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Transformation of 2,6-dimethylphenol photoinduced by excitation of $[Co(NH_3)_5N_3]^{2+}$ at 365 nm

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Abstract

Efficient induced oxidation of 2,6-dimethylphenol (DMP) occurred by excitation of azidopentaammine cobalt(III) at 365 nm. The presence of DMP did not affect significantly the quantum yields. The azide radical $N_3^{\bullet}$, produced on irradiation, efficiently reacted with DMP to yield phenoxyl radicals. In aerated as well as in deaerated solution, the coupling of such radicals yielded unequivocally 3,3′,5,5′-tetramethyldiphenoquinone as the predominant photoproduct. Trace concentrations of *para–para* coupling dimer together with polyphenyl ethers were also detected by mass spectrometry. The formation of the substituted diphenoquinone in the absence of oxygen was attributed to a subsequent oxidative pathway involving the starting Co(III) complex. No dimethyl-*p*-benzoquinone or dimethylhydroquinone was formed, suggesting that the cobalt ions play an important role in the observed reactions.

Keywords: Cobalt complex; Photoinduced transformation; 2,6-Dimethylphenol; Azide radical

1. Introduction

An increasing number of papers have been published during the last three decades covering the photochemical behaviour of azidopentaammine cobalt(III) in aqueous solutions [1–5]. On excitation of the complex, i.e. $[Co(NH_3)_5N_3]^{2+}$, involving the ligand to metal charge transfer transition (LMCT) an electron is removed from the azido group and transferred into the cobalt orbital. Thus, the photochemical behaviour is mainly characterized by an efficient redox reaction leading to Co(II) and to the azide radical $N_3^{\bullet}$:

$$[Co(NH_3)_5N_3]^{2+} \xrightarrow{h\nu\ (LMCT)} Co(II) + N_3^{\bullet} + 5NH_3$$

Because of its oxidizing properties (E_0 ($N_3^{\bullet}/N_3^-$) = +1.32 V) [6], much attention has been paid to the azide radical. It has already been used to initiate vinyl monomer polymerization on irradiation with visible as well as with near-UV light [7,8], and to induce a one-electron oxidation when suitable substrates were present in the medium, e.g. indoles [9] and phenol derivatives [10–13].

As a continuation of our work and with the aim of gaining more knowledge on the fate of phenoxyl radical in the presence of metal ions such as Co(III) or Co(II), we have undertaken the study of the oxidation of 2,6-dimethylphenol (DMP) photosensitized by $[Co(NH_3)_5N_3]^{2+}$. DMP was chosen as a model molecule, the methyl groups in the *ortho* positions being expected to make the overall mechanism simpler. This provides us with a better insight into the mechanism of the photosensitized oxidation of phenol derivatives.

2. Experimental section

2.1. Materials

Azidopentaammine cobalt(III), $[Co(NH_3)_5N_3]^{2+}$, was prepared using the procedure described by Linhard and Flygare [14]. The perchlorate salt was recrystallized from mildly acidic solution and dried under vacuum. The spectral properties (UV–visible, IR) of the prepared complex were identical to those reported in the literature ($\epsilon_{302\ nm} = 8600\ M^{-1}\ cm^{-1}$, $\epsilon_{516\ nm} = 280\ M^{-1}\ cm^{-1}$, $\nu(N_3) = 2080\ cm^{-1}$).

2,6-xylenol (DMP) was purchased from Fluka (Puriss) and used without further purification.

A literature procedure was used for the synthesis of 3,3′,5,5′-tetramethyldiphenoquinone (TMDQ) [15].

Other chemicals were of analytical grade and used as received.

The solutions were prepared with double-distilled water, and when necessary they were deaerated prior to irradiation by bubbling Ar for 30 min at 22°C. The ionic strength was

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not controlled. Unless otherwise noted, the pH, equal to 6.4, was the natural pH of the mixture. The solutions were magnetically stirred to ensure homogeneity during the irradiation.

2.2. Procedures

Irradiation at 365 nm was conducted with a high pressure mercury lamp (Osram HBO type, 125 W) equipped with a grating monochromator. The beam was parallel and the reactor was a cuvette of 1 cm, or more generally 2 cm, pathlength. Incident light intensity was determined by chemical actinometry with ferrioxalate ($I_0 \approx 2 \times 10^{15}$ photons cm^{-2} s^{-1}). For preparation purposes, an irradiation set-up delivering higher intensity at 365 nm on a larger volume was used. 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.

Electronic absorption spectra were recorded on a Cary 3 double-beam spectrophotometer and electron spin resonance (ESR) spectra were obtained with a Bruker ER 200 D spectrometer operating at 9.30 GHz with 100 kHz modulation. 2,2-diphenyl picrylhydrazyl was used as an internal standard for the determination of g values. Spin trapping experiments were performed with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trap. An Xe–Hg Hanovia lamp with appropriate cut-off filter was used for irradiation in the ESR spectrometer cavity. Since irradiation at $\lambda \leq 300$ nm generating radicals from the spin trap has been reported elsewhere [16], solutions with DMPO alone were used as blank and no ESR signal was observed under our experimental conditions.

The quantum yield of DMP degradation was determined by high performance liquid chromatography (HPLC) experiments, using a Waters 540 liquid chromatography system equipped with a Waters 990 diode UV–visible detector; a reverse phase Beckman column (250 mm×4 mm) was employed. The quantum yield of complex disappearancewas determined by means of optical density changes at $\lambda = 320$ nm where DMP and potential photoproducts have negligible absorptions, at least in the early stages of the reaction.

The total concentration of Co(II) produced was determined by means of the reaction with SCN^- [17]. The calibration curve was obtained with cobalt(II)-(acetylacetonate)$_2$. Mass spectra were obtained from the Analysis Centre of the University of Orléans. The IR spectra were obtained with KBr pellets using a Nicolet 205X Fourier transform IR spectrophotometer.

3. Results

3.1. Continuous irradiation

The absorption spectrum of the mixture of DMP with $[Co(NH_3)_5N_3]^{2+}$ was shown to be equal to the sum of the component spectra. The ligand field transition ($\lambda_{max} = 516$ nm) of the cobalt complex was not affected by the presence of DMP whereas the maximum of the LMCT transition was slightly blue shifted, or became a shoulder when the concentration of DMP was sufficiently high, as a result of the convolution with the organic compound absorption. Thus, no detectable ground state complexation or chemical reaction was observed under our experimental conditions.

Aerated solutions of azidopentaammine cobalt(III) (2.5×10^{-4} M) and DMP (5.0×10^{-4} M) underwent significant spectral changes on irradiation at 365 nm (Fig. 1). There was a continuous decrease in the CT transition and a new absorption band with a maximum at 420 nm was observed which grew with the irradiation time. The isosbestic points (351 nm and 275 nm) remained present until a significant amount of secondary products was formed. It is worth noting that for prolonged irradiation of the mixture (more than 15 min), a brown precipitate appeared. On irradiation of a solution of cobalt(III) complex alone (5.0×10^{-4} M) for 1 h, there was no sign of any precipitate formation.

Quantum yield data obtained from various solutions under different conditions are given in Table 1. When the irradiation was carried out in aerated solutions, the initial quantum yields of complex disappearance did not appear to be affected by the presence of DMP and did not exhibit a dependence on

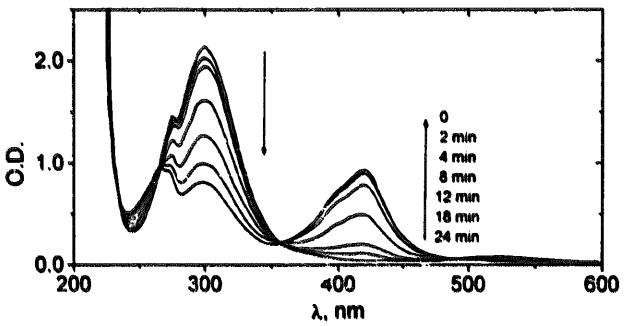


Fig. 1. UV-visible spectra of a deaerated solution of $[Co(NH_3)_5N_3]^{2+}$ (2.5×10^{-4} M) and DMP (5.0×10^{-4} M) irradiated at 365 nm.

Table 1
Quantum yields for $[Co(NH_3)_5N_3]^{+}$ disappearance and Co(II) formation [a]

[DMP] × 10^4	Medium conditions [b]	$\Phi_{complex}$ [c]	$\Phi_{Co(II)}$ [c]
0	Aerated	0.18	0.20
0	Deaerated	0.21	0.22
1.0	Aerated	0.21	0.23
10.0	Aerated	0.22	0.19
5.0	Aerated	0.20	0.23
2.5	Deaerated	0.28	0.29
5.0	pH 2.3 [d], aerated	0.20	0.21
5.0	pH 2.3 [d], deaerated	0.29	0.26

[a] $[(Co(NH_3)_5N_3)^{2+}] = 2.5 \times 10^{-4}$ M.
[b] Unless otherwise noted, the pH of the solution is 6.4.
[c] Error for quantum yields is 10% or less.
[d] The pH was adjusted with $HClO_4$ to ±0.02 units.

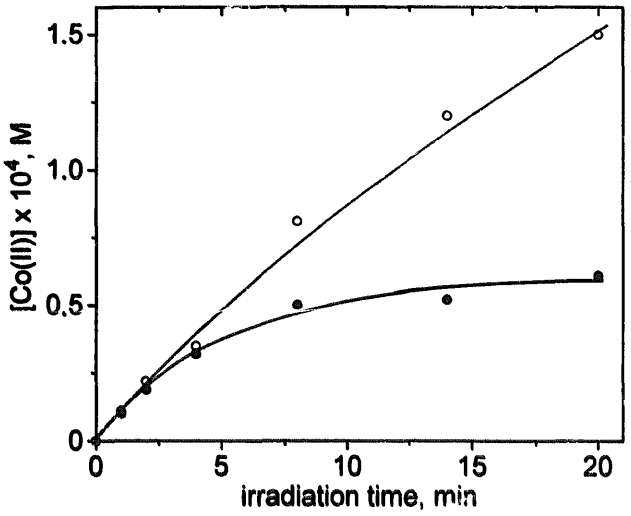


Fig. 2. Co(II) formation in the presence (○) and in the absence of DMP (●) as a function of irradiation time.

acid concentration. Similar results were obtained for the initial quantum yield of Co(II) formation. The initial quantum yield of DMP disappearance measured by HPLC is equal to 0.17, consistent, within the experimental error, with the values obtained for the complex degradation and Co(II) formation.

Photolyses in deaerated solutions at pH 6.0 or 2.3 gave similar spectral changes to those described above but with a higher initial quantum yield: the oxygen has a significant influence on the rate of the photochemical process.

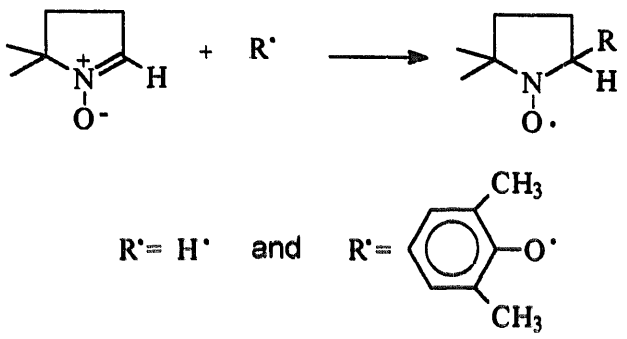
The progress of the reaction was also followed by the dependence of the photoreduction product, i.e. Co(II), on the irradiation time in the presence and in the absence of the organic compound. As shown in Fig. 2, the presence of DMP strongly enhanced the total concentration of Co(II) but, as previously indicated, the quantum yield of Co(II) formation was only slightly higher than that in the absence of DMP.

3.2. Electron spin resonance experiments

The irradiated mixture ($[Co(NH_3)_5N_3]^{2+}$–DMP) was allowed to stay in the dark for about 1 h; afterwards, the suspended solids were separated by centrifugation and dried under vacuum. The ESR spectrum of the solid product displayed a singlet at $g = 2.0036$ suggesting the presence of organic radicals. No improvement in the resolution was observed at low temperature.

In order to obtain information on the nature of the radical intermediates, ESR studies in aqueous solutions were carried out with DMPO as a spin trap. Under our experimental conditions, extensive control experiments clearly demonstrated that the observed adducts did not result from the spin trap photoreactivity.

As depicted in Fig. 3, spectrum a, irradiation of an unfiltered solution of DMP alone, 0.5 mM, in the presence of DMPO, 10 mM, gave a spectrum resulting from a mixture of spin adducts. They corresponded to the adducts with hydrogen H$^\bullet$ ($g = 2.0058$) and dimethyl phenoxyl R$^\bullet$ ($g = 2.0061$) radicals. A relative stability of the DMPO derived radical adducts was observed in the absence of light. No formation of $^\bullet$OH radical was observed: the intensity of the signal was not affected by the presence of isopropanol (2%) used as a scavenger of $^\bullet$OH.



Spin trapping experiments were also performed during irradiation ($\lambda_{exc} \geq 350$ nm) of solutions containing the Co(III) complex. As expected, on irradiation of the mixture only containing $[Co(NH_3)_5N_3]^{2+}$ (0.5 mM) and DMPO (10 mM) a quartet of triplets arising from the DMPO–N_3 radical adduct was observed ($R^\bullet = N_3^\bullet$), $g = 2.0061$ (Fig. 3, spectrum b). The adduct with $N_3^\bullet$ exhibited a fast decay in the absence of light when compared with dimethyl phenoxyl adduct. When DMP was added to the previous mixture, a different spectrum was observed. It consisted of a superimposition of two spin adducts: with azide and dimethyl phenoxyl radical (Fig. 3 spectrum c). It is noteworthy that, under these conditions ($\lambda \geq 350$ nm), no hydrogen atom was formed. Identical results were obtained when the experiments were carried out in the presence of isopropanol (2%) or in the absence of oxygen. This again ruled out any formation of hydroxyl radical.

3.3. Identification of the photoproducts

As previously mentioned, the changes in the UV–visible absorption spectra during irradiation revealed the onset of an absorption at 420 nm. Fig. 4 shows a plot of the optical density values as a function of irradiation time; no induction period was observed. The photoproduct P responsible for this absorption can be, therefore, attributed to a primary product. On further irradiation, the optical density at 420 nm reached a plateau; meanwhile, a considerable amount of suspended particles was observed.

HPLC studies were performed on the irradiated solution as well as on the precipitate. In both cases P appeared to be the dominating product formed on irradiation. By comparison with the authentic sample we synthesized, P was identified as TMDQ.

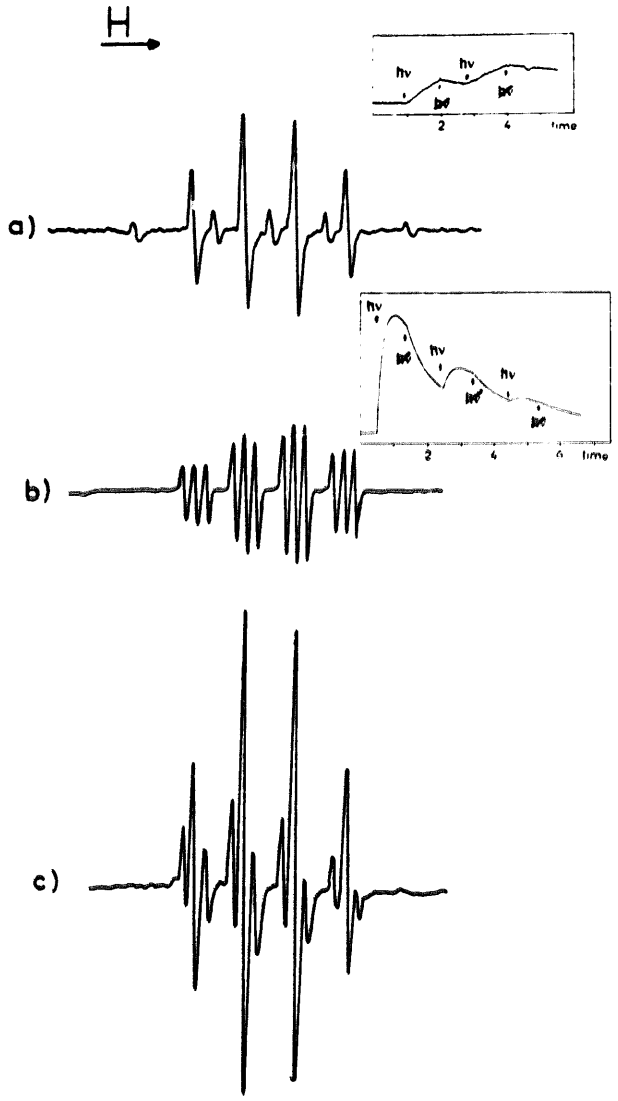
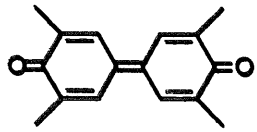


Fig. 3. ESR spectra of adducts with DMPO generated on irradiation in aerated solutions: spectrum a, DMP–DMPO (unfiltered) (DMPO–hydrogen radical adduct, $a^H(2) = 22.2$ G, $a^N(1) = 14.6$ G); DMPO–dimethylphenoxyl radical adduct, $a^H(1) = a^N(1) = 14.1$ G); spectrum b, Complex–DMPO ($\lambda > 350$ nm) (DMPO–azide radical adduct, $a^H(1) = a^N(1) = 14.1$ G, $a^N(1) = 3.24$ G); spectrum c, Complex–DMP–DMPO ($\lambda > 350$ nm).

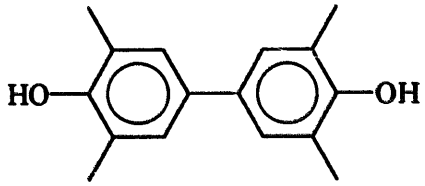


TMDQ

3,3',5,5'-tetramethyldiphenoquinone

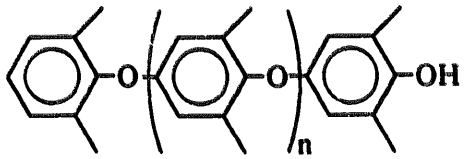
When the irradiation was limited to 5%–10% conversion of DMP and within our experimental uncertainty, the quantum yield of TMDQ formation was measured to be 0.04. No marked change was observed in the absence of oxygen.

The mass spectrometric analysis of the precipitate revealed the presence of oligomerized dimethyl phenols with molecular weights up to 482 (tetramers) together with TMDQ. All the attempts to detect these products by HPLC failed, except for the *para–para* bonded dimer which was present in trace concentrations.



3,3',5,5'-tetramethyl 4,4'-dihdroxybiphenyl

The latter product was stable in the medium and no evidence for its oxidation into TMDQ was observed. Since the two *ortho* positions were occupied by methyl substituents, the oligomers, formed upon irradiation, were expected to be the following polyphenyl ethers:



n<3

Moreover, the treatment of the precipitate with potassium thiocyanate gave evidence for the presence of a large percentage of cobalt(II). The metal ions Co^{III} or Co^{II} seemed to be associated with the organic constituent of the precipitate.

It is of interest to note that, in contrast to the results obtained on direct irradiation of DMP ($\lambda_{exc} = 254$ nm) [18], neither dimethyl *p*-benzoquinone nor dimethylhydroquinone was formed, even in the presence of oxygen. Control experiments carried out by mixing the latter products with Co(III) complex or cobalt(II)(acetylacetonate)$_2$ did not reveal any chemical reaction at room temperature and their absence cannot be attributed to some subsequent thermal degradation. They are perfectly stable in the presence of such coordination compounds. From the above information it clearly appears that the attack of the phenoxyl radical by oxygen is averted by the presence of cobalt(III) and cobalt(II) species.

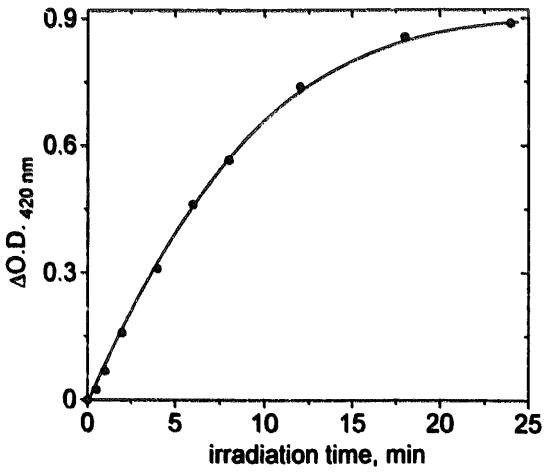
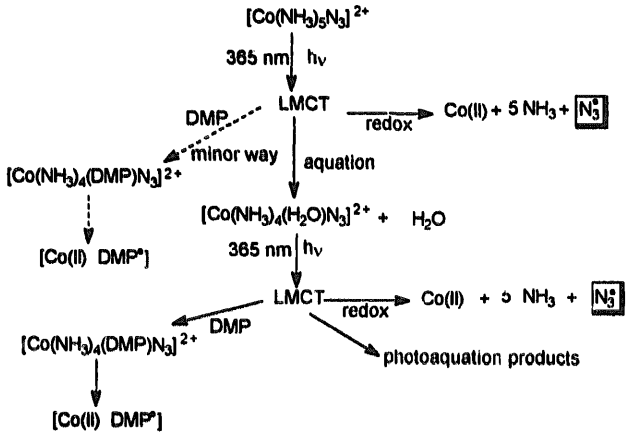


Fig. 4. The optical density changes at $\lambda = 420$ nm as a function of irradiation time.

4. Discussion

The quantitative measurements of initial quantum yields described above make evident that the presence of DMP in aerated solution does not significantly affect the complex disappearance or Co(II) formation. However, the examination of Fig. 2 reveals that, for longer irradiation times, additional pathways for Co(II) formation, probably involving the irradiation of secondary photoaquation products, must be suggested.

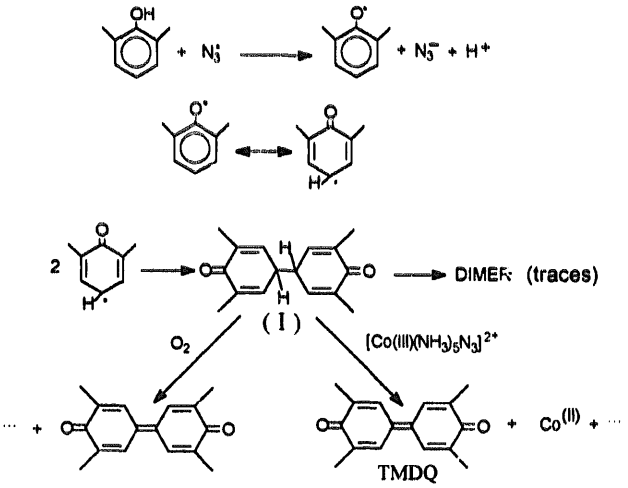
It was noted earlier that, in the precipitate, stable organic radicals were detected. The interesting possibility arises that Co(II), as already stated for other radicals [19,20], might stabilize radicals such as DMP$^{\bullet}$. Although the nature of intermediates formed after the irradiation has not been established definitely, a possible explanation might lie in a complexation of DMP with the LMCT excited state of the aquation cobalt photoproducts $[Co(NH_3)_4(H_2O)N_3]^{2+}$ and/or $[Co(NH_3)_5(H_2O)]^{3+}$. Analogous complexation might be also suggested with the excited state of the starting complex. However, since the quantum yield of $[Co(NH_3)_5N_3]^{2+}$ disappearance is not influenced by the presence of DMP, this would only represent a minor path for LMCT state deactivation.



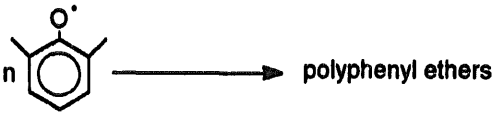
Regarding the formation of the photoproducts, the persistence of well-defined isosbestic points throughout the irradiation is strongly indicative of a main mode of photodecomposition which mainly leads to the formation of substituted diphenoquinone. The loss of such isosbestic points is only observed for prolonged irradiations. The overall mechanism involving $N_3^{\bullet}$ is displayed in the next column.

The azide radical generated on excitation of the azidopentaammine cobalt(III) complex can be involved in a direct electron transfer. Such a process, in the presence of DMP, leads predominantly to the dimethyl phenoxyl radical which was clearly detected by ESR spin trapping experiments.

The radical can dimerize to give the substituted intermediate I which may rearrange to the dimeric phenol. However, it is clear from the presence of the latter product in trace concentrations that this rearrangement only represents a minor path. In the presence of oxygen or other oxidizing agent such as Co(III) species, I leads to the symmetric diphenoquinone. From the fact that the dimeric phenol does not lead to TMDQ by a thermal oxidative process under our experimental conditions, it may be concluded that the redox potential of the cobalt(III) complex is high enough to oxidize the intermediate I but not sufficient to induce the oxidation of the C–C dimeric phenol into substituted diphenoquinone. The presence of oxygen is not necessary to the formation of the latter product but significantly decreases the quantum yield of cobalt(III) complex disappearance. This can be interpreted in terms of two competitive reactions: oxidation of I by oxygen and by azido pentaammine cobalt(III). The second reaction takes part in the additional formation of Co(II) ions.



Moreover, the mass spectrometric results obtained in aerated as well as in deaerated solution, revealing evidence for high molecular weight, require that the dimethyl phenoxyl radical disappears by oligomerization. This process leads to the only formation of polyphenylethers.



What perhaps is most significant is the fact that the same sort of photoproducts is formed under argon or oxygen and neither 2,6-disubstituted benzoquinone nor hydroquinone was formed. The failure of oxygen to oxidize the phenoxyl radical into benzoquinone as generally observed [21] seems to indicate that cobalt ions, probably Co(II), play an important role throughout the process.

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