Kinetic Studies of the Complexation of Oxalate to the $t_{2g}{}^6$ Hexaaqua Ions of Ruthenium(II) and Rhodium(III)†

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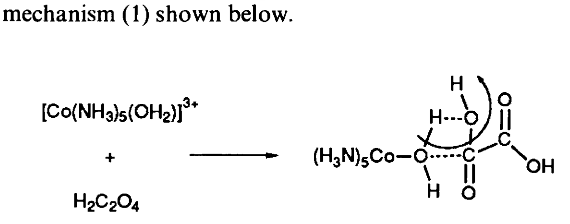
A kinetic study on the reactions of oxalate with the isoelectronic $t_{2g}{}^6$ hexaaqua ions of ruthenium(II) and rhodium(III) reveals vastly differing mechanisms occurring for the two ions. For hexaaquaruthenium(II) equilibration kinetics is relevant giving a 1:1 oxalato complex, which is presumably chelated. For the forward reaction the dependence on $[H^+]$ indicates a rate-determining reaction of $[Ru(OH_2)_6]^{2+}$ with the monoanion of oxalic acid. A comparison of rate constants and activation parameters for $HC_2O_4^-$ with those obtained for H_2O, Cl^-, Br^- or I^- as incoming ligands on $[Ru(OH_2)_6]^{2+}$ suggests the presence of an interchange reaction largely controlled by the rate of water exchange. For hexaaquarhodium(III) a two-stage process occurs ultimately giving rise to tris(oxalato) products. In the first stage, a single rate-determining anation reaction proceeds to completion giving mainly *cis*-$[Rh(OH_2)_2(C_2O_4)_2]^-$ ($\approx$90%) with a smaller amount ($\approx$10%) of the *trans* product. Rate-determining entry of the first oxalate ligand is believed to be involved. The dependence of the observed rate constants (k_{obs}) for the first stage with both temperature and $[H^+]$ is discussed as indicating involvement of a mechanism wherein interaction of $H_2C_2O_4$ occurs with both $[Rh(OH_2)_6]^{3+}$ and $[Rh(OH_2)_5(OH)]^{2+}$ in a process involving retention of the Rh–OH(OH$_2$) bond during the activation step. Rate constants are not only observed to be far in excess ($>10^3\times$) of those for water exchange on the two aqua rhodium(III) ions but also found to be extremely close to those re-evaluated with respect to the corresponding reaction on $[Ir(OH_2)_6]^{3+}$ in support of the existence of a metal independent C–O bond-breaking process. Possible reasons behind the differing behaviour observed for Ru^{2+} and Rh^{3+} are considered.

Metal-ion complexation reactions involving replacement of water by oxalic acid and its deprotonated anions have been found to be involved with a number of varied mechanistic pathways.[1–6] Reactions in which complexation involving each of $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ are all well documented as is the observation that rate-determining substitution (both associatively[1] and dissociatively[4,5] activated) or chelation[6] can be relevant. More recently a further possible mode of complexation with aqua metal ions has emerged in which water replacement appears to occur without cleavage of the M–OH$_2$ bond in the activation step. This possibility, conceivably a feature of many oxo-anion complexation reactions, was first recognised by Taube and co-workers[7] in 1970 albeit with regard to the reverse process as exhibited in the aquation of $[Co(NH_3)_5(HC_2O_4)]^{2+}$ a monodentate oxalato complex, C–O bond rupture being the dominant mechanism under acid catalysis as demonstrated by ^{18}O-labelling experiments.[7] It was conceivable that the complexation step occurred by merely the reverse process. Van Eldik and Harris[8] subsequently obtained evidence with regard to $[Co(NH_3)_5(OH_2)]^{3+}$ that in acidic solution oxalic acid complexation occurred *via* the concerted mechanism (1) shown below.



(1)

Evidence was provided by a rate far in excess of that for water exchange on the aqua pentaammine complex accompanied by a very low $\Delta H^\ddagger$ (57 kJ mol^{-1}), similar to that observed with regard to the CO_2 addition process,[9] and a noticeably negative $\Delta S^\ddagger$ (-151 J K^{-1} mol^{-1}).

The definitive oxygen labelling experiment has yet to be performed although further support for the mechanism has been gained from oxygen-18 labelling studies with regard to reactions involving the formation and aquation (hydrolysis) of *cis*-$[Co(en)_2(C_2O_4)]^+$ (en = ethylenediamine) by Miskelly and Buckingham.[10]

Recent work in our laboratory with regard to oxalate complexation on $[Ir(OH_2)_6]^{3+}$ in acidic solution ($HClO_4$–$NaClO_4$) has also demonstrated substitution rates for oxalate far in excess of the water exchange rate for this ion[11] (in this regard probably the most inert hexaaqua ion known[12]). A mechanism for oxalic acid complexation in which retention of the Ir–OH$_2$ bond occurred in the activation step was thus proposed. A low $\Delta H^\ddagger$ and markedly negative $\Delta S^\ddagger$ was observed for the oxalic acid anation path reminiscent of those observed for $[Co(NH_3)_5(OH_2)]^{3+}$. This was not only the first indication of the concerted mechanism occurring on a hexaaqua metal ion but also as a result the first successfully monitored complexation reaction on the Ir^{3+} cation.

It has thus been of interest to study oxalate substitution reactions with regard to other hexaaqua metal ions and in this respect studies on $[Ru(OH_2)_6]^{2+}$ and $[Rh(OH_2)_6]^{3+}$ are timely given recent ^{17}O NMR studies with regard to the rates and mechanism of water exchange on these two metal ions.[13] They also offer the opportunity to compare the behaviour of two isoelectronic $t_{2g}{}^6$ metal ions of the second period differing by one unit of cationic charge.

We report herein the results from a kinetic study on the reactions of oxalate with both $[Ru(OH_2)_6]^{2+}$ and $[Rh(OH_2)_6]^{3+}$ (hereafter abbreviated to Ru^{2+} and Rh^{3+}) in

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† *Supplementary data available* (No. SUP 56806, 3 pp.): Pseudo-first-order rate constants for reaction of $[Ru(OH_2)_6]^{2+}$ with oxalate. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

non-complexing acidic solution: $CF_3SO_3^-$ (Ru^{2+}), ClO_4^- (Rh^{3+}). It is clear now that the two ions behave quite differently with regard to their substitution mechanisms with this ligand.

Experimental

Preparation of Reactants.—Solutions of Ru^{2+} in trifluoromethanesulphonic acid (CF_3SO_3H) were prepared using a slightly modified method based on that described by Kallen and Earley.[14] All manipulations were carried out under air-free conditions using methods as described in previous papers.[1,15] Commercial ruthenium trichloride (Johnson Matthey) (1.0 g) was treated with commercial sodium hypochlorite solution (BDH) (200 cm^3) and the yellow RuO_4 generated was extracted with CCl_4. The combined CCl_4 extracts (200 cm^3) were then added to a flask containing 2.0 mol dm^{-3} HBF_4 (BDH, 50 cm^3) and tin powder (Aldrich, 4.0 g). Upon stirring under a stream of dinitrogen gas the aqueous layer slowly became pink and the CCl_4 layer colourless. The pink layer was separated, filtered, diluted 20 times with deoxygenated water and finally loaded onto a column (10 × 1 cm) of DOWEX 50W X2 cation-exchange resin. Following washing of the column with 0.2 mol dm^{-3} HBF_4 (200 cm^3) and water (200 cm^3) the pink band containing $[Ru(OH_2)_6]^{2+}$ was eluted with 2.0 mol dm^{-3} CF_3SO_3H (Fluka). Stock solutions (typically 0.1 mol dm^{-3}) were standardised using the peak maxima at 530 (ε 9.0) and 385 nm (10.8 dm^3 mol^{-2} cm^{-2}).[14]

Perchloric acid solutions of Rh^{3+} were prepared by the modified method of Ayres and Forrester[16] as reported by Sykes.[17] A solution of $RhCl_3 \cdot xH_2O$ (Johnson Matthey) (2.0 g) in 70% aqueous perchloric acid (BDH) (50 cm^3) was refluxed for *ca.* 2 h in a round-bottomed flask connected *via* a condenser to a water pump which allowed simultaneous concentration of the solution to about 25 cm^3. Following filtration and subsequent dilution to 0.2 mol dm^{-3} H^+ the resulting orange-yellow solution was loaded onto a column (6 × 1 cm) of DOWEX 50W X8 cation-exchange resin. Washing with 0.5 and 1.0 mol dm^{-3} $HClO_4$ resulted in the removal of chloro complexes of Rh^{III} of charge $\leqslant 2.0$. The major fraction containing $[Rh(OH_2)_6]^{3+}$ was subsequently eluted as a bright yellow band with 2.0 mol dm^{-3} $HClO_4$. Stock solutions (typically 5–10 mmol dm^{-3}) were standardised spectrophotometrically using the peak maxima at 396 (ε 62) and 311 nm (67.4 dm^{-3} mol^{-1} cm^{-1}).[17]

Solutions of $HClO_4$ and CF_3SO_3H were standardised by titration with NaOH. Stock solutions of $NaClO_4$ and $NaCF_3SO_3$ together with the background H^+ concentrations of those of the hexaaqua metal ions were standardised similarly following exchange onto a column of Amberlite IR-120H cation resin. Oxalic acid dihydrate (BDH AnalaR) was used as supplied. Doubly distilled water was used throughout.

Kinetic Studies.—For oxalate complexation on Ru^{2+} the reaction was followed at 445 nm in the presence of a 10 fold excess of oxalate over Ru^{II} in order to permit pseudo first-order kinetics. Runs were monitored over 2–5 h periods at between 20 and 45 °C using 1.0 cm quartz cells sealed with rubber septum caps under air-free conditions as previously described.[1,15] The ionic strength, I, was kept constant at 1.0 mol dm^{-3} using $NaCF_3SO_3$ to permit comparison with previous studies. In all cases good logarithmic plots of absorbance change as a function of time were obtained with linearity to greater than four half lives. First-order rate constants were obtained from the slopes and plotted as a function of total oxalate concentration (0.003–0.02 mol dm^{-3}) and as a function of $[H^+]$ (0.04–0.2 mol dm^{-3}).

For oxalate complexation on Rh^{3+} the reaction was followed at 400 nm in the presence of a similar pseudo first-order excess of oxalate over Rh^{III}. Here runs were monitored typically over 4 d periods at between 50 and 80 °C in 1.0 cm quartz cells using a Perkin-Elmer Lambda 5G model UV/visible spectrophotometer equipped with electronic thermostatting (±0.1 °C) and auto cell change facilities. The ionic strength was kept constant at 3.0 mol dm^{-3} using $NaClO_4$. A two-stage process was observed in which the absorbance changes as a function of time were fitted by a consecutive first-order reaction treatment using the non-linear least-squares program FITTING.* First-order rate constants (k_{obs} determined from the treatment were plotted as a function of total oxalate concentration 0.01–0.05 mol dm^{-3}) and $[H^+]$ (0.5–2.2 mol dm^{-3}). The latter was subsequently fitted following investigation of a number of possible mechanistic pathways.

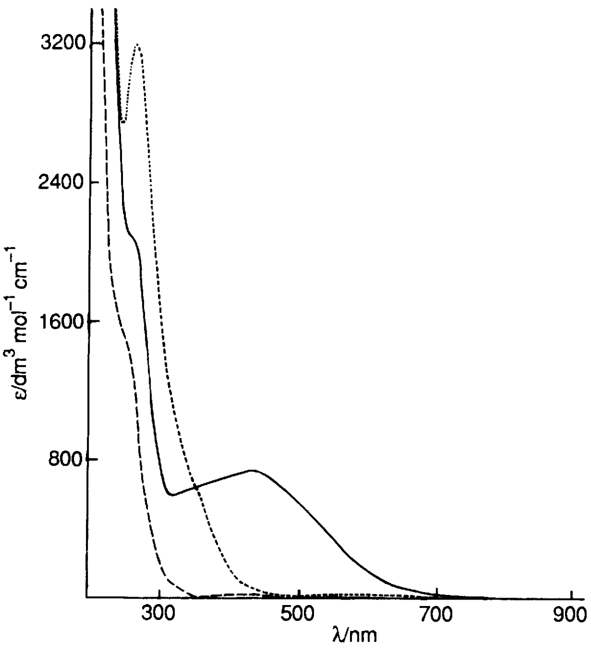

Fig. 1 Absorption spectra for solutions (25 °C) in 0.1 mol dm^{-3} CF_3SO_3H, I = 1.0 mol dm^{-3} ($NaCF_3SO_3$) of $[Ru(OH_2)_6]^{2+}$ (0.002 mol dm^{-3}) and oxalate (0.02 mol dm^{-3}) after mixing (– – – –), after 6 h (——) and then on exposure to air (• • • •)

In both studies the combined range of $[H^+]$ used (0.04–2.2 mol dm^{-3}) suggested that amounts of $C_2O_4^{2-}$ were small and could probably be neglected. The total oxalate concentration can thus be represented by equation (2).

$$[\text{Total oxalate}] = [H_2C_2O_4] + [HC_2O_4^-] \qquad (2)$$

The relevant first acid dissociation constant for oxalic acid (K_{a1}) [equation (3)] was determined as a function of

$$H_2C_2O_4 \overset{K_{a1}}{\rightleftharpoons} HC_2O_4^- + H^+ \qquad (3)$$

temperature (20–80 °C) and of ionic strength (1.0 or 3.0 mol dm^{-3}) by extrapolation from data already present in the literature.[2,3,18]

Product Analysis.—For the reaction of Ru^{2+} with oxalate the observed equilibrium kinetics and $[H^+]$ dependence (see below) suggested the rate-determining formation of a 1:1 oxalato complex; either $[Ru(HC_2O_4)(OH_2)_5]^+$ or chelated $[Ru(C_2O_4)(OH_2)_4]$. The kinetically relevant product was not isolated but its absorption spectral features are shown in Fig. 1. However on exposure to air rapid oxidation of the Ru^{II} solution

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* FITTING is a non-linear least squares program developed by Professor H. Strehlow (Max Planck Institute, Göttingen, FRG) for the treatment of both single and double exponential functions. The program takes unweighted absorbance data and computes values of the absorbance amplitude and rate constant as well as the standard deviation of the overall fit to the set function.

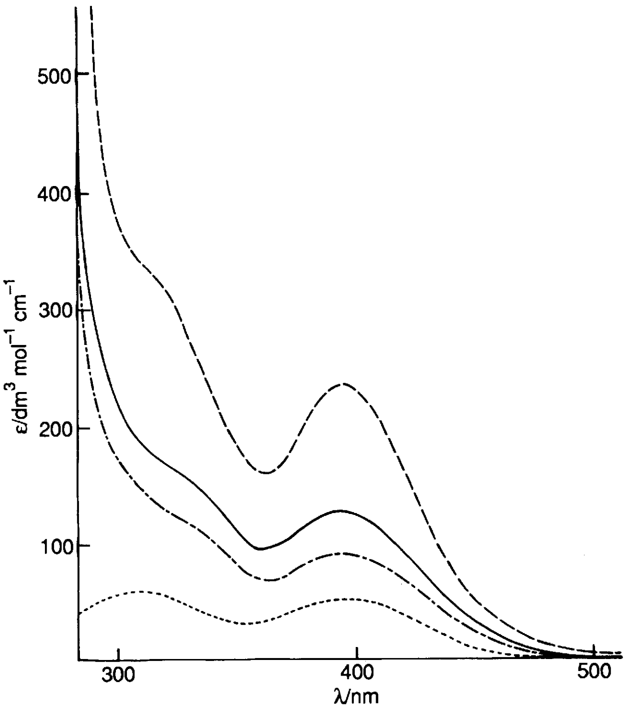

Fig. 2 Absorption spectra for $[Rh(OH_2)_6]^{3+}$ (····), *cis*-(——) and *trans* (—·—) $[Rh(C_2O_4)_2(OH_2)_2]^-$ and $[Rh(C_2O_4)_3]^{3-}$ (- - - -) (ε values taken as in ref. 20)

occurred with a clean isosbestic point to give the 1:1 chelated Ru^{III} complex $[Ru(C_2O_4)(OH_2)_4]^+$, λ_{max} 285 nm (ε = 2000 dm^3 mol^{-1} cm^{-1})[19] (Fig. 1), which was characterised additionally by a reversible one-electron reduction process back to the Ru^{II} complex at +0.04 V *vs.* the normal hydrogen electrode (NHE) (0.2 mol dm^{-3} CF_3SO_3H) thus distinguishing it from possible bis- and tris-(oxalato) products.*

Spectra for both *cis*- and *trans*-$[Rh(C_2O_4)_2(OH_2)_2]^-$ and $[Rh(C_2O_4)_3]^{3-}$ are shown in Fig. 2. Peak maxima are observed at 400 nm [ε = 120, *cis*-; ε = 92, *trans*-diaquabis(oxalato) complex; ε = 230 dm^3 mol^{-1} cm^{-1}, tris(oxalato) complex].[20] The absorbance changes at 400 nm following the two stages of reaction of Rh^{3+} with oxalate were found to be consistent with ≈90% formation of the *cis*-diaquabis(oxalato) complex and ≈10% of the *trans* complex[20] (first stage) together with equilibration to give varying amounts of tris(oxalato) complexes (second stage) the nature and extent of which depended upon $[H^+]$. Further separation and characterisation of the rhodium containing products by anion-exchange chromatography (Amberlite IRA-400) proved difficult owing to the large excess of free oxalate and perchlorate present.

Results

Oxalate Complexation with Ru^{2+}.—For runs performed over a range of total oxalate concentration from 0.003 to 0.02 mol dm^{-3} the linearity of first-order logarithmic plots over greater than four half lives suggested only a single rate-determining process to give the product spectrum shown in Fig. 1. Above 0.02 mol dm^{-3} total oxalate concentration a detectable second stage became apparent so the study was limited to concentrations ⩽0.02 mol dm^{-3}. Under these conditions the variation of rate with total oxalate concentration obeyed the relationship (4) showing evidence of equilibration kinetics with k_{obs} (= k_1 [Total oxalate] + k_{-1}) represented as below and illustrated by Fig. 3 for runs at 0.1 mol dm^{-3} H^+ conducted at six different temperatures (20–45 °C).

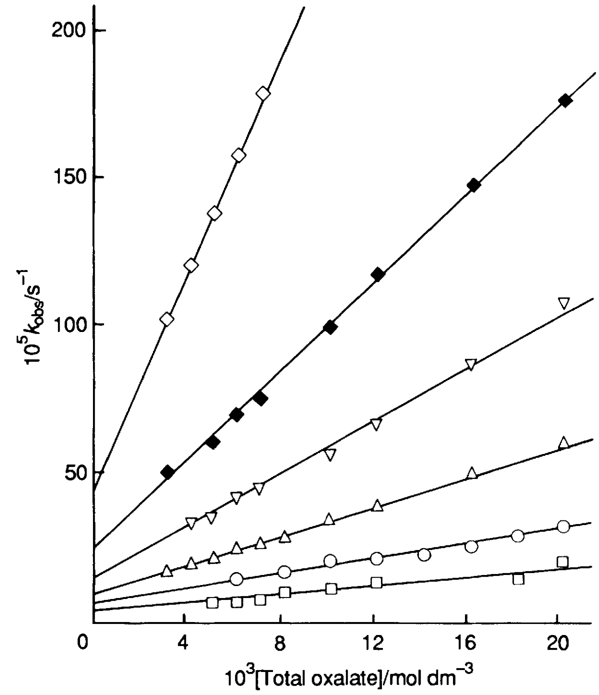

Fig. 3 First-order rate constants (k_{obs}) plotted *vs.* [Total oxalate] as a function of temperature for reaction with Ru^{2+} at $[H^+]$ = 0.1 mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaCF_3SO_3$): 20 (□), 25 (○), 30 (△), 35 (▽), 40 (◆) and 45 °C (◇)

$$-d[Ru^{2+}]/dt = k_1\,[\text{Total oxalate}][Ru^{2+}] + k_{-1}[Ru^{2+}] \quad (4)$$

The dependence of k_{obs} with total oxalate was investigated at 25 °C over the $[H^+]$ range 0.04–0.2 mol dm^{-3}. Values of k_{obs} so obtained are ilustrated by Fig. 4. The full rate law was thus found to be of the type (5) indicating that the rate-determining reaction was of Ru^{2+} reacting with the monodeprotonated anion of oxalic acid [equation (6)] with K_{a1} represented by

$$-d[Ru^{2+}]/dt = \frac{k_f K_{a1}\,[\text{Total oxalate}][Ru^{2+}]}{([H^+] + K_{a1})} + k_b[H^+][Ru^{2+}] \quad (5)$$

$$Ru^{2+} + HC_2O_4^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ru(C_2O_4) + H^+ \quad (6)$$

equation (3). With k_1 and k_{-1} defined as above, the validity of rate law (5) was confirmed by the observation of a linear plot (Fig. 5) to the dependence (7), which allows a kinetic evaluation

$$1/k_1 = [H^+]/k_f K_{a1} + 1/k_f \quad (7)$$

of K_{a1} as well as k_f. At 25 °C, the following values were obtained; K_{a1} = (0.08 ± 0.02) mol dm^{-3}, k_f = (2.6 ± 0.3) × 10^{-2} dm^3 mol^{-1} s^{-1}. Values of K_{a1} have been investigated at ionic strength 1.0 mol dm^{-3} by several workers as a function of temperature. Using the data obtained by Davies and Watkins[18] and Moorehead and Sutin[2] values of ΔH°_{a1} (−62.77 ± 0.47 kJ mol^{-1}) and ΔS°_{a1} (−33.17 ± 1.4 J K^{-1} mol^{-1}) were obtained for K_{a1}. Furthermore the K_{a1} value determined at 25 °C (0.084 mol

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* A recently completed oxalate anation study under similar conditions on $[Ru(OH_2)_6]^{3+}$ has provided cyclic voltammetric evidence, *via* ready reduction back to Ru^{II}, for the formation of the mono(oxalato) complex (E_{red} = +0.04 V *vs.* NHE) as an intermediate prior to the eventual formation of stable bis(oxalato) Ru^{III} products (E_{red} = −0.28 V *vs.* NHE) despite the absorbance changes being fitted readily to a single kinetic process. Formation of the bis(oxalato) product has been substantiated further by an aquation study on $[Ru(C_2O_4)_3]^{3-}$ (E_{red} = −0.456 V *vs.* NHE)[21] under the same conditions in which loss of one oxalate ligand is observed to give rise to the same product solution.

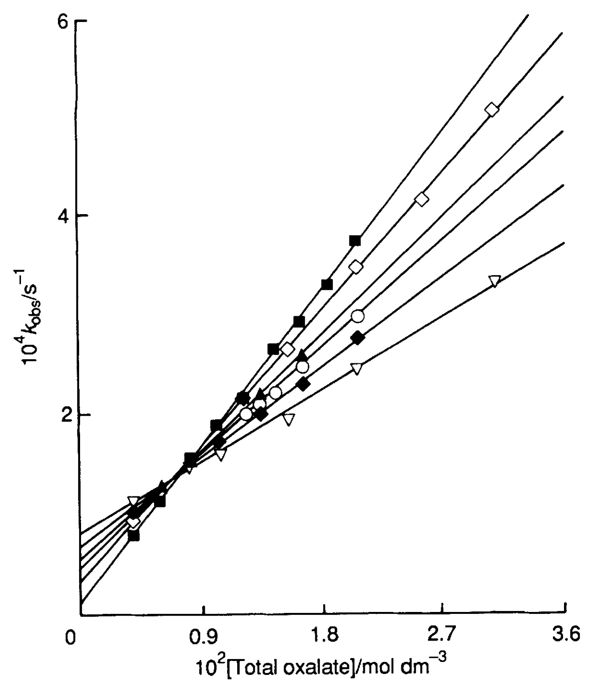


Fig. 4 First-order rate constants (k_{obs}) plotted *vs.* [Total oxalate] as a function of $[H^+]$ for reaction with Ru^{2+} at 25 °C I = 1.0 mol dm^{-3} ($NaCF_3SO_3$): $[H^+]$ = 0.04 (■), 0.07 (◇), 0.1 (△), 0.13 (○), 0.15 (◆) and 0.2 mol dm^{-3} (▽)

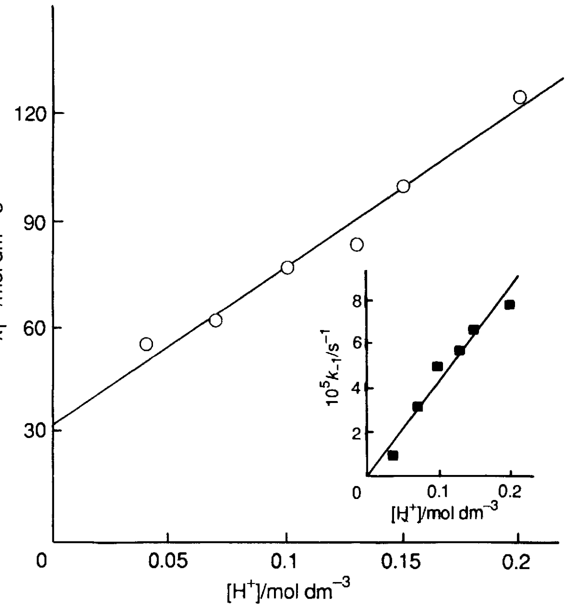


Fig. 5 Linear plot of $1/k_1$ *vs.* $[H^+]$ according to equation (7) for the reaction of Ru^{2+} with oxalate at 25 °C, I = 1.0 mol dm^{-3} ($NaCF_3SO_3$). Inset: linear plot of k_{-1} *vs.* $[H^+]$

Table 1 Values of k_f and k_b as a function of temperature for the reaction of $[Ru(OH_2)_6]^{2+}$ with oxalate, I = 1.0 mol dm^{-3} ($NaCF_3SO_3$)

T/°C	10^2k_f/ dm^3 mol^{-1} s^{-1}	10^4k_b/ dm^3 mol^{-1} s^{-1}
20	1.80	2.68
25	2.60	7.12
30	6.00	8.41
35	11.30	12.23
40	19.60	24.07
45	51.00	43.90

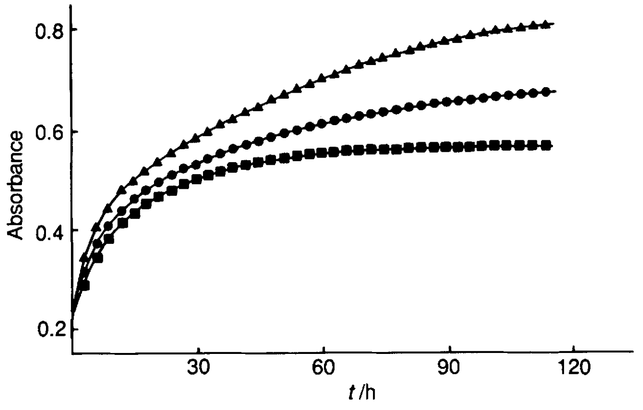


Fig. 6 Absorbance changes at 400 nm as a function of time for reaction of $[Rh(OH_2)_6]^{3+}$ (0.003 mol dm^{-3}) with oxalate (0.03 mol dm^{-3}) at 70 °C, I = 3.0 mol dm^{-3} ($NaClO_4$): $[H^+]$ = 0.2 (▲), 0.4 (●) and 2.2 mol dm^{-3} (■)

dm^{-3})^4 is an excellent agreement with the value, 0.08 mol dm^{-3}, obtained here from the fit to equation (7). Also consistent with rate law (5) a plot of k_{-1} *vs.* $[H^+]$ was linear passing through the origin giving a value of k_b (25 °C) = (7.12 ± 1.53) × 10^{-4} dm^3 mol^{-1} s^{-1}. Fitting of equation (5) to the data in Fig. 3, substituting the calculated values of K_{a1} at each temperature, allows an evaluation of the activation parameters for the forward and back reaction rate constants. A least-squares fit to the Eyring equation gave the following parameters; $\Delta H_f^‡$ = (101.07 ± 6.37) kJ mol^{-1}, $\Delta S_f^‡$ = (+65.1 ± 20.9) J K^{-1} mol^{-1}; $\Delta H_b^‡$ = (77.29 ± 7.45) kJ mol^{-1}, $\Delta S_b^‡$ = (−48.5 ± 24.4) J K^{-1} mol^{-1}. Values of k_f and k_b as a function of temperature are also listed in Table 1.

Oxalate Complexation with Rh^{3+}.—Fig. 6 shows the nature of absorbance changes at 400 nm plotted as a function of time for reaction of Rh^{3+} (0.003 mol dm^{-3}) with total oxalate (0.03 mol dm^{-3}) at 70 °C in the $[H^+]$ range 0.2–2.2 mol dm^{-3}. The two stage process is clearly seen for the 0.2 mol dm^{-3} H^+ run but becomes less apparent as the acidity was increased to approach 3.0 mol dm^{-3}. For runs at 70 °C and between 0.2 and 2.2 mol dm^{-3} H^+ the absorbance–time data was successfully fitted to two consecutive first-order reactions using FITTING giving rise to k_{obs} and absorbance amplitude values respectively for both stages.

For the first stage the dependence of k_{obs} on the total oxalate concentration between 0.01 and 0.05 mol dm^{-3} at 0.5 and 2.8 mol dm^{-3} H^+ is illustrated in Fig. 7. For each a simple linear correlation of k_{obs} with oxalate passing through the origin is observed. However, closer analysis revealed a small amount of curvature suggesting the presence of an ion-pair pre-association with a smallish equilibrium constant (K_{ip}). Values of K_{ip} are expected to be close to 1.0 dm^3 mol^{-1} from knowledge of other oxalate complexation reactions with trivalent hexaaqua ions at ionic strengths ⩾ 1.0 mol dm^{-3}.[2,3,8] To enable a comparison with the previous Ir^{3+}-study a temperature-independent value for K_{ip} of 1.0 dm^3 mol^{-1} was assumed throughout the present study. The absorption (infinity) value at 400 nm also correlated linearly with the limiting $[Rh^{3+}]$ and had slope ≈114 dm^3 mol^{-1} cm^{-1}. It was thus concluded that the first stage was involved with an irreversible complexation reaction to give *cis*-$[Rh(C_2O_4)_2(OH_2)_2]^-$ (ε_{400} = 120 dm^3 mol^{-1} cm^{-1})[20] as the major product. A smaller amount (*ca.* 10%) of the *trans*-isomer (ε_{400} = 92 dm^3 mol^{-1} cm^{-1})[20] was also produced. It remained likely however that the rate-determining step involved entry of the first oxalate ligand according to rate law (8) with chelation and complexation of the second oxalate occurring in rapid successive steps.

$$-d[Rh^{3+}]/dt = kK_{ip}[\text{Total oxalate}][Rh^{3+}] = k_{obs}[Rh^{3+}] \qquad (8)$$

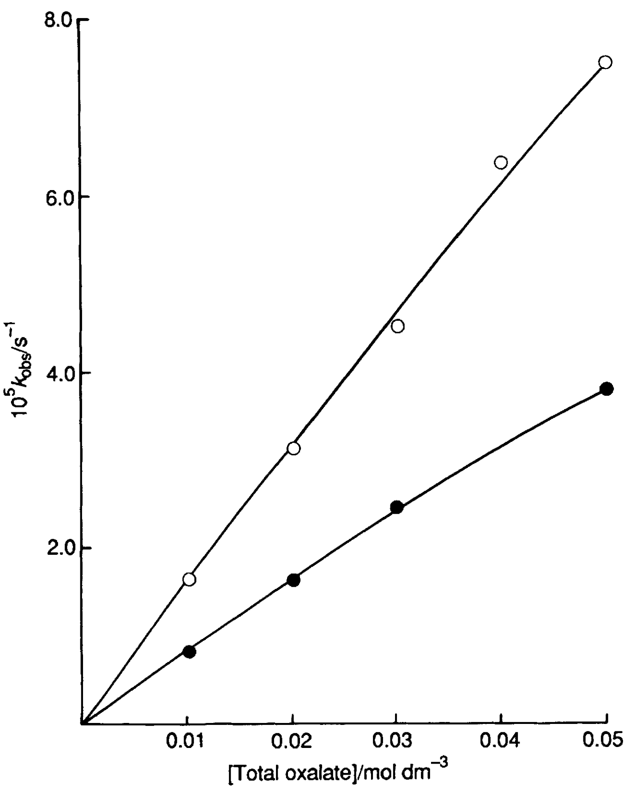


Fig. 7 First-order rate constants (k_{obs}) plotted *vs.* [Total oxalate] as a function of [H$^+$] for reaction with Rh^{3+} at 70 °C, I = 3.0 mol dm^{-3} (NaClO$_4$): [H$^+$] = 0.05 (○) and 2.8 mol dm^{-3} (●)

Values of k_{obs} were investigated subsequently as a function of [H$^+$] and temperature in the ranges 0.2–2.98 mol dm^{-3} and 50–80 °C and these are listed in Table 2. It quickly became apparent that the data, like that obtained on Ir^{3+}, could not be fitted to a rate law involving single reactant forms as found for Ru^{2+}. Plots of either k_{obs} *vs.* $[H^+]^{-1}$ or k_{obs}^{-1} *vs.* [H$^+$] showed marked curvature. Finally, as in the case of Ir^{3+},[11] the data was eventually fitted to a model in which complexation occurred in two parallel steps one involving the fully protonated forms of both of the reactants, *i.e.* $H_2C_2O_4$ and Rh^{3+}, and one involving a monodeprotonated form of one or other of them. Considering both extreme possibilities for the latter the rate law (9) may be

$$-d[Rh^{3+}]/dt = k_1[H_2C_2O_4][Rh^{3+}] + k_2K_{ip}[HC_2O_4^-][Rh^{3+}] + k_3[H_2C_2O_4][Rh(OH)^{2+}] \quad (9)$$

derived. In terms of total oxalate concentration rate law (9) may be expressed by (10); with K_{aRh} defined by equation (11) and assumed $\ll [H^+]$.

$$\frac{-d[Rh^{3+}]}{dt} = \left(\frac{k_1[H^+][Rh^{3+}] + k_2K_{ip}K_{a1}[Rh^{3+}] + k_3K_{aRh}[Rh^{3+}]}{[H^+] + K_{a1}}\right) \times [\text{Total oxalate}] = k_{obs}[Rh^{3+}] \quad (10)$$

$$[Rh(OH_2)_6]^{3+} \underset{}{\overset{K_{aRh}}{\rightleftharpoons}} [Rh(OH_2)_5(OH)]^{2+} + H^+ \quad (11)$$

Consistent with rate law (10) plots of k_{obs} ([H$^+$] + K_{a1})/[Total oxalate] *vs.* [H$^+$] were linear (Fig. 8) at each of the four temperatures studied allowing an evaluation of k_1 from the slope and of $k_2K_{a1}K_{ip} + k_3K_{aRh}$ from the intercept. Substituting in appropriate values of K_{a1} for each temperature the following parameters for k_1 were obtained; k_1 (25 °C) = (1.21 ± 0.13) × 10^{-5} dm^3 mol^{-1} s^{-1}, $\Delta H_1^‡$ = (76.70 ± 3.67) kJ mol^{-1} and $\Delta S_1^‡$ = (−81.67 ± 10.88) J K^{-1} mol^{-1}. Independent determination of corresponding values for k_2 and k_3 is, however, not possible from equation (10).

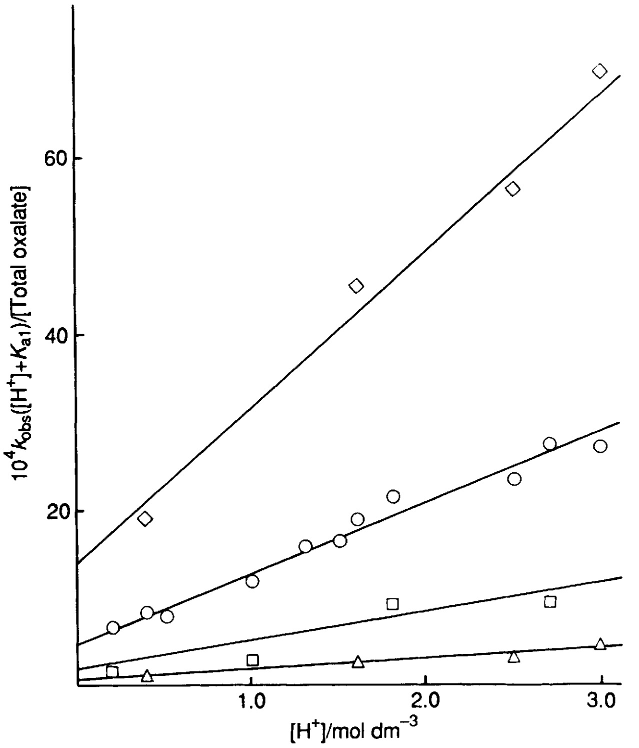


Fig. 8 Linear plot of k_{obs} ([H$^+$] + K_{a1})/[Total oxalate] *vs.* [H$^+$] according to equation (10) as a function of temperature, I = 3.0 mol dm^{-3} (NaClO$_4$): 50 (△), 60 (□), 70 (○) and 80 °C (◇)

For the second stage detailed evaluation of the kinetic data was not possible owing to the large amount of scatter observed. Furthermore, the extent of the absorbance change observed at 400 nm was found to be markedly dependent upon [H$^+$] becoming less pronounced as [H$^+$] was increased. The rate of formation of the second stage product was observed to be linearly dependent upon [Total oxalate] but independent of [H$^+$]. Further reaction of *cis*-[Rh(C$_2$O$_4$)$_2$(OH$_2$)$_2$]$^-$ with $H_2C_2O_4$, leading to tris(oxalato) products, was presumed to be involved.

Discussion

Oxalate Complexation on Ru^{2+}.—The forward rate constant for anation by $HC_2O_4^-$ on Ru^{2+} at 25 °C has a value 2.6 × 10^{-2} dm^3 mol^{-1} s^{-1} at ionic strength 1.0 mol dm^{-3}. Assuming an ion-pair constant (K_{ip}) of around 1.0 dm^3 mol^{-1} an interchange rate constant (k_i) for oxalate anation within the ion-pair [Ru(OH$_2$)$_6$]$^{2+}$, $HC_2O_4^-$ can be deduced from the model of Eigen and Wilkins [equation (12)].[22] This value is extremely

$$k_f = k_iK_{ip} \quad (12)$$

close not only to the narrow range of rate constants determined for anation by Cl$^-$, Br$^-$ and I$^-$,[14] but also to the recently determined water-exchange rate constant (1.8 × 10^{-2} s^{-1})[13] (Table 3)) and would appear initially to be strongly suggestive of a dissociative interchange mechanism. Such a conclusion gains further support by the narrow range of activation parameters observed for Cl$^-$, Br$^-$ and I$^-$ complexation and H$_2$O exchange on Ru^{2+} (Table 3).[14] However the activation parameters for $HC_2O_4^-$ in the present study are somewhat different from those observed for the above ligands and this needs to be addressed. The larger $\Delta H^‡$ observed for $HC_2O_4^-$ is

Table 2 Pseudo first-order rate constants for the reaction of $[Rh(OH_2)_6]^{3+}$ with oxalate (first stage), I = 3.0 mol dm^{-3} ($NaClO_4$)

10^2 (Total oxalate]/ mol dm^{-3}	T/°C	$[H^+]$/mol dm^{-3}	$10^5\ k_{obs}$/s^{-1}
3.0	50	0.40	0.74
		1.60	0.48
		2.50	0.38
		2.98	0.43
3.0	60	0.20	2.02
		1.00	1.68
		1.80	1.52
		2.70	1.04
3.0	70	0.20	7.98
3.0		0.40	6.26
1.0		0.50	1.62
2.0		0.50	3.15
3.0		0.50	4.52
4.0		0.50	6.36
5.0		0.50	7.51
3.0		1.00	3.47
3.0		1.50	3.60
3.0		1.60	3.48
3.0		1.80	3.53
3.0		2.50	2.78
3.0		2.70	3.00
1.0		2.82	0.88
2.0		2.82	1.62
3.0		2.82	2.47
5.0		2.82	3.78
3.0		2.98	2.68
3.0	80	0.40	12.98
		1.60	8.28
		2.50	6.67
		2.98	5.18

Table 3 Rate constants and activation parameters for substitution reactions on $[Ru(OH_2)_6]^{2+}$

Incoming Ligand	$10^2\ k$/ dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	Ref.
Cl^-	0.85^a	84.4	−1.7	14
Br^-	1.02^a	82.8	−5.0	14
I^-	0.98^a	81.5	−10.0	14
H_2O	1.8^b	87.8	+16.1	13
$HC_2O_4^-$	2.6^c	101.1	+65.1	This work

[a] I = 0.3 mol dm^{-3} (BF_4^-), [b] In s^{-1}. [c] I = 1.0 mol dm^{-3} ($CF_3SO_3^-$).

Table 4 Rate constants and activation parameters for substitution reactions on Rh^{3+}, $Rh(OH)^{2+}$ and Ir^{3+}

Ligand	k^{298}/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	Ref.
(*a*) $[Rh(OH_2)_6]^{3+}$				
Cl	$2.99 \times 10^{-9\,a}$	125.0	+11.2	27
Br	$2.75 \times 10^{-9\,a}$	120.2	−5.5	28
H_2O	2.2×10^{-9}	131.2	+29.3	26
$H_2C_2O_4$	$1.21 \times 10^{-5\,b}$	76.7	−81.7	This work
(*b*) $[Ir(OH_2)_6]^{3+}$				
$H_2C_2O_4$	$1.25 \times 10^{-5\,b}$	73.1	−94.1	13
(*c*) $[Rh(OH_2)_5(OH)]^{2+}$				
Cl	$1.01 \times 10^{-5\,a}$	127.8	+88.2	27
Br	$0.62 \times 10^{-5\,a}$	131.1	+95.0	28
H_2O	4.2×10^{-5}	103.0	—	26
$H_2C_2O_4$	$1.7 \times 10^{-2\,b}$	57.9	−85.7	This work

[a] Values refer to interchange within an ion-pair. [b] In dm^3 mol^{-1} s^{-1}.

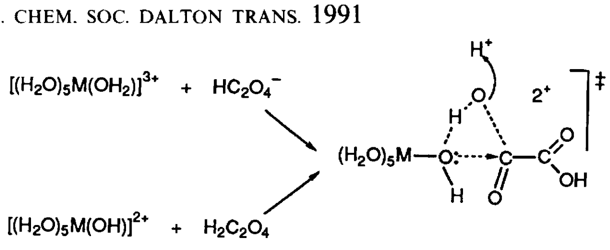
compensated for by a more positive $\Delta S^‡$ change in line with a smaller but similarly discernible trend for the other ligands. Such an effect is now recognised as likely to reflect solvational changes within the different transition states[23] and therefore cannot necessarily be used as a mechanistic diagnosis. On the other hand the measured activation volume for water exchange on Ru^{2+} is essentially zero (−0.4 ± 0.7 cm^3 mol^{-1})[13] and has been interpreted as indicating an I mechanism according to the Langford and Gray distinctions.[24] This would imply that incoming ligands may play a non-negligible role in forming the transition state and the variation in activation parameters observed may well be a reflection of this. The behaviour of $[Ru(OH_2)_6]^{2+}$ is probably unique within octahedral $(t_{2g})^6$ aqua metal ions of 2+ charge in that the only other metal complexes available for comparison are conjugate-base forms of those of Group 9 which are known to promote a more dissociatively activated mechanism.

It is generally recognised that the rates of water ligand replacement reactions on octahedral transition-metal complexes possess little dependence upon the incoming ligand. There are notable exceptions but Swaddle[25] has suggested that a more complete explanation may be to describe the varying ability of different incoming ligands to influence the pathway to formation of the transition state in what are primarily dissociatively activated processes rather than to classify them as I_a, I or I_d. Accordingly a classication of the substitution mechanism on Ru^{2+} as being I_d or even I may be placing a rather restricted and perhaps incorrect appreciation of the role played by the incoming group.

Oxalate Complexation on Rh^{3+}.—Two parallel pathways are involved in the first stage of the anation reaction to give *cis*-$[Rh(C_2O_4)_2(OH_2)_2]^-$ as the major product (90% based on the absorbance changes observed) with a smaller amount (≈10%) of the *trans* product. The reaction proceeds to completion with no evidence of build up of the 1 : 1 complex as an intermediate. It was thus concluded that rate-determining entry of the first oxalate ligand was relevant followed by rapid entry of the second to give the bis(oxalato) product paralleling that observed for the corresponding reaction on Ir^{3+}. Thus, while it may be premature to rule out involvement of an intermediate 1:1 complex on the basis of the findings with regard to complexation on Rh^{3+}, it can be deduced that the bis(oxalato) complex seems to be the preferred final product for oxalate anation on 3+ hexaaqua ions but not on those carrying a 2+ charge under the acidic conditions employed. The reasons behind this differing behaviour for Ru^{2+} and Rh^{3+} would seem to be primarily electrostatic in origin.

The two parallel pathways involve anation by (*a*) $H_2C_2O_4$ on Rh^{3+} and (*b*) a deprotonated form of one or other of the reactants and this again parallels the corresponding reaction on Ir^{3+}. The rate constant (at 25 °C) for anation by $H_2C_2O_4$ on Rh^{3+} is 1.21×10^{-5} dm^3 mol^{-1} s^{-1}. This value is four orders of magnitude greater than the recently measured rate constant for water exchange on Rh^{3+} (25 °C) (2.2×10^{-9} s^{-1}).[26] In addition the activation enthalpy (76.7 kJ mol^{-1}) and entropy (−81.7 J K^{-1} mol^{-1}) are respectively much smaller and more negative than those observed for water exchange (Table 4). Taken together these findings suggest a different mechanism for oxalate anation than that occurring for water exchange on Rh^{3+}, conceivably the same mechanism as proposed for the corresponding reaction on Ir^{3+} [11] in which the Rh–OH_2 bond remains intact throughout the activation step. In such cases one would predict that the observed rate constant for anation by $H_2C_2O_4$ might be similar for complexation on both Rh^{3+} and Ir^{3+}, *i.e.* independent of the metal ion. Reference to Table 4 shows that this is indeed the case; rate constants (k_1 for both Rh^{3+} and Ir^{3+} being virtually identical at 25 °C within experimental errors. This is believed to provide further conclusive support for the existence of a mechanism of complexation of M^{3+} with $H_2C_2O_4$ (Scheme 1) in which C–O bond breakage is the relevant process.

With regard to path (*b*) here the conclusions are more difficult



Scheme 1

owing to the so-called 'proton ambiguity' problem.[25,29] This arises wherever rapid proton transfer can take place between reactants prior to the formation of the transition state and makes a meaningful assessment of the precise nature of the reactants and hence the mechanism somewhat difficult. Conceivably two extreme sets of reactants could be considered as contributing to forming the transition state as indicated in Scheme 1.

However, bearing in mind the limitations which must be attached to meaningful conclusions when a proton ambiguity is present, an interesting result is obtained nonetheless on comparison with Ir^{III} if one considers that the reactants are $[Rh(OH_2)_5(OH)]^{2+}$ and $H_2C_2O_4$ at least in essence. Equation (10) may thus be rewritten as (13) with k_3 defined as the rate

$$\frac{-d[Rh^{3+}]}{dt} = \left(\frac{k_1[H^+] + k_3K_{aRh}}{[H^+] + K_{a1}}\right)[\text{Total oxalate}][Rh^{3+}] \quad (13)$$

constant for reaction of $Rh(OH)^{2+}$ with $H_2C_2O_4$ and K_{aRh} defined according to equation (11). Values of K_{aRh} have been evaluated as a function of temperature and at 25 °C K_{aRh} has the value 3.2×10^{-4} mol dm^{-3}.[26] From the intercepts of Fig. 8 values of k_3 can be determined as a function of temperature and at 25 °C $k_3 = 1.7 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. This value may now be compared to a similar evaluation with respect to the corresponding reaction on Ir^{3+}. Here it had been previously assumed that the reaction was between Ir^{3+} and $HC_2O_4^-$. The value of k_2(Ir) (25 °C) [from application of equation (10) assuming $k_3 = 0$] was previously deduced to be 7.2×10^{-6} s^{-1}.[11] K_{aIr} (for the first acid dissociation) has been determined by Beutler and Gamsjager[30] and has a value (at 25 °C) of $\approx 4.2 \times 10^{-5}$ mol dm^{-3}. This in turn allows an evaluation of $k_3(\text{Ir}) = 1.4 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. Values of k_3 so determined for both metals are thus found, as in the case of k_1, to be in extremely close agreement in support of the existence of a common mechanism for reaction of $H_2C_2O_4$ with $[M(OH_2)_5(OH)]^{2+}$. Consistent with this conclusion it is also noted that the value of k_3(Rh) (25 °C) is, like k_1 previously, far in excess of the water-exchange rate constant for the metal reactant (4.2×10^{-5} s^{-1}).[26] Values of K_{aIr} have not however been determined as a function of temperature to enable a full comparison with Rh^{3+} to be made. However a fit to the Eyring equation in the case of $Rh(OH)^{2+}$ gives rise to the following activation parameters for k_3; $\Delta H_3^‡ = (57.89 \pm 1.89)$ kJ mol^{-1} and $\Delta S_3^‡ = (-85.74 \pm 5.76)$ J K^{-1} mol^{-1}. These values also resemble strongly those observed for the k_1 path lending further support to the possibility that the same metal independent C–O bond breaking process is relevant.

While it is emphasised that caution must be placed on these conclusions because of the proton ambiguity it is difficult to rule out some significance being attached to the virtually identical rate parameters obtained on consideration of the mechanism as involving $H_2C_2O_4$ complexing with both $[M(OH_2)_6]^{3+}$ and $[M(OH_2)_5(OH)]^{2+}$ (M = Rh or Ir) given that interchange reactions on Ir^{III} are, in all cases known, some 10^2 to 10^3 times slower than on Rh^{III}.[31] Indeed the upper limit for the water exchange rate constant (25 °C) on Ir^{3+} has been set at $\approx 10^{-11}$ s^{-1} from experiments in progress.[32]

It is somewhat surprising to be considering the conjugate base form as being involved in such a mechanism since such complexes normally promote more dissociative character within substitution reactions (usually *via* a *trans* labilising effect).[33] However it is recognised that bound OH^-, with its two available lone pairs and higher local electron density (*vs.* H_2O), should be a more effective nucleophile for attacking the proximal carbonyl group of the oxalic acid. This would appear to be reflected in the values of k_3 which are 10^3 times larger than k_1. Furthermore, the t_{2g}^6 configuration would promote this process by disfavouring π-back-bonding from OH^- to the metal. Such a mechanism is in any case already well established as relevant to many intra- and inter-molecular hydrolysis reactions involving peptides and esters catalysed by aqua metal complexes.[34]

In the second stage of the reaction of Rh^{3+} with oxalate the lack of a detectable $[H^+]$ dependence on the rate constant but a marked $[H^+]$-dependence with regard to the extent of absorbance change suggests an equilibration reaction of *cis*-$[Rh(C_2O_4)_2(OH_2)_2]^-$ with $H_2C_2O_4$. Rate constants are *ca.* 10 times slower than for the formation of the bis(oxalato) complex and probably explained on the basis of a combination of electrostatics and statistical considerations. It is conceivable that under the reaction conditions employed the tris(oxalato) product could be a mixture of $[Rh(C_2O_4)_3]^{3-}$ and the hydrogenoxalato complex $[Rh(C_2O_4)_2(HC_2O_4)(OH_2)]^{2-}$ both having been characterised previously in crystalline samples of hydrated '$K_3[Rh(C_2O_4)_3]$.'[20,35] Such a mixture of products could also be responsible for the variation in absorbance amplitude with $[H^+]$ (Fig. 6); ε_{400} likely to be higher for the tris-chelated product whose formation will be favoured as $[H^+]$ is decreased. However the lack of solution spectroscopic data particularly in the case of the partially aquated complex does not permit a quantitative assessment of this at present.

Finally, it is likely that the greater 'inertness' with regard to interchange reactions with hard ligands as shown by Rh^{III} and Ir^{III} aqua complexes *versus* Ru^{II} is responsible for the vastly differing mechanisms of oxalate anation shown by these t_{2g}^6 metal hexaaqua ions. In the case of such a substitution with an inert metal ion such as Rh^{III} the metal ion promoted C–O bond breaking process is able to compete successfully with the much slower interchange processes as exhibited by the anation reactions with the halide ions and by water exchange (Table 4). For Ru^{2+} the interchange process here probably occurs with such a sufficiently fast rate as to allow the M–O bond breaking process to become dominant.

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