Effect of pH value of the medium on the efficiency of phenol photolysis in water

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The effect of pH value of the medium on the efficiency of phenol photolysis in water was studied by the electron absorption and fluorescence methods. It was shown that the most efficient photodecay of phenol in water under the exposure to UV radiation proceeds in acid media in the presence of ionic (anionic, cationic) forms.

Introduction

It is well-known that phenol compounds come to water reservoirs with sewage of woodworking and petroleum refining plants. They are also produced under natural conditions in the process of vital activity of microalgae and accompanying bacteria.[1] To protect water bodies from the negative impact of sewage on the internal redox processes, it should be exposed to UV irradiation both before the biological purification (intensification) and before discharge into a water reservoir (disinfection).[2] The UV irradiation is now one of important technologies of clearing water from organic admixtures, which is accompanied by photodecay of molecules. It is well-known that phototransformations of phenols in aqueous solutions depend on the presence of oxygen, concentration of the initial substance itself, and pH value of the medium. Wide variations of pK_a of phenol at excitation[3] allows its dissociation or protonation to be observed in the range of the medium acidity different from that in the ground state. Establishment of the acid–base equilibrium in the excited state is very important for realization of some or other channel in the mechanism of phototransformations of phenol under its exposure to UV radiation. In this paper, we present the comparative analysis of the efficiency of phenol photochemical decomposition in water at different values of pH by the methods of electronic absorption and fluorescence. We have studied a wide range of pH values (−1–14), in which all ionic forms of phenol took place. In strong-acid solutions ($pH < 0.9$), fluorescence of only cation is observed, and fluorescence of a neutral form arises as we pass to neutral solutions. Finally, at $pH > 10.5$ only the phenol anion fluoresces.

Technique

The absorption and fluorescence spectra were recorded by the standard technique using the Specord M40 spectrophotometer and the Hitachi M850 spectrofluorimeter. The OKN-11M high-pressure mercury lamp was used as a source of the UV and visible radiation. The time of pre-irradiation varied from 1 to 80 min. The pH values of the medium were measured by the pH-meter of pH-673 type. The phenol concentration in the solution was $5 \cdot 10^{-5}$ mol/l.

Results and discussion

The value of pH of aqueous phenol solutions changes after irradiation by the full light of the mercury lamp. It is seen from Table 1 that the pH value slightly increases at the first minutes of UV irradiation in every series of pH values. The wavelength $\lambda_1^{\max}$ corresponds to the fluorescence band maximum of the phenol neutral form at excitation into the longwave absorption band. The peaks of the bands with λ_2, λ_3, λ_4, and λ_5 arise in fluorescence spectra under irradiation of phenol solutions. We can assume that the process of photolysis involves the ionic forms of phenols as intermediate products (Table 2).

The study of photoprotolytic equilibrium of phenol in water[3] confirms the existence of ionic forms in the excited state. At excitation, the phenol molecule in water at pH = 4–9 can equiprobably exist in neutral, anionic, and cationic forms. The possibility of existence of all charged forms in the excited state is supported by quantum-chemical calculations.[4]

Formation of the hydrogen bond in the S_1^* state between hydrogen of the OH-group of phenol in the molecular plane and oxygen of the water molecule leads to appearance of minima in the electrostatic potential above and under the phenol molecular plane near oxygen of the OH-group. At excitation, phenol at pH = 4–9 can serve simultaneously both as the donor and the acceptor of proton. The possibility of further transformation depends on the particular solvation sphere: in acidulous aqueous solutions ($pH < 4$) primary phototransformations likely proceed through π-cation, and in the alkaline medium ($pH > 9$) – through proton removal with formation of active anion.

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Table 1. Variation of pH and spectral characteristics of aqueous solution of phenol after irradiation (λ_{exc}, in nm, is the fluorescence excitation wavelength)

Series #	pH	t_{irr}, min	Fluorescence			
			λ_1	λ_2	λ_3	λ_4, nm
			λ_{exc} = 270	λ_{exc} = 300		λ_{exc} = 300
1	1.85	0	296	–	–	–
	1.9	1	296	–	–	–
	1.87	2	296	345	–	–
	1.8	5	296	345	–	–
	1.85	10	296	345	–	–
	1.8	20	296	345	–	–
	1.75	40	296	345	–	–
2	4.3	0	296	–	–	–
	4.35	1	296	345	–	–
	4.33	2	296	345	–	–
	4.25	5	296	345	–	–
	4.27	10	296	345	–	–
	4.27	20	296	345	–	440
	4.25	40	296	345	–	440
3	6.35	0	296	–	–	–
	6.45	1	296	–	–	–
	6.2	2	296	–	–	–
	6.17	5	296	345	–	–
	6.05	10	296	345	–	–
	6	20	296	345	–	440
	6	40	296	345	–	440
4	7.1	0	296	345	–	–
	7.15	1	296	345	–	–
	7.2	2	296	345	–	–
	7.3	5	296	330	345	–
	7.2	10	296	330	345	–
	6.8	20	296	330	345	440
	6.7	40	296	330	345	440
5	10.3	0	298	345	–	–
	10.4	1	298	–	410	440
	10.45	2	298	–	410	440
	10.47	5	298	–	410	440
	10.5	10	298	–	410	440
	10.1	20	298	–	410	440
	9.9	40	298	–	410	440

Table 2. Spectral-luminescent properties of phenol and some its photoproducts

Form of phenol	pH	Absorption		Fluorescence	
		λ_1, nm	λ_2, nm	λ_{max}, nm	
Phenol in water	6.3	210	270	296	λ_{exc} = 270
Phenol + 10^{-1} M KOH	12.5	230	290	345	λ_{exc} = 300
Phenol + 20% H_2SO_4	−0.5	240	300	415	λ_{exc} = 300
Hydroquinone in water	6	210	290	330	λ_{exc} = 280
Hydroquinone + 10^{-1} M KOH	11.5	260	310	440	λ_{exc} = 300
n-quinone in water	6.2	250	294		–

Let us consider how the pH of the medium affects the efficiency of phenol photolysis. As a result of phototransformations followed the UV irradiation, weak diffuse increase of the absorption intensity all over the spectrum is observed in absorption spectra of phenol aqueous solutions (see Fig. 1), and this indicates the formation of several photoproducts.

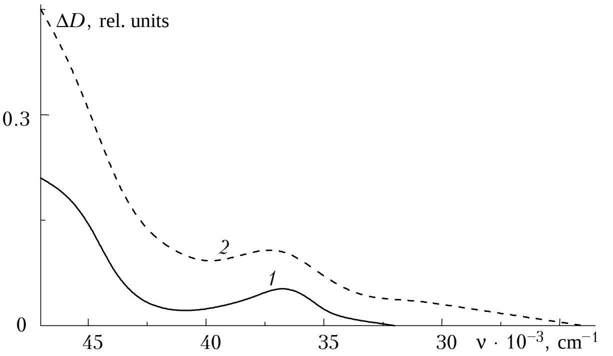


Fig. 1. Absorption spectra of the phenol aqueous solution before (*1*) and after UV irradiation for 20 min (*2*) ($c = 5 \cdot 10^{-5}$ M).

The most significant changes are observed in the fluorescent spectra (Fig. 2). The changes in phototransformations were monitored with respect to the neutral and corresponding ionic forms of phenol.

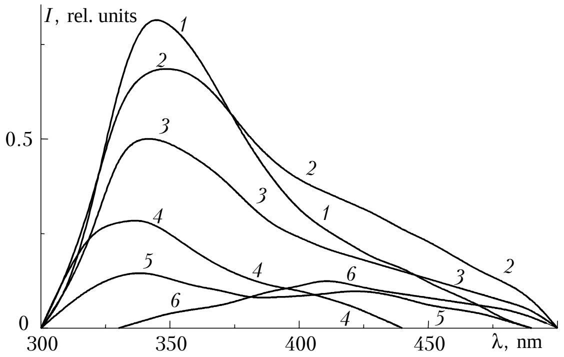
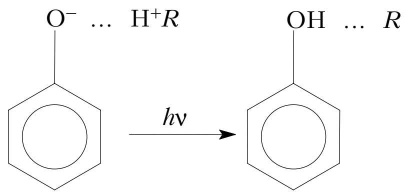


Fig. 2. Fluorescent spectra: phenol $5 \cdot 10^{-5}$ M + $5 \cdot 10^{-2}$ % H_2SO_4 (pH = 1.8), t_{irr} = 10 min, λ_{exc} = 300 nm (*1*); phenol $5 \cdot 10^{-5}$ M + $5 \cdot 10^{-4}$ % H_2SO_4 (pH = 4), t_{irr} = 20 min, λ_{exc} = 300 nm (*2*); phenol $5 \cdot 10^{-5}$ M in water (pH = 6.35), t_{irr} = 10 min, λ_{exc} = 300 nm (*3*); phenol $5 \cdot 10^{-5}$ M + 10^{-4} M KOH (pH = 7.1), t_{irr} = 10 min, λ_{exc} = 290 nm (*4*); phenol $5 \cdot 10^{-5}$ M + 10^{-4} M KOH (pH = 7.1), t_{irr} = 40 min, λ_{exc} = 300 nm (*5*); phenol $5 \cdot 10^{-5}$ M + 10^{-3} M KOH (pH = 10.5), t_{irr} = 40 min, λ_{exc} = 300 nm (*6*).

Weak fluorescence of both neutral and anionic forms of phenol is observed when adding alkali to the aqueous solution (pH = 10.5). The fluorescence band with the maximum at 296 nm corresponds to the neutral form, and that at 345 nm corresponds to the anionic form. It follows from Ref. 5 that the quantum yield of the isolated anionic form is high. In our case, the intensity of fluorescence of the anionic form is low. This corresponds to the case that the anionic form is in the H-bonded complex with solvent molecules. Under irradiation of the aqueous phenol solution with pH = 10.5 up to 20 min, the fluorescence intensity in the region of 296 nm increases. This fact is indicative of a proton transfer from the solvent to the anionic form followed by the equilibrium shift toward formation of the H-bonded neutral form of phenol (where *R* denotes the solvent):



At further increase of the irradiation time (longer than 20 min), the intensity of fluorescence at the wavelength of 296 nm decreases. This phenomenon is connected with the photodecay of the neutral form of phenol. Simultaneously with this process, the fluorescent band with the maximum at 410 nm arises. This band corresponds to fluorescence of the photoproduct. The appearance of such a fluorescent band was noticed in Ref. 6 when studying the photolysis of strong-alkali aqueous solutions of phenol. Thus, at pH = 10.5, proton is transported under UV irradiation from the solvent to the anion with formation of the neutral form of phenol. In such a way, the alkali medium decreases the efficiency of the phenol phototransformation as compared to the neutral and acid media.

In the neutral medium (pH = 6.35), phenol phototransformations are more efficient (Fig. 2). With increase of the irradiation time, the fluorescence intensity decreases nearby 296 nm and increases nearby 345 and 410 nm. Consequently, photolysis of phenol proceeds through formation of the anionic form. Thus, in the neutral medium, the OH-bond in the phenol molecule breaks down under the effect of UV irradiation with releasing proton into the medium.

Acidification of the aqueous solution leads to further increase of the efficiency of phenol phototransformation (Fig. 3). At pH = 1.8 phenol in water exists in the neutral and cationic forms. The fluorescent band with the maximum at 415 nm corresponds to the cationic form.[3] Under the UV irradiation, there arises a fluorescent band with the maximum nearby 345 nm, and its intensity increases with increasing the irradiation time (see Fig. 2). Thus, in the acid medium, phototransformations of phenol molecules are more efficient with participation of cationic and anionic forms.

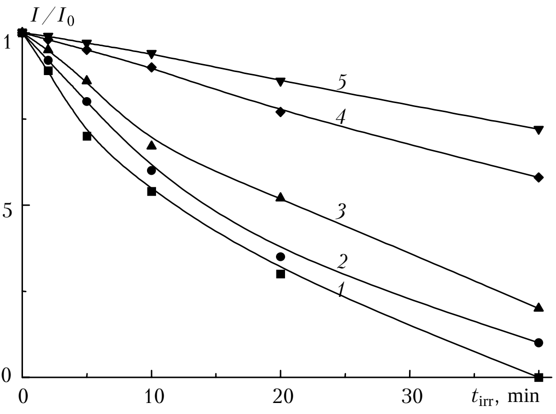


Fig. 3. Change of the fluorescence intensity of the neutral form of phenol at λ_{max} = 296 nm under UV irradiation at different values of pH: 1.8 (*1*), 4.0 (*2*), 6.35 (*3*), 7.0 (*4*), and 10.5 (*5*).

From analysis of the fluorescent data for some fixed time of irradiation, we have drawn the diagram of phenol decrease in the aqueous solution under UV irradiation (Fig. 4). The time of irradiation (10 min) corresponds to formation of primary photoproducts, and then the products decompose under the effect of UV irradiation.[7] It also follows from the diagram that the acid medium favors the photodecomposition of phenol.

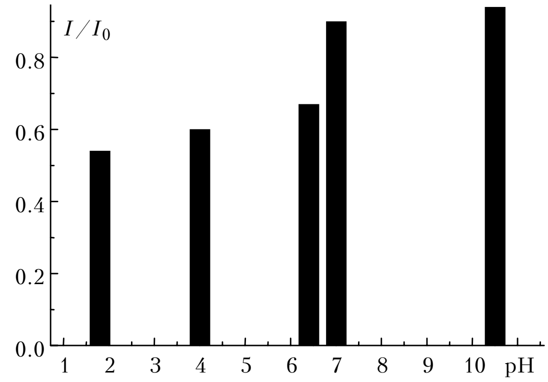


Fig. 4. Dependence of the fluorescence intensity of phenol solutions on pH; I is the fluorescence intensity of phenol solution after 10 min of UV irradiation, and I_0 is the fluorescence intensity of phenol solution before irradiation.

Conclusion

Thus, the photodecay of phenol is most efficient in the acid medium through phenol anionic and cationic forms as intermediate products. At pH = 6.35, the main intermediate product of phototransformations is the phenol anion. In the alkali medium, the equilibrium shifts towards formation of the neutral form, and this decreases the efficiency of the phenol phototransformation under the UV irradiation.

Acknowledgments

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