

Fluorescence Investigations of Phenol Phototransformation in Aqueous Solutions

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Absorption and fluorescence techniques were used to study special features of the XeCl laser-induced phototransformation of phenols in water and to compare the results obtained with those of photolysis of phenol solutions exposed to the UV radiation from mercury lamps. XeCl laser-induced phenol photolysis provided photoproducts not found on exposure to UV radiation. This is related to the two-photon population of highly excited phenol states under high-power laser pumping, which gives rise to a new phototransformation reaction pathway.

KEY WORDS: Phenol photolysis; ionic forms; fluorescence spectrum; XeCl laser.

INTRODUCTION

In recent years methods of fluorescent spectroscopy have been used to advantage for studying condensed systems. Because the fluorescence of organic compounds is sensitive to microenvironmental effects [1], it is a much used method for investigating the nature of intermolecular interactions and the structure of the microenvironment. Photodecay of phenol molecules has long attracted considerable interest of ecologists and environmentalists [2]. On the one hand, phenol is involved in biological processes occurring in living cells (redox reactions [3]). On the other hand, phenol concentrations in the Earth's water basins exceed maximum permissible levels, which may cause all living things to die [4]. The effects of the excitation photon energy, excitation power, and pH medium on the decay mechanism of the phenol molecule remains to be explored [5–8]. In Refs. 9–11 photodecay of aromatics exposed to KrCl laser radiation has been studied. How-

ever, we are not aware of the results obtained in these experiments.

In our earlier work [12] we have determined spectral-luminescence characteristics of ionic phenol forms in water (anionic and cationic) and conditions for their production (varying values of the pH medium). We have also shown that both the acidity and the basicity of phenols are increased under excitation. Phenol in the first Frank–Condon state takes an active part in molecular phototransformations and may occur in neutral, anionic, and cationic forms in neutral water (pH 6–7). Analysis of our fluorescence data leads us to conclude that these phenol forms may contribute to the phototransformation process.

This work is a continuation of our earlier research into spectral-luminescent characteristics of phenol in aqueous solutions exposed to UV mercury lamp and XeCl laser radiation ($\lambda_{\text{pump}} = 308 \text{ nm}$) and spectral-luminescent characteristics of hydroquinone, assumed to be a phenol photolysis photoproduct exposed to UV mercury lamp radiation.

Under normal conditions phenols in water do not absorb XeCl radiation at low pump intensities. Recent investigations in nonlinear optics and spectroscopy have revealed that absorption and fluorescence properties of

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organic molecules vary, as the excitation intensity is increased [13–16]. The photophysical and photochemical properties of the molecules are also found to vary in the process. For an adequate theoretical description of the relationship between photophysical and photochemical characteristics of organic molecules under high-power laser excitation, it is essential to have experimental evidence on molecular phototransformations over a wide range of pump intensities.

EXPERIMENTAL TECHNIQUES

Pre- and postirradiation electronic absorption and fluorescence spectra were recorded by a conventional procedure using a Specord M40 spectrophotometer and an Hitachi M850 spectrofluorimeter. The pH values were varied from 0 to 12 by adding KOH and H₂SO₄ to the aqueous solution of phenol. The pH medium was measured with a 673 Model pH-meter. The experiments employed high-pressure mercury lamps as ultraviolet and visible sources. The model phenol solutions (the phenol concentrations varied from 5×10^{-5} to 0.1 mol-L^{-1}) were exposed to radiation from DRSh-500 and DRLF-400-1 mercury lamps. Spectral distributions of the output energy from the mercury lamps are given in Ref. 17. The effect of the varying spectral compositions of the exciting radiation on phenol photolysis was studied using a set of colored optical glasses.

Fluorescence was induced by a XeCl laser at $\lambda = 308 \text{ nm}$ with $\tau_{\text{FWHM}} = 10 \text{ ns}$ and $E_{\text{out}} = 30\text{--}40 \text{ mJ}$. Beam focusing enabled us to produce laser fields with power densities of up to $10^{26} \text{ phot/cm}^2 \text{ s}$. The laser beam was focused by a cylindrical lens with $F = 250 \text{ mm}$ on a rectangular cell 0.2 mm thick and 1 cm wide through an $0.14 \times 0.8\text{-cm}$ aperture.

EXPERIMENTAL

UV Mercury Lamp Radiation

Our previous experiments [12] have show that the products of phenol phototransformations are quite different at various pH values. Ionic phenol forms were studied [12]. Spectral-luminescence properties of ionic forms of phenols are given in Table I. These ionic forms can participate in phototransformations as intermediate photoproducts. The data on phenol transformations with varying pH levels under identical irradiation conditions (a DRLF-400-1 mercury lamp with and without light filters at $\lambda = 365\text{--}405$ and 435 nm) have shown that the photopro-

duction rate in absorption bands around $41,000$ and $34,500 \text{ cm}^{-1}$ is higher for the anionic phenol forms than for the cationic forms, with pH values for the anionic solution decreasing from 10.6 down to 8. The effect of the phototransformation is to increase the absorption intensity of the anionic phenol form around 240 nm . This is due to photoproduct formation. In the fluorescence spectrum there is a band of low intensity around 415 nm which occurs under both anionic and cationic irradiation. This fluorescence band can be emitted by the cationic phenol form or products of second photodecay. Analysis of the phototransformations of *n*-benzoquinone studied in Ref. 18 suggests that the absorption around $41,000 \text{ cm}^{-1}$ is due to photoproduction. The increased absorption intensity observed around $37,000 \text{ cm}^{-1}$ may be attributed to the production of phenol dimers. In Ref. 19 the presence of the phenol anion in the solution is shown to result in dimer production through an anionic radical dimer on exposure to the UV radiation. The maximum dimer absorption falls at 276 nm [20,21].

We have observed more pronounced changes (shift and intensity increase of the absorption band) in the phenol absorption spectra under UV irradiation from mercury lamps around $45,500 \text{ cm}^{-1}$ (see Fig. 1, curve 3), while the absorption intensity around $37,000 \text{ cm}^{-1}$ is hardly affected by the irradiation [12]. The phenol absorption around $45,500 \text{ cm}^{-1}$ corresponds to the $S_0 \rightarrow S_2$ transition [22, 23]. The nature of this absorption band is determined exclusively by the phenyl fragment of the phenol molecule. An increase in the oscillator strength for the $S_0 \rightarrow S_2$ transition (i.e., the increased absorption intensity observed experimentally) corresponds to the case where the oxygen–hydrogen bond stretching in the OH group leads to the proton detachment, resulting in a high production probability of the anionic phenol form under irradiation. It was found that the fluorescence band around 345 nm corresponded to the anionic phenol form (see Table I). Hence it follows that the appearance of this band in the fluorescence spectrum, as the exposure time (t_{exp}) is increased, is evidence of the production of the anionic phenol form (see Fig. 2). The data on the phenol photolysis in water are given in Table II. The fluorescence intensity in the band with the maximum around 345 nm is observed to increase as t_{exp} is increased. The fluorescence is attributed to a photolysis product. At $t_{\text{exp}} = 60\text{--}120 \text{ s}$ the fluorescence intensity in the band peaks. On a further increase in t_{exp} the intensity tends to decrease, which results from the photodecay of the photolysis product.

Simultaneously with this process a fluorescence band with the maximum around 415 nm followed by a fluorescence band with a maximum around $440\text{--}460 \text{ nm}$ is observed (see Table II). The fluorescence around 415

Table I. Spectral-Luminescence Characteristics of Ionic Forms of Phenol and Hydroquinone

pH	Solution	λ_1^{abs} (nm)	λ_2^{abs} (nm)	λ^{fl} (nm) [λ_{exc} (nm)] ^a
6.8	Phenol in water	210	270	296 (270)
12	Phenol in water + $5 \cdot 10^2$ M KOH	230	290	345 (290)
-0.5	Phenol in water + 20% H ₂ SO ₄	240	300	415 (290)
-2.2	Phenol in water + 90% H ₂ SO ₄	230	320	380 (290)
7.6	Hydroquinone in water	220	290	330 (290)
11.8	Hydroquinone in water + 10^{-2} M KOH	260	320	440 (290)
-0.3	Hydroquinone in water + 20% H ₂ SO ₄	220	290	330 (290)
4.4	Phenol in water + 29% H ₂ O ₂	230	280	305 (290)

^a The fluorescence excitation wavelength.

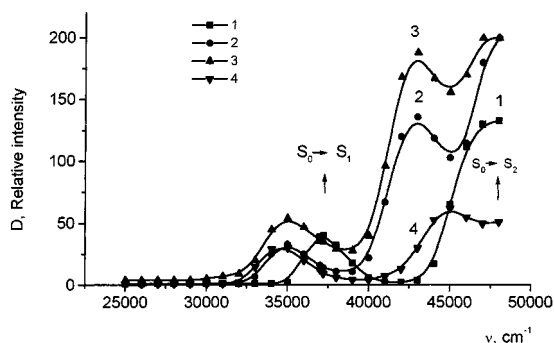


Fig. 1. Absorption spectra of phenol (1, 2, and 3) and hydroquinone (4). Solvent used: water (1 and 4), water + 5×10^{-3} mol·L⁻¹ KOH (2 and 3). Phenol or hydroquinone concentration: 5×10^{-5} mol·L⁻¹. After exposure to UV mercury radiation, $t_{\text{exp}} = 20$ min (3).

nm corresponds to the fluorescence band of the cationic phenol form (see Table I). The fluorescence of the photoproduct around 440 nm is also observed on exposure to unfiltered light from a mercury lamp with $t_{\text{exp}} = 6$ h.

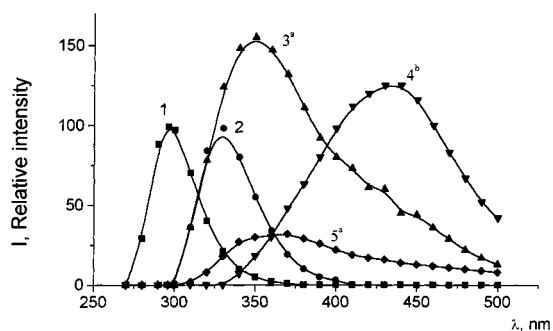


Fig. 2. Fluorescence spectra of phenol (1, 3^a, and 4^b) and hydroquinone (2 and 5^a) before (1 and 2) and after (3^a, 4^b, and 5^a) exposure to UV mercury radiation. The solvent used is water; the phenol or hydroquinone concentration is 5×10^{-5} mol·L⁻¹. The fluorescence excitation wavelengths are 270 nm (1), 290 nm (2, 3^a, and 5^a), and 333 nm (4^b). The exposure time is 20 min; the intensity is an order of magnitude lower (a) and 10 orders of magnitude lower (b) than in this figure.

On the addition of H₂O₂ to the phenol solution, the yield of the product is found to increase at $t_{\text{exp}} \ll 40$ min and to decrease at $t_{\text{exp}} > 40$ min.

It is believed that the fluorescence around 440 nm is due to the production and photodecay of hydroquinone on exposure to the UV radiation. The experiments on hydroquinone photolysis showed the fluorescence intensity to decrease in the fundamental band around 330 nm, as t_{exp} was increased (see Fig. 2). It was also found experimentally that a low-intensity band appeared around 440 nm with an increase in the exposure time. Under normal conditions (with no irradiation) the neutral hydroquinone solution does not absorb light around 330 nm, while hydroquinone does fluoresce in this band on the addition of 5×10^{-1} mol L⁻¹ KOH (pH 11.6). This corresponds to the product of the anionic hydroquinone form. It should be noted that the fluorescence of the anionic hydroquinone form, like that of the anionic phenol form, is of a low intensity in this band. The fluorescence band at 440 nm, which appears at a longer duration of phenol irradiation, coincides to the fluorescence band of the hydroquinone with KOH additions (see Table I). So this fluorescence band can be emitted by the hydroquinone anion, which can be produced by phenol photodecay to the hydroquinone with proton detachment from the last one. The proton attachment and detachment at photo-transformations cause the changes in the pH values (see Table II). On irradiation of the hydroquinone solution with the addition of 20% H₂SO₄ (pH -0.5), the absorption is found to increase around 310 nm, and the fluorescence is observed to increase around 440 nm. To sum up, both ionic phenol forms and ionic hydroquinone forms are active contributors to the phenol phototransformations.

XeCl Laser Irradiation

Comparison of the data on the mercury lamps and XeCl laser irradiation showed the following peculiarities

Table II. Spectral-Luminescence Characteristics of Phenol and Phenol Photoproducts in Water Exposed to UV Mercury Lamp and XeCl Laser Radiation^a

No.	pH,	<i>c</i>	<i>t</i> _{exp}	Photoproducts Fluorescence						
				λ_1^{abs} (nm)	λ_{exc}					
					λ^{Fl} 270	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	$\lambda_4\lambda_5$ (nm)	
1	6.75	$5 \cdot 10^{-3}$	0 s	270	296	—	—	—	—	—
2	7.24	—	10 s	270	296	345	—	—	—	—
3	6.6	—	20 s	270	296	345	—	—	—	—
4	6.5	—	30 s	270	296	345	—	—	—	—
5	6.5	—	40 s	270	296	345	—	—	—	—
6	6.8	—	50 s	270	296	345	—	—	—	—
7	6.4	—	60 s	270	296	345	—	—	—	—
8	6.3	—	120 s	270	296	345	—	—	—	—
9	6.3	—	3–10 min	270	296	370	415	—	—	—
10	7.3	—	15 min	270	296	370	415	460	—	—
11	7	—	20 min	270	296	370	415	460	—	—
12	6.7	—	30 min	270	296	370	415	460	—	—
13	6.9	—	90 min	270	296	—	415	440	—	—
14	Do not measure	0.1	2 h, 10 min	270	—	—	—	440	—	—
15	—	—	3 h	270	—	—	—	440	—	—
16	—	—	6 h	270	—	—	—	—	—	—
17*	W	—	<i>E</i>	—	—	—	—	—	—	—
17*	40	10^{-2}	0.2	270	296	—	415	460	—	—
18*	40	—	12	270	296	—	415	460	—	—
19*	170	$- + 5 \cdot 10^{-1} \text{ mol} \cdot \text{L}^{-1} \text{ KOH}$	22	270	296	—	415	460	530	600

^a *t*_{exp} is the exposure time; λ_{exc} is the fluorescence excitation wavelength (nm); *W* is the laser power density (MW/cm²); *E* is the deposition energy (J/cm³); *C* is the phenol concentration in water (mol·L⁻¹); pH was measured after irradiation.

of the behavior of phenol solutions (see Table II). On exposure to radiation from a mercury lamp the fluorescence bands were observed to appear one after another around 345 → 415 → 440–460 nm, as the exposure time was increased. With XeCl laser irradiation, no photoproduct fluorescing around 345 nm was observed. On the other hand, the photoproduct fluorescence around 415 and 440 nm was present. As indicated above, this is associated with hydroquinone production and decay. The products of the phenol phototransformation were found to fluoresce around 530 and 600 nm ($\lambda_{\text{exc}} = 500 \text{ nm}$) under laser irradiation (see Fig. 3). This effect was not observed under mercury light. The fluorescence around 530 and 600 nm under laser irradiation is due to peculiarities of laser excitation of phenol. The point is that the phenol absorption bands are in a shorter-wavelength region than the XeCl laser radiation range. Nevertheless,

the presence of the photoproducts points to the fact that the absorption of laser radiation by phenol solutions occurs through a two-photon mechanism. This is supported by the fact that the transmission of the XeCl laser radiation through phenol solutions falls off with increasing laser power density from 30 to 150 MW/cm². In response to the increase in the excitation intensity, the yield of phenol photoproducts is found to increase. It should be noted that the phenol fluorescence under two-photon excitation with the second harmonic of a Nd laser ($\lambda_{\text{pump}} = 532 \text{ nm}$) was observed in Ref. 24. However, no phototransformation data were reported in that paper.

Under identical XeCl laser excitation conditions both neutral and anionic phenol forms yield photoproducts fluorescing in the same spectral regions with maxima around 400, 460 and 490, and 530 and 600 nm (see Fig. 3). The increased absorption appears to be due to *p*-

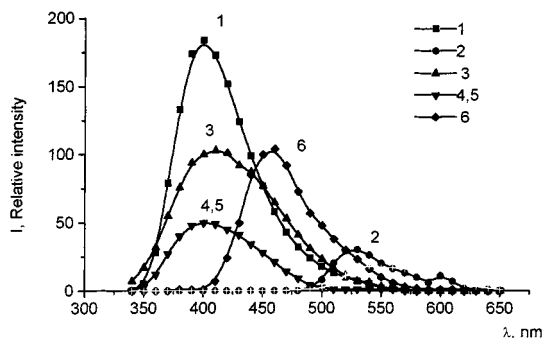


Fig. 3. Phenol fluorescence spectra after XeCl laser irradiation. The solvents used are water, with the phenol concentration being 10^{-2} mol·L $^{-1}$ (3, 4, 5, and 6), and water + 5×10^{-1} mol·L $^{-1}$ KOH, with the phenol concentration being 8×10^{-3} mol·L $^{-1}$ (1 and 2). The fluorescence excitation wavelengths are 323 nm (1, 3, 4, and 5), 400 nm (6), and 500 nm (2). E is the input excitation energy. W is the excitation power density. $E = 9.4$ J/cm 3 , $W = 170$ MW/cm 2 (1 and 2). $W = 40$ MW/cm 2 (3, 4, 5, and 6). $E = 0.2$ J/cm 3 (3); $E = 10.8$ J/cm 3 (4 and 6); $E = 22$ J/cm 3 (5). The intensity in curve 1 is an order of magnitude higher than in this figure, and the intensity in curves 2, 3, and 6 are an order of magnitude lower than in this figure.

benzoquinone production and humic acid [18], which is a *p*-benzoquinone photodecay product (see Fig. 4). The absorption around 21,000 cm $^{-1}$ corresponds to the absorption band of humic acid. Further research efforts are required to clarify the nature of the “long-wavelength” photoproducts ($\lambda = 530$ and 600 nm) formed through highly excited states ($E_{\text{exc}} \approx 64,000$ cm $^{-1}$).

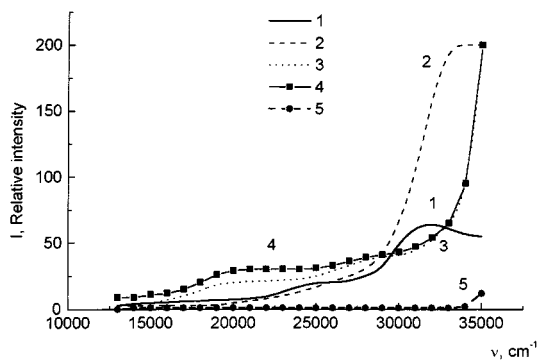


Fig. 4. Absorption spectra of phenol (2, 3, 4, and 5) and hydroquinone (1) before (1 and 5) and after (2, 3, and 4) XeCl laser irradiation. E is the input excitation energy. W is the excitation power density. Solvent used: water (3, 4, and 5) and water + KOH (1 and 2). Phenol or hydroquinone concentration: 5×10^{-5} mol·L $^{-1}$ (1), 8×10^{-3} mol·L $^{-1}$ (2), and 10^{-2} mol·L $^{-1}$ (3, 4, and 5). KOH concentration: 5×10^{-3} mol·L $^{-1}$ (1) and 5×10^{-1} mol·L $^{-1}$ (2). $E = 9.4$ J/cm 3 , $W = 170$ MW/cm 2 (2); $W = 40$ MW/cm 2 (3, 4); $E = 10.8$ J/cm 3 (3); and $E = 22$ J/cm 3 (4).

CONCLUSION

Several photodecay pathways are found to compete during phenol photolysis under Hg light excitation: photodecay through the anionic phenol form ($\lambda_{\text{fl}} = 350$ nm), phototransformations with the cationic phenol form involved ($\lambda_{\text{fl}} = 415$ nm), and photolysis of hydroquinone and ionic hydroquinone forms ($\lambda_{\text{fl}} = 330$ and 440 nm). Under XeCl laser excitation a new phototransformation mechanism comes into play: photodecay through highly excited phenol states, with photoproducts fluorescing around 530 and 600 nm. Work is under way now to identify the phenol photoproducts. We are not aware of any experiments on phototransformations through highly excited phenol states. Further research into this problem is warranted, using primarily excimer excitation delivering higher output energies.

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