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Kinetics of Aquation of the Tris(acetylacetonate) Complexes of Divalent Chromium, Cobalt, and Ruthenium. A Pulse Radiolytic Study[1]

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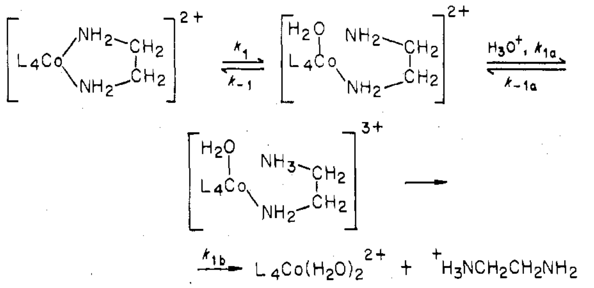
The kinetics of aquation of $Co(acac)_3^-$ and $Cr(acac)_3^-$ were studied as a function of pH. The reactions leading to the loss of each of the three ligands in $Co(acac)_3^-$ were well separated from each other while in the $Cr(acac)_3^-$ complex the first step was too fast to follow with our experimental technique. The results are in agreement with a mechanism in which the bidentate-bound ligand is in equilibrium with the ligand bound only as a monodentate. These equilibrium constants are estimated. The ligand bound as monodentate is lost by an acid-catalyzed process, with an acid-independent contribution. The aquation reaction of $Ru(acac)_3^-$ is too slow to be measured by the pulse radiolytic technique. $Ru(acac)_3H$ is a relatively strong acid. The results are compared to those obtained for the aquation reaction of $Co(en)_3^{2+}$.

Introduction

The development of the conductivity technique for following fast reactions, $t_{1/2} > 1\ \mu s$, occurring after a pulse of high-energy electrons or a flash of light is delivered to a solution, opened a new route to the study of the kinetics of ligand exchange in labile complexes.[3-7] The technique utilizes the possibility of obtaining a metal cation with an unstable ligand sphere by the fast reduction[3-6] or oxidation[7] of a complex with a stable ligand sphere. It was recently used to study the kinetics of aquation of a series of cobalt(II) amine complexes.[5] It was found that the loss of the first three NH_3 ligands from $Co(NH_3)_6^{2+}$ is too fast to be measured and the other NH_3 ligands are lost by pH-independent consecutive first-order reactions.[5] The loss of ethylenediamine, en, and triethylenetetramine is considerably slower and is acid catalyzed. The results for the latter system were interpreted in terms of the mechanism[5] in eq 1 (where L_4 are the other ligands of the cobalt, viz., H_2O or $H_2NCH_2CH_2NH_2$). The results enabled an estimate of k_1 and K_1k_{1a} or $K_1K_{1a}k_{1b}$. It seemed of interest to study the mechanism and rate of aquation of $Co(acac)_3^-$ ($acac^- \equiv$ acetylacetonate) with the hope of obtaining further information on the factors affecting the aquation reactions of labile cobalt(II) complexes. The choice of $acac^-$ as a ligand to be studied stems from the following considerations: The stability constants $K_{1L} = [ML]/[M][L]$ and $K_{2L} = [ML_2]/[ML][L]$ are similar for L = acetylacetonate or ethylenediamine, though K_{3L} is much larger for ethylenediamine.[8] However, these complexes differ considerably: (a) the donor atoms in $acac^-$ are oxygen whereas for en they are nitrogen; (b) the complex is resonance stabilized in the case of $acac^-$; (c) $acac^-$ is a charged ligand whereas en is uncharged; (d) the chelate ring size is six for the $acac^-$ complex and five for the en complex. All of these factors might affect the rate of the steps in reaction 1 or even change the mechanism of the aquation reaction. We decided to study also the aquation of $Cr(acac)_3^-$ and $Ru(acac)_3^-$ in order to obtain a better understanding of the role of the central cation.



(1)

A second reason for initiating this study was that we found[9] that the dark "back" reaction occurring in an illuminated solution containing $Ru(bpy)_3^{2+}$ and $Co(acac)_3$ is

$$Ru(bpy)_3^{3+} + acac^- \rightarrow Ru(bpy)_3^{2+} + \text{oxidn products} \quad (2)$$

where $acac^-$ is formed in the sequence

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (3)$$

$$Ru(bpy)_3^{2+*} + Co(acac)_3 \rightarrow Ru(bpy)_3^{3+} + Co(acac)_3^- \quad (4)$$

$$Co(acac)_3^- \rightarrow Co^{2+}(aq) + 3acac^- \quad (5)$$

In order to analyze the kinetics of reaction 2 a detailed knowledge of the kinetics of reaction 5 was required.

Experimental Section

Materials. $Co(acac)_3$ and $Cr(acac)_3$ were obtained from Alfa Inorganics and were recrystalized from benzene until a fresh 1×10^{-3} M solution in water had a pH <7.0 thus indicating that no free ligand, $Co(acac)_2$, or $Cr(acac)_2$ were present. In the case of $Cr(acac)_3$ it was found that the pH of the solutions changed with time and therefore all experiments were carried out within 3 h of dissolution. Within this time the ratio $[acacH]/[Cr(acac)_3]$ did not exceed 0.001. $Ru(acac)_3$ was obtained from Strem Chemicals and contained no free ligand. *tert*-Butyl alcohol, Baker analyzed, and perchloric acid, G. F. Smith, were used without further treatment. All solutions were prepared using triply distilled water and were saturated with He (99.995%, Matheson) or N_2O (99.9%, Liquid Carbonic).

Procedure. The solutions were prepared using the syringe technique. The samples were irradiated by electron pulses of 0.25 μs, 16 MeV, 0.5 A, delivering about 1000 rd to the sample.

For the transient conductivity measurements, a newly constructed apparatus, operated on-line with a Sigma 5 computer, was used. The technique is a modification of one described previously.[10,11] For measuring fast conductivity changes during and after the linac pulse, a 200-V dc pulse of about 1-ms duration is applied to the conductivity cell, and the linac is triggered at about midpoint during this pulse. The cell is connected to a special bridge circuit[10] whose output, after electronic processing, is digitized in a Biomation-8100 transient recorder and transmitted to the computer. In this mode of operation, signals of up to 500-μs duration can be measured with a time resolution of less than 0.1 μs.

For measuring longer lasting signals, a 50–100-kHz sinusoidal voltage of typically 10 V is used. The output of the (same) bridge circuit is phase-sensitively demodulated by taking samples of this signal in phase with the peaks and valleys of the input voltage. In this way we can record the conductivity change with a time resolution of as low as 10 μs, with a practically unlimited signal duration.

For dosimetry, we used the previously described Faraday cup arrangement,[10] in combination with a new integrating circuit outlined in ref 12.

The kinetics of the reactions were analyzed on a Sigma 5 computer. Rate constants were obtained using a nonlinear least-squares technique with the assumption of a single exponential decay for most cases. In

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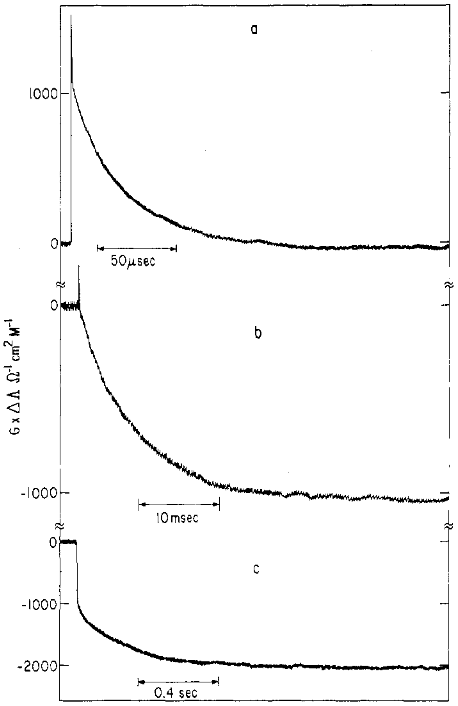


Figure 1. The three time domains of changes in conductivity as function of time after a pulse of 1000 rd was delivered to a solution containing 5 × 10^{-4} M Co(acac)$_3$, 4 × 10^{-5} M $HClO_4$, and 0.1 M *tert*-butyl alcohol. The formal units of $G \times \Delta\Lambda$ are (molecules/100 eV)(Ω^{-1} cm^2 M^{-1}).

the case of Cr(acac)$_3^-$ at higher acidities where overlap of the second and third steps was suspected, a fit to two consecutive exponential decays was carried out using the same technique. All experiments were carried out at room temperature, 25 ± 2 °C.

Results

Helium-saturated solutions containing 5 × 10^{-4} M Co(acac)$_3$ and 0.1 M *tert*-butyl alcohol in the pH range 3.1–7.0 were irradiated. To solutions containing less than 2 × 10^{-5} M H_3O^+, $NaClO_4$ was added (yielding 3.2 × 10^{-5} M concentration) in order to increase the background conductivity. In all cases an increase in conductivity immediately following the pulse was observed. Part of this conductivity increase rapidly decayed to a lower level at about half the peak height. This fast process appears also in solutions containing no Co(acac)$_3$ and is attributed to the reaction OH^-(aq) + H_3O^+(aq) → H_2O since both OH^-(aq) and H_3O^-(aq) are formed by the pulse.

Following this fast formation and decay of conductivity, further decay of the remaining conductivity signal could be observed which was well separated in time from the previous process (Figure 1a). The kinetics of this slower decay was found to obey a pseudo-first-order rate law. The conductivity at the end of this reaction always matched its initial value before the pulse. At pH ≤5, two further processes separated in time caused a further decrease in conductivity below the prepulse level (Figure 1b,c). At an initial pH of 7.0 these last two processes caused a new increase in conductivity. The kinetic analysis of the last two processes indicated that they too obey first-order rate laws. The conductivity changes and rate constants for all three first-order processes are compiled in Table I.

The pH dependence of the pseudo-first-order rate constants thus obtained for each of the three relevant processes is displayed in Figure 2. The rate constants depend linearly on [H_3O^+] with an acid-independent component which yields the intercepts in the lines of Figure 2. When the solutions were saturated with N_2O instead of He, processes with similar kinetics of the second and third reactions occurred, but the absolute changes in conductivity were only about 20% of those in the He-saturated solutions.

Table I. Kinetics of Aquation of Co(acac)$_3^-$ [a]

initial [H_3O^+], M	k_{3L}, s^{-1}	$-\Delta\Lambda_3$, Ω^{-1} cm^2 mol^{-1}	k_{2L}, s^{-1}	$-\Delta\Lambda_2$, Ω^{-1} cm^2 mol^{-1}	k_{1L}, s^{-1}	$-\Delta\Lambda_1$, Ω^{-1} cm^2 mol^{-1}
	9.7 × 10^3	208	3.3 × 10^1	−158	3.7	−98
1 × 10^{-5}	7.9 × 10^3	411	6.2 × 10^1	445	2.7	374
2 × 10^{-5}	1.6 × 10^4	415	7.8 × 10^1	430	2.8	385
4 × 10^{-5}	3.0 × 10^4	415	1.27 × 10^2	453	4.0	389
5 × 10^{-5}	3.6 × 10^4	438	1.9 × 10^2	464	5.0	336
7 × 10^{-5}	5.1 × 10^4	389	2.3 × 10^2	498	6.2	438
1 × 10^{-4}	7.2 × 10^4	415	3.1 × 10^2	498	8.4	438
2 × 10^{-4}	2.3 × 10^5	309	6.1 × 10^2	442	15.6	430
4 × 10^{-4}	*b*	*b*	1.18 × 10^3	468	29	374
7 × 10^{-4}	*b*	*b*	2.25 × 10^3	415	57	449

[a] All solutions contained 5 × 10^{-4} M Co(acac)$_3$ and 0.1 M *tert*-butyl alcohol and were He saturated. The dose was about 1000 rd/pulse. k_{iL} is the rate constant of the loss of the *i*th ligand (see discussion) and $\Delta\Lambda_i$ is the corresponding change in conductivity as obtained by extrapolation in the computer calculation assuming $G = 2.65$. [b] Too fast to be measured.

Table II. Kinetics of Aquation of Cr(acac)$_3^-$ [a]

[H_3O^+], M	k_{2L}, s^{-1}	k_{1L}, s^{-1}	$-\Delta\Lambda$,[b] Ω^{-1} cm^2 mol^{-1}
1 × 10^{-5} [c]	3.2 × 10^3	3.2 × 10^2	475
5 × 10^{-5} [c]	4.4 × 10^3	4.7 × 10^2	694
1.6 × 10^{-4} [d]	1.4 × 10^4	1.1 × 10^3	596
4 × 10^{-4} [d]	2.2 × 10^4	1.8 × 10^3	596
7 × 10^{-4} [d]	3.2 × 10^4	3.0 × 10^3	475

[a] All solutions contained 0.1 M *tert*-butyl alcohol and were He saturated. k_{iL} is the rate constant of the loss of the *i*th ligand. Accuracy ±30%; see discussion. [b] Total change in molar conductivity assuming $G = 2.65$. [c] 2 × 10^{-4} M Cr(acac)$_3$. [d] 5 × 10^{-4} M Cr(acac)$_3$.

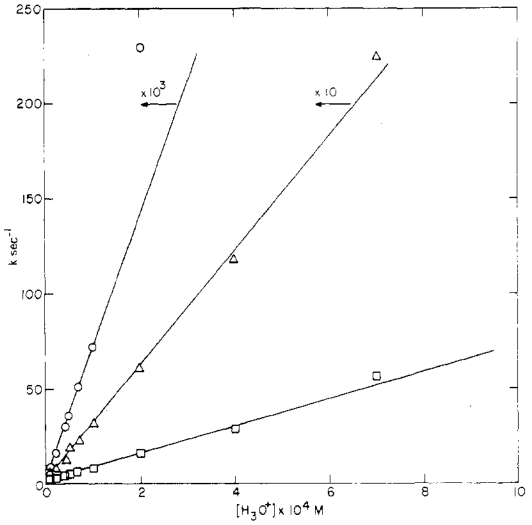


Figure 2. Dependence of the pseudo-first-order rate constants observed in the Co(acac)$_3$ solutions on pH: (○) first reaction observed, (△) second reaction observed, (□) third reaction observed.

When He-saturated solutions containing Cr(acac)$_3$ instead of Co(acac)$_3$ were irradiated, the initial increase in conductivity decayed to zero within the time required for the OH^-(aq) + H_3O^+(aq) → H_2O reaction. This reaction was followed by a negative-going signal indicating two further processes which were only poorly separated in time. The rate constants of these two processes were calculated using a nonlinear least-squares curve-fitting program assuming two consecutive first-order reactions, each of which causes half of the observed total change in conductivity. The rate constants thus calculated are summarized in Table II. The total change in conductivity decreased somewhat with decreasing pH. Results for this system are summarized in Table II. He-saturated solutions containing $Ru(acac)_3$, instead of $Co(acac)_3$ or $Cr(acac)_3$, irradiated in the pH range 7.0–3.5, also yielded an increase in conductivity. After the reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O$ was over, the remaining increase amounted to a change of $\sim 396\ \Omega^{-1}\ cm^2\ mol^{-1}$, assuming $G = 2.65$ for the product; see below. At this level, the conductivity signal was stable for at least 2 s.

Discussion

The radiolysis of water can be summarized by eq 6.[13] These

$$H_2O \rightsquigarrow\xrightarrow{\gamma,e^-} e_{aq}^-, OH, H, H_2O_2, H_2, H_3O^+(aq), OH^-(aq) \tag{6}$$

products are homogeneously distributed in the solution within less than 1 μs after the radiation is absorbed in the solution. The following yields are well documented in the literature: $G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, $G_{H_2O_2} = 0.75$, $G_{H_3O^+}(aq) = G_{e_{aq}^-} + G_{OH^-}$, and $G_{OH^-}(aq) \approx 1.0$. (G is defined as the number of product molecules formed by the absorption of 100 eV in the solution.[13]) In He-saturated solutions containing $M(acac)_3$ and *tert*-butyl alcohol reactions 7–13 have to be considered. The rate of reaction 8 for $Co(acac)_3$ is 4.6 $\times 10^{10}\ M^{-1}\ s^{-1}$ [15] and is expected to be similar for the other complexes. The rate of reaction 10 is $1.3 \times 10^9\ M^{-1}\ s^{-1}$ for the $Co(acac)_3$[17] but is unknown for the other complexes. (Our results indicate that the reaction of H atoms with $Cr(acac)_3$ is relatively slow and does not affect our results; see below.) In N_2O-saturated solutions reaction 14 will effectively compete

$$H_3O^+(aq) + OH^-(aq) \rightarrow H_2O \tag{7}$$

$k = 1.4 \times 10^{11}\ M^{-1}\ s^{-1}$ [14]

$$e_{aq}^- + M(acac)_3 \rightarrow M(acac)_3^- \tag{8}$$

$$e_{aq}^- + H_3O^+(aq) \rightarrow H \tag{9}$$

$k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}$ [15]

$$H + M(acac)_3 \xrightarrow{aq} M(acac)_3^- + H_3O^+ \tag{10}$$

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH \tag{11}$$

$k = 5 \times 10^8\ M^{-1}\ s^{-1}$ [16]

$$\cdot CH_2C(CH_3)_2OH + M(acac)_3 \rightarrow \text{products} \tag{12}$$

$$2\cdot CH_2C(CH_3)_2OH \rightarrow OH(CH_3)_2CCH_2CH_2C(CH_3)_2OH$$

$k = 1.3 \times 10^9\ M^{-1}\ s^{-1}$ [18] (13)

$$N_2O + e_{aq}^- \xrightarrow{H_3O^+} N_2 + OH \tag{14}$$

$k = 8.7 \times 10^9\ M^{-1}\ s^{-1}$ [15]

with reaction 8, and thus in neutral solutions also containing *tert*-butyl alcohol 90% of the free radicals are transformed into $\cdot CH_2C(CH_3)_2OH$, the rest being H atoms.

The conductivity changes measured are expected to be mainly due to the formation or consumption of $H_3O^+(aq)$, as its equivalent conductance $\Lambda(H_3O^+(aq)) = 350\ \Omega^{-1}\ mol^{-1}\ cm^2$ whereas $\Lambda(Co^{2+}(aq)) = 55\ \Omega^{-1}\ mol^{-1}\ cm^2$; for $Co(acac)_3^-$ and $Co(acac)^+$ the Λ values are unknown but are expected to be smaller than $50\ \Omega^{-1}\ mol^{-1}\ cm^2$. The observation that the conductivity changes in the N_2O-saturated solutions are small indicates that reaction 12 is slow relative to reaction 13. (Alternatively the products of reaction 12 might cause only minor changes in the conductivity, but we can visualize no such reaction.) The small conductivity changes observed in these solutions are attributed to reaction 10.

The changes in conductivity observed for the $Co(acac)_3$ system agree very well with the following mechanism:

$$e_{aq}^- + Co(acac)_3 \rightarrow Co(acac)_3^- \tag{15}$$

$$Co(acac)_3^- + H_3O(aq)^+ \rightarrow Co(acac)_2 + acacH \tag{16}$$

$$Co(acac)_2 + H_3O(aq)^+ \rightarrow Co(acac)^+(aq) + acacH \tag{17}$$

$$Co(acac)^+ + H_3O^+(aq) \rightarrow Co^{2+}(aq) + acacH \tag{18}$$

Contribution of reactions of the type

$$Co(acac)_3^- \rightleftharpoons Co(acac)_2 + acac^- \tag{19}$$

$$Co(acac)_2 \rightleftharpoons Co(acac)^+ + acac^- \tag{20}$$

$$Co(acac)^+ \rightleftharpoons Co^{2+}(aq) + acac^- \tag{21}$$

followed by

$$acac^- + H_3O^+(aq) \rightarrow acacH \tag{22}$$

is indicated by the intercepts in Figure 2 and by Table I.

Reaction 15 is over within less than 0.1 μs; thus the $\Delta\Lambda_0$ observed (after the $H_3O^+(aq) + OH^-$ reaction) should correspond to the formation of $Co(acac)_3^- + H_3O^+$, $\Delta\Lambda_0 = 350 + 40 = 390\ \Omega^{-1}\ cm^2\ mol^{-1}$. The yield of these products is expected to be between 2.65 and 3.25 depending whether only e_{aq}^- or e_{aq}^- and H atoms reduce the $Co(acac)_3$. The results in Table I were calculated assuming that $G(-[Co(acac)_3]) = 2.65$. The results for $\Delta\Lambda_3$ in Table I indicate that the main reducing agent during the pulse is e_{aq}^-. Reaction 16 is expected to decrease the conductivity back to its value before the pulse, as observed in Figure 1. The following reactions, (17) and (18), were expected to decrease $\Delta\Lambda_0$ further by somewhat less than $350\ \Omega^{-1}\ cm^2\ mol^{-1}$ due to the formation of the cations in these reactions. The results, Table I and Figure 1, indicate that reactions 17 and 18 indeed occur but cause a somewhat larger than expected change in $\Delta\Lambda_0$. This difference is attributed to contributions of reactions 10 and maybe 12. However, at pH 7.0 the latter two reactions are expected to cause an increase in conductivity as the consumption of $H_3O^+(aq)$ by reactions 17 and 18 at this pH causes the formation of $OH^-(aq)$. The absolute changes of conductivity at this pH are difficult to assess as the acacH acts as a buffer at pH >7.0.[8] From Figure 2 the rates of reactions 16–18 were determined as $k_{16} = (7.2 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$, $k_{17} = (3.1 \pm 0.3) \times 10^6\ M^{-1}\ s^{-1}$, and $k_{18} = (7.5 \pm 0.8) \times 10^4\ M^{-1}\ s^{-1}$. The intercepts in Figure 2 are attributed to reactions 19–21. From these intercepts (see also Table I) $k_{19} = (8 \pm 2) \times 10^3\ s^{-1}$, $k_{20} = 30 \pm 10\ s^{-1}$, and $k_{21} = 3 \pm 1\ s^{-1}$ are obtained. Using the known stability constants $-\log K_{20} = 4.14$[8] and $-\log K_{21} = 5.40$,[8] we calculate $k_{-20} = 4.1 \times 10^5\ M^{-1}\ s^{-1}$ and $k_{-21} = 7.5 \times 10^5\ M^{-1}\ s^{-1}$. The accuracy of the latter values is rather low due to the large uncertainty in k_{20}, k_{21}, K_{20}, and K_{21}. However, k_{-20} and k_{-21} are in reasonable agreement with the expected rates of anation of $Co^{2+}(aq)$.[19] If the value of k_{-19} is also similar to that of the rate of anation of $Co^{2+}(aq)$, this could yield for the unknown stability constant a value of $-\log K_{19} \approx 2.8$. The observation that the total change in conductivity is pH independent, though at $[H^+] = 7 \times 10^{-4}$ about 30% of the e_{aq}^- reacted via reaction 9 instead of reaction 8, indicates that reaction 10 occurred, as expected, in this system.

The results in the $Cr(acac)_3$ system indicate that the reaction

$$Cr(acac)_3^- \xrightarrow{H_3O^+} Cr(acac)_2 + acacH \tag{23}$$

has a rate constant larger than $2 \times 10^5\ s^{-1}$ at pH <5.0. We are therefore unable to determine whether the reaction mechanism involves a reaction of H_3O^+ with $Cr(acac)_3^-$ or the loss of an $acac^-$ ligand followed by reaction with H_3O^+. From the results in Table II we calculate $k_{24} = (4 \pm 1) \times 10^7\ M^{-1}\ s^{-1}$, $k_{25} = (4 \pm 1) \times 10^6\ M^{-1}\ s^{-1}$, $k_{26} = (3 \pm 1) \times 10^3\ s^{-1}$, and

$k_{27} = (3 \pm 1) \times 10^2\ s^{-1}$. Using the reported stability constants,

$$Cr(acac)_2 + H_3O^+ \rightarrow Cr(acac)^+ + acacH \quad (24)$$

$$Cr(acac)^+ + H_3O^+ \rightarrow Cr^{2+}(aq) + acacH \quad (25)$$

$$Cr(acac)_2 \rightleftharpoons Cr(acac)^+ + acac^- \quad (26)$$

$$Cr(acac)^+ \rightleftharpoons Cr(aq)^{2+} + acac^- \quad (27)$$

$-\log K_{26} = 5.74$[8] and $-\log K_{27} = 5.96$[8] (although these were determined in solutions with $\mu = 1.0$ M), we calculate $k_{-26} = 1.6 \times 10^9\ M^{-1}\ s^{-1}$ and $k_{-27} = 2.7 \times 10^8\ M^{-1}\ s^{-1}$, in reasonable agreement with expectation for anation reactions of $Cr^{2+}(aq)$.[19]

The results obtained in the $Ru(acac)_3$ solutions indicate that the upper limits for the rates of the reactions

$$Ru(acac)_3^- + H_3O^+ \rightarrow Ru(acac)_2 + acacH \quad (28)$$

$$Ru(acac)_3^- \rightarrow Ru(acac)_2 + acac^- \quad (29)$$

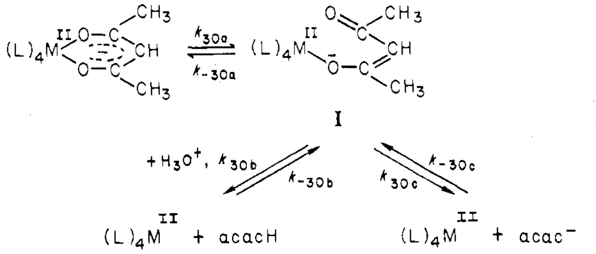
are $k_{28} < 1 \times 10^2\ M^{-1}\ s^{-1}$ and $k_{29} < 3 \times 10^{-2}\ s^{-1}$. Furthermore, the pK_a for $Ru(acac)_3^- + H_3O^+ \rightleftharpoons Ru(acac)_3H$ is smaller than 3.5. The electron density on the ligands in $Ru(acac)_3^-$ is expected to be larger than in $Cr(acac)_3^-$ and $Co(acac)_3^-$ due to the larger back-donation effect in Ru(II) complexes.[20] It is therefore reasonable to assume that $Co(acac)_3H$ and $Cr(acac)_3H$ are even stronger acids than $Ru(acac)_3H$.

The kinetic data obtained for all of these systems are compiled in Table III. Included are also data concerning the aquation reaction of $Co(en)_3^{2+}$ as calculated from the results of Lilie et al.[5] The following general features are evident:

1. The rates of aquation for the $M(acac)_3^-$ complexes are $Cr(acac)_3^- > Co(acac)_3^- \gg Ru(acac)_3^-$ as expected.

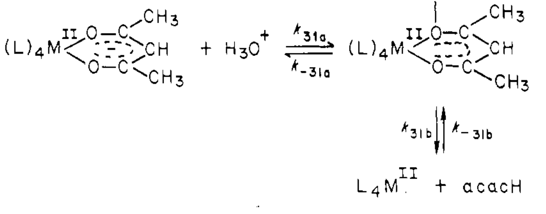
2. In comparing the rates of aquation of $Co(acac)_3^-$ and $Co(en)_3^{2+}$ it is of interest to note that $k_{3L}(acac)/k_{3L}(en) = 120$, $k_{2L}(acac)/k_{2L}(en) = 3$, and $k_{1L}(acac)/k_{1L}(en) = 0.25$. This observation might be explained by the fact that the total charge of the complex in going from $Co(acac)_3^-$ to $Co^{2+}(aq)$ changes, whereas the charge of the complex of ethylenediamine with cobalt is independent of the number of ligands.

The following detailed mechanism for the aquation reactions would explain the experimental results:



(30)

Intermediate I might have a water molecule as a ligand of M^{II} and acacH might be in the keto or enol form. An alternative mechanism would be:



(31)

In principle one could also write reaction 31 with the proton addition to the central CH group; however, this would leave keto groups as ligands which is highly improbable. Reaction 31a has to be an equilibrium reaction as one would expect $k_{31a} \approx 5 \times 10^{10}$[14] while the experimental value for the aquation is much lower.[21] The non-acid-catalyzed aquation reaction according to (31) would be a reaction with H_2O. This, however, requires the formation of $OH^-(aq)$, and as the divalent acetylacetonate complexes are strong acids (see above), this seems unreasonable. We therefore prefer mechanism 30 over mechanism 31. (In the case of $(L_4)M(en)$ only mechanism 30 is possible.)

Table III. Kinetic Data for the Aquation Reactions of $M(acac)_3^-$ and $Co(en)_3^{2+}$

	$Co(en)_3^{2+}$ [a]	$Co(acac)_3^-$	$Cr(acac)_3^-$	$Ru(acac)_3^-$
$-\log K_{3L}$ [b]	3.3	2.8[c]		
k^0_{3L}, s^{-1}	$<7 \times 10^2$	8×10^3		$\leq 3 \times 10^{-2}$
k_{3L}, $M^{-1}\ s^{-1}$	$\sim 6 \times 10^6$	7.2×10^8		$\leq 10^2$
$K_{30a}(3L)$	$<1 \times 10^{-3}$ $>1 \times 10^{-4}$	$<1 \times 10^{-1}$ $>1 \times 10^{-2}$		$>2 \times 10^{-8}$
$-\log K_{2L}$	4.9	4.14	5.74	
k^0_{2L}, s^{-1}	<60	30	3×10^3	
k_{2L}, $M^{-1}\ s^{-1}$	$\sim 1 \times 10^6$	3.1×10^6	4×10^7	
$K_{30a}(2L)$	$<2 \times 10^{-4}$ $>2 \times 10^{-5}$	$<6 \times 10^{-4}$ $>6 \times 10^{-5}$	$<8 \times 10^{-3}$ $>8 \times 10^{-4}$	
$-\log K_{1L}$	5.6	5.40	5.96	
k^0_{1L}, s^{-1}	<20	3	3×10^2	
k_{1L}, $M^{-1}\ s^{-1}$	$\sim 3 \times 10^5$	7.5×10^4	4×10^6	
$K_{30a}(1L)$	$<6 \times 10^{-5}$ $>6 \times 10^{-6}$	$<1 \times 10^{-5}$ $>1 \times 10^{-6}$	$<8 \times 10^{-4}$ $>8 \times 10^{-5}$	

[a] The kinetic data for the $Co(en)_3^{2+}$ were calculated from the figure in the paper by J. Lilie, N. Shinohara, and M. G. Simic.[5] [b] $K_{3L} = [ML_3]/[ML_2][L]$, $K_{2L} = [ML_2]/[ML][L]$, $K_{1L} = [ML]/[M][L]$ (values from ref 8); the rate constants correspond to the rate law $-d[ML_i]/dt = k^0_{iL}[ML_i] + k_i[ML_i][H_3O^+]$ for the corresponding reaction. $K_{30a}(iL)$ is the equilibrium constant for reaction 30a for the ith ligand.[23] [c] Roughly estimated from this work; see text.

In none of the reactions studied here did k_{30a} become the rate-determining step even in the most acidic conditions. (The maximal acidity that could be used was determined by the sensitivity of the conductivity system.) In this respect our results differ from those obtained in the $Co(en)_3^{2+}$ system.[5]

If one assumes that k_{-30b} is relatively slow, which is reasonable, the observed rate constant of the aquation reaction is $K_{30a}k_{30b}$. As reaction 30b is a proton-transfer reaction, its rate constant should be $5 \times 10^9 < k_{30b} < 5 \times 10^{10}\ M^{-1}\ s^{-1}$.[14] Therefore we can estimate K_{30a} for the complexes studied from the kinetic data; these estimates are included in Table III.[23] We know of no other estimates of K_{30a} for bidentate ligands (similar estimates for EDTA-type ligands are known from equilibrium studies in solution).

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Registry No. $Co(acac)_3^-$, 47177-25-3; $Cr(acac)_3^-$, 68986-53-8; $Ru(acac)_3^-$, 66560-52-9.

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(1) Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.

(2) Visiting scientist from the Nuclear Research Centre Negev and the Ben-Gurion University of the Negev, Beer-Sheva, Israel.

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(23) One of the reviewers has pointed out that "reaction 30b might be a two-step process, protonation and dissociation, where the first step may be a fast established equilibrium", and therefore the estimate of K_{30a} might be wrong. The data obtained in this study are insufficient to prove or disprove this hypothesis.

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The Di-μ-oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2−)-Dioxygen Reaction

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The reaction of di-μ-oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2−), $Mo_2O_4(cys)_2^{2-}$, I ≡ $Mo^V{}_2(cys)_2$, with O_2 has been studied in HPO_4^{2-}–$H_2PO_4^-$ and HN_3–NH_4^+ buffers. In HPO_4^{2-}–$H_2PO_4^-$ buffer at pH 6.5, excess O_2 reacted with I according to the mechanism

$$\mathrm{Mo^V{}_2(cys)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo^{IV}(cys) + Mo^{VI}(cys)}$$

$$\mathrm{O_2 + Mo^{IV}(cys)} \xrightarrow[+2\mathrm{H^+}]{k_2} \mathrm{Mo^{VI}(cys)(H_2O_2)}$$

where at least one phosphate is bound to $Mo^V{}_2(cys)_2$. When a steady-state condition is imposed on $Mo^{IV}(cys)$, the rate law becomes $-d[\mathrm{Mo^V{}_2(cys)_2}]/dt = \{k_2k_1[\mathrm{O_2}][\mathrm{Mo^V{}_2(cys)_2}]\}/\{k_{-1}[\mathrm{Mo^{VI}(cys)}] + k_2[\mathrm{O_2}]\}$ and $k_1 = (1.5 \pm 0.2) \times 10^{-3}\ \mathrm{s^{-1}}$, $k_{-1}k_2^{-1} = 0.9 \pm 0.2$ at 25.0 ± 0.2 °C. In excess I, the disappearance of O_2 follows strict first-order kinetics under all conditions. The rate constant k_{obsd} *decreases* with increasing $[O_2]$ (10^{-6}–10^{-4} M) and increases with increasing [I], the best linear plot of the data being k_{obsd}^{-1} vs. $[\mathrm{I}]^{-1}$. A mechanism is proposed involving a $Mo^V{}_2(cys)_2{\cdot}O_2$ complex which yields Mo^{VI} and H_2O_2. The resulting H_2O_2 can oxidize $Mo^V{}_2(cys)_2$ or be catalytically decomposed. The excess I–O_2 reaction was investigated at pH 9.8 in NH_3–NH_4^+ buffer. It was found that NH_3 enhances the reactivity of I toward O_2. The rate law is assumed to be rate = $\{k_{\mathrm{OH^-}} + k_{\mathrm{NH_3}}[\mathrm{NH_3}]\}[\mathrm{I}][\mathrm{O_2}]$, where $k_{\mathrm{OH^-}} = 5.5 \pm 0.5\ \mathrm{s^{-1}\ M^{-1}}$ and $k_{\mathrm{NH_3}} = (1.8 \pm 0.4) \times 10^2\ \mathrm{s^{-1}\ M^{-2}}$ at 25.0 ± 0.2 °C and $[\mathrm{O_2}]_{\mathrm{init}} = 4.1 \times 10^{-5}$ M. It should be noted that k_{obsd} for the reaction is also dependent upon $[\mathrm{O_2}]_{\mathrm{init}}$. The enhancement of I–$O_2$ reaction by the bases phosphate, ammonia, and hydroxide is explained as the addition of these bases to I, which causes a coordination asymmetry, resulting in an asymmetry in oxidation state: IV–VI vs. V–V. Such asymmetric species can be reactive toward dioxygen and possibly dinitrogen.

Introduction

The importance of molybdenum to the activity of a number of oxidation–reduction enzymes has been established for some time.[1] Complexes of molybdenum and L-(+)-cysteine, cys, have long been proposed as models for molybdenum-containing enzymes.[2,3] The participation of the complex di-μ-oxo-bis[oxo(L-(+)-cysteinato)molybdate(V)](2−), $Mo_2O_4(cys)_2^{2-}$, I ≡ $Mo^V{}_2(cys)_2$, in the reduction of dinitrogen and a series of dinitrogen analogues has been demonstrated by Schrauzer and co-workers.[4] However, a recent study suggests that I is not a good model compound for the molybdenums present in nitrogenase.[5] Due to the interest in molybdenum chemistry, the oxidation–reduction reactions of complex I warrant investigation in order to determine the reacting species. A study of the kinetics of reactions involving the oxidation of this complex by dioxygen in different media is reported here.

Experimental Section

UV–visible spectral observations were performed on Cary Model 14 and 17 spectrophotometers. Kinetic studies were executed on Cary 14 and 17 spectrophotometers and stopped-flow instruments. The stopped-flow apparatus included a Gibson-Durrum and a Durrum Model D-40 which was fitted to a Beckman UV–visible spectrophotometer. Oxygen concentrations were measured by a Beckman Fieldlab oxygen analyzer, Model 1008, which employs a polarographic oxygen sensor electrode that is sensitive to the oxygen fugacity. A Beckman Expandomatic pH meter, which was calibrated against standard buffers, was used in all pH measurements. Temperature control for all experiments was achieved through the use of either a Haab constant-temperature circulator, Model F, with Iumo contact thermometers, providing thermoregulation, or a Therimstemp temperature controller, Model 71, connected to a heating coil.

Materials. $\mathbf{Na_2[Mo_2O_4(SCH_2CHNH_2CO_2)_2]{\cdot}5H_2O \equiv I}$. I was synthesized according to literature methods.[5] Bright orange crystals were recrystallized from ethanol–water mixed solvent (50/50 by volume). C, H, N, and S were determined by Galbraith Laboratories, Inc., Knoxville, Tenn. Molybdenum was determined according to a literature method.[6] Anal. Calcd: C, 11.4; H, 3.2; N, 4.5; S, 10.1; Mo, 30.5. Found: C, 11.6; H, 3.2; N, 4.5; S, 10.0; Mo, 32.2.

All phosphate salts used for making buffer solutions were obtained from Mallinckrodt Chemical Works and were used without further purification. Aqueous solutions were prepared with distilled water which was further purified by passing through a deionizing system.

Kinetic Method. Dioxygen Reaction of I. Dioxygen reactions were run in 0.5 M phosphate buffer (HPO_4^{2-}–$H_2PO_4^-$). The pH of such a solution was 6.5 ± 0.1. All stock solutions of I were prepared by adding an appropriate amount of deaerated buffer solution to a volumetric flask that contained a weighed amount of I (solution I). The flask itself was flushed with purified N_2 or Ar gas. Plastic syringes fitted with Teflon tubing were used to transfer the solution in order to avoid metal contamination. Reactions with excess dioxygen were initiated by injecting 0.2 mL of solution I (ca. 2×10^{-3} M) into 30.0 mL of a dioxygen- or an air-saturated solution contained in a 10-cm quartz cell. The rate of reaction was monitored by following the

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