Photochemistry of Co(EDTA)⁻–I⁻ System in Aqueous Solutions

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(Received May 15, 1987)

Abstract

The $Co(EDTA)^-$ complex in aqueous solution gives rise to a specific interaction with I^- ions as evidenced by a new, relatively intense band formed at 290–300 nm. This specific interaction is attributed to the formation of an ion-pair between $Co(EDTA)^-$ and I^-, even though they are like charged ions. Irradiation of this ion-pair in air-equilibrated solutions with 313 nm light, causes the reduction of the $Co(EDTA)^-$ to $Co(EDTA)^{2-}$ and the oxidation of the I^- ion to I_3^-. The results obtained are interpreted on the basis of a mechanism in which $Co(EDTA)^{2-}$ and $I^\bullet$ are the primary photoproducts. The $I^\bullet$ radical is then scavenged by I^- to yield I_2^-, which subsequently disproportionates to I_3^- and I^- and reoxidizes $Co(EDTA)^{2-}$ to $Co(EDTA)^-$. At the beginning of the photoreaction, the I_2^- decay is equally distributed on the two reaction pathways. It was possible to determine a value of 0.2 ± 0.05 for the photoreaction quantum yield and an efficiency of the primary photochemical step almost unitary. A schematic representation of the energetics of the overall reaction is reported.

Introduction

The photochemistry of Co(III) complexes has been extensively investigated in the last 20 years [1–3]. The main feature emerging from such studies has been the strong tendency of these complexes to undergo decomposition upon irradiation in ligand-to-metal charge transfer bands. When the importance of photosensitized electron transfer reactions was realized [4–7] and the search for relays and photosensitizers became a popular research field, Co(III) complexes were discarded because they did not meet the necessary requirements. These are (i) reversible redox behaviour for a relay and (ii) reversible redox behaviour and long excited state lifetime for a photo-

sensitizer. Co(III) complexes, which show redox reversibility (e.g. those having cage-type ligands [8]) have been recently used as relays in photosensitization cycles [9–11]. Worth noting is $Co(EDTA)^-$ which acts as an electron acceptor in photoelectrochemical and photobiological systems [12]. More recently, ion-pairs formed by Co(III) complexes have been shown to be useful photosensitizers in electron transfer reactions leading to I_2 [13] and H_2 [14] formation.

As part of our on-going studies in the field of ion-pair photochemistry, we report herein some novel results on the photochemical behaviour of the unusual ion-pair formed between $Co(EDTA)^-$ and I^-.

Experimental

The $K[Co(EDTA)]$ salt was prepared as described in the literature [15]. The absorption spectrum was in full agreement with that reported by Jørgensen [16], and Shimi and Higginson [17].

The experiments were carried out at natural pH in aqueous solutions. These were air-equilibrated, or nitrogen- or oxygen-saturated by continuous bubbling.

Absorption spectra were recorded on a Perkin-Elmer λ 5 or a Kontron Uvikon 860 spectrophotometers.

Light excitation at 313 nm was carried out by means of a medium pressure Hg lamp [18]. The incident light intensity was measured by ferri-oxalate actinometry [19]. In some experiments cut-off filters for excitation at $\lambda > 400$ nm were used.

The I_3^- concentration was measured spectrophotometrically at 350 nm, by means of an appropriate calibration plot.

In the experiments performed to determine the reaction products, 100 ml of a solution containing $Co(EDTA)^-$ (10^{-2} M) and I^- (0.5 M) was irradiated until no appreciable spectral changes were recorded. The irradiated solution was subsequently treated with CCl_4. I_2 was found in the red organic phase.

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The aqueous phase was then passed through a column packed with an anionic exchange resin (Dowex 1-x8, 20–50 mesh, BDH) to separate the product of irradiation from the unreacted $Co(EDTA)^-$. The irradiation product was identified as $Co(EDTA)^{2-}$ by comparing its spectrum with that of an authentic sample. Moreover, oxidation of this product with H_2O_2 gave the initial $Co(EDTA)^-$.

Results

The spectrum of $Co(EDTA)^-$ (Fig. 1) reveals two weak bands centered at ~378 and ~536 nm and more intense bands below 300 nm. The two weak bands are attributed to MC (metal-centered) transitions and the bands growing at 300 nm arise from ligand-to-metal charge transfer (LMCT) transitions [20]. As expected the absorption spectrum of $Co(EDTA)^-$ is not sensitive to pH variations in the range 2–10*.

Irradiation of solutions of $Co(EDTA)^-$ (1×10^{-3} M) with light of $\lambda > 313$ nm did not lead to appreciable spectral variations, at least for irradiation periods comparable with those of the following experiments.

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*The invariance of the spectrum with pH is a proof that we are dealing with $Co(EDTA)^-$ and not with $Co(EDTA)$-H_2O^- which has a very similar spectrum [17].
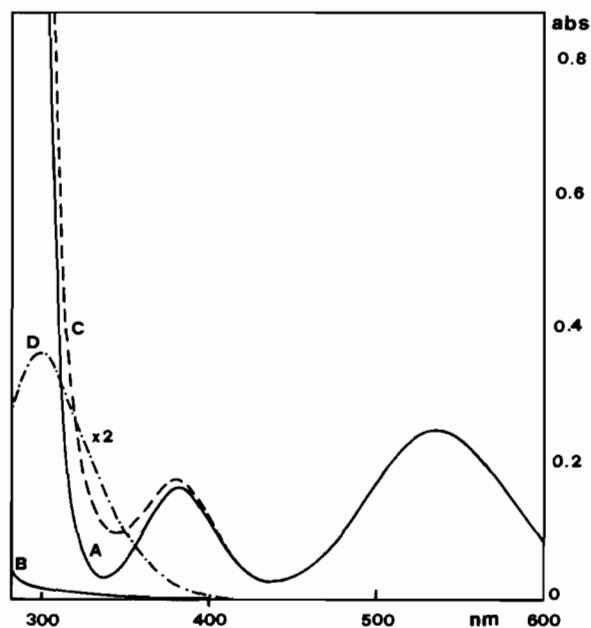

Fig. 1. Spectra of aqueous solutions of K[Co(EDTA)] in absence and in presence of KI. (A), $[Co(EDTA)^-] = 1 \times 10^{-3}$; (B) $[I^-] = 0.5$; (C) $[Co(EDTA)^-] = 1 \times 10^{-3}$ and $[I^-] = 0.5$; (D) absorbance difference between spectra C minus A. Optical path = 1 cm.

The addition of KI to solutions of $Co(EDTA)^-$ causes spectral changes in the 300 nm region. A differential spectrum showed the appearance of a new

TABLE I. Photochemistry of the $Co(EDTA)^-$–I^- System in Aqueous Solution[a]

No.	$[I^-]$	$[Co(EDTA)^-]$ $\times 10^{-3}$	A_{313}[b]	A_{350}[c]	$\Phi^l_{I_3^-}$[d]	$\Phi^u_{I_3^-}$[e]	$\Phi_{Co(II)}$[f]
1	0	5.0	1.248				
2	0.5	5.0	2.049	0.170	0.15	0.38	
3	0.1	5.0	1.394	0.038	0.03	0.33	
4	0.02	5.0	1.262	0.048[g]	4×10^{-3}	0.29	
5	0.5	2.0	0.841	0.157	0.16	0.40	
6	0.1	2.0	0.579	0.035	0.04	0.30	
7	0.5	1.0	0.411	0.111	0.16	0.40	
8	0.1	1.0	0.313	0.030	0.05	0.25	
9	0.02	1.0	0.265	0.038[g]	7×10^{-3}	0.21	
10	0.5	1.7	0.637	0.132[h]	0.15	0.39	
11	0.5	1.7	0.635	0.150[i]	0.17	0.44	
12	0.5	1.3	0.495	1.38[l]	0.08[m]		0.16[m]
13	0.5	1.3	0.497	2.76[n]	0.04[m]		0.08[m]

[a]Irradiation wavelength 313 nm; room temperature; air-equilibrated solutions; 1 minute of irradiation, unless otherwise noted; estimated errors on the quantum yields ±10%.   [b]Initial absorbance at the irradiation wavelength.   [c]Absorbance increase at 350 nm upon irradiation.   [d]Quantum yield of I_3^- production calculated from the absorbance increase at 350 nm and on the basis of all the photons absorbed by the solution (see text); it is the lower limit for the real quantum yield.   [e]Quantum yield of I_3^- production calculated from the absorbance increase at 350 nm and on the basis of the photons absorbed by the solution as a consequence of the absorbance increase at 313 nm upon mixing of $Co(EDTA)^-$ with I^- (see text); it is the upper limit for the real quantum yield.   [f]Quantum yield of Co(II) production calculated from the absorbance decrease at 536 nm, using 300^{16} and 5^{16} for the ϵ values of $Co(EDTA)^-$ and $Co(EDTA)^{2-}$ respectively.   [g]10 min of irradiation.   [h]N$_2$ saturated solution.   [i]O$_2$ saturated solution.   [l]13 min of irradiation.   [m]Quantum yields calculated on the basis of all incident photons.   [n]50 min of irradiation.

band centered at ~290–300 nm (Fig. 1). The intensity of this band depends on the concentration of the reactants, increasing with increasing I^- and/or Co-(EDTA)$^-$ concentrations (see Table I).

Irradiation ($\lambda > 410$ nm) of solutions containing Co(EDTA)$^-$ (1×10^{-3} to 5×10^{-3} M) and I^- (0.02 to 0.5 M) showed no spectral changes, but irradiation at $\lambda = 313$ nm causes noticeable spectral variations, with a clear isosbestic point (~486 nm) maintained for long irradiation periods (Fig. 2). Appropriate separation procedures, applied to irradiated solutions for the purposes of identifying the products, showed the presence of I_3^- and Co(EDTA)$^{2-}$ in agreement with the observed spectral variations.
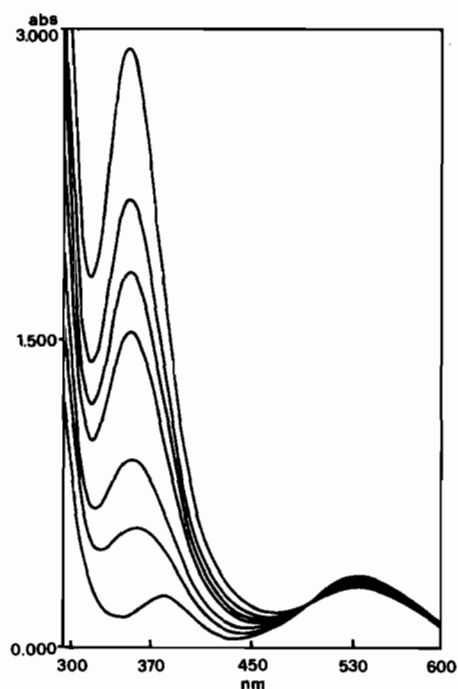

Fig. 2. Change in the absorption spectrum of an aqueous solution containing Co(EDTA)$^-$ (1.35×10^{-3} M) and I^- (0.5 M) with irradiation time.

The quantum yields of I_3^- production ($\Phi_{I_3}-$) reported in Table I were calculated from the growth of the spectral feature at 350 nm. The lower limit of $\phi_{I_3}-$ was obtained on the basis of all photons absorbed by the solutions; the upper limit was calculated taking into account only the photons absorbed by the solution as a consequence of the increase of absorbance of Co(EDTA)$^-$ solutions upon mixing with I^-. It should also be noted that the reported quantum yields are initial quantum yields calculated for 1 min of irradiation, since the production of I_3^- decreased with increasing the irradiation time, probably because of the inner filter effect of the I_3^- formed during the irradiation. Moreover these quantum yields depend on the concentration of the reactants used (see Table I).

For long irradiation experiments where the decrease of the spectrum at 536 nm was large enough to evaluate the disappearance of Co(EDTA)$^-$ with sufficient precision, we also calculated the quantum yield of Co(II) formation ($\Phi_{Co(II)}$), finding a 1:2 ratio between $\Phi_{I_3}-$ and $\Phi_{Co(II)}$ (Table I, entries 12 and 13).

The role of O_2 on the photoreaction was ascertained from experiments carried out on O_2 and N_2 saturated solutions. Within experimental error, the quantum yields are identical to those obtained in air-equilibrated solutions (see Table I, entries 10 and 11).

Discussion

Co(III) complexes with a 3+ charge in the presence of a variety of anions are known to give new bands in the UV region [13, 14]. These new bands are attributed to charge transfer transitions within the ion-pair formed between the Co(III) complex and X^-. Light excitation into these ion-pair-charge-transfer (IPCT) bands causes the promotion of an electron from the X^- species in the outer sphere to the Co(III) center, effectively giving the reduced Co(II). Since Co(II) complexes are usually labile, the excitation in the IPCT bands leads to redox decomposition reactions. When the ligand is a cryptand such as the sepulcrate (sep) species, the Co(II) complex formed in the primary photochemical step is quite inert (at least in not too acidic solutions); irradiation in the IPCT bands of these complexes does not give redox decomposition reactions. Moreover when the oxidized anion does not undergo decomposition, such complexes usually yield back electron transfer reactions, thus preventing any chemical change in deoxygenated solutions.

In the present instance, the new band observed in the near UV region of the spectrum of Co(EDTA)$^-$ in the presence of I can only be related to a charge transfer transition arising from a transfer of an electron from I^- to Co(III) in a new species formed between Co(EDTA)$^-$ and I^-. This new species can be either a new coordination compound in which the I^- anion belongs to the inner sphere of the Co(III) complex, or an ion-pair in which the I anion belongs to the outer coordination sphere of the Co(III) complex. The latter hypothesis, which may seem strange at first, is supported by the results of Margerum *et al.* [21]; these authors did not observe formation of Co–I bonds, in the oxidation of Co(EDTA)$^{2-}$ by I_2, contrary to their observations in the Br_2 oxidation of the same complex. Margerum's observations were made under conditions similar to those reported here. Examples of unusual ion-pairs between like-charged ions have been reported [22]. Both cations like N(Et)$_4^+$ and anions like

Γ are known to dimerize easily, with association constants increasing with increasing encounter radius. Evidence for close contact like that required in ion-pairs has recently been reported [23] even for coordination compounds of the same charge.

For these reasons, hereafter the new species formed between $Co(EDTA)^-$ and Γ will be considered as an ion-pair (eqn. (1))
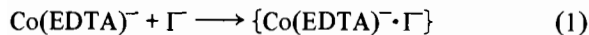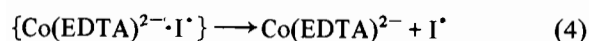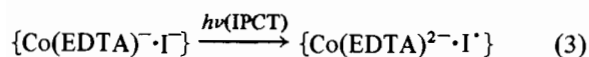
$$Co(EDTA)^- + \Gamma \longrightarrow \{Co(EDTA)^- \cdot \Gamma\} \qquad (1)$$

The results reported here show (i) that irradiation of solutions containing $Co(EDTA)^-$ and Γ leads to the formation of I_3^- and $Co(EDTA)^{2-}$ and (ii) that there is a strict correlation between the behaviour of the ion-pair-charge-transfer band and the behaviour of the I_3^- production, in agreement with the following equation:

$$2\{Co(EDTA)^- \cdot \Gamma\} \xrightarrow{h\nu;\Gamma} 2Co(EDTA)^{2-} + I_3^- \qquad (2)$$
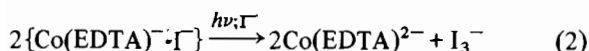
The increase in the 'initial' quantum yields of I_3^- formation (Table I) on increasing $[\Gamma]$ and/or $[Co(EDTA)^-]$ is accounted for by the corresponding increase in the concentration of the ion-pair and consequently on the corresponding fraction of absorbed light.

The details of reaction (2) are summarized in the following kinetic scheme, similar to that previously proposed for analogous systems [13, 14]:

$$\{Co(EDTA)^- \cdot \Gamma\} \xrightarrow{h\nu(IPCT)} \{Co(EDTA)^{2-} \cdot I^\cdot\} \qquad (3)$$

$$\{Co(EDTA)^{2-} \cdot I^\cdot\} \longrightarrow Co(EDTA)^{2-} + I^\cdot \qquad (4)$$

$$\{Co(EDTA)^{2-} \cdot I^\cdot\} \longrightarrow \{Co(EDTA)^- \cdot \Gamma\} \qquad (5)$$

$$I^\cdot + \Gamma \longrightarrow I_2^- \qquad (6)$$

$$I_2^- + I_2^- \longrightarrow I_3^- + \Gamma \qquad (7)$$

$$Co(EDTA)^{2-} + I_2^- \longrightarrow \{Co(EDTA)^- \cdot \Gamma\} + \Gamma \qquad (8)$$

The following considerations on this kinetic scheme are worth noting:

(i) Reaction (3) is the outer-sphere one-electron transfer process responsible for the ion-pair-charge-transfer band.

(ii) Reaction (4) is the cage escape of the radical pair produced in the preceding step, and is in competition with the subsequent reaction (5) (cage recombination).

(iii) Reaction $Co(EDTA)^{2-} + I^\cdot \to \{Co(EDTA)^{2-} \cdot I^\cdot\}$, which is the reverse of reaction (4), was not considered since it has no chance to compete with reaction (6) owing to the higher concentration of Γ with respect to $Co(EDTA)^{2-}$.

(iv) The $I^\cdot$ radical is known to react rapidly with Γ (eqn. (6); $k = 7.6 \times 10^9$ M^{-1} s^{-1} [24]) to give I_2^-. We have no direct evidence for the I_2^- formation, but note that this intermediate has been postulated in many reactions of Γ with one-electron oxidants [25, 26] and, moreover, is in keeping with the flash photolysis results of $Co(EDTA)^-$ in the presence of Br^- ($>10^{-3}$ M), in which the Br_2^- transient was observed [20]. Reactions (4) and (6) may also occur in a single step $\{Co(EDTA)^{2-} \Gamma\} + \Gamma \to Co(EDTA)_2^- + I_2^-$ (k_{4-6}).

(v) It is also known that the I_2^- radical undergoes a disproportionation reaction very efficiently (eqn. (7); $k = 7.7 \times 10^9$ M^{-1} s^{-1} [27]). The reaction $2I_2^- \to I_2 + 2\Gamma$ followed by the equilibrium $I_2 + \Gamma \to I_3^-$ have been omitted because of the almost complete displacement of the equilibrium ($K = 768$ M^{-1} [21]) towards the I_3^- species.

(vi) Reaction (8) is the back electron transfer reaction which leads to the initial situation. This reaction, which is quite exoergic, competes with with reaction (7). For analogous reactions between I_2^- and $Co(sep)^{2+}$ [28] or $Ru(NH_3)_5py^{2+}$ [29], values of 5.0×10^9 M^{-1} s^{-1} and 2.3×10^9 M^{-1} s^{-1} respectively, have been reported recently*. This means that the rate constant of reaction (8) is probably similar to the rate constant of reaction (7), leading to the conclusion that at the beginning, the I_2^- decay is equally distributed on the two reaction pathways. As the photoreaction proceeds reaction (8) may prevail over reaction (7) owing to the increase of $Co(EDTA)^{2-}$ concentration. This may again account for the non linear behaviour of the I_3^- production *versus* irradiation time.

(vii) The following reaction was not considered in the scheme:

$$2Co(EDTA)^{2-} + I_3^- \to 2\{Co(EDTA)^- \cdot \Gamma\} + \Gamma \qquad (9)$$

it reverts the products back to the reactants. In our case this reaction has little importance; Margerum *et al.* [21] reported a value of 3.1×10^{-5} M^{-1} s^{-1} for this reaction rate constant. Moreover, this reaction does not occur as written; it occurs via the following one-electron steps:

$$Co(EDTA)^{2-} + I_3^- \longrightarrow \{Co(EDTA)^- \cdot \Gamma\} + I_2^- \qquad (10)$$

$$Co(EDTA)^{2-} + I_2^- \longrightarrow \{Co(EDTA)^- \cdot \Gamma\} + \Gamma \qquad (11)$$

The reaction scheme above implies that the quantum yield of I_3^- production depends on the competition between reactions (4) and (5) and reactions (7) and (8) (neglecting reaction (9)). Thus,

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*Reaction between I_2^- and $Ru(NH_3)_5py^{2+}$ has a ΔG° value of -0.76 eV, a value close to that of reaction (8) (-0.69 eV).

$$\Phi_{I_3^-} = \tfrac{1}{2} \times k_7/(k_7 + k_8) \times k_4/(k_4 + k_5)$$

Perusal of the data in Table I shows that the reported lower and upper limits of the quantum yield of I_3^- production define such a narrow range (0.16 to 0.25) as to consider the value of 0.2 ± 0.05 as representing a true value of the 'initial' quantum yield. To the extent that approximately half of the I_2^- species produced disproportionate to I_3^- (*i.e.* $k_7/(k_7 + k_8) \sim 0.5$), the $k_4/(k_4 + k_5)$ ratio is about 1. This indicates that cage recombination is negligible with respect to cage escape, and that the quantum efficiency of the primary photochemical step is almost unitary.

A photochemical process which leads to the formation of oxidant species may, in principle, be considered as a useful process for solar energy conversion [30]. However in the specific case where excitation of the $\{Co(EDTA)^-\cdot I^-\}$ ion-pair leads to the formation of $Co(EDTA)^{2-}$ and the oxidant species I_3^-, the process is not as useful as expected owing to the low energy content of the two products combined. In fact, since the standard redox potentials of the species involved are $+0.37$ V for the $Co(EDTA)^-/Co(EDTA)^{2-}$ couple [31] and $+0.45$ V for the $\tfrac{1}{2}I_3^- \to \tfrac{1}{2}I_2^- + \tfrac{1}{2}I^-$ process*, the energy stored in the $Co(EDTA)^{2-}$ and I_3^- products is only 0.08 eV.

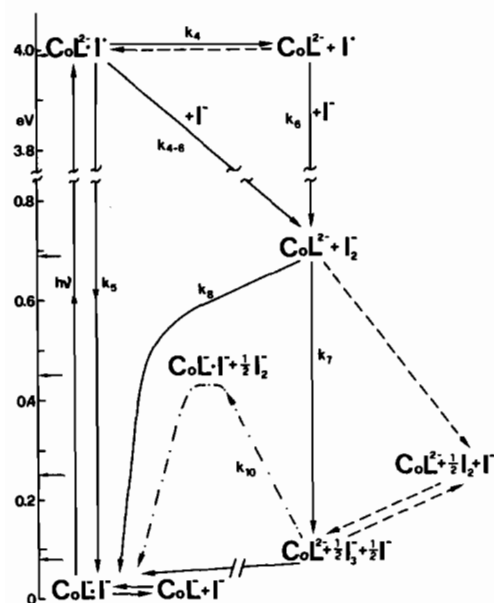A general view of the energetics of the overall reaction sequence is reported schematically in Fig. 3.

Fig. 3. Schematic representation of the energetics of the reactions that follows the Co(EDTA)$^-$–I$^-$ system. L is EDTA.

*Obtained from the potential of the $I_2^-/2I^-$ couple [32] and the ΔG° value (-0.17 eV) of the equilibrium $I_2 + I^- \to I_3^-$ [25].

Clearly, this system is meaningless in solar energy conversion since (i) it requires ultraviolet radiations to be operative and (ii) it dissipates 3.2 eV, nearly all the energy of the absorbed photons ($\sim$4 eV at 313 nm). It is also clear that the products may accumulate despite the negative ΔG° value (-0.16 eV) of reaction (9). The occurrence of this reaction is prevented by the endoergonicity of its first reaction step (reaction (10), $\Delta G^\circ = 0.37$ eV), which leads to the formation of the high energy I_2^- species.

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