of +7 and +6 for ferri- and ferrocytochrome *c*, respectively. We conclude that except possibly for high chloride concentrations binding phenomena do not interfere with our experiments.

The extent to which a dipole moment can influence a diffusion-controlled reaction with a negatively charged reactant has recently been calculated in a Brownian dynamics simulation study. When the active site is small compared to the total surface area of the protein, as is the case with cytochrome *c*, a line dipole (346 D) enhances the rate when the dipole vector pointed toward the active site, and this effect was also found at physiological ionic strength.[25] This study appears to be in qualitative agreement with the results reported here, although the reactions we studied are not diffusion-controlled.

It is remarkable that eq 1 fits the experimentally determined rate constants up to the highest ionic strength employed, while the Debye–Hückel theory breaks down above 0.1 M. We currently have no explanation for this phenomenon.

Conclusions

The data presented in this study suggest that the dipole moment of cytochrome *c* contributes to its reactivity at biologically significant ionic strength. The magnitude of this effect depends strongly on the charge of the mediator. Equation 1, proposed by Van Leeuwen et al.,[8] accounts quantitatively for this effect. Significantly, this equation requires substantial structural information about cytochrome *c* to predict the direction and magnitude of the ionic strength dependence. It seems possible that the kinetic ionic strength effect may be useful in elucidating the interaction sites of proteins about which less is known than cytochrome *c*.

Acknowledgment. Supported by Grant GM 33883 from the National Institutes of Health.

Supplementary Material Available: Table of rate constants for the reactions studied (3 pages). Ordering information is given on any current masthead page.

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Wavelength Dependence in the Ligand Field Photochemistry of Cobalt(III) Amines

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Contribution from the Chemistry Department, Concordia University, Montréal, Québec, H3G 1M8 Canada. Received July 28, 1986

Abstract: The low quantum yield ligand field excitation photosubstitution reactions of Co(III) amine complexes are shown to be plausibly interpretable as the superposition of two component reactions. The first is an excitation wavelength-independent process which is associated with the ligand field triplet which has figured strongly in discussion of photosubstitution of the analogous Rh(III) complexes. The second is a wavelength-dependent reaction which is associated with direct reaction from the ligand field singlet. This interpretation of wavelength dependence in conjunction with recent interpretations of the picosecond transient absorption spectra suggests a unified model of the photochemistry of d^6 complexes.

Adamson's introduction of the use of lasers to allow accurate evaluation of the quantum yields of inefficient photoreactions[1] initiated an era of precise evaluation of the low-yield photosubstitution pathways exhibited by Co(III) amine complexes irradiated in their ligand field bands. The results supported an earlier impression, that the large differences in quantum yield might imply a significant mechanistic difference between Co(III) amines and the other d^6 complexes such as Rh(III) or Cr, Mo, and W(0) systems where photosubstitution yields are relatively large. Recently, we have reported subnanosecond flash studies of selected Co(III) complexes which might lead us to an alternate view.[2] In these studies we found a transient absorbance which could be associated with a ligand field triplet with a short lifetime. A consistent kinetic scheme implies that the reactivity of the ligand field triplet of a Co(III) complex may be quite similar to that of a Rh(III) complex[3] and that the difference between the two is mainly in the increased (by about 2 orders of magnitude) rate of radiationless decay of the triplet. The existence of a closely spaced quintet[4] provides a mechanism for this enhanced radiationless decay, as Adamson has observed.

In contrast, some years ago it was established that the reactivity of certain Co(III) amines is lower when the triplet region of the spectrum is directly irradiated,[5] and we have recently shown that this is not an abrupt change of reactivity between the singlet and triplet regions but rather reflects a progressive decrease of the mode of reactivity which characterizes irradiation near the singlet maximum as one scans across the low-energy side of the singlet absorption band. The present report expands these observations to include several Co(III) complexes and proposes, for *future evaluation*, a model which might unify the "differing" patterns of photochemistry of d^6 systems. It is based on a wavelength-independent pattern of reactions arising from vibrationally equilibrated triplets and a wavelength-dependent reaction arising in the singlet which occurs on time scales close to vibrational and/or solvent relaxations.

Experimental Section

Materials. All starting materials were reagent grade commercial products used without further purification. Water was deionized and doubly distilled. Other solvents were spectrograde.

$[Co(NH_3)_5Cl](NO_3)_2$ was prepared following ref 6. It was characterized by the visible spectrum.[7] *trans*-$[Co(en)_2Cl_2]NO_3$ was prepared by Krishnamurthy's method.[8] The corresponding *cis*-dichloro isomer

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Table I. Quantum Yield for Photochemical Ligand Substitutions of $Co(NH_3)_5Cl^{2+}$ at 25 °C in Neutral Aqueous Solution with a 10-cm Cell^{d}

wavelength, nm	substituted ligand	laser power, mW	time, h	quantum yield (× 10^4)
488	Cl^-	200	2	16.7 ± 0.5^{a3}
				179.1 ± 1.2^{b}
	NH_3	200	2	55.0 ± 2.6^{a3}
				50.0^{b}
514	Cl^-			17.2 ± 1.0^{c}
	NH^3			50.7 ± 1.3^{c}
573	NH_3	200	2	20.9 ± 2.4^{a4}
600	Cl^-	125	2	12.8 ± 0.9^{a3}
	NH_3	125	2	23.6 ± 0.9^{a3}
622	Cl^-	80	2	10.9 ± 1.0^{a3}
	NH_3	80	2	9.1 ± 0.6^{a3}
647	Cl^-			9.6 ± 0.9^{c}
	NH_3			1.3 ± 0.4^{c}

[a] This work. [b] Pribush et al. (ref 16). [c] Langford and Vuik (ref 17). [d] Numbers in parentheses indicate the number of independent runs. The concentration of the complex is 0.01 M.

was prepared from the trans isomer by Blair's method.[9] The identity of the products was again confirmed by spectral comparisons.[10]

cis-$[Co(en)_2(NCS)Cl]NO_3$ was prepared by a modification of Werner's classic method.[11] Twenty grams of the trans isomer was dissolved in 30 mL of warm water, and a solution of 6.8 g of KNCS in 15 mL of water was slowly added with constant stirring. Gentle heating was applied until the resulting paste dissolved to produce a purple solution. This was placed in an ice bath for 2 h. Five grams of precipitate of the thiocyanate salt was collected. It was converted to nitrate by preparing a nearly saturated solution and adding concentrated HNO_3 to the solution at 0 °C. Spectra agreed with ref 12.

Photochemistry. Light intensity was measured at Ar ion laser wavelengths of 457, 488, and 514 nm as well as in the Rhodamine 6G dye laser region of 570–622 nm by the use of power meter techniques calibrated against reineckate actinometry as described by Kido and Langford.[13] Power meter readings were taken before and behind the cell and compared to readings taken before and behind the same cell filled with distilled water. The calculated absorbance values derived from power meter readings were in good agreement (1%) with those made by using conventional spectrophotometers. In order to minimize corrections for ligands released thermally, runs were normally conducted at 2–9 °C for the *trans*-dichloro and 2–6 °C for the *cis*-dichloro isomers. Runs on *cis*-chloroisothiocyanate were conducted at 0 °C. Solutions were usually prepared near the limit of ready solubility and then filtered through a 0.45-nm millipore filter. The solution was irradiated in a jacketed polarimetric cell with a volume of about 10.0 mL and a path length of 10.0 cm. In this cell, absorbance usually exceeded 1. Conversion was limited to less than 10% in all cases.

Analytical Procedures. Chloride ion release was measured by Hg(II) titration with 0.0160 M $Hg(NO_3)_2$ standardized against NaCl with diphenylhydrazine as indicator. Residual starting material was removed by ion exchange. Both photolyte and dark controls were passed through 7–8 g of Dowex HCl cation-exchange resin. The released chloride was washed from the column with 15 mL of distilled water.

Thiocyanate was determined by adding an aliquot of irradiated (or dark control) solution to a fourfold excess of reagent containing 0.100 M ferric nitrite in 0.5 M perchloric acid. The absorbance due to the resulting red complex was measured at 450 nm[14] (molar absorbance = 4.30×10^3).

Ammonia release was measured by the pH changes method of Riccieri and Schlafer.[15] Measurements were made with a four-digit precision pH meter fabricated in the Concordia science workshop. It was calibrated with acid solutions which closely surrounded the pH and ionic strength conditions of the samples. In the case of ethylenediamine complexes, the pH change measurements were taken to indicate "chelate ring opening" substitution reactions.

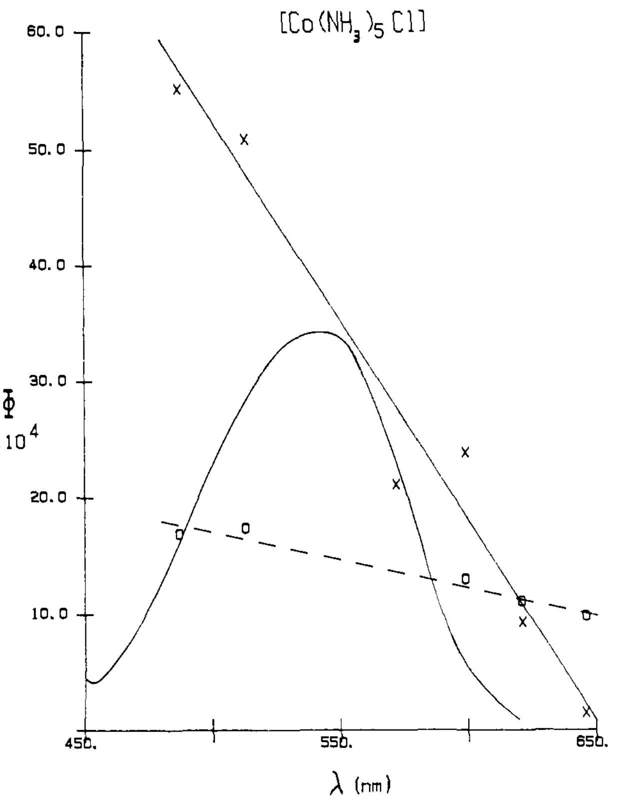

Figure 1. Quantum yield behavior for the photochemical ligand substitution of $Co(NH_3)_5Cl^{2+}$ at different irradiation wavelengths (X = ammonia substitution, O = chloride substitution).

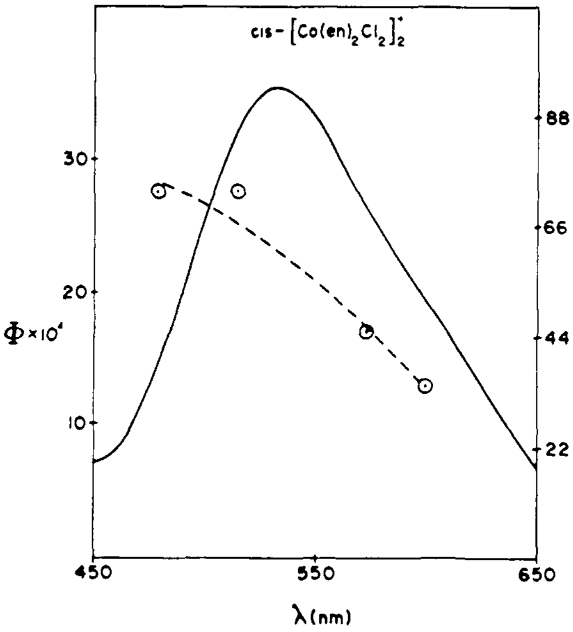

Figure 2. Quantum yield profile for photochemical Cl^- substitution vs. irradiation wavelengths for *cis*-$Co(en)_2Cl^{2+}$ (T = 2 °C).

Results

Photolysis of $Co(NH_3)_5Cl^{2+}$ ion was conducted at 25 °C since the thermal substitution rate constant is only 6.7×10^{-6} s^{-1} at this temperature and thermal blanks were small. The yields are collected in Table I. The table also includes the results from Pribush, Poon, and Adamson[1] and Langford and Vuik.[5] The results are plotted in Figure 1. Figures 2 and 3 show the wavelength dependence of chloride yields from *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III).

The results shown were demonstrated to be independent of concentrations of the complex ($3.4–5.7 \times 10^{-3}$ M) and laser intensity (180–270 mW). The yield for chelate ring opening as

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(9) Blair, J. C. *Inorg. Synth.* **1976**, *2*, 222.

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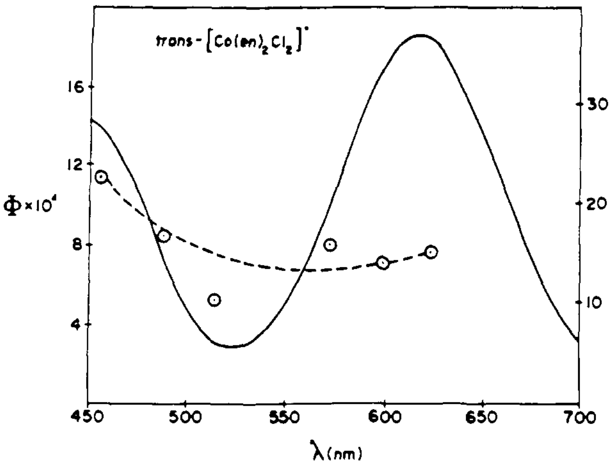

Figure 3. Quantum yield profile for photochemical Cl$^-$ substitution vs. wavelength for *trans*-Co(en)$_2$Cl^{2+} (T = 8 °C).

measured by the pH change was 4.8 × 10^{-4} for the cis isomer irradiated at 488 nm and 5.8 × 10^{-4} for the trans isomer. Thus, it is much smaller than the Cl$^-$ yield in the cis case whereas it is of the same order of magnitude as the Cl$^-$ yield in the trans case.

The quantum yields for *cis*-Co(en)$_2$(NCS)Cl$^+$ were measured at 488 and 600 nm. The 488-nm yields were 26 ± 2 × 10^{-4} for NCS$^-$ release and 4.3 ± 1 × 10^{-4} for Cl$^-$ release. Both were reduced at 600 nm. The NCS$^-$ yield was 12 ± 1 × 10^{-4}, and the Cl$^-$ yield was <1 × 10^{-4}.

The data exhibited the usual mix of ammine and halide substitution pathways. This paper will focus on halide pathways except in the case of Co(NH$_3$)$_5$Cl^{2+} because these are the ones for which we were able to characterize wavelength dependence.

Wavelength dependence is not a new feature of Co(III) photochemistry. In the redox-mediated reactions discussed by Endicott[16] which follow *charge-transfer* excitation, the changes of yield tend to respond to the solvent environment. In two recent accounts[17,18] of wavelength-dependent processes where chemical yields are determined to some degree by competition with vibrational relaxation, it has been emphasized that solvents play an important part. Thus, the solvent dependence of the wavelength-dependent reactions of *cis*-Co(en)$_2$Cl^{2+} was evaluated at 488 nm where the yield in water is sufficiently large to be sensitive. The Cl$^-$ yield in *N*,*N*-dimethylformamide is 4 ± 2 × 10^{-4} (compare 27 ± 3 × 10^{-4} in water). This yield declines to <1 × 10^{-5} in dimethyl sulfoxide. Figure 4 shows that this yield also responds to solvent viscosity as influenced by admixture of glycerol into water. Thus two solvent parameters, polarity and viscosity, have a role.

Temperature dependence of the 600-nm yields for both the wavelength-sensitive cis complex and the much less wavelength-sensitive trans complex was studied at 22 and 15 °C. The two do not differ significantly. The apparent activation energies are small in both cases and are not reliably distinguishable. The *trans*-dichloro isomer yields a value of 13.8 kJ/mol, *cis*-dichloro a value of 14.5 kJ/mol with an uncertainty of ±0.6 kJ/mol. These values are similar to those reported for analogous Rh(III) complexes by Rumfeldt and Sellan,[19] who pointed out that the values were close to activation energies for an elementary step of translational diffusion. Thus, apparent barriers are not large enough to be given specific interpretation.

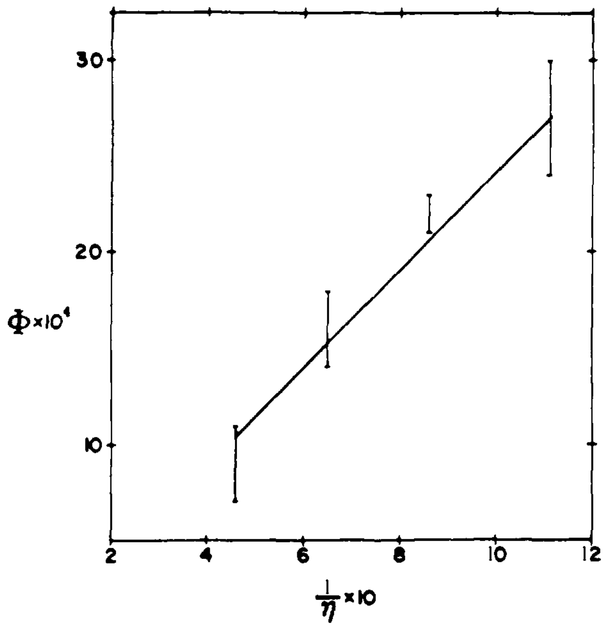

Figure 4. Relationship between the quantum yield for the photosolvolysis of *cis*-Co(en)$_2$Cl^{2+} in a water–glycerol mixture and the viscosity coefficient (η) in cp.

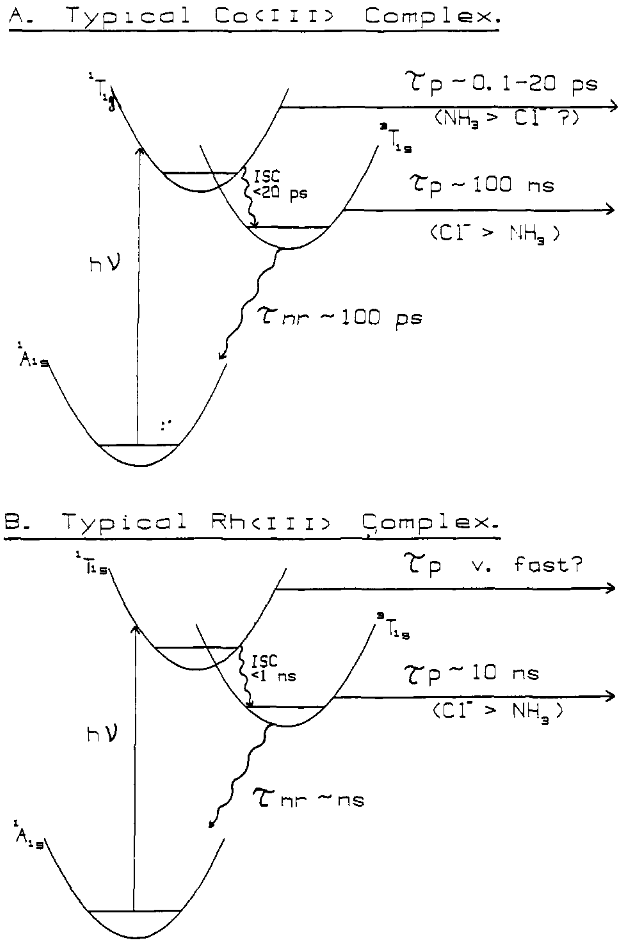

Figure 5. Reactions from $^1T_1$ are wavelength dependent and readily observed only in Co(III), where the yield from $^3T_1$ is small. In Rh(III), only yields from $^3T_1$, which are relatively large, are observed. In the figure, τ_p represents a characteristic time for product formation, τ_{nr} is nonradiative decay, and ISC represents intersystem crossing.

Discussion

Two Pathways. When irradiation (at 647 nm) of the presumed triplet regions of the spectra of Co(NH$_3$)$_6^{3+}$ and Co(NH$_3$)$_5$Cl^{2+} was first reported,[5] it was apparent that a large part of the NH$_3$ aquation yield arose from a precursor of the triplet since the amine yield, which was the major yield at 488 and 514 nm, became minor at 647 nm. The data in Table I extend the early results as has

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been partly reported in our preliminary communication.[20] The data show that yields for amine substitution approach zero as the low-energy end of the singlet absorption band is approached. In contrast, although Cl^- yields decrease, the change is less than a factor of 2, and the limit at the end of the singlet band is unambiguously distinguishable from zero. Assuming that 647-nm irrdiation did directly populate the triplet, we can summarize the reaction as shown in Figure 5, because the yields in the singlet region all exceed those for the triplet limit.

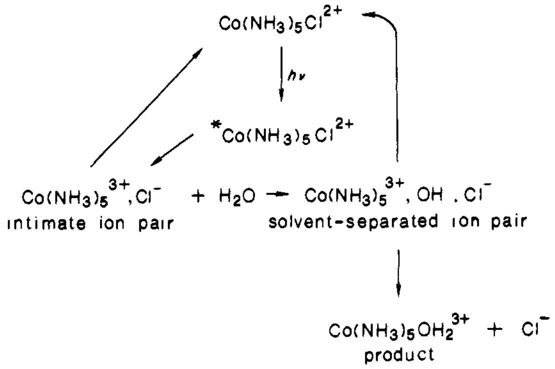
Figure 5 presents a very attractive general hypothesis for discussion of all the results. An analogue of Figure 5 can be applied to *cis*-$Co(en)_2Cl^{2+}$ by postulating a significant singlet pathway for Cl^- aquation. However, in the case of *trans*-$Co(en)_2Cl^{2+}$, the yield for Cl^- across the singlet LF region could be taken as constant within experimental error and does not require postulation of a pathway distinct from that via the triplet. (The increase in yield for *trans*-dichloro at 457 nm may reflect the onset of change-transfer excitation.) Notice that the yield is very similar to the long-wavelength limit approached for Cl^- yields in the other two cases. This hints that triplet yields for Cl^- are nearly constant in this set of complexes. *cis*-$Co(en)_2(NCS)Cl^+$ may have a triplet pathway for NCS^- loss but apparently not for Cl^- loss. The yield for Cl^- loss becomes small before the triplet is reached.

Triplet Pathway. Picosecond spectroscopy on Co(III) complexes containing a ligand permitting a metal to ligand π^* ($d - \pi^*$) transition revealed transient absorbance which indicated that the lifetime of a ligand field triplet is of the order of 50–150 ps. If we assume that the values for Cl^--containing complexes are similar, and that ISC yields are in the range 0.1–1, we can estimate the rate of reaction from the triplet. The quantum yield for reaction from the triple, ϕ, is given as eq 1, where ϕ' is the yield for

$$\phi = \phi' \frac{k_p}{k_p + k_{nr} + k_r} \qquad (1)$$

intersystem crossing (ISC), k_p is the rate constant for reaction to product, k_{nr} is the nonradiative decay rate constant, and k_r is the radiative rate constant. In the case of $Rh(NH_3)_5Cl^{2+}$[3] some representative values are $\phi = 0.18$, $\phi' = 1$, $k_n = 5 \times 10^7\ s^{-1}$, and $k_p = 11.3 \times 10^7\ s^{-1}$. If k_n is increased to the value near $1 \times 10^{10}\ s^{-1}$, characteristic of Co(III) complexes, using a ϕ observed for Co(III) and an assumed ϕ' of 0.1–1 yields a k_p between 2×10^6 and $5 \times 10^7\ s^{-1}$. We see that the available evidence points to chemical reactivity of similar order of magnitude for the triplets of representative Co(III) and Rh(III) amine complexes. The main difference in overall yields is in the much faster nonradiative decay of the LF triplets of Co(III) complexes. The shorter triplet lifetime for Co(III) may be a surprise, but it is empirically documented and may be the result of mixing with the nearby quintets.[4] It might be asked if the singlet pathway found for Co(III) complexes could be paralleled in the photochemistry of Rh(III) complexes.

Scheme I



The answer would be that a small yield comparable to those observed for Co(III) would be too small to be experimentally resolved against the background of the high yields from triplets of Rh(III). Thus, it is possible that Rh(III) complexes have a singlet pathway like that in Co(III) which remains undetected.

Singlet Pathway. The interesting feature of reaction from the singlets that precede ISC is the wavelength dependence. The higher the initial energy, the higher the aquation yields. This is a type of wavelength dependence which has been discussed widely. Most closely related to the present case is the observation of wavelength dependence in the charge-transfer excitation photochemistry of haloaminecobalt(III) complexes[16] and in the replacement of CO from $Fe(CO)_3(1,4\text{-}Me_2N_4)$. In the first of these cases, the initial critical step is the formation of a solvent-separated radical pair. This step competes with geminate recombination (although a complete account must deal with complication of this simple issue). In the substitution reactions, there is a similar competition. If the LF singlet with a σ antibonding electron is dissociative, as results on the analogous d^6 hexacarbonyl of $W(CO)_6$ which forms $W(CO)_5$ in less than 20 ps[22] might suggest, then the critical question with respect to total yield will be separation of the "geminate ion pair" vs. its recombination. Scheme I expresses the issue. Since $Co(NH_3)_5^{3+}$ has been suggested to be *exceedingly short-lived*, wavelength dependence is not a surprise. The solvent dependence data agree with this model both in the matter of reduced yields in aprotic solvents which *poorly solvate* halides (solvation energy effects) and of reduced yields in solvents of higher viscosity (dynamic effects).

Finally, it should be noted that the analysis suggested here does not exclude or refute any of our present understanding of the triplet reactions of Rh(III) amines or of the photochemical behavior of carbonyls. Rather, it offers the prospect of exploring a link among these areas of photochemistry.

Acknowledgment. We thank NSERC Canada for financial support and Dr. M. Hogben for helpful discussions.

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