

Whitesides and Bunting,¹³ which arises from the circumstance that the stereochemistry of both systems may be analyzed in terms of the same abstract model: even though the stereoisomerization processes in the two systems differ vastly in mechanistic detail (*i.e.*, torsion for **1** *vs.* pseudorotation for **2**), **1** and **2** are stereochemically correspondent.¹⁴

(13) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).

(14) D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Nat. Acad. Sci. U. S.*, **70**, 3445 (1973).

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Environmental Effects in the Photoredox Decompositions of Acidopentaamminecobalt(III) Complexes. Contributions from Charge Transfer and Ligand Centered Excited States in $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$

Sir:

Mechanistic discussions of the chemical reactions which follow the irradiation of charge transfer to metal (CTTM) absorption bands of transition metal complexes have very often been formulated around radical pair²⁻⁵ or excited state⁶⁻¹² models. Attempts to explore aspects of excited state models using triplet sensitizers¹³⁻¹⁷ have frequently been complicated by side reactions^{14, 18-20} of the sensitizer or by free radical reactions of likely photoredox products.^{17b, 21} Very recently we²² and Scandola²³ have been attempting to

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(2) (a) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); (b) A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960).

(3) R. D. Lindholm and T. K. Hall, *J. Amer. Chem. Soc.*, **93**, 3525 (1971).

(4) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(5) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Progr. Inorg. Chem.*, **17**, 1 (1972).

(6) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

(7) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970).

(8) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **92**, 6801 (1970).

(9) E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).

(10) E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76**, 2493 (1972).

(11) A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 6655 (1972).

(12) V. W. Cope, S.-N. Chen, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **95**, 3116 (1973).

(13) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1968).

(14) H. D. Gafney and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1972).

(15) I. Fujuta and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 1105 (1972).

(16) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1880 (1971).

(17) (a) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 3635 (1972); (b) *ibid.*, **95**, 2470 (1973).

(18) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970).

(19) H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(20) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **95**, 5159 (1973).

(21) (a) P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, **77**, 971 (1973); (b) *ibid.*, **77**, 1823 (1973).

(22) J. R. Barber, G. F. Ferraudi, and J. F. Endicott, work in progress.

(23) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Amer. Chem. Soc.*, **95**, 7898 (1973).

probe aspects of radical pair behavior by examining the photochemistry of cobalt(III) complexes in media of varying viscosity. Scandola's work has elegantly demonstrated opposite and proportional dependencies on viscosity of the yields of Co^{2+} and $\text{Co}(\text{NH}_3)_5\text{ONO}^{2+}$ obtained following CTTM (254 nm) excitation of $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. This kind of photochemical behavior strongly supports the contention²⁴ that the linkage isomerization reaction is the result of radical pair recombination.

Our studies²² of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{N}_3$, and NCS) complexes in a variety of solvent media appear to be leading to some unexpected insights into the nature of both radical pair species and their excited state precursors. Most importantly we find that variations of product yield with excitation wavelength ($400 \text{ nm} \geq \lambda \geq 214 \text{ nm}$) and with solvent viscosity are not always in agreement with the qualitative predictions²⁵ for the simple recombination and diffusive separation reactions of radical pair species. The most striking photochemical behavior has been found for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. For this complex the quantum yield of Co^{2+} ($\phi_{\text{Co}^{2+}}$) increases with increasing [glycerol] for deep ultraviolet ($\lambda \leq 280 \text{ nm}$) irradiations (Figure 1). This is qualitatively opposite to the behavior reported for 254-nm irradiations of $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ and qualitatively opposite to expectation if one assumes that the only factors affecting the yield of cobalt(II) are the rates of recombination and diffusive separation of primary "radical pair" products of the type $\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{R}\}$.

It is obvious from Figure 1 that the kind of variation of $\phi_{\text{Co}^{2+}}$ (*i.e.*, whether a decrease or an increase) with increasing [glycerol] is different for irradiation of different absorption features of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. Our studies indicate that the yields of Co^{2+} and $\cdot\text{NCS}$ radicals are stoichiometric over the full range of excitation in aqueous solutions. Although there are many important differences of detail, deep ultraviolet irradiations of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, and $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ have also been found to give striking increases in $\phi_{\text{Co}^{2+}}$ with [glycerol]; furthermore we have found that photoredox yields in acetonitrile are even larger while yields in 80% H_3PO_4 are the smallest we have observed.

The most striking and unique features of our observations on $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ pertain to irradiations in the near ultraviolet ($350 \text{ nm} \geq \lambda > 254 \text{ nm}$). Over this range of excitations we find: (1) $\phi_{\text{Co}^{2+}}$ (as well yields of NCS^- and oxidation products) to be nearly wavelength independent, (2) $\phi_{\text{Co}^{2+}}$ decreases, qualitatively as expected, with [glycerol], and (3) in water $\phi_{\text{Co}^{2+}}$ is strongly temperature dependent, with $\log \phi \propto T^{-1}$ (for ϕ determined at $T = 25, 35, 50$, and 60°) and $E_a \approx 18 \text{ kJ/mol}$.²⁶ In 50% glycerol we found E_a to increase to about 40 kJ/mol for 350-nm irradiations and to be

(24) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

(25) (a) R. M. Noyes, *Progr. React. Kinet.*, **1**, 128 (1961); (b) For a recent review see J. P. Lorand, *Progr. Inorg. Chem.*, **17**, 207 (1972); (c) Most pertinent among the predictions of the mechanical model are (i) the redox yield should increase monotonically (presumably to unity) with excitation energy and (ii) the formation of redox products (Co^{2+} and a ligand radical) requires the diffusive separation of the primary, solvent cage trapped, cobalt(II) and radical fragments. Thus one would predict redox yields to decrease as solvent viscosity is increased.

(26) Adamson^{2b} has reported an activation energy for formation of Co^{2+} in near-ultraviolet excitations ($\lambda \approx 370 \text{ nm}$) of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ but that no activation energy is observed for longer wavelength ($\lambda > 450 \text{ nm}$) excitations. This implies that the activation energy goes through a maximum for irradiations in this one absorption band (Figure 1).

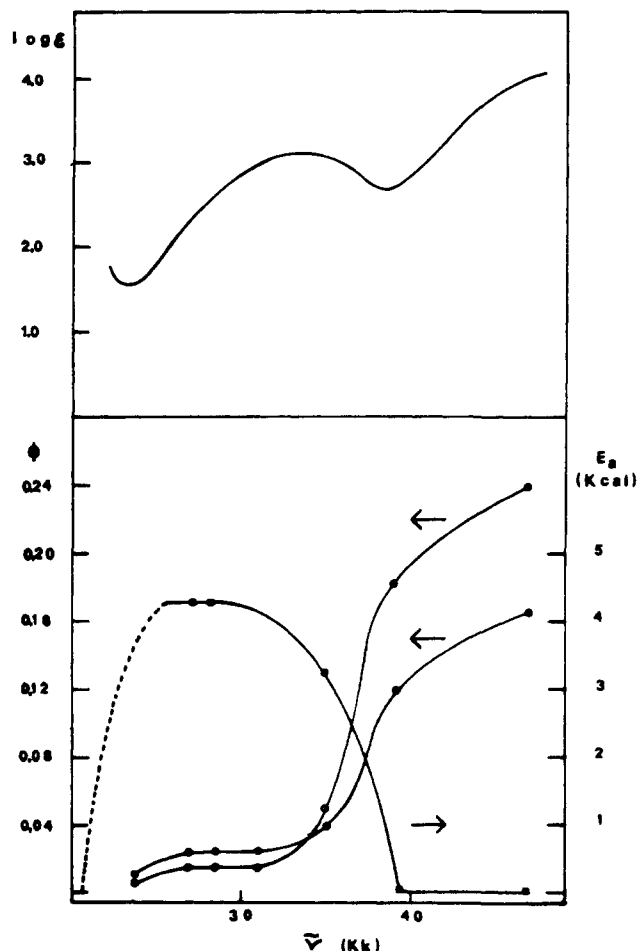
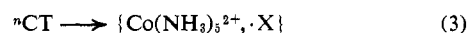


Figure 1. Absorption spectrum (upper curve) and quantum yields of Co^{2+} (lower curves) from ultraviolet irradiations of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$. For lower set of curves quantum yields were obtained in water (solid circles) or 50% glycerol-water (open circles) solutions; activation energies (solid squares) were obtained from quantum yields obtained from irradiations of aqueous solutions in the range 25–60°. Dotted portion of the curve for activation energies is drawn in accord with the report in ref 2b of an activation energy for irradiations at $\lambda > 450$ nm.

approximately zero for 254-nm irradiations. The prominent absorption feature in this spectral region, the band at 305 nm, may be a ligand centered transition.²⁷ The above observations suggest vibrational equilibration within the corresponding excited state, followed by competitive electronic relaxation to the ground state (or at least to a less reactive lower energy excited state; this complex is not very photosensitive to ligand field excitation^{2,22}) and population of a reactive charge transfer excited state. It is most significant that for this complex the decreased values of $\phi_{\text{Co}^{2+}}$ in glycerol are associated with an increased thermal activation barrier and that contrasting behavior was found for higher energy excitations. Since the medium viscosity must decrease as temperature increases, these observations again imply that while competitive diffusive and recombination processes of radical pair products may be a feature of the sequence of events following excitation in the 350–280-nm range they cannot be dominant mechanistic features for the higher energy excitations. The unexpectedly high yields of Co^{2+} which we have

(27) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Wiley, New York, N. Y., 1961.

obtained for high energy irradiations in glycerol water media may arise from either or both of two plausible mechanisms:²⁸ (1) there may be a relatively low energy onset²⁹ of a CTTM state corresponding to photo-oxidation of solvent glycerol³⁰ or (2) the shape of excited state potential energy surface, the binding energy of the CTTM excited state, etc., are to a significant extent functions of the solvent environment of complex ion substrate. Actually the first "alternative" is a limiting case of the second since CTTM excitation results in an inward flow of negative charge in the solvated complex. Clearly the Franck-Condon state (${}^1\text{CT}^*$) reached in the initial excitation must have ground state (${}^1\text{A}$) solvation, and this solvent environment must ultimately relax to solvation appropriate to the radical pair products ($\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{X}\}$); eq 1–3 describe the proposed



sequence of events, where the excited state ${}^n\text{CT}$ could in principle differ from ${}^1\text{CT}^*$ in thermal equilibration and also in spin multiplicity.³¹ It is to be observed that (1) describes an electronic transition with a large electric dipole moment, so that (1–3) would require a large adjustment in the solvent environment. We are proposing therefore that the solvent plays a more active role in CTTM photochemistry of transition metal complexes than has been previously suspected³² and that photo-physical processes affecting the quantum yield, processes such as electronic relaxation, intersystem crossing, etc., can occur within the lifetime of the CTTM states (${}^1\text{CT}^*$, ${}^n\text{CT}$, or other states populated along the coordinate for reaction 2).

(28) Possible variations in the type of radical pair species (geminate or secondary or singlet, triplet, or quintet) seem less plausible and will be discussed in detail elsewhere.

(29) That is the lowest energy manifestation of "solvent" oxidation would have to occur at about 285 nm for $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ and at about 240 nm for $\text{Co}(\text{NH}_3)_5^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{N}_3$).

(30) When glycerol oxidation has been observed, we have no means of determining unequivocally whether glycerol oxidation occurred in a primary photoredox step or in subsequent reactions of primary radicals. It is also to be noted that we prepared our glycerol solutions from reagent grade glycerol which was found to be nearly nonabsorbing at $\lambda \geq 214$ nm (absorbance of neat glycerol at 214 nm ≤ 0.1).

(31) Note that the spin of a $\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{X}\}$ radical pair containing a high spin (*i.e.*, ground state) $\text{Co}(\text{NH}_3)_5^{2+}$ species does not correlate with a singlet CTTM state.

(32) However, analogous involvements of solvent in the photophysics of charge transfer complexes have been proposed, see M. Ottolenghi, *Accounts Chem. Res.*, 6, 153 (1973).

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Vinylsilanes as Carbonyl Precursors. Use in Annelation Reactions

Sir:

The addition of a 3-ketoalkyl chain α to a carbonyl function, an important step in annelation reactions, requires either Michael addition to a suitable vinyl ketone or alkylation with a 3-ketoalkyl halide equivalent. The latter process is in principle the more general. Maximum versatility, including the important possibility of using the halide in trapping regiospecific