# Oxidation of Sulphur(IV) by Dodecatungstocobaltate(III) in Aqueous Acid Solution

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The reaction between dodecatungstocobaltate(III) and sulphite has been studied in the range pH 1.50—3.50 at 25 °C and $I$ = 0.5 mol dm$^{-3}$ ($NaClO_4$). The reaction stoicheiometry has been found to be 1 : 1 in the presence of excess of sulphite and the corresponding reaction product obtained is dithionate. However, when the complex : sulphur(IV) mole ratio is >1.5 : 1, sulphate is also obtained together with dithionate and their amounts are dependent on the mole ratio of the reactants. The stoicheiometry $[S^{IV}]_{consumed}$ : $[complex]_{consumed}$ varies in the range 0.7—1.0 : 1 on a par with the sulphate : dithionate ratio. The kinetics of the reaction path which gives a 1 : 1 stoicheiometry follows the rate law (i). A mechanism has been proposed, considering $k_0$ and $k_1'$

$$-d[\text{complex}]/dt = (k_0 + k_1'[H^+]^{-1} + k_2[HSO_3^-])[\text{complex}][HSO_3^-] \qquad \text{(i)}$$

paths to correspond to the reactions between the cobalt(III) complex with $HSO_3^-$ and $SO_3^{2-}$ respectively. The $k_2$ path is assigned to the reaction of the complex with $S_2O_5^{2-}$ or that of sulphur(IV) with an intermediate formed by the reaction between the complex and one sulphur(IV) species. The observed specific alkali-metal-ion catalysis is attributed to the formation of bridging by the alkali-metal ion between the two negatively charged reactants, facilitating the electron-transfer process.

The reactions between sulphite and different metal complexes have been the subject of interest for the last two decades,[1–15] in particular in view of their variable mechanistic aspects and other features relating to the dependence on reductant, variation of hydrogen-ion concentration, and alkali-metal-ion dependence.

In this paper we report a kinetic study of the reaction of dodecatungstocobaltate(III) with sulphite in an aqueous acidic medium. Though heteropolyanions are known to be substitution-inert, very recently the formation of inner-sphere complexes of these polyanions in non-aqueous media with different types of reagents including sulphur dioxide has been established.[16–18] Olatunji and Ayoko[19] also suggested an inner-sphere mechanism for the oxidation of diols with this complex. However in our previous studies on the oxidation of some carboxylic acids[20–22] and sugars[23] with the same complex we did not observe any stable intermediate formation either kinetically or spectrophotometrically. The present study therefore aims at (*i*) discriminating the inner- and outer-sphere interaction of the polyanion with $SO_2$ in aqueous solution and (*ii*) verifying the prediction that such a reaction would show a higher-order dependence of the rate on $[S^{IV}]$.[11]

## Experimental

*Reagents.*—The complexes, potassium salts of dodecatungstocobaltate(III), $[CoW_{12}O_{40}]^{5-}$, and dodecatungstocobaltate(II), $[CoW_{12}O_{40}]^{6-}$, were prepared, characterised, and standardised as reported earlier.[24,25] Analytical grade reagents were used without further purification. Solutions were prepared in doubly distilled water and purged with dinitrogen before mixing of the complex. The sulphite solutions were prepared by dissolving an appropriate amount of sodium sulphite in doubly distilled water which was deaerated with dinitrogen. This solution was further standardised by using an excess of iodine solution followed by back titration with standard thiosulphate, and stored under a nitrogen atmosphere. Sodium perchlorate (AG, Fluka), sodium nitrate, potassium nitrate (GR, E. Merck), lithium nitrate (AG, Fluka), and sodium sulphate (GR, E. Merck) were used for adjusting the ionic strength and also to study the effect of variation of the alkali-metal ion in this study. Sodium dithionate was prepared by the known procedure[26] and recrystallised three times before use.

*Kinetic Experiments.*—Kinetic measurements were made in a Pye-Unicam SP8-150 UV/VIS spectrophotometer equipped with thermostatted cell compartments. The temperature was controlled to 25 ± 0.1 °C using a Hakke F3 thermostat. The pH measurements were done in a Systronics digital pH meter (model 335, India). Extra precautions were taken to eliminate the loss of sulphurous acid as $SO_2$. The approximate amount of acid required to adjust the pH of the solution was first determined by trial solutions and finally the pH was adjusted by adding the requisite amount of acid just prior to the reaction. Reactions were carried out in air-tight stoppered quartz cells.

*Test for free radicals.* Generation of free radicals during the course of the reaction was confirmed by the polymerisation of acrylonitrile in aqueous solution. The reactant solutions were degassed separately with dinitrogen, mixed together, and acrylonitrile (5 cm$^3$, 20% v/v) was then added. A heavy precipitate appeared almost immediately due to the polymerisation of the monomer. No polymerisation was observed when acrylonitrile was added to the complex and sulphite solutions separately.

*Stoicheiometry and Reaction Products.*—To determine the stoicheiometry of the reaction, sulphite and $[CoW_{12}O_{40}]^{5-}$ were mixed in various ratios over a range of concentrations at pH 4.70. With excess of sulphite, the stoicheiometry was determined by measuring the unreacted sulphite titrimetrically and for the mixtures with excess of $[CoW_{12}O_{40}]^{5-}$ it was done spectrophotometrically by estimating the $[CoW_{12}O_{40}]^{6-}$

**Table 1.** Stoicheiometric results and product distribution for the reaction of $[CoW_{12}O_{40}]^{5-}$ with sulphite at pH 4.70, $I$ = 0.50 mol dm$^{-3}$, and 25 °C

| $10^3[Co^{III}]$ | $10^3[S^{IV}]$ | $10^3[Co^{III}]_c$ [a] | $10^3[S^{IV}]_c$ | $10^3[S_2O_6^{2-}]_p$ [b] | $10^3[SO_4^{2-}]_p$ |
|---|---|---|---|---|---|
| | | mol dm$^{-3}$ | | | |
| 2.00 | 0.50 | 0.72 (0.70) | 0.50 | 0.15 ± 0.03 | 0.20 ± 0.03 |
| 2.00 | 1.00 | 1.40 (1.38) | 1.00 | 0.31 ± 0.02 | 0.38 ± 0.02 |
| 2.00 | 1.50 | 1.80 (1.74) | 1.50 | 0.63 ± 0.05 | 0.24 ± 0.05 |
| 2.00 | 2.00 | 2.00 (1.94) | 1.80 | 0.85 ± 0.03 | 0.12 ± 0.03 |
| 2.00 | 2.50 | 2.00 (1.96) | 1.90 | 0.92 ± 0.02 | 0.06 ± 0.02 |
| 2.00 | 3.00 | 2.00 (2.04) | 2.00 | 0.98 ± 0.03 | 0.04 ± 0.03 |
| 2.00 | 5.00 | 2.00 (2.00) | 1.99 | 1.00 | 0 |
| 2.00 | 8.00 | 2.00 (2.00) | 2.00 | 1.00 | 0 |

[a] The values in parentheses were calculated from the $[S_2O_6^{2-}]$ and $[SO_4^{2-}]$ produced in the reaction; the suffix c stands for 'consumed.' [b] The $[S_2O_6^{2-}]$ was estimated from two sets of data; $[SO_4^{2-}]$ was calculated as $[SO_4^{2-}] = [S^{IV}]_c - 2[S_2O_6^{2-}]_p$. The suffix p stands for 'produced.'

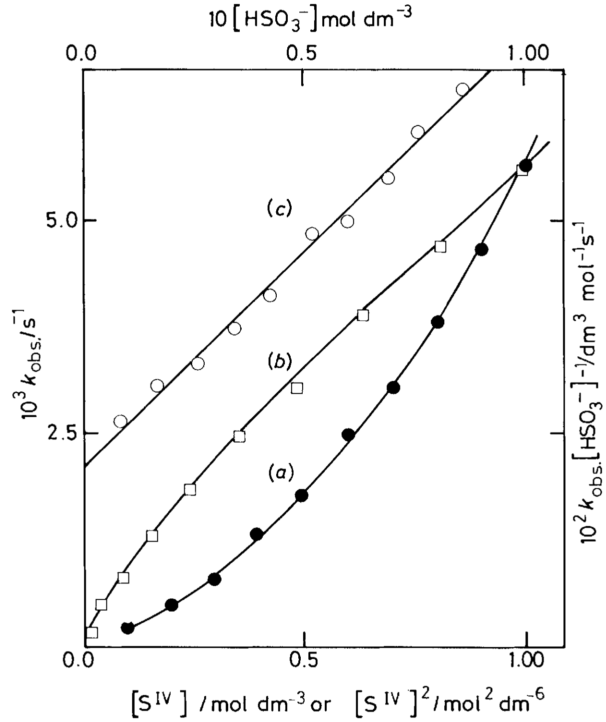

**Figure 1.** Different plots showing the dependence of the observed rate on reductant concentration. (*a*) $k_{obs.}$ *vs.* $[S^{IV}]_T$, (*b*) $k_{obs.}$ *vs.* $[S^{IV}]_T^2$, and (*c*) $k_{obs.}/[HSO_3^-]$ *vs.* $[HSO_3^-]$. Conditions are $[CoW_{12}O_{40}^{5-}] = 2.0 \times 10^{-4}$ mol dm$^{-3}$, $I$ = 0.50 mol dm$^{-3}$, pH 2.80, and 25 °C

produced at 625 nm.[24] Apparently a 1:1 $[S^{IV}]:[Co^{III}]$ stoicheiometry was favoured with excess of sulphite. Dithionate was obtained as the only reaction product under the above conditions ($[Co^{III}]:[S^{IV}]$ = 1:2.5). However, sulphate was also obtained as a reaction product together with dithionate when the complex was present in the proportions $[Co^{III}]:[S^{IV}]$ > 0.67:1 or in excess with respect to sulphite. Assuming that only dithionate and sulphate were the reaction products, their contents were determined for different $[Co^{III}]:[S^{IV}]$ mole ratios. For this purpose known quantities of sodium dithionate were allowed to react with standard potassium dichromate in a strong acid medium (5.0 mol dm$^{-3}$ $HClO_4$). The unreacted dichromate was then estimated spectrophotometrically at 348 nm[11] and thus a calibration graph with respect to known dithionate concentration was constructed. To analyse the dithionate produced, the stoicheiometric mixtures were first freed from sulphite (as $SO_2$) by bubbling dinitrogen through the acidified solution. The removal of cobalt species was accomplished by an ion-exchange method and the dithionate content was determined from the calibration graph after the completion of reaction with excess of dichromate. All these results are given in Table 1. Thus under the experimental conditions with excess of sulphite, the stoicheiometric reaction may be written as in equation (1).

$$2[CoW_{12}O_{40}]^{5-} + 2HSO_3^- \longrightarrow 2[CoW_{12}O_{40}]^{6-} + S_2O_6^{2-} + 2H^+ \quad (1)$$

## Results and Discussion

The reaction between dodecatungstocobaltate(III) with sulphite was studied in the range pH 1.50—3.50 at 25 °C. Acetic acid–sodium acetate buffer was used to adjust the pH at 3.5, but no buffer was required to hold the pH at higher acidities (pH 1.50—3.00). The reactions were monitored mainly at 388 nm, the absorption maximum of $[CoW_{12}O_{40}]^{5-}$. Some experiments carried out at 625 nm, the absorption maximum of the cobalt(II) complex, gave identical results. A typical spectral scanning of this reaction gave an isosbestic point at 510 nm indicating the absence of appreciable amounts of complex intermediate formed during the reaction. Under pseudo-first-order conditions with excess of sulphite, plots of $\log(A_t - A_\infty)$ *vs.* $t$ (where $A_t$, $A_\infty$, and $t$ have their usual significance) were linear up to *ca.* 90% completion of reaction, indicating that the reaction is first order with respect to the complex concentration. However the dependence of the rate on $[S^{IV}]$ (the total sulphite concentration) does not follow a simple order; plots of $k_{obs.}$ *vs.* $[S^{IV}]$ or $[S^{IV}]^2$ were curved. Only plots of $k_{obs.}/[HSO_3^-]$ *vs.* $[HSO_3^-]$ were linear (Figure 1) over the experimental pH range, having a positive intercept on the rate axis. This leads to a rate equation of the type (2) where $[HSO_3^-]$ was calculated

$$k_{obs.} = (k_1 + k_2[HSO_3^-])[HSO_3^-] \quad (2)$$

from the relation $[HSO_3^-] = K[S^{IV}]/(K + [H^+])$ where $K$ is the first dissociation constant of $SO_2$ [equation (3)].

$$SO_2(aq) \overset{K}{\rightleftharpoons} H^+ + HSO_3^- \quad (3)$$

The value of $K$ at 25 °C and $I$ = 0.50 mol dm$^{-3}$ ($NaClO_4$) was evaluated as $8.91 \times 10^{-3}$ mol dm$^{-3}$, in good agreement with the reported value.[27] A pH variation study revealed that the rate of reaction increases with increasing pH of the solution. We therefore investigated the effect of $[H^+]$ on $k_1$ and $k_2$ separately. The concentration of $S^{IV}$ was varied at different pH as shown in Table 2. The values of $k_1$ and $k_2$ thus obtained were then plotted against $[H^+]^{-1}$. Interestingly, the plot of $k_1$ *vs.* $[H^+]^{-1}$ is linear

**Table 2.** Variation of $[S^{IV}]$ at different pH, $[CoW_{12}O_{40}{}^{5-}] = 2 \times 10^{-4}$ mol dm$^{-3}$, $I = 0.50$ mol dm$^{-3}$, and 25 °C

| $10[S^{IV}]$/ mol dm$^{-3}$ | $10^4k_{obs.}$/s$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | pH | 1.50 | 2.00 | 2.80 | 3.00 | 3.50 |
| 0.03 | | | | | | 3.26 |
| 0.07 | | | | | 2.70 | 7.75 |
| 0.10 | | | 0.45 | 2.30 | 4.00 | 11.20 |
| 0.15 | | | | | | 17.16 |
| 0.20 | | | | 5.30 | | 23.50 |
| 0.25 | | | | | | 29.70 |
| 0.30 | | 0.35 | 1.47<br>1.91 | 8.70 | 15.00 | 36.60 |
| 0.35 | | | | | | 43.40 |
| 0.40 | | | 3.09 | 13.00 | | |
| 0.50 | | 1.09 | 5.27 | 18.00 | 28.00 | |
| 0.60 | | | | 25.20 | 37.20 | |
| 0.70 | | 1.70 | 9.50<br>8.64 | 30.60 | 49.00 | |
| 0.80 | | | | 38.20 | | |
| 0.90 | | | 12.41 | 47.00 | | |
| 1.00 | | 3.50 | 15.60 | 56.60 | | |
| 1.20 | | 4.52 | 18.87 | | | |
| 1.50 | | 7.70 | | | | |

**Table 3.** Dependence of $k_1$ and $k_2$ in $[H^+]$

| pH | $10^3[H^+]$/ mol dm$^{-3}$ | $10^3k_1$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $10k_2$/dm$^6$ mol$^{-2}$ s$^{-1}$ |
|---|---|---|---|
| 1.50 | 31.623 | 1.687 ± 0.994 | 6.345 ± 0.471 |
| 2.00 | 10.000 | 6.990 ± 1.838 | 5.324 ± 0.056 |
| 2.80 | 1.585 | 21.673 ± 0.073 | 5.177 ± 0.134 |
| 3.00 | 1.000 | 39.278 ± 0.154 | 5.724 ± 0.382 |
| 3.50 | 0.316 | 111.093 ± 0.253 | 5.160 ± 0.125 |

$k_0 = (2.05 \pm 1.37) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k'_1 = (3.50 \pm 0.10) \times 10^{-5}$ s$^{-1}$, and $k_2 = (5.55 \pm 0.23) \times 10^{-1}$ dm$^6$ mol$^{-2}$ s$^{-1}$.

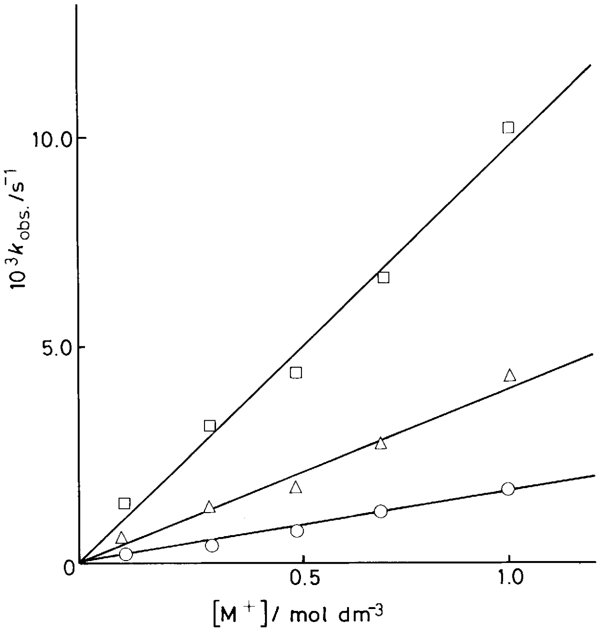

**Figure 2.** Plots of $k_{obs.}$ *vs.* $[M^+]$ at $[CoW_{12}O_{40}{}^{5-}] = 2.0 \times 10^{-4}$ mol dm$^{-3}$, $[S^{IV}] = 0.01$ mol dm$^{-3}$, pH 3.50, and 25 °C (□, $K^+$; △, $Na^+$; ○, $Li^+$).

with a positive intercept on the rate axis, but for $k_2$ no dependence on $[H^+]$ is obtained. Equation (2) can thus be modified to (4). The values of $k_0$, $k'_1$, and $k_2$ were evaluated using

$$k_{obs.} = (k_0 + k'_1[H^+]^{-1} + k_2[HSO_3^-])[HSO_3^-] \quad (4)$$

a least-squares computer procedure and listed in Table 3. It is seen that a large uncertainty is associated with the $k_0$ value $= (2.05 \pm 1.37) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$) and the value of $k'_1$ is $= (3.50 \pm 0.10) \times 10^{-5}$ s$^{-1}$. If $k_0$ is constrained to zero the value of $k'_1$ obtained is $(3.55 \pm 0.09) \times 10^{-5}$ s$^{-1}$. A comparison of these two values shows that $k'_1$ is affected only to a small extent due to this approximation and therefore the contribution of the $k_0$ path appears less significant compared to $k'_1$.

An attempt was then made to verify the effect of alkali-metal ions on the reaction rates. For this purpose, keeping the other conditions the same (pH, $[S^{IV}]$, and temperature), the concentration of the alkali-metal cations ($M^+$) added as supporting electrolyte was varied individually for each of the cations $Li^+$, $Na^+$, and $K^+$. An increase in rate with increasing $[M^+]$ was observed in each case and a plot of $k_{obs.}$ *vs.* $[M^+]$ was linear, passing through the origin (Figure 2). Since both the reacting species are negatively charged, such an increase in rate is not unlikely and the phenomenon may be attributed to specific metal-ion catalysis.[20–23] However, an effect of ionic strength may also lead to similar results. If there is no anion effect the specific metal-ion catalysis could be distinguished by keeping $[M^+]$ constant and varying the ionic strength of the solution by using a mixture of MX (*e.g.* $NaClO_4$) and $M_2Y$ (*e.g.* $Na_2SO_4$) type salts.[21] However, for the present system, variation of the anionic species causes an appreciable change in rate (see below) and thus this method is not applicable. The increase in rate on going from $Li^+$ to $Na^+$ to $K^+$ however provides evidence in favour of the catalytic effect. Such a reactivity order cannot be obtained for a simple ionic strength effect.

In equation (4), $k_0$ and $k'_1$ represent the first-order paths and correspond to the reactions of $HSO_3^-$ and $SO_3^{2-}$ respectively. Excluding protonation and ionic association, the first-order behaviour in general may be given by equation (5). The

$$[CoW_{12}O_{40}]^{5-} + S^{IV} \xrightarrow{\text{slow}} [CoW_{12}O_{40}]^{6-} + S^{V} \quad (5)$$

sulphur(V) species thus produced may reduce another molecule of $[CoW_{12}O_{40}]^{5-}$ giving $SO_4^{2-}$ as the reaction product [equation (6)] or it may recombine with a second radical to

$$\left.\begin{array}{l} H\dot{S}O_3 + [CoW_{12}O_{40}]^{5-} + H_2O \xrightarrow{\text{fast}} \\ \qquad SO_4^{2-} + [CoW_{12}O_{40}]^{6-} + 3H^+ \\ \text{or } SO_3^{\bullet -} + [CoW_{12}O_{40}]^{5-} + H_2O \xrightarrow{\text{fast}} \\ \qquad SO_4^{2-} + [CoW_{12}O_{40}]^{6-} + 2H^+ \end{array}\right\} \quad (6)$$

and

$$\left.\begin{array}{l} H\dot{S}O_3 + H\dot{S}O_3 \xrightarrow{\text{fast}} S_2O_6^{2-} + 2H^+ \\ SO_3^{\bullet -} + SO_3^{\bullet -} \xrightarrow{\text{fast}} S_2O_6^{2-} \end{array}\right\} \quad (7)$$

produce dithionate [equation (7)] in a rapid step. In the above reactions $H\dot{S}O_3$ represents the free radical produced in the $k_0$ path and $SO_3^{\bullet -}$ that in the $k'_1$ path. The $k_2$ path in equation (4) accounts for the second-order dependence in $[HSO_3^-]$ and the rate-determining step may be rationalised by either of the mechanisms (*i*) or (*ii*).*

$$(i)\ 2HSO_3^- \underset{}{\overset{(K_1 < 1)}{\rightleftharpoons}} S_2O_5^{2-} + H_2O \quad (8)$$

$$[CoW_{12}O_{40}]^{5-} + S_2O_5^{2-} \xrightarrow{\text{slow}} [CoW_{12}O_{40}]^{6-} + S_2O_5^{\bullet -} \quad (9)$$

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* In mechanism (*ii*) no oxidation state of the metal or charge on the hydrogensulphite has been assigned to the intermediate species. The intermediate may be a $Co^{III}$–$S^{IV}$ or $Co^{II}$–$S^{V}$ species.

$$S_2O_5^{\bullet -} \xrightarrow[H_2O]{\text{fast}} \text{products} \qquad (10)$$

$$(ii)\ [CoW_{12}O_{40}]^{5-} + HSO_3^- \overset{K_2}{\rightleftharpoons} \{[CoW_{12}O_{40}], HSO_3\}^{6-} \qquad (11)$$

$$HSO_3^- + \{[CoW_{12}O_{40}], HSO_3\}^{6-} \xrightarrow{\text{slow}} [CoW_{12}O_{40}]^{6-} + H\dot{S}O_3 + HSO_3^- \qquad (12)$$

$$H\dot{S}O_3 \xrightarrow[H_2O]{\text{fast}} \text{products} \qquad (13)$$

It is however difficult to distinguish between the two mechanisms from the available data. A greater reactivity of $S_2O_5^{2-}$ in comparison to $HSO_3^-$ is implied for mechanism (*i*). Though the existence of $S_2O_5^{2-}$ at $[S^{IV}] \leqslant 0.003$ mol dm$^{-3}$ at pH 3.50 could not be recognised spectrophotometrically,[28] it is likely to be present in trace amount. A second-order dependence in reductant concentration has also been noted in the oxidation of cysteine by this heteropolyion.[29]

To explore the true mechanism, it is however necessary to consider the effect of alkali-metal ions in this reaction. Since both the reacting species are negatively charged, the observed alkali-metal-ion dependence may be explained by assuming an outer-sphere complex formation *via* the alkali-metal ion where it acts as a bridge between the reactants. The catalytic activity of the alkali-metal ions follows the order $K^+ > Na^+ > Li^+$. This may be explained by considering the size of the hydrated cation which is in the order $Li^+ > Na^+ > K^+$. Thus $K^+$ would be more effective than $Na^+$ or $Li^+$ in bridging the two negatively charged species. This dependence also excludes the possibility of inner-sphere complex formation, as confirmed by the single isosbestic point obtained during spectral scanning.

Turning our attention to the hydrogen-ion dependence, we find that $k_0$ and $k'_1$ account for the $[H^+]$-independent and $[H^+]^{-1}$-dependent paths respectively. Thus $SO_3^{2-}$ seems to be more reactive than $HSO_3^-$, and has also been observed in the reactions of sulphite with iron(III)[11] and manganese(III)[30] complexes. The lower reactivity of $HSO_3^-$ has been attributed[31] to the decrease in electron density on the sulphur atom due to the associated proton. A quantitative estimation of the reactivity of $SO_3^{2-}$ may be made using the second dissociation constant ($K_2 = 4.57 \times 10^{-7}$ mol dm$^{-3}$) of $H_2SO_3$.[27] The ratio $k'_1K_2^{-1}/k_0$ (Table 3) shows that $SO_3^{2-}$ is *ca.* $3.7 \times 10^4$ times more reactive than $HSO_3^-$. The effect of dissolved oxygen on the reaction rates has been verified for this system. Under deaerated conditions the rates are *ca.* 5% faster than in the presence of dissolved oxygen. This inhibition may be attributed to scavenging of the intermediate in step (11) or $S_2O_5^{2-}$ in step (8). An examination of the effect of the reaction products on the rates revealed that the rates decrease by 20—25% when 0.50 mol dm$^{-3}$ $Na_2SO_4$ or $Na_2S_2O_6$ is used instead of 1.0 mol dm$^{-3}$ $NaClO_4$ $\{k_{NaClO_4} = (8.68 \pm 0.18) \times 10^{-3}$, $k_{Na_2SO_4} = (6.86 \pm 0.12) \times 10^{-3}$ s$^{-1}$ at pH 3.00, $[S^{IV}] = 0.03$ mol dm$^{-3}$, 25 °C$\}$. This may arise due to the lower availability of free $M^+$ (not ion-paired) for bridging. The acetate buffer used to hold the pH at 3.5 had no appreciable effect on the reaction rates.

Oxidation of $S^{IV}$ by a pathway with mixed first and second orders in $[S^{IV}]$ is unusual. Among previous studies, there are only two examples so far.[1,11] In the oxidation of $S^{IV}$ by chromium(VI) the mechanism proposed involved the formation of a sulphatochromate ester which reacted with a second sulphur(IV) species. The other example showing a higher-order dependence in $[S^{IV}]$ is the reaction between $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) and sulphite.[11] It was suggested that anionic oxidants like $[IrCl_6]^{2-}$ for which ion-pairing or specific sulphur-ligand interactions are unlikely may lead to a second-order dependence on $[S^{IV}]$. One of the objectives of our study outlined in the Introduction was to verify such generalisation, and indeed such result is corroborated with the present oxidant, $[CoW_{12}O_{40}]^{5-}$, though we have noticed some sort of ion-pair formation *via* the alkali-metal ions. In this context a recent study of the oxidation of sulphite by $[IrCl_6]^{2-}$ [13] and $[PtCl_6]^{2-}$ [14] and also a previous study[12] with $[Mo(CN)_8]^{3-}$ and $[W(CN)_8]^{3-}$ did not however reveal such an effect.

From the stoicheiometric results obtained in this study, it is evident that one-electron reduction by $S^{IV}$ is preferred at high concentrations of $S^{IV}$, and with an excess of complex over $S^{IV}$ a two-electron reduction by $S^{IV}$ takes place simultaneously with the one-electron path. The amounts of sulphate and dithionate produced are in good accord with the $[CoW_{12}O_{40}]^{5-}$ consumed for the different stoicheiometric ratios (Table 1). A similar result was obtained by Higginson and Marshall[15] in the oxidation of sulphite by $[Fe(CN)_6]^{3-}$.

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