A kinetic study of the oxidation of the tetrakisoxalatouranate(IV) ion by the octacyanotungstate(V) and the octacyanomolybdate(V) ions in an acidic oxalate buffer medium

C. Robert Dennis, et al. *[full author details at the end of the article]*

Abstract

The oxidation of the tetrakisoxalatouranate(IV) ion by the octacyanometalate(V) ion of tungsten and molybdenum was studied in an oxalate buffer medium. The reaction was first order in both $U^{IV}(C_2O_4)_4^{4-}$ and $M(CN)_8^{3-}$ (M = W, Mo), and a second order rate constant of $k_2 = 0.032 \pm 0.002$ $M^{-1}s^{-1}$ at pH 4.27 and 24.8 °C was found for the $W(CN)_8^{3-}$ reaction. For the $Mo(CN)_8^{3-}$ reaction the second order rate constant is $k_2 = 16.9 \pm 0.1$ $M^{-1}s^{-1}$ at pH 4.77 and 25.3 °C. The reactions are inversely proportional to $[H^+]$ and an equilibrium constant of $K_a \approx 1.3 \times 10^{-6}$ M^{-1} ($pK_a \approx 5.89$) at 25 °C was found for the deprotonation of $U^{IV}(C_2O_4)_3(H_2O)_2^{2-}$. Activation parameters have been obtained by a least squares fit of temperature data directly to the Eyring equation.
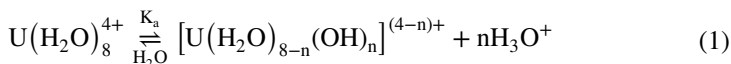
Graphical abstract
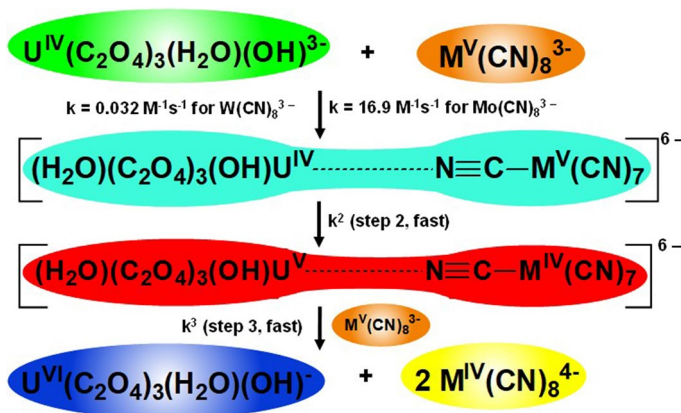
Keywords Redox kinetics · Mechanism · Rate law · Activation parameters · Aqueous medium · Oxalate buffer

Introduction

The stereochemical configuration of the octacyanotungstate(V) ion and the octacyanomolybdate(V) ion in solution has been reported to be square antiprismatic and dodecahedral [1–4]. The exchange of a cyanide ligand in aqueous solution is very slow in light, but have not been detected in diffuse light between pH 4 and pH 12 [5]. The reduction potential for $W(CN)_8^{3-}$ is $E° = 0.52$ V and for $Mo(CN)_8^{3-}$ is $E° = 0.76$ V vs NHE in 0.1 M $NaClO_4$ at 25 °C [6, 7]. Both $W(CN)_8^{3-}$ and $Mo(CN)_8^{3-}$ is one equivalent oxidants and have been used extensively in oxidation–reduction kinetic studies in alkaline medium [8–22].

Uranium(IV) octahydrate is a relative stable species in aqueous solution [23]. In aqueous solution the polar H_2O molecule compete with acidic substituted ligands by displacement reactions. Uranium(IV) cations hydrolyze in aqueous medium to form hydroxo or hydrated species which dissociate as a Brønsted acid [24]. Kraus and Nelson [25, 26] indicated that uranium(IV) cations hydrolyze in perchloric acid solution < 1.0 M to form $U(H_2O)_8^{4+}$ which dissociate as in Eq. 1.

$$U\left(H_2O\right)_8^{4+} \underset{H_2O}{\overset{K_a}{\rightleftharpoons}} \left[U\left(H_2O\right)_{8-n}(OH)_n\right]^{(4-n)+} + nH_3O^+ \tag{1}$$

Kinetic oxidation studies of U(IV) substrates with several multi-electron oxidizing agents have been reported [25–32]. The reaction mechanisms of these reactions are complicated, since both the U(IV) and the oxidizing agent hydrolyze in aqueous medium. This could influence the interpretation of hydrogen ion dependence results of these reactions. In addition, the use of two- or more-electron oxidants does not clearly indicate whether a U(V) species is formed as an intermediate when U(IV) is oxidized to U(VI). This problem may be addressed when oxidation is performed by one-electron oxidants such as $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$ or $W(CN)_8^{3-}$.

The oxidation of U(IV) hydroxo species by mono-equivalent oxidants $Fe^{III}(CN)_6^{3-}$ [33] and $Ir^{IV}Cl_6^{2-}$ [34] have also been reported. These studies were performed in $HClO_4/NaClO_4$ mediums. These mono-equivalent oxidants do not hydrolyze in aqueous medium. The initial stage of these reactions is relatively fast, corresponding to the formation of a binuclear intermediate complex [33, 34]. An important aspect of all the kinetic studies of U(IV) is that the reactions are first order in both the oxidant and reductant.

The affinity of U(IV) for oxygen is the main reason for uranium(IV) complexes containing carboxylic acid groups to be the most stable uranium(IV) chelates [24]. The only kinetic study we know of where uranium(IV) oxalate complexes have been oxidized to an uranium(VI) species is the reaction between $U^{IV}(C_2O_4)_4^{4-}$ and the one-electron oxidant $Fe^{III}(CN)_6^{3-}$ in an acidic oxalate buffer medium [35]. The $U^{IV}(C_2O_4)_4^{4-}$ complex hydrolyzes only a little in aqueous acidic solution [25] which makes it suitable for kinetic oxidation studies by relatively strong oxidizing agents. In this article, the kinetics of oxidation of $U(C_2O_4)_4^{4-}$ with the one-electron oxidants $W(CN)_8^{3-}$ and $Mo(CN)_8^{3-}$ are reported. Activation parameters have been determined and a mechanism is proposed.

Experimental

Cesium octacyanomolybdate(V)dihydrate, $Cs_3Mo(CN)_8 \cdot 2H_2O$, and cesium octacyanotungstate(V)dihydrate, $Cs_3W(CN)_8 \cdot 2H_2O$, were synthesized as previously described [36–38] and were used as a primary standard [39] after recrystallization. Potassium tetrakisoxalatouranate(IV), $K_4U(C_2O_4)_4 \cdot 5H_2O$ was synthesized as described [40] previously and it's purity was determined as 98% by a permanganate titration.

To find a suitable buffer system for the oxidation of $K_4U^{IV}(C_2O_4)_4$ by $W^V(CN)_8^{3-}$ and $Mo^V(CN)_8^{3-}$ had its difficulty. $U(C_2O_4)_4$ precipitate from a buffer solution containing a mineral acid. Several buffer systems were tested and only a carbonate/bicarbonate buffer and an oxalate/oxalic acid buffer did not show precipitation. The carbonate/bicarbonate could displace the oxalate ions from the uranium coordination sphere and thus only the oxalate/oxalic acid buffer was used in this kinetic study. This, however, means that the pH variation of the reaction mixture was limited to between pH 1.3 and pH 5.5. The oxalate buffer has been prepared by adding a KOH solution to a 0.05 M oxalic acid solution until the required pH was reached. The pH was measured with a T & C model 1002 pH meter using a glass pH electrode. The concentration of the oxalate in the reaction mixture was 0.05 M. Doubly distilled water was used throughout.

The stoichiometry of the reactions was determined spectrophotometrically by treating $M^V(CN)_8^{3-}$ (M = Mo, W) solutions with a known excess of $K_4U(C_2O_4)_4$ and then measuring the excess $K_4U(C_2O_4)_4$ at 665 nm on completion of the reaction. In both cases very good values of a 1:2 stoichiometry, $U(IV):M^V(CN)_8^{3-}$, has been obtained.

$$U^{IV}\left(C_2O_4\right)_4^{4-} + 2M^V(CN)_8^{3-} \rightarrow U^{VI}\left(C_2O_4\right)_4^{2-} + 2M^{IV}(CN)_8^{4-}$$
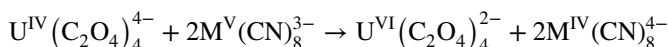
Kinetic measurements were made under pseudo first order conditions with the U(IV) species in excess and at constant ionic strength (μ) using NaCl as electrolyte, see Tables S1–S5 in Supporting Information for exact conditions. Experiments were carried out in diffuse laboratory light because the $Mo(CN)_8^{3-}$ ion in solution is sensitive to light [41]. In diffuse light at pH 1–12, the radiation effect is undetectable [5].

The oxidation of the $U(C_2O_4)_4^{4-}$ by $W^V(CN)_8^{3-}$ and $Mo^V(CN)_8^{3-}$ was monitored on a Pye Unicam SP 1700 double beam spectrophotometer connected to a Fryca-Kaltetechnik KB 300 water bath with a Thermomix 1440 thermostat for temperature control. The decrease in the absorption of the $W^V(CN)_8^{3-}$ and $Mo^V(CN)_8^{3-}$ was measured at 357 nm and 388 nm, respectively [6, 7]. From UV spectra (Fig. 1), the molar extinction coefficients of the $W^V(CN)_8^{3-}$ and $W^{IV}(CN)_8^{4-}$ was determined as 1750 and 230 $M^{-1}cm^{-1}$, respectively. The extinction coefficients of $Mo^V(CN)_8^{3-}$ and $Mo^{IV}(CN)_8^{4-}$ were determined as 1400 $M^{-1}cm^{-1}$ and 140 $M^{-1}cm^{-1}$, respectively. The extinction coefficient of the $U(C_2O_4)_4^{4-}$ ion as well as of the U^{VI} product were negligibly small at 357 nm and 388 nm, respectively [35].

Both the reagent $W^V(CN)_8^{3-}$ and it's product, $W^{IV}(CN)_8^{4-}$, and also $Mo^V(CN)_8^{3-}$ and it's product, $Mo^{IV}(CN)_8^{4-}$ absorbed light at the wavelength (λ_{max}) where the
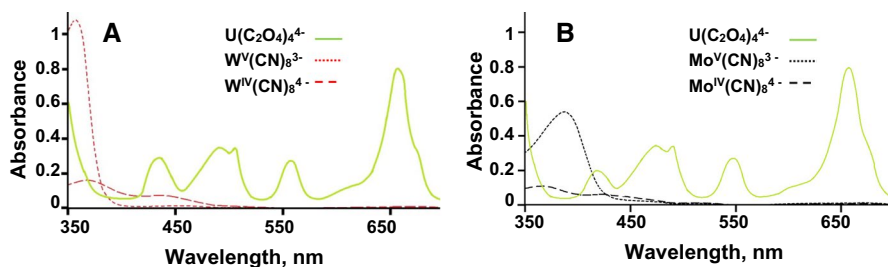
Fig. 1 UV spectra of complexes in water. **A** $[K_4U(C_2O_4)_4 \cdot 5H_2O]=0.1084$ M, $[K_4W(CN)_8 \cdot 2H_2O]=7.82 \times 10^{-4}$ M and $[Cs_3W(CN)_8 \cdot 2H_2O]=7.22 \times 10^{-4}$ M. **B** $[K_4U(C_2O_4)_4 \cdot 5H_2O]=0.1084$ M, $[K_4Mo(CN)_8 \cdot 2H_2O]=7.14 \times 10^{-4}$ M and $[Cs_3Mo(CN)_8 \cdot 2H_2O]=4.07 \times 10^{-4}$ M.
(Color figure online)

reactions were monitored. The Beer–Lambert law thus cannot be used directly to determine the concentration of $M(CN)_8^{3-}$ (M = W, Mo) at any time t. If the initial concentration of the $M(CN)_8^{3-}$ equals "a" mol dm^{-3} and if at any time t a quantity "x" has reacted to form x mol dm^{-3} $M(CN)_8^{4-}$, then the total absorbance at a time t is given by

$$A_t = \varepsilon_{M(CN)_8^{3-}} \cdot (a - x) + \varepsilon_{M(CN)_8^{4-}} \cdot x \tag{2}$$

The concentration of $M(CN)_8^{3-}$ at time t may be calculated through Eq. 3.

$$\left[M(CN)_8^{3-} \right]_t = a - x = \frac{A_t - \varepsilon_{M(CN)_8^{4-}} \cdot a}{\varepsilon_{M(CN)_8^{3-}} - \varepsilon_{M(CN)_8^{4-}}} \tag{3}$$

Activation parameters were obtained by performing reactions at various temperatures. The parameters $\Delta H^{\#}$ and $\Delta S^{\#}$, applicable only to the experimental conditions, have been obtained from the Eyring equation (Eq. 4) where k_B and h are the Boltzman and Planck constants:

$$k = \frac{k_B T}{h} \exp \left[\frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \right] \tag{4}$$

Equation 4 converted to the logarithmic form yields a linearized Eyring equation [42] (Eq. 5),

$$\ln \left(\frac{k}{T} \right) = - \left(\frac{\Delta H^{\#}}{RT} \right) + \left(\frac{\Delta S^{\#}}{R} \right) + \ln \left(\frac{k_B}{h} \right) \tag{5}$$

Here $\Delta H^{\#}$ can be obtained from the slope, $\frac{-\Delta H^{\#}}{R}$, and $\Delta S^{\#}$ from the intercept, $\frac{\Delta S^{\#}}{R} + \ln \left(\frac{k_B}{h} \right)$, of a plot of $\ln \left(\frac{k}{T} \right)$ versus $\frac{1}{T}$.

Least squares fittings of measured data were carried out by using the general fitting software Micro Math "Scientist" [43].

Results and discussion

The oxidation of the $U(C_2O_4)_4^{2-}$ ion by $M^V(CN)_8^{3-}$ ions (M = Mo, W) was performed under pseudo-order conditions with the $M^V(CN)_8^{3-}$ ion as the limiting reagent. The $[U(C_2O_4)_4^{2-}]$ was in excess of 6–20-fold. Lente provided evidence in his book [44] that an excess of fourfold is enough for a flooding (pseudo-first order) process in chemical kinetics. This was also recently experimentally confirmed [35]. In this study, the cases where the flooding excess is less than tenfold (but still larger or equal to 4), i.e. the sixfold and eightfold excess data, were also found to be acceptable for pseudo first order reaction conditions by virtue of the linearity of the k_{obsd} versus $[K_4U^{IV}(C_2O_4)_4]$ graphs (Fig. 3).

The non-linear least squares fit [43] of the data from the reaction traces, Fig. 2, to the first order rate expression, Eq. 6 [45], indicate that the reactions are first order in $M^V(CN)_8^{3-}$ (M = Mo, W). Rate constants for these reactions are summarised in Supplementary Information Tables S1 ($W^V(CN)_8^{3-}$ reaction, entries 1–6) and S2 ($Mo^V(CN)_8^{3-}$ reaction, entries 1–12)

$$\left[M^V(CN)_8^{3-}\right]_t = \left[M^V(CN)_8^{3-}\right]_0 e^{-(k_{obsd}.t)} \tag{6}$$

Variation of $[K_4U(C_2O_4)_4]$ in the $W^V(CN)_8^{3-}$ reaction mixtures (Fig. 3, left, data from Supplementary Information Table S1, entries 7–12) as well as $Mo^V(CN)_8^{3-}$ reaction mixtures (Fig. 3, right, data from Table S2, entries 13–18 at pH 1.61 and 19–25 at pH 4.93) yield a linear relationship with a direct dependence of k_{obsd} on $[K_4U(C_2O_4)_4]$. The gradients of the Fig. 3 plots yield second order rate constant, k_2, for the $W^V(CN)_8^{3-}$ oxidation of $U^{IV}(C_2O_4)_4^{4-}$ as $k_2(W^V(CN)_8^{3-}$ reaction) = 0.100 ± 0.001 $M^{-1}s^{-1}$ at pH 4.27. The second order rate constant for the $Mo^V(CN)_8^{3-}$ oxidation of $U(C_2O_4)_4^{4-}$ is $k_2(Mo^V(CN)_8^{3-}$ reaction) = 22.7 ± 0.2 $M^{-1}s^{-1}$ at pH 4.93.

Variation of the reduction product $W^{IV}(CN)_8^{4-}$ and $Mo^{IV}(CN)_8^{4-}$ in the reactions, do not have an effect on the reaction rate (Supplementary Information Table S3 entries 1–3 and Table S4, entries 1–4) indicating the rate determining step of the

Fig. 2 Reaction traces for the redox reaction $M^V(CN)_8^{3-} + U^{IV}(C_2O_4)_4^{4-}$; M = W, red plot, or Mo, black plot. $[M^V(CN)_8^{3-}] = 5.0 \times 10^{-4}$ M, $[U^{IV}(C_2O_4)_4^{4-}] = 5.0 \times 10^{-3}$ M, $\mu(NaCl) = 1.055$ M, $[C_2O_4^{2-}] = 0.05$ M. (Color figure online)
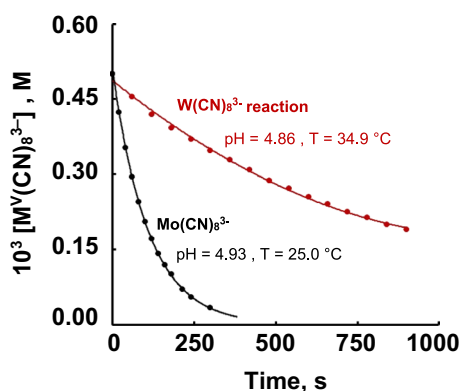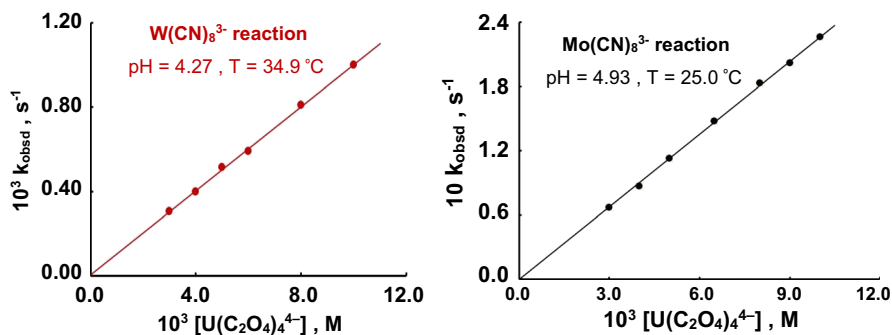
Fig. 3 Plots of k_{obsd} versus $[U^{IV}(C_2O_4)_4{}^{4-}]$ for the $[U^{IV}(C_2O_4)_4{}^{4-}]$ variation in reaction mixtures. $[W^V(CN)_8{}^{3-}] = 5.0 \times 10^{-4}$ M (red plot), $[Mo^V(CN)_8{}^{3-}] = 5.0 \times 10^{-4}$ M (black plot). For both reactions, $\mu(NaCl) = 1.055$ M, $[C_2O_4{}^{2-}] = 0.05$ M. (Color figure online)

reaction is not an equilibrium involving the reduced products $W^{IV}(CN)_8{}^{4-}$ or $Mo^{IV}(CN)_8{}^{4-}$.

Variation of the specific cation in the reaction medium, K^+ in the $W(CN)_8{}^{3-}$ reaction and Na^+ in the $Mo(CN)_8{}^{3-}$ reaction, do not have a direct proportional effect on the reaction rate. Although the alkali metal cation concentration was in large excess over both $U^{IV}(C_2O_4)_4{}^{4-}$ and $M^V(CN)_8{}^{3-}$ (M = W, Mo), plots of k_{obsd} versus [alkali metal cation] was not linear (Supplementary Information Fig. S1). This implies the effect that these alkali metals have on the reaction rate is non-specific and not pseudo-first order. Secondly, plots of log (k_{obsd}) versus log [alkali metal cation] (Supplementary Information Fig. S2) are linear but the slopes are not one. Slopes were found to be 0.47 ± 0.01 for K^+ in the $W(CN)_8{}^{3-}$ reaction and 0.34 ± 0.02 for Na^+ in the $Mo(CN)_8{}^{3-}$ reaction. These small slopes confirm that the interactions of alkali metal cations with reactants in the reactions are non-specific, i.e. they do not take part in the rate determining step of the reaction mechanism.

A theory for the influence of the ionic strength of the reaction mixture on the reaction rate was formulated by Brønsted and Bjerrum [46]. The logarithmic form of the equation, where ∂ is the Debye–Hückel solvent constant, is

$$\log k = \log k_0 + 2Z_A Z_B \partial \left(\frac{I^{1/2}}{1 + I^{1/2}} \right) \qquad (7)$$

The Debye–Hückel solvent constant (∂) for water is ~0.51 at 25 °C which simplifies the equation to:

$$\log k = \log k_0 + Z_A Z_B \left(\frac{I^{1/2}}{1 + I^{1/2}} \right) \qquad (8)$$

Should the slope of a plot of log k versus $\left(\frac{I^{1/2}}{1 + I^{1/2}} \right)$ have a positive value it follows that Z_A and Z_B have the same charge (i.e. both positive or both negative). The data

Fig. 4 Brønsted–Bjerrum plot of log k_{obsd} vs. $\frac{I^{1/2}}{1+I^{1/2}}$. $[W^V(CN)_8{}^{3-}] = 5.0 \times 10^{-4}$ M (red plot, I was controlled with KCl), $[Mo^V(CN)_8{}^{3-}] = 5.0 \times 10^{-4}$ M (black plot, I was controlled with NaCl). For both, $[U(C_2O_4)_4{}^{4-}] = 5.0 \times 10^{-3}$ M, $[C_2O_4{}^{2-}] = 0.05$ M. (Color figure online)
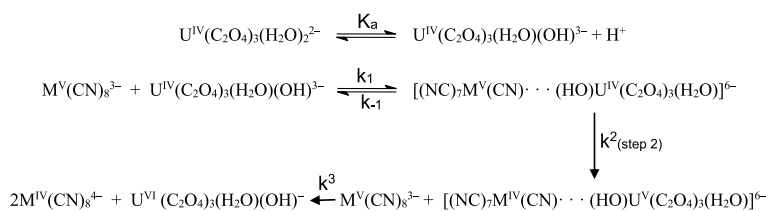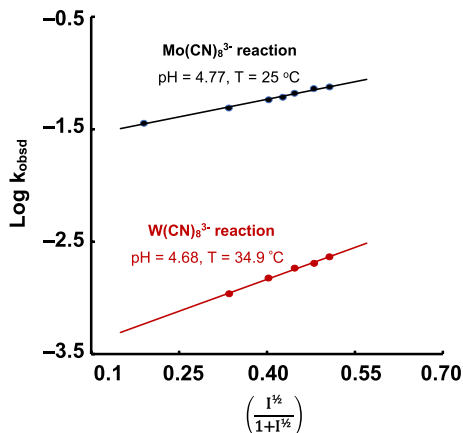
**Scheme 1** Mechanism of oxidation of $U(C_2O_4)_3(H_2O)_2{}^{2-}$ with $M^V(CN)_8{}^{3-}$ (M = Mo, W)

for varying the ionic strength (μ) of the reaction mixture for the $M(CN)_8{}^{3-}$ (M = W, Mo) oxidation of $U(C_2O_4)_4{}^{4-}$ (Supplementary Information Table S3, entries 4–8, and Table S4, entries 5–11), highlights an increase in the reaction rate with an increase in ionic strength (μ). This positive effect (slope) is also demonstrated in Fig. 4 and indicates ions of like charge react in the rate determining step. This criteria is met in the second step of the reaction mechanism, Scheme 1, where $M^V(CN)_8{}^{3-}$ react with $U^{IV}(C_2O_4)_3(H_2O)(OH)^{3-}$ to form a binuclear intermediate complex.

It has been shown before [47, 48] that in the presence of oxalate ions, $K_4U(C_2O_4)_4$ exists in solution as a mixture of $U(C_2O_4)_2$, $U(C_2O_4)_3{}^{2-}$ and $U(C_2O_4)_4{}^{4-}$. It was shown [47, 48] how the concentration of these species varies with variation in oxalate ion concentration of the solution. The oxalate ion concentration in reaction mixtures of this study was ≤ 0.05 M. From literature [47, 48] it therefore follows that the main uranium(IV) species in the reaction mixtures is $U(C_2O_4)_3{}^{2-}$ and there may also be some $U(C_2O_4)_2$. This means that two uranium(IV) species can be active in the reaction mixtures utilized in this study. However, since the concentration of $U(C_2O_4)_2$ is very low and it is very insoluble ($K_{sp} = 1 \times 10^{-22}$ [48]), its influence can be regarded as insignificantly small, and the only reactive U(IV) species of note in the reaction mixture is $U(C_2O_4)_3{}^{2-}$.

Variation of the hydrogen ion in the $W(CN)_8{}^{3-}$ reaction (Supplementary Information, Table S1, entries 13–27) and the $Mo(CN)_8{}^{3-}$ reaction (Table S2 entries

26–40) indicate a significant $[H^+]$ dependence (Fig. 5). It has been shown that $U(C_2O_4)_3^{2-}$ in aqueous medium exists as $U(C_2O_4)_3(H_2O)_2^{2-}$ [48] and that the complex ion can dissociate as shown in Eq. 9.

$$U\left(C_2O_4\right)_3\left(H_2O\right)_2^{2-} \overset{K_a}{\rightleftharpoons} U\left(C_2O_4\right)_3\left(H_2O\right)(OH)^{3-} + H^+ \tag{9}$$
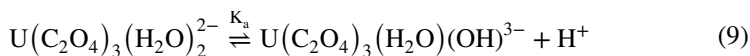
By abbreviating $U(C_2O_4)_3(H_2O)_2^{2-}$ as HA and $U(C_2O_4)_3(H_2O)(OH)^{3-}$ as A in Eq. 9, fitting of the observed experimental data for the $W(CN)_8^{3-}$ reaction at 34.9 °C to Eq. 10 [45, 49, 50]

$$k_{obsd} = \frac{k_{HA}\left[H^+\right] + k_A K_a}{\left[H^+\right] + K_a} \tag{10}$$

This yields values for the equilibrium constant $K_a = (1.6 \pm 0.5) \times 10^{-6}$ M^{-1}. The rate constants for the oxidation of $U(C_2O_4)_3(H_2O)_2^{2-}$ (HA) and $U(C_2O_4)_3(H_2O)(OH)^{3-}$ (A) by $W(CN)_8^{3-}$ was obtained from the same fit to be $k_{HA} = (5 \pm 1) \times 10^{-5}$ s^{-1} and $k_A = (1.5 \pm 0.3) \times 10^{-2}$ s^{-1}. When Eq. 10 is applied to the kinetic data of the $Mo^V(CN)_8^{3-}$ reaction at 25.0 °C, the equilibrium constant was found to be $K_a = (1.3 \pm 0.8) \times 10^{-6}$ M^{-1} while the rate constants for the $Mo^V(CN)_8^{3-}$ oxidation of $U(C_2O_4)_3(H_2O)_2^{2-}$ (HA) and $U(C_2O_4)_3(H_2O)(OH)^{3-}$ (A) were found as $k_{HA} = (9 \pm 1) \times 10^{-3}$ s^{-1} and $k_A = 1.1 \pm 0.6$ s^{-1}.

In both cases k_A is more than 100 times larger than k_{HA}. This implies k_{HA} is negligible compared to k_A and $U(C_2O_4)_3(H_2O)(OH)^{3-}$ is regarded as the dominant reactive U(IV) species in these redox reactions.

From the experimental results and discussion, a reaction mechanism, Scheme 1, is proposed.

The k_1 and k_{-1} equilibrium steps are regarded as rate determining (slow) while steps k^2 (rate constant of step 2, k^2 not to be confused with k_2 which is the second order rate constant of the k_1 step) and k^3 (rate constant of step 3) are considered fast.
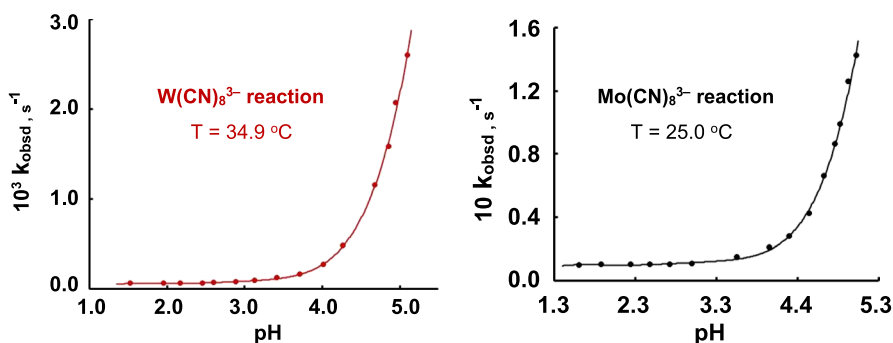

Fig. 5 Observed rate constant versus pH plots for the variation of $[H^+]$ in reaction mixtures. $[M^V(CN)_8^{3-}] = 5.0 \times 10^{-4}$ M (M = W, red plot, or M = Mo, black plot. For both, $[U^{IV}(C_2O_4)_4^{4-}] = 5.0 \times 10^{-3}$ M, μ(NaCl) = 1.055 M, $[C_2O_4^{2-}] = 0.05$ M. (Color figure online)

Applying the steady state approximation to the intermediate binuclear complexes $[(NC)_7M^V(CN)\cdots(HO)U^{IV}(C_2O_4)_3(H_2O)]^{6-}$ and $[(NC)_7M^{IV}(CN)\cdots(HO)U^V(C_2O_4)_3(H_2O)]^{6-}$ and by applying Eq. 11,

$$K_a = \frac{\left[U(C_2O_4)_3(H_2O)(OH)^{3-}\right]\left[H^+\right]}{[U(C_2O_4)_3(H_2O)_2^{2-}]} \tag{11}$$

The rate law shown in Eq. 12 can be derived. Equation 12 is also in agreement with the experimental results.

$$R = \frac{k_1 k_2 K_a}{\left[H^+\right](k_{-1} + k_2)}\left[M^V(CN)_6^{3-}\right]\left[U^{IV}(C_2O_4)_3(H_2O)_2^{2-}\right] \tag{12}$$

The activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ have been obtained by application of the Eyring equation (Eq. 4). Least squares mathematical fitting of the observed temperature variation data to the Eyring equation (Eq. 4) is the modern (and more accurate) way to obtain activation parameters [51]. Utilizing second order rate constants, k_2, a non-linear least squares fit [43] of the experimental data for varying the temperature of the reaction mixture (Supplementary Information Table S5, entries 28–34 for the $W(CN)_8^{3-}$ reaction and entries 48–55, for the $Mo(CN)_8^{3-}$ reaction) to Eq. 4 (Fig. 6), yield the activation enthalpy, $\Delta H^{\#}(W^V(CN)_8^{3-}) = 79.6 \pm 0.5$ kJ mol^{-1} and $\Delta H^{\#}(Mo^V(CN)_8^{3-}) = 36.6 \pm 0.2$ kJ mol^{-1}. The same fits yield the activation entropy, $\Delta S^{\#}(W^V(CN)_8^{3-}) = -6.4 \pm 0.2$ JK^{-1} mol^{-1} and $\Delta S^{\#}(Mo^V(CN)_8^{3-}) = -99.7 \pm 0.2$ JK^{-1} mol^{-1}. The obtained activation parameters have been validated by using Eq. 13 as explained by Lente [42] and others [22, 35].

$$\sigma\Delta S^{\#} = \frac{1}{T_{av}}\sigma\Delta H^{\#} \tag{13}$$

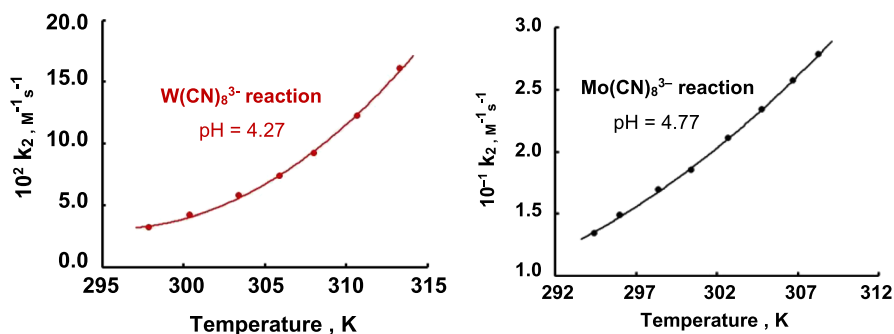**Fig. 6** A non-linear least squares fit of second order rate constant (M^{-1} s^{-1}) and temperature (K) data to the exponential Eyring equation. $[M^V(CN)_6^{3-}] = 5.0 \times 10^{-4}$ M (M=W, red plot, or M=Mo, black plot). For both $[U^{IV}(C_2O_4)_4^{4-}] = 5.0 \times 10^{-3}$ M, μ(NaCl) = 1.055 M, $[C_2O_4^{2-}] = 0.05$ M. (Color figure online)

Conclusions

The oxidation of tetrakisoxalatouranate(IV) by the octacyanotungstate(V) and octacyanomolybdate(V) ions occur stoichiometrically in the ratio $U^{IV}(C_2O_4)_4^{4-}$:$M^V(CN)_6^{3-} = 1{:}2$ (M = W, Mo) and the reactions are first order in both reactants. The reactive form of U^{IV} in these reactions in the pH range 1.6–4.99 is $U^{IV}(C_2O_4)_3(H_2O)(OH)^{3-}$. Variation of the pH of the reaction mixtures yield an acid dissociation constant of $K_a \approx 1.3 \times 10^{-6}$ M^{-1} (pK$_a \approx 5.80$) at 25.0 °C and 1.6×10^{-6} M^{-1} (pK$_a = 5.89$) at 34.9 °C for the equilibrium

$$U^{IV}(C_2O_4)_3(H_2O)_2^{2-} \overset{K_a}{\rightleftharpoons} U^{IV}(C_2O_4)_3(H_2O)(OH)^{3-} + H^+$$
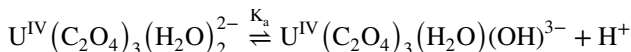
This value is mutually consistent with the value obtained from kinetic studies of the hexacyanoferrate(III) ion oxidation of the tetrakisoxalatouranate(IV) ion [35] ($K_a = 1.02 \times 10^{-6}$ M^{-1}, pK$_a = 5.99$).

Our observations agree with those of Lente [44] that a sixfold excess of one reagent (here $U^{IV}(C_2O_4)_4^{4-}$) over the concentration of the limiting reagent, (here $M^V(CN)_6^{3-}$) is sufficient to study reactions kinetically under pseudo-order conditions. The traditional view of a ten-fold excess of one reactant in a reaction over another as the minimum requirement for pseudo-order conditions, is considered an artefact from an era when computational limitations required aggressive approximations.

The advent of strong computational abilities with least square fitting programmes allows calculation of rate constants quickly and more accurately than the traditional graphical approximation methods. The same applies to calculation of the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$. As Lente [44, 51], we conclude modern computational abilities with non-linear least squares fitting programmes applied directly to the Eyring equation (Eq. 4) allows calculation of $\Delta H^{\#}$ and $\Delta S^{\#}$ more easily and accurately directly from rate constant and temperature data.

Declarations

Conflict of interest The authors are not aware of any conflict of interests.

References

1. Konig E (1962) Interpretation der absorptionsspektren der komplexionen $[Mo(CN)_8]^{4-}$, $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$ und $[W(CN)_8]^{3-}$. Theoret Chim Acta 1:23–35
2. Perumareddi JR, Liehr AD, Adamson AW (1963) Ligand field theory of transition metal cyanide complexes. Part I. The zero, one and two electron or hole configurations. J Am Chem Soc 85:249–259
3. McGarvey BR (1966) The structure of the octacyanomolybdate(V) and -tungstate(V) ions from electron spin resonance. Inorg Chem 5:476–479
4. Hayes RG (1966) EPR studies of the $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions. The geometry of the ions. J Chem Phys 44:2210–2212
5. Adamson AW, Welker JP, Volpe M (1950) Exchange studies with complex ions. I. The exchange of radiocyanide with certain heavy metal complex cyanides. J Am Chem Soc 72:4030–4036
6. Dennis CR, Fourie E, Margerum DW, Swarts JC (2020) Kinetic advantage of inner sphere electron transfer reactions of copper(III, II) peptide complexes with cyano complexes of iron, molybdenum and tungsten. Trans Met Chem 45:147–157
7. Dennis CR, Margerum DW, Fourie E, Swarts JC (2020) A kinetic study of the electron-transfer reactions of nickel(III, II) tripeptide complexes with cyano complexes of molybdenum, tungsten, and iron. Inorg Chem 59:11695–11703
8. Leipoldt JG, Bok LDC, Dennis CR (1976) A kinetic study of the octacyanomolybdate(V) ion oxidation of arsenite in an alkaline medium. J Inorg Nucl Chem 38:1655–1657
9. Leipoldt JG, Bok LDC, Van Wyk AJ, Dennis CR (1977) A kinetic study of the octacyanotungstate(V) ion oxidation of arsenite in an alkalide medium. J Inorg Nucl Chem 39:2019–2020
10. Leipoldt JG, Bok LDC, Van Wyk AJ, Dennis CR (1977) A kinetic study of the reduction of the octacyanomolybdate(V) and octacyanotungstate(V) ions by hydrazine in an alkaline medium. React Kinet Catal Lett 6:467–474
11. Leipoldt JG, Dennis CR, Van Wyk AJ, Bok LDC (1978) A kinetic study of the osmium(VIII) catalyzed reduction of octacyanomolybdate(V) and octacyanotungstate(V) ions by selenium(IV) in an alkaline medium. Inorg Chim Acta 31:187–190
12. Leipoldt JG, Bok LDC, Basson SS, Van Wyk AJ, Dennis CR, Cilliers PJ (1977) A kinetic study of the oxidation of thiourea by octacyanomolybdate(V) and octacyanotungstate(V) ions in an alkaline medium. React Kinet Catal Lett 8:93–99
13. Leipoldt JG, Dennis CR, Van Wyk AJ, Bok LDC (1979) A kinetic study of the Os(VIII) catalyzed oxidation of tellurium(IV) by octacyanomolybdate(V) and octacyanotungstate(V) ions in an alkaline medium. Inorg Chim Acta 34:237–240
14. Lamprecht GJ, Leipoldt JG, Dennis CR, Basson SS (1980) Kinetics of the octacyanomolybdate(V) ion oxidation of thiosulphate. React Kinet Catal Lett 13:269–275
15. Leipoldt JG, Dennis CR, Grobler EC (1983) Kinetics of the oxidation of the manganate ion by complex cyanides of Mo(V), W(V) and Fe(III) in alkaline solution. Inorg Chim Acta 77:L45–L46
16. Dennis CR, Basson SS, Leipoldt JG (1983) Kinetics and salt effects of the reduction of octacyanomolybdate(V) and octacyanotungstate(V) by sulphite ions. Polyhedron 2:1357–1362
17. Dennis CR, Leipoldt JG, Basson SS, Lamprecht GJ (1985) The oxidation of thiosulphate ions by octacyanotungstate(V) in weak acidic medium. Polyhedron 4:1621–1624
18. Dennis CR, Van Wyk AJ, Basson SS, Leipoldt JG (1987) Oxidation of hydrazine and methyl-substituted hydrazines by the cyano complexes of iron(III), molybdenum(V) and tungsten(V). A kinetic study. Inorg Chem 26:270–272
19. Van Wyk AJ, Dennis CR, Leipoldt JG, Basson SS (1987) A kinetic study of the oxidation of hydroxylamine by octacyanotungstate(V). Polyhedron 6:641–643
20. Dennis CR, Potgieter IM, Basson SS (2010) A kinetic study of the reduction of the octacyanomolybdate(V) ion by the hydroxide ion. Reac Kinet Mech Cat 99:63–68
21. Dennis CR, Potgieter IM, Basson SS (2011) A kinetic study of the oxidation of formaldehyde by the octacyanomolybdate(V) ion in aqueous alkaline medium. Reac Kinet Mech Cat 104:1–7
22. Dennis CR, Potgieter IM, Langner EHG, Fourie E, Swarts JC (2019) The oxidation of acetaldehyde by the octacyanomolybdate(V) ion in an aqueous alkaline medium. Transit Met Chem 44:161–165
23. Newton TW, Baker FB (1967) Aqueous oxidation-reduction reactions of uranium, neptunium, plutonium, and americium. Lanthanide/Actinide Chem 20:268–295

24. Bolotova GT, Golovnya (eds) (1964) Kompleksnye soedineniya urana, Akademiya nauk SSSR, Institut obschei i neorganicheskoi kimii (Complex uranium compounds, Academy of Sciences of the USSR, Institute of General and Inorganic Chemistry), Chapter 19

25. Kraus KA, Nelson F (1950) Hydrolytic behavior of metal ions. I. The acid constants of uranium(IV) and plutonium(IV). J Am Chem Soc 72:3901–3906

26. Kraus KA, Nelson F (1955) Hydrolytic behavior of metal ions. IV. The acid constant of uranium(IV) as a function of temperature. J Am Chem Soc 77:3721–3722

27. Betts RH (1955) Kinetics of the oxidation of uranium(IV) by iron(III) in aqueous solutions of perchloric acid. Can J Chem 33:1780–1791

28. Halpern J, Smith JG (1956) Kinetics of the oxidation of uranium(IV) by molecular oxygen in aqueous perchloric acid solution. Can J Chem 34:1419–1427

29. Newton TW (1959) The kinetics of the reaction between Pu(IV) and U(IV). J Phys Chem 63:1493–1497

30. Harkness AC, Halpern J (1959) Kinetics of the oxidation of uranium(IV) by thallium(III). J Am Chem Soc 81:3526–3529

31. Baker FB, Newton TW (1961) The reaction between uranium(IV) and hydrogen peroxide. J Phys Chem 65:1897–1899

32. Hassan RM (2011) A mechanistic approach of the kinetics of oxidation of uranium(IV) by hexachloroplatinate(IV) in aqueous perchlorate solutions. Evidence of the formation of a binuclear intermediate complex. J Phys Chem A 115:13338–13345

33. Hassan RM, Kojima T, Fukotumi H (1980) Kinetic study of the oxidation of uranium(IV) by ferricyanide ions in aqueous solutions. Bull Res Lab Nucl React Jpn 12:41–47

34. Hassan RM (1991) Kinetics of reaction of uranium(IV) and hexachloroiridate(IV) in acid perchlorate solutions. Evidence for a binuclear intermediate. J Chem Soc Dalton Trans. https://doi.org/10.1039/dt9910003003

35. Dennis CR, Van Zyl GJ, Fourie E, Basson SS, Swarts JC (2021) A kinetic study of the oxidation of the *tetrakis*oxalatouranate(IV) ion by the hexacyanoferrate(III) ion in an oxalate buffer medium. Reac Kinet Mech Cat 132:599–615

36. Leipoldt JG, Bok LDC, Cilliers PJ (1974) The preparation of potassium octacyanotungstate(IV) dihydrate. Z Anorg Allg Chem 407:350–352

37. Leipoldt JG, Bok LDC, Cilliers PJ (1974) The preparation of potassium octacyanomolybdate(IV) dihydrate. Z Anorg Allg Chem 409:343–344

38. Dennis CR, Van Wyk AJ, Basson SS, Leipoldt JG (1992) Synthesis of cesium octacyanomolybdate(V)- and cesium octacyanotungstate(V) dihydrate: a more successful method. Transit Met Chem 17:471–473

39. Basson SS, Bok LDC, Grobler SR (1974) Titrimetric and potentiometric determination of aqueous sulphide by octacyanomolybdate(V) and -tungstate(V) ions. Z Anorg Anal Chem 268:287–288

40. Marchi LE (1950) Potassium tetraoxalatouranate(IV). Inorg Synth 3:169–170

41. Gray GW, Spence JT (1971) Photochemical reduction of octacyanomolybdate(V) in aqueous solution. Inorg Chem 10:2751–2755

42. Lente G, Fabien I, Poe J (2005) A common misconception about the Eyring equation. New J Chem 29:759–760

43. "Scientist" software, version 2, MicroMath, Saint Louis, Missouri, USA

44. Lente G (2015) Chapter 3—deterministic kinetics in chemistry and systems biology. Springer, Cham, pp 61–65. https://doi.org/10.1007/978-3-319-15482-4

45. Wilkins RG (1991) The study of kinetics and mechanism of transition metal complexes, 2nd edn. Allyn and Bacon, Boston, p p8

46. Laidler KJ (1963) Reaction kinetics, vol 2. Pergamon Press Ltd, London

47. Zakharova FA, Moskvin AI (1960) The solubility product of uranium(IV) oxalate and the composition and dissociation constants of oxalato-uranium(IV) complexes in aqueous solution. Zhur Neorg Khim 5:1228–1233

48. Bolotova GT, Golovnya (eds) (1964) Kompleksnye soedineniya urana, Akademiya nauk SSSR, Institut Obschei i Neorganicheskoi Kimii (Complex uranium compounds, Academy of Sciences of the USSR, Institute of General and Inorganic Chemistry), Chapter 21

49. Swarts JC, Aquino MAS, Han J, Lam KY, Sykes AG (1995) Kinetic studies on the reduction of the tyrosyl radical of the R2 subunit of *E. coli* ribonucleotide reductase. Biochim Biophys Acta 1247:215–224

50. Han J, Swarts JC, Sykes AG (1996) Kinetic studies on the hydrazine and phenyl hydrazine reductions of *Escherichia coli* R2 subunit of ribonucleotide reductase. Inorg Chem 35:4629–4634
51. Lente G (2018) Facts and alternative facts in chemical kinetics: remarks about the kinetic use of activities, termolecular processes, and linearization techniques. Curr Opin Chem Eng 21:76–83

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Authors and Affiliations

C. Robert Dennis[1] · **Gideon J. van Zyl[1]** · **Eleanor Fourie[1]** ·
Stephen S. Basson[1] · **Jannie C. Swarts[1]**

✉ C. Robert Dennis
  crobbie.dennis@gmail.com

[1] Chemistry Department, University of the Free State, P.O. Box 339, Bloemfontein 9300, Republic of South Africa