Kinetics and Mechanism of Oxidation of Arsenous Acid by 12-Tungstocobaltate(III) Ion†

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The oxidation of arsenous acid by 12-tungstocobaltate(III) ion, $[\mathrm{Co^{III}W}]^{5-}$, studied in perchloric acid solution at constant ionic strength (1.0 mol dm^{-3}), can be expressed by the rate equation (i) where k and k_1

$$k_{\mathrm{obs}} = 2(k + k_1K_a[\mathrm{H}^+]^{-1})[\mathrm{H_3AsO_3}] \qquad \text{(i)}$$

are the rate constants for reaction paths involving $\mathrm{As(OH)_3}$ and $[\mathrm{AsO(OH)_2}]^-$ and K_a is the ionisation constant of arsenous acid. The activation parameters for the two paths are evaluated. Based on a rapid-scan spectrum of the reaction mixture, the formation of an intermediate between $[\mathrm{MCo^{III}W}]^{4-}$ and $[\mathrm{AsO(OH)_2}]^-$ in equilibrium prior to its rate-limiting decomposition is suggested where $[\mathrm{MCo^{III}W}]^{4-}$ is an ion pair between $[\mathrm{Co^{III}W}]^{5-}$ and alkali-metal ion M^+ (Li^+, Na^+ or K^+). The rate is accelerated by alkali-metal ions in the order $\mathrm{K}^+ > \mathrm{Na}^+ > \mathrm{Li}^+$. The equilibrium constant for the ion-pair formation between M^+ and $[\mathrm{Co^{III}W}]^{5-}$ is also evaluated.

The kinetics of the oxidation of arsenous acid, $\mathrm{As(OH)_3}$, by $\mathrm{Cr^{VI}}$,[1] $\mathrm{V^V}$,[2] $\mathrm{Ce^{IV}}$,[3,4] $\mathrm{Tl^{III}}$[5] in acidic and by hexacyanoferrate(III)[6] and $\mathrm{Ag^{III}}$[7] in alkaline media has been reported. An important feature of all these investigations was to seek information on whether the oxidation proceeded through an intermediate or a complex formed between the oxidant and $\mathrm{As^{III}}$. The nature of the intermediate (complex), outer- or inner-sphere, has not been satisfactorily resolved. The two complexes, $[\mathrm{Ce(H_3AsO_3)}]^{4+}$ and $[\mathrm{Ce(H_2AsO_3)}]^{3+}$, in a perchlorate medium, as evidenced by spectrophotometry, are inner-sphere complexes.

The cobalt(III) ion in 12-tungstocobaltate(III), $[\mathrm{Co^{III}O_4W_{12}O_{38}}]^{5-}\cdot 20\mathrm{H_2O}$,[8] herein after abbreviated as $[\mathrm{Co^{III}W}]^{5-}$, is deeply buried within an octahedral $\mathrm{WO_6}$ shell and is effectively caged and shielded from contact with external species.[9] The $\mathrm{WO_6}$ shell is stable even under strenuous conditions.[10] No doubt $[\mathrm{Co^{III}W}]^{5-}$ ion is considered substitution inert.[9,11] Hence an outer-sphere intermediate, if one is formed, is expected. The present study provides experimental evidence for the formation of such an intermediate.

Experimental

Materials.—12-Tungstocobaltate(II), $[\mathrm{Co^{II}W}]^{6-}$, was prepared by the method described earlier.[12] The ion $[\mathrm{Co^{III}W}]^{5-}$ was prepared by the oxidation of $[\mathrm{Co^{II}W}]^{6-}$ (75 g) in 2 mol dm^{-3} sulfuric acid (80 cm^3). The solution was boiled and solid potassium peroxodisulfate added in small amounts. The green colour progressively changed and finally became light brownish yellow. The solution was then cooled, giving light yellow needle-like prisms which were filtered off. The product was recrystallised once from water, washed with 95% ethanol and air dried.

Solutions of sodium arsenite (E. Merck, GR), sodium arsenate (Riedel), sodium and potassium nitrates (BDH, AnalaR) were prepared by direct weighing of the samples. A check on the purity of the sample of sodium arsenite was carried out by titration against permanganate ion.

Solutions of lithium and sodium perchlorate were respectively prepared by neutralising known solutions of lithium hydroxide and sodium carbonate using standard perchloric acid. The resulting solutions were cooled and adjusted to pH 7. Their concentrations were determined gravimetrically by evaporating the water from weighed aliquots on a water bath and drying to constant weight. Perchloric acid was standardised against a standard alkali.

Kinetic Measurements.—The kinetics of the reaction in perchloric acid was studied under pseudo-first-order conditions ($[\mathrm{H_3AsO_3}] \gg [\mathrm{Co^{III}W^{5-}}]$) at constant ionic strength (1.0 mol dm^{-3}) adjusted with lithium perchlorate. The rate was measured at 380 nm using a Photoelectric Instruments SFA 11 microprocessor-controlled grating colorimeter interfaced with a printer. The syringes, containing reactant solutions, were water jacketed. The desired temperature (±0.1 °C) was maintained by circulating water from a Haake D8G circulatory water-bath. The temperature of the cell, in which the reactant solutions were mixed, was read by a temperature probe placed near it. A few experiments were also studied at 620 nm (appearance of $[\mathrm{Co^{II}W}]^{6-}$). The value of the pseudo-first-order rate constant k_{obs} with respect to $[\mathrm{Co^{III}W}]^{5-}$ obtained by the two methods agreed within 3–5%; it was calculated from the slope (× 2.3) of linear plots between $\log(A_t - A_\infty)$ and time by the method of least squares using a computer program. Average values from two to three replicate runs have been deposited as SUP 56867. No attempt was made to exclude oxygen dissolved in solutions because preliminary investigations indicated that the rate was not affected by replacing oxygen with nitrogen.

Test for free radical. The reactant solutions ($10^3[\mathrm{Co^{III}W^{5-}}] = 4.0$ and $[\mathrm{As(OH)_3}] = 0.08$ in 0.1 mol dm^{-3} perchloric acid) were purged with nitrogen and mixed with acrylonitrile (1 cm^3). The reaction was initiated by mixing the two solutions and the mixture swirled occasionally. A white curdy precipitate of polyacrylonitrile was slowly obtained indicating the formation of a free radical.

Test for the intermediate. A rapid scan spectrum of a reaction mixture was taken using the RA-415 attachment of a Union Giken RA-401 stopped-flow spectrophotometer. This measures the change in absorption spectrum with time.

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† *Supplementary data available* (No. SUP 56867, 4 pp.): stoichiometry and observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

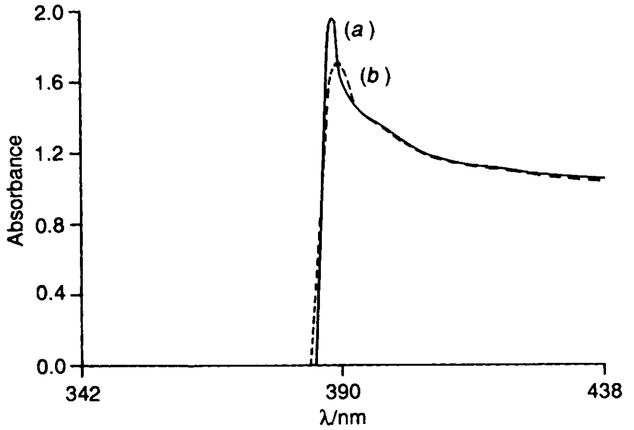

Fig. 1 Rapid-scan spectra of (*a*) $10^3[Co^{III}W^{5-}] = 2.0$ and $[H^+] = 0.05$ mol dm^{-3} and (*b*) the reaction mixture ($10^3[Co^{III}W^{5-}] = 2.0$, $[H_3AsO_3] = 0.08$ and $[H^+] = 0.05$ mol dm^{-3}) recorded at 40 °C using 390 nm as the central wavelength, slit width 3.5 mm, gate time 50 ms and zero interval time

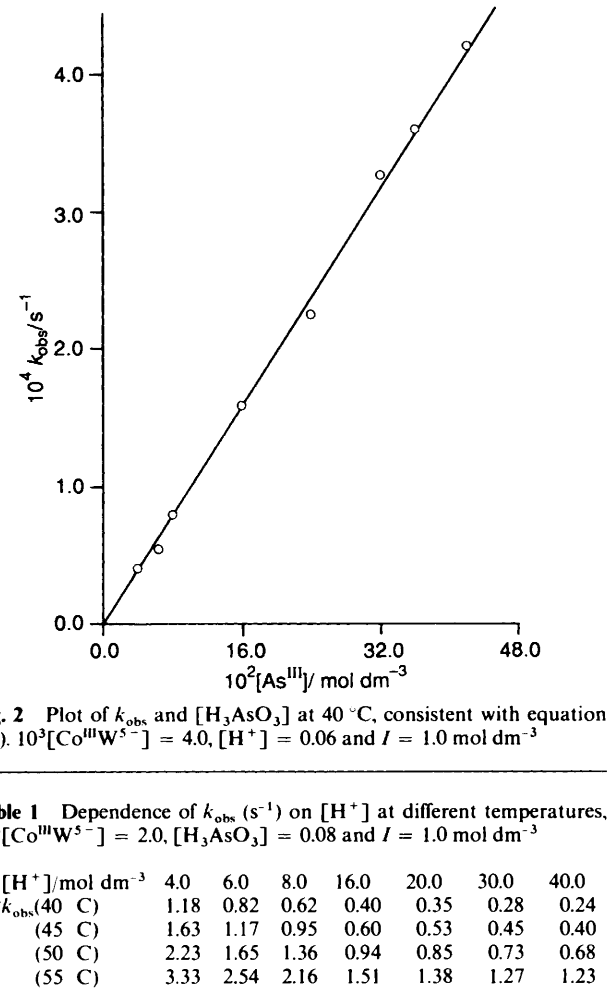

Fig. 2 Plot of k_{obs} and $[H_3AsO_3]$ at 40 °C, consistent with equation (11). $10^3[Co^{III}W^{5-}] = 4.0$, $[H^+] = 0.06$ and $I = 1.0$ mol dm^{-3}

Table 1 Dependence of k_{obs} (s^{-1}) on $[H^+]$ at different temperatures, $10^3[Co^{III}W^{5-}] = 2.0$, $[H_3AsO_3] = 0.08$ and $I = 1.0$ mol dm^{-3}

$10^2[H^+]$/mol dm^{-3}	4.0	6.0	8.0	16.0	20.0	30.0	40.0
10^4k_{obs}(40 °C)	1.18	0.82	0.62	0.40	0.35	0.28	0.24
(45 °C)	1.63	1.17	0.95	0.60	0.53	0.45	0.40
(50 °C)	2.23	1.65	1.36	0.94	0.85	0.73	0.68
(55 °C)	3.33	2.54	2.16	1.51	1.38	1.27	1.23

The detectable spectral range is 200–800 nm with a measurable spectral bandwidth of 96 nm (±48 nm of selected central wavelength). The gate time is the period between two successive scannings and the interval is the non-working period of the multichannel photodetector unit.

The spectrum of the oxidant solution ($10^3[Co^{III}W^{5-}] = 2.0$, $[H^+] = 0.05$ and $I = 1.0$ mol dm^{-3}), Fig. 1(*a*), was recorded first, then the spectrum of the reaction mixture ($10^3[Co^{III}W^{5-}] = 2.0$, $10^2[H_3AsO_3] = 8.0$, $[H^+] = 0.05$ and $I = 1.0$ mol dm^{-3}), Fig. 1(*b*). Both spectra were recorded at 40 °C using 390 nm as the central wavelength, a slit width of 3.5 mm, a gate time of 50 ms and zero interval time. The two spectra clearly showed that, although there is no shift in the wavelength of maximum absorbance, the peak height of the reaction mixture is noticeably lowered indicating the formation of some newer intermediate species which must be of outer-sphere nature as explained earlier. Considering the slow nature of the reaction, the decrease in the peak height cannot be ascribed to any redox reaction of $[Co^{III}W]^{5-}$ with H_3AsO_3 in this short period of time.

Results

Stoichiometry.—Several reaction mixtures with different initial $[Co^{III}W^{5-}]$, $[H_3AsO_3]$ and $[H^+]$ were prepared to have a varying ratio of $[H_3AsO_3]:[Co^{III}W^{5-}]$. Upon completion of the reaction the reaction mixtures were treated with a slight excess of silver(I) nitrate to ensure complete precipitation of Ag_3AsO_4. The precipitate was dissolved in dilute nitric acid and the silver(I) titrated with standard thiocyanate solution.[13] Such estimations of As^V (SUP 56867) indicate that $[Co^{III}W^{5-}]/[H_3AsO_4] = 1.98 \pm 0.04:1$. Hence, the stoichiometry of the reaction is expressed by equation (1).

$$2[Co^{III}W^5]^- + H_3AsO_3 + H_2O \longrightarrow 2[Co^{II}W]^{6-} + H_3AsO_4 + 2H^+ \quad (1)$$

Dependence on $[Co^{III}W^{5-}]$.—The value $10^4k_{obs} = 1.58 \pm 0.01$ s^{-1} (SUP 56867), determined over the range $[Co^{III}W^{5-}] = 0.0004$–$0.004$ mol dm^{-3} and at constant $[H_3AsO_3] = 0.16$, $[H^+] = 0.06$ mol dm^{-3} at 40 °C confirmed a first-order dependence on $[Co^{III}W^{5-}]$.

Dependence on $[H_3AsO_3]$.—The dependence of k_{obs} on $[H_3AsO_3]$ (SUP 56867) is illustrated in Fig. 2. The linearity of the plot and its passage through the origin indicates a first-order dependence on $[As^{III}]$.

Dependence on $[Co^{II}W^{6-}]$.—The value $10^5k_{obs} = 9.2 \pm 0.2$ s^{-1} at 40 °C over a ten-fold variation (0.0002–0.0020 mol dm^{-3}) of the initial $[Co^{II}W^{6-}]$ (SUP 56867) at $10^3[Co^{III}W^{5-}] = 2.0$, $[H_3AsO_3] = 0.08$, $[H^+] = 0.05$ and $I = 1.0$ mol dm^{-3} indicated that $[Co^{II}W]^{6-}$ is not involved in any step prior to the rate-determining step.

Dependence on $[H_3AsO_4]$.—The value $k_{obs} = (9.2 \pm 0.2) \times 10^{-5}$ s^{-1}, measured over a range of initial $[H_3AsO_4]$ (0.0002–0.0020 mol dm^{-3}) in presence of $[Co^{III}W^{5-}] = 0.002$, $[H_3AsO_3] = 0.08$, $[H^+] = 0.05$ and $I = 1.0$ mol dm^{-3} at 40 °C (SUP 56867), indicated that the rate is independent of $[H_3AsO_4]$.

Dependence on $[H^+]$.—The k_{obs} values decreased with increasing $[HClO_4]$ at constant ionic strength. The results at four temperatures are in Table 1. Plots between k_{obs} and $[H^+]^{-1}$, Fig. 3, are linear with intercepts on the rate ordinate indicating the presence of two reaction paths, one of which is dependent on $[H^+]$. The empirical rate equation (2) is therefore applicable.

$$k_{obs} = a + b[H^+]^{-1} \quad (2)$$

Dependence on Ionic Strength.—The effect of ionic strength on the observed rate was studied by varying $[LiClO_4]$. The result (SUP 56867), indicates that there is less than a 40% increase in rate over a ten-fold variation in the initial ionic strength. As suggested by one of the referees, this increase is considered to be due to the change in $[Na^+]$ as revealed by the effect of alkali-metal ions on the rate described below.

Dependence on Alkali-metal Ions.—The effect of size and

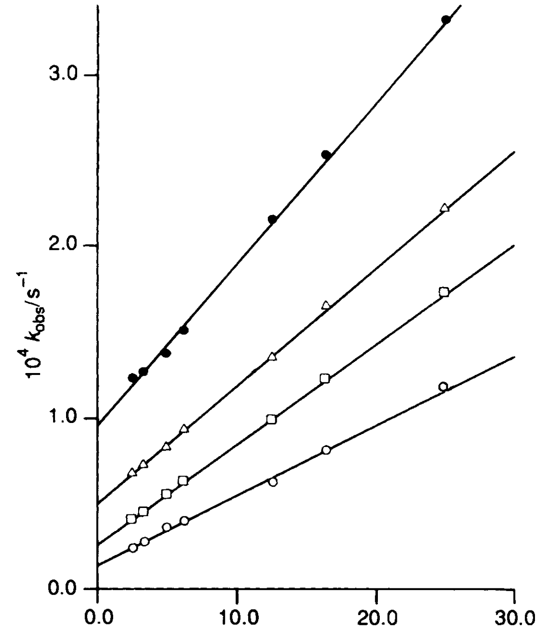

Fig. 3 Plots between k_{obs} and $[H^+]^{-1}$ at 40 (○), 45 (□), 50 (△) and 55 °C (●). $10^3[Co^{III}W^{5-}] = 2.0$, $[H_3AsO_3] = 0.08$ and $I = 1.0$ mol dm^{-3}

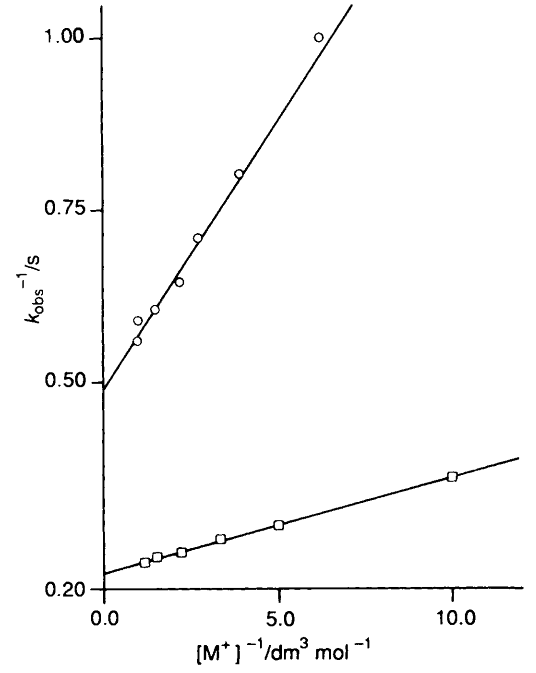

Fig. 4 Plots between k_{obs}^{-1} and $[M^+]^{-1}$ for Na^+ (○) and K^+ (□) at 40 °C

concentration of the alkali-metal ions, M^+, on the rate was investigated (SUP 56867) at constant $[H^+]$ by varying $[NaClO_4]$ and $[LiClO_4]$ so that $[ClO_4^-]$ is constant. Since $KClO_4$ is insoluble, the effect of $[K^+]$ with reference to $[Na^+]$ was studied at fixed $[NO_3^-]$ at the same $[H^+]$ by varying the concentrations of nitrate solutions of respective ions. Plots of k_{obs}^{-1} against $[M^+]^{-1}$ are linear. Fig. 4,with intercepts on the rate ordinate indicating the formation of an $[MCo^{III}W]^{4-}$ ion pair prior to its reduction by As^{III}. The formation of an $[MAsO(OH)_2]$ ion pair between M^+ and $AsO(OH)_2^-$ in effective concentrations is considered improbable.

Mechanism and Discussion

The present reaction must proceed through an outer-sphere mechanism because the oxidant is substitution inert.[11] A rapid scan of the reaction mixture, Fig. 1, indicates the formation of an outer-sphere intermediate. Any involvement of the reaction products, $[Co^{II}W]^{6-}$ or As^V, in an equilibrium prior to the rate-determining step is ruled out in view of the lack of effect of their concentrations on the observed rate.

The retardation of the rate by $[H^+]$ requires the ionisation of arsenous acid to be considered since the absorption spectrum of $[Co^{III}W]^{5-}$, monitored over the entire $[H^+]$ range used, shows no change. The acid H_3AsO_3 is expected to exist mostly in its undissociated state because its first dissociation constant K_a has the value[14] 4.23×10^{-10} mol dm^{-3} at 25 °C [values at other temperatures are obtained by using $\Delta H = 6.37$ kcal mol^{-1} (1 cal = 4.184 J)]. The H^+-independent and -dependent paths of the reaction indicate that both $As(OH)_3$ and $[AsO(OH)_2]^-$ are reactive.

Reactions (3)–(8) are considered to represent the most plausible mechanism where $M^+ = Li^+$, Na^+ or K^+ and $^{\bullet}AsO(OH)_2$ is the arsenic(IV) free radical. Evidence for As^{IV} as an unstable intermediate in oxidation-reduction processes involving As^{III} or As^V is found in a number of publications.[15] On hydration by a water molecule $HAsO_3$ is converted into arsenic acid H_3AsO_4.

$$As(OH)_3 \xrightleftharpoons{K_a} [AsO(OH)_2]^- + H^+ \qquad (3)$$

$$[Co^{III}W]^{5-} + M^+ \xrightleftharpoons{K_m} [MCo^{III}W]^{4-} \qquad (4)$$

$$[MCo^{III}W]^{4-} + [AsO(OH)_2]^- \xrightleftharpoons{K_{os}} [MCo^{III}W{\cdot}AsO(OH)_2]^{5-} \qquad (5)$$

$$[MCo^{III}W]^{4-} + As(OH)_3 \xrightarrow{k} [MCo^{II}W]^{5-} + {}^{\bullet}AsO(OH)_2 + H^+ \qquad (6)$$

$$[MCo^{III}W{\cdot}AsO(OH)_2]^{5-} \xrightarrow{k'} [MCo^{II}W]^{5-} + {}^{\bullet}AsO(OH)_2 \qquad (7)$$

$$[MCo^{III}W]^{4-} + {}^{\bullet}AsO(OH)_2 \xrightarrow{\text{fast}} [MCo^{II}W]^{5-} + HAsO_3 + H^+ \qquad (8)$$

The rate law based on the reactions (3)–(8) is given in equation (9). Further, with the assumption that $[H^+] \gg K_a$

$$\frac{-d[Co^{III}W^{5-}]}{dt} = 2K_m\left(k + \frac{k'K_{os}K_a}{[H^+]}\right) \frac{[Co^{III}W^{5-}][H_3AsO_3][H^+][M^+]}{([H^+] + K_a)(1 + K_m[M^+]) + K_aK_{os}K_m[H_3AsO_3][M^+]} \qquad (9)$$

and $K_aK_{os}K_m[H_3AsO_3][M^+]$ is negligibly small, being the product of small K_a and K_{os}, equation (9) reduces to (10), where

$$k_{obs} = \frac{2K_m(k + k_1K_a[H^+]^{-1})[H_3AsO_3][M^+]}{1 + K_m[M^+]} \qquad (10)$$

$k_1 = k'K_{os}$. Plots between k_{obs} and $[As^{III}]$, Fig. 2, and k_{obs} and $1/[H^+]$, Fig. 3, are consistent with equation (10) and so is the plot in Fig. 4 between k_{obs}^{-1} and $[M^+]^{-1}$. The value of K_m (= intercept/slope), obtained from Fig. 4, is 5.7 and 16.8 dm^3 mol^{-1} for Na^+ and K^+ respectively. Now if, as an approximation, it is assumed that $K_m[M^+]/(1 + K_m[M^+]) \approx 1$ at a constant excess of M^+, equation (10) reduces to (11). The

Table 2 Rate constants k and k_1 ($dm^3\ mol^{-1}\ s^{-1}$) at different temperatures and associated activation parameters

$T/°C$	25	40	45	50	55
10^4k	0.101	0.853	1.65	3.15	5.90
$10^{-4}k_1$	1.77	2.57	2.90	3.10	3.88

$\Delta H^‡_k = 108 \pm 2$ kJ mol^{-1}, $\Delta S^‡_k = 20 \pm 1$ J K^{-1} mol^{-1}, $\Delta H^‡_{k_1} = 17 \pm 2$ kJ mol^{-1}, $\Delta S^‡_{k_1} = -107 \pm 1$ J K^{-1} mol^{-1}.

$$k_{obs} = 2(k + k_1K_a[H^+]^{-1})[H_3AsO_3] \qquad (11)$$

values of k and k_1 are separable from the intercept and slope of the plots in Fig. 3. These values are in Table 2 along with the respective activation parameters. The distinct $\Delta H^‡$ and $\Delta S^‡$ values for the k and k_1 paths justify the nature of the reactions (6) and (7). The high $\Delta H^‡$, 108 kJ mol^{-1} and $\Delta S^‡$, 20 J K^{-1} mol^{-1}, values are of the magnitude expected for a bimolecular reaction. The values, $\Delta H^‡ = 17$ kJ mol^{-1} and $\Delta S^‡ = -107$ J K^{-1} mol^{-1} for the path k_1 ($k'K_{os}$) are combinations of two components expressed in equation (12) and (13) respectively; separation into their components is not kinetically possible.[16]

$$\Delta H^‡_{k_1} = \Delta H_{K_{os}} + \Delta H^‡_{k'} \qquad (12)$$

$$\Delta S^‡_{k_1} = \Delta S_{K_{os}} + \Delta S^‡_{k'} \qquad (13)$$

It might be added that $\Delta H^‡_{k'}$ and $\Delta S^‡_{k'}$ are not known for similar reactions but are considered to be small. For an electrostatic process such as the formation of an encounter (outer-sphere) complex, a small $\Delta H_{K_{os}}$ is reasonable.[18] There are a number of explanations, equally applicable here, for the negative $\Delta S^‡_{k_1,}$. It has been suggested that the formation of an encounter complex is a major contributor[17,18] to the negative $\Delta S_{K_{os}}$. The large negative $\Delta S^‡$ values for outer-sphere reactions are also due to the extensive solvent organisation,[19,20] and possibly a change in co-ordination of H_2O at $[Co^{III}W]^{5-}$. The negative entropy is also indicative of a highly solvated intermediate formed by ions of the same sign.[21] These considerations required the inclusion of reaction (5) in the mechanism.

The use of the K_a value did not cause any inconsistencies because the extrapolated value of k_1 at 25 °C, 1.77×10^4 dm^3 mol^{-1} s^{-1}, is still several orders of magnitude less than the diffusion-controlled limit.[22] The participation of $[AsO(OH)_2]^-$ is further supported by the catalysis of the reaction by alkali-metal ions. The order of the catalysis $K^+ > Na^+ > Li^+$ is exactly in the order of their ionic radii. The larger is the ionic radius the greater is the ability of the ion to form a bridge between negatively charged ions, helping them to come closer, by overriding the electrostatic repulsion, for the formation of an outer-sphere intermediate.

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