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Selective oxidation of *meta*- and *para*-phenylphenol photosensitized by $[Co(NH_3)_5N_3]^{2+}$ in aqueous solution

Mohamed Sarakha [a], Hugh Burrows [b], Michèle Bolte [a]

[a] *Laboratoire de Photochimie Unité de Recherche associée au CNRS 433, F-63177 Aubière Cedex, France*

[b] *Departamento de Quimica, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal*

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Abstract

The oxidation of *meta*-phenylphenol (*m*-PP) and *para*-phenylphenol (*p*-PP) was photosensitized by excitation at 365 nm in the presence of azidopentaammine cobalt(III) in neutral aqueous solution. The presence of *m*-PP or *p*-PP did not affect the initial quantum yield of cobalt(III) reduction, and oxygen had no apparent effect. By electron spin resonance spectroscopy upon irradiation, it was possible to detect the formation of both $N_3^{\bullet}$ and *m*-PP$^{\bullet}$ radicals as adducts with the spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide. Laser flash photolysis experiments gave evidence of the formation of the corresponding phenylphenoxyl radical by reaction between $N_3^{\bullet}$ and the phenols, and their constants of formation and decay were calculated. The dimers were identified as the major photoproducts. Trimers and tetramers of *m*-PP and *p*-PP were also formed. It is worth noting that no formation of quinones was observed. Cobalt appeared to prevent the reaction of oxygen with the phenoxyl radicals.

Keywords: Cobalt complex; Photoinduced oxidation; *Meta*-phenylphenol; *Para*-phenylphenol; Azide radical

1. Introduction

The photochemical behaviour of azidopentaammine cobalt(III) has been widely studied [1], and references cited therein]. The excitation in the ligand-to-metal charge transfer transition band leads mainly to the reduction of cobalt(III) into cobalt(II) and to the formation of azide radical $N_3^{\bullet}$. The oxidizing properties of the azide radical (E_0 ($N_3^{\bullet}$/N_3^-) = 1.32 V) [2] have already been used to initiate vinyl monomer polymerization [3] and to oxidize phenol derivatives [4]. We have previously described the photooxidation of *ortho*-phenylphenol by $[Co(NH_3)_5N_3]^{2+}$ in aqueous neutral solution [5]. In this paper we report the oxidation of 3-hydroxybiphenyl (*meta*-phenylphenol (*m*-PP)) and 4-hydroxybiphenyl (*para*-phenylphenol (*p*-PP)) photosensitized by $[Co(NH_3)_5N_3]^{2+}$ in aqueous solution. Special emphasis will be given to results obtained by laser flash photolysis. These will be completed with new results obtained with *ortho*-phenylphenol (*o*-PP).

2. Experimental section

The complex $[Co(NH_3)_5N_3]^{2+}$ was prepared by the published procedure [6]. The perchlorate salt was recrystallized once or twice. The IR spectrum confirmed the presence of coordinated azide, and the UV–visible absorption maxima agreed closely with the literature values ($\epsilon \approx 8600\ M^{-1}\ cm^{-1}$ and $\epsilon \approx 280\ M^{-1}\ cm^{-1}$) [6].

m-PP and *p*-PP were purchased from Janssen (99% purity) 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. Unless otherwise noted, the concentration of $[Co(NH_3)_5N_3]^{2+}$ and *m*-PP or *p*-PP was 3×10^{-4} M. The pH, equal to 6.4, was the natural pH of the mixture and no significant changes in pH were observed during the course of the 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 irradiations at 365 nm. A parallel beam was used in the reactor to irradiate a square cuvette of 1 cm or more generally 2 cm path length. The light intensity was measured by ferrioxalate actinometry ($I_0 \approx 2 \times 10^{15}$ photons $cm^{-2}\ s^{-1}$). For preparation studies, an irradiation set-up delivering higher intensity at 365 nm ($I_0 \approx 5 \times 10^{15}$ photons $cm^{-2}\ s^{-1}$) on a larger volume was used. The system consisted of a cylinder made of stainless steel built on an elliptical basis. A high

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pressure mercury lamp (Philips HPW type 125 W), with the 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 *m*-PP or *p*-PP degradation and complex disappearance were determined by high performance liquid chromatography (HPLC) experiments, using a Waters 540 liquid chromatography system equipped with a diode array UV-visible detector (Waters 990). For these studies a reverse phase Beckman (250×4 mm) column was used with a mixture of A (80:20 v/v methanol:water) and B (5:1 v/v CH_3COONa (0.03 M; pH 5):CH_3CN) as eluent, with a gradient program as described elsewhere [5].

The concentration of Co(II) produced was determined by complexometry according to the method of Katakis and Allen [7]. The calibration curve was obtained using cobalt(II)(acetylacetonate)$_2$. The Co(II) concentration was then given by the empirical formula

$$[\mathrm{Co(II)}] = 5.70\times10^{-4}(\mathrm{OD})_{620\ \mathrm{nm}}\ \mathrm{M}$$

where $OD_{620\ nm}$ is the optical density at 620 nm.

The release of NH_4^+ in the irradiated solution was followed by a spectrophotometric method using indophenol [8]. The presence of *m*-PP or *p*-PP was found not to interfere with the analysis. However, the precision of the method was limited and some discrepancy was observed among the results.

The initial quantum yields of NH_4^+ release and Co(II) formation were calculated from the initial slope of the curve, giving the concentration as a function of irradiation time.

Separation of the photoproducts was performed using a Gilson preparative high performance liquid chromatograph 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 operating at 9.30 GHz with a modulation field of 100 kHz. An Xe-Hg Hanovia lamp was used for irradiations in the ESR spectrometer cavity. To prevent the direct excitation of *m*-PP or *p*-PP, appropriate filters were used ($\lambda > 350$ nm). Spin trapping experiments were performed using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a trap. Diphenylpicrylhydrazyl (DPPH) was used as an internal standard.

Nuclear magnetic resonance (NMR) spectra were recorded in standard sample tubes on a Brucker 300 MSL (Fourier transform) spectrometer.

Mass spectra were obtained from the Analysis Center of the University of Orléans.

Laser flash photolysis experiments were carried out at the Centro de Quimica Estrutural, Instituto Superior Técnico, Lisbon, Portugal, using normally the third harmonic (355 nm; pulse width, about 10 ns) of a Nd-doped yttrium aluminium garnet laser as excitation source. Preliminary studies used the second harmonic at 532 nm for excitation. However, the signals were too weak to provide detailed information. Conventional optical detection of transients was used, with a pulsed Xe lamp, monochromator and photomultiplier. Details of the kinetic spectrophotometer and data averaging have been given elsewhere [9]. Aqueous solutions were introduced into a standard cuvette for these experiments and degassed by bubbling N_2 or Ar.

3. Results and discussion

3.1. Continuous irradiation

The photolysis of solutions of *m*-PP or *p*-PP in the presence of $[Co(NH_3)_5N_3]^{2+}$ was studied. All experiments were performed in the presence of oxygen. The absence of oxygen did not significantly affect the results. The UV-visible spectrum of a mixture 2.5×10^{-4} M $[Co(NH_3)_5N_3]^{2+}$ and 2.5×10^{-4} M *m*-PP or *p*-PP (so-called "PP") at pH 6.2 was the sum of the component spectra. The LF transition of the cobalt complex at 516 nm was not affected by the presence of "PP" whereas the maximum of the charge transfer transition at 302 nm became a shoulder owing to the convolution with "PP" absorption. "PP" does not absorb at $\lambda > 320$ nm. There was no detectable spectral evidence for ground-state association between $[Co(NH_3)_5N_3]^{2+}$ and "PP". When allowed to stand in the dark, the solution was stable. However, when aerated solutions of azidopentaammine cobalt(III) 3×10^{-4} M and "PP" 3×10^{-4} M were irradiated at 365 nm, and the UV–visible absorption spectra were recorded (Fig. 1) there was a continuous decrease in the charge transfer transition. The quantum yield of the complex disappearance was determined both by HPLC and by UV spectroscopy monitored at 320 nm, with the assumption of a negligible absorption of the photoproduct at that wavelength. The initial quantum yield did not appear to be affected by the presence of "PP". Similar results were obtained for the initial quantum yield of Co(II) formation:

$$\Phi_{\mathrm{complex\ dis.}} = \Phi_{\mathrm{Co(II)form}} = 0.18$$

both in the presence and in the absence of "PP".

The concentrations of free NH_3 and Co(II) were determined during the photoreaction. The ratio $[NH_3]_{rel}/[Co(II)]_{form}$ was roughly constant and equal to 4 which revealed a deficit in NH_3 compared with the stoichiometric ratio expected for the photoreduction of $[Co(NH_3)_5N_3]^{2+}$. The quantum yields of *m*-PP and *p*-PP disappearance were equal to 0.18 and 0.20, in good agreement with yields of Co(III) loss and Co(II) formation.

The variations in concentrations of cobalt(III) complex, of cobalt(II) and of *p*-PP as functions of irradiation time are given in Fig. 2. For comparison, the results obtained in the absence of *p*-PP are also reported. The results were analogous to those obtained with *m*-PP, showing that the presence of "PP" did not affect the rate of the initial photoreaction.

However, two important differences appeared in the presence of the phenylphenols: Co(II) formation was always more important in the presence of "PP"; from the beginning

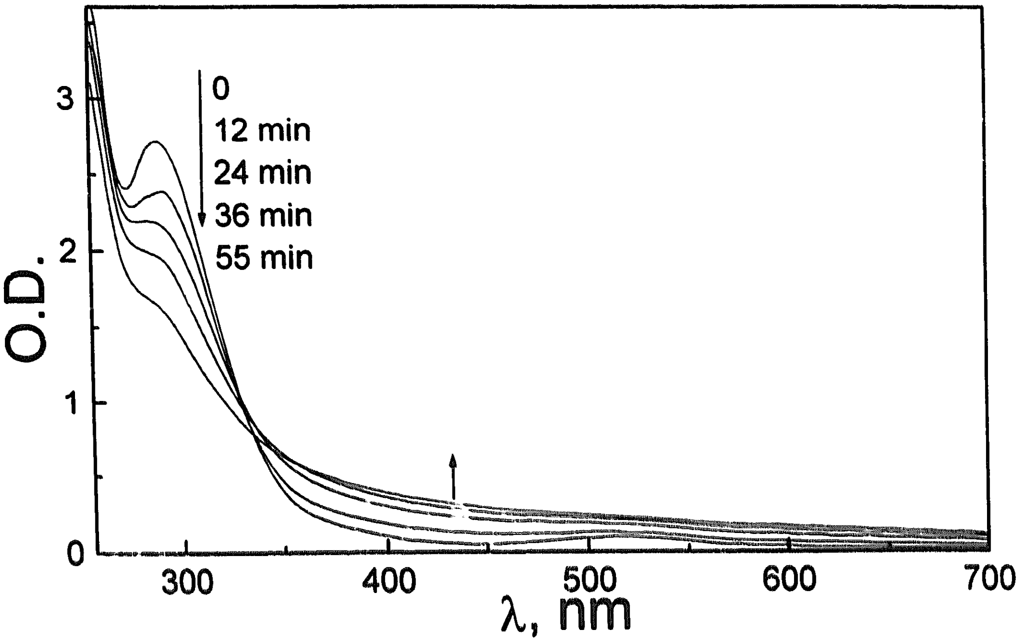


Fig. 1. Spectral evolution of a solution $[Co(NH_3)_5N_3]^{2+}$ (2.5×10^{-4} M) and *m*-PP (2.5×10^{-4} M) upon irradiation at 365 nm: O.D., optical density.

of the reaction, the formation of a brown precipitate was observed.

3.2. *Laser flash photolysis experiments*

To obtain mechanistic information on these reactions, the kinetic behaviour of transient species was monitored by laser flash photolysis. Unpublished results relating to *o*-PP are also reported. Following excitation of degassed aqueous solutions of *o*-, *m*- or *p*-PP in the presence of $[Co(NH_3)_5N_3]^{2+}$ (1×10^{-3} M), absorptions around 400 nm were observed to increase over a few microseconds. A typical example is shown in Fig. 3(a). Location of the absorption maxima was limited by the strong light absorption of the cobalt complex, and the limited solubility of the phenols. However, comparison with spectra for related species [10,11] suggests that these absorptions are due to the corresponding phenoxyl radicals. No transient absorptions were observed in this region upon photolysis of solutions of the cobalt complex without the phenols. Support for this assignment comes from the fact

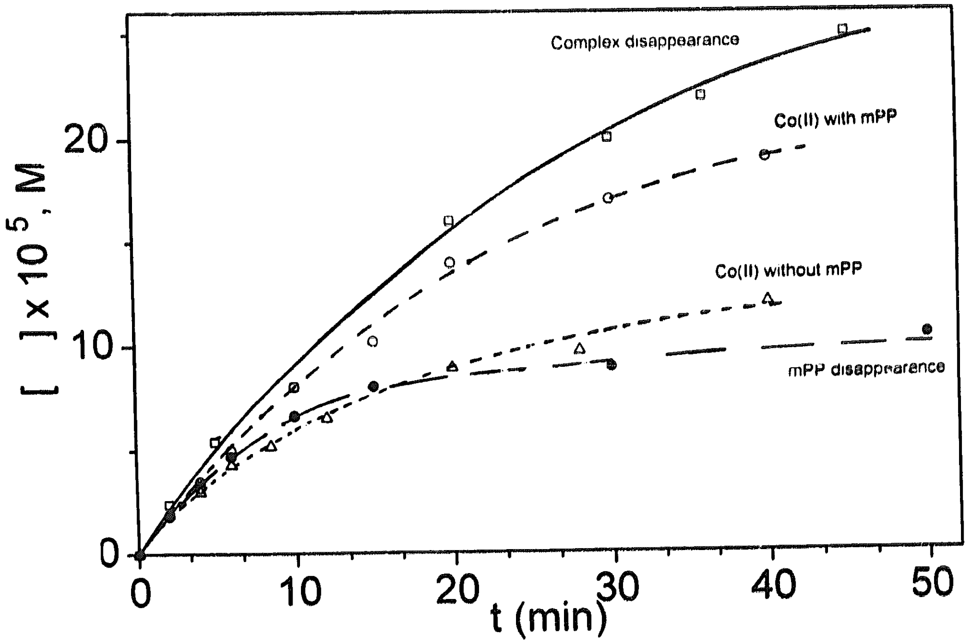


Fig. 2. Disappearance of $[Co(NH_3)_5N_3]^{2+}$ and *p*-PP, Co(II) formation in the presence and in the absence of *p*-PP, as a function of irradiation time (λ_{exc} = 365 nm).

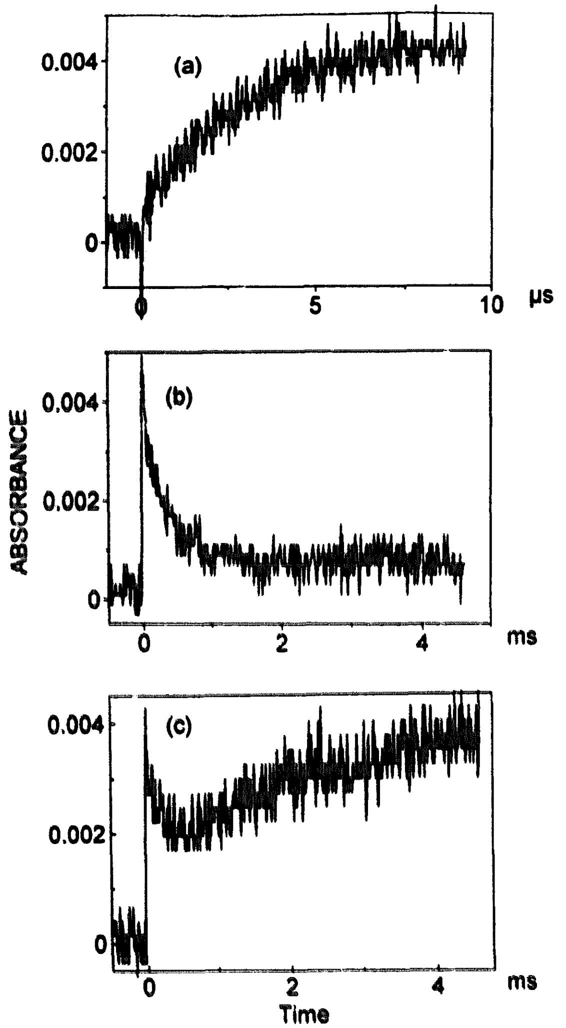


Fig. 3. Kinetic traces observed at 400 nm following laser flash photolysis (355 nm) of degassed aqueous solutions of $[Co(NH_3)_5N_3]^{2+}$ (1×10^{-3} M) in the presence of (a), (b) *p*-PP (3×10^{-4} M) and (*c*) *o*-PP (2.25×10^{-4} M).

that $N_3^{\bullet}$, which is expected to be the primary product of $[Co(NH_3)_5N_3]^{2+}$ photolysis, is suggested to react quantitatively with phenols by electron transfer to give the phenoxyl radical [4]:

$$N_3^{\bullet} + PhOH \rightarrow N_3^- + PhO^{\bullet} + H^+ \qquad (1)$$

Further, other potential candidates for these transients, such as the $N_3^{\bullet}$ radical or cyclohexadienyl derivatives formed by radical addition to the phenols, absorb at shorter wavelengths; $N_3^{\bullet}$ has $\lambda_{max} = 274$ nm [12] whilst the $H^{\bullet}$ and $HO^{\bullet}$ adducts of phenols typically absorb in the 300–350 nm region [13–15]. In all cases, the increase in absorption follows good pseudo-first-order kinetics. For *o*-PP, the rate of this was found to depend upon the phenol concentration (up to 2.5×10^{-3} M), with the overall rate law

$$\text{rate} = k_2[N_3^{\bullet}][PhOH]$$

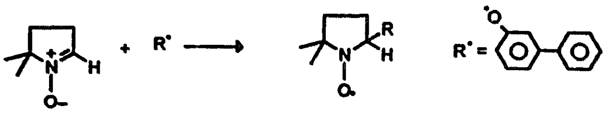
For the other derivatives, kinetic studies were limited by solubility. However, comparison with results from [4] suggests that in all cases we are looking at reaction (1), for which second-order rate constants of $k = 5.9\times10^8$ M^{-1} s^{-1} (*o*-PP), 6.0×10^8 M^{-1} s^{-1} (*m*-PP) and 8.0×10^8 M^{-1} s^{-1} (*p*-PP) were calculated. These are within the range of values observed for oxidation of phenols by azide radicals in neutral aqueous solutions [4].

In all cases, the phenoxyl radical was observed to decay on a millisecond time scale. However, differences were observed between the behaviour of *o*-PP and the other two derivatives. With *o*-PP, the initial decay of this transient was followed by the increase in a new transient absorption in the 400 nm region (Fig. 3(c)). In the absence of spectral information, this somewhat complex behaviour was not followed further. With *p*-PP, the phenoxyl radical decayed by second-order kinetics (to greater than 70% reaction) (Fig. 3(b)). A value for the decay constant of $2k/\epsilon_{400} = 7.3\times10^5$ cm s^{-1}, where ϵ is the extinction coefficent for this radical at 400 nm, was found. This is close to values observed for other phenoxyl radicals in water [11]. Whilst we do not have a value for ϵ_{400} for the *p*-PP radical, from absorption spectra of related radicals [11], a second-order rate constant of about 10^9 M^{-1} s^{-1} can be estimated for the bimolecular decay of the *p*-PP radical for this species in aqueous solutions. Values for the bimolecular decay of this radical in benzene and chlorobenzene are 10–100 times smaller [16]. However, it has been emphasized that the rate of this reaction is strongly solvent dependent and is likely to be catalysed in protic solvents [17]. With *m*-PP, the transient absorption also decayed on a millisecond time scale. Whilst the signal was too noisy to permit accurate kinetic analysis, a decay constant of $2k/\epsilon_{400} \approx 3\times10^5$ cm s^{-1} was estimated, assuming that the reaction also follows a bimolecular process.

3.3. Electron spin resonance spectroscopy

ESR spectroscopy was used to characterize both intermediate species and final products. A singlet at $g = 2.0036$ G was observed in the ESR spectrum of the dried precipitates obtained with *m*-PP and *p*-PP.

To identify transient species, ESR spectroscopy experiments were performed during irradiation of solution containing [Co(III) complex] $= 5\times10^{-4}$ M and ["PP"] $= 10^{-3}$ M in the presence of DMPO as a spin trap. The excitation light was filtered at $\lambda > 350$ nm to avoid the absorption of the light by "PP" or DMPO. As previously described, two types of signal were observed corresponding to the adducts from $N_3^{\bullet}$ and the phenoxyl radical [5]:



Experiments carried out in the presence of ethanol as a scavenger of $^{\bullet}$OH radicals or in the absence of oxygen yielded identical results.

Differences were observed with the two phenylphenols; in the system with *m*-PP, the signal (Fig. 4) was the sum of the two signals due to the adducts $N_3^{\bullet}$ and *m*-PP, whereas the signal of the solution containing *p*-PP mainly revealed the presence of the $N_3^{\bullet}$ adduct, the contribution due to the *p*-PP being very weak.

3.4. Identification of the photoproducts

In contrast with what was obtained upon direct excitation [18], no evidence for formation of quinones was observed either with *m*-PP or *p*-PP. The results relating to the probable nature of photoproducts obtained with *m*-PP and *p*-PP will be reported separately.

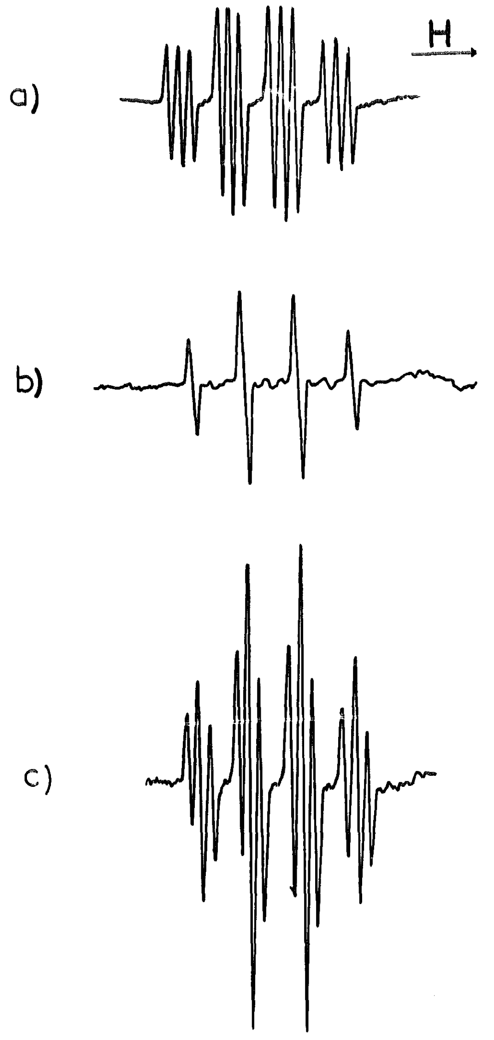
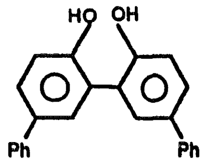


Fig. 4. ESR spectra of adduct with DMPO recorded after irradiation in aerated solutions. (a) Complex concentration 2.5×10^{-4} M ($\lambda > 350$ nm); $a^N(1) = a^H(1) = 14.2$ G; $a^N(2) = 2.7$ G; $g = 2.0060$. (b) *m*-PP concentration, 3×10^{-4} M (unfiltered); $a^N(1) = a^H(1) = 14.2$ G; $g = 2.0060$.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

3.4.1. p-PP

Here, only a small amount of precipitate was produced. The high performance liquid chromatogram of an irradiated solution showed the formation of only one soluble photoproduct provided that the conversion was lower than 30%. After isolation by preparative HPLC, the NMR spectrum (Fig. 5) and the mass spectrum ($m/z = 338$) are in agreement with formation of the dimer 2.2′-dihydroxy 55′diphenylbiphenyl:

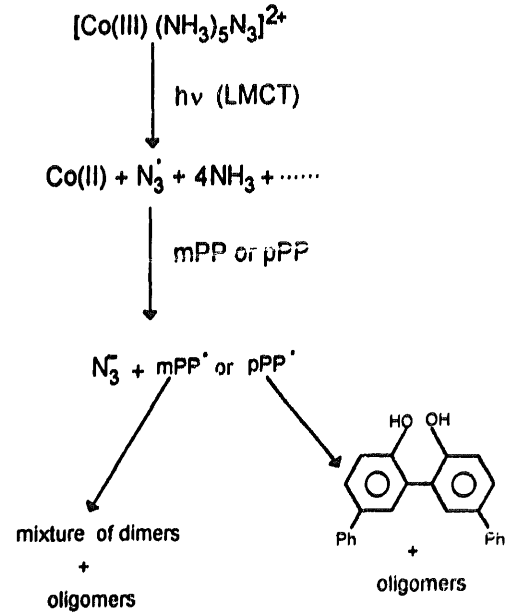


In addition, the mass spectrum of the precipitate showed the presence of different oligomers ($m/z = 338$), trimer ($m/z = 506$) and tetramer ($m/z = 674$) together with peaks at $m/z = -18$. These peaks are assigned to the product of a very easy dehydration due to the proximity of two hydroxyl groups.

3.4.2. m-PP

In this case, more significant yields of precipitate were produced. The mass spectrum of the product revealed the presence of dimers ($m/z = 338$), trimers ($m/z = 506$) and tetramers ($m/z = 674$). The major photoproducts separated by preparative HPLC after dissolution in methanol and characterized by mass spectroscopy ($m/e = 338$) were the dimers (44′, 42′ or 22′), although all attempts to separate these failed.

The overall mechanism can be described as follows:



4. Conclusion

The cobalt(III) complex $[Co(NH_3)_5N_3]^{2+}$ appears to be an efficient and selective photo-oxidative agent of *m*-PP and

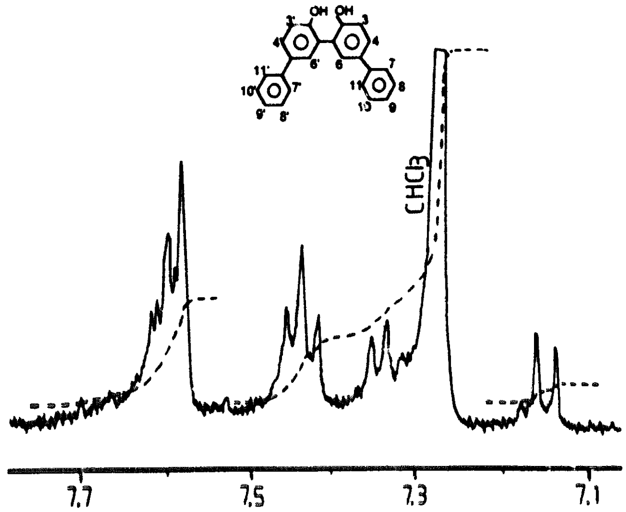


Fig. 5. 400 MHz ^{1}H NMR spectrum of the water-soluble photoproduct of *p*-PP oxidation (in $CDCl_3$): δ = 7.15 (d, H_3 and $H_{3'}$); 7.33 (t, H_9 and $H_{9'}$); 7.44 (t, H_8, $H_{10}H_{8'}$ and $H_{10'}$); 7.59 (s, H_6 and $H_{6'}$); 7.61 (t, H_4 and $H_{4'}$); 7.62 (d, H_7, H_{11} $H_{7'}$ and $H_{11'}$).

p-PP. The exclusive formation of oligomers is observed, with the dimers being the major photoproducts. There is no formation of quinones, in contrast with what has been observed during the direct photo-oxidation of "PP" [18].

ESR and flash photolysis studies suggest that the mechanism of the oxidation goes through the reaction of azide radical on the phenol derivative, giving rise to the corresponding phenylphenoxyl radical via an overall second-order reaction. These radicals are long lived and decay on a millisecond time scale by second-order kinetics. Even though the lifetime of the radicals is sufficiently long, there is no evidence for their reaction with oxygen as seen by the absence of quinone formation. The decay of the phenoxyl radicals by bimolecular reaction appears to account for the major route to the formation of dimers.

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