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Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 217–222

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

After-effect in the oxidation of hydroquinone photoinduced by cobalt azide complex

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Abstract

The mechanism of the oxidation of hydroquinone (QH_2) photoinduced by the azide complex has been studied in aqueous acidic solution. Such an oxidation is shown to proceed selectively through an electron transfer reaction producing the semiquinone radical. 1,4-Benzoquinone (Q) appears to be the primary product in the presence and in the absence of oxygen. The ratios $[Co(II)]_{form}/[QH_2]_{disap}$ and $[Q]_{form}/[QH_2]_{disap}$ are found to be equal to 2 and 1, respectively. This fits well with the disproportionation of the semiquinone radical. The resulting quinone is unstable in acidic medium and reacts with the azide anion (N_3^-) to generate azidohydroquinone and azidobenzoquinone. An overall mechanism describing the photochemical and the dark reaction has been established. © 1997 Elsevier Science S.A.

Keywords: Hydroquinone; Photoinduced oxidation; Cobalt azide complex; Semiquinone radical

1. Introduction

It is well known that when the cobalt(III) azidopentaammine complex is irradiated into the ligand-to-metal charge transfer transition ($N_3^- \rightarrow Co(III)$), the azide radical $N_3^{\bullet}$ is generated together with the reduced metal Co(II) [1,2]. The selective and high reactivity of $N_3^{\bullet}$ towards aromatic compounds [3], coupled with the high quantum yield of the redox process have made $[Co(NH_3)_5N_3]^{2+}$ an attractive complex to photoinduce oxidations.

In previous work, we reported the oxidation of various phenol derivatives induced by excitation of $[Co(NH_3)_5N_3]^{2+}$ in aqueous solution [4–6]. The electron transfer process was clearly established by direct observation of the corresponding radicals. High rate constants of the bimolecular decays were measured. The coupling of the phenoxyl radicals occurred with the same efficiency in deaerated as well as in aerated solution leading to dimers and oligomers. A striking result was the absence of the corresponding quinones which reflected the inhibition of the reaction between oxygen and the phenoxyl radical. This result was in favour of the ‘‘protection’’ of the radical by cobalt(II) by a cage phenomenon preventing it from the attack of molecular oxygen and favouring the formation of dimers.

With the aim of considering a general strategy for this reaction to be extended to other compounds, we chose to investigate the photoinduced oxidation of a highly oxidizable substrate, hydroquinone. The dimeric form of such a compound (2,5,2′,5′-tetrahydroxybiphenyl) can be formed upon direct photolysis. Its formation was faster when benzoquinone was initially present in the solution whereas it was inhibited in the presence of 3-chlorophenol [7]. The triplet state of hydroquinone was shown to be the precursor of such a coupling reaction.

2. Experimental

2.1. Reactants and standards

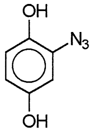
The cobalt(III) complex, $[Co(NH_3)_5N_3](ClO_4)_2$, was available from previous work [4]. The IR and UV–visible spectra of the purified complex agreed well with the published data [8].

Hydroquinone was obtained from Merck (> 99.5%) and used without further purification.

1,4-Benzoquinone, purchased from Fluka (purum, ≥ 98%), was vacuum sublimed and was stored in the refrigerator.

Azidohydroquinone and 2-azido-1,4-benzoquinone were synthesized as follows:

- *Azidohydroquinone (QH_2N_3)*



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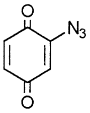
PII S1010-6030(97)00135-4

To a yellow solution of 1,4-benzoquinone (13 mmol) in distilled ethanol (50 ml) was slowly added a freshly prepared acidic aqueous solution of sodium azide (1.0 g NaN_3 in 10 ml, pH ≈ 1.2). The mixture was stirred for 20 min at room temperature. The solution colour turned deep red. High performance liquid chromatography (HPLC) analyses of the mixture during the progress of the reaction showed the presence of several products among them the expected azidohydroquinone which was found to be the major product. The evaporation of the solvent was carried out under reduced pressure with a rotatory evaporator at ambient temperature. The desired product was isolated from the crude mixture by chromatography on silica (eluent, hexane/AcEth 7/3 by volume). UV (λ_{max}): 249 nm, 309 nm. ^{1}H NMR ($CDCl_3$), δ ppm: 6.53 (dd, 1H, $J = 8.8$ and 2.6 Hz), 6.62 (d, 1H, $J = 2.6$ Hz), 6.79 (d, 1H, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$), δ ppm: 105, 113, 117, 127, 1425, 150. Mass spectrum, m/e: 151 (M^+), 123, 95, 82, 67. IR (KBr), ν (cm^{-1}): 2140 cm^{-1} (N_3).

- *2-Azido-1,4-benzoquinone (QN_3)*



During the progress of the above synthesis and in the early stages of the reaction, the HPLC analyses clearly showed the formation of another major product which rapidly disappeared when an excess of sodium azide was used. In order to isolate this product, an analogous procedure was followed by using a less concentrated solution of the reactant, N_3^- (0.04 g in 10 ml of distilled water, pH ≈ 1.2). The major product, identified as azidobenzoquinone, was then isolated in low yield by chromatography on silica (eluent, hexane/AcEth 7/3 by volume). It should be noted that the 2-azido-1,4-benzoquinone appeared to decompose rapidly at room temperature. The mass and NMR spectra were thus performed immediately after synthesis. UV (λ_{max}): 242 nm, 400 nm. ^{1}H NMR ($CDCl_3$), δ ppm: 6.42 (dd, 1H, $J = 2.27$ Hz), 6.95 (d, 1H, $J = 9.19$ Hz), 6.79 (d, 1H, $J = 10.1$ Hz). Mass spectrum, m/e: 121 ($M^+ - 28$), 93, 67, 65. IR (KBr), ν (cm^{-1}): 2140 cm^{-1} (N_3), 1680 cm^{-1} (C=O).

Other chemicals were analytical grade and used as purchased. Water was purified by a Millipore Milli-Q system. The pH of the solution was obtained by addition of a small amount of concentrated $HClO_4$. The pH meter was an ORION research 811, used with an ORION electrode. The solutions were freshly prepared and, when necessary, they were deaerated prior to irradiation by bubbling either Ar or N_2 for 30 min at 22°C.

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 cell of 1 cm path length. Incident light intensity was determined by chemical actinometry with ferrioxalate ($I_o \approx 6.5 \times 10^{14}$ photons cm^{-2} s^{-1}).

Flash photolysis studies used a Nortech FPX-1 flash lamp emitting 130 J, with a rise time of 10 μs. Transient absorption spectra were recorded using a standard lamp–source–monochromator–photomultiplier set-up and the photomultiplier signal passed to a Technotronic 564 storage oscilloscope. Appropriate filters ($\lambda > 320$ nm) were used to prevent the direct excitation of hydroquinone.

Electronic spectra were recorded on a CARY 3 double beam spectrophotometer using 1.0 cm quartz cells.

The quantum yields of hydroquinone disappearance and 1,4-benzoquinone formation were determined by HPLC experiments using a Waters 540 liquid chromatography system equipped with a Waters 990 diode UV–visible detector. The quantum yield of complex disappearance and Co(II) formation were determined as described elsewhere [4,9].

The infrared spectra were run as KBr pellets using a Nicolet 2105X Fourier Transform IR spectrophotometer.

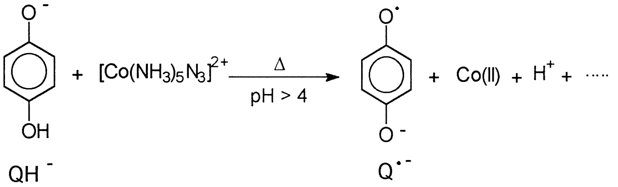
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a BRUCKER 300MSL (Fourier Transform) spectrometer in deuterated chloroform purchased from Aldrich.

GC–MS analyses were performed on a Hewlett-Packard 5985 model equipped with a capillary column Supelco (30 m length, i.d. 0.25 mm and a film thickness of 25 μm). The injection and detector temperatures were 250 and 200°C, respectively. A high grade helium was used as a carrier gas.

3. Results

3.1. Continuous irradiation

The cobalt(III) complex reacted with hydroquinone (QH_2) in the dark at the natural pH of the mixture, pH ≈ 6.5, to yield 1,4-benzoquinone (Q) and cobalt(II) as the dominant products. During the course of the reaction, small but increasing absorbance with maxima at 405 and 430 nm could be detected. These features indicated the formation of the well-characterized semiquinone anion radical ($Q^{\bullet -}$) [10]. This thermal behaviour was found to be strongly pH dependent in the range 4 < pH < 9. In contrast, acidic mixtures at pH < 4 did not show any significant chemical reaction within several hours. An easy oxidation of the monoanionic form of hydroquinone (QH^-) by the cobalt(III) azidopentaammine complex appears to be a plausible explanation of this thermal behaviour.



In acidic medium, no evidence for ground state complexation was found when the UV–visible spectrum of the mixture (hydroquinone/complex) was compared to the individual

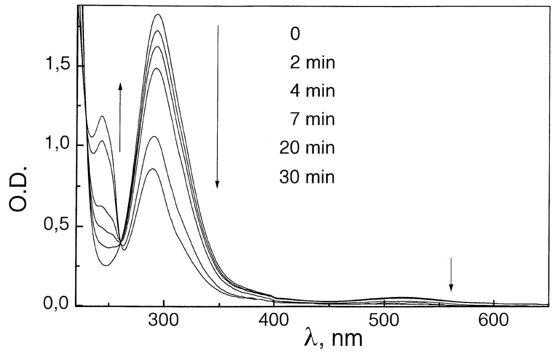


Fig. 1. Spectral evolution of a solution of $[Co(NH_3)_5N_3]^{2+}$ (2.0×10^{-4} M) and hydroquinone (2.0×10^{-4} M) upon irradiation at 365 nm.

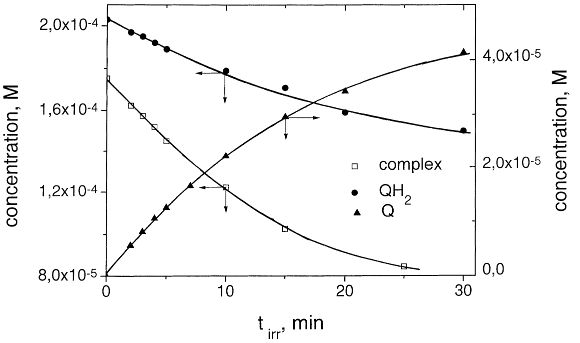


Fig. 2. Kinetics of formation of benzoquinone (Q) and disappearance of the Co(III) complex and hydroquinone (QH_2) as a function of irradiation time.

spectra of the components. This again ruled out any significant dark reaction under our experimental conditions.

Continuous irradiation at 365 nm of $[Co(NH_3)_5N_3]^{2+}$ (2.0×10^{-4} M) in the presence of hydroquinone (2.0×10^{-4} M) induced important spectral changes (Fig. 1): (i) the disappearance of 302 and 520 nm bands; (ii) a new absorption band at 246 nm which was easily attributed to the formation of 1,4-benzoquinone and which continuously grew with irradiation time; (iii) a well-defined isosbestic point is also observed ($\lambda = 263$ nm).

Since the cobalt(III) complex and hydroquinone had no appreciable absorption at 246 nm, the quantum yield of the quinone formation was determined from the optical density changes at that wavelength. The progress of the photochemical reaction was also followed by HPLC measurements. They showed the formation of 1,4-benzoquinone as the main photoproduct. However, because of the subsequent thermal evolution of the irradiated solution (see below), these analyses were carried out immediately after irradiation.

Fig. 2 shows that the hydroquinone disappears quantitatively to yield 1,4-benzoquinone. Throughout the irradiation, the ratio $[Co(II)]_{formed}/[QH_2]_{disappeared}$ remained equal to 2. The different quantum yields are presented in Table 1. It is worth noting that no direct or induced photoreactivity of quinone was observed under our experimental conditions. This was confirmed by irradiating the azide complex at 365 nm in the presence of benzoquinone; no disappearance was observed.

On the basis of the above results, it can be concluded that the presence of hydroquinone does no affect the intrinsic photochemistry of the azidopentaammine cobalt(III) complex. Within the experimental errors, the hydroquinone disappearance quantum yield appeared to be quite similar to that of quinone formation and about two times smaller than the quantum yield of the photoredox process, i.e. formation of Co(II). Neither oxygen nor the initial concentration of hydroquinone affects the values of the quantum yields.

3.2. Flash photolysis

Flash photolysis experiments were carried out under conditions where the cobalt azide complex was the only absorbing species ($\lambda > 320$ nm). The flash photolysis of a deaerated solution of cobalt(III) complex (5.0×10^{-5} M) and hydroquinone (1.0×10^{-4} M, pH = 1.3) produced the semiquinone radical which was observed 200 μs after the flash and easily identified from its characteristic absorption spectrum ($\lambda_{max} = 410$ nm and 390 nm (sh)). Fig. 3 shows the radical absorption spectra obtained at different millisecond time scale intervals. Its decay is kinetically of second order, $2k/\varepsilon_{410\,nm} = 3.6\times10^5\ s^{-1}$ cm, and did not show any dependence on oxygen concentration. From the given extinction coefficient at 410 nm ($\varepsilon = 5500\ mol^{-1}\ cm^{-1}$) [10], the bimolecular rate constant was found to be $1.0\times10^9\ mol^{-1}\ s^{-1}$. This was in good agreement with that measured in reported pulse radiolysis studies [10].

3.3. Subsequent thermal reactions

As mentioned previously, 1,4-benzoquinone is the main organic product observed upon 365 nm irradiation of $[Co(NH_3)_5N_3]^{2+}$ in the presence of hydroquinone and in acidic medium. However, significant evolution was observed when an irradiated solution was allowed to stand in the dark for several minutes. HPLC analysis showed that the quinone disappeared while two other products with longer retention

Table 1
Results from continous irradiation of $[Co(NH_3)_5N_3]^{2+}$ in the presence and in the absence of hydroquinone at 365 nm

	$[QH_2]$/M	$\Phi_{complex\ disap}$	$\Phi_{QH2\ disap}$	$\Phi_{Q\ form}$	$\Phi_{Co(II)\ form}$
Aerated solution, pH 1.3	0	0.22			0.20
	2.0×10^{-4}	0.21	0.09	0.10	0.19
Deaerated solution, pH 1.3	0	0.21			0.21
	2.0×10^{-4}	0.20	0.10	0.11	0.18

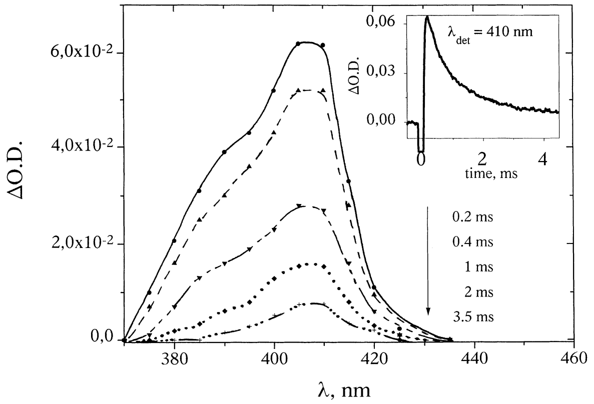


Fig. 3. Spectrum obtained on flash photolysis of a deaerated aqueous solution of Co(III) azide complex and hydroquinone. The insert shows a typical trace recorded at 410 nm. [Co(III) complex] $=5.0\times10^{-5}$ M, [hydroquinone] $=1.0\times10^{-4}$ M.

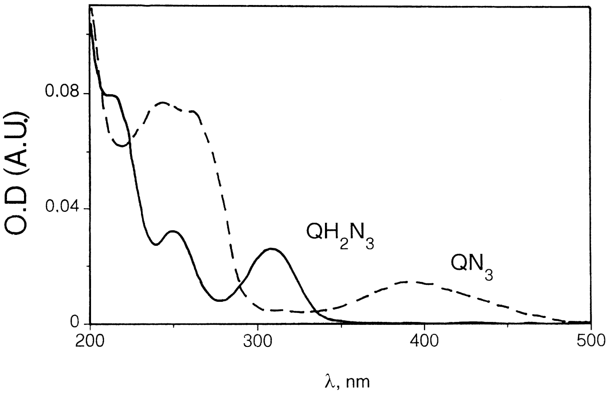


Fig. 4. UV–visible absorption spectra of azidohydroquinone (QH_2N_3, ———) and azidobenzoquinone (QN_3, - - -).

times were formed. Their absorption spectra are given in Fig. 4. They were synthesized and identified as azidohydroquinone and 2-azido-1,4-benzoquinone, respectively (see Section 2). This clearly indicates a conversion of benzoquinone into such products. It must be pointed out that the mixture of $[Co(NH_3)_5N_3]^{2+}$ and quinone did not show any thermal evolution when kept in the dark at room temperature.

It has been reported that 1,4-benzoquinone reacts with hydrazoic acid (HN_3) in benzene and leads to the formation of azidohydroquinone [11]. To our knowledge, the formation of azidobenzoquinone has never been reported in the literature. Analogous azidoquinone derivatives were generally obtained by the displacement of the chloride by the azide group from the corresponding chloroquinones [12–15]. Hence, we decided to investigate the mechanism of azidobenzoquinone formation in the benzoquinone/azide anion system.

At room temperature, 1,4-benzoquinone reacted thermally with sodium azide in acidic medium to give three major products: azidohydroquinone (QH_2N_3), hydroquinone (QH_2) and azidobenzoquinone (QN_3) Fig. 5. Other minor products with longer retention times were also observed but they appeared to be rather unstable under our experimental conditions. Similar results were observed in the presence and in the absence of oxygen. The formation of the three products was followed by HPLC measurements, their evolution as a function of reaction time is reported in Fig. 6. It clearly appears that QH_2N_3 accumulates in the solution whilst QH_2 reaches a limiting value. Such a limiting value remains the same throughout the reaction. What perhaps is most significant is the fact that the QN_3 concentration reaches a maximum value and decreases quite rapidly. The rate of this disappearance was sodium azide concentration dependent. By using a high concentration, with respect to benzoquinone concentration (>5 times), it was not possible to detect any traces of QN_3. This is probably the reason why such a product was not observed in the previously reported work [11].

4. Discussion

On the basis of the above experimental observations, we will discuss the mechanism of the photoinduced oxidation of hydroquinone in terms of two different steps, the photochemical and the subsequent thermal reaction.

4.1. Photochemical reaction

The photochemistry of the cobalt(III) azidopentaammine complex in aqueous solution as far studied shows that the

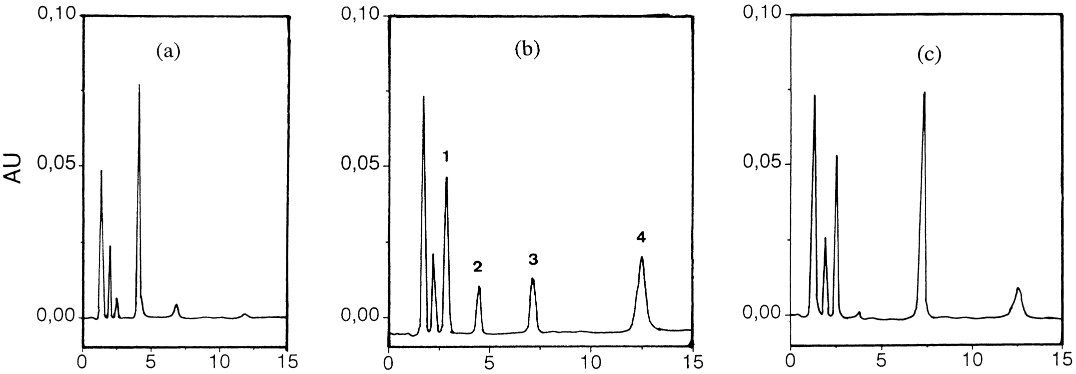


Fig. 5. High performance liquid chromatograms observed on products of thermal evolution of aerated acidic solutions of quinone (10^{-4} M) and N_3^- (2.0×10^{-4} M): (A) initial mixture; (B) 1 h 15 min; (C) 8 h 30 min. 1, hydroquinone; 2, benzoquinone; 3, azidohydroquinone; 4, azidobenzoquinone. $\lambda_{detection}=220$ nm.

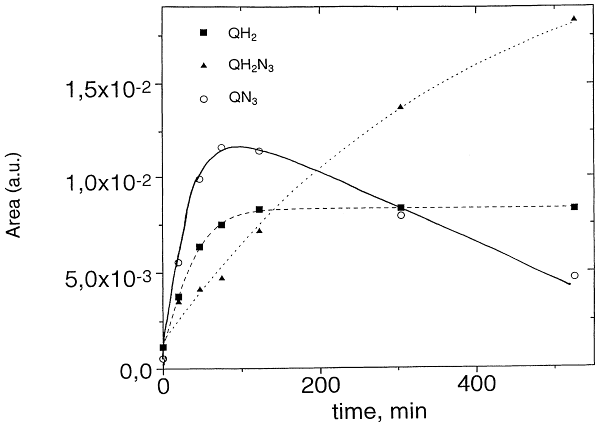


Fig. 6. The variation of the distribution of the products as a function of reaction time.

process is dominated by the photoredox reaction leading to Co(II) and the azide radical $N_3^{\bullet}$. In acidic medium, the presence of hydroquinone does not significantly affect this behaviour. The 365 nm irradiation of a mixture of $[Co(NH_3)_5N_3]^{2+}$ and hydroquinone (QH_2) leads to the quite important formation of *para*-benzoquinone (Q) and to the reduced metal centre Co(II). A comparison of the different quantum yields revealed the following relationships:

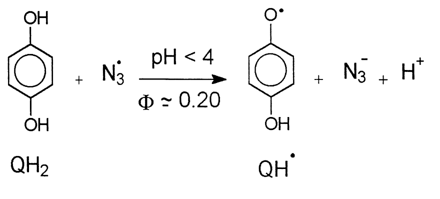
$$\Phi_{(QH_2\ \mathrm{disappearance})} = \Phi_{(Q\ \mathrm{formation})} = \frac{\Phi_{(Co(II)\ \mathrm{formation})}}{2} = \frac{\Phi_{(\mathrm{Complex\ disappearance})}}{2}$$

The quantitative formation of Q came from the oxidation of QH_2 by an electron transfer process leading to the formation of the semiquinone radical. Indeed, Alfassi and Schuler [3] reported that upon pulse radiolysis, the azide radical $N_3^{\bullet}$ selectively reacts with hydroquinone via an electron transfer reaction. Evidence for the semiquinone radical ($QH^{\bullet}$) formation in our system came from flash photolysis experiments. The disproportionation accounts for the second-order dependence of the disappearance rate on the semiquinone radical concentration. The observation that the Φ_{QH_2} and Φ_Q values are equal to the ratio $\Phi_{Co(II)}/2$ is in agreement with such a reaction.

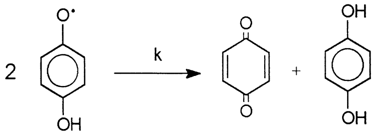
Hence we can put forward the following mechanism for the photochemical formation of benzoquinone

$$[Co(NH_3)_5N_3]^{2+} \xrightarrow[365\ \mathrm{nm}]{h\nu} Co(II) + N_3^{\bullet} + 5\ NH_3 \qquad (1)$$

$$\Phi \simeq 0.20$$



(2)



(3)

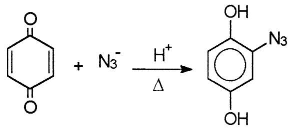
In contrast to the results obtained with phenylphenols and 2,6-dimethylphenol substrates [4–6], it is worth noting: (i) that there is no evidence for the semiquinone radical–metal ion pair formation as evidenced by the similar values of the bimolecular rate constant in the presence and in the absence of cobalt ions; (ii) the lack of any detectable traces of the dimer 2,5,2′,5′-tetrahydroxybiphenyl.

4.2. Thermal reaction

The primary product, quinone, undergoes an efficient thermal reaction. It only occurred after irradiation and involved the azide anion formed during the photochemical process (reaction 1). This mainly leads to the formation of three major products: hydroquinone (QH_2), azidohydroquinone (QH_2N_3) and azidobenzoquinone (QN_3).

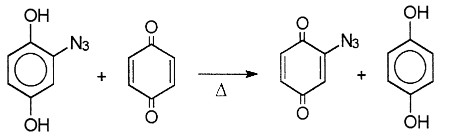
This complex behaviour may involve different reactions.

It is well known that 1,4-benzoquinone reacts with hydrazoic acid (HN_3) to yield azidohydroquinone. In this process benzoquinone behaves as an electron acceptor towards the azide anion.



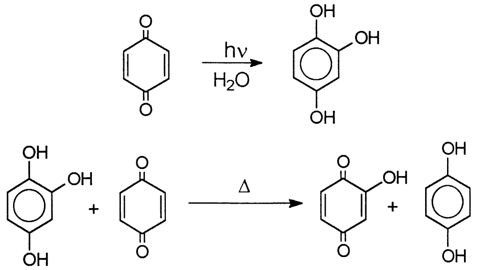
(4)

An intermolecular redox reaction involving QH_2N_3 and Q leads to the formation of QN_3 and QH_2. The concentration of the latter products rapidly reaches a limit value corresponding to the complete uptake of the starting quinone.



(5)

This reaction was written by analogy with what was previously described for the subsequent thermal reaction occurring after benzoquinone photolysis in acidic or alkaline medium [16–18].



When N_3^- is present in excess, the disappearance of QN_3 observed in Fig. 6 could be explained by a reaction similar to that written for quinone (reactions 4). It would mainly lead to diazidohydroquinone. Under our experimental conditions the generation of such a product was not categorically observed. The diazido derivatives are known to undergo an easy cleavage [19].

5. Conclusion

The oxidation of hydroquinone photoinduced by excitation of $[Co(NH_3)_5N_3]^{2+}$ involved the attack of the azide agent $N_3^{\bullet}$ with the formation of a semiquinone radical. However, contrary to what was observed in previous work, no dimer was formed and the main photoproduct was benzoquinone which, in the presence of the azide anion, underwent a thermal reaction leading to the formation of the azidohydroquinone and azidobenzoquinone.

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