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Redox Photochemistry of Diethyldithiophosphatecobalt(III)

L. L. COSTANZO, I. FRAGALA', S. GIUFFRIDA and G. CONDORELLI

Istituto di Chimica Generale dell'Università di Catania, 95125 Catania, Italy

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The photochemical behavior of Co(dtp)₃ [dtp⁻ = (C₂H₅O)₂PS₂⁻] in CH₂Cl₂ solution was investigated as a function of irradiating wavelength along all the absorption spectrum. The dependence on the triplet sensitizer energy was also investigated. The reaction Co(dtp)₃ → Co(dtp)₂ occurred by irradiating in the charge transfer or intramolecular ligand spectral regions, whereas the complex was essentially inert by irradiating in the ligand field region. The quantum yields monotonically decreased by increasing the irradiation wavelength. The reaction was quenched by dicyclopentadienyliron. Benzophenone and 2'-acetonaphthone sensitized the redox reaction through an energy transfer mechanism; with the first sensitizer a diffusion controlled process occurred and therefore the energy gap between the donor–acceptor triplet states is greater than 2.9 Kcal; with the second a probable reversible energy transfer was operating, suggesting that the 2'-acetonaphthone and complex triplet energies lie close to each other. With benzil as sensitizer the photoreactive state was not populated enough for the redox process to be observed. The overall results indicate that the photoreactive state is a charge transfer triplet state, whose population depends either on the intersystem crossing being faster than thermal equilibration from excited states or on the energy transfer from sensitizers having a triplet energy ⩾59 Kcal.

Introduction

The photochemistry of Co^{III} complexes in aqueous solution has been widely studied [1]. Photoredox reactions have been shown to occur when charge transfer bands are irradiated, although reduction may also occur when ligand field absorptions are irradiated. Unfortunately, complexes of the reduced metal are kinetically unstable and rapidly exchange ligands in solution, consequently the characterization of the primary photoproduct by conventional means is very difficult. Despite these inconveniences, very little is known about the photochemistry in aprotic solvents, the role of which was expected to be less significant than that of water or hydroxylic solvents and therefore secondary reactions as thermal solvatation may be absent. Besides, few reports [2, 3] have been concerned with the investigation of quantum yield variation as a function of irradiation wavelength in all absorption bands.

TABLE I. Absorption Spectra of Co^{III} and Co^{II} Diethyldithiophosphates in CH_2Cl_2 Solution.

Compounds	Assignment[a]	λ (nm)	ε
$Co(dtp)_3$	d–d ($^1A_{1g} \rightarrow {}^1T_{1g}$)	738	477
	d–d ($^1A_{1g} \rightarrow {}^1T_{2g}$)	540	440
	CTTM ($\pi_1 \rightarrow e_g$)	406	6,950
	CTTM ($\pi_2 \rightarrow e_g$)	334	18,450
	Intra Ligand	232	9,950
$Co(dtp)_2$	d–d ($^4A_2 \rightarrow {}^4T_1$)	662	275
		588	105
	CTTL	382	2,980
	CTTL	314	5,200
		275	3,950

[a] Ref. 4, 5.

In the present paper, which is part of our continuing research on photoredox reactions of metal complexes, we investigated the photochemical of diethyldithiophosphatecobalt(III), $Co(dtp)_3$, in CH_2Cl_2 solution with regard to the photochemical mechanism, the excited state origin, the wavelength dependence of the quantum yields and the effect of potential sensitizers and quenchers. The chelate $Co(dtp)_3$ was selected for several reasons: the ligand $(C_2H_5O)_2PS_2^-$ is coordinated by sulfur atoms, unlike most complexes studied in which oxygen or nitrogen are donor atoms; both $Co(dtp)_2$ and $Co(dtp)_3$ were well characterized and are chemically stable to thermal reaction in N_2 atmosphere [4, 5]; the charge transfer bands and ligand-field bands are well separated (Table I), so that it is easy to obtain excited states of a different nature by exciting with radiations of suitable wavelength.

Experimental

Materials

$Co(dtp)_2$ was prepared by gradually adding the NH_4dtp salt to concentrated, freshly boiled aqueous

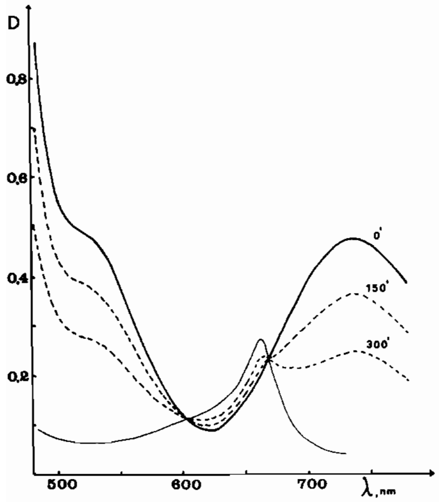


Figure 1. Spectral changes of the CH_2Cl_2 solution of Co(dtp)$_3$ 10^{-3} *M* with irradiation time at 333 nm. (——) Absorption spectrum of Co(dtp)$_2$.

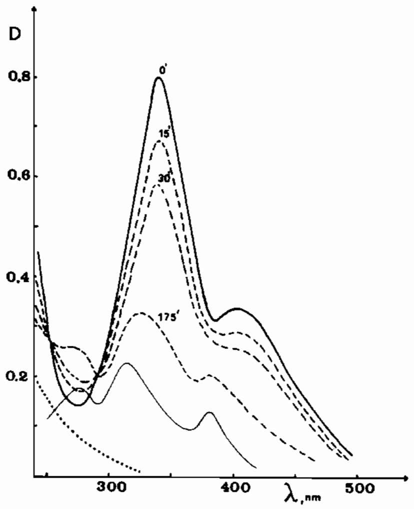


Figure 2. Spectral changes of the CH_2Cl_2 solution of Co(dtp)$_3$ 0.55 × 10^{-4} *M* with irradiation time at 333 nm. Absorption spectra of Co(dtp)$_2$ (——) and (dtp)$_2$ (······).

solution of $CoCl_2 \cdot 6H_2O$, extracting the complex with freshly boiled CH_2Cl_2 and rapidly removing the solvent under vacuum [5].

Co(dtp)$_3$ was prepared by oxidation of the Co(dtp)$_2$ with H_2O_2 [4]. Bis(diethossiphosphinothioyl)-disulfide $[(C_2H_5O)_2PS_2]_2$, abbreviated as (dtp)$_2$, was prepared by adding iodine to concentrated aqueous solution of NH$_4$dtp and by extracting the obtained oleum with CH_2Cl_2 [6].

Benzophenone,2'-acetonaphthone, benzil and dicyclopentadienyliron (Bacher) were suitable for sensitizer "use". Dichloromethylene was of spectroscopic grade. All other common chemicals were reagent grade.

Apparatus

The irradiation equipment was described previously [7]. The radiation of 254 nm was obtained from a low pressure Hg vapor lamp (Hanau NN 15/44) by means of a suitable filter combination. Radiations of 313, 333, 365, 405 and 436 nm were isolated from a Hg vapor lamp (Hanau Q 400) by means of interference filter (Schott Gen.). The radiations of 491 and 540 nm were obtained from tungsten incandescent lamp by means of interference filter (Zeiss Jena). The intensity of the incident light measured by a ferric oxalate actinometer was of the order of 10^{-7} Nh ν/min.

Spectrophotometric measurements were made with an Optical CF4NI spectrophotometer with the cell compartment thermostated at 25 °C. Luminescence spectra were recorded with a MPF-3L Perkin–Elmer spectrophotofluorometer.

Procedures

Sample or sample–sensitizer mixture solutions, of suitable concentration, were introduced into standard spectrophotometric cells, sealed after deoxygenation with pure nitrogen and irradiated at the desired wavelength. During irradiation, the solutions were stirred with a small magnetic stirrer. Kinetics of the reaction were followed spectrophotometrically in the suitable absorption region. For measurements of the sensitizer emission, the solutions were purged with nitrogen until there was no further increase in the phosphorescence intensity.

Results

Preliminary experiments indicated that on direct irradiation the Co(dtp)$_3$ in CH_2Cl_2 solution underwent photoreaction detectable by recording spectra at various intervals, as shown in Fig. 1 for 10^{-3} *M* solution. The isosbestic points and the successive spectra matched those of a mixture of Co(dtp)$_3$ and Co(dtp)$_2$ with a combined concentration equal to that of the starting chelate. By dilution of the irradiated solution and by recording spectra in the ultraviolet region, the presence of a third species absorbing below 300 nm was easily observable. When solutions of concentration about 10^{-5} *M* were irradiated and the photoreaction was followed in the UV region the spectral variations, above 300 nm, could be fitted assuming reduction of Co(dtp)$_3$ to Co(dtp)$_2$ (Fig. 2). The presence of two isosbestic points below 300 nm not consistent with the spectra of complexes indicated that a third species was

TABLE II. Quantum Yields for the $Co(dtp)_3 \rightarrow Co(dtp)_2$ Photoreduction.

λ_{exc} (nm)	$\phi_{Co^{II}}$
254 (IL)	0.053 ± 0.001
313 (CTTM)	0.053 ± 0.001
333 (CTTM)	0.048 ± 0.001
365 (CTTM)	0.039 ± 0.001
405 (CTTM)	0.022 ± 0.002
436 (CTTM)	0.017 ± 0.002
491 (CTTM + d–d)	0.004
546 (d–d)	–

produced in stoichiometric ratio with two chelates of cobalt; it was identified as $(dtp)_2$ by comparing its UV spectrum and that of the compound independently prepared [6].

Thus the overall reaction can be written as

$$2\ Co(dtp)_3 \xrightarrow{h\nu} 2\ Co(dtp)_2 + (dtp)_2$$

The photoreduction cannot be carried out to completion because of side reactions depending on the length of work time. Solutions photolysed for various lengths of time and kept in the dark showed no change in absorbance after 12 hours. $Co(dtp)_3$ was also photolysed in other solvents; in cyclohexane and acetonitrile the results were similar to those described. This suggests that the photoreduction is essentially intramolecular and that the primary photoprocess does not involve reactions with solvent molecules. The rate of photoreduction was studied as a function of the initial concentration of the chelate from 10^{-3} to 3×10^{-5} *M*. Solutions of absorbance greater than 2 at the irradiating wavelength were zero order in chelate concentration. The initial quantum yield was calculated by the equation

$$-\frac{\Delta[Co(dtp)_3]}{\Delta t} = \Phi I$$

Solutions of low concentration with absorbance less than 1 obey a first order rate law

$$-\frac{d[Co(dtp)_3]}{dt} = \Phi\frac{I}{V}\ \epsilon[Co(dtp)_3]\ \frac{1-10^{-D}}{D}$$

where D is total optical density, Φ the quantum yield for the $Co(dtp)_3$ decrease and the other symbols have their usual meaning. By rearrangement

$$-\frac{D}{1-10^{-D}}\ \frac{d[Co(dtp)_3]}{[Co(dtp)_3]} = \Phi\frac{I}{V}\epsilon dt$$

By plots of the term on the left $F([Co(dtp)_3])$ *vs.* time [8] good straight lines were obtained, and from slopes the quantum yields were calculated. The quantum yields of photoreaction, determined as a function of wavelength through all the absorption bands, are independent of the initial concentration and strongly dependent on the irradiation wavelength (Table II).

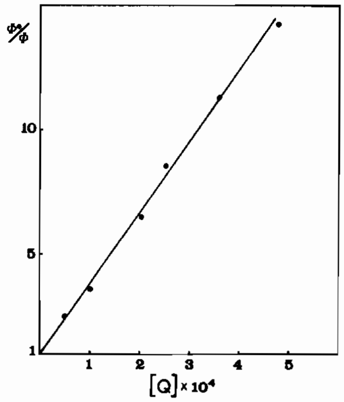


Figure 3. Stern–Volmer plot for the quenching of the $Co(dtp)_3$ 0.48 × 10^{-3} *M* photoreduction by dicyclopentadienyliron, Q.

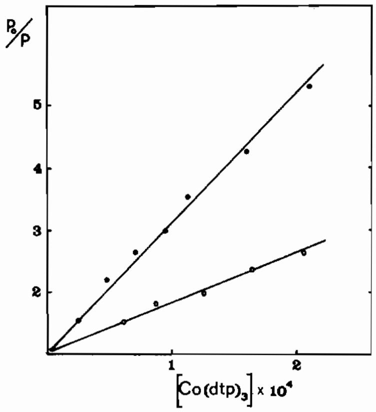


Figure 4. Stern–Volmer plots of the quenching of benzophenone (●) and benzil (○) phosphorescence by $Co(dtp)_3$.

Some experiments demonstrated that the $Co(dtp)_2$ solutions are insensible to irradiation in the charge transfer bands. Attempts to quench the redox photoreaction have been carried out with dicyclopentadienyliron, Q, ($E_T < 42$ Kcal) using light of 333 nm absorbed only by $Co(dtp)_3$ (0.48 × 10^{-3} *M*). The quantum yields decrease with quencher concentration and the plot of Φ^0/Φ *vs.* [Q] gives a good straight line (Fig. 3). By the slope the value of the Stern–Volmer constant $k_q\tau = 28{,}000$ was obtained (k_q bimolecular quenching constant and τ lifetime of the quenchable excited state). Since the quenching rate can be equal or lower than the diffusion controlled limit (k_d in $CH_2Cl_2 = 1.5 \times 10^{10}\ M^{-1}\ sec^{-1}$), a lower value for τ of the order of 10^{-6} sec was calculated.

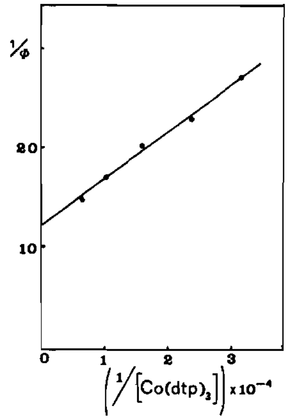


Figure 5. Photoreduction of $Co(dtp)_3$ sensitized by benzophenone.

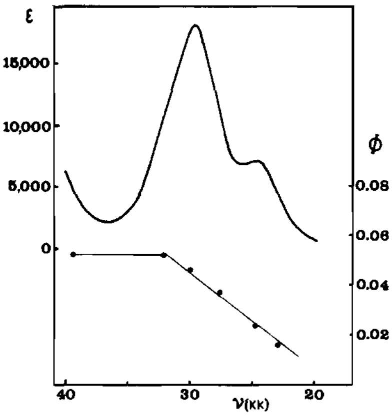


Figure 6. Absorption spectrum (left scale) and photoredox quantum yields (right scale) of $Co(dtp)_3$.

Experiments were performed in order to find out whether benzophenone (E_T = 69 Kcal), 2′-acetonaphthone (E_T = 59 Kcal) and benzil (E_T = 55 Kcal) could sensitize the photoreaction. All data concerning the emission were appropriately corrected for the absorption by the complex, when it was necessary.

In the $Co(dtp)_3$-benzophenone system, the emission of sensitizer (0,25 *M*) under the same conditions as those of the photochemical experiments was strongly quenched by various complex concentrations ($0.2–2 \times 10^{-4}$ *M*). The data plotted on a Stern–Volmer diagram (Fig. 4) yielded a bimolecular quenching constant (k_q) of 1.7×10^{10} M^{-1} sec^{-1} (lifetime for benzophenone $\tau = 1.9 \times 10^{-6}$ sec) [9]. The irradiation at 333 nm caused spectral variations which could be exactly fitted, assuming a conversion $Co(dtp)_3 \rightarrow Co(dtp)_2$.

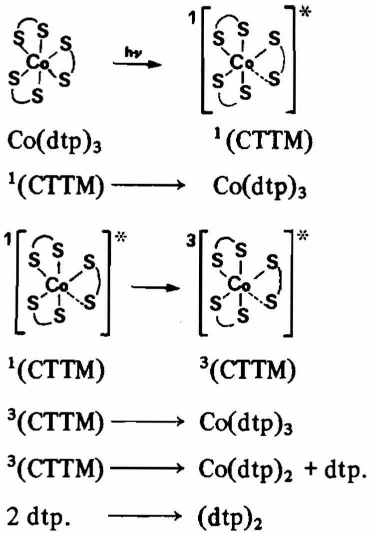
In the experimental conditions, the light absorption by the complex was completely negligible. The apparent quantum yields of the initial reaction increased with the $Co(dtp)_3$ concentrations. From the intercept and from the intercept/slope ratio of the Stern–Volmer sensitization plot (Fig. 5) the limit quantum yield and the bimolecular constant for the sensitization k_s are respectively calculated: ϕ_{lim} = 0.08, $k_s = 1.7 \times 10^{10}$ M^{-1} sec^{-1}. It is gratifying to note that the values of k_q and k_s are the same and are in satisfactory agreement with the quenching constant controlled by diffusion. In the system $Co(dtp)_3$–2′-acetonaphthone, the irradiation at 333 nm with the light almost completely absorbed by the sensitizer (0.05 *M*) led to the formation of $Co(dtp)_2$. The apparent quantum yields increased with $Co(dtp)_3$ concentration ($0.45–1.4 \times 10^{-4}$ *M*). Additional experiments carried out with a constant substrate concentration (10^{-4} *M*) and a variable sensitizer one (in the range 0.01–0.5 *M*) showed two significant features: (i) the apparent quantum yield of the sensitized photoreduction decreased as the 2′-acetonaphthone concentration increased and (ii) in identical conditions the quantum yields of the direct reaction at 436 nm, at which wavelength the sensitizer does not absorb, decreased in the same way as (i).

In the system $Co(dtp)_3$–benzil, the sensitizer (0.01 *M*) phosphorescence was quenched by $Co(dtp)_3$ ($0.5–1.7 \times 10^{-4}$ *M*) (Fig. 4). Assuming for the lifetime of benzil a value of 6×10^{-5} sec [10] the bimolecular quenching constant can be calculated by the slope of the Stern–Volmer plot, $k_q \approx 0.5 \times 10^8$ M^{-1} sec^{-1}. This value is about two orders of magnitude smaller than the theoretical diffusion controlled value. The irradiation at 333 nm with light absorbed in optimal conditions by substrate and by sensitizer, respectively 10 and 90%, demonstrated that only direct reaction is observable, therefore no sensitization occurred.

Discussion

The photochemical behavior of $Co(dtp)_3$ is strongly dependent on the spectral region irradiated (Fig. 6). The redox reaction occurs from charge transfer states; however it is interesting to note that, since the charge transfer transitions occur at energies lower than ligand excited states, reduction occurs also from these latter by means of rapid internal conversion or intersystem crossing to photoreactive charge transfer state. Assuming [11] that this state is the charge transfer excited state of lowest energy, the relative transition involves excitation of an electron from a π orbital localized primarily on the ligand to the antibonding orbital, primarily metal in character. Thus the predominant primary photoreduction is the oxidation of the ligand whose bond to reduced metal will consequently be greatly weakened. The instantaneous CTTM species can undergo primary recombination or can release the photolabilized ligand to give a tetracoordinate metal complex of Co^{II}

which in turn may undergo stereochemical rearrangement to a tetrahedral one [4]. It is not important for this argument whether the excited state under consideration be triplet or singlet, but the experiments carried out using dicyclopentadienyliron as quencher triplet indicated clearly that the photoreactive state is a triplet excited state of a long enough lifetime. The photochemical reaction pathway can be adequately described by the following scheme:



$\mathrm{Co(dtp)_3} \qquad {}^1\mathrm{(CTTM)}$

$${}^1\mathrm{(CTTM)} \longrightarrow \mathrm{Co(dtp)_3}$$

${}^1\mathrm{(CTTM)} \qquad {}^3\mathrm{(CTTM)}$

$${}^3\mathrm{(CTTM)} \longrightarrow \mathrm{Co(dtp)_3}$$

$${}^3\mathrm{(CTTM)} \longrightarrow \mathrm{Co(dtp)_2} + \mathrm{dtp.}$$

$$2\,\mathrm{dtp.} \longrightarrow \mathrm{(dtp)_2}$$

One interesting and uncommon feature of the results of direct irradiation is the definite decrease of the quantum yields also within each of the two CTTM bands, even though these do not extensively overlap. No appreciable discontinuity is observed to occur in the quantum yield variation when the irradiation wavelength changes from one to another of the two CTTM bands. There is a definite energy threshold E = 59 Kcal below which $\Phi_{Co}{}^{II}$ is very small; this corresponds to the energy threshold for absorption in the spectroscopic CTTM bands. Because the lifetime of the photoreactive state rules out the hypothesis of a dissociative state, these results point to the interpretation that in the CTTM singlet excited states, unreactive by themselves, physical events leading to chemical reaction are fast enough to prevent thermal equilibration. Therefore the trend of the quantum yield variation represents that of the intersystem crossing efficiency, η^i_{IS}. Furthermore it should be noted that $\Phi_{Co}{}^{II}$ reaches a limiting value at a higher excitation energy; this implies rapid vibrational relaxation within the spectroscopic excited state, followed by the electronic relaxation characteristic of the equilibrated excited state.

By considering the simplest pertinent energy-level diagram (Fig. 7) the overall quantum yield for Co(dtp)$_2$ formation by means of excitation at vibronic level ith, would be given by

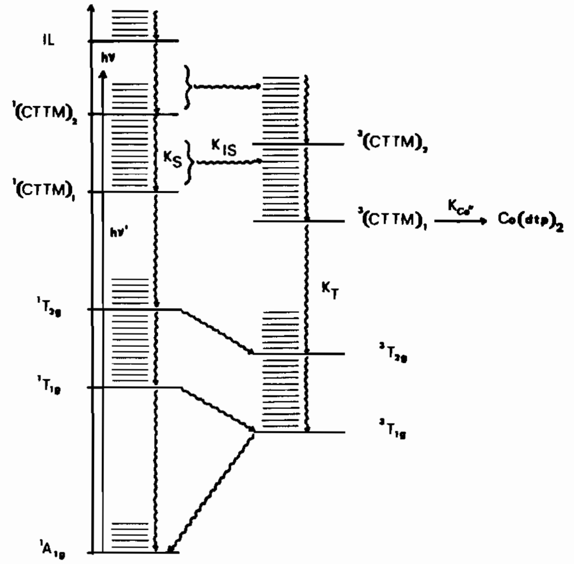


Figure 7. Hypothetical energy level scheme for the Co(dtp)$_3$.

$$\Phi^i_{Co^{II}} = \frac{K_{Co^{II}}}{(K_T + K_{Co^{II}})}\,\frac{K^i_{IS}}{(K^i_S + K^i_{IS})}$$

where K^i_{IS} and K^i_S are the rate constants respectively for intersystem crossing and for the other decay processes (internal conversion and associated loss of vibrational energy) from the vibronic level ith and

$$\frac{K^i_{IS}}{(K^i_S + K^i_{IS})} = \eta^i_{IS}.$$

Additional informations on the photoreactive state and its approximate energy come from sensitization experiments using sensitizers of various triplet energies. Although most sensitized reactions of Co^{III} complexes involve electron transfer [12], in this case two features – the stoichiometric formation of the intramolecular oxidation compound (dtp)$_2$, detectable by isosbestic points in the UV region, and the behavior of sensitizers, clearly functions of their triplet energy – are consistent with sensitization energy transfer.

In the classical scheme

$$\mathrm{S} + h\nu \longrightarrow {}^1\mathrm{S}^* \qquad (1)$$

$${}^1\mathrm{S}^* \longrightarrow {}^3\mathrm{S}^* \qquad (2)$$

$${}^1\mathrm{S}^* \longrightarrow \mathrm{S} + h\nu' \qquad (3)$$

$${}^1\mathrm{S}^* \longrightarrow \mathrm{S} + \mathrm{heat} \qquad (4)$$

$${}^3\mathrm{S}^* \longrightarrow \mathrm{S} + h\nu'' \qquad (5)$$

$${}^3\mathrm{S}^* \longrightarrow \mathrm{S} + \mathrm{heat} \qquad (6)$$

$${}^3\mathrm{S} + \mathrm{C} \xrightarrow{k_s} \mathrm{S} + {}^3\mathrm{C}^* \qquad (7)$$

$${}^3\mathrm{C}^* \longrightarrow \mathrm{C} + \mathrm{heat} \qquad (8)$$

$${}^3\mathrm{C}^* \longrightarrow \mathrm{Co(dtp)_2} \qquad (9)$$

were S = sensitizer, C = $Co(dtp)_3$ and $^3C^*$ = lowest triplet state of charge transfer ^{3}(CTTM), the steady state assumption for $^3S^*$ and $^3C^*$ leads to the following equation for the quantum yield of the $Co(dtp)_2$ that is formed:

$$\frac{1}{\Phi_{Co^{II}}} = \frac{1}{\Phi_{lim}}\left(1 + \frac{1}{k_s\tau[C]}\right)$$

where

$$\Phi_{lim} = \eta_{IS}^{sens}\,\frac{K_{Co^{II}}}{K_T + K_{Co^{II}}}$$

and

η_{IS}^{sens} = intersystem crossing efficiency of sensitizer

When benzophenone is used as sensitizer, k_s and k_q values are comparable to those expected for an energy transfer process controlled by diffusion, where the energy gap between the donor and acceptor triplet states is greater than 2.9 Kcal mol^{-1} [13]. Provided that for benzophenone $\eta_{IS}^{sens} = 1$, the Φ_{lim} coincides with the quantum yield of the triplet state redox reaction. Then, if the assumption is made that the charge transfer triplet is the only reactive state in the direct photoreaction, the efficiency of the intersystem crossing from vibronic levels of singlet states can be calculated:

$$\eta_{IS}^{i} = \frac{\Phi_{dir}}{\Phi_{sens}}\,.$$

When 2′-acetonaphthone is used as sensitizer the above scheme is not correct, because reaction [7] is probably reversible; indeed the experimental results of the system $Co(dtp)_3$–2′-acetonaphthone are consistent with a possible mechanism of reversible energy transfer [14], favoured by the long lifetime of the complex triplet. This indicates that the triplet donor–acceptor energies lie close to each other (about 59 Kcal).

This value agrees with the energy threshold found in the direct photoreduction and with the results of the benzil sensitization. The bimolecular constant of the phosphorescence quenching of benzil is two orders lower than the diffusion constant and the extent of the sensitized reaction is negligible compared to the direct one, namely the photoreactive state of $Co(dtp)_3$ is not significantly populated by energy transfer from benzil, because it lies at energy higher than 55 Kcal. The phosphorescence quenching could involve an energy transfer which produces the lowest excited states of the ligand field [15].

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