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Photochemistry of $Co(sep)^{3+}$–Oxalate Ion Pairs: A Novel System for Dihydrogen Evolution from Aqueous Solutions

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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 oxalate ions that exhibit a charge-transfer absorption band in the near-UV region. Excitation of the ion pairs in deoxygenated solution with 313-nm light causes the reduction of $Co(sep)^{3+}$ to $Co(sep)^{2+}$ and the oxidation of oxalate ions to carbon dioxide. The quantum yield of the photoreaction depends on oxalate concentration and pH. When the photoreaction is carried out in the presence of colloidal platinum, no net reduction of $Co(sep)^{3+}$ takes place and, besides carbon dioxide, dihydrogen also evolves from the solution. The turnover number of $Co(sep)^{3+}$ is higher than 700. The peculiar aspects of this novel system for the photosensitized evolution of hydrogen from water based on the use of $Co(sep)^{3+}$ as a sensitizer and oxalate ions as sacrificial agents are discussed. In air-equilibrated or oxygen-saturated solutions $Co(sep)^{2+}$ is oxidized to $Co(sep)^{3+}$ by dioxygen. When this reaction is carried out in the presence of oxalate ions, a new product is obtained that presumably originates from a reaction between $Co(sep)^{2+}$ and the CO_2^- radical. For comparison purposes, the photochemistry of the $Co(en)_3^{3+}$–oxalate ion pair (en = ethylenediamine) has also been briefly investigated.

Introduction

Photosensitized electron-transfer reactions are currently the object of much interest for theoretical reasons as well as for practical applications.[2-9] Most of the investigations in this field have so far been focused on the use of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine)[10,11] as a photosensitizer. There is now the need to explore the potentiality of other systems in order to achieve further progress in this very important branch of chemical research.

We have found that the recently synthesized[12] $Co(sep)^{3+}$ complex (Figure 1; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) 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 another paper[13] we have shown that $Co(sep)^{3+}$ can sensitize the photoassisted oxidation of iodide ions to iodine by dioxygen. In this paper we report results concerning the use of $Co(sep)^{3+}$ as a photosensitizer for the evolution of dihydrogen from aqueous solutions with oxalate ions as "sacrificial" agents. Other interesting aspects of the photochemistry of the $Co(sep)^{3+}$–oxalate ion pairs are reported and discussed.

Experimental Section

$Co(sep)Cl_3{\cdot}H_2O$ was prepared following the method of Sargeson et al.[12] as modified by Indelli.[14] The absorption spectrum and the electrochemical behavior of the compound so obtained were in full agreement with the data reported in the literature.[12] $Co(en)_3Cl_3$ (en = ethylenediamine) was prepared as described by Work.[15] The colloidal Pt catalyst was prepared following the method described by Wilenzick et al.[16] Other chemicals were of reagent grade.

The experiments were carried out in aqueous solutions that were air equilibrated, oxygen saturated, or deoxygenated by N_2 bubbling. The absorption spectra were recorded with a Cary 19 spectrophotometer, and the electrochemical measurements were performed by an Amel Model 563 Electrochemolab equipment. The gaseous products were removed from the irradiation vessel through a trap cooled with a liquid N_2/methanol slush by an automatic Toepler pump and collected in a gas buret. The gas was then injected into a Dani 3600 gas chromatograph equipped with a silica gel column using He as the carrier gas. The concentration of $Co(sep)^{2+}$ formed upon irradiation was measured from the decrease in absorbance at 475 nm, where the extinction coefficients of $Co(sep)^{3+}$ and $Co(sep)^{2+}$ are 106 and 8 $M^{-1}\,cm^{-1}$, respectively. The amounts of Co(II) were determined by extraction of Co(II) as the thiocyanate complex into 4-methyl-2-pentanone and then measuring the absorption of the organic solution at 620 nm.[17] The concentration of Co(II) was determined by reference to a calibration curve.

The irradiation cell was a 3-mL spectrophotometric cell connected by a side arm to a vessel equipped with a high-vacuum stopcock. Light excitation at 313 nm was carried out by a medium-pressure Hg lamp as previously described.[18] The incident light intensity, measured by ferric oxalate actinometry,[19] was 0.37×10^{-6} *Nhν*/min (*N* = Avogadro's number). For the quantum yield measurements, the irradiation time was usually on the order of 30 min. The quantum yield values are based on the total light intensity absorbed by the solution (i.e., by $Co(sep)^{3+}$ and by its ion pairs).

Results

Sargeson et al.[12] showed that $Co(sep)^{3+}$ is quite inert in neutral and acid solution, and we demonstrated[13] that it is also inert toward photodecomposition (Table I, entry 1).

When solutions of $Co(sep)Cl_3$ and $(NH_4)_2C_2O_4$ were combined, no spectral change was observed at pH 0.5, but an increase in absorbance took place in the UV region when the pH of the solution was 3.0 or 5.5. Difference spectra (Figure 2) demonstrated the presence of a new band with maximum at 275 nm at both pH 3.0 and pH 5.5. The intensity of this band was about twice as intense as at pH 5.5.

Light excitation (λ = 313 nm) of deoxygenated solutions containing $Co(sep)Cl_3$ and $(NH_4)_2C_2O_4$ at pH 0.5 did not cause any spectral change (Table I, entry 2). At higher pH values, however, an absorbance decrease in the entire spectral region was observed (Figure 3) and CO_2 was found to evolve from the solution. Bubbling dioxygen or air into such irradiated solutions caused a fast recovery of absorbance, leading to a final spectrum (Figure 3) that was exactly the same as that shown by the solution before irradiation in the visible region, but was somewhat more intense in the UV region. This increase in absorption over the absorbance of $Co(sep)^{3+}$ was more noticeable at pH 5.5 than at

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Table I. Photochemistry of the Ion Pairs Formed by $Co(sep)^{3+}$ or $Co(en)_3{}^{3+}$ with Oxalate Ions[a]

entry no.		10^3[Co(III) complex], M	$[(NH_4)_2C_2O_4]$, M	pH[b]	O_2[c]	10^5[Pt],[d] M	$\Phi_{\text{-Co(III)}}$[e,f]	Φ_{CO_2}[f]	Φ_{H_2}[f]
1	$Co(sep)Cl_3$	5.0	–	3.0	air satd		$<10^{-6}$[g]		
2		5.0	0.1	0.5	deoxyg		$<10^{-3}$[h]		
3		5.0	0.1	3.0	deoxyg		0.13[h]	0.13	
4		5.0	0.1	5.5	deoxyg		0.29[h]	0.28	
5		5.0	0.01	3.0	deoxyg		0.03[h]		
6		1.0	0.1	3.0	deoxyg		0.08[h]		
7		5.0	0.1	3.0	deoxyg	5.0	$<10^{-3}$[h]	0.14	0.07[i]
8		5.0	0.1	5.5	deoxyg	5.0	$<10^{-3}$[h]	0.24	0.10
9		5.0	0.1	3.0	O_2 satd		$<10^{-3}$[h]	0.17	
10	$Co(en)_3Cl_3$	5.0	0.1	3.0	deoxyg		0.13[j]	0.12	

[a] Room temperature (20 °C); $\lambda_{exc} = 313$ nm, except otherwise noted. [b] Controlled by HCl. [c] The solutions were saturated with air, saturated with oxygen, or deoxygenated by nitrogen bubbling. [d] Colloidal Pt catalyst. See text. [e] Quantum yield of disappearance of the Co(III) complex. The Co(II) species formed is specified in the footnotes. [f] Estimated uncertainty <20%. [g] Quantum yield for $Co_{aq}{}^{2+}$ formation; $\lambda_{exc} = 254$ nm.[13] [h] Quantum yield for $Co(sep)^{2+}$ formation. [i] Turnover number of $Co(sep)^{3+}$ with respect to H_2 >700; $\lambda_{exc} >$ 300 nm. [j] Quantum yield for $Co_{aq}{}^{2+}$ formation.

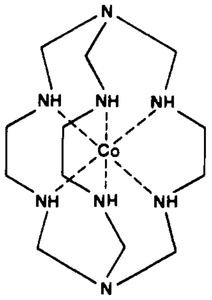

Figure 1. Schematic representation of the $Co(sep)^{3+}$ complex.

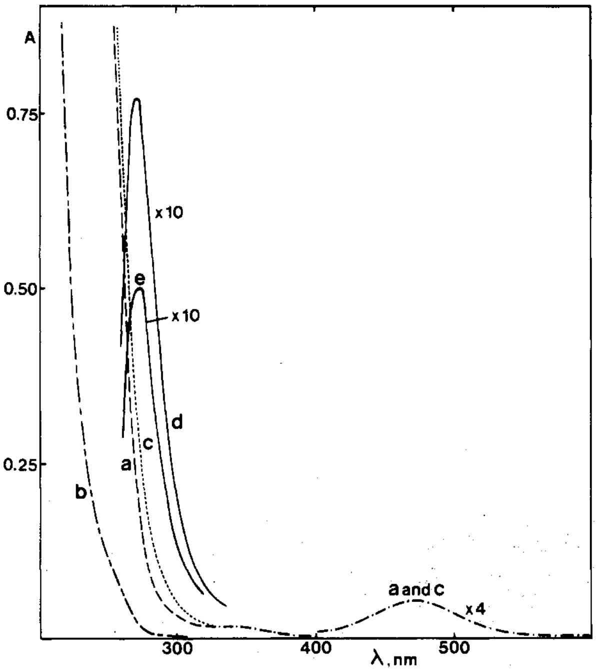

Figure 2. Spectra of aqueous $Co(sep)Cl_3$ in the absence and in the presence of $(NH_4)_2C_2O_4$: (a) $[Co(sep)Cl_3] = 2.5 \times 10^{-3}$ M, pH 6.0; (b) $[(NH_4)_2C_2O_4] = 0.1$ M, pH 5.5; (c) $[Co(sep)Cl_3] = 2.5 \times 10^{-3}$ M, $[(NH_4)_2C_2O_4] = 0.1$ M, pH 5.5; (d) difference of spectrum c minus (spectrum b plus spectrum a), pH 5.5; (e) same as in spectrum d, pH 3.0. Optical path: 0.45 cm.

pH 3.0. The quantum yield of $Co(sep)^{2+}$ formation was found to depend on the pH of the solution (Table I, entries 2–4) and on the oxalate concentration (entry 5). The amount of CO_2 formed was in a 1:1 stoichiometric ratio with the amount of $Co(sep)^{2+}$ produced (entry 3).

When a colloidal Pt catalyst was present in the irradiated solution, no spectral change was observed in the entire spectral region and CO_2 and H_2 were produced in a 2:1 stoichiometric ratio.

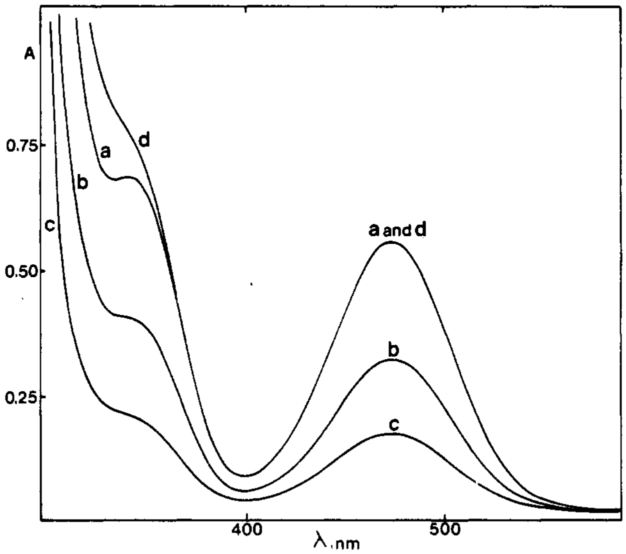

Figure 3. Change in absorption spectrum with irradiation time: (a) zero time; (b) 70-min irradiation; (c) 190-min irradiation; (d) solution from (c) after saturation with O_2. Experimental conditions: $[Co(sep)Cl_3] = [(NH_4)_2C_2O_4] = 5.0 \times 10^{-3}$ M; $\lambda_{exc} = 313$ nm.

The quantum yield of CO_2 and H_2 formation depended on the pH of the solution (entries 7 and 8). In an experiment carried out at pH 3 irradiating the solution for 24 h, about 1 mL of H_2 was produced. In the same experiment, no decrease in absorbance was observed at 475 nm within the experimental error. The lower limit for the turnover number of $Co(sep)^{3+}$ with respect to H_2 production was evaluated to be >700.

When air-equilibrated or oxygen-saturated solutions were irradiated for short irradiation periods, the absorption spectrum did not change in the visible but an increase in absorbance was observed in the near-UV region; CO_2 was again produced with a quantum yield (entry 9) that was practically the same as that obtained for deoxygenated solutions. For long irradiation periods an increase in absorbance was observed even in the visible region.

Additional experiments were performed in order to elucidate the reason why an increase in absorbance is observed when the photoreaction is carried out in the presence of oxygen or when oxygen is introduced after irradiation. $Co(sep)^{3+}$ solutions (5.0×10^{-3} M) were reduced to $Co(sep)^{2+}$ electrochemically and then reoxidized either electrochemically or by dioxygen bubbling. In agreement with the results of Sargeson et al.,[12,20] in both cases the final spectrum coincided with that of the original $Co(sep)^{3+}$ solution. In other experiments, ammonium oxalate was added to the electrochemically produced $Co(sep)^{2+}$ solution before its

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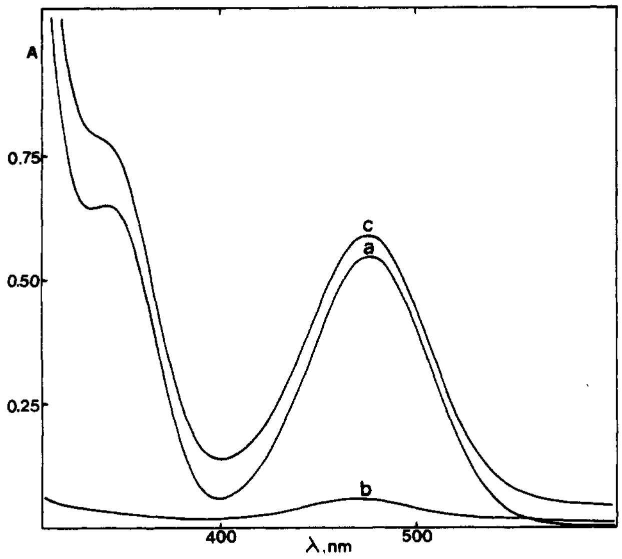

Figure 4. Absorption spectra: (a) $[\mathrm{Co(sep)Cl_3}] = 5.0 \times 10^{-3}$ M, $[(\mathrm{NH_4})_2\mathrm{C_2O_4}] = 0.1$ M; (b) solution from (a) after electrochemical reduction; (c) solution from (b) after saturation with O_2.

reoxidation so as to make the solution 0.1 M in $(\mathrm{NH_4})_2\mathrm{C_2O_4}$. Under such conditions, while the electrochemical reoxidation yielded a solution showing again the spectrum of $\mathrm{Co(sep)}^{3+}$, reoxidation by dioxygen yielded a solution whose spectrum was higher than that of $\mathrm{Co(sep)}^{3+}$ in the entire spectral region (Figure 4).

For comparison purposes, the photochemistry of the $\mathrm{Co(en)_3}^{3+}$–oxalate ion pairs was also investigated. When a deoxygenated aqueous solution containing 5.0×10^{-3} M $\mathrm{Co(en)_3Cl_3}$ and 0.1 M $(\mathrm{NH_4})_2\mathrm{C_2O_4}$ at pH 3 was excited by 313-nm light, a decrease in absorbance was observed in the entire spectral region. CO_2 was found to evolve from the solution and $\mathrm{Co_{aq}}^{2+}$ was formed (Table I, entry 10). The quantum yield was the same for both products, showing that the formation of CO_2 is accompanied by the decomposition of a stoichiometric amount of $\mathrm{Co(en)_3}^{3+}$. No spectral change was observed when dioxygen was bubbled in the solution after light irradiation.

Discussion

$\mathrm{Co(sep)}^{3+}$, as well as the other Co(III) complexes that exhibit 3+ electric charge,[21,22] forms ion pairs with most anions.[13,14,23] The pK_a values of oxalic acid are 1.23 and 4.19.[24] Thus, $H_2C_2O_4$ is the only species present at pH 0.5, and no ion pair with $\mathrm{Co(sep)}^{3+}$ can be formed. At pH 3.0 and 5.5 the prevailing species are the monoanion $\mathrm{HC_2O_4}^-$ and the dianion $\mathrm{C_2O_4}^{2-}$, which, as one can see from Figure 2, form ion pairs with $\mathrm{Co(sep)}^{3+}$, exhibiting a CT band with maximum at 275 nm. The higher intensity of the IPCT band at pH 5.5 is related to the higher ion-pair concentration when $\mathrm{C_2O_4}^{2-}$ is available and, presumably, also to the larger overlap between donor and acceptor orbitals in the ion pair involving the dianion.

Light excitation in the CT band of the ion pairs formed by Co(III) complexes with anions causes the promotion of an electron from the anion to the Co(III) center, which is thus reduced to Co(II).[25-27] When the Co(II) complex is labile, as is the case of the hexaamine complex, a redox decomposition reaction is obtained. For example[25]

$$[\mathrm{Co^{III}(NH_3)_6}]^{3+},\mathrm{I}^- \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} \tag{1a}$$

$$[\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} \rightarrow [\mathrm{Co^{III}(NH_3)_6}]^{3+},\mathrm{I}^- \tag{1b}$$

$$[\mathrm{Co^{II}(NH_3)_6}]^{2+},\mathrm{I} + 6\mathrm{H_3O^+} \rightarrow \mathrm{Co_{aq}}^{2+} + 6\mathrm{NH_4}^+ + {}^1/_2\mathrm{I_2} \tag{1c}$$

For the $[\mathrm{Co^{III}(en)_3}]^{3+},\mathrm{HC_2O_4}^-$ (or $[\mathrm{Co^{III}(en)_3}]^{3+},\mathrm{C_2O_4}^{2-}$) ion pairs, IPCT excitation leads to the labile[28] $[\mathrm{Co^{II}(en)_3}]^{2+}$ complex and the unstable $\mathrm{HC_2O_4}$ (or $\mathrm{C_2O_4}^-$) radical, which is known[29] to decompose into CO_2 and the strongly reducing $\mathrm{HCO_2}$ (or $\mathrm{CO_2}^-$) species (eq 2a–e). A secondary thermal reaction can then occur,

$$[\mathrm{Co^{III}(en)_3}]^{3+},\mathrm{HC_2O_4}^- \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(en)_3}]^{2+},\mathrm{HC_2O_4} \tag{2a}$$

$$[\mathrm{Co^{II}(en)_3}]^{2+},\mathrm{HC_2O_4} \rightarrow [\mathrm{Co^{III}(en)_3}]^{3+},\mathrm{HC_2O_4}^- \tag{2b}$$

$$[\mathrm{Co^{II}(en)_3}]^{2+},\mathrm{HC_2O_4} + 6\mathrm{H_3O^+} \rightarrow \mathrm{Co_{aq}}^{2+} + 3\mathrm{enH_2}^{2+} + \mathrm{HC_2O_4} \tag{2c}$$

$$\mathrm{HC_2O_4} \rightarrow \mathrm{CO_2} + \mathrm{HCO_2} \tag{2d}$$

$$\mathrm{HCO_2} \rightleftarrows \mathrm{H^+} + \mathrm{CO_2}^- \qquad \mathrm{p}K_a = 1.4^{30} \tag{2e}$$

leading to the redox decomposition of another $[\mathrm{Co^{III}(en)_3}]^{3+}$ molecule[31] (eq 2f). The overall photochemical reaction can thus

$$[\mathrm{Co^{III}(en)_3}]^{3+} + \mathrm{CO_2}^- + 6\mathrm{H_3O^+} \rightarrow \mathrm{Co_{aq}}^{2+} + 3\mathrm{enH_2}^{2+} + \mathrm{CO_2} \tag{2f}$$

be represented as in eq 2g, in agreement with the 1:1 stoichiometric ratio of the $[\mathrm{Co^{III}(en)_3}]^{3+}$ molecules decomposed and CO_2 molecules produced (Table I, entry 10).

$$2[\mathrm{Co^{III}(en)_3}]^{3+} + \mathrm{HC_2O_4}^- + 11\mathrm{H_3O^+} \xrightarrow{h\nu(\mathrm{ICPT})} 2\mathrm{Co_{aq}}^{2+} + 6\mathrm{enH_2}^{2+} + 2\mathrm{CO_2} \tag{2g}$$

When the ligand is a capsule like sep, the Co(II) complex obtained in the primary photochemical step is quite inert (at least in not too acidic solutions).[12] Thus, when the oxidized anion does not undergo decomposition, back-electron-transfer reactions prevent any net chemical change in deoxygenated solution[32] (eq 3a–d).

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

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

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

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

In the case of the $[\mathrm{Co^{III}(sep)}]^{3+},\mathrm{HC_2O_4}^-$ and $[\mathrm{Co^{III}(sep)}]^{3+},\mathrm{C_2O_4}^{2-}$ ion pairs, IPCT excitation can be followed by the decomposition of the oxidized anion (eq 4a–c). The reducing

$$[\mathrm{Co^{III}(sep)}]^{3+},\mathrm{HC_2O_4}^- \xrightarrow{h\nu(\mathrm{IPCT})} [\mathrm{Co^{II}(sep)}]^{2+},\mathrm{HC_2O_4} \tag{4a}$$

$$[\mathrm{Co^{II}(sep)}]^{2+},\mathrm{HC_2O_4} \rightarrow [\mathrm{Co^{III}(sep)}]^{3+},\mathrm{HC_2O_4}^- \tag{4b}$$

$$[\mathrm{Co^{II}(sep)}]^{2+},\mathrm{HC_2O_4} \rightarrow [\mathrm{Co^{II}(sep)}]^{2+} + \mathrm{CO_2} + \mathrm{CO_2}^- + \mathrm{H^+} \tag{4c}$$

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[32] In eq 3c and d, I represents the various oxidized species obtained upon one-electron oxidation of I^- (i.e., I, $\mathrm{I_2}$, $\mathrm{I_2}^-$, and $\mathrm{I_3}^-$). Note also that quite different behavior is observed in aerated or oxygen-saturated solutions, as discussed in ref 13.

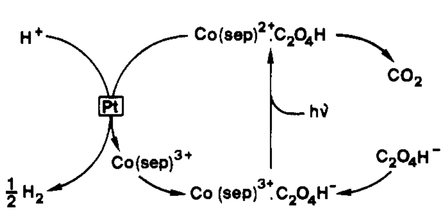

Figure 5. Schematic representation of photosensitized evolution of dihydrogen from water based on the excitation of the $Co(sep)^{3+},C_2O_4H^-$ ion pairs.

radical CO_2^- then reduces another $[Co^{III}(sep)]^{3+}$ molecule (eq 4d). The overall reaction in deoxygenated solution is thus given

$$[Co^{III}(sep)]^{3+} + CO_2^- \rightarrow [Co^{II}(sep)]^{2+} + CO_2 \qquad (4d)$$

$$k = 4.3 \times 10^8\ M^{-1}\ s^{-1}\ {}^{33}$$

by the equation (4e), in agreement with the 1:1 stoichiometric

$$2[Co^{III}(sep)]^{3+} + HC_2O_4^- \xrightarrow{h\nu(IPCT)} 2[Co^{II}(sep)]^{2+} + 2CO_2 + H^+ \qquad (4e)$$

ratio found for $[Co^{III}(sep)]^{3+}$ reduced and CO_2 evolved (Table I, entry 3). The increase in the quantum yield of the photoreaction on going from pH 3.0 to pH 5.5 (Table I, entries 3 and 4) is accounted for by the corresponding increase in the fraction of light absorbed by the ion pairs (see Figure 2). The same explanation holds for the increase in the quantum yield with increasing oxalate concentration (compare entry 5 with entry 3). When the $Co(sep)^{3+}$ concentration decreases in the presence of excess oxalate, no change in the fraction of $Co(sep)^{3+}$ ions involved in ion pairs is expected.

The $[Co^{II}(sep)]^{2+}$ complex produced by reactions 4c and 4d is a reductant strong enough ($E = -0.28$ V for $Co(sep)^{3+/2+}$)[34] to reduce H^+ to $^1/_2\ H_2$ at both pH 3.0 and pH 5.5. When a Pt catalyst was present in the solution, such a reaction indeed occurred (Table I, entries 7 and 8) and a stoichiometric amount of H_2 replaced $[Co^{II}(sep)]^{2+}$ as a reaction product (compare entry 7 with entry 3 and entry 8 with entry 4). Under such condition the overall reaction is

$$HC_2O_4^- + H^+ \xrightarrow[Co(sep)^{3+}]{h\nu} 2CO_2 + H_2 \qquad (5)$$

and $Co(sep)^{3+}$ plays the role of a photosensitizer as it can be better seen from Figure 5. The turnover number of $Co(sep)^{3+}$ was found to be higher than 700 at pH 3.0. The photosensitized evolution of hydrogen from water based on $Co(sep)^{3+}$ as a sensitizer and oxalate ions as sacrificial agents is a process in some way analogous to the hydrogen-evolving processes based on the photoredox reactions involving $Ru(bpy)_3^{2+}$ or other photosensitizers, $Co(sep)^{3+}$ or other relays, and EDTA or other sacrificial donors.[34-39]

When the Pt catalyst is not present and the solution is oxygen saturated, the $[Co^{II}(sep)]^{2+}$ complex produced by reactions 4c and 4d is reoxidized to $[Co^{III}(sep)]^{3+}$ by dioxygen (Table I, entry 9). Such a reaction has been thoroughly studied by Sargeson et al.[20] and is known to proceed by the steps (6a)–(6e). We have found

$$[Co^{II}(sep)]^{2+} + O_2 \xrightarrow{H^+} [Co^{III}(sep)]^{3+} + HO_2/O_2^- \qquad (6a)$$

$$HO_2 \rightleftarrows O_2^- + H^+ \qquad pK_a = 4.69^{40} \qquad (6b)$$

$$HO_2 + Co(sep)^{2+} \xrightarrow{H^+} Co(sep)^{3+} + H_2O_2 \qquad (6c)$$

$$O_2^- + Co(sep)^{2+} \xrightarrow{2H^+} Co(sep)^{3+} + H_2O_2 \qquad (6d)$$

$$2HO_2/O_2^- \xrightarrow{H^+} H_2O_2 + O_2 \qquad (6e)$$

that when this oxidation process takes place in the presence of oxalate ions, a new species exhibiting a broad absorption is formed. Similar spectral changes were observed during continuous γ irradiation of $Co(sep)^{3+}$-aerated solutions containing HCOONa or bubbling O_2 into a deaerated solution containing radiolytically produced $Co(sep)^{2+}$ and HCOONa.[33] This suggests that the new species originates from a reaction between $Co(sep)^{2+}$ and the CO_2^- radical. Further investigations are in progress on this system.

Conclusion

The photochemistry of Co(III) complexes has been extensively investigated in the last 20 years.[26,41,42] The main feature emerged from such studies has been the strong tendency of these complexes to undergo redox decomposition upon irradiation in ligand-to-metal charge-transfer or ion-pair charge-transfer bands. Such photodecomposition reactions are interesting but useless. When the importance of photosensitized electron-transfer reactions was realized[43-46] and the search for relays and photosensitizers became a popular research field, Co(III) complexes were discarded because they did not meet the main requirements needed that are (i) reversible redox behavior for a relay and (ii) reversible redox behavior and long excited-state lifetime for a photosensitizer. The synthesis by Sargeson et al.[12,47] of Co(III) complexes having cage-type ligands has allowed one to overcome the problem of redox reversibility and to use Co(III) complexes as relays in photosensitization cycles.[35,38,48] The ion-pair approach described in this and in the previous paper[13] allows us to overcome the problem of the short excited-state lifetime and to use Co(III) complexes as photosensitiziers. Useful photochemistry can thus be obtained, in principle, even from Co(III) complexes.

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Registry No. $Co(sep)^{3+}$, 72496-77-6; $Co(sep)^{2+}$, 63218-22-4; $Co(en)_3^{3+}$, 14878-41-2; $C_2O_4^{2-}$, 338-70-5; $HC_2O_4^-$, 920-52-5; CO_2, 124-38-9; H_2, 1333-74-0; H_2O, 7732-18-5.

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