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Sensitized photooxidation of 2,3- and 2,7-dihydroxynaphthalenes in alkaline water

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Abstract

The Rose Bengal sensitized photooxidation of 2,3-dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN) in pH 12 water yields 1,1′-dimeric products, the appearance of which can be explained by the coupling of radicals formed by primary electron transfer from the anionic form of each starting dihydroxynaphthalene to singlet molecular oxygen or to the excited sensitizer. The dimer from 2,7-DHN is further oxidised during the irradiation to 6,7-dihydroxyperylene-1,12-quinone (DHPQ). In the case of 2,3-DHN, phthalic acid has also been detected. © 1998 Elsevier Science S.A.

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1. Introduction

Hydroxylated aromatic contaminants are widely distributed in water and soils [1,2]. Phenols, polyphenols, naphthols and their derivatives are raw materials and byproducts in the synthesis of many pesticides, and can be frequently found in industrial wastes and petroleum spills. Furthermore, chlorinated aromatic contaminants and polyaromatic hydrocarbons produce phenolic compounds under environmental conditions [3–5], and naphthalene pesticides such as 2-naphthyloxyacetic acid and 1-naphthol methyl carbamate are also degraded to the corresponding naphthols, and then to higher hydroxylated compounds, among other products [6,7]. A route for the natural degradation from the environment of all these contaminants, that can be the most important one under favourable conditions, is the photochemical oxidation, i.e., the combined action of light and oxygen [5]. In order to understand and, hence, to be able to control this photochemical decay, the mechanism and kinetics of the reactions involved in the light-induced processes are being studied in detail, in order to determine both the structure of the photoproducts and the photodegradation rates of the contaminants, under different experimental conditions [8–11]. From a practical point of view, the knowledge of said structures is of utmost interest, because the photoproducts derived from the contaminants can also be contaminants, and then the phototransformations would only produce toxicity changes.

When visible light, oxygen, and a sensitizer (i.e., a dye or even a coloured contaminant) coincide in a liquid medium, singlet molecular oxygen [$O_2(^1\Delta_g)$] can be generated. The [$O_2(^1\Delta_g)$]-mediated photooxidation appears as a very promising option for the photodegradation of contaminants. We have previously studied the kinetics of this type of photooxidation applied to several dihydroxynaphthalenes [12], and have found that in water solution the photooxidation rate constants of these compounds are in general much higher in pH 12 solution, i.e., when the hydroxy substituents are in ionized form. This pH dependence can be used for the programmed photodegradation of these dihydroxynaphthalenes. However, the full understanding of the photodegradation process requires the identification of the photooxidation products. In the present paper we report for the first time on the analysis of the photoproducts found in the Rose Bengal sensitized photooxidation in alkaline water (pH 12) of 2,3-dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN), two representative compounds with the hydroxy substituents in the same or in different aromatic nucleus.

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2. Experimental

2.1. Materials

2,3-Dihydroxynaphthalene and 2,7-dihydroxynaphthalene (both Fluka) were purified by recrystallization from hexane. The photosensitizer Rose Bengal, bound to polystyrene or as free dye (both Fluka), was used as received. Water was double distilled. Organic solvents were distilled.

For comparative purposes three compounds were synthesized. (a) 2,2′,3,3′-Tetrahydroxy-1,1′-binaphthyl (Di-2,3-DHN) was obtained by solid phase oxidation of 2,3-DHN with $FeCl_3$ [13]; UV, λ_{max} (nm) (log ε): in EtOH, 234 (4.87), 286 (3.98), 298 (3.92), 312 (3.69), 327 (3.69); in pH 12 water, 248 (4.82), 339 (3.92); MS of the tetramethylated derivative, *m/z* (%): 376 (4), 375 (27), 374 (M^+, 100), 328 (43), 285 (18). (b) 2,3-Dihydroxy-1,4-naphthoquinone (isonaphthazarine) was synthesized by hydrogen peroxide oxidation of 2-hydroxy-1,4-naphthoquinone (Aldrich) [14,15]; UV, λ_{max} (nm) (log ε): in EtOH, 274 (4.29), 333 (3.22), 438 (3.12); MS of the dimethylated derivative, *m/z* (%): 218 (M^+, 33), 203 (67), 173 (74), 147 (35), 104 (100). (c) 6,7-Dihydroxyperylene-1,12-quinone (DHPQ) was obtained by air oxidation of 2,7-DHN in MeOH–water 1:9 v/v [16]; UV, λ_{max} (nm) (log ε): in $CHCl_3$, 294 (4.43), 327(4.41), 694 (3.70); in basic EtOH, 332 and 610 nm.

2.2. Photooxidations

A solution in alkaline water (250 ml, pH 12 with NaOH) containing 2,3-DHN (100 mg, 2.5×10^{-3} M) and Rose Bengal bound to polystyrene (150 mg), or 2,7-DHN (28 mg, 7×10^{-4} M) and Rose Bengal (ca. 5×10^{-6} M, maximum visible absorbance at 546 nm of ca. 0.5) was placed into a pyrex flask and irradiated with the light from an air-cooled 200-W tungsten lamp, while bubbling air and with stirring. Flask and lamp were located in the focal points of an elliptical reflector [17]. The photooxidation reactions were followed by UV–vis absorption spectroscopy after dilution with water (separating the sensitizer by filtration in the case of the irradiation of 2,3-DHN), and by thin layer chromatography (TLC) (silica gel Merck 60 F_{254}, $CHCl_3$–EtOH 4:1 v/v as eluent, detection with 254 or 366 nm light) of the ethyl acetate extracts of acidified samples.

2.3. Products analysis

The photoproducts from each DHN were analyzed in two irradiated samples with absorption spectral changes at 340 nm of ca. 20 and 80%, in order to study the evolution of the primarily obtained products. Each reaction mixture was acidified (HCl) and extracted (ethyl acetate); the extract was dried and the solvent was vacuum evaporated. The residue was analyzed by TLC as before. In the case of 2,3-DHN, GC-MS analysis of the isolated reaction mixture, its methylated form (obtained with diazomethane in methanol), the ethyl acetate extracts of the separated TLC spots, and their methylated forms (obtained as before) were also carried out. Conditions: HP G1800A (GCD system) gas chromatograph equipped with a mass detector in the EI mode (ionization energy 70 eV), scanning the range 40–425 amu, and controlled by an HP 3365 ChemStation software; a laboratory-made capillary column (25 m × 0.32 mm × 0.8 μm) coated with methylsilicone OV-1, was employed, using helium (0.8 ml min^{-1}) as carrier gas; temperature program from 80 to 220°C at 5°C min^{-1}, inlet block and detector at 250°C, split mode. Percentages of products were based on the total area of the chromatographic peaks (total ion current, TIC), including the peak area of the residual 2,3-DHN. In the case of 2,7-DHN, the irradiation product was separated and purified by preparative TLC.

Alkaline solutions of 2,3-DHN are stable in the dark or when irradiated in the absence of sensitizer, at least during the irradiation times herein used. On the contrary, alkaline solutions of 2,7-DHN (7×10^{-4} M) become blue (absorbance at 600 nm ca. 0.2) after 1 h of stirring in the dark, while bubbling air.

3. Results and discussion

3.1. Sensitized photooxidation of 2,3-dihydroxynaphthalene

The photooxidation of 2,3-DHN in alkaline water was carried out with Rose Bengal bound to polystyrene as sensitizer because this form of the dye can be readily separated from the reaction medium by filtration, facilitating the analysis of the reaction products. The free dye generates singlet molecular oxygen with quantum yields in the range 0.70–0.81 [18,19], depending on the solvent and on the purity of the dye, and previous kinetic studies on the photooxidation of 2,3-DHN and 2,7-DHN [12] unambiguously indicated that singlet oxygen mediated processes (Type II mechanism) predominate with this dye as sensitizer. The spectral changes observed in the photooxidations (Figs. 1 and 2) were practically suppressed in the presence of 1 mM sodium azide, a

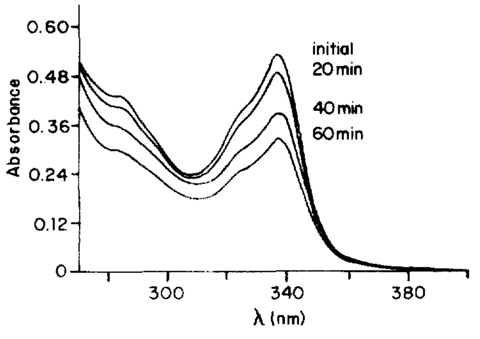

Fig. 1. Absorption spectral changes during the Rose Bengal (polystyrene-bound) sensitized photooxidation of 2,3-dihydroxynaphthalene (2.5×10^{-3} M in pH 12 water, 3:100 v/v dilution).

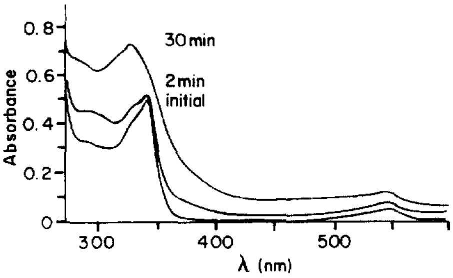

Fig. 2. Absorption spectral changes during the Rose Bengal sensitized photooxidation of 2,7-dihydroxynaphthalene (7×10^{-4} M in pH 12 water, 1:10 v/v dilution).

well-known singlet oxygen quencher [20], and time resolved phosphorescence detection of the generated singlet oxygen clearly indicated an important singlet oxygen quenching by each DHN [12].

During the photooxidation of 2,3-DHN, an UV absorption decrease in the 280–400 nm range was observed (Fig. 1). The irradiated mixture with 20% UV change at 340 nm showed on TLC plates the presence of at least five products, as well as the unreacted 2,3-DHN. Complex mixtures of products have also been observed before in the photooxidation of other 2-hydroxynaphthalenes under similar conditions [5]. In our case, the dimer 2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl (Di-2,3-DHN) and phthalic acid were unequivocally detected in the mixture, as such or in the form of methylated derivatives, by comparison with the corresponding standard compounds by TLC and by GC-MS (retention times and mass spectra). Their percentages in the whole reaction mixture, with still ca. 82% initial 2,3-DHN (based on volatile products analyzed by GC-MS), were 2% each. Two other minor products (less than 0.5% each, by GC-MS) could not be identified. A fifth product, soluble in alkaline water and strongly retained on TLC plates when eluting with solvents of moderate polarity, was tentatively identified as a polymeric material because its UV spectrum in ethanol resembles that of the dimer Di-2,3-DHN, although with wider bands, and because its GC-MS analysis showed only small, unidentified peaks, probably arising from the decomposition of non-volatile material. The percentage of this product in the former reaction mixture was 15% by weight, as estimated from the UV spectrum of the extract in ethanol of the corresponding TLC spot from the separation of a weighed reaction mixture, assuming the same molar absorption coefficient at 300 nm as Di-2,3-DHN. A polymer of undefined structure has also been described before as the main result of the MnO_2 oxidation of 2,3-DHN [21]. However, in our case it must be pointed out that a very polar, low molecular weight species of undefined structure can't be discarded. GC-MS analysis of the other irradiated mixture, with 80% UV change, showed only a trace (ca. 0.2%) of Di-2,3-DHN, while the content of phthalic acid was 5%. The formation of the dimer and the tentative polymer is difficult to detect from the observed UV changes because the spectra of 2,3-DHN, Di-2,3-DHN and the material retained on TLC plates have similar shapes. The absence of isonaphthazarine in both irradiated samples was inferred by GC-MS comparison of the methylated reaction mixture with 2,3-dimethoxy-1,4-naphthoquinone.

The presence of the dimeric compound Di-2,3-DHN and the tentative polymer in the reaction mixture suggests the primary photoformation of a radical by an electron transfer process from 2,3-DHN (in anionic form in the medium) to singlet molecular oxygen (Type II photooxidation) or to the excited sensitizer (Type I) (Fig. 3) [22]. Radical dimerization at the 1-position and subsequent rearomatization would yield the observed dimer. Di-2,3-DHN has also been obtained before by solid phase oxidation of 2,3-DHN with $FeCl_3$ [13], and a similar 1,1′-dimeric compound has been found in the oxidation of 2-naphthol with hydrogen peroxide in aqueous solution, in the presence of horseradish peroxidase [23].

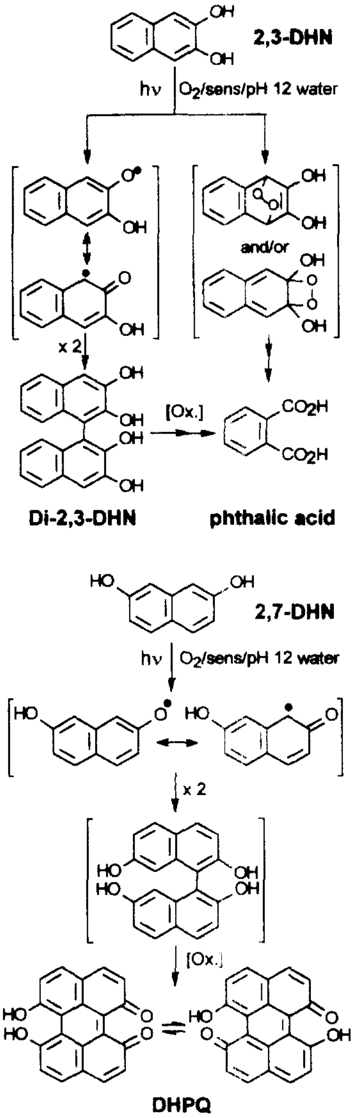

Fig. 3. Proposed mechanism for the sensitized photooxidation of 2,3-dihydroxynaphthalene (2,3-DHN) and 2,7-dihydroxynaphthalene (2,7-DHN) in pH 12 water. For the sake of clarity the phenol groups are depicted in non-ionized form.

Phthalic acid, the other identified reaction product, can be formed from the endoperoxide or from the dioxethane obtained by [4+2] or [2+2] cycloaddition of singlet molecular oxygen to the 1,4 or 2,3 positions of 2,3-DHN, respectively, after ring cleavage and further thermal or photochemical oxidation (Fig. 3). Phthalic acid can also be generated through a similar oxidation of the dimer Di-2,3-DHN (as the observed percentage changes suggest) or polymer. The related compound *o*-carboxyphenylglyoxylic acid (phthalonic acid), a possible intermediate in the oxidation to phthalic acid [24], has not been detected in any reaction mixture. It has been reported [25] that phthalic acid is also the major product of the potassium superoxide oxidation of 2,3-DHN in *N,N*-dimethylformamide in the presence of 18-crown-6 ether. From the point of view of its environmental impact, this acid, as well as its mono and diesters, show very low acute or chronic toxicity to mammals, without carcinogenic properties, although high doses of some of its esters have been found to be teratogenic [26].

3.2. *Sensitized photooxidation of 2,7-dihydroxynaphthalene*

The sensitized photooxidation of 2,7-DHN in alkaline water gave rise in a few minutes to a blue reaction mixture with an UV–vis spectrum with increasing absorption throughout the 270–800 nm range (Fig. 2). The main product of the photooxidation was identified as 6,7-dihydroxyperylene-1,12-quinone (DHPQ, Fig. 3) in equilibrium with its tautomeric form, on the basis of its comparison (UV–vis and MS spectra, TLC) with a pure sample. Its estimated yield was ca. 90% on modified starting naphthalene, as deduced by spectroscopic analysis of the corresponding TLC extracts. The photogeneration of DHPQ must follow a mechanism similar to that operating in the case of 2,3-DHN, through the intermediate dimer 2,2′,7,7′-tetrahydroxy-1,1′-binaphthyl (not observed). The same intermediate has been previously described as the result of the oxidative coupling of 2,7-DHN with oxygen and alumina-supported Cu(II) sulfate [27]. The perylenequinone DHPQ can also be obtained by in-dark air oxidation of 2,7-DHN in an alkaline aqueous medium [16], although at lower rate than under the photooxidation conditions herein described. By comparing the absorbance changes at 600 nm, it can be deduced that the photooxidation process is 10–50 times faster, depending on the irradiation time.

The toxicity and ecological impact of the quinone DHPQ is not known. Some natural polynuclear quinones such as Cercosporin [28] or Hypericin [29] are photodynamically active pigments with anticancer and antiviral properties.

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