Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 231–237

Azidopentaammine cobalt(III) complex: a selective photo-oxidant of *ortho*-phenylphenol in aqueous solution

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Received 16 May 1994; accepted 5 July 1994

Abstract

Excitation of azidopentaammine cobalt(III) ($[Co(NH_3)_5N_3]^{2+}$), in the presence of *ortho*-phenylphenol (OPP) in neutral solution, leads to the disappearance of OPP and the formation of Co(II). The presence of OPP does not affect the initial quantum yields significantly. No oxygen effect is observed.

Flash photolysis and electron spin resonance (ESR) spectroscopy provide evidence for the formation of azide ($N_3^{\cdot}$) and *ortho*-phenylphenoxyl ($OPP^{\cdot}$) radicals. Cobalt(II) plays the role of a stabilizer for $OPP^{\cdot}$ radicals.

At high conversion, a brown precipitate is formed. Various analytical results (high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) spectroscopy, mass specrometry) show that the "para–para" and "ortho–ortho" dimers of OPP are the major photoproducts. Trimers and tetramers are also observed as minor photoproducts. There is no formation of quinone derivatives.

Keywords: Indexwords missing

1. Introduction

The photochemistry of Co(III) coordination compounds has been studied extensively [1–10]. It has been reported that the irradiation of pentaammine cobalt(III) complexes ($[Co(NH_3)_5X]^{2+}$) leads to the formation of aquation and redox photoproducts with the quantum yields depending on the irradiation wavelength.

The photoreduction of the Co(III) centre is favoured by irradiation at the ligand-to-metal charge transfer transition band; excitation corresponding to the ligand field (LF) transition mainly provokes aquation of the complex and the redox process is of minor importance. In the particular case of irradiation of the azidopentaammine cobalt(III) complex ($[Co(NH_3)_5N_3]^{2+}$) at 254 nm, the photoredox process gives rise to Co(II) and $N_3^{\cdot}$ [11]; this is also true in the domain $254 < \lambda < 450$ nm [3]. The azide radical, a powerful oxidizing agent ($E_0(N_3^{\cdot}/N_3^-) =$ 1.32 V [12]), has been reported to initiate vinyl monomer polymerization [13] and to oxidize indoles and phenol derivatives [14,15] in aqueous solution, but cannot attack aromatic rings.

The direct photo-oxidation of *ortho*-phenylphenol (2-hydroxybiphenyl (OPP)) has been studied in our laboratory [16–18]; the irradiation of an air-saturated aqueous solution of OPP at 296 nm leads to the formation of various photoproducts of which phenylbenzoquinone and phenylhydroquinone are the most important in addition to hydroxylation products. In the absence of oxygen, no photoproducts could be detected directly, although the OPP concentration decreased. It was impossible to obtain dimers and oligomers of OPP. Therefore we decided to photosensitize the oxidation of OPP by $[Co(NH_3)_5N_3]^{2+}$ on irradiation at longer wavelength ($\lambda = 365$ nm).

2. Experimental section

The complex $[Co(NH_3)_5N_3]^{2+}$ was prepared as described by Linhard and Flygare [19]. The perchlorate salt was recrystallized at least once but generally twice. The IR spectrum indicated the presence of coordinated azide and the absorption spectrum agreed within a few per cent with the literature values ($\epsilon_{302\ nm} \approx 8600\ M^{-1}\ cm^{-1}$, $\epsilon_{516\ nm} \approx 280\ M^{-1}\ cm^{-1}$) [19].

OPP was purchased from Janssen (purity, 99%) and used without further purification.

The solutions were deaerated by bubbling with argon for 30 min at 22 °C; the ionic strength was not controlled.

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SSDI 1010-6030(94)03917-J

Unless otherwise noted, the concentrations of $[Co(NH_3)_5N_3]^{2+}$ and OPP were 5×10^{-4} M. The pH of 6.4 was the natural pH of the mixture and no significant change was observed during the course of irradiation.

2.1. Apparatus and procedure

A high-pressure mercury lamp (Osram HBO type 125 W), with a Bausch and Lomb grating monochromator, was used for irradiation at 365 nm. The beam was parallel and the reactor was a square cuvette of 1 cm or generally 2 cm path length. The light intensity was measured by ferrioxalate actinometry ($I_0 \approx 2 \times 10^{15}$ photons cm^{-2} s^{-1}). An irradiation apparatus delivering high intensities at 365 nm (5×10^{15} photons cm^{-2} s^{-1}) over a larger volume was used to prepare large amounts of the precipitate. A stainless steel cylinder was used. A high-pressure mercury lamp (Philips HPW type 125 W) (emission at 365 nm selected by an inner filter) was located at the focal axis of the elliptical cylinder and the reactor, a water-jacketed Pyrex tube, was located at the second focal axis.

UV–visible spectra were recorded on a Cary 3 double-beam spectrophotometer.

The quantum yields of OPP degradation and complex disappearance were determined by high performance liquid chromatography (HPLC) experiments. The HPLC apparatus was a Waters 540 liquid chromatography system equipped with a diode array UV–visible detector (Waters 990). A reverse phase Beckman column (250 mm × 4 mm) was employed and the eluent was a mixture of A (80 : 20 (v/v) methanol–water) and B (5 : 1 (v/v) CH_3COONa (0.03 M) (pH 5) plus CH_3CN) used with the gradient programme given in Fig. 1. The gradient programme was adapted to the simultaneous detection of OPP and the cobalt complex. OPP was eluted during the first part, whereas the complex was eluted with a longer retention time: $[Co(NH_3)_5N_3]^{2+}$, $t = 10.3$ min; OPP, $t = 4.9$ min. The detection of the organic compounds (OPP and the photoproducts) was carried out with a methanol–water mixture gradient.

The concentration of Co(II) formed was determined by complexometry according to the method of Katakis and Allen [20]. The calibration curve was obtained with cobalt(II)-(acetylacetonate)$_2$. The Co(II) concentration was given by the empirical formula: $[Co(II)] = 5.70 \times 10^{-4} \times (OD)_{620}$ M, where OD_{620} is the optical density at 620 nm.

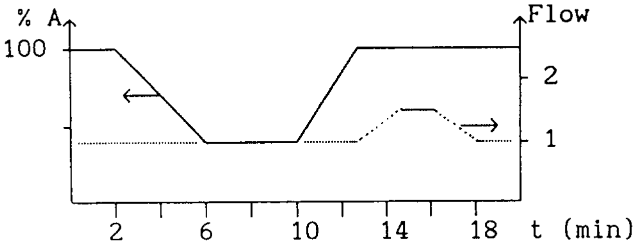


Fig. 1. Gradient programme for HPLC.

The release of NH_3 in the irradiated solution was followed by the indophenol spectrophotometric method [21]. The calibration curve was established with NH_4Cl in the domain corresponding to the NH_4^+ concentration resulting from irradiation. Correction was always made for the absorbance at 625 nm of identically treated aliquots of irradiated and dark solutions. We checked that the presence of OPP did not interfere with the analysis. However, the method was not very precise and some discrepancy was observed between the results. The initial quantum yields of NH_4^+ release and Co(II) formation were calculated from the initial slope of the curve of the concentration vs. irradiation time.

Transient spectra were recorded using a Nortech FPX-1 flash lamp emitting 130 J, with a rise time of 10 μs. The output of the multiplier was passed to a Tektronix 564 storage oscilloscope. In order to prevent the direct excitation of OPP, appropriate filters ($\lambda > 320$ nm) were placed in front of the flash lamp.

The IR spectra of the precipitate were run as KBr pellets using a Nicolet 205X Fourier transform IR (FTIR) spectrophotometer.

Separation of the photoproducts was obtained using a Gilson preparative HPLC apparatus equipped with a 115 UV detector and a 201 fraction collector.

Electron spin resonance (ESR) spectra were recorded using a Brucker ER 200 D spectrometer at 9.30 GHz with a modulation field of 100 kHz. A Xe–Hg Hanovia lamp was used for irradiation in the ESR spectrometer cavity. To prevent the direct excitation of OPP, appropriate filters were used ($\lambda > 350$ nm). Spin trapping experiments were performed using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a trap. DPPH was used as an internal standard.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured in standard sample tubes on a Brucker 300 MSL (Fourier transform) spectrometer.

Mass spectra were obtained from the Analysis Centre of the Centre National de la Recherche Scientifique (CNRS).

3. Results

3.1. Continuous irradiation

In a systematic manner, we performed experiments in the presence and absence of OPP. All the experiments were performed in the presence of oxygen. The absence of oxygen did not affect the results significantly. The UV–visible spectrum of a mixture of 2.5×10^{-4} M $[Co(NH_3)_5N_3]^{2+}$ and 2.5×10^{-4} M OPP at pH 6.2 was the sum of the component spectra. The LF transition of the cobalt complex at 516 nm was unaffected by the presence of OPP, whereas the maximum of the charge transfer (CT) transition at 302 nm was changed to a shoulder due to convolution with the OPP absorption. OPP showed no absorption above $\lambda = 320$ nm. There was no detectable spectral evidence of complexation between $[Co(NH_3)_5N_3]^{2+}$ and OPP in the ground state. When allowed to stand in the dark, the solution was stable. Aerated solutions of azidopentaammine cobalt(III) (2.5×10^{-4} M) and OPP (2.5×10^{-4} M) were irradiated at 365 nm, and the UV–visible absorption spectra were recorded (Fig. 2): there was a continuous decrease in the CT band.

The quantum yield of $[Co(NH_3)_5N_3]^{2+}$ disappearance was calculated to be 0.20 regardless of the method of determination (HPLC or UV spectroscopy at a suitable wavelength (302 nm in the absence of OPP and 320 nm in the presence of OPP with the assumption of negligible absorption of the photoproduct at these wavelengths)). It is worth noting that the presence of OPP does not affect the initial quantum yield.

The initial quantum yield of Co(II) formation was measured to be 0.17 in the absence and 0.20 in the presence of OPP. There was no acceleration of cobalt(II) formation during the process.

The concentrations of free NH_3 and Co(II) and their ratios were measured during the photoreaction in the absence and presence of OPP. The results are given in Table 1. In every case, the ratio remains roughly equal to four. The initial quantum yield of OPP disappearance measured by HPLC is equal to 0.19 which is, within experimental error, similar to that of complex consumption and Co(II) formation.

In conclusion, apart from a quantum yield of Co(II) formation slightly higher than that in the absence of OPP, the presence of OPP did not affect the photochemical phenomenon at least in the early stages of the reaction.

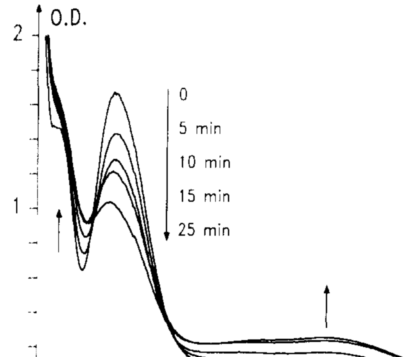


Fig. 2. Evolution of the UV–visible spectrum of an air-saturated solution of $[Co(NH_3)_5N_3]^{2+}$ (2.5×10^{-4} M) and OPP (2.5×10^{-4} M) on irradiation at 365 nm.

For longer irradiation times, the general shapes of the curves of NH_3 release, Co(II) formation and $[Co(NH_3)_5N_3]^{2+}$ disappearance were similar in the absence and presence of OPP. The curve levelled off for a conversion percentage higher than 30% (Fig. 3). However, two differences appeared in the presence of OPP: a brown precipitate was formed and Co(II) formation always remained more important. Changes were also observed in the difference between the starting complex concentration and cobalt(II) formation. An autoacceleration was observed after 10 min of irradiation; this was true with and without OPP. However, the difference assigned to the aquation phenomenon was of less importance in the presence of OPP.

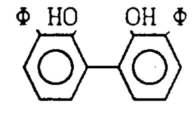
Deaerated solutions of the complex and OPP were irradiated under similar conditions. No significant differences from the previous case were observed. In particular, the general shapes of the curves were identical.

3.2. Analysis and identification of the products

The determination of Co(II) was performed separately on the crude solution, the precipitate and the filtered solution. In the latter case, the concentration of Co(II) rapidly reached a maximum at 5×10^{-5} M, whereas in the precipitate, there was a continuous increase with irradiation time. The percentage of Co(II) in the dry precipitate was 22% by mass.

The irradiated solution together with the precipitate and the isolated precipitate dissolved in CH_3OH were studied by HPLC. Attempts were made to characterize the products formed after irradiation. No quinone derivatives were detected.

The filtered solution contained OPP and one photoproduct P_1 which was separated by preparative HPLC. The mass spectrum showed a main peak at $m/e = 338$ attributed to a dimeric form of OPP. The assignment of the ^1H NMR spectrum of P_1 (Fig. 4(A)) agreed with the ortho–ortho dimer of OPP (2,2′-dihydroxy-3,3′-diphenyl biphenyl).



2,2'-dihydroxy 3,3'-diphenyl biphenyl

The IR spectrum of the precipitate showed the absence of the N_3^- group (2080 cm) and the carbonyl group. The mass spectrum revealed the presence of a tetramer ($m/e = 674$), trimer ($m/e = 506$), dimer ($m/e = 338$) and "monomer" of OPP. The curing of the precipitate by CH_3OH yielded an insoluble Co(II) salt and a yellow solution. A typical chromatogram of this solution is given in Fig. 5. The major photoproduct P_2

Table 1
NH_3 release and Co(II) formation on irradiation of $[Co(NH_3)_5N_3]^{2+}$ (5×10^{-4} M) at 365 nm and pH 6.2

	t (min) of irradiation	$[NH_3]\times10^4$ (M)	$[Co(II)]\times10^4$ (M)	$R=[NH_3]/[Co(II)]$
Without OPP	6	2.7	0.75	3.6
	10	3.7	0.9	4.1
	20	6.8	1.4	4.8
	45	8.2	2.0	4.1
With OPP (5×10^{-4} M)	2	1.4	0.39	3.6
	5	2.5	0.64	3.9
	10	4.6	1.2	3.8
	15	6.3	1.5	4.2
	25	7.5	2.0	3.7

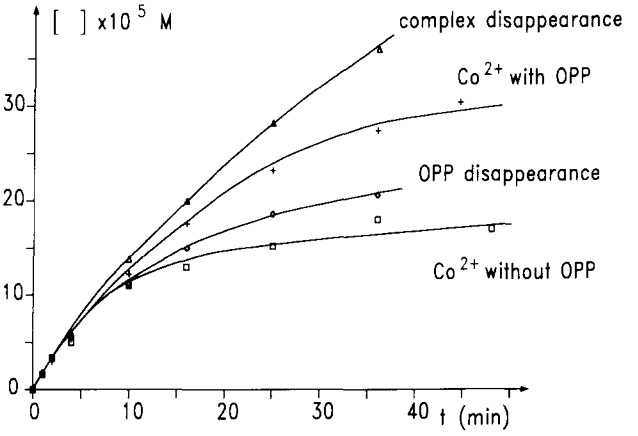
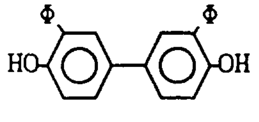


Fig. 3. Disappearance of Co(III) and OPP and appearance of Co(II) as a function of irradiation time.

was isolated by HPLC; the ^1H NMR spectrum (different from the NMR spectrum of P_1) (Fig. 4(B)) and the mass spectrum ($m/e=338$) were in agreement with the para–para dimer of OPP (4,4′-dihydroxy- 5,5′-diphenyl biphenyl). P_2 is the major photoproduct of the reaction.



4,4'-dihydroxy 5,5'-diphenyl biphenyl

In addition to OPP, P_1 and P_2, other products were observed whose UV–visible spectra were analogous and characterized by a broad band at $\lambda=420$–480 nm. This absorption disappeared when the precipitate was cured by an NaSCN solution to eliminate Co(II). Therefore these peaks are assigned to complexes between cobalt(II) and dimers or oligomers of OPP.

3.3. Flash photolysis experiments

The flash photolysis of $[Co(NH_3)_5N_3]^{2+}$ alone did not produce any transient; $N_3^{\cdot}$ does not absorb significantly and cannot be observed under our experimental conditions. The flash photolysis of an aerated solution of $[Co(NH_3)_5N_3]^{2+}$ (5×10^{-4} M) and OPP (5×10^{-4} M) at $\lambda>320$ nm produced a transient with a strong absorption in the 350–410 nm region. Three

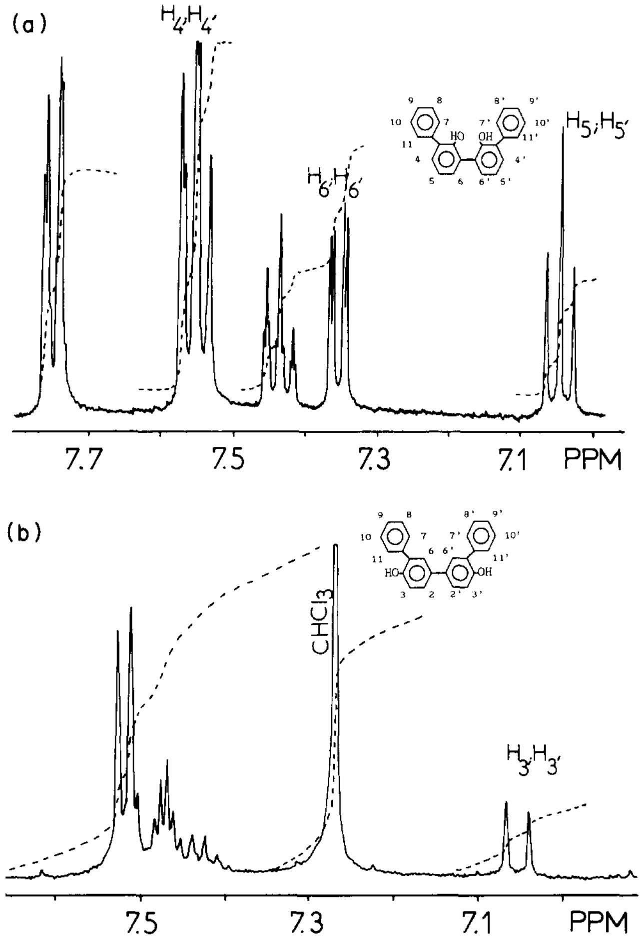


Fig. 4. (A) 300 MHz ^1H NMR spectrum of photoproduct P_1 in $CDCl_3$. $\delta=7.04$ t (H_5 and $H_{5'}$); 7.36 dd (H_6 and $H_{6'}$); 7.43 tt (H_9 and $H_{9'}$); 7.56 t (H_8, H_{10}, $H_{8'}$ and $H_{10'}$); 7.57 dd (H_4 and $H_{4'}$); 7.74 dd (H_7, H_{11}, $H_{7'}$ and $H_{11'}$). Coupling constants: ortho coupling, 7.5 Hz; meta coupling, 1.9 Hz. (B) 300 MHz ^1H NMR spectrum of photoproduct P_2 in $CDCl_3$. $\delta=7.05$ d (H_3 and $H_{3'}$); 7.50 m (14 H).

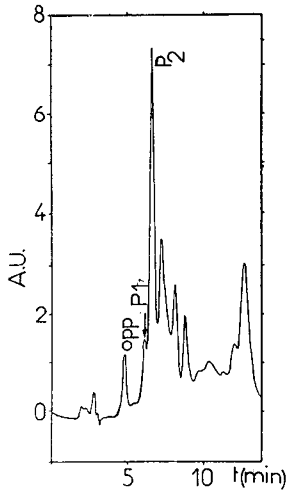


Fig. 5. High performance liquid chromatogram of a methanol solution of the precipitate. $\lambda_{detection} = 260$ nm, MeOH–H_2O = 80 : 20.

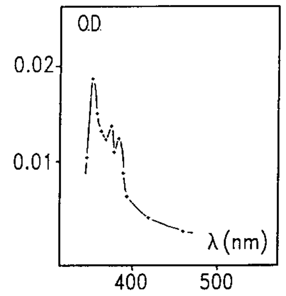
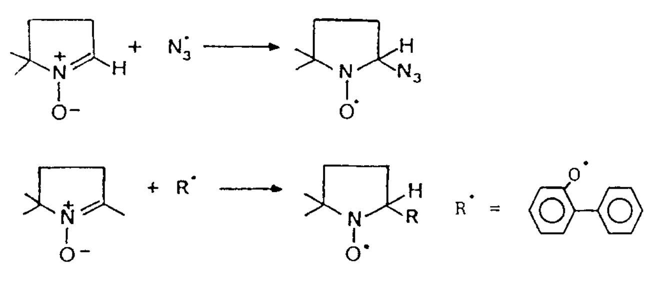


Fig. 6. Spectrum of the *ortho*-phenylphenoxyl radical observed by flash photolysis in the presence of 5×10^{-4} M of $[Co(NH_3)_5N_3]^{2+}$ on irradiation at $\lambda > 320$ nm.

well-defined maxima were observed at 355, 375 and 395 nm (Fig. 6).

3.4. ESR spectroscopy

The ESR spectrum of the precipitate, at room temperature, exhibited a singlet at $g = 2.0036$ G characteristic of an organic radical. On washing the precipitate with methanol, the intensity of the signal decreased strongly. Spin trapping experiments on irradiation were performed using DMPO as a trap. This compound is water soluble and does not absorb light at $\lambda > 330$ nm. Two adducts can be formed during the photoredox process



The ESR spectra of the adducts are given in Figs. 7(a) and 7(b); a quartet was observed with OPP$^\bullet$ ($g = 2.0061$) and a quartet of triplets with $N_3^\bullet$ ($g = 2.0061$). The formation of a quartet instead of a triplet of doublets is due to the identical value of the coupling between O$^\bullet$ and N on the one hand and N and H on the other.

When a mixture of $[Co(NH_3)_5N_3]^{2+}$ and OPP was irradiated at $\lambda > 350$ nm, the signal observed (Fig. 7(c)) was the sum of the two signals (a) and (b), providing evidence for the presence of the two types of radical in the solution.

On–off experiments performed with $N_3^\bullet$ and OPP$^\bullet$ adducts showed the stability of the OPP$^\bullet$ adduct compared with the $N_3^\bullet$ adduct whose signal rapidly decreased in the absence of light. The same set of experiments performed in the presence of ethanol (used as a scavenger of $^\bullet$OH) or in the absence of oxygen yielded identical results. There was no $^\bullet$OH radical formation.

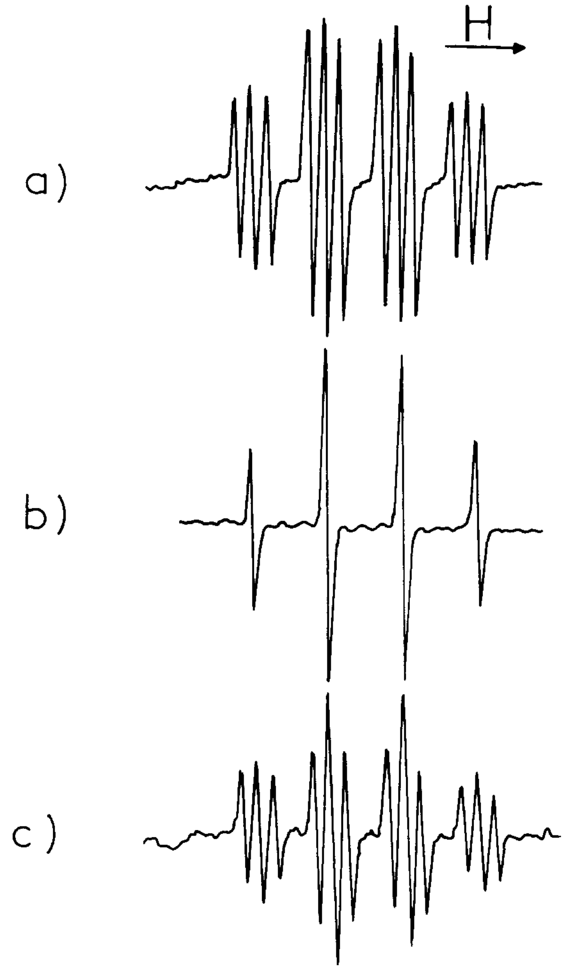


Fig. 7. ESR spectra of DMPO spin adducts recorded after about 10 min of irradiation in aerated solutions. (a) Complex concentration, 2.5×10^{-4} M ($\lambda > 350$ nm): $a^N(1) = a^H(1) = 14.2$ G, $a^N(2) = 2.7$ G, $g = 2.0060$. (b) OPP concentration, 2.5×10^{-4} M (unfiltered): $a^N(1) = a^H(1) = 14.2$ G, $g = 2.0060$. (No signal appears if filtered at $\lambda > 350$ nm.) (c) Complex/OPP concentrations, 2.5×10^{-4} M/10^{-3} M; $\lambda > 350$ nm; $g = 2.0060$.

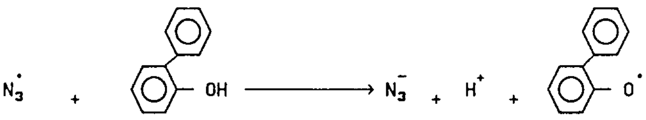
4. Discussion

It has been widely reported that the irradiation of $[Co(NH_3)_5N_3]^{2+}$ at the $N_3^- \rightarrow Co(III)$ CT absorption band causes an efficient redox reaction together with ligand substitution (in most cases). The quantum yield of cobalt(II) formation is reported either to remain constant for $\lambda_{irr} = 365$ nm [3] or to increase with the conversion percentage when $\lambda_{irr} = 254$ nm [10]. This latter phenomenon is assigned to the formation of the aquation photoproduct $[Co(NH_3)_4(H_2O)N_3]^{2+}$, a better absorber and very efficient in terms of the redox process.

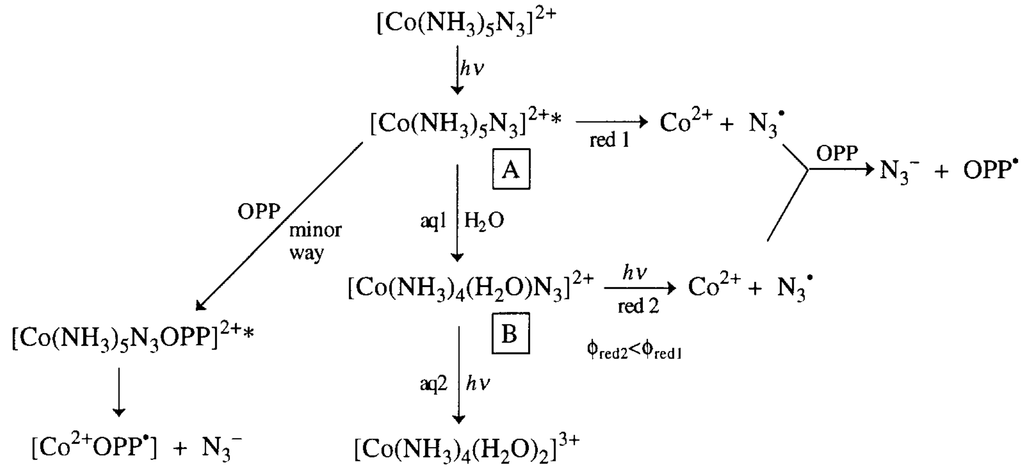
The reported values of $\phi_{Co(II)} = 0.44$ with $\lambda_{irr} = 365$ nm were measured at very high concentrations of the cobalt complex ($[Co(NH_3)_5N_3]^{2+} = 0.01$ M) [2]. The value of 0.2, obtained on irradiation at 365 nm, is identical with the value reported in the literature for $\lambda_{irr} = 254$ nm, but in contrast with the phenomenon described for the latter case, we did not observe the acceleration of Co(II) formation. The quantum yield of NH_3 release is approximately four times higher, which reflects a deficit of one ammonia molecule released per reduced cobalt(III) atom. It is worth noting that the ratio $[NH_3]_{rel}/[Co(II)]_{form}$ is roughly constant during the oxidoreduction process.

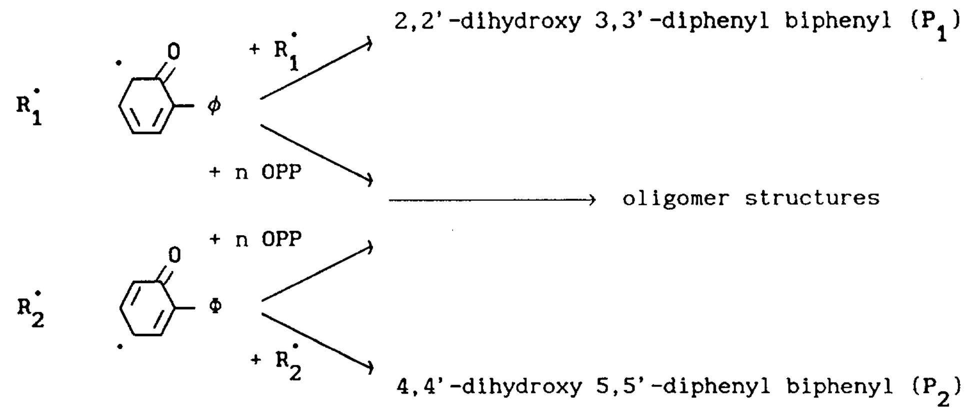
In terms of the initial quantum yields, the presence of OPP does not affect the complex disappearance, but the rate of Co(II) formation appears to be slightly higher. As a result, the additional formation of Co(II) can only occur at the expense of the photoaquation process.

In addition, in our experimental conditions (complex concentration, 5×10^{-4} M; OPP concentration, 5×10^{-4} M), the quantum yield of OPP consumption is analogous to that of Co(II) formation. Thus the redox reaction giving rise to Co^{2+} and $N_3^{\bullet}$ can be followed by the reaction of $N_3^{\bullet}$ with OPP.



The quantum yield of OPP disappearance sensitized by $[Co(NH_3)_5N_3]^{2+}$ is one order of magnitude higher than that obtained by direct excitation. The flash photolysis experiments ($\lambda > 320$ nm) give evidence for the presence of a transient assigned to $OPP^{\bullet}$. By direct excitation ($\lambda > 280$ nm) of OPP, we were unable to detect the formation of any transient. Similar experiments performed with *meta*-phenylphenol (MPP) and *para*-phenylphenol (PPP) show the presence of the



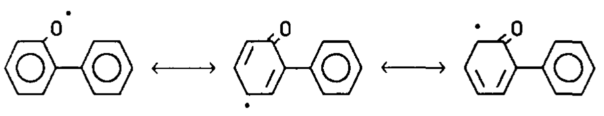


radicals MPP$^{\cdot}$ and PPP$^{\cdot}$ (*meta*- and *para*-phenylphenoxyl radicals) when flashed in the presence of $[Co(NH_3)_5N_3]^{2+}$ at $\lambda > 330$ nm [22]. However, in contrast with OPP, MPP$^{\cdot}$ and PPP$^{\cdot}$ can be easily observed on direct excitation at $\lambda > 280$ nm [23]. It has been reported in the literature that cobalt(II) gives a long-lived complex radical with tert-butylperoxy radical [24,25] and semiquinone radicals [26]. In the precipitate, OPP$^{\cdot}$ or an oligomeric radical detected by ESR spectroscopy is stable for days, the stability probably due to the presence of Co(II). However, the stabilization, by cobalt(II), of the OPP$^{\cdot}$ radical formed by reaction with $N_3^{\cdot}$ implies a reaction in the cage between $[Co(NH_3)_5N_3]^{2+}$ and OPP.

Looking at the fate of $N_3^{\cdot}$ radicals, also detected by ESR spectroscopy, when released in the solution, the following reactions can be observed

$$N_3^{\cdot} + N_3^{\cdot} \longrightarrow 3N_2$$

$$N_3^{\cdot} + OPP \longrightarrow N_3^{-} + OPP^{\cdot} + H^{+}$$



Several forms of the *ortho*-phenylphenoxyl radical can react with OPP to yield dimeric, trimeric and tetrameric structures. It should be noted that the presence of cobalt prevents the attack of these radicals by O_2 to yield quinone derivatives. We can rule out the oxidative termination of OPP$^{\cdot}$ by the starting cobalt(III) complex which would yield a higher complex disappearance in the presence of OPP.

In the early stages of the reaction, as demonstrated by the quantum yields, the photoaquation process is either only a minor deactivation pathway or the aquated photoproduct presents similar features in terms of absorption, physical properties and photoreactivity compared with the starting complex $[Co(NH_3)_5N_3]^{2+}$ (A). According to Refs. [11,27], $[Co(NH_3)_4(H_2O)N_3]^{2+}$ (B) complies with these conditions.

In conclusion, the following simplified scheme can be put forward which accounts for all the experimental results.

$[Co(NH_3)_5N_3]^{2+}$ appears to be a very efficient and selective photosensitizer of OPP oxidation: only OPP oligomers are obtained even in the presence of oxygen. The formation of quinone derivatives, observed in high yield by direct photo- oxidation, is completely inhibited. The presence of a new species, probably cobalt(II), prevents the attack of the *ortho*-phenylphenoxyl radical (OPP$^{\cdot}$) by oxygen. In addition, the formation of the symmetric dimers P_1 and P_2 is favoured under these conditions.

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