

Oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by peroxomono-sulfate in strong and weak acid solutions, an example of zero-order kinetics

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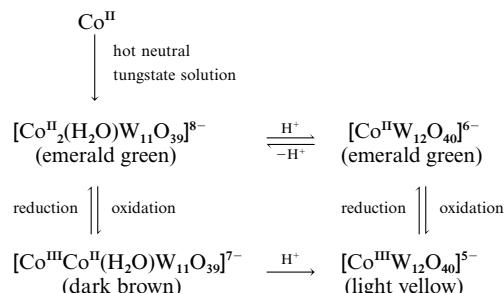
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Oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by HSO_5^- in both strong and weak acid solution (the latter in the presence of added $[\text{WO}_4]^{2-}$) gives $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. The kinetics of oxidation was examined at 15–35 °C over the range $[\text{H}^+] = 0.05\text{--}0.625 \text{ mol dm}^{-3}$ and found to exhibit pseudo-zero-order kinetics, $-d[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/dt = 2k_{\text{ox}}[\text{HSO}_5^-]/[\text{H}^+]$ where $k_{\text{ox}} = 1.03(7) \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 25.0 °C. The rate expression may be accounted for by a mechanism arising from the deprotonation of HSO_5^- to give SO_5^{2-} as the oxidant species, enabling oxidation of two $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ ions by an SO_5^{2-} ion, presumably through an outer-sphere electron-transfer mechanism given the stability of the polyoxotungstate framework under highly acidic conditions. Over the pH range 4.2–5.7 and 5–25 °C the reaction exhibits pseudo-first-order reaction kinetics which is independent of the oxidant concentration and involves breakdown of the polyoxotungstate framework as the limiting step, with removal of a W_3O_{13} unit as a precursor to oxidation through the loss of three $[\text{HWO}_4]^-$ ions following attack by water molecules. The reaction kinetics for the oxidation by HSO_5^- of the related Co^{II}-substituted Keggin ion $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ to give $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$ was also investigated, and likely involves initial oxidation of the framework Co^{II} to Co^{III} followed by fast electron transfer to give a central cobalt(III) heteroatom.

Over the last few years we have been involved in a program of study of the kinetics of formation reactions of heteropolyoxometalate compounds, with a view to elucidating their mechanism(s) of formation. Almost no investigations of this type had previously been made despite the fact that many such compounds have been known for a considerable period of time. To date, the kinetics of oxidation of manganese(II) by peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$), peroxomonosulfate (HSO_5^-) and hypochlorous acid (HOCl), of nickel(II) by $\text{S}_2\text{O}_8^{2-}$, and of cobalt(II) by HSO_5^- , all in aqueous solution in the presence of molybdate, have been examined, resulting in formation of the species $[\text{MnMo}_9\text{O}_{32}]^{6-}$, $[\text{NiMo}_9\text{O}_{32}]^{6-}$ and $[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-}$.^{1–4} These studies have established that the main building units of heteropolyoxomolybdates are $[\text{HMnO}_4]^-$ and, to a lesser extent, $[\text{MoO}_4]^{2-}$. These species have appeared as major components in the experimentally established rate laws, whether involved in the assembly of the polyoxomolybdate framework, or in breakdown of the framework prior to oxidation. We now report the kinetics of oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by HSO_5^- in both strong and weak acid solutions and, in a limited study, we have also looked at the kinetics of oxidation of the related Co^{II}-substituted Keggin species $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ by HSO_5^- at high pH to give the Co^{III}-centred species $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$.

The four cobalt polyoxotungstate anions listed above and their chemical interrelationships are summarised in Scheme 1. Both $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ have the well known twelve-tungsten atom Keggin structure,⁵ while $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ and $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$ have modified Keggin structures where a $\text{Co}(\text{H}_2\text{O})^{2+}$ unit replaces a WO_4^{4-} unit in the peripheral polyoxotungstate framework of the conventional Keggin structure.^{5,6}

While our previous studies have involved primarily the assembly or fragmentation of the polyoxometalate framework in the formation of the heteropolyoxometalate, this study has allowed some examination of oxidation reactions of heteropolyoxotungstate species where the anion remains intact, so



Scheme 1

that the central heteroatom is still enclosed within the polyoxometalate framework (or partial polyoxometalate framework); the only change is in the oxidation state of the central tetrahedrally co-ordinated heteroatom, in this case Co^{II}, and an associated change in the anionic charge. Prior to this study, the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in strong acid solution has been the subject of a number of investigations with other oxidants such as bromate (BrO_3^-), peroxodisulfate, periodate (IO_4^-), chlorate (ClO_3^-) and permanganate (MnO_4^-).^{7–11} In each case the oxidation was found to follow pseudo-first-order kinetics and outer-sphere reaction mechanisms were proposed on the basis of the stability of the anion under the highly acidic reaction conditions. Interestingly, in the present study, oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in strongly acid solution ($[\text{H}^+] = 0.05\text{--}0.625 \text{ mol dm}^{-3}$) resulted in an example of pseudo-zero-order kinetics, which is rarely observed in inorganic systems, while under less acidic conditions (pH 4.2–5.7) evidence for the breakdown of the polyoxotungstate framework prior to oxidation was observed. Oxidation of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ to $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$ is also examined, and is believed to involve oxidation of the framework Co^{II} to Co^{III}, followed by fast electron transfer to give a Co^{III} at the core of the heteropolyoxotungstate anion.

Experimental

Syntheses

Hexapotassium dodecatungstocobaltate(II) 16-hydrate, $K_6[CoW_{12}O_{40}] \cdot \approx 16H_2O$. The synthesis was adapted from that reported by Baker and McCutcheon¹² (syntheses A, B and G). Sodium tungstate dihydrate, $Na_2WO_4 \cdot 2H_2O$ (99.0 g, 0.30 mol), was dissolved in water (200 cm³), and the solution adjusted to between pH 6.5 and 7.5 by the addition of glacial acetic acid (20 cm³). A solution (65 cm³) of $Co(CH_3CO_2)_2 \cdot 4H_2O$ was also prepared (12.45 g, 0.05 mol). The Na_2WO_4 solution was heated to near boiling and the $Co(CH_3CO_2)_2$ solution added slowly with stirring. The resulting mixture was boiled gently for 10 min and filtered while still hot to remove traces of insoluble matter. A hot, saturated solution (150 cm³) of KCl (65.0 g, 0.87 mol) was added to the above solution, which had been returned to the boil, and the resulting solution allowed to cool to room temperature. The green precipitate which formed was allowed to settle for 24 h, and the resulting pale blue solution removed by decantation. To the dark green precipitate (which also contained a significant amount of light green sludge) was added 2 mol dm⁻³ H_2SO_4 (200 cm³). The solution immediately became dark blue (a result of the conversion of $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ into $[Co^{II}W_{12}O_{40}]^{6-}$). It was evaporated slowly on a hotplate over 4 h to a volume of 50 cm³. The light green needles described by Baker and McCutcheon¹² were observed to form during this procedure. The solution was then filtered while still hot and cooled in an ice-bath. Dark blue crystals formed which were isolated within 24 h and allowed to dry in the air (40.7 g, 47% yield). After 24 h a white precipitate had formed in the remaining solution and no further material could be obtained. The crystals were used to prepare the stock solution for the kinetic studies, while a small portion was retained for recrystallization from water (pH ≈ 4) in order to obtain X-ray quality crystals. Subsequently, the product was structurally characterized by X-ray crystallography, which will be reported separately.¹³ Thermogravimetric analysis was used to establish the actual water content of the compound. This study resulted in a loss of mass of 8.57% up to 400 °C, indicating 16.3 H₂O molecules per $K_6[CoW_{12}O_{40}]$ formula unit, so that the composition of the compound was close to $K_6[CoW_{12}O_{40}] \cdot 16H_2O$. The UV/VIS spectrum profile and molar absorptivity agreed with those reported by Simmons¹⁴ and Ayoko *et al.*,⁷ indicating the purity of the compound. λ_{max}/nm (water, pH 5.1) 625 ($e/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 214). Infrared spectrum (KBr disc): 938s (W=O stretching), 874s, 735s cm⁻¹ (W–O–W and Co–O–W stretching).

Octapotassium aquaundecatungstodicobaltate(II) 17-hydrate, $K_8[Co_2(H_2O)W_{11}O_{39}] \cdot 17H_2O$. The synthesis of this compound was essentially as reported by Baker and McCutcheon.¹² The product was recrystallized from water (pH 5) three times. The product did not contain any of the insoluble pink material, $K_6[Co(H_2O)_4(H_2W_{12}O_{42})] \cdot 14H_2O$, which has been reported by Giménez-Saiz *et al.*,¹⁵ and was characterized spectroscopically for use in the kinetic studies, as described below. UV/VIS (water, pH 5.8): λ_{max}/nm 600 ($e/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 211). The visible spectrum agreed with that reported by Simmons.¹⁴

Physical methods

Electronic spectra were recorded on an Hitachi 150-20 or U-2000 spectrophotometer, infrared spectra as KBr discs using a Bio-Rad FTS-7 Fourier-transform spectrophotometer. Thermogravimetric analysis was accomplished using a Stanton Redcroft TG-750 instrument with a Eurotherm model 94 temperature controller. Sample masses of about 10–15 mg were used, with a heating rate of 10 °C min⁻¹, and analyses were performed in a static air atmosphere. Electron spin resonance studies (X-band) were carried out on a Bruker ESP300 spectrometer at a resonance frequency of 9600 MHz employing 100

kHz field modulation. A flat cell appropriate for aqueous solutions was employed, and measurements were made at 21 °C.

Kinetic studies

The oxidation of $[Co^{II}W_{12}O_{40}]^{6-}$ to $[Co^{III}W_{12}O_{40}]^{5-}$ was monitored at 625 nm on an Hitachi 150-20 or U-2000 spectrophotometer fitted with a thermostatted compartment stable to ± 0.1 °C. Owing to the speed of the oxidation of $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ to $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$, the reactions in this case were monitored on an Applied Photophysics SX.17MV stopped-flow spectrophotometer. The data were collected and analysed using an interfaced Archimedes 440/1 computer. The reactions were monitored between 580 and 640 nm in 10 nm intervals. A first-order globalization procedure involving singular value decomposition of the resulting matrix of absorbance vs. time data and subsequent non-linear least-squares fitting was then used to obtain the rate constants.¹⁶ The spectrophotometer was fitted with a thermostatted compartment stable to ± 0.1 °C.

Millipore Milli-Q water was used throughout the kinetic studies. Investigation of the oxidation of $[Co^{II}W_{12}O_{40}]^{6-}$ to $[Co^{III}W_{12}O_{40}]^{5-}$ in highly acidic solution involved mixing equal volumes of $[Co^{II}W_{12}O_{40}]^{6-}$ stock solution (in 0.05 mol dm⁻³ H_2SO_4 , no added $[WO_4]^{2-}$) and HSO_5^- solution giving final reaction mixtures containing 6.1×10^{-4} mol dm⁻³ $[Co^{II}W_{12}O_{40}]^{6-}$, and variable amounts of “Oxone” (2KHSO₅·KHSO₄·K₂SO₄; purity determined as 97.4% using the method for K₂S₂O₈) (Aldrich)¹⁷ and $[H^+]$ with enough NaNO₃ (UNIVAR, AR Grade) to yield a total ionic strength of 0.75–1.75 (for the ionic strength dependence), 1.8 (for the $[HSO_5^-]$ dependence and wavelength dependences), 1.00 (for the $[H^+]$ dependence) or 0.40 mol dm⁻³ (for the reaction stoichiometry determination). The hydrogen ion concentration was varied by addition of H_2SO_4 . For the different acid medium study, the $[Co^{II}W_{12}O_{40}]^{6-}$ stock solution contained 0.75 mol dm⁻³ HClO₄. In the deuterium isotope effect study, $[Co^{II}W_{12}O_{40}]^{6-}$ was made up in D₂O with a $[D^+] = 0.05$ mol dm⁻³ using D₂SO₄ (98 wt. % solution in D₂O, Aldrich).

For the oxidation of $[Co^{II}W_{12}O_{40}]^{6-}$ to $[Co^{III}W_{12}O_{40}]^{5-}$ in weakly acidic solution, equal volumes of buffered stock solutions of $[Co^{II}W_{12}O_{40}]^{6-}$, also containing an excess of $[WO_4]^{2-}$, and HSO_5^- solutions were mixed together to obtain the final solutions. Final reaction mixtures contained variable amounts of $[Co^{II}W_{12}O_{40}]^{6-}$ stock solution, $Na_2WO_4 \cdot 2H_2O$ (UNIVAR, AR Grade) and “Oxone” as appropriate, with enough NaNO₃ (UNIVAR, AR Grade) to yield a total ionic strength of 1.00 mol dm⁻³. For the tungstate-dependence study, however, in order to obtain a wide range of $Co^{2+} : [WO_4]^{2-}$ ratios, solutions were prepared with a total ionic strength of 1.60 mol dm⁻³.

For the oxidation of $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ to $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$ only an oxidant dependence was investigated. Equal volumes of buffered $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ stock solutions, also containing an excess of $[WO_4]^{2-}$, and ones containing HSO_5^- were mixed to obtain the final solutions. Final reaction mixtures were buffered at pH 5.69 and contained 0.0020 mol dm⁻³ $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$, 0.0625 mol dm⁻³ $[WO_4]^{2-}$ ($Na_2WO_4 \cdot 2H_2O$, UNIVAR, AR Grade), variable amounts of “Oxone”, with enough NaNO₃ (UNIVAR, AR Grade) to yield a total ionic strength of 1.00 mol dm⁻³.

All reaction mixtures for the studies at lower acidity were initially prepared using 6 mol dm⁻³ acetic acid–NaOH buffer solutions. The high concentration of buffer solutions was necessary to stabilize the pH due to both the acidity of “Oxone” and the basicity of $[WO_4]^{2-}$ in solution during polymerization to $[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$. As a result, only a slight variation in pH (0.08 unit, $[Co^{II}W_{12}O_{40}]^{6-}$ to $[Co^{III}W_{12}O_{40}]^{5-}$) was observed over the range of $[WO_4]^{2-}$ concentrations used at any fixed pH and, similarly, a minor variation in pH (0.02 unit for oxidation of $[Co^{II}W_{12}O_{40}]^{6-}$ to $[Co^{III}W_{12}O_{40}]^{5-}$,

Table 1 Observed zero-order rate constants for the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by HSO_5^- under highly acidic conditions ($[\text{H}^+] = 0.05\text{--}0.625 \text{ mol dm}^{-3}$, $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 6.1 \times 10^{-4} \text{ mol dm}^{-3}$)

$[\text{HSO}_5^-]/\text{mol dm}^{-3}$	$[\text{H}^+]/\text{mol dm}^{-3}$	$I/\text{mol dm}^{-3}$	$T/\text{^\circ C}$	$10^7 k_{\text{ox}}/\text{mol dm}^{-3 \text{ s}^{-1}}$
0.010	0.05	1.8	25.0	2.41(8)
0.020	0.05	1.8	25.0	4.30(15)
0.030	0.05	1.8	15.2	1.80(7)
0.030	0.05	1.8	20.4	3.88(15)
0.030	0.05	1.8	25.0	6.45(30)
0.030	0.05	1.8	29.9	11.24(50)
0.030	0.05	1.8	34.4	18.62(80)
0.030	0.125	1.0	25.0	2.57(9)
0.030	0.125	1.75	25.0	2.32(10)
0.030	0.25	1.0	25.0	1.23(6)
0.030	0.25	1.50	25.0	1.17(6)
0.030	0.375	1.0	25.0	0.81(4)
0.030	0.375	1.25	25.0	0.79(4)
0.030	0.50	1.0	25.0	0.59(3)
0.030	0.625	0.75	25.0	0.44(2)
0.030	0.625	1.0	25.0	0.47(2)
0.040	0.05	1.8	25.0	8.90(5)
0.050	0.05	1.8	25.0	11.43(6)

and 0.01 unit for oxidation of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ to $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$ was observed over the range of HSO_5^- concentrations used.

Results and discussion

As indicated in Scheme 1, conversion of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ into $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ occurs in acidic solution. The preparation of the latter is usually accomplished by addition of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{8-}$ to *ca.* 2 mol dm⁻³ H_2SO_4 , followed by purification through recrystallization. The lower limit of stability of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in acidic solution has not been accurately established and, indeed, all kinetic studies of oxidation of this anion have been performed in quite strongly acidic solution ($[\text{H}^+] = 0.02\text{--}1.5 \text{ mol dm}^{-3}$).⁷⁻¹¹ Before examination of the kinetics of oxidation of this anion under weakly acidic conditions was begun, in the presence of added tungstate, a study of the oxidation kinetics in strongly acidic solution using the oxidant HSO_5^- was performed. To our surprise, this reaction exhibited zero-order kinetics (at a given HSO_5^- concentration), which is extremely rare in simple inorganic systems. Previous studies of the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by a variety of oxidants (BrO_3^- , $\text{S}_2\text{O}_8^{2-}$, IO_4^- , ClO_3^- and MnO_4^-) under highly acidic conditions have been analysed in terms of pseudo-first-order rate constants. Various rate laws have been established involving first-order dependences on reductant, oxidant and in some cases a catalyst concentration, with either acid independence ($\text{S}_2\text{O}_8^{2-}$), first-order acid dependence (MnO_4^-), or parallel pathways involving acid independence and first- or second-order acid dependence (BrO_3^- , IO_4^- and ClO_3^-). In each case an outer-sphere mechanism for the oxidation reaction was proposed based on the inert nature of the polyoxotungstate framework surrounding the central Co^{II} .

In our studies, oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ at high acid concentrations ($[\text{H}^+] = 0.05$ to $0.625 \text{ mol dm}^{-3}$) and in weakly acidic solution (pH 4.2–5.7) using HSO_5^- as the oxidant exhibited relatively slow kinetics at room temperature to give $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. With the exception of the temperature dependence studies, all oxidation kinetics for both studies was monitored at 25.0 °C.

1. Oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by HSO_5^- in highly acidic solution

In the present study, oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in highly acidic solution by HSO_5^- occurred slowly at room temperature and below to give $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. Surprisingly, all absorbance

vs. time traces observed for the loss of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{5-}$ at 625 nm were $\geq 99.9\%$ linear over the course of a kinetic run, indicative of zero-order kinetics. However, for the final few percent of the reactions, some slight curvature of the traces was noted. In order to verify the zero-order nature of the reaction, the kinetics was examined at 40 nm to either side of the broad band maximum, with identical results. Consequently, the kinetic data were analysed in terms of a (pseudo) zero-order rate law governed by k_{ox} which, as shown below, subsumes dependences on both $[\text{HSO}_5^-]$ and $[\text{H}^+]$. A list of rate constants obtained under various conditions is given in Table 1. The reaction stoichiometry was established by adding an excess of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to HSO_5^- , allowing the reaction to proceed to completion and establishing the ratio of the number of mols of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ consumed per mol of HSO_5^- . This value was 1.96, indicating that HSO_5^- is acting as a two-electron oxidant. Thus the rate expression (1) may be written.

$$-\text{d}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/\text{dt} = 2k_{\text{ox}} \quad (1)$$

The rate constant k_{ox} shows a first-order dependence on $[\text{HSO}_5^-]$ at a $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$, so that a plot of $\log k_{\text{ox}}$ against $\log [\text{HSO}_5^-]$ gives a straight line with a slope of 0.97(4) ($R^2 = 0.9952$). The plot of k_{ox} against $[\text{HSO}_5^-]$ was linear, passing through the origin. This results in the expanded rate expression (2), where $k'_{\text{ox}} = 2.24(10) \times 10^{-5} \text{ s}^{-1}$ at 25.0 °C. This

$$-\text{d}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/\text{dt} = 2k'_{\text{ox}}[\text{HSO}_5^-] \quad (2)$$

value is an average over each of the HSO_5^- concentrations employed (Table 1).

The rate constant k_{ox} also shows an inverse first-order dependence on $[\text{H}^+]$, with a plot of $\log k_{\text{ox}}$ against $\log [\text{H}^+]$ giving a straight line of slope $-1.053(5)$ ($R^2 = 0.9999$). A plot of k_{ox} against $1/[\text{H}^+]$ passed through the origin, with no evidence for any intercept. This results in the expanded rate expression (3), where $k_{\text{ox}} = 1.03(7) \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 25.0 °C based

$$-\text{d}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/\text{dt} = 2k_{\text{ox}}[\text{HSO}_5^-]/[\text{H}^+] \quad (3)$$

upon $k_{\text{ox}} = k'_{\text{ox}}[\text{H}^+]$, averaged over all of the relevant data given in Table 1.

An alternative form of this rate expression involves incorporation of the deprotonation reaction $\text{HSO}_5^- \rightleftharpoons \text{SO}_5^{2-} + \text{H}^+$, where $K_a = 4.0(9) \times 10^{-10} \text{ mol dm}^{-3}$,¹⁸ resulting in a rate expression of the form (4), where $k'_{\text{ox}} = 2.6(7) \times 10^3 \text{ s}^{-1}$ at 25.0 °C.

$$-\text{d}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}/\text{dt} = 2k'_{\text{ox}}[\text{SO}_5^{2-}] \quad (4)$$

Although the pK_a for the above deprotonation reaction is 9.4(1) and in this study the $[\text{H}^+]$ ranges from 0.05 to 0.625 mol dm⁻³, with SO_5^{2-} concentrations therefore of the order of $10^{-11}\text{--}10^{-10} \text{ mol dm}^{-3}$, the resulting rate equation suggests that SO_5^{2-} is the active species with dissociation of HSO_5^- occurring prior to oxidation of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$.

The reaction was also investigated under conditions of a slight excess of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$. For a single kinetic run with $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 6.1 \times 10^{-4}$, $[\text{HSO}_5^-] = 5.0 \times 10^{-4}$, $[\text{H}^+] = 0.05$ and $I = 0.40$ (NaNO_3) mol dm⁻³ at 25.0 °C the reaction becomes effectively first order, with a rate constant of $1.26 \times 10^{-4} \text{ s}^{-1}$. This is consistent with the observation of a slight curvature of the linear absorbance vs. time traces near completion of the reaction, when performed with an excess of oxidant, as noted above.

Temperature dependence. The temperature dependence of the oxidation was studied from 15.2 to 34.4 °C. The data (at $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$) are given in Table 1. An Arrhenius plot of $\ln k_{\text{ox}}$ against $1/T$ gives a straight line ($R^2 = 0.9977$) and an Arrhenius activation energy, E_a , of 88(2) kJ mol⁻¹. The data

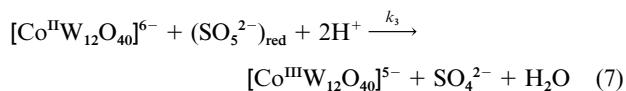
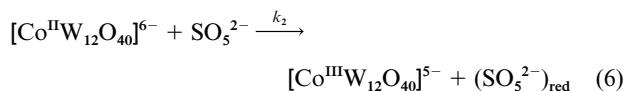
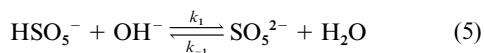
(following conversion of k_{ox} into k'_{ox} , which removes all concentration interdependencies) may also be used to estimate the enthalpy and entropy of activation, $\Delta H^\ddagger = 86 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -20 \text{ J K}^{-1} \text{ mol}^{-1}$. Solvation effects can be expected to dominate in reactions between ionic species, so that the negative activation entropy is consistent with some solvent rearrangement and an increase in solvation during formation of the transition state of this reaction.

Investigation of potential ionic strength dependence and the zero-order reaction in a different acid medium (HClO_4). The oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by HSO_5^- has been shown above to have an inverse first-order dependence on $[\text{H}^+]$. In order to investigate any potential ionic strength effect a second $[\text{H}^+]$ dependence was studied, but under conditions whereby the ionic strength was allowed to vary by more than a factor of two by adjustment with added NaNO_3 . The data are given in Table 1. A plot of $\log k_{\text{ox}}$ against $\log [\text{H}^+]$ gives a slope of $-1.02(2)$ ($R^2 = 0.9990$), indicating an inverse first-order dependence on $[\text{H}^+]$. Again, a plot of k_{ox} against $1/[\text{H}^+]$ was linear and passed through the origin, with no evidence for any intercept. As no deviation from the inverse first-order dependence was observed, which was originally obtained under constant ionic strength conditions, this indicates that the oxidation reaction is not dependent on ionic strength in the range studied.

A typical zero-order reaction was also carried out in a different acid medium, HClO_4 , to determine if the reaction was dependent on the type of electrolyte. Using the conditions $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 5.9 \times 10^{-4}$, $[\text{HSO}_5^-] = 0.030$, $[\text{HClO}_4] = 0.75$, $I = 1.00$ (NaNO_3) mol dm^{-3} and 25.0°C , the reaction again exhibited zero-order kinetics with the pseudo-zero-order rate constant $k_{\text{ox}} = 1.0 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Isotope effect. The effect of the deuterium isotope rate effect was investigated by conducting a single reaction in $\text{D}_2\text{O}-\text{D}_2\text{SO}_4$. Under identical reaction conditions ($[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 6.1 \times 10^{-4}$, $[\text{HSO}_5^-] = 0.030$ and $I = 1.8 \text{ mol dm}^{-3}$) apart from the H_2SO_4 -water medium being replaced by $\text{D}_2\text{SO}_4-\text{D}_2\text{O}$ where $[\text{H}^+] = [\text{D}^+] = 0.05 \text{ mol dm}^{-3}$, the ratio $k_{\text{ox}}^{\text{D}} : k_{\text{ox}}^{\text{H}} = 0.38 : 1$ at 25.0°C was obtained. The ratio indicates that hydrogen bonds have some involvement in the activation process, and further discussion of this is given below.

Mechanistic considerations. The form of the rate equation (3) and the derived form (4) provide considerable insight into the rate-determining step of the reaction mechanism, and suggest that this involves the deprotonation of HSO_5^- by OH^- , even under the highly acidic conditions used in this study.



The first reaction involves the deprotonation of HSO_5^- to give SO_5^{2-} and its reverse, while the second and third steps are both rapid, with the third included to account for the observed stoichiometry. Application of the steady-state approximation to the $[\text{SO}_5^{2-}]$ leads to the expression (8). Introduction of the

$$-\frac{d}{dt}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 2k_1k_2[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}[\text{HSO}_5^-][\text{OH}^-]/(k_2[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} + k_{-1}[\text{H}_2\text{O}]) \quad (8)$$

expression for K_w , i.e. $K_w = [\text{H}^+][\text{OH}^-]$, yields eqn. (9). Now,

$$-\frac{d}{dt}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 2k_1k_2K_w[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}[\text{HSO}_5^-]/[\text{H}^+](k_2[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} + k_{-1}[\text{H}_2\text{O}]) \quad (9)$$

assuming that $k_2[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} \gg k_{-1}[\text{H}_2\text{O}]$, this expression reduces to eqn. (10) which is identical to the experimentally

$$-\frac{d}{dt}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 2k_1K_w[\text{HSO}_5^-]/[\text{H}^+] \quad (10)$$

determined rate expression (3). Thus the observed rate constant $k_{\text{ox}} = k_1K_w$ [where $k_{\text{ox}} = 1.03(7) \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$], so that $k_1 = (1.03 \times 10^{-6})/(1.008 \times 10^{-14}) \approx 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Moreover, as k_1 and k_{-1} are related through the equilibrium expression for eqn. (5), and are also linked to the expression for the pK_a of HSO_5^- and that of pK_w , then k_{-1} can be evaluated as ca. $45 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The values for k_1 and k_{-1} are only approximate, as the ion product used, K_w , is that for pure water and is inappropriate in the presence of such a high ionic strength with the concentrations employed in the present studies ($[\text{H}_2\text{SO}_4] = 0.05$ to $0.625 \text{ mol dm}^{-3}$).¹⁹

The forward reaction in eqn. (5) is, not surprisingly, very fast, but is somewhat slower than the upper limit of about $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for a bimolecular rate constant in solution. This is consistent with reaction (5), which involves the interaction of two like-charged anions and so the rate constant would be expected to be somewhat less than the upper limit given above. The negative entropy of activation is also consistent with the interaction of two ions of similar charge forming the activated state and the increased solvation required for a dianion. Reaction (5) is thus the rate-limiting step in the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by virtue of the low concentration of OH^- , which under the strongly acid conditions of the present study is extremely low, despite the magnitude of the bimolecular rate constant involved in this step. The deuterium isotope rate effect also suggests involvement of hydrogen bonds in the rate-determining step, which is again consistent with deprotonation of HSO_5^- as given in the forward reaction of eqn. (5). However, some further discussion is warranted. The general observation of $k_D : k_H \leq 1$ (0.38 : 1 in the present case) is related to differences in solvation, and has been well established for solvolysis reactions of organic halides and sulfonates in aqueous media as well as, for example, hydrolysis and isomerization reactions of some co-ordination compounds.²⁰⁻²³ Most macroscopic and molecular properties of H_2O and D_2O are almost identical, although properties related to the disruption of the structure are different, such as viscosity and melting point. Also, differences in the thermodynamic properties of H_2O and D_2O have been qualitatively interpreted in terms of a somewhat stronger O-D···O hydrogen bond than a O-H···O hydrogen bond. This results from the larger moment of inertia of D_2O compared to H_2O . Thus there is a widely held view that D_2O is a more structured (rigid) solvent than H_2O . A solvent isotope effect on reaction rate is thus related to solvation effects in the two solvents, although whether a species is less strongly solvated in the more structured D_2O solvent or whether more of the hydrogen-bonding network is broken in forming the transition state in D_2O is difficult to answer. Without further studies, in the present case it is simply pointed out that the $k_D : k_H < 1:1$ is consistent with solvent and hence hydrogen bond involvement in formation of the transition state.

A key point in determining the zero-order nature of the reaction is the assumption that $k_2[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} \gg k_{-1}[\text{H}_2\text{O}]$. While k_{-1} is relatively fast (ca. $45 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), k_2 must be very fast for this assumption to be valid, given the extent of reaction over which zero-order kinetics is exhibited. Indeed, as noted above, only at the very end of each reaction some curvature of the absorbance vs. time traces was observed and, when the reaction

Table 2 Observed rate constants for the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ by HSO_5^- under weakly acidic conditions ($\text{pH } 4.17\text{--}5.68$, $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 0.0025 \text{ mol dm}^{-3}$).

$[\text{HSO}_5^-]/\text{mol dm}^{-3}$	$[\text{WO}_4^{2-}]_T/\text{mol dm}^{-3}$	$[\text{WO}_4^{2-}]_{\text{calc}*}/\text{mol dm}^{-3}$	pH	T/°C	$I/\text{mol dm}^{-3}$	$10^4 k_{\text{diss}}/\text{s}^{-1}$
0.005	0.0625	—	5.22	25.0	1.00	4.54(15)
0.010	0.0625	—	5.22	25.0	1.00	4.62(15)
0.020	0.0625	—	5.22	25.0	1.00	4.79(15)
0.030	0.0125	1.42×10^{-4}	5.18	25.0	1.60	6.85(25)
0.030	0.0250	1.49×10^{-4}	5.17	25.0	1.60	6.72(25)
0.030	0.0438	1.53×10^{-4}	5.16	25.0	1.60	5.21(20)
0.030	0.0625	—	5.00	5.0	1.00	1.85(7)
0.030	0.0625	—	5.00	10.2	1.00	2.30(9)
0.030	0.0625	—	5.00	14.8	1.00	2.94(10)
0.030	0.0625	—	5.00	20.2	1.00	4.04(14)
0.030	0.0625	—	5.00	24.9	1.00	5.92(20)
0.030	0.0625	1.07×10^{-5}	4.17	25.0	1.00	13.4(5)
0.030	0.0625	2.44×10^{-5}	4.47	25.0	1.00	9.21(30)
0.030	0.0625	5.38×10^{-5}	4.76	25.0	1.00	6.26(25)
0.030	0.0625	1.03×10^{-4}	5.00	25.0	1.00	5.40(20)
0.030	0.0625	1.59×10^{-4}	5.16	25.0	1.60	5.03(20)
0.030	0.0625	1.92×10^{-4}	5.23	25.0	1.00	4.85(20)
0.030	0.0625	2.72×10^{-4}	5.36	25.0	1.00	4.51(15)
0.030	0.0625	6.41×10^{-4}	5.68	25.0	1.00	3.90(15)
0.030	0.125	1.69×10^{-4}	5.16	25.0	1.60	5.02(20)
0.030	0.1875	1.81×10^{-4}	5.17	25.0	1.60	5.70(20)
0.030	0.250	2.07×10^{-4}	5.21	25.0	1.60	6.19(25)
0.040	0.0625	—	5.22	25.0	1.00	5.06(20)

* Calculated from data provided in ref. 25.

was performed in the presence of a slight excess of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$, the reaction exhibited first-order kinetics as a result of the breakdown of the assumption involved in producing the zero-order kinetics. One surprising result of this study is that the active oxidant is SO_5^{2-} rather than the protonated form HSO_5^- , given the anionic nature of the $[\text{CoW}_{12}\text{O}_{40}]^{6-}$. As the latter has shown no evidence of structural disassembly in previous reactions with a wide variety of oxidants under similar acid conditions,^{7–11,24} it is speculated that the E° values of HSO_5^- and SO_5^{2-} differ markedly (and perhaps also their one-electron reduced forms). Thus the reaction is assumed to follow an outer-sphere oxidation, with no major structural changes of the polyoxotungstate framework other than that caused by oxidation of Co^{II} to Co^{III} , which involves a slight increase in size of the polyoxotungstate framework.¹³ Presumably electron transfer across the polyoxotungstate framework is rapid, with the latter acting as a “conducting sphere”, prior to donation of the electron to SO_5^{2-} . Indeed, the polyoxometalate framework of the Keggin structure is well known as allowing extremely rapid electron mobility, evidenced by the facile electron transport in reduced heteropoly species.⁵ Strictly speaking these are not equivalent, as the oxidation process involves electron transfer from the heteroatom at the core of the structure to the periphery of the polyoxotungstate framework and thence to the oxidant, rather than around the polyoxotungstate framework, although many of the same atoms are involved in these processes.

2. Oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by HSO_5^- in weakly acidic solution

The oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ over the range pH 4.2–5.7 by HSO_5^- in the presence of added $[\text{WO}_4^{2-}]$ occurs slowly at room temperature to give $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$. The kinetic data were analysed in terms of the first-order rate law governed by k_{diss} , a pseudo-first-order rate constant which is essentially independent of $[\text{HSO}_5^-]$ and exhibits complex dependences on $[\text{H}^+]$ and $[\text{WO}_4^{2-}]$. A list of rate constants obtained under various conditions is given in Table 2.

The rate constant k_{diss} is found to be almost independent of $[\text{HSO}_5^-]$ at pH 5.22. While the slight variation in k_{diss} with increasing $[\text{HSO}_5^-]$ {for a plot of $\log k_{\text{diss}}$ vs. $\log [\text{HSO}_5^-]$,

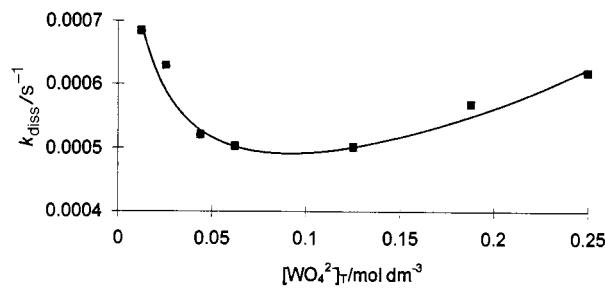


Fig. 1 Dependence of k_{diss} on total added tungstate under weakly acidic conditions: $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 0.0025$, $[\text{HSO}_5^-] = 0.030$, $I = 1.00 \text{ mol dm}^{-3}$, pH 5.18 ± 0.03 , 25.0°C .

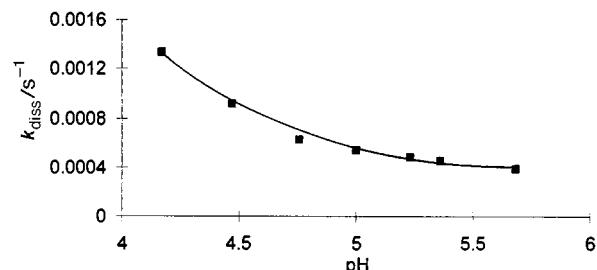


Fig. 2 Dependence of k_{diss} on pH under weakly acidic conditions: $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-} = 0.0025$, $[\text{WO}_4^{2-}]_T = 0.0625$, $[\text{HSO}_5^-] = 0.030$, $I = 1.00 \text{ mol dm}^{-3}$, 25.0°C .

the slope = 0.05(1); $R^2 = 0.945$ } could be attributable to the changing ionic make-up of the solution, it is more likely a result of the presence of several species in solution, each with different oxidation behaviour. In the main, however, oxidation of the central Co^{II} to Co^{III} appears not to be the rate-determining step, indicating that the species which gives rise to this contribution is not a major species in solution at these acid levels.

In order to determine the dependences of the rate on $[\text{H}^+]$ and $[\text{WO}_4^{2-}]$, the variations of k_{diss} with both pH and $[\text{WO}_4^{2-}]$ were examined. The variations with total added tungstate (at pH 5.2), $[\text{WO}_4^{2-}]_T$ (Fig. 1), and pH (Fig. 2) both appear complex. While the behaviour in each case can be attributed to changes in the speciation of tungstate with both pH and

concentration, the complexity of the observed dependences suggests that other influences are affecting the rate of oxidation, as will be shown below. Currently, the only reported study of the speciation of tungstate over the required pH range and total added tungstate concentration is that by Cruywagen and van der Merwe.²⁵ This was carried out in 1 mol dm⁻³ NaCl, over the pH range from 4.5 to 6.5. The present kinetic study was carried out at $I = 1.00$ (pH dependence) or 1.60 mol dm⁻³ ($[WO_4^{2-}]$ dependence) in acetic acid–NaOH buffer solution, with pH values as low as 4.2. Although the ionic medium used by Cruywagen and van der Merwe is somewhat different from that of the present study, the reported formation constants have been found to be satisfactory under the conditions employed in this investigation.²⁶

For the tungstate dependence study, over the range of concentrations examined ($[WO_4^{2-}]_T = 0.0125\text{--}0.250 \text{ mol dm}^{-3}$), the major species in solution reported by Cruywagen and van der Merwe are $[H_2W_{12}O_{42}]^{10-}$, $[W_7O_{24}]^{6-}$ and $[WO_4]^{2-}$, with considerably lower concentrations of $[HWO_4]^-$, $[HW_7O_{24}]^{5-}$ and $[W_6O_{20}(OH)_2]^{6-}$. Tungsten-183 NMR studies have confirmed the presence of the first three in solution, but could find no evidence for the last three over the pH range studied, although the concentration of total added tungstate in the two studies was very different.²⁷ However, as long as the free $[WO_4]^{2-}$ is accurately modelled by the reported stability constants, the calculated $[WO_4]^{2-}$ concentrations can be used to analyse the kinetic data. Thus the actual $[WO_4]^{2-}$ concentrations in solution, *i.e.* $[WO_4]^{2-}_{\text{calc}}$, for various amounts of total added tungstate, at constant pH, may be used to examine the actual tungstate dependence. However, a plot of $\log k_{\text{diss}}$ against $\log [WO_4]^{2-}_{\text{calc}}$ was found to be non-linear, exhibiting a parabolic-like curve. This is attributed to disassembly of the $[Co^{II}W_{12}O_{40}]^{6-}$ ion over the pH range chosen for this study, possibly into more than one component as evidenced above. Examination of the limiting slopes of the parabolic dependence over the range of added tungstate concentrations gives values of $-3.1(1.1)$ ($R^2 = 0.80$) at low $[WO_4]^{2-}_{\text{calc}}$ and $+1.0(0.3)$ ($R^2 = 0.91$) at high $[WO_4]^{2-}_{\text{calc}}$. Although the standard deviations in these limiting slopes are substantial, the inverse third order observed for low added tungstate suggests plausible loss of a W_3O_{13} (or W_3O_{12}) unit from the polyoxotungstate framework, which would then open up the central Co^{II} to attack by the oxidant (HSO_5^- or SO_5^{2-}) following co-ordination of the latter. The first-order dependence at the higher $[WO_4]^{2-}_{\text{calc}}$ suggests that with a higher tungstate concentration the speciation may have changed and indicates that the reassembly of the polyoxotungstate framework is slow for this new species. The acid dependence is less straightforward to interpret, as the $[WO_4]^{2-}_{\text{calc}}$ dependence at the added tungstate concentration used in this study is unknown. A $\log k_{\text{diss}}([WO_4]^{2-}_{\text{calc}})^n$ vs. $\log [H^+]$ plot, where n was varied over the range of -4 to $+3$, gave linear or almost linear plots ($R^2 > 0.94$) in every case. The best fit was for a value of $n = -2$, where a slope of $-2.00(3)$ ($R^2 = 0.999$) was obtained, indicating an inverse second-order dependence on $[H^+]$. This may, however, just be fortuitous given the likelihood of several species being in solution, as noted above. All other slopes were non-integral for integral values of n . Thus for $n = -3$ the resulting slope was $-3.18(3)$ ($R^2 = 0.999$). Notably, however, the order with respect to $[H^+]$ is effectively identical to that of the $[WO_4]^{2-}_{\text{calc}}$ dependence at the likely value(s) of n established in the tungstate dependence study above. Combining the results from the total added tungstate and pH dependence studies suggests that the oxidation of $[Co^{II}W_{12}O_{40}]^{6-}$ under less acidic conditions, *i.e.* pH 4.2–5.7, involves the breakdown of the polyoxotungstate framework, probably involving loss of a W_3O_{13} unit. As an inverse third-order dependence on $[WO_4]^{2-}$ is matched by an inverse third-order dependence on $[H^+]$, this strongly suggests that the species lost from the polyoxotungstate framework of $[Co^{II}W_{12}O_{40}]^{6-}$ are three $[HWO_4]^-$ ions, following attack by water molecules. This would lead to the loss

of a “ W_3O_{12} ” group (*i.e.* formally three “[$WO_4]^{2-}$ ” ions), with access to the inner co-ordination sphere of the central Co^{II} being accomplished by fast attack of H^+ and ultimately elimination of a further water molecule, leading to effective loss of a “ W_3O_{13} ” unit. This would leave the Co^{II} susceptible to co-ordination by the oxidant (HSO_5^- or SO_5^{2-}), followed by loss of the reduced oxidant (or a radical species, such as OH^\cdot) and ultimately fast build-up of the polyoxotungstate framework to yield $[Co^{III}W_{12}O_{40}]^{5-}$. All attempts to observe an ESR signal at 21 °C over a 10 min period after initiating a typical oxidation reaction were unsuccessful (within 40–60 s following mixing of reagents), indicating that no long-lived radical species were produced as the oxidation reaction took place. This indicates the fast loss of any possible radical reduction products (*e.g.* OH^\cdot , which has bimolecular rate constants for reaction with solutes typically ranging from 10^7 to $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25 °C).²⁸

It is worth noting at this point that $[Co^{III}W_{12}O_{40}]^{5-}$ produced in the oxidation reactions is unstable at low concentrations of added tungstate (<0.01 mol dm⁻³, pH 5.2) and the reactions do not go to completion, with reduction back to $[Co^{II}W_{12}O_{40}]^{6-}$ occurring within the experimental time frame of reaction (*ca.* 3 h). This effect becomes enhanced at higher pH values where oxidation is incomplete at higher concentrations of added tungstate (<0.125 mol dm⁻³, pH 5.7). Indeed, most of the $[Co^{III}W_{12}O_{40}]^{5-}$ in solution formed as a product of these reactions slowly reverts back to $[Co^{II}W_{12}O_{40}]^{6-}$ (either partially or completely) within 1 to 3 d. Thus within the pH range used in this study, the polyoxotungstate framework must be sufficiently labile to expose the Co^{III} at the core of the $[Co^{III}W_{12}O_{40}]^{5-}$ ion, leading to oxidation of the water solvent and reversion back to Co^{II} .

The temperature dependence of the oxidation was studied at 5.0–25.0 °C and at pH 5.0. Notably, a plot of $\ln k_{\text{diss}}$ vs. $1/T$ is not linear and the limiting slopes gave E_a values from *ca.* 27 to 59 kJ mol⁻¹, increasing as the temperature increases over the range studied. The fact that E_a varies so much over the temperature range is consistent with the breakdown of the polyoxotungstate framework and the presence of multiple species in solution.

3. Oxidation of $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ to $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$ by HSO_5^- in weakly acidic solution

Oxidation of the related Co^{II} -substituted Keggin species $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ to $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-}$ by HSO_5^- at pH 5.7 occurs quickly at room temperature (less than *ca.* 15 s for oxidant concentrations from 0.005 to 0.035 mol dm⁻³), and so a stopped-flow method was employed to monitor the kinetics of these reactions. The pH range of this study was strictly limited due to the conversion of $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ into $[Co^{II}W_{12}O_{40}]^{6-}$ even under weakly acid conditions. The minimum pH at which $[Co^{II}_2(H_2O)W_{11}O_{39}]^{8-}$ was found to be relatively stable within the experimental time frame was pH 5.7, which is also close to the maximum pH at which an acetic acid–NaOH buffer solution can operate. Hence, a pH dependence study could not be performed. A tungstate dependence was also difficult to determine due to the limited change in the concentration of $[WO_4]^{2-}$ in solution with total added tungstate at pH 5.69 (6.01×10^{-4} to $7.62 \times 10^{-4} \text{ mol dm}^{-3}$ over the $[WO_4]^{2-}$ range 0.025 to 0.3 mol dm⁻³). The other polymerized species change much more significantly with total added tungstate, and this effect reduces the $[WO_4]^{2-}$ concentration dependence. Reactions for the oxidant dependence were monitored at 25.0 °C, between 580 and 640 nm at 10 nm intervals using an automated point-by-point method, followed by global non-linear least-squares fitting.¹⁶

The kinetic data were analysed in terms of the first-order rate law governed by k , a pseudo-first-order rate constant which subsumes a dependence on $[HSO_5^-]$. The data, with an initial

$[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}] = 0.002$, $[\text{WO}_4^{2-}]_{\text{T}} = 0.0625$ and $I = 1.00 \text{ mol dm}^{-3}$, are $[\text{HSO}_5^-]/k$, $0.005/0.30$, $0.020/0.96$ and $0.035 \text{ mol dm}^{-3}/1.52 \text{ s}^{-1}$, and indicate that the rate constant k shows a slight deviation from first-order dependence on $[\text{HSO}_5^-]$, with a plot of $\log k$ against $\log [\text{HSO}_5^-]$ giving a straight line with a slope of $0.835(4)$ ($R^2 = 0.9999$), thereby yielding the expanded rate expression (11), where k' is $25.1(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at

$$+d[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{7-}]/dt = k'[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}][\text{HSO}_5^-]^{0.84} \quad (11)$$

25.0°C . This value is an average over each of the HSO_5^- concentrations employed. The slight deviation from first-order dependence on $[\text{HSO}_5^-]$ is most likely a reflection of some conversion of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}]$ into $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and then oxidation to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ even under the weakly acidic conditions employed, so that while $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}]$ appeared stable at pH 5.69, a small amount of conversion may have occurred within the experimental time frame. This would reduce the order of the acid dependence, as the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ shows essentially no dependence on $[\text{HSO}_5^-]$, as established above.

Mechanistic considerations. The structure of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}]$ is based on that of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ with a framework WO_4^{4-} unit being replaced by a $\text{Co}(\text{H}_2\text{O})^{2+}$ unit. The product species, $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{7-}]$, is similar, except that the Co^{III} is the central heteroatom.¹⁴ The rate of the reaction for the oxidation of $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{8-}]$ to $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{7-}]$ is considerably faster than the oxidation reactions examined above, and is plausibly accounted for by an inner-sphere mechanism. The Co^{II} is located in a distorted octahedral environment of five (formal) " O^{2-} " ions and one H_2O molecule as its nearest neighbours. As octahedral Co^{II} is labile, the water molecule is readily exchanged, in this case by a potential oxidant such as a HSO_5^- or SO_5^{2-} ion. Oxidation of the framework Co^{II} then occurs, followed by fast electron transfer from the internal Co^{II} to the external Co^{III} to give a central cobalt(III) heteroatom. This would involve the agency of the four co-ordinate oxygen atoms. The oxidation step of the external Co^{II} is rate-determining. Protonation and/or loss or addition of $[\text{WO}_4]^{2-}$ to the anion is unlikely to affect the rate of oxidation, hence it is probable that dependences on $[\text{H}^+]$ and $[\text{WO}_4^{2-}]$ may not have been observed had they been able to be determined.

Although the above is only a limited study and necessarily incomplete because of the inherent nature of the reaction, it is the first time that the kinetics of oxidation of a substituted Keggin ion has been examined. The study illustrates that the mechanism of oxidation is substantially different to the oxidation of the unsubstituted Keggin ions in strongly acidic solution, which appear to follow an outer-sphere mechanism, and which exhibit much slower oxidation kinetics (typically *ca.* 3 h compared to *ca.* 15 s at room temperature) than that proposed for the substituted Keggin ion. The fact that oxidation is so fast and must involve the four-co-ordinate oxygen atoms surrounding the central heteroatom is consistent with the fast electron transfer across the polyoxotungstate framework implicated in the oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ under strongly acidic conditions.

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