Photosensitized Reactions of Cobalt(III) Complexes. II. The Biphenyl–Hexaamminecobalt(III) and Biacetyl–Hexaamminecobalt(III) Systems[1]

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Abstract: Biphenyl and biacetyl have been investigated as potential sensitizers for the redox decomposition of the hexaamminecobalt(III) complex ion. When hydroalcoholic solutions containing 3.5×10^{-3} *M* biphenyl and 7.5×10^{-4}–5×10^{-3} *M* $[Co(NH_3)_6](ClO_4)_3$ were irradiated with 254-nm radiation, an efficient redox decomposition of the complex was observed even though the light absorption by the complex was negligible. The apparent quantum yields of the sensitized reaction increased with increasing the concentration of the complex and were markedly enhanced by deoxygenation. These results have been interpreted on the basis of a mechanism involving energy transfer from the biphenyl triplet to a triplet charge-transfer state of the complex which then undergoes a redox decomposition having almost unitary efficiency. With biacetyl, no sensitization of the redox decomposition of the complex was obtained. On the other hand, a very efficient quenching of the biacetyl phosphorescence by the complex was observed. The quenching has been attributed either to an induced deactivation of the biacetyl triplet not involving electronic energy transfer or to an energy-transfer process leading to ligand-field states of the complex.

In the field of inorganic photochemistry, the study of photosensitized reactions has only been undertaken in the last few years.[1–5] Two reports have appeared concerning the photosensitized redox decomposition of Co(III)–ammine complexes. In the first one, Vogler and Adamson[2] reported that the redox decomposition of the hexaamminecobalt(III) and aquopentaamminecobalt(III) complex ions was sensitized by *trans*-stilbene-4-carboxylic acid, benzophenone, benzil, and biacetyl. The quenching of the biacetyl phosphorescence by the hexaammine complex led Vogler and Adamson to conclude that the redox decomposition of the complexes was the result of an energy-transfer process from the donor triplet to a triplet charge-transfer state of the complex. In a subsequent paper, Scandola, *et al.*,[1] studied the redox decomposition of the hexaamminecobalt(III) complex ion sensitized by naphthalene. On the basis of the quenching of the naphthalene fluorescence and of the insensitivity of the photosensitized reaction to the concentration of dissolved oxygen, a mechanism was proposed involving a singlet–singlet energy transfer leading to a charge-transfer state of the complex.

In this article, we wish to report the results of an investigation on the hexaamminecobalt(III) complex ion, carried out by using biphenyl and biacetyl as potential sensitizers.

Experimental Section

Materials. Reagent grade biacetyl (BDH Chemicals, Poole, England) was used without further purification. Reagent grade biphenyl (BDH Chemicals) was purified by crystallization from ethanol. $[Co(NH_3)_6](ClO_4)_3$ was prepared from the chloride salt[6] by crystallization in the presence of excess $HClO_4$. Spectrograde ethanol was used to prepare the hydroalcoholic solvent mixtures.

Apparatus. Radiations of 254 and 404 nm were obtained as described elsewhere.[7,8] The reaction cells were standard 1-cm spectrophotometer cells (capacity, 3 ml) which were thermostated at 25°. The incident light intensity was always of the order of 10^{-7} einstein/min. Absorption spectra were recorded with an Optica CF4 NI spectrophotometer. Emission spectra were measured with a CGA DC 3000/1 spectrophotofluorimeter.

Procedures. With biphenyl as donor, solubility requirements suggested the use of a 30% ethanol–water mixture as solvent. With biacetyl, both aqueous and 50% water–ethanol solutions could be used. $[Co(NH_3)_6](ClO_4)_3$ was used, instead of the more common chloride salt, in order to avoid spectral and photochemical complications arising from intermolecular charge-transfer transitions within the $Co(NH_3)_6{}^{3+}$–Cl^- ion pair.[9] All of the solutions were made acid with 10^{-2} *M* $HClO_4$ in order to prevent air oxidation of Co^{2+}, which is the relevant expected photoproduct. The determination of the Co^{2+} concentration was carried out using the ferrous–phenanthroline method.[10] In order to obtain the quantum yields of the photoredox decomposition (either direct or sensitized), the irradiation was only carried on until a small percentage of the complex concentration was decomposed, so that the formation of Co^{2+} appreciably followed zero-order kinetics. In some experiments, most of the dissolved oxygen was removed from the solutions by saturation with pure nitrogen. When such a procedure was carried out carefully, the residual concentration of dissolved oxygen was sufficiently low as to allow the observation of the biacetyl phosphorescence. The observed ratio of phosphorescent to fluorescent emission was about 9:1 and only a small increase in phosphorescence intensity[11] was observed on irradiation.

Results

The spectra of biphenyl, biacetyl, and $Co(NH_3)_6{}^{3+}$ are shown in Figure 1. Since the results obtained with the two sensitizers are quite different, they will be illustrated separately.

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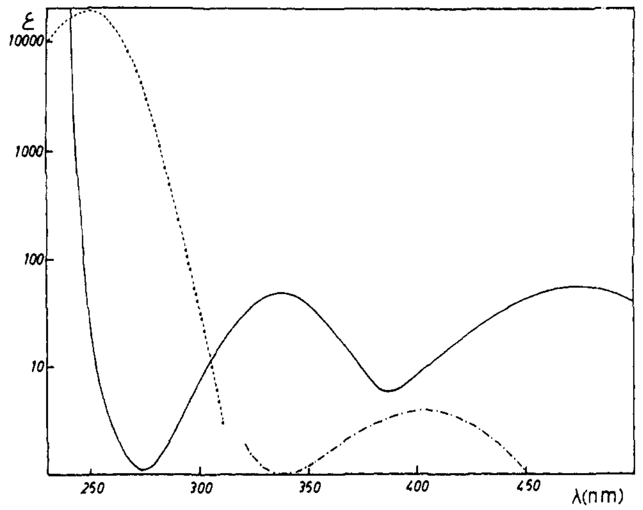

Figure 1. Absorption spectra of: —, $[Co(NH_3)_6](ClO_4)_3$ in 30% ethanol–water solution; ----, biphenyl in 30% ethanol–water solution; -·-·-·-·, biacetyl in aqueous solution.

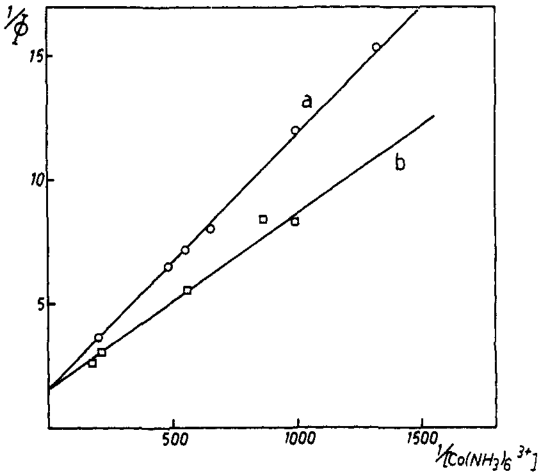

Figure 2. Variation of the quantum yield of the biphenyl-sensitized redox decomposition with complex concentration: (a) aerated solutions, (b) deaerated solutions.

The Biphenyl–$Co(NH_3)_6^{3+}$ System. An investigation of the direct photochemical behavior of the complex in the particular solvent system used (see Procedures) showed that 254-nm radiation caused the redox decomposition of the complex with the same quantum yield, 0.16, as in aqueous solution.[9] Radiations of wavelength higher than 280 nm did not cause any appreciable redox decomposition.

When solutions containing 3.5×10^{-4} *M* biphenyl and 7.5×10^{-4}–5×10^{-3} *M* $Co(NH_3)_6^{3+}$ were irradiated with 254-nm light, an efficient redox decomposition of the complex was observed. In these conditions, light absorption by the complex was completely negligible (less than 1% of the total absorbed light). A spectrophotometric check of the photochemical stability of biphenyl in these experiments showed that the decomposition of biphenyl was absolutely negligible (less than 1%) as compared with the amount of Co^{2+} formed. The apparent quantum yield of the photosensitized reaction (*i.e.*, the ratio between the rate of Co^{2+} formation and the rate of light absorption) increased with increasing complex concentration, according to curve a in Figure 2. The deoxygenation of the solutions prior to irradiation brought about an increase in the quantum yields of the sensitized reaction (curve b in Figure 2).

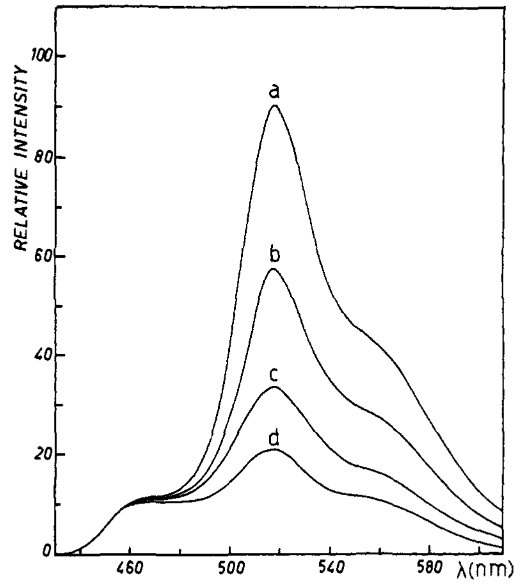

Figure 3. The effect of complex concentration on the luminescence spectrum of biacetyl in deaerated aqueous solutions. The complex concentrations are (a) 0, (b) 1×10^{-5} *M*, (c) 5×10^{-5} *M*, (d) 1×10^{-4} *M*.

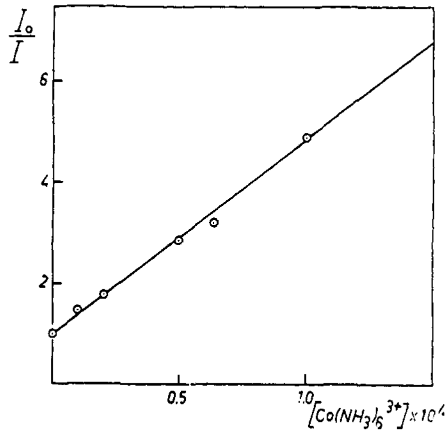

Figure 4. Stern–Volmer plot for the quenching of the biacetyl phosphorescence by the complex.

Experiments performed on the fluorescent emission of biphenyl in the presence of various concentrations of the complex failed to show any quenching effect.

The Biacetyl–$Co(NH_3)_6^{3+}$ System. In agreement with previous observations,[9] no detectable amounts of Co^{2+} were formed when aqueous or hydroalcoholic solutions of the complex were irradiated with light of wavelength higher than 280 nm.

Experiments were then performed in order to find out whether biacetyl could sensitize the redox decomposition of the complex. Carefully deaerated aqueous solutions containing 0.15 *M* biacetyl and 1×10^{-3}–1×10^{-2} *M* $Co(NH_3)_6^{3+}$ were irradiated with 404-nm light (which, under such conditions, was mostly absorbed by biacetyl). Even after prolonged irradiation, no detectable amounts of Co^{2+} were formed.

A study of the luminescence spectra of deaerated aqueous solutions of biacetyl with various complex concentrations (Figure 3) showed that the biacetyl fluorescence was practically unaffected by the complex, whereas the phosphorescence was strongly quenched.

The phosphorescence quenching data were plotted on a Stern–Volmer diagram (Figure 4) which yielded a quenching constant of 3.8×10^4 l. mol^{-1}.

When a 50% water–ethanol mixture was used as solvent, slightly different results were obtained. Under such conditions, very small traces of Co^{2+} were produced in the sensitization experiments (the upper limit for the quantum yield was estimated to be 5×10^{-3}). The biacetyl phosphorescence was also quenched but to a lower extent than in aqueous solutions. This effect is clearly the result of competitive quenching by ethanol.

The above experimental results were not appreciably altered by changing the anion of the complex salt from perchlorate to chloride or by using neutral solutions instead of the acid ones.

Discussion

The results obtained with biphenyl strongly suggest that the observed sensitized photodecomposition occurs as the result of an electronic energy-transfer process. In fact, a trivial emission–reabsorption process can be easily ruled out owing to the insensitivity of the complex to radiations in the wavelength range of the biphenyl fluorescence. On the other hand, the photochemical stability of biphenyl in the presence of the complex rules out chemical processes like reaction between the excited biphenyl and the complex or irreversible electron transfer within a donor–acceptor molecular complex.[12]

Both the observed lack of quenching of the biphenyl fluorescence and the dependence of the photosensitized reaction on the concentration of dissolved oxygen suggest that the biphenyl triplet is responsible for the sensitization and that the energy-transfer process is of the triplet–triplet type. The observed reaction mode (reduction at the cobalt center) suggests that a N → Co charge-transfer state of the complex is the reactive state.[13] Thus, the overall mechanism may be schematized as follows.

$$\text{biphenyl}(S_0) \xrightarrow{h\nu} \text{biphenyl}(S_1) \tag{1}$$

$$\text{biphenyl}(S_1) \longrightarrow \text{biphenyl}(S_0) \tag{2}$$

$$\text{biphenyl}(S_1) \longrightarrow \text{biphenyl}(T_1) \tag{3}$$

$$\text{biphenyl}(T_1) \longrightarrow \text{biphenyl}(S_0) \tag{4}$$

$$\text{biphenyl}(T_1) \xrightarrow{O_2} \text{biphenyl}(S_0) \tag{5}$$

$$\text{biphenyl}(T_1) + Co(NH_3)_6{}^{3+}(S_0) \longrightarrow \text{biphenyl}(S_0) + Co(NH_3)_6{}^{3+}(T_{ct}) \tag{6}$$

$$Co(NH_3)_6{}^{3+}(T_{ct}) \longrightarrow Co(NH_3)_6{}^{3+}(S_0) \tag{7}$$

$$Co(NH_3)_6{}^{3+}(T_{ct}) \longrightarrow Co^{2+} + \text{other products} \tag{8}$$

According to this mechanism, the quantum yield of the photosensitized reaction is given by

$$\Phi = \frac{k_3}{k_2 + k_3} \frac{k_6[Co(NH_3)_6{}^{3+}]}{k_4 + k_5[O_2] + k_6[Co(NH_3)_6{}^{3+}]} \frac{k_8}{k_7 + k_8} \tag{9}$$

Upon rearrangement, one obtains

$$1/\Phi = 1/\Phi_{lim}(1 + 1/K_s[Co(NH_3)_6{}^{3+}]) \tag{10}$$

where

$$\Phi_{lim} = \frac{k_3}{k_2 + k_3} \frac{k_8}{k_7 + k_8} = \Phi_{ISC}{}^{D}\Phi_{R}{}^{A} \tag{11}$$

and

$$K_s = \frac{k_6}{k_4 + k_5[O_2]} = k_6\tau_D \tag{12}$$

Figure 2 shows that the experimental data fit eq 10 for both aerated and deoxygenated solutions. Contrary to what happens to K_s, the upper limit for the quantum yield of the sensitized reaction, Φ_{lim}, is independent of most experimental conditions (in particular of the concentration of dissolved oxygen). Figure 2 gives $\Phi_{lim} = 0.63$. From this value, one can calculate the quantum yield of redox decomposition of the triplet charge-transfer state of the complex, provided that the quantum yield of intersystem crossing of biphenyl in fluid solutions is known (see eq 11). On the basis of the quantum yield of the biphenyl fluorescence in ligroin (0.23) reported by Bowen,[14] an upper limit for the intersystem crossing yield can be obtained, *i.e.*, $\Phi_{ISC}{}^{D} \leqslant 0.77$. This, in turn, should set a lower limit for the quantum yield of reaction of the triplet charge-transfer state of the complex, *i.e.*, $\Phi_{R}{}^{A} \geqslant 0.82$. Within the limits of such an estimate, it appears therefore that the triplet charge-transfer state of the complex decomposes with a very high (almost unitary) efficiency. Then, if the assumption is made that the charge-transfer triplet is the only reactive state in the direct photoreaction, the quantum yield of the direct photoreaction, 0.16, roughly represents the yield of intersystem crossing from the singlet charge-transfer state to the reactive triplet. If, on the contrary, some reaction is assumed to occur also in the singlet, the yield of intersystem crossing must be even lower than that.

The results obtained with biacetyl disagree with those reported for the same system by Vogler and Adamson.[2] These authors claim that an efficient redox decomposition is sensitized in hydroalcoholic solutions and that the same process occurs also in aqueous solutions, but with a very low efficiency. By relating these findings to the observed quenching of the biacetyl phosphorescence, Vogler and Adamson proposed for this system, as well as for similar ones, a mechanism involving energy transfer from the donor triplet to a triplet charge-transfer state of the complex.

By contrast, our experiments failed to show any evidence for sensitization in aqueous solutions, while only very small traces of Co^{2+} could be detected in hydroalcoholic solutions. This shows that the charge-transfer states of the complex are not significantly populated following light absorption by biacetyl. It follows that the efficient quenching of the biacetyl phosphorescence must occur by some mechanism different from that proposed by Vogler and Adamson. The most likely candidates appear to be (a) a complex-catalyzed intramolecular deactivation of the biacetyl triplet, (b) a chemical quenching not involving redox decomposition of the complex, or (c) energy transfer to ligand-field

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(12) Of course, these arguments cannot be used to rule out a biphenyl-to-complex charge transfer followed by reductive decomposition of the complex and fast reequilibration of the oxidation state of biphenyl. This, however, seems to be a rather *ad hoc* hypothesis.

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triplets of the complex, which are in a favorable energetic position and are known[13] to be unreactive toward redox decomposition.

The comparison between the results obtained with biphenyl and with biacetyl suggests that the triplet charge-transfer state of the hexaamminecobalt(III) complex ion is too high in energy to be reached from the triplet state of biacetyl (which is placed at about 19,000 cm^{-1} in aqueous solution) but low enough to accept energy transfer from the biphenyl triplet (which has an energy of about 23,000 cm^{-1}).

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Conformational Structure, Energy, and Inversion Rates of Cyclohexane and Some Related Oxanes[1a]

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Abstract: The conformations of cyclohexane, *s*-trioxane, *p*-dioxane, *m*-dioxane, and tetrahydropyran are defined in terms of a new coordinate system which allows the structure and energy of all the significant conformations to be specified by only two coordinates. Using a potential derived from vibrational and geometrical data, detailed maps of conformational energy are constructed. These maps show that the more symmetric molecules are almost freely pseudorotating in the transition state between the chair and boat-twist forms. From calculated structural and potential data, the kinetic parameters for chair inversion are determined. A detailed picture of the chair-chair inversion process is given and the calculated rates are compared to experiment. As a result of the pseudorotation, values of $\Delta S^{\ddagger}$ are found which are positive and large.

The conformations of cyclohexane and of related six-membered rings have been of active interest since at least 1890.[2] Since then a large number of methods have been used to attempt to calculate the geometry and relative energy of the various conformations.[3] There have been a number of continuing difficulties with these attempts.[4] The exact structures have been difficult to determine or even to enumerate accurately, although most workers have had at least a qualitative understanding of the chair and boat conformers. The conformations that are in some sense intermediate between the boat and the chair structures have been especially elusive. Another major difficulty has been the lack of experimental information on any but the most stable forms of the molecules. For most of the simple ring compounds this, of course, means that the only direct evidence concerns the chair form. Derivatives of the simple saturated ring systems have been found to have a variety of the possible conformations, but this has led to quantitative understanding of the conformational possibilities only indirectly.[5] Only a relatively few properties of the simple ring systems are sensitive to the various possible conformations. The geometry and vibrational properties of the chair form give some information concerning the forces which hold it in its conformation.[6] The thermodynamic properties especially at high temperature are sensitive to the existence of the boat form.[7] Finally, the rate of inversion of the rings—a property that has been carefully and repeatedly measured in recent years—is sensitive to the nature of the transition state.[8] Unfortunately, the last two characteristics depend on thermal averages over the dynamical coordinates of the conformations and this makes it difficult to work backward from the experimental measurements to precise statements about the nature of the conformations.

In this paper we present a relatively complete conformational analysis of cyclohexane, *s*-trioxane, *p*-dioxane, *m*-dioxane, and tetrahydropyran. We first present a new set of internal coordinates which makes it easy to define the various conformations precisely and we then evaluate the energies of all the significant conformations using a potential function we have previously derived from vibrational and geometrical data.[6] Finally, we consider the chair-chair inversion process in detail and derive values for its rate. Many aspects of our system of coordinates and our consideration of symmetry are immediately extendable to the conformational properties of all the medium rings, but in this paper we will confine ourselves to six-membered ring systems and leave the larger rings for a later paper.

The Out-of-Plane Coordinates

We start by considering the coordinates which describe the out-of-plane motion of a planar six-membered

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[1] (a) Supported in part by the National Science Foundation; (b) National Science Foundation Predoctoral Fellow; (c) Alfred P. Sloan Foundation Fellow; address correspondence to this author.

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