The concentrations of the various species and the calculated and observed intensities are given in Table IV. The agreement between calculated and observed intensities is reasonable, considering the assumptions made and the accuracy of measurement with relatively weak peaks. It should be recalled that two serious assumptions have been made: (a) $f_{SeBr_6^{2-}} = f_{SeBr_5^-}f_{Br^-}$; (b) the activity factors, a/y^4 and a/y^2, calculated for pure HBr solutions are applicable to mixtures of the strong acids HBr, $HSeOBr_3$, $HSeBr_5$, and H_2SeBr_6. Both of these assumptions will be more dangerous with increasing concentration, particularily where the Se(IV) acids assume a greater proportion of total acid concentration.

Conclusion

The principal species present in solutions of SeO_2 in hydrobromic acid are H_2SeO_3, $HSeO_2Br$, $SeOBr_3^-$, $SeBr_5^-$, and $SeBr_6^{2-}$. While the Raman spectra give no clear evidence for the presence of SeO_2Br^-, $SeOBr_2$, and $SeOBr_4^{2-}$, their presence in low concentration cannot be ruled out. It is interesting that $SeBr_4$ decomposes to Se_2Br_2, $SeBr_2$, and Br_2 in nonaqueous solvents, yet no evidence for such decomposition is found in this work. Apparently coordination by the bromide ion stabilizes the Se(IV) oxidation state. In comparison to chloroselenates in hydrochloric acid, bromoselenates in hydrobromic acid are formed more readily. For instance, in 5 M HCl (1 M SeO_2), all of the Se(IV) is still present as H_2SeO_3,[4] whereas in 5 M HBr (1 M SeO_2), no $H_{S}eO_3$ remains, all of the Se(IV) being present as $HSeO_2Br$ and $SeOBr_3^-$. Moreover, the chloro species formed in HCl is $SeOCl_2$, while in HBr, $SeOBr_3^-$ is formed. In the SeO_2–HF system, even at 26 M HF, no bands for fluoroselenate(IV) species can be seen in the Raman spectrum.[14] Thus, the order of ease of haloselenate(IV) formation, Br > Cl > F, follows the order of HX activities in water.[1,4,17] Both hexabromo-[7] and tribromoselenate(IV)[8] compounds can be isolated from the HBr solutions of SeO_2, thus reflecting the presence of these anions as the predominant forms of bromoselenate found in these solutions, depending upon the HBr concentration involved (Table IV). On the basis of the relatively low concentration of pentabromoselenate(IV) in these solutions, it appears unlikely that compounds containing this anion can be prepared from aqueous HBr solutions.

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada is thanked for financial support.

Registry No. H_2SeO_3, 7783-00-8; $HSeO_2Br$, 88212-41-3; $SeOBr_3^-$, 86238-39-3; $SeBr_5^-$, 94598-25-1; $SeBr_6^{2-}$, 20130-45-4; SeO_2, 7446-08-4; HBr, 10035-10-6.

Contribution from the Istituto Chimico "G. Ciamician" and Istituto di Scienze Chimiche,
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Electron-Transfer Photosensitization via Ion Pairs. Co(sepulchrate)$^{3+}$–Iodide Ion System

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The Co(sep)$^{3+}$ complex (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) in aqueous solution forms ion pairs with I^- ions that exhibit a relatively intense charge-transfer absorption. In deoxygenated solutions at natural pH, light excitation of the ion pair does not cause any net reaction. In deoxygenated acid solutions a photochemical reaction takes place with formation of I_3^- and Co_{aq}^{2+} in a 1:2 stoichiometric ratio, with quantum yield 3.4×10^{-3} at pH 1. In oxygen-saturated solutions at natural pH, a photoassisted oxidation of I^- to I_3^- by O_2 is obtained with turnover number >40 for Co(sep)$^{3+}$ and quantum yield 1.6×10^{-3} for $^1/_2$ I_3^- formation. The quantum yield increases with increasing H^+ and I^- concentrations, and in acid solution, it also increases with irradiation time. The results obtained are interpreted on the basis of a mechanism in which the primary photoproducts Co(sep)$^{2+}$ and I are involved in the following secondary reactions: (i) The I radical is scavenged by I^- to yield I_2^-, which then undergoes disproportionation to I_3^- and I^-. (ii) In deoxygenated neutral solutions Co(sep)$^{2+}$ is quantitatively reoxidized to Co(sep)$^{3+}$ by I, I_2^-, or I_3^-. (iii) In deoxygenated acid solution Co(sep)$^{2+}$ undergoes a decomposition reaction, yielding Co_{aq}^{2+}. (iv) In the presence of oxygen, Co(sep)$^{2+}$ can be oxidized to Co(sep)$^{3+}$ with concomitant formation of H_2O_2, which in acid solution oxidizes I^- to I_3^-. The potentiality of the ion-pair approach to the design of photosensitizers for cyclic redox processes is briefly discussed.

Introduction

The recently synthesized[2] Co(sep)$^{3+}$ complex (Figure 1) (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) exhibits interesting electron-transfer properties[2,3] and has already been used as a relay species in homogeneous[4–6] and heterogeneous[7,8] photochemical cyclic processes for solar energy conversion. We have found that Co(sep)$^{3+}$ can give ion pairs with a variety of anions, and that, once involved in such ion pairs, it can play the role of an electron-transfer photosensitizer. In this paper we report the results obtained on light excitation of the Co(sep)$^{3+}$,I^- ion pair under a variety of experimental conditions.

Experimental Section

$Co(sep)Cl_3 \cdot H_2O$ was prepared following the method of Sargeson et al.[2] as modified by Indelli et al.[9] The absorption spectrum and the electrochemical behavior of the compound so obtained were in full agreement with the data reported in the literature.[2]

The experiments were carried out in aqueous solutions that were air equilibrated or nitrogen or oxygen saturated by continuous bubbling. The absorption spectra were recorded with a Cary 19 spectrophotometer, and the electrochemical measurements were performed by an AMEL Model 563 Electrochemolab equipment.

Light excitation at 254 or 313 nm was carried out by low- and medium-pressure Hg lamps as previously described.[10] The incident light

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[2] Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

[3] Creaser, I. I.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Springborg, J. *J. Am. Chem. Soc.* **1977**, *99*, 3181.

[4] Houlding, V.; Geiger, T.; Kolle, V.; Graetzel, M. *Chem. Commun.* **1982**, 681.

[5] Scandola, M.; Scandola, F.; Indelli, A.; Balzani, V. *Inorg. Chim. Acta* **1983**, *76* L67.

[6] Lay, P. A.; Mau, A. W. H.; Sasse, W. M. F.; Creaser, I. I.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2349.

[7] Geiger, T.; Nottemberg, R.; Pelaprat, M.; Graetzel, M. *Helv. Chim. Acta* **1982**, *65*, 2507.

[8] Heller, A.; Ballardini, R.; Balzani V., unpublished results.

[9] Indelli, A., private communication.

0020-1669/85/1324-0844$01.50/0

Table I. Photochemistry of the $Co(sep)^{3+},I^-$ System in Aqueous Solution[a]

entry no.	$10^3[Co(sep)^{3+}]$, M	$[I^-]$, M	pH[b]	O_2[c]	Φ[d]	remarks
1	5.0		3.0	air satd		$\Phi < 10^{-6}$ [e]
2	1.0	0.1	~5.5	deoxyg	$<10^{-6}$	
3	1.0	0.1	1.0	deoxyg	3.4×10^{-3}	$\Phi(Co_{aq}^{2+}) = \Phi(^1/_2 I_3^-)$
4	1.0	0.1	~5.5	air satd	0.6×10^{-3}	
5	5.0	0.1	~5.5	air satd	0.5×10^{-3}	
6	5.0	0.1	3.0	air satd	3.2×10^{-3}	
7	5.0	0.1	1.0	air satd	9.6×10^{-3} [f]	
8	5.0	0.02	~5.5	O_2 satd	0.2×10^{-3}	
9	5.0	0.1	~5.5	O_2 satd	2.4×10^{-3}	TON > 40[g]
10	2.0	0.1	~5.5	O_2 satd	1.1×10^{-3}	
11	5.0	0.1	4.5	O_2 satd	5.4×10^{-3}	
12	5.0	0.1	4.0	O_2 satd	5.6×10^{-3}	
13	5.0	0.1	3.8	O_2 satd	7.2×10^{-3}	
14	5.0	0.1	3.0	O_2 satd	8.8×10^{-3}	
15	5.0	0.1	1.5	O_2 satd	1.5×10^{-2} [f]	
16	5.0	0.1	1.0	O_2 satd	5.1×10^{-2} [f]	TON > 20[g]
17	2.0	0.02	1.0	O_2 satd	1.8×10^{-2} [f]	
18	2.0	0.1	1.0	O_2 satd	4.3×10^{-2} [f]	

[a] Room temperature (~20 °C); $\lambda_{exc} = 313$ nm, except otherwise noted. The quantum yields were calculated on the basis of all the photons absorbed by the solution (see text). [b] Controlled by HCl. [c] The solutions were saturated with air, saturated with oxygen, or deoxygenated by nitrogen bubbling. [d] Quantum yield of $^1/_2 I_3^-$ formation; estimated uncertainty 10%. [e] Quantum yield of $Co(sep)^{3+}$ disappearance or Co_{aq}^{2+} formation; $\lambda_{exc} = 254$ nm. [f] After 1-min excitation. [g] Turnover number of $Co(sep)^{3+}$; $\lambda_{exc} > 300$ nm.

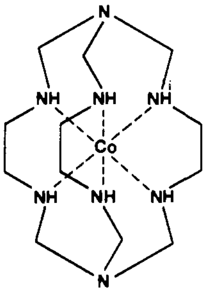

Figure 1. Schematic representation of the $Co(sep)^{3+}$ complex.

intensity was measured by ferric oxalate actinometry.[11] In some experiments cutoff filters for excitation at $\lambda > 300$ nm or $\lambda > 400$ nm were used.

The I_3^- concentration was measured spectrophotometrically at 350 nm. The Co_{aq}^{2+} concentration was determined spectrophotometrically at 620 nm after complexation with NCS^- and extraction with methyl isobutyl ketone. In both cases appropriate calibration plots were used. In the experiments performed to determine the turnover number of $Co(sep)^{3+}$, I_2 was continuously extracted from the aqueous phase by methyl isobutyl ketone.

Results

As previously reported by Sargeson and co-workers,[2,3] we have found that $Co(sep)^{3+}$ can be reversibly reduced to $Co(sep)^{2+}$ in aqueous solution. The reduced complex is not stable in acid solution where it quantitatively decomposes to Co_{aq}^{2+} and other products ($k = 1.2 \times 10^{-2}$ M^{-1} s^{-1}).[2] We have also confirmed the results of Sargeson and co-workers[2,12] on the oxidation of $Co(sep)^{2+}$ by O_2 and H_2O_2. Oxidation by O_2 leads to $Co(sep)^{3+}$ and H_2O_2, and it is fast enough ($k = 43$ M^{-1} s^{-1})[2] to prevail over the $Co(sep)^{2+}$ decomposition even in acid solution. Oxidation by H_2O_2 is much slower: when 1.0×10^{-3} M $Co(sep)^{2+}$ and 1.0×10^{-3} M H_2O_2 solutions were mixed, quantitative oxidation of $Co(sep)^{2+}$ to $Co(sep)^{3+}$ was obtained at pH 5.5, whereas at pH 1 only 90% of $Co(sep)^{2+}$ was oxidized, the remaining 10% being decomposed to Co_{aq}^{2+}.

$Co(sep)^{3+}$ is quite inert in both neutral and acid aqueous solution.[2] Its absorption spectrum is shown in Figure 2. Light excitation in the ligand-to-metal charge-transfer bands does not cause any photochemical decomposition ($\Phi_{redox} < 10^{-6}$, entry 1 in Table I).

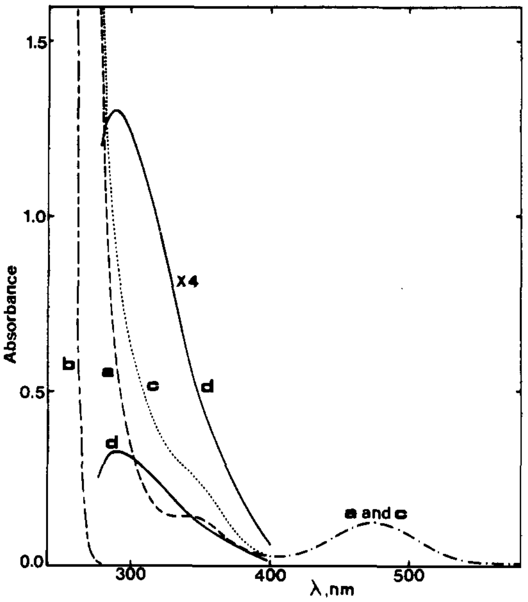

Figure 2. Spectra of aqueous $Co(sep)^{3+}$ in the absence and in the presence of iodide: (a) $[Co(sep)Cl_3] = 2.5 \times 10^{-3}$ M; (b) [NaI] = 0.05 M; (c) $[Co(sep)Cl_3] = 2.5 \times 10^{-3}$ M, [NaI] = 0.05 M; (d) difference of spectrum c minus [spectrum b plus spectrum a]. Optical path: 0.45 cm.

When I^- ions are added to aqueous solutions of $Co(sep)^{3+}$, spectral changes are observed (Figure 2) that indicate the formation of ion pairs. The formation constant for the 1:1 ion pair is quite similar[13] to those of the analogous ion pairs involving $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$.[14] When a strong excess of I^- ion is present, ion triads $Co(sep)^{3+},2I^-$ are also formed.[13]

The results obtained upon light excitation of $Co(sep)^{3+}$ solutions containing I^- ions are summarized in Table I. Most of the experiments were carried out with 313-nm excitation. Qualitatively similar results were obtained by excitation at 254 nm or with $\lambda > 300$ nm and $\lambda > 400$ nm. The quantum yield values reported in Table I refer to the formation of $^1/_2$ I_3^- (which corresponds to the one-electron oxidation of I^-) and were calculated on the

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(10) Gandolfi, M. T.; Manfrin, M. F.; Juris, A.; Moggi, L.; Balzani, V. *Inorg. Chem.* **1974**, *13*, 1342.

(11) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London Ser. A* **1956**, *235*, 518.

(12) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624.

(13) Pina, F.; Moggi, L., unpublished results.

(14) (a) Beck, M. T. *Coord. Chem. Rev.* **1968**, *3*, 91. (b) Katayama, S.; Tomamushi, R. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 606. (c) Yokoyama, H.; Yametra, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1725.

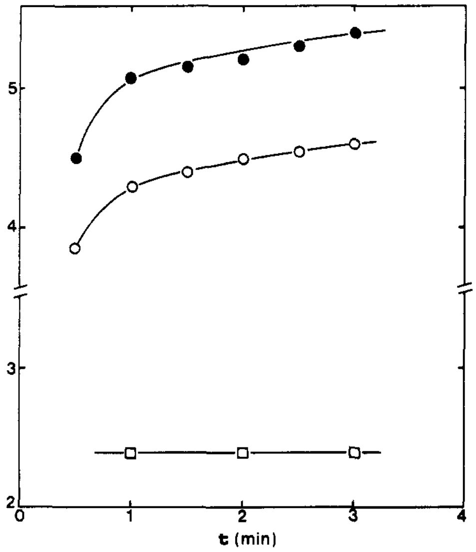

Figure 3. Variation of the quantum yield of $^1/_2$ I_3^- formation with irradiation time (λ_{exc} = 313 nm, O_2-saturated solutions: (●) [Co(sep)$^{3+}$] = 5 × 10^{-3} M, [I^-] = 0.1 M, pH 1; (○) [Co(sep)$^{3+}$] = 2 × 10^{-3} M, [I^-] = 0.1 M, pH 1; (□) [Co(sep)$^{3+}$] = 5 × 10^{-3} M, [I^-] = 0.1 M, pH 5.5.

basis of all the photons absorbed by the solution (i.e., by free Co(sep)$^{3+}$ and by its ion pairs). Of course, a more meaningful way to calculate the quantum yields would have been to consider only the light absorbed by the ion pairs, since excitation of free Co(sep)$^{3+}$ is not expected to cause any reaction. However, such a calculation is not possible because the association constant for the Co(sep)$^{3+}$,I^- couple is unknown. The quantum yield values reported in Table I are therefore lower limits for the quantum yields of ion-pair reaction. Upper limiting values for the quantum yields can be calculated on the basis of the IPCT contribution to the 313-nm absorption as evaluated from the spectral changes caused by ion-pair formation (see, e.g., Figure 2). Such values are 2–3 times larger than those given in Table I.

As one can see from entry 2 of Table I, no net photoreaction was observed in deoxygenated aqueous solutions at their natural pH (~5.5). In deoxygenated acid solutions, however, a photoredox reaction was observed with formation of I_3^- and Co_{aq}^{2+} in a 1:2 ratio (entry 3). In air-saturated (entries 4–7) or oxygen-saturated (entries 8–18) solutions, formation of I_3^- was obtained both at natural pH and in acid solution. For long irradiation periods a precipitate was obtained that was identified as Co(sep)$(I_3)_3$ from elemental analysis and absorption spectrum. The formation of the precipitate could be prevented by continuous extraction of I_2 with methyl isobutyl ketone, at least for not too long irradiation periods. Under such conditions, the turnover number of Co(sep)$^{3+}$ was >20 at pH 1 and >40 at pH 5.5 for oxygen-saturated solutions. For solutions at pH >3, formation of I_3^- followed zero-order kinetics and no post-photochemical effect was observed. In more acidic solutions, however, the formation of I_3^- continued for some time after the end of the irradiation and the quantum yield increased with irradiation time (see, for example, Figure 3). The quantum yield values given in Table I for such experimental conditions are those measured after 1 min of irradiation. As one can see, the quantum yield increases with increasing I^- concentration (entries 8 vs. 9 and 17 vs. 18) and Co(sep)$^{3+}$ concentration (entries 9 vs. 10 and 16 vs. 18). The same trends are shown by the upper limiting values of the quantum yields (see above).

Discussion

Photochemistry of Co(sep)$^{3+}$. Excitation of Co(III) complexes into their ligand-to-metal charge-transfer (LMCT) bands leads to an excited state that is formally a Co(II) complex.[15] The Co(II) complexes are usually very labile because of the presence of σ^* (e_g) electrons.[16] For example, $Co(NH_3)_6^{2+}$ releases the first three NH_3 ligands with $k > 10^6$ s^{-1}.[17] It follows that excitation of Co(III) complexes into their LMCT bands usually leads to an efficient redox decomposition reaction.[15] For example, the photoredox decomposition of $Co(NH_3)_6^{3+}$ upon LMCT excitation (eq 1) takes place with relatively high quantum yield (Φ = 0.16 for λ_{exc} = 254 nm).[18]

$$[\mathrm{Co^{III}(NH_3)_6}]^{3+} \xrightarrow{h\nu(\mathrm{LMCT})} [\mathrm{Co^{II}(NH_3)_5(NH_3^+)}]^{3+} \tag{1a}$$

$$[\mathrm{Co^{II}(NH_3)_5(NH_3^+)}]^{3+} \xrightarrow{\text{fast}} [\mathrm{Co^{III}(NH_3)_6}]^{3+} \tag{1b}$$

$$[\mathrm{Co^{II}(NH_3)_5(NH_3^+)}]^{3+} \xrightarrow{\text{fast}} \mathrm{Co_{aq}}^{2+} + 5\mathrm{NH_4}^+ + \text{products} \tag{1c}$$

Because of the cage nature of the sep ligand, Co(sep)$^{2+}$ is relatively inert even in acid medium ($k = 1.2 \times 10^{-2}$ M^{-1} s^{-1}).[2] It follows that, once a LMCT excited state is obtained, radiationless conversion to the ground state (i.e., back-electron-transfer) strongly predominates over ligand dissociation (eq 2). This explains the observed photoinertness (Table I, entry 1) of the Co(sep)$^{3+}$ complex.

$$[\mathrm{Co^{III}(sep)}]^{3+} \xrightarrow{h\nu(\mathrm{LMCT})} [\mathrm{Co^{II}(sep^+)}]^{3+} \tag{2a}$$

$$[\mathrm{Co^{II}(sep^+)}]^{3+} \xrightarrow{\text{fast}} [\mathrm{Co^{III}(sep)}]^{3+} \tag{2b}$$

$$[\mathrm{Co^{II}(sep^+)}]^{3+} \xrightarrow{\text{slow}} \mathrm{Co_{aq}}^{2+} + \text{products} \tag{2c}$$

Photochemistry of the Co(sep)$^{3+}$$I^-$ System. Co(III) complexes with 3+ electric charge are known to give ion pairs with most anions.[14,19,20] When the anion is a reducing species, ion-pair charge-transfer (IPCT) bands appear in the near-UV spectral region. Light excitation into such IPCT bands causes the promotion of an electron from the anion in the outer coordination sphere to the Co(III) center, which is reduced to Co(II).[15,20] Since Co(II) complexes are usually labile (see above),[16] light excitation into the IPCT bands eventually leads to a redox decomposition reaction. For example, in the $Co(NH_3)_6^{3+}$,I^- system[20] IPCT excitation leads to redox decomposition (eq 3) with high quantum yield.[15,20]

$$[\mathrm{Co^{III}(NH_3)_6}]^{3+},\mathrm{I}^- \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} \tag{3a}$$

$$[\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} \rightarrow [\mathrm{Co^{III}(NH_3)_6}]^{3+} + \mathrm{I}^- \tag{3b}$$

$$[\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} \xrightarrow{\mathrm{H}^+} \mathrm{Co_{aq}}^{2+} + 6\mathrm{NH_4}^+ + {}^1/_2\mathrm{I_2} \tag{3c}$$

When the ligand is a capsule like sep, the Co(II) complex is inert in neutral solution (see above). Thus, IPCT excitation (eq 4a) is followed by either the back-electron-transfer reaction within the solvent cage (eq 4b) or the separation of the primary photoproducts (eq 4c). The I radical is then scavenged by I^- ions (eq 4d; $k = 7.6 \times 10^9$ M^{-1} s^{-1})[21] to yield I_2^-, which is able to oxidize

$$[\mathrm{Co^{III}(sep)}]^{3+},\mathrm{I}^- \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(sep)}]^{2+},\mathrm{I} \tag{4a}$$

$$[\mathrm{Co^{II}(sep)}]^{2+},\mathrm{I} \rightarrow [\mathrm{Co^{III}(sep)}]^{3+},\mathrm{I}^- \tag{4b}$$

$$[\mathrm{Co^{II}(sep)}]^{2+},\mathrm{I} \rightarrow [\mathrm{Co^{II}(sep)}]^{2+} + \mathrm{I} \tag{4c}$$

$$\mathrm{I} + \mathrm{I}^- \rightarrow \mathrm{I_2}^- \tag{4d}$$

$$[\mathrm{Co^{II}(sep)}]^{2+} + \mathrm{I_2}^- \rightarrow [\mathrm{Co^{III}(sep)}]^{3+} + 2\mathrm{I}^- \tag{4e}$$

$$\mathrm{I_2}^- + \mathrm{I_2}^- \rightarrow \mathrm{I_3}^- + \mathrm{I}^- \tag{4f}$$

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(15) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: London, 1970.

(16) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980.

(17) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516.

(18) Manfrin, F.; Varani, G.; Moggi, L.; Balzani, V. *Mol. Photochem.* **1969**, *1*, 387.

(19) (a) Heck, L. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 701, 709. (b) Cannon, R. D. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 179.

(20) (a) Adamson, A.; Sporer, A. *J. Am. Chem. Soc.* **1958**, *80*, 3865. (b) Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630.

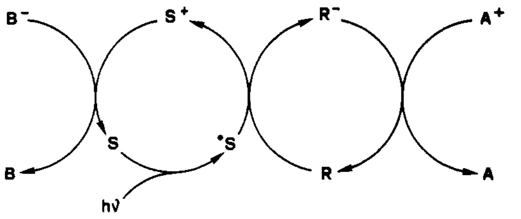

Figure 4. Schematic representation of conventional photosensitized electron-transfer processes in homogeneous solution: S = sensitizer; R = relay.

[Co^{II}(sep)]$^{2+}$ (eq 4e) or to undergo a disporportionation reaction (eq 4f; $k = 7.7 \times 10^9$ M^{-1} s^{-1}).[22] In its turn, I_3^- produced by eq 4f is still an oxidant strong enough to oxidize [Co^{II}(sep)]$^{2+}$ (eq 4g). As a consequence, no net reaction takes place under such experimental conditions (entry 2, Table I).

$$2[\text{Co}^{II}(\text{sep})]^{2+} + I_3^- \rightarrow 2[\text{Co}^{III}(\text{sep})]^{3+} + 3I^- \quad (4g)$$

In acid medium, however, the [Co^{II}(sep)]$^{2+}$ decomposition (eq 4h; $k = 1.2 \times 10^{-2}$ M^{-1} s^{-1})[2] is fast enough to compete with the

$$[\text{Co}^{II}(\text{sep})]^{2+} \xrightarrow{H^+} \text{Co}_{aq}{}^{2+} + \text{products} \quad (4h)$$

[Co^{II}(sep)]$^{2+}$ oxidation (eq 4e,g). Co$_{aq}{}^{2+}$ is thus formed that can be reoxidized to Co$_{aq}{}^{3+}$ by neither I_2^- nor I_3^-. As a consequence, a stoichiometric amount of $^1/_2$ I_3^- accumulates in the solution (Table I, entry 3).

In the presence of oxygen eq 4i comes into play ($k = 43$ M^{-1} s^{-1}).[2] Because of the high O_2 concentration (compared with the I_2^- and I_3^- concentrations), eq 4i competes with eq 4e,g.

$$[\text{Co}^{II}(\text{sep})]^{2+} + {}^1/_2O_2 \xrightarrow{H^+} [\text{Co}^{III}(\text{sep})]^{3+} + {}^1/_2H_2O_2 \quad (4i)$$

Moreover, H_2O_2 can also oxidize [Co^{II}(sep)]$^{2+}$ (eq 4j; $k \simeq 4$ M^{-1} s^{-1}).[2] In conclusion, some I_3^- accumulates while [Co^{III}(sep)]$^{3+}$

$$[\text{Co}^{II}(\text{sep})]^{2+} + {}^1/_2H_2O_2 \xrightarrow{H^+} [\text{Co}^{III}(\text{sep})]^{3+} + H_2O \quad (4j)$$

is regenerated (Table I, entries 4–18). The net photoreaction is thus the oxidation of I$^-$ to I_3^- by dioxygen, photoassisted by [Co^{III}(sep)]$^{3+}$. As expected, the initial quantum yield of I_3^- formation increases with increasing O_2 concentration (entries 5 vs. 9, 6 vs. 14, and 7 vs. 16). The turnover number of [Co^{III}(sep)]$^{3+}$ is presumably higher in neutral than in acid solution (entry 9 vs. 16) because in acid solution eq 4h plays some role.

In acid medium the following secondary reaction can also take place:[23]

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O \quad (4k)$$

This reaction may account for (i) the post irradiation I_3^- formation, (ii) the increase in the quantum yield of I_3^- formation with increasing irradiation time, and (iii) the pH dependence of the quantum yield. The dependence of the I_3^- quantum yield upon I$^-$ concentration (entries 8 vs. 9 and 17 vs. 18) may also depend on reaction 4k. However, qualitatively the same effect is also expected because of the increase in ion-pair concentration.[24] In the same way, increasing Co(sep)$^{3+}$ concentration causes an increase in the quantum yield presumably because of an increase in the ion-pair concentration (entries 9 vs. 10 and 16 vs. 18).

Photosensitization via Ion Pairs. Photochemical electron-transfer reactions involving a sensitizer (S) and a relay (R) species (Figure 4) are currently the object of much interest because of their potentiality in the fields of light energy conversion[25] and photochemical synthesis.[26] Both S and R must be able to undergo reversible electron-transfer processes, and S must also have suitable spectroscopic and excited-state properties. The normal Co(III) complexes decompose upon one-electron reduction, and thus they cannot be used as S or R in the cyclic systems of Figure 4. By contrast, the Co(sep)$^{3+}$ complex can be reversibly reduced and has already been used as a relay in the conventional (Figure 4) cyclic processes for solar energy conversion.[4-8] It cannot be used, however, as a sensitizer in such processes because of its too short excited-state lifetime.

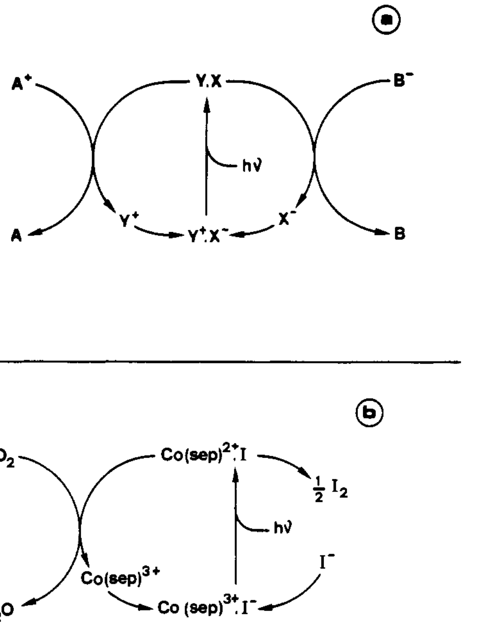

Figure 5. Schematic representation: (a) photosensitized electron-transfer processes via ion pairs; (b) the oxidation of I$^-$ by O_2 photosensitized by Co(sep)$^{3+}$ via ion pairs.

As we have seen above, light excitation of the [Co^{III}(sep)]$^{3+}$,I$^-$ ion pair in the presence of dioxygen leads to oxidation of I$^-$ to I_3^- as a net reaction (eq 5). In this photoassisted reaction Co(sep)$^{3+}$ plays the role of a sensitizer.

$$4I^- + O_2 + 4H^+ \xrightarrow[\text{Co(sep)}^{3+}]{h\nu} 2I_2 + 2H_2O \quad (5)$$

A general scheme for photosensitization via ion pairs is shown in Figure 5a. For the system studied in this paper, the actual scheme is that shown in Figure 5b. It can be noted that this system is in some way analogous to the so-called sacrifical processes based on the cycle of Figure 4 when S$^+$ is prevented from reacting with the reduced relay R$^-$ by the reaction with an appropriate sacrifical species B$^-$.

Studies on other photosensitized reactions based on ion pairs involving Co(sep)$^{3+}$ are currently in progress in our laboratories.

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Registry No. Co(sep)$^{3+}$, 72496-77-6; I_3^-, 14900-04-0; Co^{2+}, 22541-53-3.

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[21] Baxendale, J. M.; Bevan, P. L. T.; Stott, D. A. *Trans Faraday Soc.* **1968**, *64*, 2389.

[22] Grossweiner, L. I.; Matheson, M. S. *J. Phys. Chem.* **1957**, *61*, 1089.

[23] Durrant, D. J.; Durrant, B. "Introduction to Advanced Chemistry"; Longmans, Green and Co.: New York, 1962.

[24] Increasing I$^-$ concentration may also cause the formation of [Co^{III}(sep)]$^{3+}$2I$^-$ ion triads. In the primary photoproduct of an ion triad the scavenging of I by I$^-$ may be more effective.

[25] (a) Connoly, J. S., Ed. "Photochemical Conversion and Storage of Solar Energy"; Academic Press: London, 1981. (b) Rabani, J., Ed. "Photochemical Conversion and Storage of Solar Energy"; Weizmann Science Press: Jerusalem, 1982. (c) Balzani, V.; Scandola, F. In "Energy Resources by Photochemistry and Catalysis"; Graetzel, M., Ed.; Academic Press: London, 1983; p 1.

[26] Albini, A. *Synthesis* **1981**, 249. Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.