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Sensitized Photochemistry of the Nitropentamminecobalt(III) Complex Ion

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Sensitization of the photochemistry of $Co(NH_3)_5NO_2^{2+}$ *in water or water/ethanol solutions has been attempted using a number of triplet energy donors. Acetone, benzaldehyde, and thioxanthone were found to be efficient sensitizers of the redox decomposition reaction of the complex. In the one experimentally accessible case,* i.e., *with acetone, the nitro–nitrito linkage isomerization reaction was also found to be sensitized, in the same ratio to redox decomposition as observed in the direct photochemistry. Limit sensitization quantum yields for redox decomposition were 0.35 and 0.25 with acetone and benzaldehyde, respectively. Michler's ketone, biacetyl and benzil did not appreciably sensitize the photochemistry of the complex, although the biacetyl phosphorescence was efficiently quenched by* $Co(NH_3)_5NO_2^{2+}$*. The correlation of the triplet energy of the donors with their sensitizing ability, and the simultaneous sensitization of redox decomposition and linkage isomerization are taken as evidence of an energy-transfer sensitization mechanism, as opposed to an electron transfer one. The results are discussed in terms of an excited state model which includes ligand-to-metal charge transfer states of various multiplicities corresponding to high-spin and low-spin cobalt(II) as well as ligand field states.*

Introduction

Sensitization has been a powerful tool for mechanistic investigations in both organic [1] and inorganic [2] photochemistry. The charge transfer photochemistry of Co(III) complexes is one of the most thoroughly studied areas of inorganic photochemistry [3]. This field, however, has derived little benefit from the use of sensitization techniques, in spite of the effort spent in this direction [4–16]. Two reasons may account for this situation. First, much confusion has arisen from the use of incorrect descriptions of the ligand-to-metal charge transfer (LMCT) states of Co(III) complexes. In fact, most of the discussion on sensitization studies has been made in terms of singlet and triplet LMCT states, without taking into account the possibility of low-spin and high-spin configurations at the metal center. The relevant types of LMCT states in the photochemistry of Co(III) complexes have now been clearly described by Endicott and Ferraudi [17].

A further major drawback of sensitization studies on Co(III) complexes is represented by the possibility of electron-transfer mechanisms being responsible for the observed results. It has become apparent that, if the observed sensitized reaction is simply the redox decomposition of the complex, there is no unequivocal way of experimentally discriminating between energy-transfer and electron-transfer sensitization. Actually, most of the sensitization studies on Co(III) complexes published until now are suspected of being vitiated by electron-transfer processes [16].

The direct photochemistry of $Co(NH_3)_5NO_2^{2+}$ has been investigated in considerable detail in recent years. The photochemical behavior of the complex in aqueous solution was shown by Balzani *et al.* [18], to consist of simultaneous redox decomposition (reaction 1) and linkage isomerization (reaction 2).

$$Co(NH_3)_5NO_2^{2+} \longrightarrow Co^{2+}_{aq} + 5NH_3 + NO_2 \qquad (1)$$

$$Co(NH_3)_5NO_2^{2+} \longrightarrow Co(NH_3)_5ONO^{2+} \qquad (2)$$

The two photoreactions occur in a constant ratio following irradiation of both LMCT and ligand field (LF) bands with quantum yield values which decrease with decreasing energy of the irradiated band. These results were interpreted [18] on the basis of the following proposals: (i) a Co–NO$_2$ LMCT state is eventually populated regardless of the type of absorption band which is irradiated; (ii) a Co–NO$_2$ bond splitting in the LMCT state is the common precursor of both photoreactions; (iii) the quantum yield values of both processes are accounted for by a radical-pair mechanism in which linkage isomerization is the result of cage recombination while redox decomposition arises from diffusion of the radicals into bulk solution. Some of these mechanistic proposals have subsequently been investigated in more detail. In particular, the cage recombination hypothesis was demonstrated through the viscosity dependence of the quantum yields of redox decomposition and linkage isomerization [19]. Moreover, a detailed study of the wavelength dependence of the redox decomposition quantum yields [20] confirmed the dissociative nature of the LMCT singlet states and indicated that crossing of the reactive LMCT state near to the minimum of the lowest ligand field singlet allows efficient population of the LMCT state following ligand field irradiation. A semi-quantitative model developed by Endicott [21], which also considers the role of the solvent in the dynamics of the LMCT state relaxation, actually predicted essentially dissociative potential energy surfaces for the LMCT states of $Co(NH_3)_5NO_2^{2+}$.

We have now performed a sensitization study on $Co(NH_3)_5NO_2^{2+}$. This complex seems to be better suited than most other Co(III) complexes for this aim. In fact, the presence of a characteristic LMCT excited state pathway like linkage isomerization in addition to the usual redox decomposition process makes it easier, in principle, to discriminate between energy-transfer and electron-transfer sensitization mechanisms.

Experimental

Materials

$[Co(NH_3)_5NO_2](NO_3)_2$ was prepared according to Murman and Taube [22] and twice recrystallized from water. Acetone, biacetyl and benzaldehyde were reagent grade products and were distilled under reduced pressure before use. Benzyl, thioxanthone, and Michler's ketone were Baker special purity products ("suitable for sensitizer use") and were used without any further purification. Spectrograde ethanol and triply distilled water were used as solvents.

Apparatus

Lamps and filters for obtaining 290 and 405 nm radiations and the general irradiation equipment were as previously described [20]. Spectrophotometric measurements were performed with Shimadzu QV-50 (single beam) and Optica CF4NI (double beam) spectrophotometers. Emission measurements were performed with a Hitachi–Perkin Elmer MPF2A spectrofluorimeter.

Procedures

Different solvent systems were used depending on the sensitizer. The solutions were always made 10^{-2} *M* in $HClO_4$ in order to avoid air oxidation of the Co^{2+} product. After irradiation, the solutions were analyzed for Co^{2+} by standard methods [23] and, when allowed by the sensitizer absorption, for the occurrence of linkage isomerization by spectral analysis in the 300–350 nm range [24]. Quantum yields for the two photoprocesses were straightforwardly obtained in conditions of zero-order kinetics by comparison with ferrioxalate actinometry [25]. When necessary, deoxygenation of the solutions was achieved by bubbling pure nitrogen into the reaction cell for a period of one hour. The adequacy of such a procedure was checked by comparison with standard freeze–pump–thaw methods. During the irradiations, the solutions were always stirred with a magnetic stirrer. Luminescence intensity measurements were always performed in the frontal irradiation mode, owing to the high absorbance of the solutions used.

Results

Different solvent systems, namely water, 1:1 ethanol/water, 4:1 ethanol/water, have been used according to the solubility requirements of the sensitizers used. The direct photochemistry of $Co(NH_3)_5NO_2^{2+}$ is qualitatively the same in all the solvent systems. Quantum yields in 4:1 ethanol/water are the same as in 1:1 ethanol/water and both are about 20% higher than those obtained in pure water [20].

Several organic molecules which are usually considered as triplet energy donors [1] were tried as potential sensitizers of the photochemistry of $Co(NH_3)_5NO_2^{2+}$. With some of these systems, however, the lack of oxygen effects and/or the occurrence of donor fluorescence quenching strongly suggested the involvement of singlet rather than triplet states in the sensitization. Naphthalene, phenanthrene, biphenyl and, more surprisingly, also xanthone and acetophenone were discarded due to these drawbacks. The results obtained with the other, "well behaved" donors are reported in detail below and are schematically summarized in Table I.

TABLE I. Sensitized Photochemistry of $Co(NH_3)_5NO_2^{2+}$.

Donor	E_T[a] (kcal/mol)	Sensitization[b]	ϕ_{red}/ϕ_{isom}	ϕ_{red}^{lim}
Acetone	78	+	3.0	0.35
Benzaldehyde	72	+	c	0.25
Thioxanthone	66	+	c	d
Michler's Ketone	61	–		
Biacetyl	55	–		
Benzil	53	–		

[a] Values from ref. 1. [b] (+) indicates sensitization and (–) lack of sensitization. [c] Isomerization not accessible for experimental reasons. [d] Not measured.

Acetone

The experiments were performed in aqueous solution. The wavelength of irradiation was 290 nm, which corresponds very closely to the first absorption band of acetone. Acetone was used at a constant concentration of 2.7 *M*, while the $Co(NH_3)_5NO_2^{2+}$ concentration was varied in the 1.2×10^{-2}–5.0×10^{-4} *M* range. In these experimental conditions, light absorption by the complex was always less than 7% of the total absorbed light intensity.

Under these conditions, efficient redox decomposition of the complex was observed. At all complex concentrations, the observed Co^{2+} yields were considerably higher in deaerated solutions than in aerated ones. Quantum yields for the sensitized reaction were calculated by applying a small correction for direct light absorption by the complex. The sensitized quantum yields are plotted according to the usual Stern–Volmer relation in Figure 1. Both the aerated and deaerated values extrapolate to a limit quantum yield of 0.35 ± 0.04.

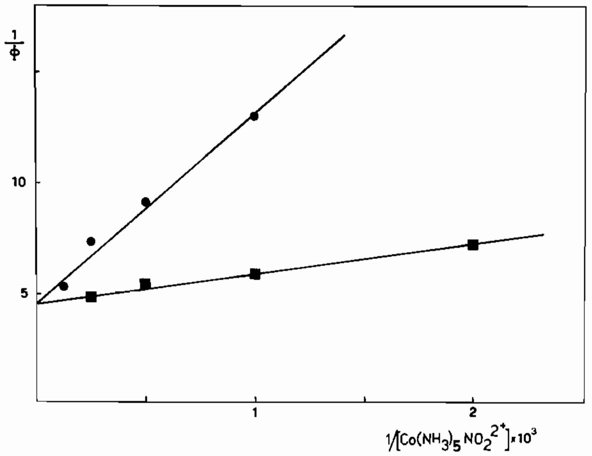

Fig. 1. Stern–Volmer plot of the photoredox decomposition of $Co(NH_3)_5NO_2^{2+}$ sensitized by acetone.

The absorbance of acetone in the 300–350 nm region allowed the analysis of the spectral variations of solutions containing 0.5×10^{-3} to 2.0×10^{-3} *M* $Co(NH_3)_5NO_2^{2+}$ for the occurrence of linkage isomerization. Nitro–nitrito linkage isomerization was found to occur in this concentration range simultaneous to redox decomposition. The ratio between the two reaction modes was $\phi_{redox}/\phi_{isom} = 3.0 \pm 0.5$.

The fluorescence of acetone was monitored as a function of complex concentration up to 2.0×10^{-3} *M*. No genuine quenching effect was detected.

Benzaldehyde

For solubility requirements, the experiments were performed in ethanol/water 1:1 by volume. The wavelength of irradiation was 290 nm. The benzaldehyde concentration was 5.0×10^{-2} *M*, while that of the complex was varied over the range 5.0×10^{-4}–8.0×10^{-3} *M*. In these experimental conditions, the direct light absorption by the complex was always less than 7%.

In these conditions, efficient redox decomposition of $Co(NH_3)_5NO_2^{2+}$ was observed. Sensitization quantum yields were obtained by applying small corrections due to direct light absorption by the complex. The Stern–Volmer plots for aerated and deaerated solutions are shown in Figure 2. The extrapolated limit quantum yield is 0.25 ± 0.03.

Owing to the high absorbance of the irradiated solutions in the 300–350 nm range, spectrophotometric detection of the linkage isomerization reaction was forbidden in this case.

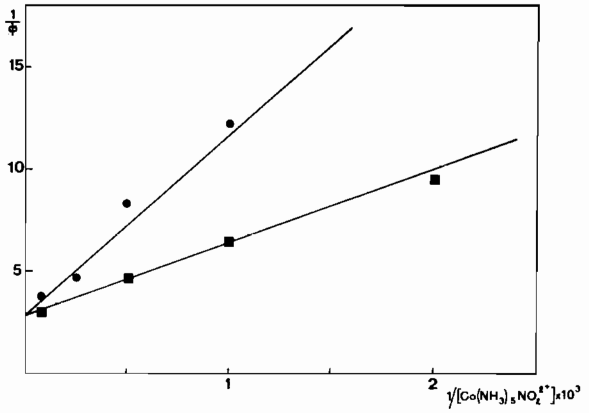

Fig. 2. Stern–Volmer plot of the photoredox decomposition of $Co(NH_3)_5NO_2^{2+}$ sensitized by benzaldehyde.

Thioxanthone

The experiments were performed in 1:1 water/ethanol solvent. The wavelength of irradiation was 405 nm. The thioxanthone concentration was 1.8×10^{-3} *M* and that of the complex 2.0×10^{-3} *M*. These conditions correspond to 3.7% direct light absorption by the complex.

Under these conditions, moderately efficient redox decomposition of the complex was observed. The sensitized quantum yield, corrected for direct light absorption, was 0.016 ± 0.002 and 0.031 ± 0.003 in aerated and deaerated solutions, respectively. Owing to the relatively low efficiency of the sensitization process, no concentration dependence study was performed.

No analysis for the occurrence of linkage isomerization was allowed by the experimental conditions. The fluorescence of the sensitizer was not appreciably quenched by the complex at the concentration used.

Michler's Ketone

The experiments were performed in 1:1 ethanol/water solvent. The wavelength of excitation was 290 nm. The ketone concentration was 1×10^{-3} *M* and that of the complex was 2×10^{-3} *M*. In these conditions, direct light absorption by the complex was about 2%.

No appreciable Co^{2+} concentration could be detected upon irradiation of these deaerated solutions, in addition to the low amount produced by direct light absorption by the complex. The absorbance in the 300–350 nm range was too high to allow sensitive detection of any possible isomerization process.

Biacetyl

The experiments were performed in aqueous solution. The biacetyl concentration was 3×10^{-1} *M*, while that of the complex was varied in the 5×10^{-4}–2×10^{-3} *M* range. The wavelength of excitation was 405 nm. The direct light absorption by the complex was less than 3%.

Irradiation of these deaerated solutions did not produce any appreciable photoreaction, in addition to that arising from direct light absorption by the complex.

The phosphorescent emission of biacetyl (λ_{max} = 520 nm) is completely quenched in the experimental conditions used. Good Stern–Volmer plots were obtained by working at lower complex concentrations. The Stern–Volmer constant for the quenching of biacetyl phosphorescence by $Co(NH_3)_5NO_2^{2+}$ was 2.8×10^4 M^{-1}.

Benzil

The experiments were performed in 1:1 ethanol/water solvent. The benzyl and complex concentrations were both 1×10^{-3} *M*. Direct light absorption by the complex was about 2%.

Irradiation of these deaerated solutions did not produce any appreciable Co^{2+} in addition to that arising from direct light absorption by the complex.

Discussion

Photosensitization Mechanism

Sensitization processes can occur by a variety of mechanisms [1, 2, 26], which for our purposes can be divided into "chemical" and "energy transfer" mechanisms. The chemical mechanisms involve a bimolecular reaction between the excited sensitizer (or some photoproduct of the sensitizer) and the substrate, and their study can only be of some interest with regard to the excited-state reactivity of the sensitizer. Energy transfer mechanisms involve electronic excitation of the substrate and can be used, in favourable cases, to obtain information about the photoreaction mechanism of the substrate.

With Co(III) complexes as substrates, the possibility of chemical sensitization mechanisms is a very serious one. The main direct photochemical reaction of these complexes in the MLCT spectral region is redox decomposition [3, 27]. In direct photochemical studies on acidopentamminecobalt(III) complexes, the redox decomposition photoreaction (reaction 3)

$$Co(NH_3)_5X^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + \cdot X \qquad (3)$$

is usually identified by the formation of Co^{2+} and ammonia, while particularly favourable cases only allow the detection of X ligand radicals.

When a sensitizer (S) is used to sensitize the photochemistry of these complexes, both energy transfer (reaction 4) and chemical mechanisms (*e.g.*, electron transfer, reaction 5) can give rise to some common reaction products, namely, Co^{2+} and ammonia.

$$^{*}S + CO(NH_3)_5X^{2+} \rightarrow S + {}^{*}Co(NH_3)_5X^{2+} \rightarrow S + Co^{2+} + 5NH_3 + \cdot X \qquad (4)$$

$$^{*}S + Co(NH_3)_5X^{2+} \rightarrow S^{+} + Co(NH_3)_5X^{+} \rightarrow S^{+} + Co^{2+} + 5NH_3 + X^{-} \qquad (5)$$

Actually, it has proved exceedingly difficult in many cases to discriminate experimentally between these alternative mechanisms. As to the possibility of detecting intermediates, LMCT states of Co(III) complexes have never been characterized by either emission or absorption, and the Co(II) complexes which should be formed in the chemical mechanisms are expected to collapse to Co^{2+} in a microsecond time scale [28]. On the other hand, the observed oxidation states of S and X cannot be confidently used as a diagnostic tool, because of the possibility of fast secondary redox processes between these species (reaction 6).

$$S^{+} + X^{-} \rightleftharpoons S + \cdot X \qquad (6)$$

Problems of this type have generated a number of controversial interpretations in sensitization studies of Co(III) complexes [2, 7, 9, 11, 16]. Prevailing emphasis is recently being placed on electron transfer rather than energy transfer interpretations [2, 29] and Gafney and Adamson [16] have actually come to the conclusion that "virtually all sensitized reactions of Co(III) complexes so far reported involve electron rather than energy transfer".

The $Co(NH_3)_5NO_2^{2+}$ ion seems to be better suited than other pentammine Cobalt(III) complexes for investigating the nature of the sensitization mechanism. In fact, direct irradiation of this complex gives, besides the usual redox decomposition reaction, an efficient linkage isomerization process [18] which has been shown [19] to proceed via cage recombination of the primary radical pair $Co(NH_3)_5^{2+}\cdot NO_2$. While this species can obviously arise as a consequence of bond homolysis in a LMCT excited state of the complex, there seems to be no reasonable way of obtaining such radical pair following intermolecular electron transfer from a sensitizer to the complex. This offers, in principle, a possibility of testing the

TABLE II. Ligand-to-Metal Charge Transfer Excited States of $Co(NH_3)_5X^{2+}$ Complexes.

Orbital Configuration[a]	Symmetry (C_{4v})	Spin State (2S + 1)	Type[b]
$(p_z)_X^2 (p_x, p_y)_X^3 (d_{xz}, d_{yz})^4 (d_{xy})^2 (d_{z^2})$	E	1, 3	LSπ1
$(p_z)_X^2 (p_x, p_y)_X^3 (d_{xz}, d_{yz})^4 (d_{xy})^2 (d_{x^2-y^2})$	E	1, 3	LSπ2
$(p_z)_X (p_x, p_y)_X^4 (d_{xz}, d_{yz})^4 (d_{xy})^2 (d_{z^2})$	A_1	1, 3	LSσ1
$(p_z)_X (p_x, p_y)_X^4 (d_{xz}, d_{yz})^4 (d_{xy})^2 (d_{x^2-y^2})$	B_1	1, 3	LSσ2
$(p_z)_X^2 (p_x, p_y)_X^3 (d_{xz}, d_{yz})^3 (d_{xy})^2 (d_{z^2}) (d_{x^2-y^2})$	A_1, B_1, A_2, B_2	3, 5	HSπ1
$(p_z)_X^2 (p_x, p_y)_X^3 (d_{xz}, d_{yz})^4 (d_{xy}) (d_{z^2}) (d_{x^2-y^2})$	E	3, 5	HSπ2
$(p_z)_X (p_x, p_y)_X^4 (d_{xz}, d_{yz})^3 (d_{xy})^2 (d_{z^2}) (d_{x^2-y^2})$	E	3, 5	HSσ1
$(p_z)_X (p_x, p_y)_X^4 (d_{xz}, d_{yz})^4 (d_{xy}) (d_{z^2}) (d_{x^2-y^2})$	A_2	3, 5	HSσ2

[a] Molecular orbitals of the complex are indicated by the parent metal and X-ligand atomic orbitals. [b] LS and HS indicate the low-spin and high-spin Co(II) configuration at the metal; σ and π indicate the origin of the transition on the X ligand; 1 and 2 indicate the low-energy and high-energy tetragonal component of the state.

energy transfer or chemical nature of the sensitization mechanism.

The experimental results (Table I) show that acetone, benzaldehyde and thioxanthone but not Michler's ketone, biacetyl and benzil sensitize the redox decomposition of $Co(NH_3)_5NO_2^{2+}$. Unfortunately, with two out of three working sensitizers, the experimental conditions forbid the analysis for the occurrence of linkage isomerization. In the case of acetone, however, the results unequivocally show that linkage isomerization is sensitized together with redox decomposition, in essentially the same 1:3 ratio as observed in direct photochemistry [18]. This constitutes a rather compelling piece of evidence for the energy transfer nature of the sensitization of the photochemistry of $Co(NH_3)_5NO_2^{2+}$ by acetone. For benzaldehyde and thioxanthone such direct evidence is lacking. As far as possible chemical mechanisms are concerned, electron transfer from the excited triplet sensitizer to the complex seems unlikely, since excited triplet carbonyl compounds are only known to be good oxidants [30]. On the other hand, photoreduction of the sensitizer (particularly in water/ethanol solvent) followed by secondary reduction of the complex seems to be ruled out by the inefficiency of other carbonyl compounds like biacetyl, Michler's ketone, and benzyl.

Finally, additional support for the general occurrence of electronic energy transfer rather than chemical sensitization in these systems is given by the reasonable correlation observed (Table I) between the sensitizing efficiency of the sensitizers and their triplet energy. In conclusion, direct evidence as well as indirect general arguments indicate that the results of the present study are the consequence of excitation energy transfer rather than of chemical sensitization mechanisms.

Triplet vs. *Singlet Excitated State Behavior*

The possibility that spin forbidden excited states of LMCT character may be involved in the photoredox decomposition of Co(III) complexes was first suggested by Vogler and Adamson [4] who attempted to test this hypothesis by sensitizing the redox decomposition of $Co(NH_3)_6^{3+}$. Since then, several sensitization studies have been published [6, 7, 9, 11, 14, 15] in which the observed photochemistry was attributed to the reactivity of triplet LMCT states. The nature of these spin-forbidden LMCT states, however, has not been discussed in any detail until very recently [17].

A relatively large number of states of the LMCT type is expected to lie in the near UV range for a Co(III) complex. In a typical acidopentammine complex, the number and type of LMCT states are determined by three main factors, namely, the tetragonal splitting of the *d* orbitals, the possibility of σ or π origin of the transition on the acido ligand, and the possibility of different spin states of the Co(II) configuration at the metal. The type, symmetry and spin multiplicity of LMCT states occurring at low energies in $Co(NH_3)_5X^{2+}$ complexes are summarized in Table II. The two typical LMCT bands found in the spectra of these complexes [31] correspond to transitions from the ground state to LSπ1 and LSσ1 singlet states.

It has become customary to discuss the excited-state behavior of Co(III) complexes in terms of hypothetical energy profiles of the excited states as a function of the reaction coordinate [3, 18, 20, 21, 32]. The LMCT state situation shown in Table II is sufficiently complex as to prevent any theoretical treatment of this system as a function of internuclear distances. A number of broad considerations can nevertheless be made concerning the relative energy ordering of the various types of states.

(i) The energy differences between LMCT states of the same one-electron configuration (*i.e.*, of the same "type" in Table II, but of different spin multiplicity and/or symmetry) should be small at ground-state equilibrium geometry since repulsion terms between metal-localized and ligand-localized electrons should be small. These small energy differences are further expected to decrease regularly along the reaction coordinate for metal–ligand bond breaking.

(ii) At the ground-state equilibrium geometry, states of tetragonal types 1 and π are lower in energy than corresponding states of type 2 and σ [31]. This ordering should be maintained along the reaction coordinate. The energy differences between states differing in their σ or π character decreases to vanishing as the metal–ligand bond is stretched. The energy difference between states of tetragonal type 1 and 2 should decrease steadily with increasing metal–ligand bond length for HS states (notice that d_{xy}, d_{xz}, and d_{yz} are all essentially nonbonding in the $Co(NH_3)_5^{2+}$ product), while remaining sizeable even at long distances for LS states.

(iii) In the ground-state equilibrium geometry, the HS states lie at considerably higher energies than the corresponding LS states. In the $Co(NH_3)_5^{2+}{\cdot}X$ radical pair product, however, the ordering must be reversed, with the HS states lower than the LS ones.

Endicott and Ferraudi [17] have recently pointed out a very important consequence of the energy situation described in point (iii), namely, the fact that somewhere along the reaction coordinate for redox decomposition of $Co(NH_3)_5X^{2+}$ complexes a crossing of LS and HS surfaces must occur. They have actually suggested that a predominant photoreaction path in these systems may be the relaxation of the initially excited LS states through this crossing region to yield the HS $Co(NH_3)_5^{2+}{\cdot}X$ products. Since HS and LS states are of quintet/triplet and triplet/singlet multiplicities, respectively, a true surface crossing is expected to occur in all cases except for triplet LS and HS states, which should exhibit a typical "avoided crossing" [33] situation. A picture of this type is schematized in Figure 3 for the lowest LMCT states (LSπ1 and HSπ1) of a typical $Co(NH_3)_5X^{2+}$ complex.

An interesting consequence of Endicott and Ferraudi's picture is that triplet LMCT states can proceed smoothly on a single potential energy surface down to HS Co(II) products, while an intersystem crossing process is required in order to reach the same products starting from a singlet LMCT state. This argument would imply some inefficiency in singlet reactions caused by direct irradiation as compared to a higher efficiency for the triplet reactions which can be induced by sensitization. A comparison of direct and sensitized quantum yields of photoredox decomposition of Co(III) pentammine complexes should be valuable in this regard. It is unfortunate that most, if not all, of the sensitization results in Co(III) photochemistry are suspected of being generated by chemical sensitization mechanisms [16]. As previously discussed, the results of this study, especially those obtained with acetone, seem to be free of this type of objection.

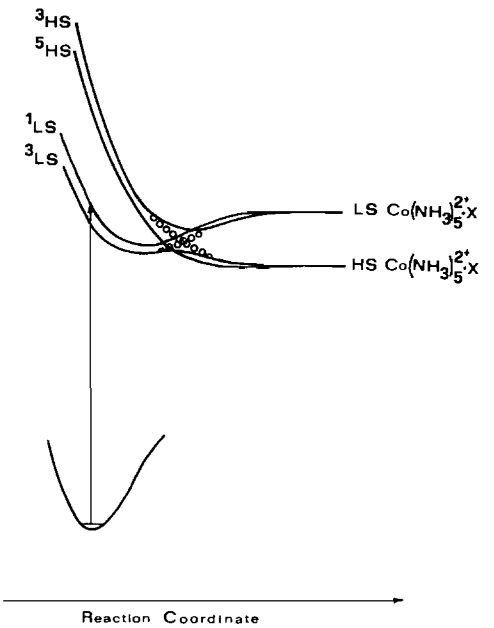

Fig. 3. Typical ordering of the lowest LMCT excited states of a $Co(NH_3)_5X^{2+}$ complex as a function of the photoredox reaction coordinate. Symbols are described in the text and in Table II.

Before comparing the direct and sensitized quantum yields in the case of $Co(NH_3)_5NO_2^{2+}$ one should recognize the wavelength dependent nature of the direct quantum yields, brought about by the operation of a cage recombination mechanism [20]. The most significant comparison, therefore, seems to be that between sensitized quantum yields and direct quantum yields for excitation wavelengths of the same energy as the triplet energies of the sensitizers. Acetone has a triplet energy [1] corresponding to about 360 nm, while that of benzaldehyde corresponds to about 400 nm. A comparison of the limit quantum yields in Table I with the direct quantum yields [20] in this wavelength range indicates that the two sets of quantum yields are essentially the same. This conclusion seems to be at odds with the above arguments on singlet *vs.* triplet reaction efficiencies.

A closer look at the energetics of the $Co(NH_3)_5NO_2^{2+}$ system, however, may reconcile this discrepancy. The method proposed by Endicott [3, 32] for estimating the redox energetics of Co(III) complexes requires the knowledge of the activation enthalpy for the thermal X-ligand substitution reaction of the complex. This figure is unknown for $Co(NH_3)_5NO_2^{2+}$. If a typical value for Co(III) pentammine complexes is assumed [28], *e.g.*, 9 ± 3 kK mol^{-1}, and ΔH^0_{IP} is calculated according to Endicott *et al.* [32, 34] the energy of the $Co(NH_3)_5^{2+}{\cdot}NO_2$ radical pair, ΔH_c^0, is 17 ± 3 kK mol^{-1}. This value is appreciably lower than the onset of LMCT absorption (about 24 kK), indicating that the LS LMCT states are essentially dissociative in nature. Thus, the LMCT excited state situation in the case of $Co(NH_3)_5NO_2^{2+}$ is more likely that depicted in Figure 4. The figure shows that in this case it is not necessary to use the avoided crossing between LS and HS triplet states to achieve the dissociation in a non-activated process. Prompt dissociation of both singlet and triplet LS LMCT states should account in this case for similar photoreaction quantum yields obtained in direct and sensitized irradiation. It should be stressed that this situation is likely to be rather exceptional among Co(III) pentammine complexes, since the low H_c^0 and thus the dissociative nature of LS LMCT states come from the low oxidation potential of the NO_2 group as compared to other acido ligands.

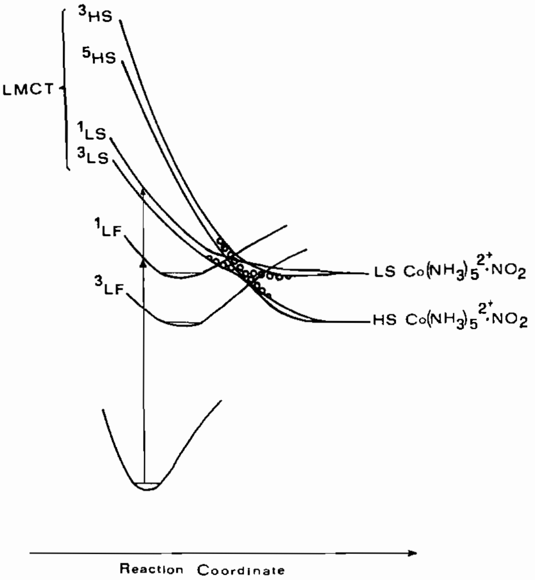

Figure 4. Qualitative representation of the excited state situation of $Co(NH_3)_5NO_2^{2+}$. Symbols are described in the text and in Table II.

A final comment is deserved by the results obtained using biacetyl as the energy donor. In fact, the triplet state of biacetyl was found to be quenched by the complex, but no sensitized photochemistry was observed. Most likely, this indicates energy transfer from the sensitizer to some unreactive triplet of the complex. The obvious candidate for this type of energy transfer is the lowest LF triplet state of the complex. The interesting observation here is that the singlet LF state which is reached by direct LF irradiation leads to reaction [18] while the corresponding triplet reached by energy transfer from biacetyl does not. Quite probably, this is due to the relatively high singlet–triplet splitting of LF states as compared with that of LMCT states. Thus, although the crossing from singlet LF to LMCT states is energetically allowed in this system [20], the crossover from relaxed LF triplet to LMCT states may be substantially endothermal. A situation of this kind is also schematized in Figure 4.

References

1 A. A. Lamola, "Energy Transfer and Organic Photochemistry", P. A. Leermakers and A. Weissberger, Eds., Interscience, New York, N.Y. (1969) Chapter II.
2 V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and G. S. Laurence, *Coord. Chem. Rev., 15,* 321 (1975).
3 J. F. Endicott, "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Interscience, New York, N.Y. (1975) Chapter III.
4 A. Vogler and A. W. Adamson, *J. Am. Chem. Soc., 90,* 5943 (1968).
5 M. A. Scandola, F. Scandola and V. Carassiti, *Mol. Photochem., 1,* 403 (1969).
6 M. A. Scandola and F. Scandola, *J. Am. Chem. Soc., 92,* 7278 (1970).
7 H. D. Gafney and A. W. Adamson, *J. Phys. Chem., 76,* 1105 (1972).
8 P. Natarajan and J. F. Endicott, *J. Phys. Chem., 77,* 971 (1973).
9 P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc., 94,* 3635 (1972).
10 H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc., 94,* 8283 (1972).
11 P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc., 95,* 2470 (1973).
12 P. Natarajan and J. F. Endicott, *J. Phys. Chem., 77,* 1823 (1973).
13 J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc., 95,* 5159 (1973).
14 P. Natarajan and J. F. Endicott, *J. Phys. Chem., 77,* 2049 (1973).
15 L. Moggi, N. Sabbatini and O. Traverso, *Mol. Photochem., 5,* 11 (1973).
16 H. Gafney and A. W. Adamson, *Coord. Chem. Rev., 16,* 171 (1975).
17 J. F. Endicott and G. J. Ferraudi, *Inorg. Chem., 14,* 3133 (1975).
18 V. Balzani, R. Ballardini, N. Sabbatini and L. Moggi, *Inorg. Chem., 7,* 1398 (1968).
19 F. Scandola, C. Bartocci and M. A. Scandola, *J. Am. Chem. Soc., 95,* 7898 (1973).
20 F. Scandola, C. Bartocci and M. A. Scandola, *J. Phys. Chem., 78,* 572 (1974).
21 J. F. Endicott, *Inorg. Chem., 14,* 448 (1975).
22 R. K. Murman and H. Taube, *J. Am. Chem. Soc., 78,* 4886 (1956).
23 F. Vydra and R. Pribil, *Talanta, 5,* 44 (1960).
24 The determination of the linkage isomerization reaction was carried out by first subtracting the redox decomposition reaction from the overall spectral variations and then analyzing the resulting spectral changes in terms of the product spectra of ref. 18.
25 C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A, 253,* 518 (1956).
26 P. S. Engel and B. M. Monroe, *Adv. Photochem., 8,* 245 (1971).

27 V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y. (1970).

28 F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y. (1967).

29 G. Navon and N. Sutin, *Inorg. Chem., 13,* 2159 (1974).

30 P. J. Wagner, *Topics in Current Chemistry, 66,* 1 (1976).

31 V. M. Miskowski and H. B. Gray, *Inorg. Chem., 14,* 401 (1975).

32 J. F. Endicott, G. J. Ferraudi and J. R. Barber, *J. Phys. Chem., 79,* 630 (1975).

33 L. Salem, C. Leforestier, G. Segal and R. Wetmore, *J. Am. Chem. Soc., 97,* 479 (1975).

34 ΔH^0_{IP} can be estimated as about 8 kK mol^{-1}, starting from the reported value for $Co(NH_3)_5^{2+}$·Br [32] and knowing that NO_2 is about 1 V weaker an oxidant than Br [3]; this argument assumes similar entropy contributions for the nitro and bromo cases.