Kinetics and Mechanism of the Oxidation of Dodecatungstocobaltate(II) by Peroxodisulphate and Periodate in Aqueous Acidic Solution

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The kinetics of oxidation of $[CoW_{12}O_{40}]^{6-}$ by peroxodisulphate and periodate have been studied spectrophotometrically in aqueous acidic media. In the case of peroxodisulphate the reaction is zero order in [complex] and follows a rate law $-d[CoW_{12}O_{40}{}^{6-}]/dt = 2k_s[S_2O_8{}^{2-}]$. However, with periodate the reaction is first order in [complex] and a limiting dependence on both [oxidant] and $[H^+]$ is obtained. An interesting stoichiometric result was also obtained: at high [complex]:[periodate] ratio (> 6:1) the stoichiometry is 2, but under pseudo-first-order conditions with excess of periodate the stoichiometry is less than 1. An inhibition of the reaction by alkali-metal salts added to adjust the ionic strength has also been observed. All these results have been explained successfully by considering a free-radical mechanism where the free radical produced in the rate-determining step either may decompose thermally or react with a second complex molecule. An inverse dependence of the rate on the concentration of alkali-metal cation and a high value of the association constant obtained from periodate variation suggest an inner-sphere pathway for this reaction.

Heteropolyanions find wide applications as active photosensitisers,[1] electron acceptors in biological processes,[2–4] and possible antiviral and antitumour agents.[5,6] Dodecatungstocobaltate(III) is one of the important examples of this class. Although a number of papers have appeared on its reduction by a variety of organic[7–14] and inorganic[15–20] reagents, there is no report on the oxidation of the corresponding cobalt(II) analogue which is also equally interesting from the chemical viewpoint. In the present study we report the oxidation of dodecatungstocobaltate(II) $[CoW_{12}O_{40}]^{6-}$ by peroxodisulphate and periodate in aqueous solution. Peroxodisulphate shows variable kinetic features,[21–25] and periodate is a typical inner-sphere oxidant often featuring complex redox chemistry.[26–29] Thus it seems importat to study the oxidation of a substitution-inert complex with these oxidants.

Experimental

Materials and Reagents.—The complexes, potassium salts of dodecatungstocobaltate(III), $[CoW_{12}O_{40}]^{5-}$, and dodecatungstocobaltate(II), $[CoW_{12}O_{40}]^{6-}$ were prepared and standardised by usual procedures.[16,30] Analytical grade potassium peroxodisulphate and potassium periodate were recrystallised three times before use, then analysed titrimetrically.[31,32] Sodium nitrate, sodium sulphate, and potassium nitrate of analytical grade for the cation-variation study were used after recrystallisation. The acid strength of the reaction solutions was maintained by using acids corresponding to the alkali-metal salts (*e.g.* H_2SO_4 for Na_2SO_4 medium).

Kinetic Measurements.—The experiments were carried out in a Philips Analytical SP8-150 UV/VIS spectrophotometer equipped with thermostatted cell compartments. The reactions were followed by monitoring the increase in $[CoW_{12}O_{40}]^{5-}$ concentration at 388 nm (its absorption maximum). A few runs conducted at 625 nm (the absorption maximum of $[CoW_{12}O_{40}]^{6-}$ give identical results. Dissolved oxygen has no effect on the rate of reaction.

Stoichiometry and Reaction Products.—The stoichiometries of these reactions were determined spectrophotometrically by measuring the decrease in absorbance of $[CoW_{12}O_{40}]^{6-}$ at 625 nm and determining the unreacted [oxidant] titrimetrically.[31,32] For this purpose a set of solutions containing various concentration ratios of $[CoW_{12}O_{40}]^{6-}$ with periodate and peroxodisulphate were prepared. For $S_2O_8{}^{2-}$ oxidation, the stoichiometry was $[CoW_{12}O_{40}{}^{6-}]:[S_2O_8{}^{2-}]$ 1.98 ± 0.04. However for the periodate reaction the stoichiometry was dependent on $[CoW_{12}O_{40}{}^{6-}]/[I^{VII}]_T$ where $[I^{VII}]_T$ indicates the total periodate concentration. When this ratio was 1:10 the stoichiometry was 0.9 ± 0.02. However, with increasing $[CoW_{12}O_{40}{}^{6-}]$ the stoichiometric ratio increased, finally to 2.01 ± 0.03 at $[CoW_{12}O_{40}{}^{6-}]:[I^{VII}]_T = 6:1$. The results obtained are given in Table 1. The reaction products in the peroxodisulphate and periodate reactions are sulphate and iodate respectively.

Test for Free Radicals.—The reactions proceed with the generation of free radicals which was confirmed by polymerisation of acrylonitrile as reported earlier.[15]

Results and Discussion

Oxidation of $[CoW_{12}O_{40}]^{6-}$ *by Peroxodisulphate.*—The stoichiometry for the peroxodisulphate oxidation is given by equation (1). The reactions have been carried out under pseudo-first-order conditions using excess of peroxodisulphate over $[CoW_{12}O_{40}]^{6-}$. Absorbance *vs.* time plots were linear up to 90% completion of the reaction indicating a zero-order dependence of the rate in complex concentration. The reaction is first order in $[S_2O_8{}^{2-}]$ (Table 2) and follows the rate law in equation (2). In contrast to previous studies,[21–25] no effect of

$$2[CoW_{12}O_{40}]^{6-} + S_2O_8{}^{2-} \longrightarrow 2[CoW_{12}O_{40}]^{5-} + 2SO_4{}^{2-} \quad (1)$$

$$-d[CoW_{12}O_{40}{}^{6-}]/dt = 2k_s[S_2O_8{}^{2-}] = k_{obs} \quad (2)$$

Table 1 Stoichiometric results for the reaction of $[CoW_{12}O_{40}]^{6-}$ with periodate at $[H^+] = 0.50$ mol dm^{-3} and $[K^+] = 0.10$ mol dm^{-3}

$10^3[CoW_{12}O_{40}^{6-}]$	$10^3[I^{VII}]$	$10^3[CoW_{12}O_{40}^{6-}]_c$	$10^3[I^{VII}]_c$	$[CoW_{12}O_{40}^{6-}]_c/[I^{VII}]_T$
mol dm^{-3}				
1.00	1.00	0.98 ± 0.03	1.00	0.98
2.00	1.00	1.57 ± 0.02	1.00	1.57
3.00	1.00	1.68 ± 0.03	1.00	1.68
4.00	1.00	1.90 ± 0.02	1.00	1.90
6.00	1.00	1.99 ± 0.03	1.00	1.99
1.00	2.00	1.00	1.04 ± 0.03	0.96
1.00	5.00	1.00	1.08 ± 0.03	0.93
1.00	8.00	1.00	1.10 ± 0.02	0.91
1.00	12.00	1.00	1.13 ± 0.03	0.88
1.00	15.00	1.00	1.12 ± 0.02	0.89
1.00	20.00	1.00	1.10 ± 0.03	0.91
1.00	30.00	1.00	1.11 ± 0.03	0.90

The subscript c indicates consumed.

Table 2 Kinetic and thermodynamic parameters for the reaction of dodecatungstocobaltate(II) with peroxodisulphate

$10^4[CoW_{12}O_{40}^{6-}]$	$[S_2O_8^{2-}]$	$[H^+]$	10^8k_{obs}/mol dm^{-3} s^{-1}		
mol dm^{-3}			40	50	60 °C
2.00	0.01	0.50	0.40	1.41	6.29
2.00	0.02	0.50	0.68	2.90 (2.86)	11.60
2.00	0.03	0.50		4.21	16.80
2.00	0.04	0.50	1.43	5.59 (5.56)	25.61
2.00	0.05	0.50		7.30 (7.32)	28.38
2.00	0.06	0.50	2.31	8.80	34.51
2.00	0.07	0.50		10.31 (10.37)	
2.00	0.08	0.50	2.85	11.82 (11.91)	
0.20	0.08	0.50		36.12	
0.35	0.08	0.50		35.32	
0.50	0.08	0.50		39.08	
0.75	0.08	0.50		10.96	
1.00	0.08	0.50		11.72	
3.00	0.08	0.50		11.66	
5.00	0.08	0.50		11.82	
8.00	0.08	0.50		12.05	
2.00	0.08	0.10		11.59	
2.00	0.08	0.01		12.02	
2.00	0.08	0.005		11.99	
2.00	0.08	0.001		11.75	

$\Delta H^\ddagger = 117 \pm 7$ kJ mol^{-1}, $\Delta S^\ddagger = 29 \pm 4$ J K^{-1} mol^{-1}. In general the ionic strength varies between 1.03 and 1.24 mol dm^{-3} but $[K^+] = 0.50$ mol dm^{-3} in all cases. Parenthetical values denote average rates with an error limit ± 0.05 with $I = 1.56$ and 2.06 mol dm^{-3} maintained by addition of the requisite amount of KNO_3.

$[H^+]$ has been encountered over a wide range of concentration, 1.0×10^{-3}–0.50 mol dm^{-3} (Table 2). The effect of ionic strength on the reaction rate is also negligible (Table 2).

Since the oxidation process is independent of $[H^+]$ and zero order with respect to $[CoW_{12}O_{40}^{6-}]$, a plausible mechanism is that in equations (3) and (4). The value of k_s obtained at 50 °C

$$S_2O_8^{2-} \xrightarrow{k_s} 2SO_4^{\cdot -} \qquad (3)$$

$$SO_4^{\cdot -} + [CoW_{12}O_{40}]^{6-} \xrightarrow{\text{fast}} SO_4^{2-} + [CoW_{12}O_{40}]^{5-} \qquad (4)$$

[$(0.73 \pm 0.03) \times 10^{-6}$ s^{-1}] for the present system agrees well with the literature value[26] (1.0×10^{-6} s^{-1}) and thus supports the proposed mechanism. It is to be noted here that though the reaction is independent of $[CoW_{12}O_{40}^{6-}]$ in the range 1.0×10^{-4}–1.0×10^{-3} mol dm^{-3}, at very low concentration ($< 1.0 \times 10^{-4}$ mol dm^{-3}) a complicated dependence of the rate on $[CoW_{12}O_{40}^{6-}]$ is obtained (Table 2). This type of behaviour has also been encountered in the oxidation of vanadium(IV) by peroxodisulphate[23] and may be due to an additional catalytic pathway. We have not investigated it further because of difficulties involved in measuring the rates at very low concentration of $[CoW_{12}O_{40}]^{6-}$.

The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values obtained from the temperature variation (40–60 °C) (Table 2) are in good agreement with the reported[25] values and support the proposed mechanism.

Oxidation of $[CoW_{12}O_{40}]^{6-}$ *by Periodate*.—The oxidation of $[CoW_{12}O_{40}]^{6-}$ with periodate has been studied in the ranges $[I^{VII}]_T = 1.0 \times 10^{-3}$–0.06 mol dm^{-3} and $[H^+] = 1.0 \times 10^{-3}$–0.20 mol dm^{-3} at various alkali-metal-ion concentrations. A typical spectral scanning of the reaction shows a single isosbestic point at 510 nm. In the UV region the spectrum of a mixture of $[CoW_{12}O_{40}]^{6-}$ and periodic acid showed no change in peak position or increase in absorption relative to that of either periodic acid or $[CoW_{12}O_{40}]^{6-}$, being simply additive of the two.

The reaction of $[CoW_{12}O_{40}]^{6-}$ with periodate is first order in complex concentration. To determine the dependence of the rate on periodate, experiments have been carried out over the range, $[I^{VII}]_T = 1.0 \times 10^{-3}$–0.06 mol dm^{-3} at $[H^+] = 0.10$ and $[K^+] = 0.10$ mol dm^{-3} and temperature 60 °C. At low

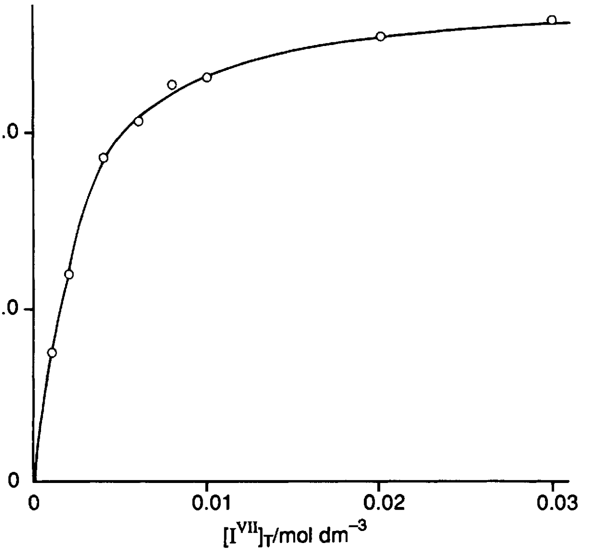

Fig. 1 Plot of k_{obs} *vs.* $[I^{VII}]_T$ at $[CoW_{12}O_{40}^{6-}] = 2 \times 10^{-4}$, $[H^+] = 0.10$, $[K^+] = 0.10$ mol dm^{-3} and 60 °C

Table 3 Variation of $[H^+]$ and $[M^+]$ (M = Na or K) in the oxidation of $[CoW_{12}O_{40}]^{6-}$ by periodate at $[I^{VII}] = 0.002$ mol dm^{-3}, $[CoW_{12}O_{40}^{6-}] = 2.0 \times 10^{-4}$ mol dm^{-3} and 60 °C

$10[H^+]$	$[M^+]$	$10^3k/s^{-1}$	
mol dm^{-3}		obs.[a]	calc.[b]
0.01	0.10	0.15	0.14
0.05	0.10	0.58	0.51
0.08	0.10	0.73	0.67
0.10	0.10	0.95	0.75
0.20	0.10	1.18	1.00
0.50	0.10	1.20	1.22
1.00	0.01	2.20 (1.81)	
1.00	0.05	1.61 (1.24)	
1.00	0.10	1.22 (1.00)	1.32
1.00	0.30	0.57 (0.50)	
1.00	0.50	0.37 (0.31)	
1.00	0.50	(0.30)[c]	
1.00	0.50	(0.31)[d]	
1.00	0.50	(0.31)[e]	
1.50	0.10	1.22	1.36
2.00	0.10	1.22	1.38

[a] At constant $[K^+]$. The parenthetical values are for the corresponding reactions at constant $[Na^+]$. [b] The average value of $k_r = \{\frac{1}{2}(3.10 + 3.50) = 3.30\} \times 10^{-3}$ s^{-1} was taken to calculate k_{calc}. [c] 0.10 mol dm^{-3} Na_2SO_4 + 0.30 mol dm^{-3} $NaNO_3$. [d] 0.15 mol dm^{-3} Na_2SO_4 + 0.20 mol dm^{-3} $NaNO_3$. [e] 0.20 mol dm^{-3} Na_2SO_4 + 0.10 mol dm^{-3} $NaNO_3$.

periodate concentration the reaction is first order in [oxidant] but becomes independent at high concentrations (Fig. 1).

The effect of the hydrogen-ion concentration on the oxidation rate was investigated in the range $[H^+] = 1.0 \times 10^{-3}$–0.20 mol dm^{-3}, $[K^+] = 0.10$ mol dm^{-3} at 60 °C and at low $[I^{VII}]_T$ (2.0×10^{-3} mol dm^{-3}), where a first-order dependence on $[I^{VII}]_T$ prevails. As shown in Table 3, rate increases with increasing $[H^+]$. A plot of k_{obs} *vs.* $[H^+]$ is a limiting curve of decreasing slope with a nearly zero intercept, which indicates that the anionic forms of periodic acid ($H_4IO_6^-$, IO_4^-) are unreactive towards $[CoW_{12}O_{40}]^{6-}$ and H_5IO_6 is the only reactive species in this system.

The proton association of periodic acid can be described as in equation (5), but periodate anion can exist both in IO_4^- and $H_4IO_6^-$ forms and $[HL^-]_T = [IO_4^-] + [H_4IO_6^-]$; thus K actually represents the apparent proton association constant, reported[33] to be 43 dm^3 mol^{-1} at 25 °C.

$$HL^- + H^+ \xrightleftharpoons{K} H_2L \qquad (5)$$

The effect of specific ions on the rate of this reaction has been studied by using salts of selected cations and anions as the supporting electrolytes. Interestingly, the reaction rate decreases with increasing alkali-cation concentration, showing a minimum and then becoming constant. The extent of inhibition is slightly greater in the case of Na^+ than that of K^+ and these results are summarised in Table 3. To determine whether this effect is due to the ionic strength or a specific effect of the alkali-metal cations, some reactions were studied at constant $[Na^+]$ but varying ionic strength using a mixture of $NaClO_4$ and Na_2SO_4. As it is seen from Table 3, no appreciable change in rate was observed with increasing ionic strength at constant $[Na^+]$.

Considering the foregoing observations, two different reaction schemes may be proposed to account for the oxidation of $[CoW_{12}O_{40}]^{6-}$ by periodic acid. The rate law corresponding to Scheme 1 may be formulated as in equation (10), similarly Scheme 2 leads to rate law (11). These equations are identical with $k_r = k_c$ and $Q = k_a/k_b$. They are however in terms of $[H_5IO_6]$. Using equation (10), the general rate law (12) in terms of total periodate concentration $[I^{VII}]_T$ may be formulated. Since periodate is present in large excess, it may be assumed that most of the $[CoW_{12}O_{40}]^{6-}$ is used up for ion pairing with H_5IO_6 and hence $Q[CoW_{12}O_{40}^{6-}]_{free} \ll 1$ and can be neglected. So the general equation is (13). Rearranging, we obtain equation (14).

$$H_5IO_6 + [CoW_{12}O_{40}]^{6-} \xrightleftharpoons{Q} \{[CoW_{12}O_{40}]^{6-}, H_5IO_6\} \qquad (6)$$

$$\{[CoW_{12}O_{40}]^{6-}, H_5IO_6\} \xrightarrow{k_r} [CoW_{12}O_{40}]^{5-} + H_3IO_5^{\bullet -} + H_2O \qquad (7)$$

Scheme 1

$$[CoW_{12}O_{40}]^{6-} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [CoW_{12}O_{40}]^{6-*} \text{ (modified species)} \qquad (8)$$

$$[CoW_{12}O_{40}]^{6-*} + H_5IO_6 \xrightarrow{k_c} [CoW_{12}O_{40}]^{5-} + H_3IO_5^{\bullet -} + H_2O \qquad (9)$$

Scheme 2

$$-d[CoW_{12}O_{40}^{6-}]/dt = k_rQ[H_5IO_6][CoW_{12}O_{40}^{6-}]/(1 + Q[H_5IO_6]) \qquad (10)$$

$$-d[CoW_{12}O_{40}^{6-}]/dt = (k_ck_a/k_b)[H_5IO_6][CoW_{12}O_{40}^{6-}]/\{1 + (k_a/k_b)[H_5IO_6]\} \qquad (11)$$

$$k_{obs} = \frac{k_rQK[H^+][I^{VII}]_T}{1 + \{K[H^+](1 + Q[I^{VII}]_T + Q[CoW_{12}O_{40}^{6-}]_{free})\}} \qquad (12)$$

$$k_{obs} = \frac{k_rQK[H^+][I^{VII}]_T}{1 + \{K[H^+](1 + Q[I^{VII}]_T)\}} \qquad (13)$$

$$1/k_{obs} = 1/k_r + (K[H^+] + 1)/k_rKQ[H^+][I^{VII}]_T \qquad (14)$$

A plot of $1/k_{obs}$ *vs.* $[I^{VII}]_T^{-1}$ yields a straight line with intercept = $1/k_r$ and slope = $(K[H^+] + 1)/k_rKQ[H^+]$. Taking $K = 43$ dm^3 mol^{-1}, the values of k_r and Q thus obtained are $(3.10 \pm 0.10) \times 10^{-3}$ s^{-1} and 391 ± 10 dm^3 mol^{-1} respectively. Further rearrangement of equation (13) yields (15). From a plot

$$1/k_{\text{obs}} = \{1/k_r + 1/k_rQ[\text{I}^{\text{VII}}]_T\} + 1/k_rKQ[\text{H}^+][\text{I}^{\text{VII}}]_T \quad (15)$$

of $1/k_{\text{obs}}$ *vs.* $[\text{H}^+]^{-1}$, and using the above value of Q, the values of k_r and K calculated from a least-squares fitting program were $(3.49 \pm 0.50) \times 10^{-3}$ s^{-1} and 61 ± 9 dm^3 mol^{-1} respectively. There is a good agreement between the kinetically determined value of K and that reported.[33] Utilising the general rate expression and the experimentally determined values of k_r, K and Q as above, the values of k_{obs} were calculated at different $[\text{H}^+]$. There is also an excellent agreement between the experimental and calculated k_{obs} (Table 3) and this supports the proposed mechanism.

One of the interesting features of this study is the stoichiometric results. Though a 2:1 stoichiometry prevails at high $[\text{CoW}_{12}\text{O}_{40}{}^{6-}]:[\text{I}^{\text{VII}}]_T$ ratio (6:1), under the experimental conditions it reaches a value of 0.9:1.0. This is rather unusual and the possible pathways for periodate consumption may be explained by considering the reactions (16)–(19). However, at high $[\text{CoW}_{12}\text{O}_{40}{}^{6-}]:[\text{I}^{\text{VII}}]$ ratio a second complex ion may react either with the free radical produced in (7) or (16), giving a 2:1 stoichiometry [equations (20) and (21)]. The generation of $\dot{\text{O}}\text{H}$ radical through the breakdown of $\text{H}_3\text{IO}_5{}^{\bullet-}$ was tested by the hydroxylation of benzoic acid.[27] For this purpose, 0.01 mol dm^{-3} I$^{\text{VII}}$ was treated with $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ to which 0.01 mol dm^{-3} benzoic acid was added and pH adjusted to 2 by HClO_4. The concentrations are critical and were chosen to avoid the preferential formation of iron(III) benzoate and iron(III) periodate both of which mask the colour of iron(III) salicylate. After completion of the reaction the complex was separated by ion exchange and the eluent was then treated with iron(III) chloride solution which gave a purple colouration characteristic of iron(III) salicylate. In the presence of excess of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ no such polymerisation was observed.

$$\text{H}_3\text{IO}_5{}^{\bullet-} \xrightarrow[\text{decomposition}]{\text{thermal}} \text{H}_2\text{O} + \text{IO}_3{}^- + \dot{\text{O}}\text{H} \quad (16)$$

$$2\dot{\text{O}}\text{H} \xrightarrow{\text{fast}} \text{H}_2\text{O}_2 \quad (17)$$

$$\dot{\text{O}}\text{H} + \text{H}_5\text{IO}_6 \xrightarrow{\text{fast}} \text{H}_2\text{O}_2 + \text{H}_3\text{IO}_5{}^{\bullet-} + \text{H}^+ \quad (18)$$

$$\text{H}_2\text{O}_2 + \text{H}_5\text{IO}_6 \xrightarrow{\text{fast}} \text{HIO}_3 + 3\text{H}_2\text{O} + \text{O}_2 \quad (19)$$

$$\text{H}_3\text{IO}_5{}^{\bullet-} + [\text{CoW}_{12}\text{O}_{40}]^{6-} \xrightarrow{\text{fast}} [\text{CoW}_{12}\text{O}_{40}]^{5-} + \text{H}_3\text{IO}_5{}^{2-} \quad (20)$$

$$\dot{\text{O}}\text{H} + [\text{CoW}_{12}\text{O}_{40}]^{6-} \xrightarrow{\text{fast}} [\text{CoW}_{12}\text{O}_{40}]^{5-} + \text{OH}^- \quad (21)$$

The redox reactions of $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ are generally of outer-sphere type.[7–12] Pope and co-workers[34–36] however observed inner-sphere type adduct formation in the reactions of heteropolyanions in non-aqueous media. The reaction of $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ with alkanediols[19] has been proposed to occur by the formation of an intermediate complex followed by electron transfer through a hopping mechanism. On the other hand, periodate is known to be an inner-sphere oxidant though the oxidation of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ by periodate[29] is a controversial issue. In the present system the observations (*i*) of a large value of Q (= 391 dm^3 mol^{-1}) (*ii*) an inhibiting effect of alkali-metal cations in contrast to the cation-bridged outer-sphere reactions of $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ suggest the formation of a precursor complex prior to electron transfer. In such a case, the intermediate complex may be assumed to be formed by bonding of a periodate oxygen to a surface tungsten atom.

The alternative mechanism (Scheme 2), as suggested by one of the referees, involves some modified $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ species probably in which a WO_6 unit has partly opened up or partly broken away from the main structure. This mechanism has as its basis the fact that no spectral evidence in favour of intermediate complex formation is obtained in the UV region, particularly with such a large association constant (Q = 391 dm^3 mol^{-1}). However, this mechanism also lacks support since a recent ^{183}W NMR study of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ in solution gives a single peak[37] indicating that all the WO_6 octahedra are structurally identical. Another fact which disfavours this mechanism comes from the bromate ion oxidation[38] of this complex, which shows similar redox patterns to those in the present system, under identical conditions. If Scheme 2 is assumed to be correct, the value of k_a/k_b [equation (8)] should be constant irrespective of the nature of the oxidant. From the bromate-ion oxidation of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ the value obtained is 0.20 at $[\text{H}^+]$ = 0.10 mol dm^{-3}, $[\text{K}^+]$ = 0.10 mol dm^{-3}, and 60 °C which is *ca.* 10^4 times lower than the desired value. From the above discussion it may be proposed that the reaction goes *via* the formation of an inner-sphere intermediate from which the electron transfer occurs through a hopping mechanism. It should also be mentioned in this context that though an inner-sphere mechanism was suggested in the reduction of $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ by alkanediols,[19] no spectral evidence in favour of intermediate complex formation was obtained. A decrease in reaction rate with increasing metal-ion concentration is explained by the decrease in formal charge on $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ on ion pairing, which in turn decreases upon association of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ and H_5IO_6 and thereby lowers the reaction rate. The values of k_r and Q thus obtained are not absolute but could well incorporate the ion-pairing constant between M$^+$ and $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ especially where the charges are significant.

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