*Coordination Chemistry Reviews*, 16 (1975) 171—184

# ACRIDINIUM AND QUINOLINIUM ION SENSITIZATION OF $[Co(NH_3)_5Br]^{2+}$

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## INTRODUCTION

The photochemistry of cobalt complexes has been studied extensively for a number of years [1,2,3], yet many aspects remain to be well understood. Some recent work especially has shown that irradiation of various ammine complexes in the wavelength region of the first ligand field ($L_1$) band leads predominately to substitution reactions, often antithermal as well as stereospecific [4]. Ligand field analyses suggest that the chemistry is indeed that of a low lying ligand field excited state [5]. Irradiation in the region of the first charge transfer (CT) band or even of ligand field bands if the latter have higher than usual extinction coefficients (indicating some mixing with CT character) leads to redox decomposition but with varying degrees of concomitant substitution [1—3]. An early and still viable mechanism [1—3] explains the occurrence of the two reaction modes as alternative consequences of cage reactions following homolytic bond fission and studies have provided some direct support to this mechanism [6,7]. Sensitization studies have usually led only to redox decomposition even though the available donor energy was insufficient to populate even the thermally equilibrated excited (thexi [8]) CT state, presumably $^1$CT. As a possible explanation it was proposed that the sensitizer actually populated a low lying $^3$CT state which, while not observed in absorption spectroscopy, should in principle exist [9]. Such a state should still have a chemistry of redox decomposition and this explanation of sensitization has been widely invoked [10].

The present study was undertaken to probe further into this type of explanation. The direct photolysis of $[Co(NH_3)_5Br]^{2+}$ in the 450 nm and shorter wave length region gives comparable amounts of redox decomposition and of $Br^-$ aquation [11], which, as noted above, has been explained in terms of cage processes following homolytic bond fission. If sensitization produced a $^3$CT

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state of the complex, then the same mix of reaction modes should be observed. The actual results were unexpected and will be seen to be more informative about the nature of the sensitization process itself than about the chemistry of the excited states of the complex.

## EXPERIMENTAL

### *Materials*

$[Co(NH_3)_5Br]Br_2$ was prepared by a standard method [12]. The same procedure, using $^{60}CoCl_2$, yielded $^{60}Co$ labeled complex. The corresponding nitrate salts were prepared by recrystallization from $NaNO_3$ solution. The spectra of the labeled and unlabeled preparations were verified to be identical, both agreeing with the published spectra [13]. $[Co(NH_3)_5(H_2O)]Cl_2$ and the corresponding $^{60}Co$ labeled complex were prepared again by a standard method [14] and were converted to the perchlorate salts by recrystallization from perchloric acid solution. Their spectra agreed with the published spectrum [13].

Reagent grade quinoline was purified by fractional distillation, taking the 235—238°C fraction, and was then stored in the dark. Acridine was purified by precipitation from a saturated 95% ethanol solution by the addition of water. The pale yellow-white solid had a melting point of 111°C. Aqueous stock solutions were prepared by adding known amounts of quinoline and of acridine to water, followed by the dropwise addition of glacial acetic acid until dissolution occurred. The stock solutions were stored in the dark. Spectra recorded periodically agreed with published ones [15]; there was no indication of any thermal decomposition on standing.

### *Procedures*

The photolysis apparatus was that previously described [16]. Monochromatization was by means of a Balzer 408 nm interference filter of 10 nm wavelength width at half transmission. In the case of 305 nm irradiations, an Optics Technology interference filter was used, of half-width 15 nm. Corning UV blocking filters were used in addition, to ensure that no shorter wavelength radiation was being passed. Light intensities were determined by ferrioxalate actinometry [17].

Solutions were irradiated in a water jacketed pyrex cell or in a 5 cm quartz spectrophotometer cell. Solutions were stirred during photolysis by nitrogen or compressed air bubbling, the bubbler being arranged so that there was no interception of the incident light beam. To investigate the effect of various gases on the sensitization yield, solutions to be photolyzed were saturated with either nitrogen, argon, oxygen, or compressed air, by bubbling the appropriate gas through them for 20 mins prior to the start of photolysis (and then during photolysis).

Sensitization by acridinium ion, $AcH^+$, was studied at 408 nm with solutions $7 \times 10^{-4}$ *M* in $AcH^+$, $10^{-3}$ *M* in complex, and buffered to pH 4 by being $1.25 \times 10^{-2}$ *M* in acetic acid and $2.64 \times 10^{-3}$ *M* in sodium acetate. Under this pH condition 98% of the acridine was present as $AcH^+$. The extinction coefficient of this is $2.98 \times 10^3$ $M^{-1}$ $cm^{-1}$ at 410 nm; 97% of the incident light was absorbed by $AcH^+$. In the cases with quinolinium ion, $QH^+$, as sensitizer, solutions were $4.6 \times 10^{-4}$ *M* in $QH^+$ and buffered to pH 4 with the same acetate buffer mixture. Irradiations were at 305 nm (in the region of absorption of $QH^+$) and because of the relatively large extinction coefficient of $[Co(NH_3)_5Br]^{2+}$ at this wavelength, complex concentrations were limited to $2.5 \times 10^{-4}$ *M*; 94% of the incident light was absorbed by the $QH^+$ whose extinction coefficient at this wavelength is $6.68 \times 10^3$ $M^{-1}$ $cm^{-1}$. The photolyses were carried out at 24 ± 1°C and normally under air saturation since initial experiments showed that the sensitization yields were unaffected by dissolved oxygen.

Analysis of the solutions for $Co^{II}$ was made by the thiocyanate procedure [18]. The procedure produces a $Co^{II}$ thiocyanate complex absorbing at 625 nm and the $Co^{II}$ produced by photolysis was determined from the difference in absorbances of the photolysed and dark solutions. Tests with known concentrations of $Co^{II}$ showed that there was no interference by either sensitizer.

The amount of $Co(NH_3)_5(H_2O)^{2+}$ formed during the direct photolysis of $^{60}Co$ labeled $[Co(NH_3)_5Br]^{2+}$ was determined by a previously described fractional recrystallization procedure [11], but modified to minimize the amount of coprecipitation of the bromopentaammine complex. A 2 ml aliquot of a saturated solution of $[Co(NH_3)_5Br]^{2+}$ was added to a 5-ml aliquot of the solution to be analyzed, then 5 ml of saturated aqueous $[Co(NH_3)_5(H_2O)]^{3+}$ was added as carrier for the labeled aquopentaamine formed during photolysis. $[Co(NH_3)_5Br]Cl_2$ was then precipitated by the addition of solid NaCl, and after centrifugation the precipitate was partially dissolved in water and reprecipitated. The two supernatants were combined and the $[Co(NH_3)_5(H_2O)]^{3+}$ present was precipitated by the addition of solid $NaClO_4$; the precipitate was centrifuged down and dissolved in a minimum amount of water, a small additional amount of $Co(NH_3)_5(H_2O)^{3+}$ added and then $NaClO_4$, to again precipitate the aquopentaamine perchlorate salt. The procedure was repeated twice more. A number of tests with $^{60}Co$ labeled $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(NH_3)_5Br]^{2+}$ showed that 74 ± 4% of original $[Co(NH_3)_5(H_2O)]^{3+}$ was recovered after the four precipitations and that the final precipitate was contaminated by 0.6 ± 0.02% of original $[Co(NH_3)_5Br]^{2+}$. Additional tests showed that the above percentages were not noticeably affected by the presence of either sensitizer.

It was determined that no loss of sensitizer occurred in the sensitization experiments. This was shown approximately by correcting the final spectrum for the change in absorbance due to the reaction of the complex, and observing that the original spectrum resulted. Fluorescence analyses provided an independent check. Aliquots of the photolyzed and unphotolyzed solutions were diluted with 0.1 *M* $HClO_4$ to yield solutions with an absorbance of 0.05 $cm^{-1}$. At this low absorbance the fluorescence intensity is directly proportional to the concentration of the sensitizer. Absorption and emission spectra were recorded on a Cary Model 14R spectrophotometer and on an Aminco spectrofluoremeter, respectively.

$[Co(NH_3)_5Br]^{2+}$ absorbs appreciably in the region of the fluorescence emission of the sensitizers, and two techniques were used to allow for this. In one approach, the fluorescence emission of buffered solutions containing $7 \times 10^{-4}$ *M* $AcH^+$ or $4.6 \times 10^{-4}$ $QH^+$ and varying amounts of complex were measured in 1-cm cells at right angles to the exciting light. The true emission intensity was determined by correcting the observed emission for the fraction of the exciting light absorbed by the complex and the fraction of emitted light similarly absorbed assuming an effective path length of 0.5 cm. This correction was appreciable at the higher complex concentrations and an alternative technique of monitoring the emission from the front face of the cell, that is, the face illuminated by the exciting light. To minimize the scatter of the latter, a 1-mm path length quartz cell was mounted at an angle of 40° to the exciting light beam and at 50° to the emission detector. Under these conditions, corrections for trivial reabsorption of the emission was negligible. Measurements by the two procedures agreed well.

A DuPont 911 curve analyzer was used to resolve the absorption spectrum of $[Co(NH_3)_5Br]^{2+}$ into gaussian components, as shown in Fig. 1.

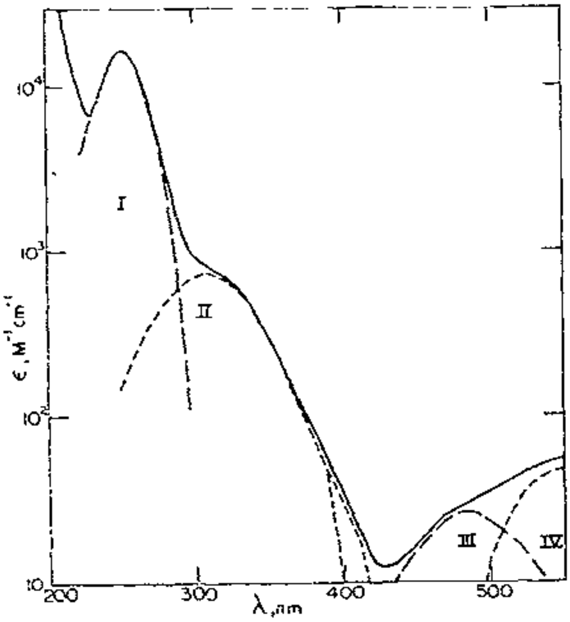

**Fig. 1. Absorption Spectrum of aqueous $[Co(NH_3)_5Br]^{2+}$. Dashed lines show estimated gaussian components.**

## RESULTS

### *Direct photolyses of $[Co(NH_3)_5Br]^{2+}$*

A number of direct photolysis experiments were made using $2.5 \times 10^{-3}$ *M* $[Co(NH_3)_5Br]^{2+}$ in pH 4 aqueous buffer solutions. Most were carried out using 408 ± 5 nm light, the wavelength used in the sensitization studies, and irradiations were to 10—15% reaction. The results are summarized in Table 1.

First, the average of eight experiments at 408 nm gave $\Phi_R = 0.071 \pm 0.001$ and $\Phi_A = 0.031 \pm 0.002$, where R and A denote formation of $Co^{II}$ (redox decomposition) and of $[Co(NH_3)_5(H_2O)]^{3+}$ (aquation), respectively. The ratio $\Phi_R/\Phi_A$ is thus 2.3. These results were obtained by means of the analytical procedures described under Experimental. Other reaction modes, such as ammonia aquation, were not of major importance since spectrophotometric analysis of irradiated solutions yielded nearly the same quantum yield values. Thus the amount of redox decomposition was found from the decrease in absorbance at 514 nm, the isosbestic point between $[Co(NH_3)_5Br]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$, to give a $Co^{II}$ yield of 0.061. The absorbances at 550 nm and 487 nm, the respective $L_1$ band maxima for the two complexes, then

TABLE 1

Spectral features and photochemistry of $[Co(NH_3)_5Br]^{2+}$

| Wavelength (nm) | Feature[a] | Quantum yields | |
|---|---|---|---|
| | | $\phi_R$ | $\phi_A$ |
| 250 | $^1$CTTM ($\epsilon = 16{,}700$) | | |
| 254 | | 0.19[b] | |
| 285 | $^1$CTTM (thexi) | | |
| 305 | | 0.17 | |
| 310 | $^1L_2$ ($\epsilon = 730$) | | |
| 340—400 | | 0.15[c] | 0.067 |
| ca. 380 | | 0.15[d] | |
| 408 | | 0.071 ± 0.001 | 0.031 ± 0.002 |
| 405—425 | | 0.071[c] | 0.069[c] |
| 425 | $^1L_2$ (thexi)[d] | | |
| 425—550 | | 0.020 ± 0.003 | 0.011 ± 0.001 |
| 450 | | $8.0 \times 10^{-3}$ [c] | 0.027[c] |
| 480 | $^1L_1'$ ($\epsilon = 26$) | | |
| 550 | $^1L_1$ ($\epsilon = 53$) | $1 \times 10^{-5}$ [c] | $1.5 \times 10^{-3}$ [c] |
| 560 | $^1L_1'$ (thexi) | | |

[a] Extinction coefficient estimated from the maximum of the gaussian components, in $M^{-1}$ $cm^{-1}$. Thexi state wavelength estimated from the foot of the gaussian component.

[b] See ref. 1 and also J.F. Endicott and M.Z. Hoffman, J. Amer. Chem. Soc., 87 (1965) 3348

[c] Ref. 11.

[d] Assuming some long wavelength tailing.

allowed calculation of the aquation yield, which was found to be 0.036. We believe the analytical results to be the more accurate because of the sensitivity of the direct spectrophotometric method to errors in absorbance measurements.

One experiment using 425 nm light gave $\Phi_R = 0.051$ and $\Phi_A = 0.033$, or $\Phi_R/\Phi_A = 1.5$. Two runs were made using a broad band filter passing 425—550 nm light, in approximation of the emission from $AcH^+$. The spectral distribution of the Hg lamp used is such that the irradiating light was mainly in the 436 nm region. These experiments gave $\Phi_R = 0.020 \pm 0.003$ and $\Phi_A = 0.011 \pm 0.001$, or $\Phi_R/\Phi_A = 1.8$. Finally, one irradiation at 305 nm gave $\Phi_R = 0.17$. Thus $\Phi_R$ drops steadily with increasing wavelength of irradiation, as does $\Phi_A$; the ratio of the two yields is relatively constant over the region studied, but does decrease slowly.

### *Fluorescence quenching*

Both $AcH^+$ and $QH^+$ exhibit strong fluorescence in room temperature aqueous solution [19,20]. The maxima in the emission spectra occur at 475 nm and 420 nm, respectively, and the emission intensities are independent of the presence or absence of dissolved oxygen. The results of our quenching studies are summarized in the Stern—Volmer plots of Fig. 2. The data have been corrected for trivial reabsorption of fluorescent light (amounting to no more than 10% correction). Least squares analyses give Stern—Volmer constants (see Discussion) of 143 $M^{-1}$ and 8 $M^{-1}$ for the quenching of $AcH^+$ and of $QH^+$, respectively, by $[Co(NH_3)_5Br]^{2+}$. The latter figure is within experimental error of zero.

### *Sensitization results*

Photosensitization appears to occur with either $AcH^+$ or $QH^+$ as donors. There is no oxygen effect; the yield of $Co^{II}$ and of aquopentaamine complex

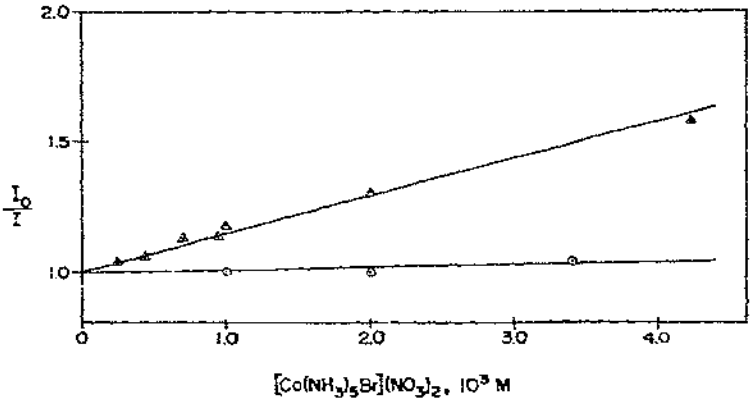

Fig. 2. Emission quenching by aqueous $[Co(NH_3)_5Br]^{2+}$. (⊙): $QH^+$; (△): $AcH^+$.

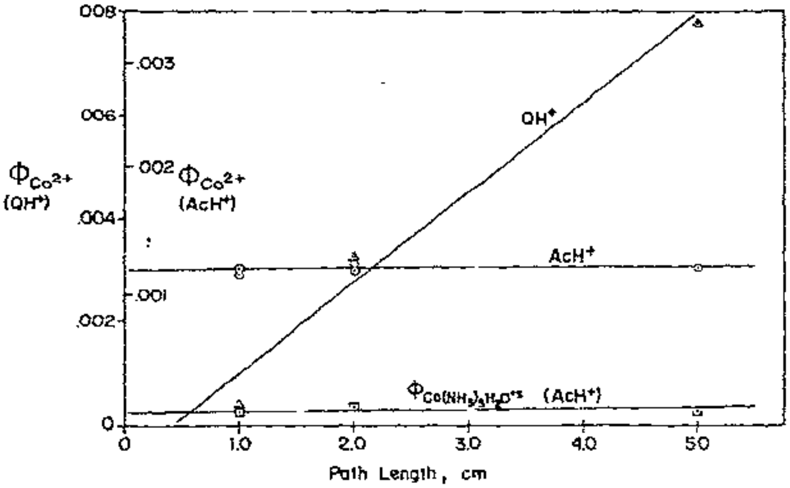

Fig. 3. Tests for fluorescence photolysis of aqueous $[Co(NH_3)_5Br]^{2+}$. Outer ordinate scale: $\phi_R$ using $QH^+$; Inner ordinate scale: $\phi_R$ $\phi_A$ using $AcH^+$.

were the same for solutions saturated with Ar, $N_2$, air, or $O_2$. We were concerned, however, that fluorescence photolysis might be occurring since the emission spectra of $AcH^+$ and of $QH^+$ overlap, respectively, the $L_1$ and $L_2$ bands of the bromopentaamine complex. The correction for this effect was determined by obtaining quantum yields for systems irradiated in cells of varying depth, and extrapolating the resulting yields to zero cell depth [16,21]. The results are shown in Fig. 3.

It is evident that little, if any, fluorescence photolysis occurred in the $AcH^+$ systems, as might be expected in view of the emission being in the region of the relatively insensitive $L_1$ band of the complex. In the case of the $QH^+$ systems, however, extrapolation of the apparent sensitization yields to zero cell depth gives zero yield, and we assign the photolysis observed in the various actual experiments to varying degrees of fluorescence photolysis. As a matter of convenience, only the yields for redox decomposition were obtained in this last series of experiments.

Returning to the $AcH^+$ sensitization, Fig. 2 gives $\Phi_{S,R} = 0.0012$ and $\Phi_{S,A} = 1.4 \times 10^{-4}$, where the subscript denotes sensitization. Note that the ratio of yields is 9 : 1 as compared to the 2.3 : 1 ratio found on direct photolysis at 408 nm.

Two additional experiments were carried out to establish that the high proportion of redox decomposition in the $AcH^+$ sensitized reaction was not due to sensitized decomposition of $[Co(NH_3)_5(H_2O)]^{3+}$. Solutions containing $7 \times 10^4$ *M* $AcH^+$, $1 \times 10^{-3}$ *M* $[Co(NH_3)_5Br]^{2+}$, either $1 \times 10^{-4}$ *M* or $5 \times 10^{-4}$ *M* labeled $[Co(NH_3)_5(H_2O)]^{3+}$, and buffered to pH 4 were irradiated at 408 nm to about 8% decomposition of the bromopentaammine complex. Analysis of the photolyzed solutions by the fractional precipitation techniques were carried out, and 71% of the $[Co(NH_3)_5(H_2O)]^{3+}$ was recovered in both cases. This is the normal yield as established by the calibration experiments and we conclude that no significant decomposition of the added $[Co(NH_3)_5(H_2O)]^{3+}$ occurred and hence that the sensitized decomposition of this species was not important.

The variation of the $AcH^+$ sensitized yield of $Co^{II}$ was determined as a function of $[Co(NH_3)_5Br]^{2+}$ concentration, with results as shown in Fig. 4. Solutions were at the usual buffered pH of 4 and were $7 \times 10^{-4}$ *M* in $AcH^+$. As discussed in the next section, the slope and intercept of the plot yield a Stern—Volmer constant of 126 $M^{-1}$ and a limiting $\Phi_{S,R}$ of 0.0084.

Finally, it was possible to determine whether any chemical decomposition of the acridine occurred. First, solutions $1 \times 10^{-3}$ *M* in $[Co(NH_3)_5Br]^{2+}$ and either $7.6 \times 10^{-4}$ or $2.9 \times 10^{-4}$ *M* in $AcH^+$ (and at pH 4) were photolyzed to 7% decomposition to $Co^{II}$. The spectra of the photolyzed and initial solutions were identical in the 380—410 nm region of the $AcH^+$ absorption maximum. Further, after photolysis of the first solution, a 2-ml aliquot was diluted to 50 ml with 0.1 *M* $HClO_4$ and the fluorescence intensity compared with that for unphotolyzed solution treated in the same way. The two emission intensities were the same within experimental error. We conclude that less than 1% of the sensitizer was decomposed in these experiments, or that less than 0.05 mole of sensitizer could have decomposed per mole of complex sensitized.

The above results imply that no direct photolysis of $AcH^+$ occurred under our conditions, and this conclusion was confirmed by irradiation at 408 nm of solutions containing only $AcH^+$. It has been reported that the first excited singlet state of acridine can effect hydrogen abstraction in ethanol solvent medium, to yield (eventually) acridone [22]. We find no literature on the photosensitivity in aqueous media.

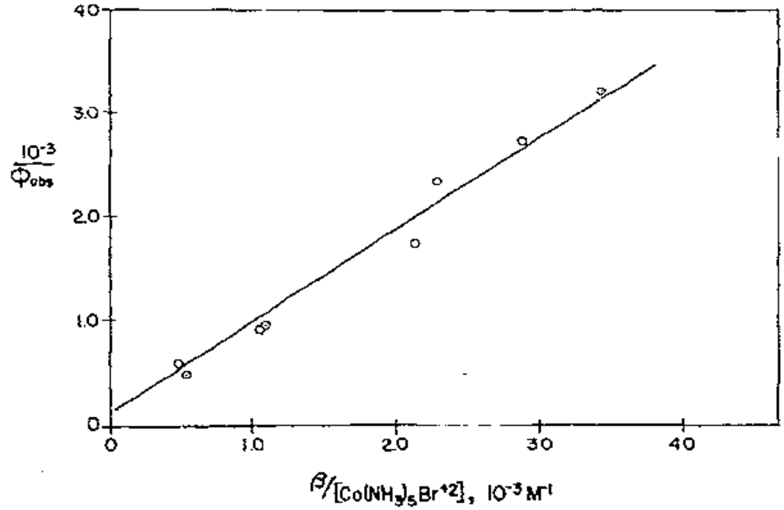

Fig. 4. $AcH^+$ sensitized redox decomposing of aqueous $[Co(NH_3)_5Br]^{2+}$.

## DISCUSSION

### *Excited state energies*

Resolution of the absorption spectrum of $[Co(NH_3)_5Br]^{2+}$ into components yields the series of bands shown in Fig. 1. These components are essentially gaussian, but for component II in particular some tailing on the long wavelength side must be allowed if the spectrum is to be represented in the 400—450 nm region. Component I, centered at 250 nm, undoubtedly represents a charge transfer to metal, CTTM, transition, the donor ligand being Br. That is, judging from the hexaammine and aquopentaammine spectra, the CTTM absorption for ammonia as donor is centered around 200 nm, or at a much shorter wavelength. Proceeding to longer wavelengths, the shoulder in the spectrum yields component II which we assign as the second ligand field or $L_2$ band. This centers at 310 nm, as compared to 340 nm for the $L_2$ band in the hexaammine and about 350 for the fluoropentaamine [13]. However, the relatively large extinction coefficient, about 720 $M^{-1}$ sec$^{-1}$, strongly suggests that some mixing with charge transfer excited states is involved. The next, or $L_1$ band, shows a shoulder on the short wavelength side, and we find components III and IV, centered at 480 nm and 550 nm, respectively. These presumably derive from the splitting of the $L_1$ band in $C_{4V}$ symmetry. The $L_1$ band for the hexaammine is at 475 nm, for example [2].

The positions of band maxima, while useful in ligand field theory, may not be directly relevant to photochemistry or to sensitization processes since these very likely involve thexi states. The donor species are presumably thermally equilibrated before making the energy transfer encounter, and, for the complex the thexi state energy is essentially the minimum needed if that excited state is to be populated. Table 2 gives thexi state energies for $AcH^+$ and $QH^+$, estimated where possible from the crossings of the absorption and emission spectra.

TABLE 2

Thexi state energies

| Species | State and energy in kcal mole$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | Singlet | Triplet | $^1$CTTM | $L_2$ | $L_1'$ | $L_1$ |
| $AcH^+$ | 66[a] | 50[b], 45[c] | | | | |
| $QH^+$ | 82[a] | 62[d] | | | | |
| $[Co(NH_3)_5Br]^+$ | | | 99[e] | 73[e] | 51[e] | <45[e] |

[a] Determined from the crossing of the absorption and emission spectra.
[b] See V. Erinolaw and I. Katlgar, Optics and Spec., 9 (1960) 183.
[c] See D.F. Evans, J. Chem. Soc. (London), (1957) 1351.
[d] See G. Jackson and G. Porter, Proc. Roy. Soc. (London), A260, 13 (1961).
[e] Estimated from the long wavelength tail of the absorption bond component.

In the absence of emission, as in the case of the bromopentaamine, the thexi state energies for the various components are roughly estimated as close to the long wavelength foot of each component [23]. Note that these estimates indicate that neither sensitizer can populate the CTTM state of the complex, that the $L_2$ state can be populated only by the first singlet excited state of $QH^+$ and that the $L_1$ state can probably be populated by the singlet or the triplet excited state of either sensitizer.

### *Direct photolysis of $[Co(NH_3)_5Br]^{2+}$*

Our data as well as various literature results are summarized in Table 1. Clearly, irradiation at wavelengths below the CTTM or $L_2$ states leads to extensive redox decomposition, while irradiation into the $L_1$ state leads to virtually only aquation, and in low yield. An interesting feature of this system is that irradiation in the $L_2$ band region also leads to substantial aquation. The earlier results gave $\Phi_A = 0.069$ whereas we find the lower value of 0.031. The difference may reflect an improved fractional precipitation procedure, although the present study differs in using buffered rather than merely slightly acidified solutions. We have assumed that this high aquation yield is characteristic of the state populated (either CTTM or $L_2$), explainable in terms of the cage mechanism discussed in Refs. 1—3. It seems unlikely that the aquation mode of reaction derives from a crossing to produce some $L_1$ state in view of the low $\Phi_A$ found on direct irradiation into this state. Furthermore, a direct test of this last type of mechanism has been made, using the complex *trans*-$[Co(en)_2(NCS)Cl]^+$ which shows two aquation modes; the ratio of yields for these was found to be different on photolysis in the wavelength region of important redox decomposition from the ratio on photolysis at longer wavelengths [6].

### *Sensitization*

The $AcH^+$ sensitized decomposition of $[Co(NH_3)_5Br]^{2+}$ does not appear to involve the donor triplet state. The yield is not oxygen sensitive. An important consideration is that the concentration dependence of $\Phi_R$ directly implicates the first singlet excited state. Steady state analysis of the standard scheme,

$$D \xrightarrow{h\nu} {}^1D^* \quad (1)$$

$$ {}^1D^* \xrightarrow{k_m} D \quad \text{(medium quenching)} \quad (2)$$

$$ {}^1D^* \xrightarrow{k_f} D \quad \text{(emission)} \quad (3)$$

$$ {}^1D^* + C \xrightarrow{k_q} D + \text{products} \quad (4)$$

where eqn. (4) shows bimolecular quenching to form products, yields the relationships

$$\Phi_f^\circ/\Phi_f = 1 + K_{SV}(C) \tag{5}$$

$$1/\Phi_s = 1/\Phi_s^\circ + (1/K_{SV}\Phi_s^\circ)\beta/C \tag{6}$$

The Stern—Volmer constant, $K_{SV}$, is given by $k_q/(k_m + k_f)$, $\Phi_s^\circ$ is the efficiency whereby reaction results from a quenching encounter, and the function $\beta$ corrects, for the loss of complex during the photolysis [9].

The fluorescence quenching data give $K_{SV} = 143\ M^{-1}$ while the sensitization data give $\Phi_s^\circ = 0.0093$ and $K_{SV} = 123\ M^{-1}$, where $\Phi_s = \Phi_{s,R} + \Phi_{s,A}$ and the ratio of these last two yields is that given in Fig. 2 and is taken to be independent of complex concentration. The $K_{SV}$ value of 123 $M^{-1}$ is very sensitive to the value of the intercept of Fig. 3, and we regard it as within experimental error of the value of 143 $M^{-1}$ found from the fluorescence quenching studies. We therefore conclude that it is indeed the first excited singlet state of $AcH^+$ that is involved in the sensitization.

The fluorescence lifetime of $AcH^+$ in 0.1 $N$ $H_2SO_4$ is $4.3 \times 10^{-8}$ sec [16] and is $3.8 \times 10^{-8}$ sec in water [24]. If we assume a lifetime of $4 \times 10^{-8}$ sec for our medium, then $k_q = 143/4 \times 10^{-8} = 3.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. This last value compares well with the diffusion limited rate constant of about $3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ estimated using the Smoluchowski equation.

The usual interpretation of these results would be that eqn. (4) leads to excited state complex, C*, which then undergoes reaction with some efficiency $\Phi^*$. Since $\Phi_s^\circ$ is 0.0093, or about 0.1 of the direct photolysis redox yield at the wavelength corresponding to the first singlet thexi state energy of $AcH^+$, one would then conclude that about 10% of the quenching encounters lead to C*.

There are two difficulties with this standard interpretation. First, the data illustrated in Fig. 2 show that in the sensitized reaction the ratio of the redox to aquation modes is 9 : 1, or quite different from the 2.3 : 1 value found in direct photolysis in the wavelength region corresponding to the energy of the donor thexi state. It must then be supposed that in direct photolysis the two reaction modes stem from two distinct excited states, only one of which is populated in sensitization. Since the first part of this supposition is contraindicated the second part is not substantiated. The second set of problems involves energetics. The singlet thexi state of $AcH^+$ should not be able to populate either the CTTM or the $L_2$ state of the complex, yet these are the possible states whose reaction is one of redox decomposition. An explanation that we [9] and others [10] have resorted to is to suppose that a lower lying triplet CTTM (or even $L_2$ type) state is populated in sensitization. For the present system one must add the stipulation that this triplet state is not involved in direct photolysis and has a different chemistry than the corresponding singlet state. This stipulation seems unavoidable if the 9 : 1 vs. 2.3 : 1 ratio is to be explained. The stipulation seems awkward and ad hoc. A further point is that the $QH^+$ first singlet thexi state should be able to populate $L_2$ state of the complex, yet no sensitization is observed. The result may be rationalized if one assumes that the donor thexi state lifetime is at least 20 times shorter than that of $AcH^+$, to be consistent with the low observed upper limit to $K_{SV}$. This rationalization seems awkward and ad hoc. While the fluorescence lifetime of $QH^+$ seems not be have been reported, that of 6-methoxyquinoline is not very different from that of $AcH^+$ [25]. Also, neither the shape, nor the intensity of the first allowed absorption band of $QH^+$ suggest an unusually short excited state lifetime.

A very different explanation is that the $AcH^+$ sensitization is due to the excited state redox process

$$AcH^{+*} + Co^{III}\text{ complex} \rightarrow Ac^{+} + H^{+} + Co^{II} \qquad (7)$$

Oxidation of solvent or of the released ligands by $Ac^+$ then regenerates $AcH^+$ so that no net consumption of sensitizer is observed. This type of mechanism was proposed in the case of $Ru(bipyr)_3^{2+}$ [26] and now seems to be well demonstrated [27—29]. Such a mechanism accounts, of course, for the large ratio of sensitized redox to aquation reaction modes. The dominant process, electron transfer, now leads only to redox decomposition. Interestingly most of the quenching encounters could still lead to excitation energy transfer if the $L_1$ state of the complex were produced, and then underwent aquation with the yield of about $10^{-3}$ observed on direct photolysis. This situation could give the observed 9 : 1 ratio of redox to aquation mode. The lack of any appreciable sensitization by $QH^+$ is now to be explained in terms of redox potentials and electron transfer rates rather than in terms of excited state energies.

There is some further qualitative support for the above analysis. While no excited state oxidation potentials are available for $AcH^+$ or $QH^+$, the existence (and, indeed, the spectrum) of $Ac^+$ has been reported [30]. Also, an indication that singlet excited state acridine is more easily oxidized than singlet excited state quinoline is that in ethanol solution the former but not the latter undergoes oxidation [31].

While the electron transfer mechanism thus seems reasonably possible, there is insufficient data to account for the non-reactivity of singlet thexi state $QH^+$. The reported ionization potentials for ground state Ac and Q and the available excited state $pK_a$'s [32] combine with the energy data of Table 2 to suggest that the oxidation potentials of singlet thexi state $AcH^+$ and $QH^+$ may be comparable. The previously reported quinoline sensitized redox decomposition of $[Co(NH_3)_6]^{3+}$ may also actually involve electron rather than excitation energy transfer. If so, the process must be quite sensitive to medium as well as to pH. Such potential complexities make it difficult to say whether the difference found here between $AcH^+$ and $QH^+$ as sensitizers for $[Co(NH_3)_5Br]^{2+}$ is consistent with the electron transfer mechanism.

Returning to $[Ru(bipyr)_3]^{2+}$ as sensitizer, the electron transfer mechanism has been considered unlikely in the case of [Co(HEDTA)X] complexes because both redox decomposition and aquation was found to be sensitized. A two excited state, excitation energy transfer mechanism was therefore proposed [33]. It should be pointed out, however, that the electron transfer mechanism found for other $[Ru(bipyr)_3]^{2+}$ sensitizations of $Co^{III}$ ammines could still apply to the $[Co(HEDTA)X]^-$ systems. The point is that reduction at the cobalt center would give a $Co^{II}$ complex which would be labile with respect to the X group but which might remain partially coordinated to the EDTA. The $[Ru(bipyr)_3]^{3+}$ product of the electron transfer could then generate the observed final products, i.e., coordinated $Co^{II}$ would be oxidized to the $Co^{III}$ aquo product, $Co(HEDTA)(H_2O)$. Aquation via reoxidation of a chelated $Co^{II}$ appears to be important in the photolysis of $Co^{III}(PnAO)X_2$ complexes, for example [34]. However, where partial or complete dissociation of the EDTA occurred for $Co^{II}$, it would be the ligand that would be oxidized by $[Ru(bipyr)_3]^{3+}$, yielding the observed net redox products.

## CONCLUSION

The present study leads us strongly to suspect that vitually all sensitized reactions of $Co^{III}$ complexes so far reported involve electron rather than excitation energy transfer. The small component of sensitized aquation found here for $AcH^+$ may be an exception since aquation by reoxidation is not likely for $[Co(NH_3)_5Br]^{2+}$ in view of the fact that on reduction all ligands should be shed rapidly in acid solution.

## ACKNOWLEDGEMENTS

This investigation was supported in part by contract DA-ARO-D-31-124-G87 between the University of Southern California and the Army Research Office (Durham).

## REFERENCES

1 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1971.
2 A.W. Adamson, W.L. Waltz, E. Zinato, D.W. Watts, P.D. Fleischauer and R.D. Lindholm, Chem. Rev., 68 (1968) 541.
3 J. Endicott in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, in press.
4 R.A. Pribush, C.K. Poon, C.M. Bruce and A.W. Adamson, J. Amer. Chem. Soc., 96 (1974) 3027; P.S. Sheridan and A.W. Adamson, ibid., 96 (1974) 3032 and Inorg. Chem., 13 (1974) 2482.
5 J.I. Zink, Inorg. Chem., 12 (1973) 1018; M. Wrighton, H.B. Gray and G.S. Hammond, Mol. Photochem., 5 (1973) 165.
6 A. Vogler and A.W. Adamson, J. Phys. Chem., 74 (1969) 67.
7 V. Balzani, R. Ballardini, N. Sabbatini and L. Moggi, Inorg. Chem., 7 (1968) 1398.
8 A.W. Adamson, Proc. Int. Conf. Coord. Chem., 14th, 1972.

9 A. Vogler and A.W. Adamson, J. Amer. Chem. Soc., 90 (1958) 5943.
10 See for example, P. Natarajan and J.F. Endicott, J. Amer. Chem. Soc., 95 (1973) 3257 and ref. 3.
11 A.W. Adamson, Discuss. Faraday Soc., 29 (1960).
12 H.H. Willard, H. Diehl and H. Clark, Inorg. Syn., 1 (1939) 186.
13 M. Linhard and M. Weigel, Z. Anorg. Allg. Chem., 266 (1951) 4.
14 H.S. Booth, Inorg. Syn., 1 (1939) 187.
15 N. Mataga, Y. Kaifu and M. Koijumi, Bull. Chem. Soc. Jap., 29 (1956) 373; N. Mataga and S. Tsuno, Bull. Chem. Soc. Jap., 30 (1957) 368.
16 J.E. Martin and A.W. Adamson, Theoret. Chim. Acta, 20 (1971) 119.
17 C.A. Parker, Proc. Roy. Soc., Ser. A, 220 (1953) 104; C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., Ser. A, 235 (1956) 518.
18 R.G. Bennett, Rev. Sci. Instrum., 31 (1960) 1275.
19 H.D. Gafney and A.W. Adamson, J. Phys. Chem., 76 (1972) 1105 and references therein.
20 N. Mataga and S. Turro, Bull. Chem. Soc. Jap., 29 (1956) 373.
21 J.B. Birks, Photophysics of Aromatic Molecules, Wiley—Interscience, New York, 1970, p. 521.
22 F.W. Wilkinson and J.T. Dubois, J. Chem. Phys., 48 (1968) 2651.
23 P.D. Fleischauer, A.W. Adamson and G. Sartori, in J.O. Edwards, (Ed.), Inorganic Reaction Mechanisms, Wiley (1972).
24 C.A. Parker, Photoluminescence of Solutions, Elsevier, New York 1968.
25 R.F. Chen, G.G. Vurek and N. Alexander, Science, 156 (1967) 949.
26 H.D. Gafney and A.W. Adamson, J. Amer. Chem. Soc., 94 (1972) 8238.
27 J.N. Demas and A.W. Adamson, J. Amer. Chem. Soc., 95 (1973) 5159.
28 G. Navon and N. Sutin, Inorg. Chem., 13 (1974) 2159.
29 C.R. Bock, T.J. Meyer and D.G. Whitten, J. Amer. Chem. Soc., 96 (1974) 4710.
30 C. David, P. Janssen and G. Geuskens, Spectrochim. Acta, 27A (1971) 367.
31 J.P. Ray and T.D.S. Hamilton, Nature (London), 206 (1965) 1040.
32 M.A. El-Bayoumi and O.S. Khalil, J. Chem. Phys., 47 (1967) 4863; M.F. El-Sayed, M. Kasha and Y. Tanaka, J. Chem. Phys., 34 (1961) 334.
33 P. Natarajan and J.F. Endicott, J. Amer. Chem. Soc., 95 (1973) 3257.
34 F. Diomedi-Camassei, E. Nochi, G. Sartori and A.W. Adamson, Inorg. Chem., 14 (1975) 25.