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Phototransformation of 3-hydroxybenzonitrile in water

Florent Bonnichon, Claire Richard*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS No. 6505, 63177, Aubière Cedex, France

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Abstract

The photolysis of 3-hydroxybenzonitrile in water yields 2-amino-5-hydroxybenzaldehyde (**I**), 3-hydroxybenzaldehyde (**II**) and cyanohydroquinone (**III**). **I** is only observed at pH < 4 whereas **II** is yielded whatever the pH. Oxygen has no influence on the formation of **I** but partly inhibits that of **II**. **III** is only observed in oxygenated solutions and at pH < 7. The photoionization is likely to be the primary step in the mechanism of formation of **II** and **III**. On the other hand, the production of **I** might be explained by the photoisomerization of 3-hydroxybenzonitrile into a cyclic imine followed by hydrolysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: 3-Hydroxybenzonitrile; Phototransformation; Water; Photoisomerization; Photoionization

1. Introduction

It was recently shown that 4-hydroxybenzonitrile (4-OHBN) is photoisomerized into 4-hydroxybenzoisonitrile (4-OHBIN) which is stable in alcohols and hydrolyzed into 4-hydroxyformanilide in acidic water [1]. Triplet-quenching experiments and kinetic studies revealed that the photoisomerization proceeds via the triplet in a two-stage photoprocess. On the basis of laser-flash photolysis experiments and mechanistic considerations, it was suggested that the intermediate species absorbing the second photon is an azirine which might be formed after an intramolecular electron transfer via the triplet excited state [1] (Scheme 1).

The photolysis of 2-hydroxybenzonitrile (2-OHBN) leads to benzoxazole [2,3] (Scheme 2). This reaction is likely to involve again the intermediate formation of an isonitrile even though this species failed to be detected. It can be argued that the neighbourhood of the substituents OH and NC results into a very fast cyclisation avoiding the detection of the isonitrile. On laser-flash photolysis of 2-OHBN and benzoisoxazole both of which are finally converted into benzoxazole, the same long-lived transient was detected: it might be the azirine [1].

In the case of the 3-hydroxybenzonitrile, the *meta* position of CN with respect to OH makes the formation of an azirine unfavourable and the question arises whether the photoisomerization into an isonitrile is even though possible. The photochemical transformation of 3-hydroxybenzonitrile in water was investigated in this perspective and we report here the results of the products studies and the nanosecond laser-flash photolysis experiments.

2. Experimental

2.1. Materials and methods

3-Hydroxybenzonitrile (3-OHBN) and 3-methoxybenzonitrile (3-OMeBN) were purchased from Aldrich (purity 99% and 98%, respectively), and used without further purification. Other reagents were of the highest grade available. Water was purified with a Milli-Q (Millipore) device. UV spectra were recorded on a Cary 3 (Varian) spectrophotometer. ^{1}H NMR spectra were taken on a Brucker AC400 spectrometer. Mass analyses were performed on a HP 5985 gas chromatography coupled with mass. Analytical HPLC was carried out on a Waters apparatus equipped with a photodiode array detector using a conventional reverse phase column. Preparative HPLC was performed on a Gilson apparatus with UV detection using a semi-preparative microsorb 3 μm column. Irradiations were carried out at 292 and 320 nm (half-width about 10 nm) using a xenon arc (1600 W) equipped with a high intensity Schoeffel monochromator. For preparative runs, samples were irradiated in a device equipped with six sunlamps emitting within the range 280–350 nm with a maximum of emission located at 310 nm. Potassium ferrioxalate was used as chemical

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*Corresponding author. Tel.: +33-04-7340-7169; fax: +33-04-7340-7700.

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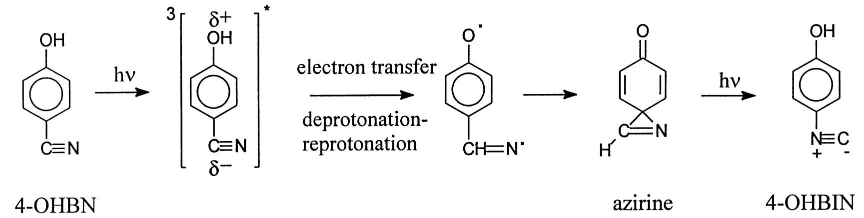
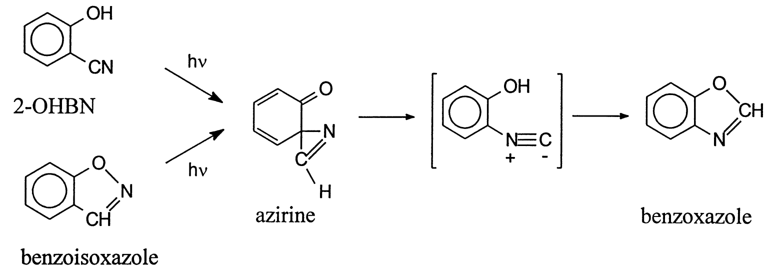


Scheme 1.



Scheme 2.

actinometer. The pH of 3-OHBN solutions were adjusted with perchloric acid, phosphate buffers or NaOH. Solutions of $K_4Fe(CN)_6$ were buffered between 3.7 and 4.9 with citrate buffers.

Transient absorption experiments in the 20 ns to 500 μs region were carried out on a nanosecond laser-flash photolysis spectrometer from Applied Photophysics (LKS.60). The laser excitation at 266 nm from Quanta Ray GCR130-1 Nd:YAG (pulse width ≈ 9 ns) was used in a right angle geometry with respect to the monitoring light beam. The transient absorbances were monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and IP28 or R928 photomultipliers. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. It also houses the high voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 Bit RISC-processor kinetic spectrometer workstation was used to analyze the digitized signal. Potassium peroxodisulfate was used as chemical actinometer. The formation of sulfate radicals was monitored at 450 nm ($\varepsilon \times \phi = 1900 \pm 150$ [4–6]). To measure the $\varepsilon \times \phi$ product of the transients formed from 3-OHBN, we used solutions of 3-OHBN having the same optical densities at 266 nm than that of $K_2S_2O_8$.

2.2. *Identification of the photoproducts*

2-Amino-5-hydroxybenzaldehyde (**I**) was produced by irradiating 3×100 ml of 3-OHBN (5×10^{-4} M) at pH = 3.7 in a quartz vessel for 1 h with six sunlamps. Samples were evaporated to 10 ml and **I** was separated by preparative HPLC. $\lambda_{max} = 387$ nm in H_2O, $\varepsilon_{387} = 4300 \pm 200\ M^{-1}\ cm^{-1}$; ^1H NMR (CD_3CN, ppm) 9.75 (s, 1H), 6.92 (d, 1H, $J = 2.8$ Hz), 6.89 (dd, 1H, $J = 8.8$ and 2.9 Hz), 6.64 (d, 1H, $J = 9.0$ Hz), 6.47 (s, 1H), 5.98 (s, 2H); EI-GCMS *m/z*: 137, 109, 108, 92 and 80.

2,5-Dihydroxybenzonitrile (**III**) was synthesized according to [7]: a basic (NaOH = 2 M) solution of 2-hydroxybenzonitrile (0.04 M) and $K_2S_2O_8$ (0.04 M) was stirred at room temperature for 48 h. 5-Sulfo-2-hydroxybenzonitrile potassium salt was recovered after cooling the solution and hydrolyzed into **III** upon stirring in hot acidic solution. $\lambda_{max} = 317$ nm in H_2O, pH = 3 and $\varepsilon_{317} = 3500 \pm 200\ M^{-1}\ cm^{-1}$; ^1H NMR (CD_3OD, ppm) 7.1 (d, 1H, $J = 7.9$ Hz), 7.1 (d, 1H, $J = 2.9$ Hz), 7.0 (dd, 1H, $J = 7.9$ and 2.9 Hz); EIMS *m/z*: 135.

3. Results and discussion

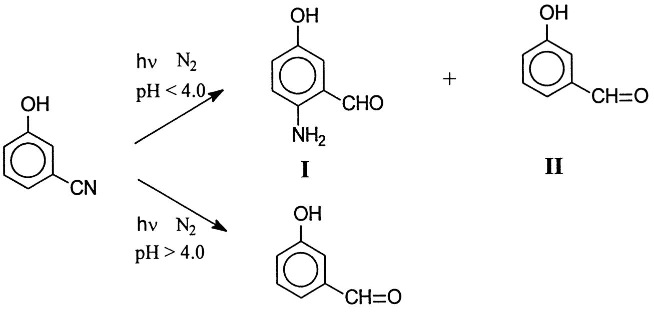
3.1. *Continuous irradiations*

The pK_a of 3-OHBN is equal to 8.34 ± 0.03 [8]. The maximum of absorption of the molecular 3-OHBN is located at 292 nm ($\varepsilon = 2940\ M^{-1}\ cm^{-1}$). The anionic form absorbs at longer wavelength ($\lambda_{max} = 320$ nm with $\varepsilon = 3800\ M^{-1}\ cm^{-1}$).

Aqueous solutions of 3-OHBN (5×10^{-4} M) were irradiated at several pH laying within the range 1.9–10. Results are summarized in Table 1. In deoxygenated solutions, **I** and **II** are the main photoproducts (see Scheme 3). At pH = 1.9, the quantum yield of 3-OHBN consumption is equal to 0.0023. **I** and **II** account for 67% and 11% of converted 3-OHBN, respectively. As the pH is increased from 1.9 to 3.9, the quantum yield of **I** formation decreases falling down to 0 at pH 3.9, whereas that of **II** increases. The quantum yield of 3-OHBN transformation decreases when the pH is

Table 1
Quantum yields of 3-OHBN (5×10^{-4} M) disappearance and **I**, **II** and **III** formation

Conditions	$\Phi_{3\text{-OHBN}}$	$\Phi_{\mathbf{I}}$	$\Phi_{\mathbf{II}}$	$\Phi_{\mathbf{III}}$
$pH = 1.9$	0.0027 ± 0.0003	0.0018 ± 0.0002	0.00031 ± 0.00004	0
$pH = 1.9$ oxygenated solution	0.0033 ± 0.0003	0.0017 ± 0.0002	0.00015 ± 0.00002	0.00020 ± 0.00003
$pH = 1.9$ (MA) $= 10^{-2}$ M	0.0019 ± 0.0002	0.0010 ± 0.0001	Traces	
$pH = 3.0$	0.0023 ± 0.0003	0.0009 ± 0.0001	0.0006 ± 0.0001	
$pH = 3.0$ (2-propanol) $= 0.34$ M	0.0019 ± 0.0003	0.0009 ± 0.0001	0.0006 ± 0.0001	
$pH = 3.4$	0.0023 ± 0.0003	0.00079 ± 0.0001	0.00074 ± 0.0001	
$pH = 3.7$	0.0023 ± 0.0003	0.0004 ± 0.00005	0.0010 ± 0.0001	
$pH = 3.7$ oxygenated solution	0.0035 ± 0.0003	0.00048 ± 0.00005	0.0004 ± 0.00005	0.0006
$pH = 3.9$	0.0023 ± 0.0003	<0.0001	0.0015 ± 0.0002	
$pH = 5.2$	0.00073 ± 0.0002	0	0.00049 ± 0.00005	
$pH = 5.2$ oxygenated solution	0.0011 ± 0.0003	0	0.00025 ± 0.0003	0.0006
$pH = 7.1$	0.0008 ± 0.0002	0	0.0005 ± 0.0001	
$pH = 7.1$ oxygenated solution	0.00015 ± 0.0003	0	0.0003 ± 0.00005	<0.0001
$pH = 10$	<0.0002		0.0001 ± 0.00002	



Scheme 3.

raised above 4. It falls down to 0.0008 between 5 and 7. At $pH = 10$, it is less than 0.0002. Above $pH = 3.9$, **II** becomes the main photoproduct with a chemical yield of the order of 68%.

In the presence of oxygen, cyanohydroquinone **III** appears as third photoproduct. On addition of oxygen, the quantum yield of 3-OHBN disappearance is increased by 22% at $pH = 1.9$ and 50% at $pH = 3.7$, 5.2 and 7.1 (see Table 1). Oxygen does not affect the formation of **I**, but reduces by a half that of **II**. At $pH = 1.9$, methyl acrylate (10^{-2} M) inhibits completely the formation of **II** and by a half that of **I**. The addition of 2-propanol (0.34 M) has no effect on the reaction at $pH = 3$.

For comparison we also studied the phototransformation of the methoxy derivative at 292 nm. In neutral deoxygenated medium, the quantum yield of 3-OMeBN transformation is about four times lower than that of 3-OHBN. Two main photoproducts exhibiting maximum of absorption at 254 nm are observed. These products are neither the 3-methoxybenzoisonitrile that is expected to be hydrolyzed in acidic medium nor the 2-amino-5-methoxybenzaldehyde that should absorb at longer wavelength. It can be concluded that the phenolic OH plays a major role in the formation of **I** and **II**.

3.2. Laser-flash photolysis experiments

3.2.1. Photolysis of 3-OHBN

Several absorption bands appear when neutral aqueous 3-OHBN (10^{-3} M) is irradiated at 266 nm. The transient species exhibiting a maximum at 320 nm and reacting with H^+ is assigned to the 3-cyanophenolate anion which is produced by deprotonation of the singlet excited state because of the low pK^* value (1.89 [8]). From the $\varepsilon \times \phi$ product and the known ε value at 320 nm, we got: $\Phi = 0.089$. The hydrated electrons ($\lambda_{max} = 720$ nm) are also detected as well as the corresponding 3-cyanophenoxyl radical ($\lambda_{max} = 410$ and 390 nm) which can be produced independently by photolysis of acidic solutions containing $K_2S_2O_8$ and 3-OHBN. In solutions of 3-OHBN, the absorbance at 550 nm increases in a quadratic manner with the incident light intensity (P) indicating that the ionization is mainly biphotonic (Fig. 1). However, the linear plot of the ratio of the absorbance at 550 nm over P against P gives an intercept of 0.0005 ± 0.00025 showing that monophotonic ionization also occurs (see inset of Fig. 1). Using an appropriate actinometry (see Section 2) we deduced from this value that the quantum yield of the monophotonic ionization is equal to 0.007 ± 0.003.

In ethanol, the triplet–triplet absorption is detected ($\lambda_{max} = 325$ nm) (Fig. 2). The $\varepsilon_{320} \times \phi$ product was found to be equal to 1800 ± 200 M^{-1} cm^{-1} and the rate constant of reaction of the triplet with oxygen to 4.2×10^9 M^{-1} s^{-1}.

3.2.2. Reaction of 3-OHBN with hydrated electrons and $H^{\cdot}$

The fact that monophotonic ionization occurs, implies that hydrated electrons are produced under continuous irradiation of 3-OHBN with low light energy. Reaction of 3-OHBN with these electrons or with $H^{\cdot}$ in acidic solution should therefore, take place. To get a better insight into the mechanism of reduction, we studied the reactivity of 3-OHBN with electrons and $H^{\cdot}$, these species being

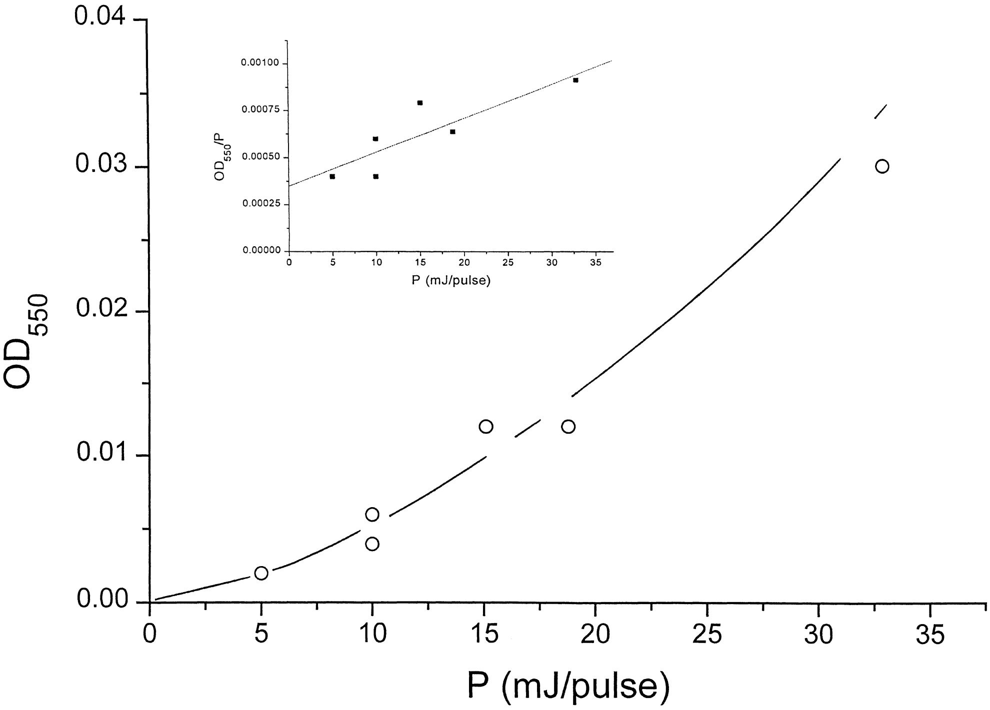


Fig. 1. Dependence of the absorbance at 550 nm (OD_{550}) on the laser pulse energy from a neutral solution of 3-OHBN (5.0×10^{-4} M). Absorbance at 266 nm is equal to 0.94. inset: plot of OD_{550}/P vs. P.

produced by photolysing ferrocyanide ions at 266 nm ($\phi = 0.52$ [9]).

The photolysis of solutions containing $K_4Fe(CN)_6$ (5.0×10^{-4} M) and 3-OHBN (5.0×10^{-4} M) acidified at pH = 2.2 yields the transient spectra shown in Fig. 3. At this pH, the H-adduct should be produced by addition of $H^{\cdot}$ radicals on 3-OHBN. Actually, two transients are detected. The first one ($\lambda_{max} = 425$ nm) is observed 0.2 µs after the pulse in the absence and in the presence of 2-propanol used as $H^{\cdot}$ scavenger. As a consequence, this long-lived transient ($\tau > 400$ µs) is not the H-adduct. The second transient appears 1 µs after the pulse and decays with a first-order rate constant equal to 6.5×10^4 s^{-1}. This species is likely to be the H-adduct as it is not observed on the addition of 2-propanol. The absorption spectrum of this H-adduct, T_1H, was obtained by substracting the spectrum measured 80 µs

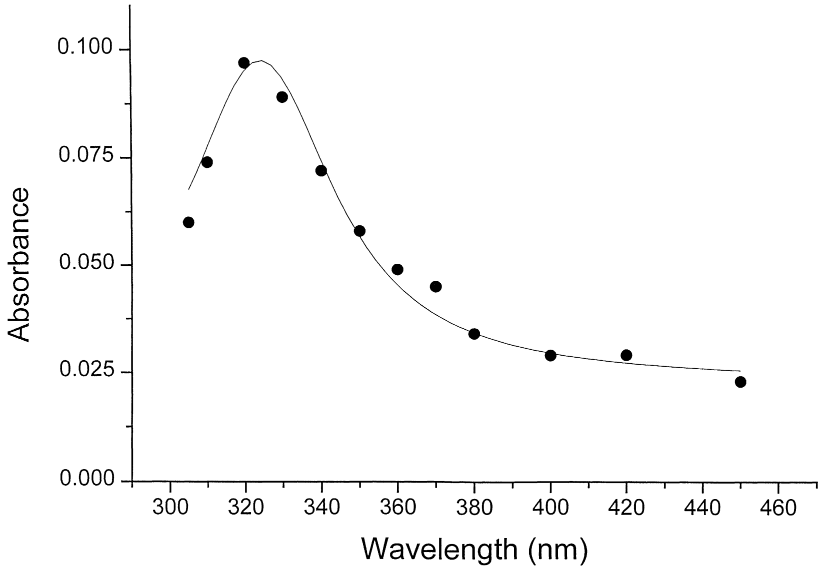


Fig. 2. Transient absorption spectrum obtained at end of pulse by photolysis of 3-OHBN (5×10^{-4} M) in ethanol. Absorbance at 266 nm is equal to 1.1.

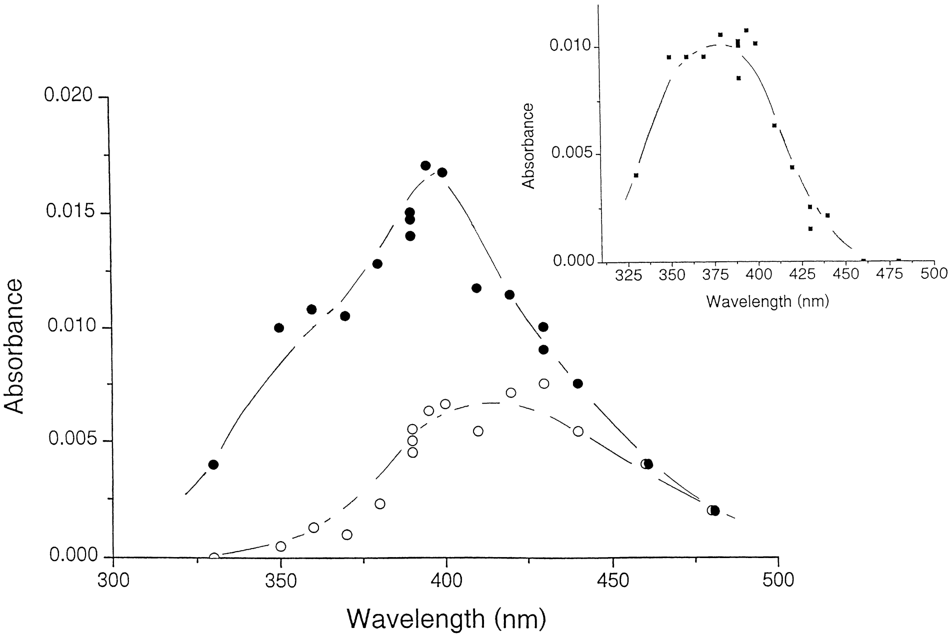


Fig. 3. Transient absorption spectra obtained by photolysis of a deoxygenated solution of $K_4Fe(CN)_6$ (5.0×10^{-4} M) and 3-OHBN (5.0×10^{-4} M) acidified at pH = 2.2. ●: 1 μs after the pulse ○: 80 μs after the pulse inset: difference between the absorption spectra measured at 1 and 80 μs.

after the pulse from that measured 1 μs after the pulse (see insert of Fig. 3). The maximum of absorption is located around 390 nm.

The irradiation of a deoxygenated and neutral aqueous solution containing $K_4Fe(CN)_6$ (5.0×10^{-4} M) and 3-OHBN (5.0×10^{-4} M) yields 1 μs after the pulse the transient shown in Fig. 4 ($\lambda_{max} = 315$ nm). According to the results obtained by pulse radiolysis of benzonitrile [10], this transient can be assigned to the radical anion formed by reaction of the hydrated electrons with 3-OHBN, T_2^-. From the first-order rate constant of T_2^- formation (7.2×10^6 s^{-1}), it can be deduced that the bimolecular reaction rate constant between electrons and 3-OHBN is equal to 1.4×10^{10} M^{-1} s^{-1}. The first-order decay of T_2^- is accelerated on acidification of the solution. From the linear dependence of the apparent rate constant vs. $[H^+]$ within the pH range 3.7–5, we computed $k_{H^+} = (9.0 \pm 0.2) \times 10^9$ M^{-1} s^{-1} (Fig. 5). In order to get the transient spectrum of the protonated species, T_2H, we measured the absorbances 6 μs after the pulse from solutions buffered at pH = 4.2. We

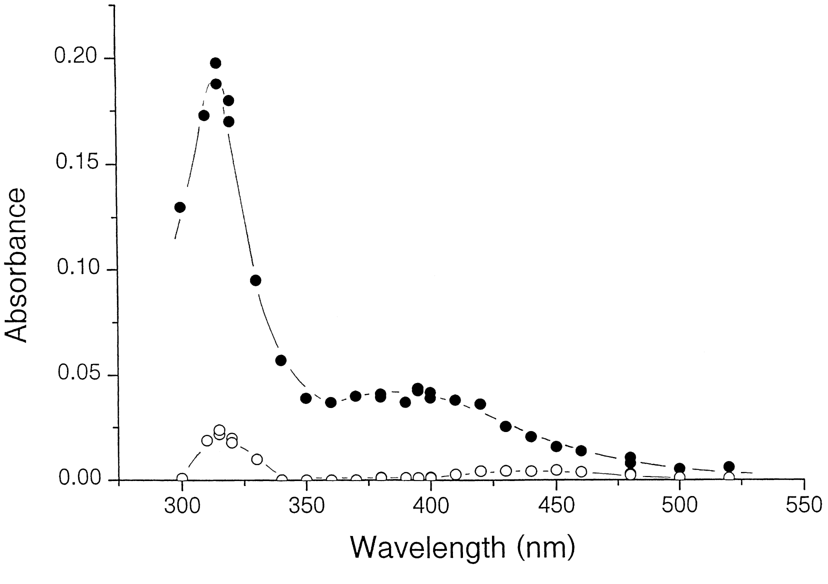


Fig. 4. Transient absorption spectra measured by photolysis of a neutral and deoxygenated solution of $K_4Fe(CN)_6$ (5.0×10^{-4} M) and 3-OHBN (5.0×10^{-4} M). ●: 1 μs after the pulse ○: 45 μs after the pulse.

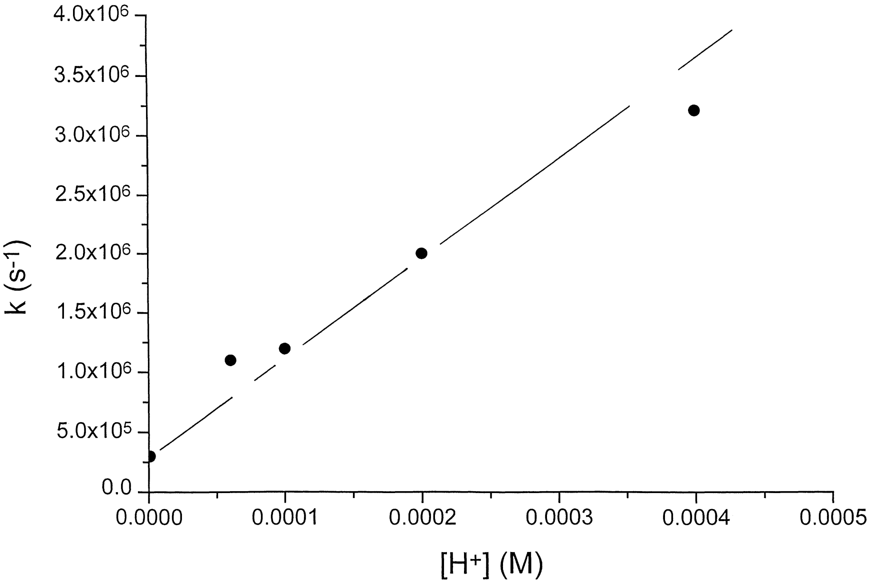


Fig. 5. Plot of the first-order rate constant decay of T_2^- vs. H^+ concentration.

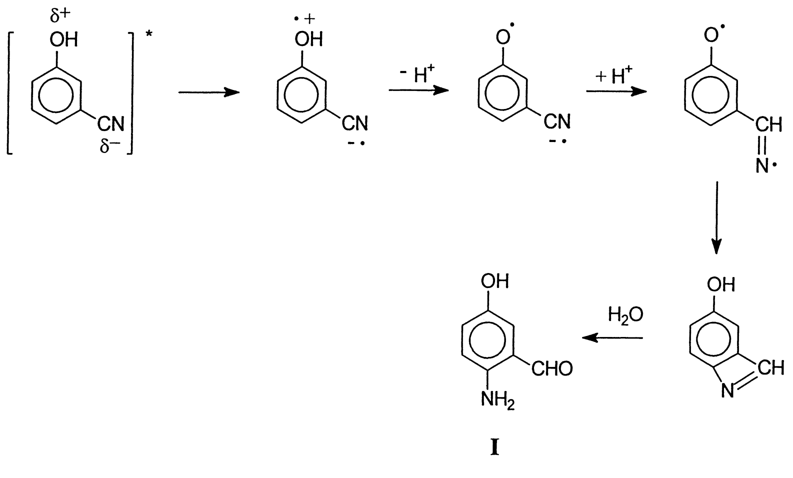
found a spectrum very similar to that of T_2^- therefore, different from that of T_1H indicating that T_1H and T_2H are distinct species in accordance with the results obtained by pulse radiolysis of benzonitrile [10].

From all these data, it can be concluded that three species can be produced: T_1H ($\lambda_{max} = 390$ nm) predominates at $pH < 3$, T_2H within the pH range 3.5–5 and T_2^- ($\lambda_{max} =$ 315 nm) at $pH > 6$.

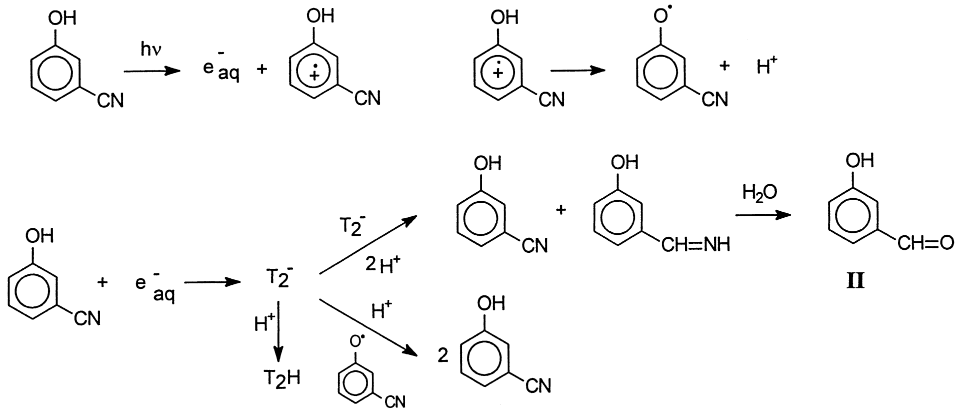
3.3. Mechanism of formation of I

Results obtained by continuous irradiations indicate that **I** is only formed at $pH < 4$, this formation being neither influenced by oxygen nor by a hydrogen atom scavenger such as 2-propanol. It can be therefore, concluded that **I** is not produced via the reduction of 3-OHBN by the solvated electrons or the H˙ atoms.

An alternative route for the formation of **I** might be the photoisomerization into the cyclic imine shown in Scheme 4, followed by an hydrolysis. This reaction is likely to involve the intermediary formation of a diradicalar species. Such intermediates were also assumed to be produced on irradiation of 2- and 4-OHBN (see Scheme 1) [1]. Unlike the diradicals formed from 2- and 4-OHBN, the diradical arising from 3-OHBN has no possibility to rearrange into an azirine but could yield, instead, an imine by addition of the nitrogen atom on the ring. The mechanisms of formation of the diradicals are not fully understood. The excited states of 4-OHBN are polar as the electron-donating group and the electron-withdrawing group are *para* to each other and lie in the transition moment axis. As a consequence, it was proposed that the diradical is produced after an intramolecular electron transfer followed by a deprotonation–reprotonation sequence [1]. The same reaction may occur with the



Scheme 4.



Scheme 5.

meta derivative, although the relative position of the two substituents is less favorable.

The formation of **I** is partly inhibited by methyl acrylate (10^{-2} M) but is not affected by oxygen (1.3×10^{-3} M). The involvement of the triplet in the reaction is therefore, possible but not proved. The reason why **I** is only detected at pH > 4 might be a better reactivity of the triplet in molecular than in anionic form and a pK^* value lower than 4.

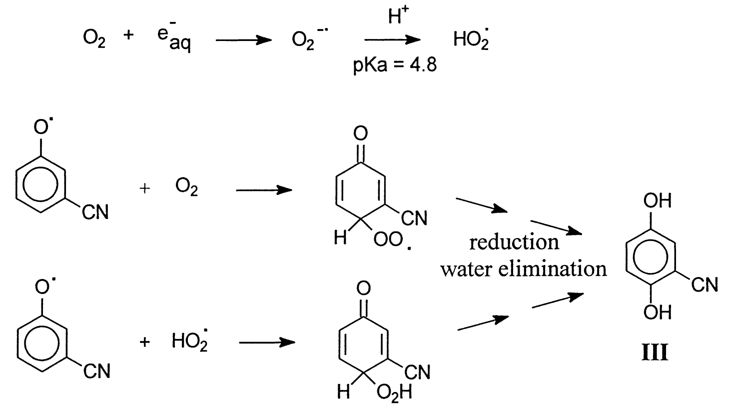
3.4. *Mechanisms of formation of* **II** *and* **III**

It was previously reported that 2-, 3-, 4-hydroxy and 4-aminobenzonitriles are photoreduced into aldehydes in basic medium (10^{-2} M NaOH), and a reduction mechanism involving the solvated electrons was proposed [11]. In the present work we show that the photochemical reduction is much more efficient in moderately acidic than in basic medium, the highest quantum yields of **II** formation being observed around pH = 4. The primary step in the mechanism of **II** formation is the reaction of 3-OHBN with hydrated electrons or $H^{\cdot}$ as indicated by the fact that the reaction is partly inhibited by oxygen (1.3×10^{-3} M) and completely inhibited by methyl acrylate (1.0×10^{-2} M). Results show that electrons rather than $H^{\cdot}$ are responsible for the formation of **II**. First, at pH = 3, the hydrogen atom scavenger 2-propanol has no effect on the reaction indicating that $H^{\cdot}$ play a minor role in the formation of **II**. Second, the quantum yield of **II** production increases from pH = 1.9 to 3.9 as the H^+ concentration decreases.

In neutral medium, the formation of **II** can be explained by the Scheme 5. The dismutation of two T_2^- radicals is likely to produce an imine which is hydrolyzed into **II**. T_2^- can also react with the 3-cyanophenoxyl radical giving back 3-OHBN. The fact that the highest quantum yield value is observed at pH = 4 indicates that the imine formation is more efficient from T_2H than from T_2^- or T_1H.

From Scheme 5, we should have only 33% of 3-OHBN converted into **II**. Actually, chemical yields as high as 68% are measured indicating that other routes of **II** formation must exist.

The production of **III** in oxygenated solutions can be explained either by the oxidation of the 3-cyanophenoxyl radical by molecular oxygen or by its reaction with $HO_2^{\cdot}/O_2^{-\cdot}$. In both cases, reduction steps are necessary for the final formation of **III** (Scheme 6). The pk_a of **III** is likely to resemble that of 3-OHBN (8.34) [8]. It means that, at pH = 7, **III** is partly dissociated and should be therefore,



Scheme 6.

oxidized. This oxidation explains why **III** is not observed in neutral and basic solutions.

In conclusion, the phototransformation of 3-hydroxybenzonitrile is tentatively explained by two distinct reaction paths: photoionization and diradical formation by an intramolecular electron transfer. The photoionization leads to 3-hydroxybenzaldehyde via the reduction of 3-hydroxybenzonitrile by solvated electrons and to cyanohydroquinone through the oxidation of the 3-cyanophenoxyl radical by molecular oxygen or through the reaction of the radical with $HO_2^{\cdot}/O_2^{-\cdot}$. On the other hand, the production of 2-amino-5-hydroxybenzaldehyde can be rationalized by the intermediate formation of a diradical. Such a formation is not proved but it is in line with the mechanisms proposed to explain the photoisomerization of 4-OHBN and 2-OHBN in 4-hydroxybenzoisonitrile and benzoxazole, respectively. In both cases, azirines are likely to be produced as intermediates and we suggested that these azirines resulted from the rearrangement of diradicals. In the case of 3-OHBN, the rearrangement of the diradical into an azirine is impossible due to the relative position of CN and OH and a cyclic imine would be formed instead, yielding 2-amino-5-hydroxybenzaldehyde after hydrolysis. The fact that photoisomerization of CN into NC is not observed with 3-OHBN validates the assumption that this reaction requires the intermediate formation of an azirine.

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