zero-order AOM orbital energies can be used to show that the trans → cis barrier on $^3A'$ should be nearly the same as the $\Lambda \rightleftarrows \Delta$ barrier on $^3A''$.)

Both σ and π ligand properties may be selected to cause a low lying $^3A''$ state and photoracemization. Figure 1c illustrates the effect of $e_\pi^{A} > e_\pi^{X}$ (A is a π donor and X is a π acceptor). The σ effect arises from $(z^2)/(x^2 - y^2)$ mixing and electron-repulsion energies. $e_\sigma^{X} \neq e_\sigma^{A}$ is required for $(z^2)/(x^2 - y^2)$ mixing; the perturbed (z^2) MO, which always lies lower than the $(x^2 - y^2)$ MO, has the form $(z^2) + \lambda(x^2 - y^2)$. As $\lambda <$ or > 0 the (z^2) torus becomes ellipsoidal, with the major axis along the y or x axis, respectively. Thus $\lambda > 0$ results in less electron repulsion for the $^3A''$ than $^3A'$ state. First-order perturbation theory may be used to show that $\lambda > 0$ whenever the off-diagonal Hamiltonian element between (z^2) and $(x^2 - y^2)$ is negative. This requirement is met whenever $e_\sigma^{X} > e_\sigma^{A}$, as in Figure 1b (note that the σ effect overides the fact that $e_\pi^{X} > e_\pi^{A}$ in this case).

Theoretical Methods

The computational technique used is the same as that used by V/C, by one of us previously,[4] and by others.[5] In short, the AOM approximation to the full, one-electron Hamiltonian matrix is established for structures along the reaction coordinate, in a basis of metal d and ligand σ and π orbitals. Diagonalization of this matrix produces a basis of one-electron MO's and energies. The latter serve as a basis for construction of Slater determinants for *all* d^6 configurations possible. This basis is made diagonal under the S^2 operator, and a full CI calculation is performed with Racah B and C parameters to include state mixing by electron repulsion forces. The results are presented in terms of orbital and state correlation diagrams.

As the purpose of this study was limited to investigation of relative A and X σ- and π-bonding effects on the triplet-state surface characteristics, we have utilized a range of the AOM e_σ and e_π parameters so as to encompass a variety of M/A/X combinations. These values (in μm^{-1}) are $(0.5 \leq e_\sigma^{A} \leq 1.16)$, $(0 \leq e_\pi^{A} \leq 0.1)$, $(0.5 \leq e_\sigma^{X} \leq 1.16)$, and $(-0.1 \leq e_\pi^{X} \leq 0.1)$. These values include those of V/C for NH_3 ($e_\sigma = 1.14$, $e_\pi = 0$) and for Cl^- ($e_\sigma = 0.86$, $e_\pi = 0.14$). The nominal values for B and C of 0.035 and 0.14, respectively, were used.[6]

Experimental Methods

The *trans*-$[Co(en)_2(CN)Cl]Cl$ complex was prepared by a previously reported procedure.[7] The *trans*-$[Co(en)_2(CN)(H_2O)^{2+}$ ion was prepared by the addition of perchloric acid to *trans*-$[Co(en)_2(CN)(OH)]Cl$.[7] The stereochemistry of the *cis*-$[Co(en)_2(CN)(H_2O)]^{2+}$ photolysis product was confirmed by electronic absorption spectroscopy[8] and ^{13}C NMR spectroscopy by using techniques previously described.[9,10] The trans starting materials show only one carbon peak in the ethylenediamine region, while the cis product shows four nonequivalent ethylenediamine carbon atoms.

Photolysis reactions utilized the 488-nm (1.5-W) line of a Spectra-Physics argon-ion laser and procedures previously described.[11] Usable light intensities were determined by using Reineckate actionometry.[12]

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Registry No. *trans*-$Co(en)_2(CN)Cl^+$, 51321-29-0; *trans*-$Co(en)_2(CN)(H_2O)^{2+}$, 19414-12-1; *cis*-$Co(en)_2(CN)(H_2O)^{2+}$, 45978-53-8.

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The 254-nm Photochemistry of the Rhodo Chromium(III) Complex: Observation of New Photosubstitution Reactions

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The thermal reactions of the binuclear rhodo chromium(III) complex $[Cr(NH_3)_5OHCr(NH_3)_5]^{5+}$ and the related aquo erythro $[Cr(NH_3)_5OHCr(NH_3)_4OH_2]^{5+}$ and chloro erythro $[Cr(NH_3)_5OHCr(NH_3)_4Cl]^{4+}$ complexes have been extensively investigated.[1,2] In acidic solution the bridge in the rhodo ion is cleaved to produce $Cr(NH_3)_5OH_2^{3+}$ in $HClO_4$ and $Cr(NH_3)_5OH_2^{3+}$ together with $Cr(NH_3)_5Cl^{2+}$ in HCl.

The photochemical reactions of the aquo and chloro erythro complexes, following excitation into the two lowest lying quartet excited states, traditionally labeled L_1 and L_2, have also been reported.[3] The photochemical reactions that were observed consisted solely of ligand substitution and isomerization processes that retained the binuclear structure of the initial complexes. Once the data were corrected for the thermal reaction, no bridge-cleavage products were obtained. We have recently studied the ligand field photochemistry of the rhodo complex in a variety of acid media.[4] Our findings parallel those obtained in ref 3 for the erythro complexes. No bridge cleavage is observed when the rhodo complex is excited into L_1 and L_2 over the temperature range 5–35 °C.

We report here a study of the 254-nm photochemistry of the rhodo ion in aqueous acid media and the observation of photoinduced bridge cleavage.

Experimental Section

The rhodo complex was prepared as the chloride salt according to the method of Linhard and Weigel.[5] Anal. Calcd for $[Cr(NH_3)_5OHCr(NH_3)_5]Cl_5 \cdot nH_2O$: mole ratio N/Cr = 5.00. Found: mole ratio N/Cr = 5.00. The chloride salt was converted to solutions of the nitrate and perchlorate salts by the addition of $AgNO_3$ and $AgClO_4$, respectively. The precipitated AgCl was removed by filtration. Subsequent tests showed no evidence of residual Ag^+ or Cl^- in the solutions. The absorption spectra and extinction coefficients of the rhodo ion were independent of the anion, in the L_1 and L_2 bands, and were in quantitative agreement with those published previously.[1,6]

Solutions were photolyzed in a Rayonet Model RPR-100 photochemical reactor equipped with 12 Rayonet RPR 1849-Å/2537-Å lamps. The output of these lamps is concentrated (>95% of the light into the cell) in the 254-nm Hg line. The solutions were contained in a thermostated, jacketed quartz photolysis cell which can be stirred during photolysis and purged with gas. In some experiments the solutions were put through several freeze–thaw cycles prior to irradiation and purged with N_2 during photolysis. Temperature control was good to ±1 °C.

Reaction products were ion exchanged by using Sephadex C-25 cation-exchange resin. The various cationic species were eluted with

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varying concentrations of $HClO_4$. Absorption spectra were run on a Cary 14 spectrophotometer. Chromium analyses were performed on all samples following oxidation to CrO_4^{2-} in basic peroxide.

Table I. Quantum Yields for the Products of the 254-nm Photolysis of $[Cr(NH_3)_5OHCr(NH_3)_5]^{5+}$ [a, b]

species	quantum yield (at $t = 0$)	species	quantum yield (at $t = 0$)
$Cr(NH_3)_5OH_2^{3+}$	0.021 ± 0.001	OH_2 erythro	0.179 ± 0.020
Cl erythro	0.087 ± 0.006	total erythro	0.266 ± 0.023

[a] $T = 5$ °C. [b] Initial moles of rhodo = 8.47×10^{-5} in all cases; solution 0.10 M in HCl.

Results

When the chloride salt of the rhodo ion, in 0.10 M HCl, is put through three freeze–thaw cycles to remove dissolved oxygen and then photolyzed at 254 nm at 5 °C, in an N_2 atmosphere, three products are obtained in the ion-exchange separation of the reaction mixture: the aquo and chloro erythro ions and the aquopentaamminechromium(III) ion. The quantum yields for three replicate experiments (initial rhodo, as chloride salt, 8.47×10^{-5} mol), corrected for the small amount thermal reaction at 5 °C, are presented in Table I. When the unreacted rhodo ion was also eluted and analyzed, an average of 98% of the chromium was recovered in the experiments summarized in Table I. Similar results are obtained when the rhodo ion is photolyzed in HCl solution with O_2 present and in HNO_3 and $HClO_4$ solutions ([acid] = 0.1 M) in both oxygenated and deoxygenated solutions. In the experiments in HNO_3 and $HClO_4$ solutions the rhodo complex was first converted to the nitrate and perchlorate salts, respectively. Under some experimental conditions a small amount of the chromium ends up as Cr(VI).[7]

The apparent quantum yield for the production of $Cr(NH_3)_5OH_2^{3+}$ from the rhodo ion is constant at 0.021 ± 0.001 for irradiation times up to 10 min, corresponding to 45% conversion of the starting complex. During this same time the ratio $\phi(Cr(NH_3)_5OH_2^{3+})/\phi(\text{erythro complexes})$ is constant at 0.088 ± 0.006 and the apparent quantum yield for the total production of the erythro complexes remains constant at 0.266 ± 0.023. During this same time period, the ratio of the apparent quantum yields for the individual erythro complexes $[\phi(\text{Cl erythro})/\phi(OH_2\text{ erythro})]$ varies from 0.48 at 2.5 min to 0.75 at 10 min. At longer times the ratio continues to rise, reaching 1.0 after 20 min of irradiation. In previous experiments on the L_1 photochemistry of the rhodo ion this latter ratio ranged from 0.0 at 1.5 min to 0.65 at longer times for similar conversion percentages.

Discussion

Several previous reports regarding ligand substitution reactions following excitation into the charge-transfer region of Cr(III) complexes have appeared in the past decade.[9-11] In those cases where two distinct photoaquation reactions were possible, it has been noted that the thermal reaction mode, which in the cases studied turns out to be the least probable photoreaction following excitation into L_1 and L_2, becomes more prominant upon excitation into the charge-transfer region. The observation of bridge-cleavage products following 254-nm excitation of the rhodo complex is another example of this phenomenon. In the reaction studied here, no thermal reaction mode products are observed following excitation into L_1 and L_2. The detection limits of our experiments are such that, if $Cr(NH_3)_5OH_2^{3+}$ is formed on L_1 or L_2 photolysis, its quantum yield is $\leq 10^{-4}$ of its yield following charge-transfer excitation.

The data reported here suggest a model in which essentially all of the photochemical reactions following 254-nm excitation of the rhodo ion arise from the charge-transfer state or the third quartet state, L_3 (this is the $^4T_1$ (^4F) state in *O* microsymmetry), which is buried under the lower energy edge of the charge-transfer band. In addition, any states which can be reached from the charge-transfer (CT) or L_3 states, but not from L_1 or L_2, could contribute to the observed photochemistry. Included in this latter set of states are highly excited vibrational levels of the ground electronic state. Other than the fact that the thermal reaction mode product is seen to become an important photoproduct following 254-nm excitation, there are currently no data which compel us to choose the "hot ground state" as the photoactive state. Quantum yield data as a function of excitation wavelength, over the range of wavelengths producing $Cr(NH_3)_5OH_2^{3+}$, would provide a more significant test of the "hot ground state" mechanism.

Hoppenjans, Hunt, and Penzhorn have shown that the bridge cleavage of the chloro erythro complex is catalyzed by Cr(II).[12] Since it is likely that the charge-transfer state in the rhodo complex involves a ligand to metal charge transfer, which may result in the formation of Cr(II), it is interesting to see if Cr(II)-catalyzed hydrolysis can account for the formation of $Cr(NH_3)_5OH_2^+$ in the experiments reported here. First of all, the proposed mechanism of Cr(II) catalysis of the chloro erythro complex involves formation of a Cl bridge to the Cr(II) and is thus not directly transferable to the rhodo complex. Recent experiments in ClO_4^- solutions show that the bridge-cleavage quantum yield is very similar to that in Cl^- media, ruling out an electron-transfer process involving chloro bridges. Second, the relatively low quantum yield for bridge cleavage does not demand that Cr(II) catalysis be invoked. Third, in none of our experiments is there any evidence for $Cr_2(H_2O)_8(OH)_2$, the product formed on air oxidation of Cr(II), or for any species such as $Cr(OH_2)_5Cl^{2+}$ or $Cr(OH_2)_6^{3+}$.

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Registry No. $[Cr(NH_3)_5OHCr(NH_3)_5]^{5+}$, 23329-46-6; $Cr(NH_3)_5OH_2^{3+}$, 15975-47-0; $[Cr(NH_3)_5OHCr(NH_3)_4Cl]^{4+}$, 48063-42-9; $[Cr(NH_3)_5OHCr(NH_3)_4OH_2]^{5+}$, 73465-00-6.

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Bis(η^8-1,3,5,7-tetramethylcyclooctatetraene) Compounds of Protactinium, Neptunium, and Plutonium

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Although many reports have appeared on the chemistry of the bis(cyclooctatetraene) complexes of uranium and thorium,[2]

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