Kinetic Studies of the Complexation of Oxalate to Hexa-aquairidium(III)

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A kinetic study of the oxalate anation of hexa-aquairidium(III) perchlorate in $HClO_4$–$NaClO_4$ solution, I = 1.5 mol dm^{-3} ($NaClO_4$), is reported. The acidity dependence ($[H^+]$ = 0.14 – 1.00 mol dm^{-3}) is consistent with the existence of two parallel pathways involving anation by both $H_2C_2O_4$ and $HC_2O_4^-$. Rate constants (25 °C) and activation parameters for the two paths are: $H_2C_2O_4$, k_1 = (1.3 ± 0.2) × 10^{-5} dm^3 mol^{-1} s^{-1}, $\Delta H_1^\ddagger$ = 73.1 ± 4.6 kJ mol^{-1}, $\Delta S_1^\ddagger$ = −94.1 ± 13.9 J K^{-1} mol^{-1}; and $HC_2O_4^-$, k_2 = (7.2 ± 1.2) × 10^{-6} s^{-1}, $\Delta H_2^\ddagger$ = 108 ± 7 kJ mol^{-1}, $\Delta S_2^\ddagger$ = +20.3 ± 22.4 J K^{-1} mol^{-1}. Ion-pair association of $HC_2O_4^-$ is small as expected and a temperature-independent value of 1.0 dm^3 mol^{-1} has been assumed for its association constant in evaluating the k_2 path, although this does not affect the overall conclusions reached. Widely differing activation parameters are seen for the two paths suggesting that different mechanisms may operate. Anation by $HC_2O_4^-$ is discussed in terms of an ion-pair interchange mechanism. However, anation by $H_2C_2O_4$ is suggested to involve a concerted mechanism in which replacement of the aqua ligands is achieved in the rate-determining step without Ir–OH_2 bond cleavage, similar to that thought to operate in the corresponding anation reaction of $[Co(NH_3)_5(OH_2)]^{3+}$. The results highlight the first successfully monitored anation reaction of $[Ir(OH_2)_6]^{3+}$ and are discussed with respect to anation of $[Rh(OH_2)_6]^{3+}$ and in the context of anation by both $H_2C_2O_4$ and $HC_2O_4^-$ of trivalent aqua metal ions in general.

Hexa-aquairidium(III) perchlorate was first characterised by Beutler and Gamsjager in 1976 [1] and its hexa-aqua structure has since been verified.[2] These workers [3] later reported first and second acid dissociation constants (pK_a values) of 4.37 and 5.20 respectively in I = 1.0 mol dm^{-3} ($NaClO_4$) at 25 °C. Since then few, if any, kinetic studies of successfully monitored anation reactions (including the fundamental process of water exchange) have been reported. Hexa-aquairidium(III) is probably the most inert transition-metal hexa-aqua ion yet obtained.[4] Attempts at measuring the water exchange in perchloric acid solutions by an oxygen-18 isotopic dilution method in sealed tubes at 120 °C were impaired by sporadic oxidation to give purple solutions containing iridium(IV), probably as a result of reactions with perchlorate ion at these high temperatures. Separate studies have shown that these purple iridium(IV) solutions contain dimeric oxygen-bridged species.[5] Furthermore, anation of $[Ir(OH_2)_6]^{3+}$ (1 mmol dm^{-3}) by both Cl^- and Br^- ions (3.7 mol dm^{-3}) could not be detected following monitoring at 40 °C over 10—15 d.[4] It is not yet clear whether this reflects an immeasurably slow rate of halide anation at these concentrations or an extremely small formation constant for the halogenoaqua complex reflecting a relatively large aquation rate. Similar studies with thiocyanate are impaired by the competing acid decomposition of thiocyanate at the elevated temperatures and prolonged reaction times needed. Oxalato complexes of iridium(III) have however been characterised since the early 1900s and both bis and tris complexes are known.[6—9] Furthermore, the complexes absorb strongly in the u.v. region thus lending themselves potentially towards monitoring of the anation process.

We report herein the results from a kinetic study of the successfully monitored oxalate anation reaction of $[Ir(OH_2)_6]^{3+}$ under conditions which give the diaquabis(oxalato) complex, $[Ir(OH_2)_2(C_2O_4)_2]^-$, as product. The results are discussed in terms of possible mechanisms and in relation to anation studies of $[Rh(OH_2)_6]^{3+}$ and to other oxalate-anation reactions with trivalent aqua metal ions.

Experimental

Preparation of Reactants.—Perchloric acid solutions of hexa-aquairidium(III) perchlorate were prepared by hydrolysis of either samples of $Na_2[IrCl_6]\cdot6H_2O$ or $Na_3[IrCl_6]\cdot12H_2O$ (Johnson Matthey) in solutions of sodium hydroxide (0.1 mol dm^{-3}) as described previously.[1,3] Following precipitation of $[Ir(OH)_3(OH_2)_3]$, solutions were purified by Dowex ion-exchange chromatography (50W X2 column). Elution with 2.0 mol dm^{-3} $HClO_4$ gave stock solutions (0.03 mol dm^{-3} in Ir^{III}) with peak maxima at 267 (36.4) and 313 nm (ε 32.5 dm^3 mol^{-1} cm^{-1}) (ratio 1.12). The lower ε value for the peak at 267 nm reported here represents an improvement in purity following the column treatment. Solutions were stored under an argon atmosphere at −18 °C to prevent sporadic oxidation to oligomeric products. Freshly columned solutions of $[Ir(OH_2)_6]^{3+}$ were used for the kinetic runs where possible. Oxalic acid dihydrate, perchloric acid (70%), and sodium perchlorate (all BDH Analar) were used as supplied. Solutions of sodium perchlorate and $[Ir(OH_2)_6]^{3+}$ (background acidity) were standardised by exchange onto a column of Amberlite IR 120 resin (H^+ form) followed by titration of the liberated H^+. Potassium tris(oxalato)iridate(III) tetrahydrate was prepared by the modified method of Delépine [7] as recently reported by Milburn and co-workers.[8] Solutions in water possessed a peak maximum at 286 nm (ε = 4 080 dm^3 mol^{-1} cm^{-1}) in agreement with the literature value.

Kinetic Studies.—Absorbance increases below 400 nm were observed following addition of an excess of oxalic acid to solutions of $[Ir(OH_2)_6]^{3+}$ in perchloric acid over 1-d periods at 70 °C. Runs were followed over 1-week periods at the maximum observed change in absorbance at 254 nm in 1.0-cm quartz cells using a Perkin-Elmer Lambda 5G model u.v.–visible recording spectrophotometer with electronic thermostatting and auto cell-change facilities. The temperature was controlled to ±0.1 °C. The ionic strength was kept constant throughout at 1.5 mol dm^{-3} with sodium perchlorate. Runs were

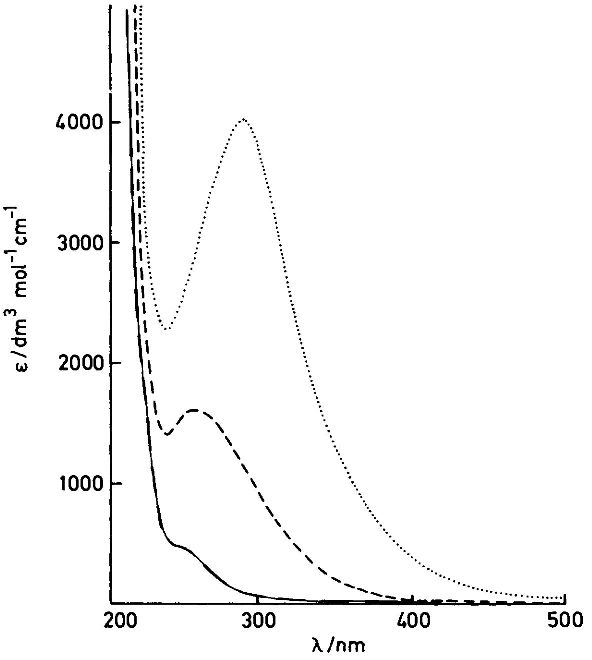

Figure 1. U.v.-visible spectra for solutions of oxalato iridium(III) species: (· · · ·) $[Ir(C_2O_4)_3]^{3-}$ in water at pH 7; (– – – –) $[Ir(OH_2)_2(C_2O_4)_2]^-$ in 1.0 mol dm^{-3} $HClO_4$; (———) solution following mixing of $[Ir(OH_2)_6]^{3+}$ with a 10-fold excess of oxalic acid in 1.00 mol dm^{-3} $HClO_4$; and (— —) a simulation of the same mixture

followed with either total oxalate or $[Ir(OH_2)_6]^{3+}$ concentration in at least 10-fold excess to permit first-order kinetics. Where stable infinity absorbance readings were obtained, plots of absorbance changes, $\ln(A_\infty - A_t)$, against time (t) were linear to three half-lives in all cases. Frequently, however, varying and unstable infinity readings were obtained accompanied by some detectable formation of a faint purple colour due to iridium(IV) over the long reaction times and high temperatures (>40 °C) employed, even when conducted in an argon atmosphere. Since first-order kinetics is operative this problem was overcome by analysing only the initial 2—3 half-lives of reaction using the method of Kezdy and Swinbourne.[10] In the cases of runs at temperatures <60 °C, this was a necessity due to the extremely long reaction times needed (weeks) to attain infinity readings. In all cases, good linear plots of the absorbance at time t against that at time $(t + \Delta t)$ were obtained for Δt values up to one half-life as required. First-order rate constants ($k_{obs.}$/s^{-1}) were obtained from evaluation of ln(slope)/Δt. Satisfactory agreement (±10%) was found for $k_{obs.}$ values so determined compared with those from the slopes of $\ln(A_\infty - A_t)$ against t where this was possible. The first acid dissociation constant, K_a^1, for oxalic acid [equation (1)] was taken as 0.076 mol dm^{-3}

$$H_2C_2O_4 \overset{K_a^1}{\rightleftharpoons} HC_2O_4^- + H^+ \qquad (1)$$

by an extrapolation of existing data[11] to the conditions used here. It was assumed to have a negligible temperature dependence in the range studied, consistent with recent findings.[12] The value of K_a^2 for oxalic acid (2.5×10^{-4} mol dm^{-3}) suggested that in the range of acidity used (0.14 – 1.00 mol dm^{-3}) the amounts of $C_2O_4^{2-}$ are small and can probably be neglected. The total oxalate concentration can thus be represented by equation (2).

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

Table 1. Pseudo-first-rate constants for oxalate anation of hexaaquairidium(III) perchlorate, $[H^+]$ = 1.00, I = 1.5 mol dm^{-3} ($NaClO_4$)

θ_c/°C	10^2[Total oxalate] mol dm^{-3}	$10^3[Ir^{III}]$ mol dm^{-3}	$10^6k_{obs.}$/s^{-1}
50.0	0.50	0.50	1.41
	1.00	1.00	1.19
	2.00	2.00	2.66
	3.00	3.00	3.18
70.0	0.50	0.50	3.69
	0.05	5.00	4.61
	1.00	1.00	7.68
	1.50	1.50	10.7
	2.00	2.00	14.4
	0.05	20.0	15.6
	3.00	3.00	20.3
	0.05	30.0	20.8
80.0	0.01	1.00	1.90
	0.02	2.00	3.49
	0.025	2.50	4.02
	0.02	3.00	5.22
	0.035	3.50	6.48
	0.02	4.00	7.19
	0.045	4.50	7.73
	0.02	5.00	8.28
	0.50	0.50	8.70

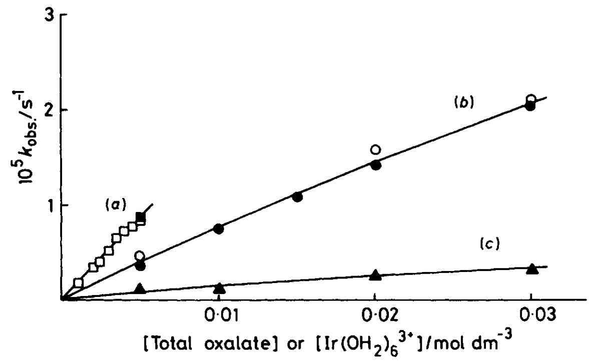

Figure 2. First-order rate constants for runs followed at 254 nm, $[H^+]$ = 1.0 mol dm^{-3}, with either total oxalate (■, ●, ▲) or iridium(III) (□, ○) in ⩾10-fold excess: (a) 80, (b) 70, and (c) 50 °C

Product Analysis.—The u.v.-visible spectrum of absorbance infinity solutions following reaction of an excess of oxalic acid with $[Ir(OH_2)_6]^{3+}$ at 70 °C ($[H^+]$ = 1.0 mol dm^{-3}) showed a single maximum at 260 nm (ε = 1 600 dm^3 mol^{-1} cm^{-1}) clearly not consistent with formation of the tris chelated product (maximum expected at 286 nm, ε = 4 100 dm^3 mol^{-1} cm^{-1}; Figure 1). However, this solution, following dilution to 0.01 mol dm^{-3} in H^+, passed straight down a column of Dowex 50W X2 cation-exchange resin with no detectable retention of any iridium-containing material (by Zinser and Page[13] iridium analysis). It was concluded therefore that an anionic product was formed. Finally, an identical absorption spectrum to that from this solution was obtained from a solution of $[Ir(C_2O_4)_3]^{3-}$ in 1.0 mol dm^{-3} perchloric acid at 70 °C for 1 d. Subsequent precipitation of the liberated oxalate and titration with permanganate established the loss of one oxalate ligand per complex. It was concluded that the product of the anation reaction under these conditions was the diaquabis(oxalato) complex, $[Ir(OH_2)_2(C_2O_4)_2]^-$, presumed to be a mixture of *cis* and *trans* isomers.

Table 2. Pseudo-first-order rate constants for oxalate anation of hexa-aquairidium(III) perchlorate as a function of acidity, $I = 1.5$ mol dm^{-3} ($NaClO_4$). Total oxalate in $\geqslant$10-fold excess over Ir^{III} (number of runs averaged in parentheses)

θ_c/°C	10^2[Total oxalate]	$[H^+]$	$10^6k_{obs.}/s^{-1}$	θ_c/°C	10^2[Total oxalate]	$[H^+]$	$10^6k_{obs.}/s^{-1}$
	mol dm^{-3}				mol dm^{-3}		
40.0	2.00	0.35	1.10	70.0	0.50	0.15	5.60 (2)
	2.00	0.55	0.83		0.50	0.20	5.56 (2)
	2.00	0.75	0.86		0.50	0.30	5.28 (3)
	2.00	1.00	0.87		0.50	0.40	4.32
					0.50	0.50	4.67 (3)
50.0	1.00	0.14	2.40		0.50	0.60	3.77
	2.00	0.40	2.91		0.50	0.70	4.40
	2.00	0.70	3.70		0.50	0.80	3.75
	2.00	1.00	3.19		0.50	0.90	3.73
60.0	1.00	0.14	3.68	80.0	0.50	0.14	15.9
	2.00	0.40	11.6		0.50	0.30	12.4
	2.00	0.70	8.36		0.50	0.70	10.2
	2.00	1.00	7.79		0.50	1.00	8.69

Results

The linearity of pseudo-first-order plots over three half-lives suggests only one rate-determining process. Since no rapid absorbance changes were observed (Figure 1) following mixing of solutions of oxalic acid and $[Ir(OH_2)_6]^{3+}$, it was concluded that rate-determining entry of the first oxalate ligand is relevant. Chelation as the rate-determining step was discounted owing to the observed dependence of the rate on the concentration of either total oxalate or $[Ir(OH_2)_6]^{3+}$ when present in 10-fold excess (Figure 2). It was concluded that chelation and subsequent entry of the second oxalate ligand are relatively rapid processes succeeding rate-determining entry of the first monodentate oxalate ligand. Pseudo-first-order rate constants ($k_{obs.}$) are listed in Table 1 as a function of reactant concentration and temperature ($[H^+] = 1.0$ mol dm^{-3}) and in Table 2 as a function of both temperature and acidity.

The values of $k_{obs.}$ show an inverse dependence on acidity in the range used. However, closer analysis of the dependence shows it not to be consistent with the presence of simple $[H^+]^{-1}$ terms. Plots of $k_{obs.}$ against $[H^+]^{-1}$ show marked curvature and it was quickly apparent that the major contributor to the observed H^+ dependence was the deprotonation of oxalic acid with a value of $K_a^1 \approx [H^+]$. The observed dependence was successfully fitted by a least-squares treatment to a rate law whereby anation by both $H_2C_2O_4$ and $HC_2O_4^-$ contributed.* With the total oxalate concentration in 10-fold excess, the rate law (3) was obtained. Rate constants k_1 (dm^3 mol^{-1} s^{-1}) and k_2

$$\frac{-d[Ir(OH_2)_6{}^{3+}]/dt}{[Ir(OH_2)_6{}^{3+}]} = k_{obs.} = \frac{k_1[H_2C_2O_4] + k_2K_2[HC_2O_4{}^-]}{1 + K_2[HC_2O_4{}^-]} \qquad (3)$$

(s^{-1}) represent the two parallel anation pathways and K_2 (dm^3 mol^{-1}) is the ion-pair association constant for the formation of $[Ir(OH_2)_6]^{3+}$, $HC_2O_4^-$. As can be seen from Figure 2, the dependence of $k_{obs.}$ on reactant concentration shows almost negligible curvature for concentrations up to 0.03 mol dm^{-3} (highest studied). Ion-pair association is therefore small, under these conditions with oxalic acid as the major species in solution, $K_2[HC_2O_4] \ll 1$, and equation (3) can be simplified to (4). The lack of appreciable ion-pair association is also

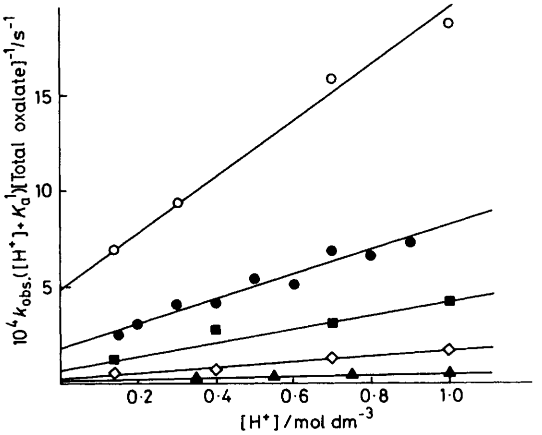

Figure 3. Acidity dependence for runs followed at 254 nm with total oxalate in $\geqslant$10-fold excess over Ir^{III} at 80 (○), 70 (●), 60 (■), 50 (◇), and 40 °C (▲)

$$\frac{-d[Ir(OH_2)_6{}^{3+}]/dt}{[Ir(OH_2)_6{}^{3+}]} = k_{obs.} = k_1[H_2C_2O_4] + k_2K_2[HC_2O_4{}^-] \qquad (4)$$

consistent with no detectable rapid absorbance changes (Figure 1) following mixing and with behaviour to be expected at such ionic strengths. Similarly, little association between $[Ir(OH_2)_6]^{3+}$ and $H_2C_2O_4$ can be assumed from the data. The slight amount of curvature is too small to allow an estimate of K_2. However, a value between 0.5 and 2.0 dm^3 mol^{-1} would be in agreement with those found for a number of other $3+/1-$ anation reactions including those of $HC_2O_4^-$ under similar conditions.[11,14] Equation (4) can be written as (5) in terms of the total concentration of oxalate according to (2) with $k_{obs.}$ and $K_a^1(H_2C_2O_4)$ defined as before. Consistent with equation (5), plots of $k_{obs.}([H^+] + K_a^1)$/[Total oxalate] or $[Ir(OH_2)_6{}^{3+}]$

$$\frac{-d[Ir(OH_2)_6{}^{3+}]/dt}{[Ir(OH_2)_6{}^{3+}]} = k_{obs.} = \frac{(k_1[H^+] + k_2K_2K_a^1)[\text{Total oxalate}]}{K_a^1 + [H^+]} \qquad (5)$$

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* Fits to the rate equation $k_{obs.} = kK_a^1[\text{Total oxalate}]/(K_a^1 + [H^+])$ involving $HC_2O_4^-$ as the sole reactant were not consistent with the dependence on acidity or the known value of $K_a^1(H_2C_2O_4)$.

Table 3. Temperature dependence of oxalate anation rate constants for hexa-aquairidium(III) perchlorate, $I = 1.5$ mol dm^{-3} ($NaClO_4$)

θ_c/°C	10^4k_1/dm^3 mol^{-1} s^{-1}	10^4k_2*/s^{-1}
40.0	0.47	0.46
50.0	1.52	3.08
60.0	3.69	8.76
70.0	6.30	24.7
80.0	14.1	67.6

* K_2 assumed to have a value of 1.0 dm^3 mol^{-1} (independent of temperature).

against [H$^+$] are linear and data for five temperatures covering the range 40—80 °C are shown in Figure 3. If a reasonable value for K_2 of 1.0 dm^3 mol^{-1} (independent of temperature) is assumed consistent with the previously reported values,[11] this allows evaluation of both k_1 and k_2 as a function of temperature. Least-squares fits to the Eyring equation gave: k_1 (25 °C) = $(1.3 \pm 0.2) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}, $\Delta H_1^\ddagger = 73.1 \pm 4.6$ kJ mol^{-1}, $\Delta S_1^\ddagger = -94.1 \pm 13.9$ J K^{-1} mol^{-1}; and k_2 (25 °C) = $(7.2 \pm 1.2) \times 10^{-6}$ s^{-1}, $\Delta H_2^\ddagger = 108 \pm 7$ kJ mol^{-1}, $\Delta S_2^\ddagger = +20.3 \pm 22.4$ J K^{-1} mol^{-1} (Table 3).

Discussion

Oxalate anation of hexa-aquaririidium(III) perchlorate has been observed to proceed by pathways involving both $H_2C_2O_4$ and $HC_2O_4^-$. Under the conditions used ([H$^+$] = 0.14—1.00 mol dm^{-3}), the only detectable product is the diaquabis(oxalato) complex, $[Ir(OH_2)_2(C_2O_4)_2]^-$, with no evidence for further anation to give the tris(oxalato) product. The instability of $H_3[Ir(C_2O_4)_3]$ with respect to acid-catalysed displacement of one oxalate ligand is in fact well documented.[6,9] Attempts at its synthesis by heating suspensions of $Ir_2O_3{\cdot}nH_2O$ in oxalic acid solutions resulted only in the isolation of bis(oxalato) products.[9] The observed relatively rapid and irreversible acid-catalysed aquation of $[Ir(C_2O_4)_3]^{3-}$ to give bis(oxalato) products ($t_{\frac{1}{2}} \approx 12$ h, 50 °C, [H$^+$] = 1.0 mol dm^{-3}) contrasts with the much slower corresponding aquation of $[Rh(C_2O_4)_3]^{3-}$ ($t_{\frac{1}{2}} \sim 47$ h, 50 °C, 0.97 mol dm^{-3} H$^+$ [15]). The detection of an appreciable kinetic isotope effect (^{1}H *vs.* ^{2}H) on the rhodium(III) reaction is evidence in support of a rapid protonation step followed by rate-determining loss of the protonated oxalate ligand. The faster aquation for Ir^{III} could reflect an enhanced basicity of the oxalate ligands or of the complex as a whole towards likewise protonation but this remains to be proved.

A preliminary investigation into oxalate anation on $[Rh(OH_2)_6]^{3+}$ at 70 °C has allowed the detection of appreciable amounts of the tris(oxalato) complex as a kinetically significant product consistent with its much slower and reversible acid-catalysed aquation.* The ion $[Ir(C_2O_4)_3]^{3-}$, as with $[Rh(C_2O_4)_3]^{3-}$, is much more stable towards aquation at higher pH and solutions of $K_3[Ir(C_2O_4)_3]$ are reported not to racemise in boiling water at pH 7 over 1-h periods.[16] In short, acid-catalysed aquation seems to have elevated importance for $[Ir(C_2O_4)_3]^{3-}$.

Water exchange in $[Rh(OH_2)_6]^{3+}$ is known to proceed through a dominant conjugate-base-assisted mechanism presumed strongly dissociative with the monohydroxo form 10^3 times more reactive than the aqua ion.[17] Pathways involving $[Rh(OH)]^{2+}$ also dominate anation by both Cl$^-$ and Br$^-$ ions on $[Rh(OH_2)_6]^{3+}$ with the mechanism proposed involving rate-determining dissociation of an aqua ligand.[18] The dominating H$^+$ dependence involving the oxalate ligand in the present anation studies makes difficult an accurate assessment of a similar involvement of $[Ir(OH)]^{2+}$, particularly if only a partial involvement is relevant. Certainly a dominant contribution from this species is not suggested from the acidity dependence [additional H$^+$ terms would appear in the denominator of equation (5)].

Oxalate anation involving both $H_2C_2O_4$ and $HC_2O_4^-$ has been observed for a number of mixed aqua-amine complexes of Co^{III}. With *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ (en = ethylenediamine) and *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ (tn = trimethylenediamine) an ion-pair interchange mechanism for both anating species has been proposed.[19,20] The faster rates observed with tn *versus* en as ligand were interpreted in terms of a facilitation by the larger chelate ring towards dissociative loss of aqua ligand.[20] The large ion-pair association constants observed for the tn complex (1.7 dm^3 mol^{-1}, $H_2C_2O_4$; 11.5 dm^3 mol^{-1}, $HC_2O_4^-$) were explained by strong hydrogen bonding with the *cis* diaqua ligands, facilitated by the *cis* conformation of the chelating amine ring.[20] However, with monoaqua complexes such as $[Co(NH_3)_5(OH_2)]^{3+}$ and *cis*-$[Co(en)_2(NH_3)(OH_2)]^{3+}$, a feature of the oxalate-anation reactions is the markedly differing activation parameters for the $H_2C_2O_4$ and $HC_2O_4^-$ pathways and much lower ion-pair association constants.[14,21] For $[Co(NH_3)_5(OH_2)]^{3+}$, Van Eldik and Harris[14] proposed a mechanism for anation by $H_2C_2O_4$ involving a four-centred transition state leading to anation by oxalate without involving Co–OH$_2$ bond cleavage. Such a consideration arose from the low $\Delta H^\ddagger$ value (57.3 kJ mol^{-1}), similar to that observed in the CO_2 addition process,[22] and the large and negative $\Delta S^\ddagger$ value (−150.6 J K^{-1} mol^{-1}). Consistent with this, Taube and co-workers[23] had earlier observed C–O bond cleavage during the reverse process, namely acid-catalysed aquation of $[Co(NH_3)_5(HC_2O_4)]^{2+}$ (normal Co–O bond cleavage is observed at higher pH). Furthermore, recent oxygen-18 labelling studies of the base hydrolysis of *cis*-$[Co(en)_2(C_2O_4)]^+$ have demonstrated[24] that pathways exist even in alkaline solution which involve attack by OH$^-$ on carbon leading to Co–C_2O_4 bond cleavage without Co–O bond rupture. Anation by $HC_2O_4^-$ of $[Co(NH_3)_5(OH_2)]^{3+}$ was envisaged to proceed by the expected dissociative interchange mechanism.[14]

For the present study, a similar set of differing activation parameters for anation by $H_2C_2O_4$ and $HC_2O_4^-$ of $[Ir(OH_2)_6]^{3+}$ is observed which lends strong support to a similar interpretation. As for $[Co(NH_3)_5(OH_2)]^{3+}$, anation by $H_2C_2O_4$ is characterised by a relatively low $\Delta H^\ddagger$ value and highly negative $\Delta S^\ddagger$ value when compared with the pathway involving $HC_2O_4^-$. The proposal of a similar concerted transition state for anation by $H_2C_2O_4$ (Scheme) not involving Ir–OH$_2$ bond rupture cannot therefore be discounted and remains a likely mechanism. Additionally such a mechanism would not involve necessarily a dominating contribution from $[Ir(OH)]^{2+}$ in agreement with what is observed. For anation by $HC_2O_4^-$, the data lend support to an ion-pair interchange mechanism as proposed for $[Co(NH_3)_5(OH_2)]^{3+}$. Lack of conjugate-base involvement is harder to rationalise here. However, such an involvement is unlikely to play a dominant role for anation of $[Co(NH_3)_5(OH_2)]^{3+}$ in acidic solution and, given the similar activation parameters to the present system, involvement of $[Ir(OH)]^{2+}$ need not necessarily be invoked. As listed in Table 4, at 40 °C, rate constants for oxalate anation of

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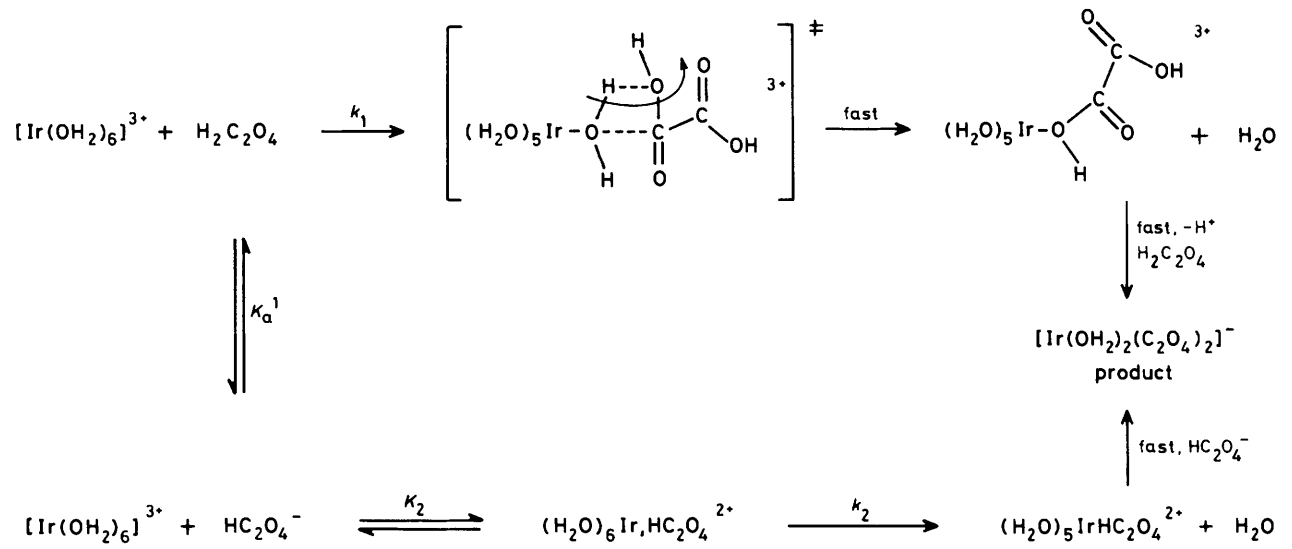
* Absorbance *vs.* time plots (400 nm) following mixing of solutions of $[Rh(OH_2)_6]^{3+}$ (2×10^{-3} mol dm^{-3}) with a 10-fold excess of oxalic acid at 70 °C are noticeably biphasic with equilibration occurring in the second stage to give amounts of the tris(oxalato)rhodate(III) complex depending on acidity. Above [H$^+$] = 2.00 mol dm^{-3}, formation of the tris complex is retarded and only a single kinetic stage to give the bis complex is relevant. At lower acidities an equilibrium mixture of the two complexes is present. Full kinetic details will be reported subsequently in a separate paper.

Table 4. Rate constants and activation parameters for anation of trivalent cations by $H_2C_2O_4$ and $HC_2O_4^-$

Complex	Anating species	10^5k (40 °C)/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
$[Ir(OH_2)_6]^{3+}$	$H_2C_2O_4$	4.68[a]	73.1	−94.1
	$HC_2O_4^-$	4.60	108	+20.3
$[Co(NH_3)_5(OH_2)]^{3+}$ [b]	$H_2C_2O_4$	2.03[a]	57.3	−150.6[c]
	$HC_2O_4^-$	1.94	93.7	−37.6
cis-$[Co(en)_2(NH_3)(OH_2)]^{3+}$ [b]	$H_2C_2O_4$	0.54[a]	95.8	−37.6[d]
	$HC_2O_4^-$	1.76	108.8	+12.6

[a] Units of dm^3 mol^{-1} s^{-1}. [b] I = 1.00 mol dm^{-3}. [c] Ref. 14. [d] Ref. 21.



Scheme. Possible mechanisms involved in anation by oxalate species of hexa-aquairdium(III) perchlorate in perchloric acid solution

$[Ir(OH_2)_6]^{3+}$ are only a factor of 2 greater than for $[Co(NH_3)_5(OH_2)]^{3+}$. Water exchange in $[Co(NH_3)_5(OH_2)]^{3+}$ is slow but easily observed [k_{ex} (25 °C) = 5.7 × 10^{-6} s^{-1}].[25] A similar order of magnitude for water exchange in $[Ir(OH_2)_6]^{3+}$ does not however seem relevant from preliminary measurements performed recently in CF_3SO_3H solutions.* Values much less than 10^{-6} s^{-1} at 25 °C are relevant, indeed it is already clear that oxalate anation proceeds with a rate that far exceeds that of water exchange which lends further support to the mechanisms proposed.

The question remains however as to why anation of $[Ir(OH_2)_6]^{3+}$ by Cl^- and Br^- ions cannot be detected. Iridium(III) being much softer than Rh^{III} or Co^{III} may be expected to have a lower affinity for such anions. An increasingly likely possibility is that halide anation of $[Ir(OH_2)_6]^{3+}$ is much less extensive due to a very small equilibration constant reflecting a high aquation rate for the monohalogeno complex. This would however seem to be in conflict with the behaviour of the halogenopenta-amines of Ir^{III} and Rh^{III} in which the equilibrium position of a mixture of the complexes $[M(NH_3)_5(OH_2)]X_3$ and $[M(NH_3)_5X]X_2$ (X = Cl, Br or I) lies well over in favour of the halogeno co-ordinated product in all cases.[26] The situation for a bidentate chelating ligand such as oxalate is somewhat different with the observed stability of $[Ir(OH_2)_2(C_2O_4)_2]^-$ towards acid-catalysed aquation probably reflecting an extremely slow aquation rate responsible for driving the anation reaction through to the observed product. Conversely, as already suggested, the measurable anation rate for oxalate may be due to a favourable mechanism operating for substitution perhaps unique to oxalate as incoming ligand.

Aquation of $[IrCl_6]^{3-}$ proceeding as far as $[Ir(OH_2)_4Cl_2]^+$ has been claimed.[27] The aquation behaviour of the unknown ion $[Ir(OH_2)_5Cl]^{2+}$ has therefore yet to be addressed. In this context, it should be noted that Cl^- anation of $[Rh(OH_2)_6]^{3+}$ proceeds to give $[Rh(OH_2)_4Cl_2]^+$ in a single step with Cl^- labilisation of the *trans*-aqua ligand in $[Rh(OH_2)_5Cl]^{2+}$ (never isolated) thought to be responsible.[18] Further studies aimed at isolating and assessing the solution chemistry of $[Ir(OH_2)_5Cl]^{2+}$ would be of interest.

In conclusion, the present findings highlight the first successfully monitored anation reaction of hexa-aquairidium(III) using oxalate as ligand. Formation of the bis(oxalato) complex and not the tris complex occurs under the conditions employed. Anation is observed involving both $H_2C_2O_4$ and $HC_2O_4^-$ as incoming ligands. The activation parameters for the two pathways suggest different mechanisms operating for each which may be unique to oxalate in facilitating detectable anation of Ir^{III} in this case. Anation by $H_2C_2O_4$ is thought to proceed through a concerted mechanism without involving Ir–OH_2

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* An oxygen-17 n.m.r. study is underway using samples of $[Ir(O^{17}H_2)_6][CF_3SO_3]_3$ in aqueous CF_3SO_3H solution which are stable at elevated temperatures (> 100 °C) and the prolonged reaction times needed for measurement of the water-exchange process. Preliminary results indicate k_{ex} values much less than 10^{-6} s^{-1} (25 °C) (D. T. Richens, D. Zbinden, L. Helm, and A. E. Merbach, unpublished work).

bond cleavage. A similar mechanism is thought to occur with $[Co(NH_3)_5(OH_2)]^{3+}$ and may be common to a number of other $M(OH_2)_n{\cdot}H_2C_2O_4$ anation reactions. Such processes may be more akin to the complexing nature of oxalate as a ligand rather than to the nature of the inert trivalent metal centre.

The results of an on-going study to measure the rate and mechanism of water exchange for $[Ir(OH_2)_6]^{3+}$ and of the corresponding anation reaction of $[Rh(OH_2)_6]^{3+}$ with oxalate (to be reported subsequently) remain of interest in the context of the present findings.

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References

1 P. Beutler and H. Gamsjager, *J. Chem. Soc., Chem. Commun.*, 1976, 554.
2 R. S. Armstrong, J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1973.
3 H. Gamsjager and P. Beutler, *J. Chem. Soc., Dalton Trans.*, 1979, 1415.
4 S. E. Castillo-Blum, A. G. Sykes, and H. Gamsjager, *Polyhedron*, 1987, **6**, 101.
5 S. E. Castillo-Blum, D. T. Richens, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1986, 1120.
6 A. Duffour, *Ann. Chim. Phys.*, 1913, **30**, 435.
7 M. Delépine, *Bull. Soc. Chim. Fr.*, 1917, **21**, 157.
8 H. G. Kruszyna, I. Bodek, L. K. Libby, and R. M. Milburn, *Inorg. Chem.*, 1974, **13**, 434.
9 F. M. Jaeger, *Recl. Trav. Chim.*, 1919, **38**, 271.
10 E. S. Swinbourne, 'Analysis of Kinetic Data,' Studies in Modern Chemistry Series, Nelson, London, 1971; F. J. Kezdy, J. Jaz, and A. Bruylands, *Bull. Soc. Chim. Belg.*, 1958, **67**, 687; E. S. Swinbourne, *J. Chem. Soc.*, 1960, 2371.
11 E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1866; O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1973, 1232; G. Davies and K. O. Watkins, *Inorg. Chem.*, 1970, **9**, 2735; 'Stability Constants of Metal Complexes,' *Special Publ.*, The Chemical Society, London, 1971, vol. 25, p. 245.
12 J. E. Finholt, P. Leupin, and A. G. Sykes, *Inorg. Chem.*, 1983, **22**, 3315.
13 E. J. Zinser and J. A. Page, *Anal. Chem.*, 1970, **42**, 787.
14 R. Van Eldik and G. M. Harris, *Inorg. Chem.*, 1975, **14**, 10.
15 K. Krishnamurty, *Inorg. Chem.*, 1962, **1**, 422; D. Barton and G. M. Harris, *ibid.*, p. 251.
16 R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 1964, 2417; R. W. Olliff, A. L. Odell, and F. B. Seaton, *ibid.*, 1965, 2280.
17 W. Plumb and G. M. Harris, *Inorg. Chem.*, 1964, **3**, 542.
18 K. Swaminathan and G. M. Harris, *J. Am. Chem. Soc.*, 1966, **88**, 4411; R. J. Buchacek and G. M. Harris, *Inorg. Chem.*, 1976, **15**, 927.
19 P. Brown and G. M. Harris, *Inorg. Chem.*, 1968, **7**, 1872; R. Van Eldik and G. M. Harris, *ibid.*, 1979, **18**, 1997.
20 A. C. Dash, R. K. Nanda, and N. Ray, *J. Coord. Chem.*, 1982, **12**, 91.
21 A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1161.
22 E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Am. Chem. Soc.*, 1973, **95**, 4169.
23 C. Andrade and H. Taube, *Inorg. Chem.*, 1966, **5**, 1087; C. Andrade, R. B. Jordan, and H. Taube, *ibid.*, 1970, **9**, 711.
24 G. M. Miskelly and D. A. Buckingham, 'Comments on Inorganic Chemistry,' eds. N. Sutin and P. Gütlich, Gordon and Breach, London, 1985, vol. 4, p. 163 and refs. therein.
25 H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, 1958, **80**, 2642.
26 A. B. Lamb and L. T. Fairhall, *J. Am. Chem. Soc.*, 1923, **45**, 378; A. B. Lamb, *ibid.*, 1939, **61**, 699.
27 W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals: Os, Ru, Ir and Rh,' Interscience, London, 1967, p. 244; E. Blasius and W. Preetz, *Z. Anorg. Allg. Chem.*, 1965, **335**, 1; J. C. Chang and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 209; A. J. P. Domingos, A. M. T. S. Domingos, and J. M. Cabral, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2563.

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