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Photodecomposition of *cis*-Azidoamminebis(2,4-pentanedionato)cobalt(III): Energy Transfer

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It has been reported that $Co(acac)_2N_3NH_3$ is decomposed in photolysis to yield $Co(acac)_2$ and azide radicals. The threshold energy for this process has been bracketed between 21.3×10^3 and 17.2×10^3 cm^{-1} and a triplet charge-transfer photoactive state is implicated. The sensitizers benzil, benzophenone, and phenanthrene sensitize the decomposition of $Co(acac)_2N_3NH_3$ to yield cobalt(II) with a quantum efficiency comparable to, but somewhat smaller than, that observed in direct photolysis. Biacetyl sensitizers the decomposition with 1 order of magnitude greater efficiency. The phosphorescences of both benzophenone and biacetyl are quenched by $Co(acac)_2N_3NH_3$, whereas the fluorescences of biacetyl and zinc tetraphenylporphyrin are unaffected. The quenching of the benzophenone phosphorescence follows Stern–Volmer kinetics, yielding a quenching constant of 2.16×10^3 M^{-1}. The sensitization by benzil further narrows the bracketing of photoactive state energies to $(18.5–17.2) \times 10^3$ cm^{-1}.

Introduction

In two recent communications from these laboratories, the photodecomposition of *cis*-azidoamminebis(2,4-pentanedionato)cobalt(III) ($Co(acac)_2N_3NH_3$) was examined in considerable detail.[1,2] The photochemistry of this complex is surprisingly simple in that it exhibits a single mode of photodecomposition for excitations througout the 250–580-nm region. Upon irradiation the complex yields $Co(acac)_2$ and azide radicals with near constant quantum efficiency for radiations of energies greater than 21.3×10^3 cm^{-1} (470 nm). There are several unusual features in the photochemistry of this complex. It is surprisingly simple considering the number of modes of photodecomposition which have been observed for other complexes containing the ligands which comprise this complex.[3-8] The quantum efficiency is very low (0.019–0.034 above 21.3 $\times 10^3$ cm^{-1}). The threshold for photodecomposition is between 21.3×10^3 and 17.2×10^3 cm^{-1} which is much lower than the charge transfer to metal state involving the azido group (CTTM(N_3)). Photodecomposition occurs with an apparent activation energy of 11.7 kcal/mol, and finally the respective optical electronegativities of the 2,4-pentanedionato and azido[9,10] ligands suggest that the CTTM(acac) is the lower energy charge-transfer state. So that these results could be explained, a triplet charge-transfer state involving the azido group was proposed.[2]

The implication of a photoactive triplet charge-transfer state is not unique to this work and was first proposed by Adamson and co-workers.[11] In their study and those of others, energy transfer has been used to help characterize the photoactive state.[11-17] The use of sensitizers of known singlet and triplet energies should permit a further bracketing of the photoactive state energy. It should also provide further support for its assignment as a triplet state.

Experimental Section

Materials. $Co(acac)_2 \cdot 2H_2O$ was prepared by the method of Ellan and Ragsdale.[18] The product was recrystallized several times from ethanol and dried in air. Prior to use in the preparation of calibration curves, it was dried under vacuum, at 55 °C for 6 h to yield $Co(acac)_2$.

K(*trans*-Co(acac$_2$(N_3)$_2$)) was prepared by the method of Boucher and Herrington.[19]

Zinc tetraphenylporphyrin was prepared from tetraphenylporphyrin and zinc acetate by the method of Adler and co-workers.[20] The crude product was purified by chromatography on alumina and development with 1:1 (v/v) benzene–chloroform.

$Co(acac)_2N_3NH_3$ was prepared by treating 1.0 g of K(*trans*-Co(acac)$_2$(N_3)$_2$) with 20 mL of methanol which was ca. 50% saturated with ammonia. The suspension was warmed to 60 °C for a few minutes after which time all of the solid had dissolved. The solution was allowed to evaporate to dryness, and the residue was taken up in a minimum of chloroform and filtered. The product precipitated from the filtrate upon the addition of two volumes of mixed hexanes. After it was collected by filtration, it was purified by chromatography on silica gel. The column was developed with 5% (v/v) methanol in chloroform, and the product was isolated from the eluents by the addition of two volumes of mixed hexanes and allowing the product to crystallize overnight. The solid was collected and air-dried.

Reagent grade benzophenone, phenanthrene, and ammonium thiocyanate were recrystallized from ethanol prior to use. Methanol was freshly distilled from magnesium turnings prior to use. Biacetyl and benzil were also freshly distilled.

Photolysis Procedures. The optical train used in the photolyses has been described elsewhere.[1] For irradiation requiring visible radiation, McCarthy 100-4750, 100-5350, or a soft-glass filter was used to remove the second-order spectrum of the monochromator. Unless otherwise specified, all quantum yield determinations were made at 25.0 ± 0.1 °C and 90% of the exciting radiation was contained in a 10-nm band-pass. Light intensities were determined with ferrioxalate[19] actinometry. Quantum yield determinations were made from plots of concentrations vs. time of irradiation. These plots were linear, and at no time was the reaction carried beyond 5% conversion to products. There was no evidence for secondary photolysis or an internal filter effect. Unless otherwise specified, photolyses were performed without prior deaeration of solutions. For sensitized photolyses, however, the solvent was aerated immediately after distillation and when deaerated solutions were required, nitrogen which had been saturated with solvent was passed through the solution for 20 min prior to irradiation.

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Table I. Quantum Yield for the Formation of Cobalt(II) by Sensitized Photolysis

sensitizer	[sens], M	$10^4 \times$ [Co(acac)$_2$N$_3$NH$_3$], M	λ_{ex}, nm	$\phi_{Co(II)}{}^{sens}$	triplet E, cm^{-1} $\times$ 10^3	conditions
benzil	1.50	4.91	300	0.0064	18.5[a]	deaerated
biacetyl	0.30	7.62	300	0.116	19.7[b]	deaerated
phenanthrene	0.041	7.14	330	0.014	21.6[c]	deaerated
benzophenone	0.30	6.93	300	0.0103	24.2[b]	deaerated
benzophenone	0.30	12.24	300	0.0069		aerated
benzophenone	0.30	10.94	300	0.0066		aerated
benzophenone	0.30	6.93	300	0.0051		aerated
benzophenone	0.30	5.09	300	0.0043		aerated
benzophenone	0.30	4.09	300	0.0039		aerated

[a] Reference 22. [b] Reference 23. [c] Reference 24.

For sensitized photolyses the absorbance of Co(acac)$_2$N$_3$NH$_3$ was kept less than 10% of the total absorbance of the solution at the exciting wavelength, and the observed quantum yields were corrected for direct photolysis. These corrections were usually small. In luminescence quenching experiments it was not possible to use solutions for which the absorbance of Co(acac)$_2$N$_3$NH$_3$ at the exciting wavelength was negligible compared to that of the luminescing compound, thus it was necessary to correct for absorbance by Co(acac)$_2$N$_3$NH$_3$. A Stern–Volmer plot was prepared for the quenching of benzophenone phosphorescence by Co(acac)$_2$N$_3$NH$_3$.

The concentration of cobalt(II) in the photolytes was determined by pipetting 2 mL of the photolytes into a 5-mL volumetric flask and diluting to the mark with 1 M methanolic NH$_4$SCN and recording the optical density at 618 nm. Calibration curves were prepared with authenic samples of Co(acac)$_2$.

Physical Measurements. Optical spectra were recorded on either a Cary Model 17, Hitachi Model 100-60, or a Sargent Welch SM optical spectrophotometer. Infrared spectra were recorded on a Beckman Model 4240 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer Model MPF-44A spectrofluorometer.

Results and Discussion

The mechanism for the photodecomposition of Co(acac)$_2$N$_3$NH$_3$ has been described in some detail.[1,2] The primary photochemical process involves reduction of the metal center and formation of azide radical intermediates.[1] A single mode of photodecomposition is observed with similar quantum efficiencies whether an internal ligand, charge-transfer, or ligand field state is initially populated by direct photolysis. The photoactive state is postulated to be nondissociative with an apparent activation energy of 11.7 kcal/mol, and solvent assistance in the radical dissociation step is implicated.[2] Secondary radical pair recombination is unimportant under the conditions used in photolysis.[1]

The photoactive state has been described as a triplet charge-transfer excited state involving the azido group (^{3}CTTM(N$_3$)). There are several lines of evidence which suggest that this is the case. The quantum yields for the photodecomposition of this complex are more than 1 order of magnitude lower than those observed for the photodecomposition both Co(acac)$_3$[8] and Co(NH$_3$)$_5$N$_3$.[2,6] The quantum yields are nearly wavelength independent for excitations of energies greater than 21.3 × 10^3 cm^{-1}, and the threshold for redox photochemistry occurs between 21.3 × 10^3 (470 nm) and 17.2 × 10^3 cm^{-1} (580 nm). These results suggest facile interconversion among singlet excited states followed by inefficient intersystems crossing into the triplet manifold. Although azido group oxidation is the only observed mode of photodecomposition, the optical electronegativities of the azido and pentanedionato groups suggest that the latter is lower in energy by some 3 × 10^3 cm^{-1}. Furthermore, it is this state (^{1}CTTTM(acac)) that is primarily populated by 350-nm excitation. The results of spectral curve fitting and comparisons with other complexes suggest that the vibrationally equilibrated ^{1}CTTM(N$_3$) excited state is at about 30 × 10^3 cm^{-1} or at least 8.7 × 10^3 cm^{-1} above the threshold for redox photodecomposition. This separation is considerably greater than the apparent activation energy of 11.7 kcal (4.09 × 10^3 cm^{-1}). These results support the nonparticipation of the ^{1}CTTM(N$_3$) excited state in the observed photochemistry and further implicate a ^{3}CTTM(N$_3$) photoactive state.

The photodecomposition of Co(acac)N$_3$NH$_3$ was effected by the sensitizers benzophenone, benzil, biacetyl, and phenanthrene. It was not effected by zinc tetraphenylporphyrin, however. In all cases in which sensitized photolysis occurred, a cobalt(II) photoproduct formed. The quantum efficiencies for the sensitized photolysis of Co(acac)$_2$N$_3$NH$_3$ by these sensitizers were determined. The yields were determined in deaerated solutions and under nitrogen and may be found in Table I. Because of the intense absorption of Co(acac)$_2$N$_3$NH$_3$ in the region in which the sensitizers were excited, it was necessary to correct the quantum yields for direct photolysis. The known extinction coefficients of the complex and sensitizer and the quantum efficiency for direct photolysis were used to make these corrections. The relative concentrations of sensitizer and Co(acac)$_2$N$_3$NH$_3$ were determined as to permit at least 85% of the absorbed radiation to be absorbed by the sensitizer. In the cases of benzophenone- and biacetyl-sensitized photolyses, the Co(acac)$_2$N$_3$NH$_3$ concentration was sufficient to completely quench the sensitizer phosphorescence. Because the sensitizer concentrations were fairly high (1.5–0.40 M), new calibration curves for the determination of cobalt(II) were prepared for each sensitizer solution. Because Co(acac)$_2$N$_3$NH$_3$ at these concentrations did not absorb significantly in the regions in which these sensitizers luminesce, the mechanism for sensitized photolysis by which sensitization occurs by absorption of luminescence can be ruled out.

The triplet-state energies of each of the sensitizers are also given in Table I. Of the molecules which sensitize Co(acac)$_2$N$_3$NH$_3$ photodecomposition, benzil has the lowest triplet-state energy (18.5 × 10^3 cm^{-1}).[22] The quantum yield for this process is comparable to that of the other sensitizers, and the bracketing of the photoactive state energy is further narrowed to (18.5–17.2) × 10^3 cm^{-1}. With the exception of biacetyl, whose yield is 1 order of magnitude greater than that of the other sensitizers, the quantum yield for senisitized photolysis is about half of that found in direct photolysis. A low yield for sensitized photolysis can be attributed to several factors. Among these are inefficient energy transfer, inefficient population of the energy transfering state in the sensitizer, or low reactivity of the photoactive state in the acceptor. In that the intersystems crossing quantum yield for benzophenone is unity,[23,24] it seems unlikely that the low quantum yields can

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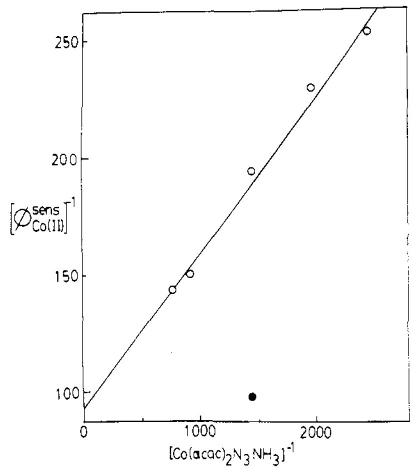

Figure 1. Plot of the quantum yield of cobalt(II) resulting from the benzophenone (0.30 M) sensitized photolysis of $Co(acac)_2N_3NH_3$ vs. the concentration of $Co(acac)_2N_3NH_3$. Photolyses were performed in aerated methanol with 300-nm exciting radiation: (●) determined under N_2.

generally be attributed to inefficient population of the donor state. The similarity in the quantum yields argues against inefficiency in energy transfer being a dominant factor in the low yields. The observation of an apparent activation energy of 11.7 kcal, the solvent dependence of the direct photolysis quantum yield, and a near constancy of quantum yield throughout the $(17.2–40.0) \times 10^3$ cm^{-1} region point to a photoactive state of low reactivity. This being the case sensitized photolysis by biacetyl must be occurring via a mechanism other than energy transfer. Sensitized photolysis by other than energy transfer has been observed in other metal complexes.[13,25]

Because of its unitary intersystems-crossing quantum yield, benzophenone was selected for more detailed examination. Monitoring of the optical spectrum of a solution, 1.23×10^{-4} M in benzophenone and 2.14×10^{-5} M $Co(acac)_2N_3NH_3$, in which benzophenone absorbed at least 72% of the incident radiation (280 nm), revealed the maintenance of isosbestic points. These isosbestic points occurred at the same wavelengths as observed in the direct photolysis of methanolic solutions containing only $Co(acac)_2N_3NH_3$. (The extinction coefficients of benzophenone and $Co(acac)_2N_3NH_3$ are comparable at these wavelengths.) These results suggest that the photodecomposition of $Co(acac)_2N_3NH_3$ by both direct and sensitized photolysis is clean and yields the same products and that benzophenone is not consumed during photolysis.

The quantum yield for benzophenone-sensitized photolysis was dependent on the presence or absence of molecular oxygen. Since triplet excited states are often effectively quenched by molecular oxygen ($^3Co(acac)_2N_3NH_3$ is not, however), this suggests that $Co(acac)_2N_3NH_3$ must compete with molecular oxygen for energy transfer from triplet benzophenone. So that this could be substantiated, the quantum yields for sensitized photolysis in solutions of varying $Co(acac)_2N_3NH_3$ concentration but constant sensitizer and oxygen concentrations were determined. Solutions were prepared from freshly distilled methanol through which methanol saturated air had been passed for 20 min. Failure to carry out aeration of the fresly distilled solvent resulted in erratic quantum efficiencies because of the variance in the concentration of oxygen in the solvent. As with the other sensitized photolyses, the quantum yields were corrected for direct photolysis. The results may be found in Table I. A plot of $[Co(acac)_2N_3NH_3]^{-1}$ vs. $[\phi_{Co(II)}^{sens}]^{-1}$ is linear with a slope of 0.0677 M and an intercept of 93.84 (Figure 1). The result of sensitized photolysis by benzophenone in deaerated solutions is included in the figure for comparison.

Table II. Benzophenone Phosphorescence Quenching by $Co(acac)_2N_3NH_3$[a]

no.	$10^5 \times [Co(acac)_2N_3NH_3]$, M	I_0/I(cor) (417 nm)
1	0.00	1.00
2	6.10	1.11
3	12.20	1.25
4	24.40	1.56
5	6.10	1.12
6	18.30	1.32
7	30.50	1.65
8	6.10	1.14
9	12.2	1.29

[a] The solutions were oxygenated and excited with 370-nm radiation. The benzophenone concentration was 0.0262 M.

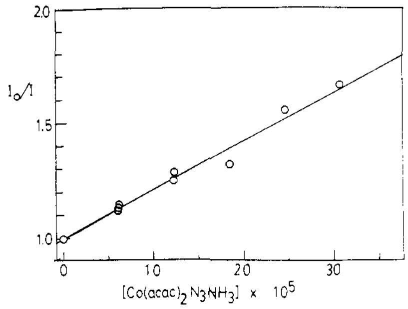

Figure 2. Plot of the relative corrected intensity of the 417-nm emission of 2.62×10^{-2} M benzophenone in deoxygenated methanol containing various concentrations of $Co(acac)_2N_3NH_3$. The exciting wavelength was 370 nm.

The competitive quenching between $Co(acac)_2N_3NH_3$ and O_2 is depicted in eq 1–5, where S is the sensitizer and Q any

$$S + h\nu \xrightarrow{\Phi_{ISC}I_a} {}^3S^* \qquad (1)$$

$$^3S^* + O_2 \rightarrow S + O_2^* \qquad (2)$$

$$^3S^* + Co(acac)_2N_3NH_3 \rightarrow S + {}^3Co(acac)_2N_3NH_3 \qquad (3)$$

$$^3S^* + Q \rightarrow S + Q^* \qquad (4)$$

$$^3Co(acac)_2N_3NH_3 \rightarrow \text{products} \qquad (5)$$

other triplet quencher in the system. Assuming a steady-state concentration of $^3S^*$, one obtains eq 6, where $\Phi_{Co(II)}^{sens}$ and

$$\phi_{Co(II)}^{sens^{-1}} = \Phi_{Co(II)}^{sens^{-1}}\Phi_{ISC}^{-1}\left[1 + \frac{k_2[O_2] + k_4[Q]}{k_3[Co(acac)_2N_3NH_3]}\right] \qquad (6)$$

Φ_{ISC} are primary quantum yields for sensitize photolysis and intersystems crossing. This relationship is consistent with that indicated in Figure 1. Futhermore, the intercept in the plot (Figure 1) equals the reciprocal quantum yield determined in the deoxygenated solution, which indicates that oxygen is the only triplet quencher competing with $Co(acac)_2N_3NH_3$. If this is the case, $k_2[O_2]/k_3 = 7.21 \times 10^{-4}$, and if $[O_2]$ is taken to be about 5×10^{-4} M, then $k_2/k_3 = 1.4$. Such a large rate constant for $Co(acac)_2N_3NH_3$ quenching would seem to support the argument for efficient $Co(acac)_2N_3NH_3$–

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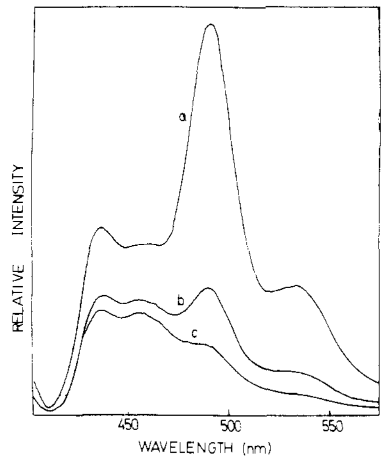

Figure 3. Emission spectra of biacetyl in deoxygenated methanol containing various concentrations of $Co(acac)_2N_3NH_3$. The exciting radiation was 430 nm, and the biacetyl concentration was 0.342M; the concentrations of $Co(acac)_2N_3NH_3$ were 0.0 M (a), 1.90×10^{-4} M (b), and 5.69×10^{-4} M (c).

^{3}benzophenone energy transfer and that sensitization occurs via an energy-transfer mechanism.

Concomitant with sensitizing the decomposition of $Co(acac)_2N_3NH_3$, benzophenone's phosphorescence is quenched by $Co(acac)_2N_3NH_3$. Emission-quenching determinations were carried out in deoxygenated solutions with a benzophenone concentration of 2.62×10^{-2} M. A plot of I_0/I (I is intensity), which is corrected for the fraction of exciting radiation absorbed by benzophenone, vs. $Co(acac)_2N_3NH_3$ concentration is given in Figure 2. As might be expected the quenching exhibits Stern-Volmer kinetics with a quenching constant of 2.16×10^3 M^{-1}.

Biacetyl emits both flourescence and phosphorescence in fluid solution. Excitation of a 3.34 M deoxygenated methanolic solution made 5.70×10^{-4} M in $Co(acac)_2N_3NH_3$ resulted in quenching 80% of the phosphorescence and 45% of the flourescence compared to a solution containing no $Co(acac)_2N_3NH_3$ (Figure 3). The extent to which the flourescence was quenched might be easily accounted for as a result of internal filtering by $Co(acac)_2N_3NH_3$. Zinc tetraphenylporphyrin fluoresces strongly at 603 and 654 nm. No significant fluoresces of the emission resulting from 400-nm excitation is observed when a 2.69×10^{-5} M zinc tetraphenylporphyrin solution is made 6.31×10^{-5} M in $Co(acac)_2N_3NH_3$. In addition, excitation into the 420-nm soret band of zinc tetraphenylporphyrin did not sensitize any photodecomposition of 5.79×10^{-5} M $Co(acac)_2N_3NH_3$.

Sensitized-photolysis results are consistent with the mechanistic proposals put forth in our previous communication.[1,2] Whereas the singlet-state emissions of excited molecules are not quenched by $Co(acac)_2N_3NH_3$, emitting triplet states are quenched by $Co(acac)_2N_3NH_3$. The emission quenching obeys Stern-Volmer kinetics and in the presence of oxygen exhibits kinetics consistent with competitive quenching between $Co(acac)_2N_3NH_3$ and O_2. Several molecules with low-energy triplet states sensitize the decomposition $Co(acac)_2N_3NH_3$ in the same manner as by direct photolysis. The lowest energy sensitizer, benzil, has a triplet energy of 18.5×10^3 cm^{-1}, thus bracketing the photoactive state energy within $(18.5-17.2) \times 10^3$ cm^{-1}.

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Oxidative Transformations in Nickel(II) Chelates of Tetradentate Schiff Bases

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Nickel(II) chelates of tetradentate β-keto enamines undergo aerial oxidation at the ethylene bridge to form a variety of monomeric nickel(II) chelate species. Chromatographic separation and identification of the products obtained from the oxidation of several chelates are reported, and, in some cases, structural isomers of the original and oxidized forms are identified. The sensitivity of the chelates to oxidation, studied by cyclic voltammetry and thermal analysis, are strongly influenced by substituents in the ligand. Oxidation of a Schiff base chelate with hydrogen peroxide removes the ethylene bridge, giving a ternary nickel(II) complex.

Tetradentate Schiff bases are known[2,3] to give highly stable chelates with bivalent metal ions. Indeed, certain chelates of Cu(II), Ni(II), Pd(II), and V(IV) are sufficiently stable to be volatilized and eluted intact from chromatographic columns at temperatures above 250 °C.[4-8] The stability of these derivatives, however, is markedly influenced by the substituents in the ligand. In the general structure I, a two-carbon bridge between the β-keto enamine rings, with fluoroalkyl substituents at R_1 or R_2, produces greatest chelate stability for a given bivalent metal ion, M. Longer bridging groups, or substituents in place of hydrogen at R_4 (such as halogens or alkyl groups), dramatically reduce stability,[7] probably by steric strain in the chelate rings.

Thermal stability of the chelates is limited by the dehydrogenation reaction which can occur at the two-carbon bridge. This reaction is affected by the type of substituent on the

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