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Mercury(II)-Catalyzed Aquation of *fac*-$RhCl_3(OH_2)_3$ in Aqueous Solution

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In the presence of excess Hg^{2+} ion, the title complex in strongly acidic aqueous solution changes fairly rapidly to *cis*-$RhCl_2(OH_2)_4^+$ at room temperature. Subsequent catalyzed aquations to produce successively $RhCl(OH_2)_5^{2+}$ and $Rh(OH_2)_6^{3+}$ are much slower, and all three steps are readily separable kinetically. The reaction mechanism appears to involve preassociation of Hg^{2+} with the parent complex and each of its two chloride-containing products, followed by dissociative interchange of water for $HgCl^+$. The rate law for each step thus takes the form $k_{obsd} = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$. By determining k_{obsd} over a range of $[Hg^{2+}]$ values, it is possible to evaluate both the interchange rate constants (k) and the reactant association constants (K). The latter are essentially temperature independent over the experimental range and have the values 137 ± 5, 10.0 ± 1.0, and 3.0 ± 0.6 M^{-1} for the tri-, di-, and monochloro species, respectively. The corresponding interchange rate constants at 40 °C are $(10.7 \pm 0.4) \times 10^{-3}$, $(4.3 \pm 0.3) \times 10^{-5}$, and $(8.9 \pm 1.8) \times 10^{-6}$ s^{-1}. These have the following temperature parameters, respectively: $\Delta H^\ddagger$ (kcal mol^{-1}), 19.0 ± 0.4, 22.2 ± 0.7, and 23.3 ± 0.3; $\Delta S^\ddagger$ (cal deg^{-1} mol^{-1}), −6.4 ± 1.5, −7.5 ± 2.2, and −5.0 ± 0.9. Some significant comparisons are made with recently published studies of Hg(II)-catalyzed reactions of several haloaminerhodium(III) complex ions.

The aquation and anation reactions of the whole series of chloroaquorhodium(III) complexes have been previously studied in our laboratory,[1] as has the bromide anation of the hexaaquorhodium(III) species.[2] Our most significant and conclusive finding is that the steric course of all these reactions in strongly acidic solution is controlled almost entirely by the trans effect of the halide ligands of each reactant species. Thus, for example, one observes that $RhCl_6^{3-}$ undergoes stepwise aquation only by the release of Cl^- trans to another Cl^- in a short chain of reactions which produces only cis complexes, with *fac*-$RhCl_3(OH_2)_3$ as the apparent end product. In these preceding studies, where the *fac* complex solution contained some excess Cl^-, the aquation would not proceed further even when the solution was refluxed for several hours.[1] However, we have recently prepared the *fac* complex in aqueous solution free of ionic Cl^-, and we observed that the aquation does indeed take place very slowly (half-time between 3 and 4 h) under reflux to form *cis*-$RhCl_2(OH_2)_4^+$. There is, nevertheless, no evidence for further loss of Cl^- to form either $RhCl(OH_2)_5^{2+}$ or $Rh(OH_2)_6^{3+}$ by means of the refluxing technique.

Several recent studies involving halorhodium(III) complexes have demonstrated the efficacy of aqueous Hg^{2+} ion as a catalyst for the aquation reaction. Thus, in the Hg(II)-catalyzed aquation of $Rh(NH_3)_5X^{2+}$ (where X = Cl or Br), the process exhibits[3,4] simple second-order kinetics, at least when [Hg(II)], although greatly in excess of [Rh(III)], is relatively low. However, when X = I, a limiting rate is approached at the higher Hg(II) concentrations,[4b] which the authors explained in terms of an associative mechanism involving the formation of the species $[Rh(NH_3)_5IHg]^{4+}$ as an intermediate. Subsequent work by the same investigators[5] has dealt with complexes of the type *trans*-$Rh(am)_4Cl_2^+$, where am = NH_3, pyridine, or $^1/_2$ ethylenediamine. Again, an associative intermediate is proposed, which in this case takes the form $[Rh(am)_4Cl_2Hg]^{3+}$, and the rate studies indicate that the mercury-induced replacement of the first chloride by water occurs very much more rapidly than that of the second. The purpose of the present study is to find out to what extent Hg(II) can effectively catalyze a stepwise aquation of the extremely stable neutral species *fac*-$RhCl_3(OH_2)_3$ and to determine the kinetics and possible mechanisms of the various reactions involved.

Experimental Section

All chemicals used were of reagent grade and were used without further purification. K_3RhCl_6 was prepared by heating powdered rhodium metal mixed with potassium chloride in a stream of Cl_2 at 750 °C, as suggested by Ayres and Young.[6] The spectrum of the compound formed agreed exactly with that reported by Wolsey.[7] *fac*-$RhCl_3(OH_2)_3$ was prepared by a method similar to that of Palmer and Harris.[1] Refluxing K_3RhCl_6 for 30 min in 0.2 M $HClO_4$ solution gives mainly the *fac* trichloro complex. The solution is then fed into an 80-cm ion-exchange column containing a mixed-bed resin composed of equivalent amounts of anion-exchange resin in the ClO_4^- form, Bio-Rad 1 X8 (200–400 mesh), and protonated cation-exchange resin, Bio-Rad 50W-X8 (200–400 mesh). The temperature of the column is maintained at approximately 2 °C by passing ice-cold water through a water jacket surrounding the column. Elution with a weak perchloric acid solution (pH 3.5) results in the development of two bands in the column. The first of these, which occupies the initial 4-cm portion, remains more or less fixed during further elution. The lower portion of the second band is eluted and discarded. The complex constituting the remainder of this band is then recovered by continued elution and its spectrum determined by means of a Cary Model 118 spectrophotometer. Peaks occur at the same wavelengths as those reported earlier[1] for *fac*-$RhCl_3(OH_2)_3$, with some small differences found in the molar extinction coefficients.[8] Analysis of the complex showed that the average Cl:Rh ratio was 3.00.[9] Mercury(II) perchlorate solution was prepared by dissolving HgO in an excess of $HClO_4$, and the solution was standardized with thiocyanate.[10]

Three separate product species were readily identifiable spectrophotometrically by means of the Cary 118 instrument as *cis*-$RhCl_2(OH_2)_4^+$, $RhCl(OH_2)_5^{2+}$, and $Rh(OH_2)_6^{3+}$, since the rates of the stepwise Hg(II)-catalyzed aquations are so widely separated (see data to follow). Also, complete scans of the spectral changes during any one step of the aquation exhibit persistent isosbestic points for at least 4 half-times indicative of a single-stage reaction. The visible absorption spectra of the three successive species involved in the process agree well with the findings of earlier studies in our laboratory.[11]

Kinetic data were obtained by following the spectral changes in the presence of excess Hg^{2+} at a wavelength appropriate to a given step in the reaction,[12] using either the Cary 118 or a Beckman DU spectrophotometer fitted with a Gilford digital readout attachment. These measurements were generally made "in situ" using a channeled metal-block cell holder through which water was circulated from an external thermostat, although for the slow reactions carried out at temperatures above 60 °C a successive sampling technique was satisfactory. Temperature control was always within ±0.1 °C. The ionic strength was fixed at 3.0 M and the acid concentration at 2.0 M, using appropriate mixtures of $LiClO_4$ and $HClO_4$. Under the various experimental conditions established for each step of the aquation, pseudo-first-order kinetics were always obeyed over at least 2 half-times of reaction. The observed rate constants, k_{obsd}, were evaluated from conventional $\ln(D_t - D_\infty)$ vs. time plots, where D_t is the observed absorbance at time t and D_∞ is the known final absorbance at the chosen wavelength of the pure product species for that step of the process.[12]

Results and Discussion

The kinetics data are presented in Tables I–III. It is noted that for all three successive reactions, k_{obsd} is *not* proportional

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Table I. Mercury(II)-Catalyzed Aquation of *fac*-$RhCl_3(OH_2)_3$

A. Rate Variation as a Function of $[Hg^{2+}]^a$

$10^2[Hg^{2+}]$, M	1.20	1.80	3.00	4.80	6.00	8.00
$10^4 k_{obsd}$, s^{-1}	9.67	11.3	12.8	13.4	14.0	14.3

B. Rate Variation as a Function of Temperature^b

T, °C	10.0	15.0	20.0	25.0
$10^4 k_{obsd}$, s^{-1}	3.07	5.70	9.67	17.9
$10^4 k_1$, s^{-1}	4.9	9.2	15.6	28.8

$\Delta H_1{}^{\ddagger} = 19.0 \pm 0.4$ kcal mol^{-1}
$\Delta S_1{}^{\ddagger} = -6.4 \pm 1.5$ cal deg^{-1} mol^{-1}

^{a} $t = 20$ °C, [complex] = 1.20 mM. ^{b} [complex] = 1.20 mM, $[Hg^{2+}] = 12.0$ mM.

Table II. Mercury(II)-Catalyzed Aquation of *cis*-$RhCl_2(OH_2)_4{}^+$

A. Rate Variation as a Function of $[Hg^{2+}]^a$

$10^2[Hg^{2+}]$, M	0.967	1.45	1.93	2.42	2.90
$10^6 k_{obsd}$ at 40.0 °C, s^{-1}	3.81	5.46	6.94	8.47	9.87
$10^6 k_{obsd}$ at 50.0 °C, s^{-1}	13.1		23.5	28.6	33.3

B. Rate Variation as a Function of Temperature^b

T, °C	30.0	40.0	45.0	50.0
$10^6 k_{obsd}$, s^{-1}	1.24	3.81	7.08	13.1
$10^5 k_2$, s^{-1}	1.4	4.3	8.0	14.8

$\Delta H_2{}^{\ddagger} = 22.2 \pm 0.7$ kcal mol^{-1}
$\Delta S_2{}^{\ddagger} = -7.5 \pm 2.2$ cal deg^{-1} mol^{-1}

^{a} [complex] = 0.967 mM. ^{b} [complex] = 0.967 mM, $[Hg^{2+}] =$ 9.67 mM.

Table III. Mercury(II)-Catalyzed Aquation of $RhCl(OH_2)_5{}^{2+}$

A. Rate Variation as a Function of $[Hg^{2+}]^a$

$10^2[Hg^{2+}]$, M	1.95	2.93	3.90	5.93	7.58
$10^5 k_{obsd}$ at 60.0 °C, s^{-1}	0.750	1.08	1.42	2.07	2.46
$10^5 k_{obsd}$ at 70.0 °C, s^{-1}	2.31		4.30	6.41	7.95

B. Rate Variation as a Function of Temperature^b

T, °C	50.0	55.0	60.0	70.0
$10^6 k_{obsd}$, s^{-1}	2.50	4.41	7.50	23.1
$10^5 k_3$, s^{-1}	4.5	8.0	13.6	41.8

$\Delta H_3{}^{\ddagger} = 23.8 \pm 0.3$ kcal mol^{-1}
$\Delta S_3{}^{\ddagger} = -5.0 \pm 0.9$ cal deg^{-1} mol^{-1}

^{a} [complex] = 0.976 mM. ^{b} [complex] = 0.976 mM; $[Hg^{2+}] = 19.5$ mM.

to $[Hg^{2+}]$ but in fact tends to approach a maximum at the highest mercury(II) concentrations. This behavior is assumed to be indicative of a mechanism involving reactant association followed by an interchange of H_2O for $HgCl^+$, as follows:[13]

$$fac\text{-}RhCl_3(OH_2)_3 + Hg^{2+} \overset{K_1}{\rightleftharpoons} RhCl_3(OH_2)_3{\cdot}Hg^{2+} \xrightarrow{k_1} cis\text{-}RhCl_2(OH_2)_4{}^+ + HgCl^+ \quad (1)$$

$$cis\text{-}RhCl_2(OH_2)_4{}^+ + Hg^{2+} \overset{K_2}{\rightleftharpoons} RhCl_2(OH_2)_4{\cdot}Hg^{3+} \xrightarrow{k_2} RhCl(OH_2)_5{}^{2+} + HgCl^+ \quad (2)$$

$$RhCl(OH_2)_5{}^{2+} + Hg^{2+} \overset{K_3}{\rightleftharpoons} RhCl(OH_2)_5{\cdot}Hg^{4+} \xrightarrow{k_3} Rh(OH_2)_6{}^{3+} + HgCl^+ \quad (3)$$

Since each step in the process is observable separately and $[Hg^{2+}]$ is in considerable excess, the observed rate constant for each is given by an expression of the form

$$k_{obsd} = kK[Hg^{2+}]/(1 + K[Hg^{2+}]) \quad (4)$$

A double-reciprocal plot of $1/k_{obsd}$ vs. $1/[Hg^{2+}]$ should yield a straight line of slope $1/kK$ and intercept $1/k$, enabling determination of each of the constants. Typical plots of data from Tables IA–IIIA are given in Figure 1 and are seen to be satisfactorily linear. The values for the various k's and K's determined in this manner are recorded in Table IV, together with their standard deviations. It is noted that the K values for the second and third steps are independent of the temperature within experimental error, and similar behavior can be assumed for K_1.[14,15] Using these K values, we may calculate by use of eq 4 the various k_i's from the k_{obsd} data obtained at other temperatures, as shown in Tables IB–IIIB. These k_i values can then be treated in the conventional manner to yield the $\Delta H_i{}^{\ddagger}$ and $\Delta S_i{}^{\ddagger}$ data, also shown in Tables IB–IIIB.

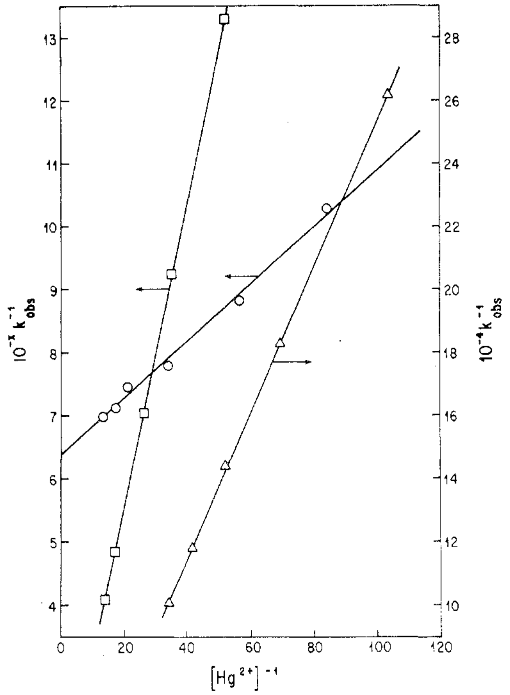

Figure 1. Double-inverse plot of rate data for mercury(II)-catalyzed aquation of some chloroaquorhodium(III) complexes: (○) *fac*-$RhCl_3(OH_2)_3$, left-hand ordinate (x = 2), 20 °C; (△) *cis*-$RhCl_2(OH_2)_4{}^+$, right-hand ordinate, 40 °C; (□) $RhCl(OH_2)_5{}^{2+}$, left-hand ordinate (x = 4), 60 °C.

Table IV. Association and Rate Constants for the Mercury(II)-Catalyzed Aquation of Chloroaquorhodium(III) Complexes

complex	T, °C	k_i, s^{-1}		K_i, M^{-1}
fac-Cl_3	20.0	$(15.7 \pm 0.2) \times 10^{-4}$		137 ± 5
cis-Cl_2	40.0	$(4.7 \pm 0.3) \times 10^{-5}$		9.1 ± 0.5
	50.0	$(13.8 \pm 1.1) \times 10^{-5}$		10.8 ± 0.9
			av	10.0 ± 1.0
Cl	60.0	$(12.6 \pm 1.6) \times 10^{-5}$		3.2 ± 0.4
	70.0	$(46.0 \pm 9.3) \times 10^{-5}$		2.7 ± 0.5
			av	3.0 ± 0.6

One can now make a specific rate comparison by means of the three sets of rate parameters at a selected reference temperature. The magnitudes of the k_i's at 40 °C as taken from Table IIB for the dichloro complex and as calculated from the tabulated $\Delta H_i{}^{\ddagger}$ and $\Delta S_i{}^{\ddagger}$ values for the other two are $k_1 = (10.7 \pm 0.4) \times 10^{-3}$, $k_2 = (4.3 \pm 0.3) \times 10^{-5}$, and $k_3 = (8.9 \pm 1.8) \times 10^{-6}$ s^{-1}, for a ratio of 1200:5:1. When the largely temperature-independent association constants K_i are included, the second-order limiting rate constants at low $[Hg^{2+}]$ are even more widely divergent. Thus, the ratio of k_iK_i values at 40 °C is 55000:16:1, although the corresponding falloff in the K_i values is much less pronounced, dropping only from 137 to 10 to 3 (see Table IV). These values are, in fact, reasonably in agreement with simple Coulomb law prediction on the following grounds. One can visualize the aquated Hg^{2+} ion as being symmetrically disposed relative to the electronegative chloride ligands in all three types of associated reactant pairs. Further, the effective charge on the segment of the chlororhodium complex ion adjacent to the Hg^{2+} ion should not be assumed to have the appropriate formal charge for the tri-, di-, and monochloro complexes of 0, 1+, or 2+ but some value intermediate between this formal charge and the total negativity of the cis chloride ligands. Assuming this value to be one unit less than the total available negativity, one arrives at charge values of 2–, 1–, and 0 for the three complexes, each in close association with the compact mercuric ion of charge 2+. On this basis, electrostatic theory[16] predicts K_i values of 170, 10, and 0.5, respectively, assuming a value of 5 Å for the distance of closest approach of each pair of associating rectants. While this rough method of estimation cannot of course be expected to lead to exact agreement with observation, it is sufficiently close to support the concept of essentially Coulombic chlororhodium(III) complex/mercury(II) pairing. However, some incipient directional chemical bond formation must contribute, to account for the fact that the entering Hg^{2+} ion is symmetrically related to each of the available chloride ligands.

The sharp decrease in the k_i values continues the trend in uncatalyzed aquation rates as noted for more highly chlorinated members of the same series of chloroaquo complexes. Thus, the first-order aquation rate constants for $RhCl_6^{3-}$, $RhCl_5(H_2O)^{2-}$, and *cis*-$RhCl_4(H_2O)_2^-$ are in the ratio[18] at 40 °C of 325:7:1. Though the trend is not quite as marked between the first and second species in this series as in our present study, it still exhibits the strong accelerative influence of the presence of additional Cl^- ligands on Rh–Cl bond fission. This is clearly related to the decreased positivity of the Rh(III) center, as well as to the trans effect of the remaining Cl^- ligands, and is fully consistent with the proposed dissociative mechanism[1] as recently supported by independent pressure-effect studies.[19] Though the chloride trans effect is absent in the Hg(II)-catalyzed reactions, it may be thought of as being replaced by incipient Hg–Cl bond making as a contributor to Rh–Cl bond weakening. The temperature parameters we record in Tables I–III are in keeping with this concept. There are almost constant negative $\Delta S^{\ddagger}$ values of about –6 cal deg^{-1} mol^{-1}, indicative of very similar bonding and solvation-shell rearrangements in forming the transition state. However, there are significant increases in $\Delta H^{\ddagger}$ as the number of Cl^- ligands is decreased, indicative of a strengthening of the Rh–Cl bond in the successive transition states.

Some interesting parallels may be drawn by comparison of our data with the published data concerning the haloaminerhodium(III) Hg(II)-catalyzed aquation reactions. It has been observed, for example, that the chloropentaammine species exhibits no kinetic evidence for formation of an identifiable Hg(II) complex reaction intermediate.[3,4a] Our work shows that the association constant may be quite small for a monochloro complex (~3 M^{-1}) and would therefore not cause appreciable deviation from second-order kinetics unless [Hg^{2+}] is pushed well above 0.03 M, which was not done in either of the referenced studies. Significantly, as has already been mentioned, for *trans*-$Rh(NH_3)_4Cl_2^+$ the constant K also has a relatively low value (~2.5 M^{-1}), which was rendered observable by varying [Hg^{2+}] to as high as 0.2 M in the rate studies.[5] One notes that it appears to make little difference to the magnitude of the stability constant of the associative intermediate whether water (as in the pentaaquo species) or chloride (as in the trans dichloro complex) is the trans ligand. But there is a large difference in the rate constants for the subsequent dissociative interchange of water for the $HgCl^+$ entity, the magnitudes at 40 °C being ~10^{-5} s^{-1} (as quoted above) and[5] ~2×10^{-2} s^{-1}. This is in keeping with expectation since the kinetic trans effect of chloride ligand in other substitution reactions of rhodium(III) complexes is usually greater than that of water by a factor of several thousand.[2] Once the trans chloride is replaced by water, however, the remaining chloride is much more difficult to remove, even with the help of Hg^{2+} catalysis as has been noted experimentally.[5] By contrast, although the data are anything but conclusive,[20] it is claimed that the rates of the two successive steps in the uncatalyzed aquation of *trans*-$Rh(en)_2Cl_2^+$ ion are of the same order of magnitude. However, for *trans*-$Co(en)_2Cl_2^+$, the ratio of the rates of uncatalyzed aquation for successive loss of Cl^- at 25 °C is approximately 14, while for the corresponding Hg^{2+} promoted process, the rate ratio is about 300.[21]

The complex ion $Rh(NH_3)_5I^{2+}$, unlike its chloride analogue, does form an associative complex with Hg^{2+} which has a large formation constant (~200 at 25 °C).[4] This fact can possibly be ascribed to the increased "softness" of the iodide ligand as a Lewis base as compared to the "softness" of chloride. There is in consequence a much greater degree of incipient mercury-to-iodide chemical bond formation than is possible for the relatively "hard" chloride, for which the binding in the associative complex is, to a considerable extent at least, Coulombic, as pointed out above.

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Registry No. Hg^{2+}, 14302-87-5; *fac*-$RhCl_3(OH_2)_3$, 54595-36-7; *cis*-$RhCl_2(OH_2)_4^+$, 37498-46-7; $RhCl(OH_2)_5^{2+}$, 15696-62-5.

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(12) The wavelengths selected and the corresponding molar extinction coefficients were as follows: step 1, 500 nm, ϵ(trichloro) 68.0, ϵ(dichloro) 37.7; step 2, 480 nm, ϵ(dichloro) 50.5, ϵ(monochloro) 22.1; step 3, 450 nm, ϵ(monochloro) 48.2, ϵ(hexaaquo) 26.9.
(13) No allowance is made for a parallel uncatalyzed reaction since our preliminary experiments (mentioned in the introduction) show that even for the trichloro species uncatalyzed aquation is negligibly slow.
(14) A small temperature coefficient for these constants is to be expected since, as discussed below, the bonding is probably of a relatively weak "nonchemical" type.
(15) It is of interest that a similar absence of temperature dependence for K has been noted[5] for the Hg(II)-catalyzed aquation of both *trans*-$Rh(NH_3)_4Cl_2$ and *trans*-$Rh(en)_2Cl_2^+$ and that in both instances $K \approx$ 2.5 M^{-1}, close to our value of 3.0 M^{-1} for the pentaaquochloro species (Table IV).
(16) This estimate is based on use of the well-known equation for the equilibrium constant for complex formation between species A and B in a fluid system but not involving "true" chemical bonding,[17] viz., $K = (4\pi a^3 N_0/3000)$ $\exp(Z_A Z_B e^2/\epsilon k T a)$, where Z_A and Z_B are the magnitudes of the charges

on A and B, ϵ is the dielectric constant of the fluid, a is the distance of closest approach of A and B, and the other constants have their usual meanings.

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Photochemical and Thermal Reactions of Tris(acetylacetonato)chromium(III) in Water–Ethanol Solution

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Irradiation of 50% v/v water–ethanol solutions of Cr(acac)$_3$ at 16 wavelengths between 230 and 730 nm leads to replacement of one acetylacetonate ligand by two water molecules. The photoproduct is cationic, neutral, or anionic depending on solution pH and was characterized by absorption spectra, chemical analysis, ion exchange, and conductivity. The photoaquation quantum yields are pH independent between pH 0 and pH 13, are wavelength independent between 350 and 730 nm, and are atypically low for a Cr(III) complex ($\phi \approx 0.01$). A fourfold increase in quantum yield is observed upon 250-nm excitation, with no evidence for redox processes. The system is photochromic, as photoinduced acetylacetonate labilization is opposed by thermal anation of acetylacetone, and photostationary states can occur. The results are interpreted in terms of two distinct reactive excited states: a relatively unreactive ligand field (LF) state and a higher energy ligand-localized (LL) state.

Introduction

The remarkable stability,[1] the well-characterized structural properties,[2] absorption[3] and emission[4] spectra, and the variety of electronic transitions make tris(acetylacetonato)chromium(III) especially interesting from a photochemical point of view.[5] Previous investigations of Cr(acac)$_3$ and of other, variously substituted, β-diketonatochromium(III) chelates have focused on photoisomerization[6,7] and on partial photoresolution.[8-12] These studies, however, have been performed in organic, noncoordinating media such as hexane,[6,7] benzene,[10] and chlorobenzene,[8,9,12] where only intramolecular processes (either twisting or bond rupture and recoordination) are possible.

An understanding of the photochemical behavior of Cr(acac)$_3$ in a coordinating solvent is important for a number of reasons. (i) The solvent is thought to play a crucial role in the photochemical reactivity of many Cr(III) complexes,[13] so studies in noncoordinating solvents exclude an important reactant. (ii) The exceptional inertness[1] and extensive π-electron system[1-3] of the acetylacetonato ligand introduce factors which are rather unusual in photochemical studies of chromium(III).[13] (iii) The diversity of the absorption spectrum gives access to several types of electronic excitation, corresponding to ligand field (LF), charge-transfer (CT), and ligand-localized (LL) transitions.[5] Selective irradiation may yield some insight into the relative photochemical importance of the different excited states involved. (iv) The photochemical reactivity of Cr(acac)$_3$ can then be compared to the patterns established for the β-diketonates of other first-row transition metals, such as iron(III),[14] cobalt(III),[15] nickel(II),[16] and copper(II).[17] To date only qualitative observations have been reported on the photolysis of three β-diketonatochromium(III) complexes in alcoholic solvents, and only upon 254 nm irradiation.[5,18]

Experimental Section

Materials. Cr(acac)$_3$ was prepared and recrystallized following a described procedure.[19] The principal maxima of its absorption spectrum in 50% v/v water–ethanol solution are observed at 730 (sh, ϵ 0.4), 558 (68), 413 (sh, 200), 390 (435), 383 (440), 332 (16 700), and 257 nm (12 200) (Figure 1), in agreement with literature values.[3] [Co(NH$_3$)$_5$F](NO$_3$)$_2$ was obtained by a standard method.[20] Other chemicals and solvents were of reagent grade.

Analytical Methods. Free acetylacetone was determined spectrophotometrically, by use of a 0.02 M solution of *o*-phenylenediamine in 1 M HClO$_4$.[21] To an aliquot of the reaction mixture an equal volume of the reagent solution was added, and the optical density was measured at 490 nm (ϵ 840) after at least 10 min. At this wavelength the absorbance of Cr(acac)$_3$ is relatively low (ϵ 20.5). Standardization plots were linear in the 10^{-3}–10^{-5} M range. The reproducibility was not affected by the presence of the complex, up to at least 1 h after mixing. When Cr(acac)$_3$ was photolyzed in the presence of Co(NH$_3$)$_5$F^{2+}, Co^{2+} was analyzed spectrophotometrically at 625 nm (ϵ 1850) by the thiocyanate–acetone method.[22]

Optical densities of solutions were measured with a Beckman DU, and absorption spectra were recorded with either a Beckman DB or Cary 17 spectrophotometer. A glass microelectrode (Schott Model U 9258/81) immersed in the spectrophotometer cell and an Orion 801 digital potentiometer were used for pH determination. Electrical conductivity was measured with a Halosis S–Au bridge. Ion-exchange studies were performed with 4 × 1 cm columns by use of either Sephadex SP-C25 cationic resin in the proton form or Amberlite IRA-900 anion exchanger in the hydroxide form. Columns were preconditioned with 50% v/v water–ethanol mixtures before the photoproduct solution was loaded. Elution was with 50% v/v water–ethanol, HClO$_4$, or NaOH solutions.

Procedures. The general photolysis apparatus has been described previously.[23] Light sources consisted of either a 500-W, high-pressure Xe lamp or a 200-W, high-pressure Hg lamp. Irradiation wavelengths were selected by means of either Baird Atomic interference filters, which gave bands of ca. 10-nm half-width, or a Baush & Lomb high-intensity grating monochromator. The 254-nm radiation was obtained by filtering the emission of a Minerallight UVSL-25 lamp through 2 cm of CoSO$_4$- and NiSO$_4$-saturated solution. Light intensities were about 2×10^{-8} and 2×10^{-9} einstein s^{-1}, respectively, and were either continuously monitored by a thermopile[23] or measured using the reineckate[24] and ferrioxalate[25] actinometers. The actual absorbed energy was determined as described elsewhere.[26]

Solutions of Cr(acac)$_3$ in 50% v/v water–ethanol were photolyzed in thermostatted, standard spectrophotometer cells under continuous magnetic stirring. Complex concentrations ranged from 10^{-2} M (for

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