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Correspondence

A Model to Account for Differences in Excited-State Reactivity and Cage Recombination Processes in the Photoredox Chemistry of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5NO_2^{2+}$ [1]

AIC403760

Sir:

The photoredox behavior of coordination complexes has long been of interest and several models, usually involving radical-pair species, have been proposed to account for both the charge-transfer spectra and photochemistry.[2-6] We have recently been systematically examining the energetics of charge transfer to metal (CTTM) spectra of $Co(NH_3)_5X^{2+}$ complexes and attempting to use this information together with the variations in product yield with composition of the solvent medium to provide insight into the mechanistic details of photoredox decompositions of these complexes.[7,8] In the progress of these studies it has become evident that $Co(NH_3)_5NO_2^{2+}$ is unique among the simple acidopentaammine complexes (*i.e.*, for X = Br, Cl, N_3, and NCS, as well as NO_2). Among the contrasts in photochemical behavior are the following. (1) A limiting value of the redox quantum yield, $\phi^{\lim}(Co^{2+})$, has been found for ultraviolet charge-transfer excitation of each complex except $Co(NH_3)_5NO_2^{2+}$.[6-9] (2) The photoredox yield has been found to be a far more complicated function of solvent (*e.g.*, in alcohols, acetonitrile, phosphoric acid, etc.) for $Co(NH_3)_5X^{2+}$ (X = Br, Cl, N_3, NCS)[8] than for $Co(NH_3)_5NO_2^{2+}$.[9] (3) The photoredox, Co^{2+} + NO_2, and the photoisomerization, $Co(NH_3)_5ONO^{2+}$, products have been found to be competitively formed from a common precursor[9b]—this precursor has been postulated to be a radical-pair species which dissociates to form redox products or recombines to form the linkage isomer; however, *recombination does not appear to produce the more stable $Co(NH_3)_5NO_2^{2+}$ isomer*.[9b,10] (4) For the $Co(NH_3)_5X^{2+}$ (X = Br, Cl, NCS, N_3) complexes we have found that the extrapolated threshold excitation energy for appreciable photoredox decomposition, E_{th}, is within 2 kK of the threshold energy for CTTM absorbance, E'_{th};[7,8] for $Co(NH_3)_5NO_2^{2+}$, $E'_{th} - E_{th} \simeq 6$ kK.[6,9,11]

Consideration of the above points suggests that some dynamic components should be introduced into models for the chemistry of CTTM excited states and this can lead to an interpretation of the photoredox behavior of $Co(NH_3)_5NO_2^{2+}$. Few features of the approach employed in the present report appear to have been anticipated in previous mechanistic discussions,[2-9] but the general approach does seem to have some mechanistic generality.

A. General Considerations. 1. Energetics. We have recently shown that $\Delta H_{IP}°$, for reaction 1, and $\Delta H_c°$, for reaction 2,

$$\{Co(NH_3)_6{}^{3+}, X^-\} \xrightarrow{\Delta H_{IP}°} {}^1\{Co(NH_3)_6{}^{2+}, \cdot X\} \qquad (1)$$

$$Co^{III}(NH_3)_5X \xrightarrow{\Delta H_c°} {}^1\{Co(NH_3)_5{}^{2+}, \cdot X\} \qquad (2)$$

may be estimated from thermodynamic and kinetic parameters[12] and that comparison of these parameters with CTTM spectra of the cobalt(III) complexes implies an appreciable Franck–Condon contribution to the spectra of the ion-pair complexes.[7,8b] For several $Co(NH_3)_5X^{2+}$ complexes (*i.e.*, with X = Cl, Br, N_3, NCS) our estimates of thermodynamic and spectroscopic parameters are such that $\Delta H_c° - E_{th} = 2 \pm 1$ kK/mol, and $E_{th} \simeq E'_{th}$; *i.e.*, these quantities are nearly equal within the expected precision of our estimates. It is useful to take $Co(NH_3)_5Br^{2+}$ as a prototype of the class of compounds; for this complex we estimate $E_{th} = 22$ kK/mol, $E'_{th} = 22$ kK/mol, and $\Delta H_c° = 24$ kK/mol. Allowing for some small Franck–Condon contribution to E'_{th}, this quantity may be taken to be an approximation to the vibrationally thermalized energy of potential energy manifold describing the spectroscopic CTTM excited state (^{1}CT), and $\Delta H_c°$ may be taken as an approximation of the minimum energy required to form a geminate "radical pair" of net singlet spin multiplicity[1] $\{Co(NH_3)_5{}^{2+}, \cdot Br\}$. It may also be estimated that a radical pair of net triplet spin multiplicity containing high-spin cobalt(II), ${}^3\{Co(NH_3)_5{}^{2+}, \cdot Br\}$, lies about 4 kK lower in energy than ${}^1\{Co(NH_3)_5{}^{2+}, \cdot Br\}$.[7,8b] A qualitative representation of a potential energy surface connecting points corresponding to these estimated energy differences is shown in Figure 1.

2. Franck–Condon Components. The spectroscopic transition $Co(NH_3)_5Br^{2+}(^1A_1) \rightarrow Co(NH_3)_5Br^{2+}(^1CT)$ generates the Franck–Condon excited state in a ground-state solvation environment and with ground-state metal–ligand bond distances. Both of these factors contribute repulsively to cause the initial Franck–Condon state to be higher in energy than a thermally equilibrated CTTM excited state with the same electronic configuration. If no other factors intervened, one would expect the initial Franck–Condon state to relax smoothly (along an "antibonding" trajectory) to primary radical-pair products, ${}^1\{Co(NH_3)_5{}^{2+}, \cdot Br\}$. An approach to generating such a trajectory is available if one considers the back-reaction, *i.e.*, the compression of the bonds in the radical-pair species and repolarization of the solvent to regenerate metal–ligand distances and solvation appropriate to the ground state. Very similar processes have been considered in detail for electron-transfer reactions[13,14] and in charge-transfer transitions in mixed dinuclear complexes.[15] The total free energy change involved in this process may be estimated from, $\Delta G_R = (\lambda_i + \lambda_o)/4$, with $\lambda_i \simeq 2k(\Delta r)^2$, where k is a force constant and Δr the difference in bond lengths between equilibrated radical pair and initial excited-state species, and with λ_o given by (3)[13,14,16] at any distance of separation r of cobalt(II) and

$$\lambda_o = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_{el}}\right)e^2 \qquad (3)$$

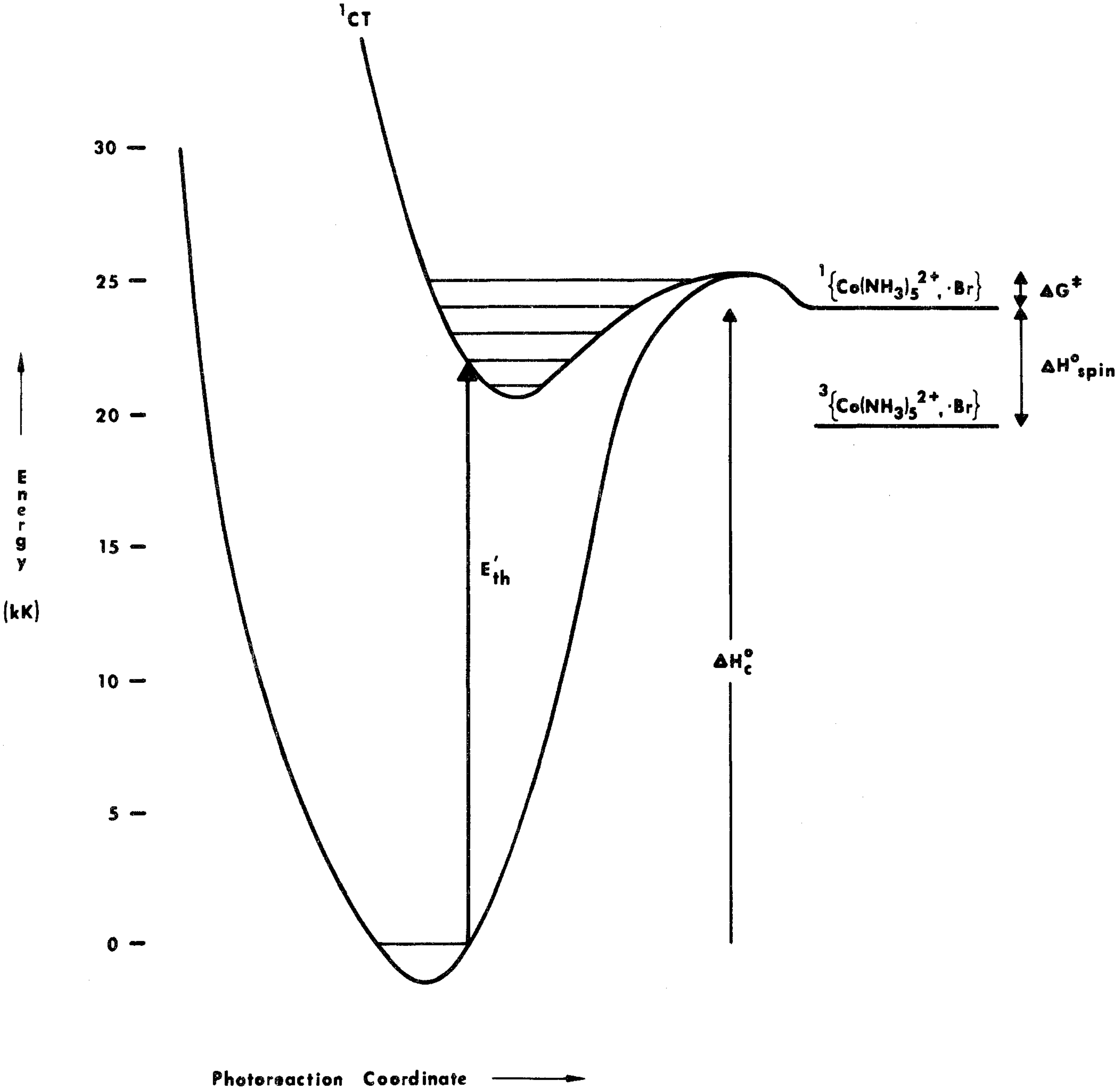

Figure 1. Hypothetical potential energy surfaces for the photoredox chemistry of $Co(NH_3)_5Br^{2+}$. Energy quantities indicated are drawn to scale per the estimates discussed in the text. Only the lowest energy CTTM excited state is indicated.

the radical fragment. Since the Jahn–Teller distortion in low spin cobalt(II) complexes can amount to 0.5 Å in each of two bonds along the axis of distortion[17] and since $\lambda_o/4$ is of the order of 4 kK/mol for systems of the type being considered, the initial Franck–Condon state should be of the order of 10 kK/mol higher in energy than the equilibrated radical-pair species.

B. A Primitive Model. In view of the above it seems reasonable to take $E'_{th} - 2$ kK (allowing for a small Franck–Condon contribution to E'_{th} for the cobalt complexes) as an estimate of the energy difference between the ground state and the lowest energy vibronic state in the CTTM manifold. Thus, it is proposed that the energy of the system along the photoreaction coordinate may be approximated by $[((\lambda_o + \lambda_i)/4) - (\text{covalent bond energy})]$. This approach[18] does assume that vibrational relaxation within a Franck–Condon state is rapid compared to dielectric relaxation of the surrounding solvent.[19] In order to obtain an estimate of the barrier to excited-state dissociation (4) one may further assume

$$Co(NH_3)_5Br^{2+} + h\nu \rightarrow {}^1CT \xrightarrow{k_4} {}^1\{Co(NH_3)_5{}^{2+}, \cdot Br\} \quad (4)$$

either (a) that dielectric relaxation and excited-state dissociations are coupled so that there is a net activation barrier to (4) as indicated in Figure 1 or (b) that dielectric relaxation is rapid compared to excited-state dissociation resulting in no significant barrier to excited-state dissociation. In order to estimate a barrier appropriate to assumption (a), it is convenient to assume that the covalent bond energy is much smaller than $(\lambda_i + \lambda_o)/4$ in the transition state for the cage recombination reaction (5) and to use the resulting reorg-

$${}^1\{Co(NH_3)_5{}^{2+}, \cdot Br\} \xrightarrow{k_5} Co(NH_3)_5Br^{2+} \quad (5)$$

anizational barrier as appropriate to both (4) and (5). This "transition state" involves some compression of bond lengths on the cobalt(II) fragment, some electrical repolarization of

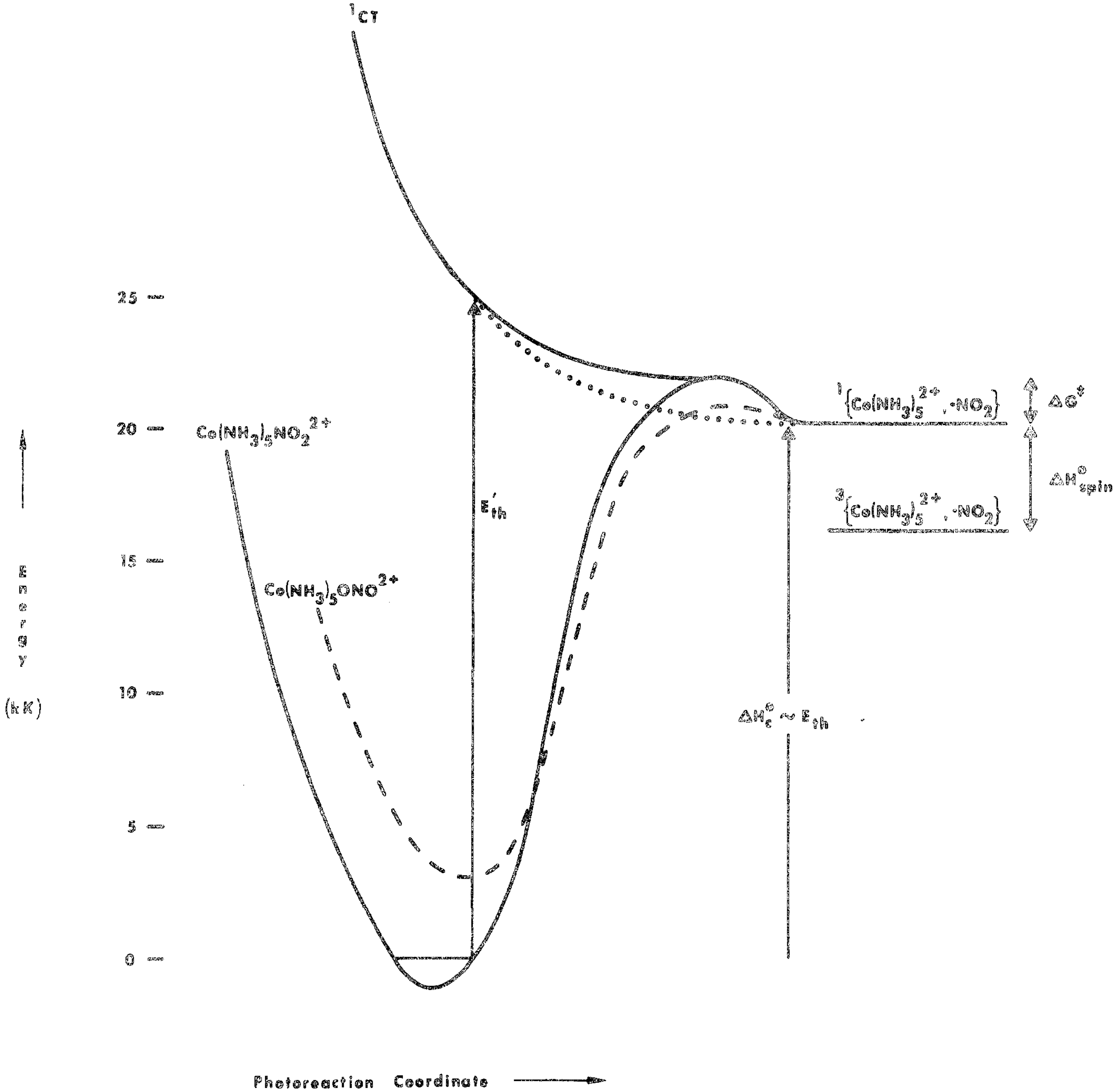

Figure 2. Hypothetical potential energy surfaces for the photoredox chemistry of $Co(NH_3)_5NO_2^{2+}$. Energy quantities indicated are drawn to scale per the estimates discussed in the text. States other than the lowest energy CTTM state are omitted for simplicity. Solid curves are for $Co(NH_3)_5NO_2^{2+}$, the dashed curve is for the ground state of $Co(NH_3)_5ONO^{2+}$, and the dotted curve is for a fully dissociative state, equivalent to that proposed in ref 6 and 9a.

the solvent cavity, and some changes in size of the solvent cavity, but no net transfer of charge.

As a final assumption the Jahn–Teller distorted, low-spin $Co(N_4)(OH_2)_2^{2+}$ complexes, containing relatively saturated (N_4) ligands,[16a] are taken as models of the cobalt fragment in $^1\{Co(NH_3)_5^{2+}, \cdot Br\}$, so $\lambda_i/4 \simeq 1.5$ kK/mol and $\lambda_o/4 \simeq 4$ kK/mol,[20,21] for a reorganizational free energy of about 5.5 kK/mol. Equation 6[22] may be used with $\lambda/4 \simeq 5.5$ kK/mol

$$\Delta G^{\ddagger} = \frac{\lambda}{4} + \frac{\Delta G^{\circ}}{2} + \frac{(\Delta G^{\circ})^2}{4\lambda} \tag{6}$$

and $\Delta G^{\circ} \approx 11.8$ kK/mol[7,8b] to obtain $k_5 \approx 2 \times 10^{10}$ sec^{-1}; use of these same values to estimate k_4 results in an unreasonably small number which suggests (1) an appreciable reduction in $\lambda/4$ due to covalent bonding in the "transition state," (2) that the reaction of photochemical significance is (7), or (3) that dielectric relaxation is rapid compared to

$$^1\text{CT} \xrightarrow{k_7} {}^3\{\text{Co(NH}_3)_5{}^{2+}, \cdot\text{Br}\} \rightarrow \text{products} \tag{7}$$

excited-state dissociation. Although present information does not permit a clear choice between these alternatives, it is likely that some reaction combination other than (4) and (5) is required in order to account for the observation that $\phi^{\lim}(Co^{2+}) \simeq 0.32$;[7,8,23,24] this observation excludes the third alternative unless the vibrationally equilibrated charge-transfer excited state has an energy $E_0 < \Delta H_c^{\circ}$.

If (7) and (8) were adiabatic processes (spin-relaxation rate large compared to k_7 and k_8), then $k_7 \approx 3 \times 10^4$ sec^{-1} ($\lambda/4 \approx 4.0$ kK/mol) and $k_8 \approx 5 \times 10^{12}$ sec^{-1} ($\lambda/4 \approx 5.5$ kK/mol); if (7) and (8) were largely nonadiabatic processes, one would

$$^3\{\mathrm{Co(NH_3)_5}{}^{2+}, \cdot\mathrm{Br}\} \xrightarrow{k_8} \mathrm{Co(NH_3)_5Br^{2+}} \tag{8}$$

anticipate that $k_7 > k_8$ since the relaxation rate should depend inversely on the energy gap[25] and since the ^{3}CT state corresponding to the high-spin cobalt electronic configuration would become the excited-state precursor to $^3\{Co(NH_3)_5{}^{2+}, \cdot Br\}$.

While present experimental information does not allow the above mechanistic approach to provide a completely unambiguous description of all the significant photoreaction pathways of $Co(NH_3)_5Br^{2+}$, the approach does provide a basis for describing a bound ^{1}CT state in which vibrational relaxation and other photophysical processes can occur, at least qualitatively accounting for the observation that the redox quantum yield approaches a limit less than unity for high-energy excitation. Application of this same approach to the photochemistry of $Co(NH_3)_5NO_2{}^{2+}$ is very instructive and provides a plausible account of many of the observations noted in the opening paragraphs of this paper. (See Figure 2.)

The NO_2[26] radical is about 1 V weaker an oxidant than $\cdot Br$,[27] but the aquation rate of $Co(NH_3)_5NO_2{}^{2+}$ is sufficiently slow that the value of $\Delta H^\ddagger$ is unknown,[28] making it impossible to estimate $\Delta H_c°$ in the usual manner (*i.e.*, using $\Delta H_c = \Delta H^\ddagger + \Delta H_{IP}°$).[8b,12] On the other hand, for most complexes $\Delta H_c° \simeq E_{th}$, so a value of $\Delta H_c° \simeq 19$ kK/mol will be employed here; a value of $\Delta H_c° \simeq 19$ kK/mol would imply $\Delta H^\ddagger \simeq 12$ kK/mol[29] for aquation. Since E_{th} is appreciably less than E'_{th}, this implies that the equilibrated Franck–Condon state is higher in energy than the final radical-pair products—a situation which would always obtain if there were no Co^{II}–$(\cdot X)$ covalent bonding in the excited state. The NO_2 radical is in no sense spherical;[21] however the existence of O- and N-bonded isomers suggests that one should estimate λ_0 for different limiting directions of approach of $Co(NH_3)_5{}^{2+}$ and NO_2 in the radical pair; for each direction of approach we will assume the charge in $NO_2{}^-$ to be largely centered on N.[30] For approach along the Co–O–N– direction $a_2 \simeq 1.94$ Å, $a_1 = 3.0$ Å, and $r = 3.3$ Å in (3); this leads to $\lambda_o \simeq 7.8$ kK/mol. For approach along the Co–NO_2 direction, $a_2 \simeq 0.75$ Å, $r = 2.10$ Å, and $\lambda_o \simeq 22.0$ kK/mol. In order to estimate the total reorganizational barrier for each of the two radical recombination reaction modes, it is necessary to estimate λ_i' for the NO_2–$NO_2{}^-$ couple. Structural data exist for $Co(NH_3)_5NO_2{}^{2+}$ [31] and for NO_2.[21] For $Co(NH_3)_5ONO^{2+}$ it has been assumed that the N–O bond lengths are similar to those in μ-nitrito-cobalt(III) complexes.[32] On the basis of these data, Stranks' method for estimating bond distances in the transition state,[33] force constants for NO_2, $Co(NH_3)_5NO_2{}^{2+}$, and $Co(NH_3)_5ONO^{2+}$,[34] and a harmonic oscillator model for estimating bond compression and expansion energies, the values of λ_i' are about 0.5 and 1.1 kK/mol, respectively. With $\lambda_i \approx 5$ kK/mol for the cobalt component of the couple, $\lambda \simeq 36$ kK/mol, $\Delta G^\ddagger \simeq 2.0$ kK/mol, and $k_5' \sim 0.4 \times 10^9$ sec^{-1} for formation of $Co(NH_3)_5NO_2{}^{2+}$; the respective calculated kinetic parameters for formation of $Co(NH_3)_5ONO^{2+}$ are $\lambda \simeq 21.7$ kK/mol, $\Delta G^\ddagger \approx 0.5$ kK/mol, and $k_5'' \approx 5 \times 10^{11}$ sec^{-1}.[35–37] The actual situation should lie between these limits, but cage recombination ought to favor formation of $Co(NH_3)_5ONO^{2+}$ over formation of $Co(NH_3)_5NO_2{}^{2+}$ owing to the larger reorganizational barrier involved in formation of the latter. The actual ratio of products is reasonably sensitive to the relative stabilities of those products as well as the actual values of molecular parameters; values used above, would predict over 99% formation of $Co(NH_3)_5ONO^{2+}$ in the cage recombination. If the formation of a secondary radical pair had only the effect of increasing the effective value of a_1 (*e.g.*, through coordination of water), the discriminatory effect noted in λ_0 for the two different recombination modes would not be qualitatively altered, so the above argument is not sufficient to discriminate between the possibilities of geminate and secondary recombination.

C. Refinements and Conclusions. The argument above does provide a theoretical explanation for the experimental observation that cage recombination gives predominantly the nitrito isomer, but the kinetic model sketched above and the experimental evidence both imply that deactivation processes leading to regeneration of $Co(NH_3)_5NO_2{}^{2+}$ must occur in an excited-state precursor to the radical pair species. This necessary inference seems to contradict other evidence for a dissociative excited-state reaction coordinate in this system.[6,9] However, potential energy surfaces such as those indicated in Figures 1 and 2 are computed assuming that vibrational relaxation is rapid and that dielectric relaxation and excited-state dissociation processes are coupled as discussed above; the resultant surfaces should probably be regarded as an envelope for the collection of intermediate surfaces corresponding to different arrangements of ligands and solvent around the metal, orientations varying from those of the ground state to those of the radical pair. If the rates of dielectric and vibrational relaxation were very similar, the resultant potential energy surface could be expected to reflect many of the features of a dissociative excited state, even though some electronic relaxation might occur in the initial Franck–Condon excited state and its immediate successors. In principle the rate of dielectric relaxation should vary with solvent viscosity;[38] however specific solvation of the highly charged and hydrogen-bonding substrates may mask such effects.

In terms of the mechanistic approach outlined above, the differences in the photoredox chemistry of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5NO_2{}^{2+}$ may be ascribed to (a) more metal–radical covalent bonding in the charge-transfer excited states of the former than the latter and (b) more rapid vibrational relaxation than dielectric relaxation for $Co(NH_3)_5Br^{2+}$, but competing relaxation processes for $Co(NH_3)_5NO_2{}^{2+}$. It is not evident that either effect should be related to the "reducing nature of the $NO_2{}^-$ ligand."[9a] The mechanistic approach suggested here provides at least a qualitative, and perhaps a semiquantitative, account of the photoredox behavior of several cobalt(III) complexes; the dissociative charge-transfer excited states proposed by Scandola, *et al.*,[9a] are not compatible with these workers' observation that cage recombination gives only the linkage isomer while the net photoprocesses produce both isomers.[9] The mechanistic approach employed in the present report specifically involves the solvent in the dynamic processes of charge-transfer excited states and suggests that these excited states must be very short-lived. Such a significant role of the solvent seems required by our preliminary studies[8] and is being investigated further.

Registry No. $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5NO_2{}^{2+}$, 16633-04-8.

References and Notes

(1) Partial support of this research by the National Science Foundation (Grant GP 36888X) is gratefully acknowledged.

(2) For reviews see (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970; (b) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1970); (c) D. R. Eaton, *Spectrosc. Inorg. Chem.*, **1**, 29 (1970); (e) D. W. Watts, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, **52** (1972); (f) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Progr. Inorg. Chem.*, **17**, 1 (1972).

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(5) (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).

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

(7) J. F. Endicott in "Concepts of Inorganic Photochemistry," A. W. Adamson and P. W. Fleischauer, Ed., Wiley, New York, N. Y., Chapter 3, in press.

(8) (a) G. Ferraudi and J. F. Endicott, *J. Amer. Chem. Soc.*, **96**, 3681 (1974); (b) J. F. Endicott, G. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, in press; (c) submitted for publication in *J. Amer. Chem. Soc.*

(9) (a) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Phys. Chem.*, **78**, 572 (1974); (b) *J. Amer. Chem. Soc.*, **95**, 7898 (1973); (c) F. Scandola, private communication.

(10) The author is grateful to Professor V. Balzani for his recognition of this important point.

(11) This extrapolated value of E_{th} corresponds to about the origin of the low-energy ligand field absorption band of this complex, as noted previously by Scandola, *et al.*[9a] Irradiation of the ligand field band gives wavelength-independent yields of linkage isomerization and redox. The ratio of photoredox and photoisomerization is wavelength independent for this complex,[6,9] and at 254 nm $\phi(Co^{2+}) \simeq 0.5$.

(12) Note that (2) must be decomposed into two steps,

$$Co^{III}(NH_3)_5X \xrightarrow{\Delta H^{\ddagger}} \{Co^{III}(NH_3)_5, X^-\} \xrightarrow{\Delta H_{IP}{}^{\circ\prime}} \{Co^{II}(NH_3)_5, \cdot X\}$$

so that $\Delta H_c{}^{\circ} \simeq \Delta H^{\ddagger} + \Delta H_{IP}{}^{\circ\prime}$.

(13) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); **67**, 853 (1963).

(14) See also discussion by N. Sutin, "Inorganic Biochemistry," Vol. 2, G. Eichhorn, Ed., American Elsevier, New York, N. Y., 1973, p 611.

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(16) The quantities in (3) are as follows: λ_o, Marcus' outer-sphere reorganizational parameter; a_1 and a_2, radii of the reactants; r, distance of separation of the reactant centers in the transition state; D_{op}, square of the index of refraction of the medium; D_s, dielectric constant of the medium; e, charge on the electron.

(17) (a) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 5097 (1973); (b) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *ibid.*, **96**, 5661 (1974).

(18) An alternative procedure would treat the CTTM transition as an intervalence transition and use the absorption maximum and bandwidth to estimate the reorganizational barriers[15] for (4) and (5); however this approach leads to relatively high energies for the thermally equilibrated CTTM states (E_0) and to activation barriers which seem inappropriately large (by about 15 kK/mol). The energy parameters so deduced could be interpreted as characteristics of the initial Franck–Condon state but are probably appreciably in error due to the large free energy changes associated with (5) and to a failure of the assumption of weak interaction between reactant centers. On the other hand Hush's equation $E^* = (E_{op})^2/4(E_{op} - E_0)$, with energy quantities estimated in the text, leads to barriers to ^{1}CT dissociation which vary from ~2 kK (for $E_0 = 20$ kK) to ~9 kK (for $E_0 = 22$ kK). The values of $\lambda/4$ obtained in the text lie within this range.

(19) The bulk dielectric relaxation time of water can be estimated to be in the range of 10^{-11}–10^{-12} sec, *e.g.*, using eq 7 in K. Fueki, D.-F Feng, and L. Kevan, *J. Phys. Chem.*, **78**, 393 (1974).

(20) In this estimate the following numerical values have been used in (3): $a_1 = 2.4$ Å (Co^{II}), $a_2 = 1.14$ Å (Br),[19] and $r = (1.4 + a_2)$ Å; the last value substitutes the covalent radius of Br for that of O in the transition state of the $Co(N_4)(OH_2)_2{}^{3+}$–$Co(N_4)(OH_2)_2{}^{2+}$ self-exchange reaction (see ref 16a). In obtaining $\lambda_i/4$, the inner-sphere reorganizational barrier estimated in ref 16a has been reduced by a factor of 2, assuming the major barrier is in compression of the Co^{II}–N bond and half of the resulting value (for a hypothetical self-exchange reaction) was used.

(21) See J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York, N. Y., 1972, p 184.

(22) Actually (6) may underestimate k_4 for very exoergic recombinations: see (a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970); (b) R. D. Van Duyne and S. F. Fischer, submitted for publication (private communication from Professor Fischer); (c) S. F. Fischer, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR 20.

(23) The quantum yield actually is a complex function of several rate constants, k_9 the rate constant for electronic relaxation $^1CT \rightarrow {}^1A_1$ and k_D the rate constant for separation of radical-pair fragments: $\phi(Co^{2+}) = [k_4/(k_9 + k_4)][k_D/(k_5 + k_D)]$. For $k_d \approx 5 \times 10^{10}$ sec^{-1}, and $k_4 > 10^8$ sec^{-1}, estimates in the text lead to $\phi(Co^{2+}) \leq 7 \times 10^{-4}$, hence the statement that the estimated value of k_4 is too small. However, the value for k_4 is extremely sensitive to the energy difference of the equilibrated ^{1}CT state and $\Delta H_c{}^{\circ}$; if this energy difference had been taken to be 0 kK/mol rather than −4 kK/mol, $k_4 \approx 10^{10}$ sec^{-1} and $\phi(Co^{2+}) \leq 0.7$. Since the present estimates of $\Delta H_c{}^{\circ}$, E_{th}, and E'_{th} are each uncertain to about 2 kK/mol, it is unrealistic to expect information now available to permit accurate evaluation of quantum yields. The possibility that quantum yields may be used with this model to estimate more precise energy differences of species along the photoreaction coordinate will be considered elsewhere. The purpose of the present report is to provide a semiquantitative account of the contrasts in photochemical behavior noted in the introductory part of this paper.

(24) A frequently cited alternative is that k_5 is very large, consistent with present estimate, and that the photoproducts are formed from a secondary or solvent separated radical pair.[5,6] The possibility of observing a limiting yield for such alternatives is dependent on the lability of the solvent.[7,8]

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Migration of Ether Ligands in Etherates of Triborane

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Sir:

While the ^{11}B nmr spectra of most of the Lewis base adducts of B_3H_7 are known to show the presence of *two* kinds of boron,[1–3] those of ether adducts were reported to consist of a single multiplet peak.[2,4] In an earlier work, however, somewhat unsymmetrical ^1H hyperfine structure in the ^{11}B resonance peak of $B_3H_7 \cdot THF$ was pointed out.[1a] This dissymmetry of the peak could be due to an overlap of two different resonance peaks.

It was thought important to confirm the experimental facts with the aid of better instrumentation available now, because the observation of only one resonance peak in the B_3H_7 etherates has led one to speculate[2] that the ether molecule migrates in the adduct molecule or that a rapid base exchange is taking place, whereas the presence of two peaks would not necessitate such a speculation.

The sample of $B_3H_7 \cdot THF$ was prepared by the method described earlier.[5] Approximately 1 *M* solutions of the compound in tetrahydrofuran, methylene chloride, and benzene were prepared in 10-mm o.d. nmr sample tubes. The sample of $B_3H_7 \cdot O(C_2H_5)_2$ was prepared by treating a diethyl ether solution of NaB_3H_8 with a stoichiometric amount of anhydrous HCl in a 10-mm o.d. nmr sample tube at −80°.[6] The concentration was about 1 *M* and a precipitate of NaCl was retained in the sample tube. The sample of NaB_3H_8 was prepared by the reaction of $NaBH_4$ with B_4H_{10} in diethyl ether.[7] The ^{11}B nmr spectra were recorded on a Varian XL-100 spectrometer operating at 32.1 MHz, temperature of the probe being at 20°.

The spectra of $B_3H_7 \cdot THF$ and $B_3H_7 \cdot O(C_2H_5)_2$ are shown in Figures 1 and 2, respectively. Contrary to the two previous descriptions[2,4] that were based on the spectra obtained with lower frequency spectrometers (10–19.3 MHz), the resonance peaks, Figures 1a and 2a, are both unsymmetrical. The spectrum of $B_3H_7 \cdot THF$, Figure 1a, is compatible with that presented earlier.[1] The proton-decoupled spectra, Figures 1b and 2b, show two peaks separated clearly. The high-field peaks, which are attributed to the boron atoms attached to