17.4
10.0	1.0	1.0	2.0	13.9
10.0	1.0	3.0	2.0	6.5
10.0	1.0	5.0	2.0	6.4
10.0	1.0	7.0	2.0	6.9
10.0	1.0	10.0	2.0	7.7
10.0	1.0	10.0	3.0	9.8
10.0	1.0	10.0	4.0	10.7
10.0	1.0	10.0	6.0	11.8
10.0	1.0	10.0	8.0	14.5
10.0	1.0	10.0	10.0	16.3
10.0	1.0	1.0	1.1	13.5
10.0	1.0	1.0	2.0	12.4
10.0	1.0	1.0	3.0	12.1
10.0	1.0	1.0	5.0	12.0
10.0	1.0	1.0	7.0	13.1

Sethuram *et al.* [6–9] made kinetic studies of diperiodatocuprate(III) oxidations in alkaline medium. In most of their work they observed an increase in reaction rate with an increase in alkali concentration, and a decrease in rate with that of periodate which was attributed to a change in the complex species. The alkali effect on the reaction rate indicated a deprotonation equilibrium for the DPC species, while the periodate effect clearly indicated that a dissociation equilibrium exists for DPC species, through which the diperiodato complex dissociates to give a monoperiodato species. The question then to be addressed is, whether the dissociation of the diperiodato species occurs prior to deprotonation, such that the monoperiodato species formed undergoes deprotonation, or deprotonation occurs prior to the dissociation. In the first case, two monoperiodato species and one diperiodato species exist in solution, while in the second one monoperiodato species and two diperiodato species should exist in solution. Considering the observations of Lister, Sethuram *et al.* assumed the latter to be the case, *i.e.* that the alkali effect could be attributed to a reaction between alkali and diperiodatocuprate(III) to form a deprotonated diperiodato species, and the periodate effect to dissociation of the deprotonated diperiodato species to give a monoperiodato species. These results again cannot be explained by employing the formula $[Cu(HIO_6)_2]^{5-}$ for the diperiodato species, since it is unlikely that such a species could react with a negatively charged hydroxide ion, or liberate a proton. Furthermore, the periodate ion is known to exist as $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$ in strongly alkaline medium. Therefore, when $[Cu(HIO_6)_2]^{5-}$ dissociates to give a monoperiodate species, the HIO_6^{4-} species liberated should be protonated. Such protonation should give rise to an inverse alkali effect on the rate of oxidation by diperiodatocuprate(III) along with an inverse order in periodate, thus contradicting the work of Sethuram *et al.* Probably a species of the type $[Cu(HIO_6)_2]^{5-}$ exists only at extremely high alkali concentrations and is protonated to a different extent at low alkali concentrations.

Sethuram *et al.* considered the extent of periodate protonation in the complex to be undetermined, formulated the complex as $Cu(HL)_2$ and represented the equilibria existing for diperiodatocuprate(III) in solution as:

$$Cu(HL)_2 + OH^- \rightleftharpoons Cu(HL)L + H_2O$$
$$Cu(HL)L \rightleftharpoons Cu(HL) + L$$

For the oxidation of sulfite by diperiodatocuprate(III), we observed that the rate of reaction increased with ionic strength and that an inverse first order dependence on periodate and fractional order dependence on alkali exist. Further, a plot of *k versus* $[OH^-]$ was found to be linear with an intercept. Although the effect of alkali is similar to the observation by Sethuram *et al.*, by assuming the equilibria proposed by them for the DPC species, we could not explain the fact that the plot of *k versus* $[OH^-]$ was linear with an intercept. Furthermore, periodate exists as an equilibrium mixture of $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$, a fact which was ignored by Sethuram *et al.* in some of their reactions and considered in others. This lead us to the conclusion that the equilibria proposed by Sethuram *et al.* may not be correct. Our results could be explained by assuming the equilibria,

$$Cu(HL)_2 \rightleftharpoons Cu(HL) + HL$$
$$HL + OH^- \rightleftharpoons L + H_2O$$

However, in this study the extent of protonation of the DPC species could not be determined conclusively, since to determine the actual diperiodatocuprate(III) species it is necessary to study its reaction with another charged species over a wide range of alkali concentrations.

Unlike the case of sulfite, the alkali dependence of *k* for the present reaction was found to be complex. It is clear from the plot of *k versus* alkali shown in Figure 2 that, with an increase in alkali concentration, *k* initially decreased steeply and then slowly increased. In the 1.0×10^{-3}–1.0×10^{-2} mol dm^{-3} region of alkali, the decrease in *k* with an increase in alkali can be expressed by the empirical equation,

$$k = k'\{a + b[OH^-]\}/c[OH^-]$$

where *a*, *b* and *c* are constants, since a plot of *k versus* $1/[OH^-]$ was found to be linear with an ordinate intercept (Figure 3). The oxidation of sulfite could not be studied in this region. In alkali concentrations greater than 0.05 mol dm^{-3}, the plot of *k versus* $[OH^-]$ was linear with an intercept (Figure 4). In this region the alkali dependence may be expressed as:

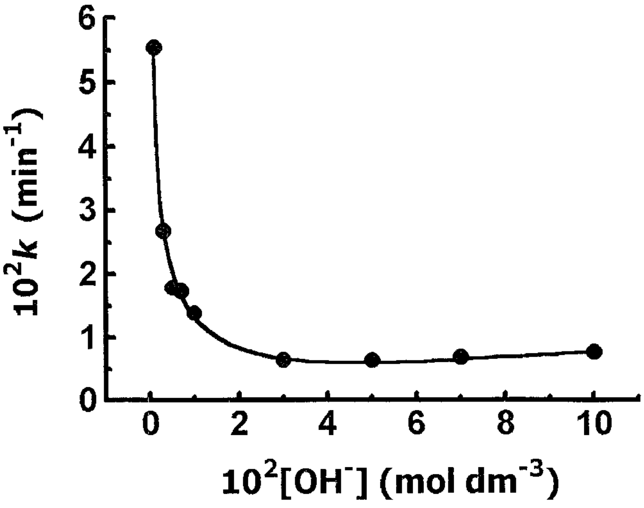

Fig. 2. Plot of *k versus* $[OH^-]$, in the entire alkali range.

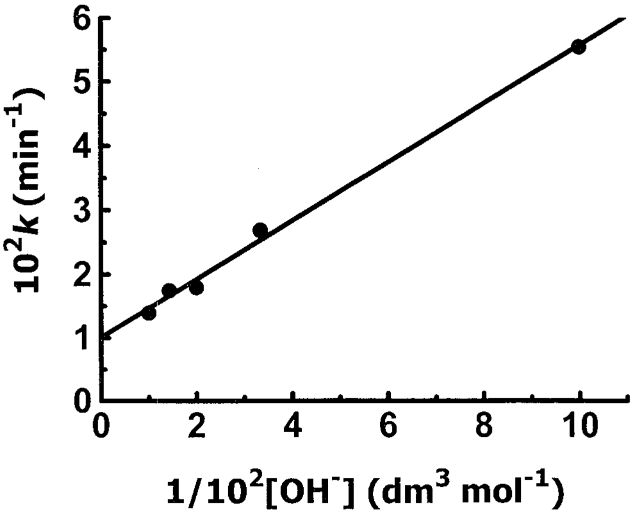

Fig. 3. Plot of *k versus* $1/[OH^-]$, in the low alkali concentration range.

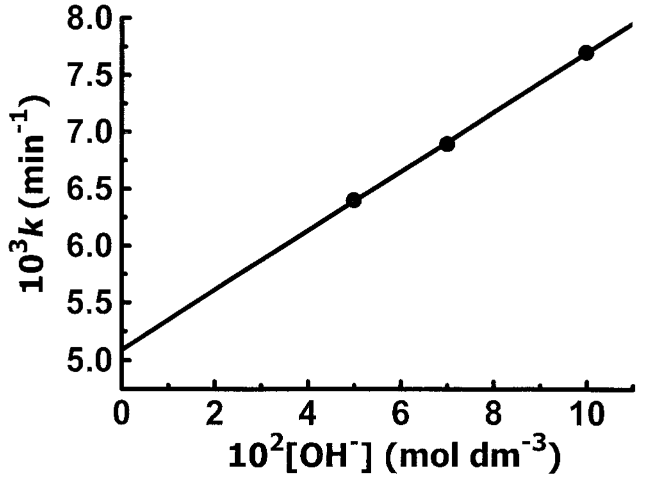

Fig. 4. Plot of k *versus* [OH$^-$], in the high alkali concentration range.

$$k = m + n[\mathrm{OH}^-]$$

If these two equations are combined, a general equation of the form

$$k = \{p + q[\mathrm{OH}^-] + r[\mathrm{OH}^-]^2\}/s[\mathrm{OH}^-] \quad (1)$$

may be obtained, where p, q, r and s are constants. This general equation accounts for the effect of alkali on k over the entire range studied, and the plot obtained for k *versus* [OH$^-$] (Figure 2).

Although from Figure 2 the increase in rate with increase in alkali concentration in the high concentration range appears to be small, it is evident from Figure 4, which is a reproduction of the same with a better scale, that the reaction rate constant increased almost one and a half times, which is much larger than the experimental accuracy of ±8% for our data. Furthermore, this study was made in a medium of constant ionic strength. Thus, it is clear that although the increase in k with alkali concentration appears to be small at high alkali concentration regions, it cannot be due to experimental error or other medium effects which are usually marginal.

In addition to such an alkali effect it was found that in 1.0×10^{-2} mol dm^{-3} as well as in 0.1 mol dm^{-3} alkali concentrations, $1/k$ *versus* [KIO$_4$] plots were linear with an intercept, implying that the effect of periodate is similar at both the alkali concentrations (Figure 5). This effect indicates that the monoperiodato species of copper(III) is the reactive DPC species over the entire alkali range studied. If only one monoperiodato species were to exist throughout the alkali concentration range studied, the dependence of k on alkali concentrations should be the same at lower as well as at higher regions, in order for the similar periodate effect to be observed. But since a small change in alkali concentration of the medium is causing a difference in rate constant, it is obvious that the monoperiodato species existing in the two regions of alkali concentrations are different. This fact is further supported by the observed ionic strength effect in the two regions of alkali concentration, as explained below.

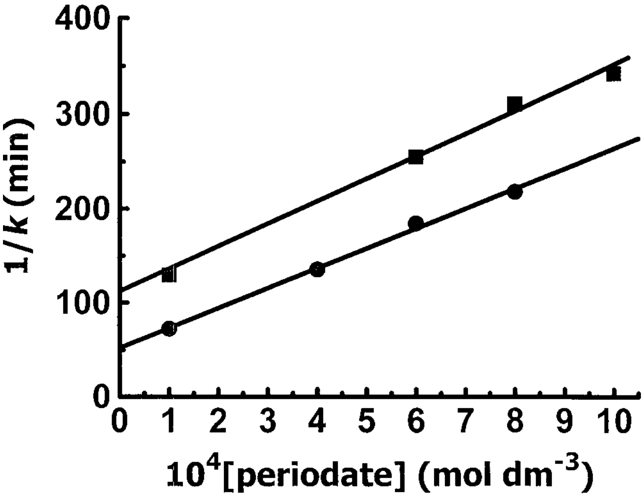

Fig. 5. Plot of $1/k$ *versus* [periodate]. ● In 1.0×10^{-2} mol dm^{-3} alkali; ■ in 0.1 mol dm^{-3} alkali.

In the oxidation of sulfite by diperiodatocuprate(III) in 0.1 mol dm^{-3} of alkali, a plot of log k *versus* $\sqrt{\mu}$ was linear with a slope corresponding to +2. Since the sulfite ion carries a charge of 2–, the reactive species of DPC, existing in that alkali concentration, should be uninegative. In the present reaction, the ionic strength effect was observed to be negligible at a 1.0×10^{-2}mol dm^{-3} alkali concentration, indicating that the reactive copper(III) species is neutral at this alkali concentration. However, at higher alkali concentration *i.e.*, in 0.1 mol dm^{-3}, when the ionic strength of the reaction mixtures was increased, the rate increased and a plot of log k *versus* $\sqrt{\mu}$ was linear (Figure 6), agreeing with the ionic strength effect observed for sulfite in a similar alkali concentration range. Since iodide only exists as a uninegative ion over the entire alkali range employed, and since only the monoperiodato species is reactive at both alkali concentration ranges, these ionic strength effects also support the existence of two different monoperiodatocuprate(III) species in the two

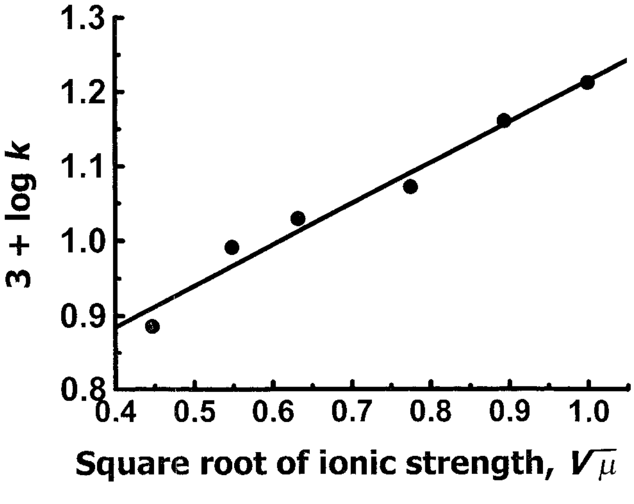

Fig. 6. Effect of ionic strength on k.

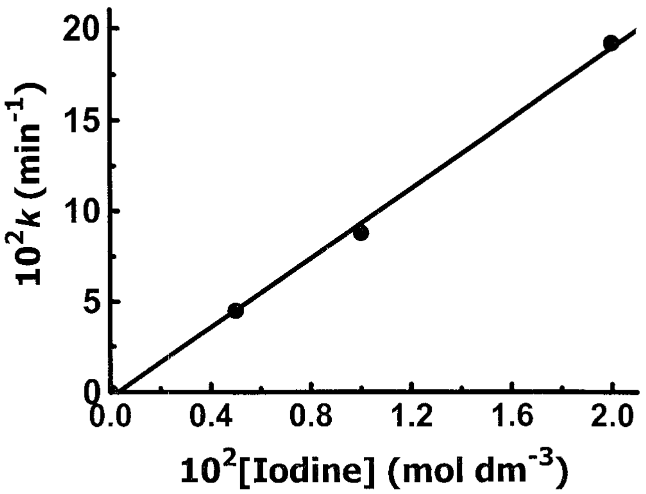

Fig. 7. Effect of added iodine on rate in 1.0 × 10^{-2} mol dm^{-3} alkali.

alkali concentration ranges. Thus it may be presumed that diperiodatocuprate(III) dissociates prior to deprotonation, and it is the monoperiodato species thus formed that undergoes deprotonation. These results indicate an additional equilibrium for the DPC species to the one we proposed earlier.

As mentioned earlier, at higher alkali concentrations the monoperiodato species is negatively charged, while at lower alkali concentrations it is neutral. The only possible neutral monoperiodato species of copper(III) is $[Cu(H_2IO_6)]$. In order to explain the ionic strength effect it can be assumed that the monoperiodato species existing at lower alkali concentration is $[Cu(H_2IO_6)]$ and that in higher alkali is $[Cu(HIO_6)]^-$ and the diperiodato species as $[Cu(H_2IO_6)_2]^{3-}$. Thus, we may assume the following equilibria for the DPC species in the 1.0 × 10^{-3}–0.1 mol dm^{-3} alkali concentration range.

$$[Cu(H_2IO_6)_2]^{3-} \overset{K_1}{\Longleftrightarrow} [Cu(H_2IO_6)] + H_2IO_6^{3-} \qquad (2)$$

$$[Cu(H_2IO_6)] + OH^- \overset{K_2}{\Longleftrightarrow} [Cu(HIO_6)]^- + H_2O \qquad (3)$$

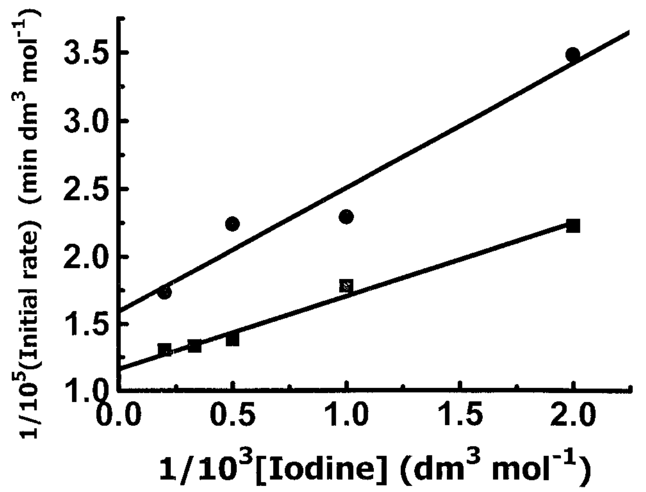

Fig. 8. Effect of added iodine on rate in higher alkali concentrations. ● In 5.0 × 10^{-2} mol dm^{-3} alkali; ■ in 0.1 mol dm^{-3} alkali.

Since, in this alkali concentration range periodate exists as an equilibrium mixture of $[H_3IO_6]^{2-}$ and $[H_2IO_6]^{3-}$ [11, 12], and the order with respect to DPC and iodide is unity in each, we can write the mechanism for the reaction as follows:

$$[Cu(H_2IO_6)_2]^{3-} \overset{K_1}{\Longleftrightarrow} [Cu(H_2IO_6)] + H_2IO_6^{3-} \qquad (2)$$

$$[Cu(H_2IO_6)] + OH^- \overset{K_2}{\Longleftrightarrow} [Cu(HIO_6)]^- + H_2O \qquad (3)$$

$$[H_3IO_6]^{2-} + [OH^-] \overset{K_3}{\Longleftrightarrow} [H_2IO_6]^{3-} + H_2O \qquad (4)$$

$$[Cu(H_2IO_6)] + I^- \xrightarrow[\text{(slow)}]{k_1} Cu(II) + I^{\bullet} \qquad (5)$$

$$[Cu(HIO_6)] + I^- \xrightarrow[\text{(slow)}]{k_2} Cu(II) + I^{\bullet} \qquad (6)$$

$$2I^{\bullet} \xrightarrow[\text{fast}]{} I_2 \qquad (7)$$

This mechanism gives rise to the following rate expression.

$$\begin{aligned} \text{Rate} &= \frac{-d[DPC]}{dt} = \frac{d[I^-]}{2dt} \\ &= \tfrac{1}{2}\, k_1[Cu(H_2IO_6)][I^-] + k_2[Cu(HIO_6)][I^-] \\ &= [Cu(H_2IO_6)][I^-]\{k_1 + k_2K_2[OH^-]\}/2 \end{aligned} \qquad (8)$$

or,

$$\text{Rate} = \frac{K_1[Cu^{III}]_t[I^-](1+K_3[OH^-])\{k_1+k_2K_2[OH^-]\}}{2\{K_3[per]_t[OH^-]+(K_1+K_1K_2[OH^-])(1+K_3[OH^-])\}} \qquad (9)$$

where $[Cu^{III}]_t$ represents the total concentration of all the DPC species and $[per]_t$ represents that of periodate. The pseudo-first order rate constant k may be given from Equation (8) as,

$$k = \frac{K_1[I^-](1+K_3[OH^-])\{k_1+k_2K_2[OH^-]\}}{2\{K_3[per]_t[OH^-]+K_1(1+K_2[OH^-])(1+K_3[OH^-])\}} \qquad (10)$$

If K_2 is very small such that $K_2[OH^-]$ is negligible compared to unity, Equation (10) reduces to,

$$k = \frac{K_1[I^-](1+K_3[OH^-])\{k_1+k_2K_2[OH^-]\}}{2\{K_3[per]_t[OH^-]+K_1(1+K_3[OH^-])\}} \qquad (11)$$

and if K_1 is small compared to $K_3[OH^-](K_1 + [per]_t)$, Equation (11) reduces to

$$k = \frac{K_1[I^-](1+K_3[OH^-])\{k_1+k_2K_2[OH^-]\}}{2\{K_3[OH^-]([per]_t+K_1)\}} \qquad (12)$$

It may be seen that Equation (12) is in the form of the general Equation (1) derived above.

If it is assumed that $k_2K_2[\mathrm{OH^-}] \ll 1$, Equation (12) reduces to

$$k = \frac{k_1K_1[\mathrm{I^-}][1 + K_3[\mathrm{OH^-}]]}{2K_3[\mathrm{OH^-}](K_1 + [\mathrm{per}]_t)} \tag{13}$$

At constant periodate concentration, Equation (13) leads to a straight line when k is plotted *versus* $1/[\mathrm{OH^-}]$, as has been observed experimentally. It may be seen that the ratio of the intercept of the plot to its slope should give the K_3 value from which the third dissociation constant of orthoperiodic acid may be estimated. The value thus obtained from our experimental data was 1.6×10^{-12} mol dm^{-3}, which is in good agreement with the literature value [11, 12]. Upon rearranging Equation (13) we get,

$$\frac{1}{k} = \frac{2K_3[\mathrm{OH^-}]}{k_1[\mathrm{I^-}][1 + K_3[\mathrm{OH^-}]]} + \frac{2K_3[\mathrm{OH^-}][\mathrm{per}]_t}{k_1K_1[\mathrm{I^-}][1 + K_3[\mathrm{OH^-}]]} \tag{14}$$

Equation (14) supports the fact that at lower alkali concentrations, a plot of $1/k$ *versus* [periodate] is linear with an intercept. It is also obvious that the ratio of the intercept to the slope of the plot should be equal to K_1. The value of K_1, thus computed, was found to be 4.1×10^3 mol dm^{-3}.

At alkali concentrations $> 5.0 \times 10^{-2}$ mol dm^{-3}, if $K_3[\mathrm{OH^-}]$ is much greater than unity, Equation (12) reduces to

$$k = \frac{K_1[\mathrm{I^-}]\{k_1 + k_2K_2[\mathrm{OH^-}]\}}{2\{[\mathrm{per}]_t + K_1\}} \tag{15}$$

This equation accounts for the observed linear plot of k *versus* $[\mathrm{OH^-}]$ ion at higher alkali concentrations, as shown in Figure 4. As with low alkali concentrations, Equation (15) again implies that the plot of $1/k$ *versus* periodate should be linear with an intercept and that the ratio of the intercept of the plot to its slope should be equal to K_1. The value obtained this time is 2.2×10^3 mol dm^{-3} which is very similar to that obtained earlier. This further confirms the equilibria assumed for the species of DPC.

The effect of iodine on the rate was studied at three different alkali concentrations, 1.0×10^{-2}, 5.0×10^{-2} as well as at 0.1 mol dm^{-3} (Table 2). In the presence of added iodine, the reaction rate was accelerated at all three alkali concentrations. At the lowest alkali concentration employed for this study, a plot of initial rate *versus* [iodine] was linear, passing through origin. This suggests that, in the presence of added iodine, the rate of the reaction between iodide and DPC is negligible compared to that of the reaction between iodine and DPC, while the latter is negligible compared to the former in the absence of added iodine. The greater reactivity of iodine at higher concentrations may be assigned to the known lower standard reduction potential of the iodate–iodine system compared to that of the iodine–iodide system at higher alkali concentration. It is important to note here that although iodine is known to react with alkali giving rise to iodate and iodide, this reaction is probably suppressed in the reaction mixtures under review, which contain large quantities of iodide ion in addition to periodate. This is further supported by the fact that the reaction between alkali and iodine proceeds with an overall order of three in iodine, but no such higher orders are observed in the present investigation.

Table 2. Effect of added product, iodine on the reaction rate. [DPC] = 5.0×10^{-5} mol dm^{-3}, [KI] = 0.1 mol dm^{-3}, [$\mathrm{KIO_4}$] = 1.0×10^{-4} mol dm^{-3} and temp = 303 K

10^3 [iodine] (mol dm^{-3})	10^2 $[\mathrm{OH^-}]$ (mol dm^{-3})	Initial rate × 10^6 (mol dm^{-3} min^{-1})
0.5	1.0	4.5
1.0	1.0	8.8
2.0	1.0	19.2
0.5	5.0	2.9
1.0	5.0	4.4
2.0	5.0	4.5
5.0	5.0	5.8
0.5	10.0	4.5
1.0	10.0	5.6
2.0	10.0	7.2
3.0	10.0	7.5
5.0	10.0	7.7

At the other two alkali concentrations, a plot of 1/(initial rate) *versus* 1/[iodine] was linear, indicating that the copper(III) species and iodine exist in equilibrium to form an intermediate complex which decomposes into the products. The equilibrium may be written:

$$\mathrm{Cu^{III}} + \mathrm{I_2} \overset{K'}{\Longleftrightarrow} \mathrm{C} \tag{16}$$

$$\mathrm{C} \xrightarrow{k_3} \text{products} \tag{17}$$

where C represents the complex intermediate formed between DPC and $\mathrm{I_2}$ and $\mathrm{Cu^{III}}$ represents the uncomplexed DPC.

This mechanism gives rise to the rate equation:

$$\text{Rate} = \frac{-d[\mathrm{DPC}]}{dt} = \frac{d[\mathrm{I^-}]}{2dt} = k_3[\mathrm{C}]_e/2 \tag{18}$$

$$\text{Rate} = k_3K'[\mathrm{Cu^{III}}]_e[\mathrm{I_2}]_e/2 \tag{19}$$

Since iodine was employed in considerable excess over DPC, $[\mathrm{I_2}]_e$ may be assumed to be equal to the total iodine concentration, $[\mathrm{I_2}]$. Then the rate may be given as,

$$\text{Rate} = k_3K'[\mathrm{Cu^{III}}]_e[\mathrm{I_2}]/2 \tag{20}$$

If the total concentration of DPC is assumed to be equal to the sum of the concentrations of the intermediate complex and uncomplexed DPC, then

$$[\mathrm{DPC}] = [\mathrm{Cu^{III}}]_e + [\mathrm{C}]_e \tag{21}$$

where [DPC] is the total concentration of DPC.

From this equation we may write,

$$[\mathrm{Cu^{III}}]_e = \frac{[\mathrm{DPC}]}{\{1 + K'[\mathrm{Cu^{III}}]_e[\mathrm{I_2}]\}} \tag{22}$$

Upon substituting in the rate Equation (20) we obtain,

$$\mathrm{Rate} = \frac{k_3K'[\mathrm{DPC}][\mathrm{I_2}]}{2(1 + K'[\mathrm{I_2}])} \tag{23}$$

Upon rearranging the above equation,

$$\frac{1}{\mathrm{Rate}} = \frac{2}{k_3K'[\mathrm{DPC}][\mathrm{I_2}]} + \frac{2}{k_3[\mathrm{DPC}]} \tag{24}$$

Equation (24) accounts for the linearity of the 1/(rate) *versus* 1/$[\mathrm{I_2}]$ plot observed experimentally. It can also be seen that the ratio of the intercept of the plot to its slope should be equal to K'. The K' values computed from the plots obtained at 5.0×10^{-2} and 1.0×10^{-1} mol dm^{-3} alkali concentrations were found to be 1.74×10^{4} and 2.18×10^{4} dm^{3} mol^{-1} respectively.

In 1.0×10^{-2} mol dm^{-3} alkali, the plot of initial rate *versus* $[\mathrm{I_2}]$ was linear. It may be seen from Equation (23), that such a plot would arise if $K'[\mathrm{I_2}]$ is very small compared to unity. At low alkali concentration, probably the value of K' is sufficiently small to give rise to this result. The alkali dependence of K' might arise due to the change in the DPC species with varying alkali concentrations.

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