

Effect of heavy atom substitution on spectral-luminescent properties and photolysis of phenol

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Analysis of the spectral-luminescent properties of phenol and its derivatives has shown that quantum yield of fluorescence decreases in the series: phenol, 4-chlorophenol, 4-bromophenol. According to quantum-chemical calculations, the low quantum yield of fluorescence is caused by intercombination conversion which is more efficient than the radiation decay of the state S_1 ($k_r = 3 \cdot 10^7 \text{ s}^{-1}$, $k_{ST} = 10^8 \cdot \text{s}^{-1}$). Substitutions lead to the increase in the efficiency of $S-T$ conversion, decrease in the quantum yield in 4-chlorophenol, and quenching of fluorescence in 4-bromophenol ($\gamma_{\text{ph}} = 0.23$, $\gamma_{\text{Cl-ph}} = 0.09$, $\gamma_{\text{Br-ph}} = 10^{-4}$). The efficiency of photolysis in phenol and its derivatives under the exposure to UV radiation was compared using both theoretical and experimental methods.

Introduction

Natural waters contain large amounts of phenol and its derivatives. These compounds come to the soil or water medium through intense application of fungicides, insecticides, and herbicides.¹ Pollution of the environment and, especially, subsoil waters with phenol and its compounds is of toxic hazard. Biological transformations are often the efficient way for decomposition of these compounds. However, photochemistry presents an alternative method for decomposition of ecotoxicants. Photophysical properties and primary photoreactions of phenol in aqueous solution are considered in sufficient detail in Refs. 1 and 2.

The photolysis efficiency depends on the excitation energy, temperature, and pH of a medium. Under the effect of temperature differences, solar radiation, biotic and abiotic transformations, and medium pH variations of water objects, the initial phenols often give a spectrum of new, more dangerous products. Thus, at chlorination of drinking water containing phenols, they can produce dibenzodioxines being the 1st class carcinogens.³ As known,^{4,5} photochemical properties of phenols depend on both the type of a substituent and its position in the ring.

In this paper we study the effect of heavy atom substitution on spectral-luminescent properties and photolysis of phenol in water.

Technique

Electronic absorption and fluorescence spectra of phenol and its substituted molecules before and after irradiation were recorded with a Specord M40 spectrophotometer and a Hitachi 850 spectrofluorimeter. As a source of UV radiation for photochemical studies,

we used pulsed barrier discharge excilamps* employing mixtures of rare gases and halogens: XeBr ($\lambda = 283 \text{ nm}$) and KrCl ($\lambda = 222 \text{ nm}$). To interpret spectral-luminescent properties and reveal the mechanism of photo-break of O-H, C-Cl, and C-Br bonds of isolated phenol molecules, we involved quantum-chemical calculation, namely, the Intermediate Neglect of Differential Overlap (INDO) method with spectroscopic parameterization.

Results and discussion

Spectral-luminescent properties

Absorption and fluorescence spectra of aqueous solutions of the compounds under study were obtained (Figs. 1 and 2). After strong acids and alkalis were added to aqueous solutions of phenols, we observed reversible changes in the absorption and fluorescence spectra, which were attributed to production of various ionic (cation, anion) forms of phenols (Table 1).

Quantum-chemical calculations of the absorption spectra of phenols have shown that heavy atom substitution in the *para*-position of phenol does not lead to considerable changes in the spectra. This substitution leads to a longwave shift of absorption bands and increase of intensity in the longwave and medium spectral regions (Table 2). The heavy atom substitution leads to appearance of the state $S_2(\pi\sigma^*)$, formation of whose σ^* -orbital involves atoms of the C-Hal (carbon-halogen, where Hal = Br or Cl) bond. The electronic transition $S_0 \rightarrow S_2(\pi\sigma^*)$ in

* Exciplex lamps were put at our disposal by Prof. V.F. Tarasenko (Laboratory of Optical Radiation, Institute for High-Current Electronics SB RAS) within the framework of collaboration under AS RF Grant No. 407.

the studied substituted molecules lies in the region of the longwave absorption band (see Table 2).

The experiment has shown that the intensity of the fluorescence band decreases at transition from phenol to chlorine-substituted phenol; in bromphenol

no fluorescence was observed. To explain this fact, we used quantum-chemical calculations. With the wave functions obtained by the INDO method, we calculated the rate constants of photophysical processes (radiation decay, internal and singlet-triplet conversion).

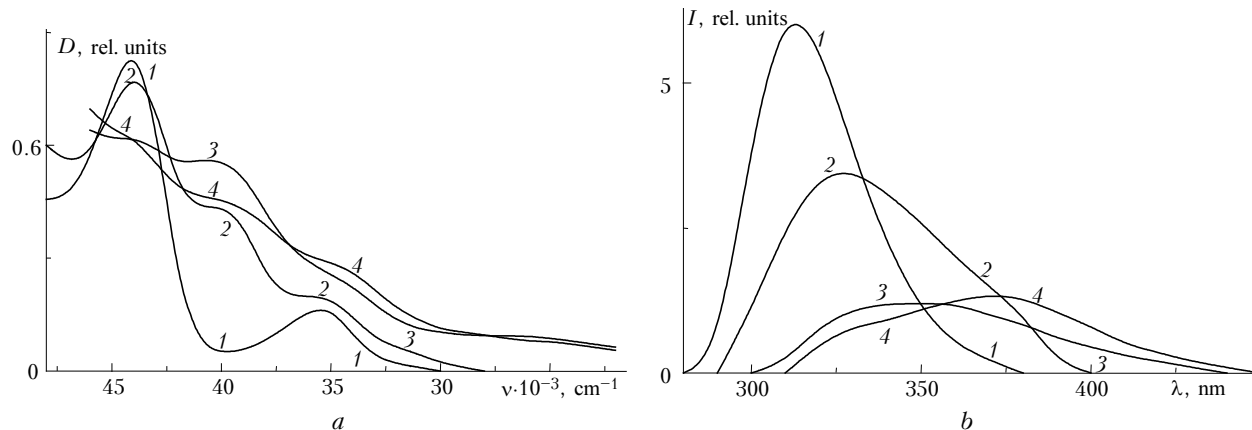


Fig. 1. Absorption (a) and fluorescence (b) spectra of aqueous solution of 4-chlorophenol before (1) and after the exposure to radiation of XeBr (2, 3) and KrCl (4) lamps: $E_{\text{pump}} = 0.6$ (2) and 6 J/cm^3 (3, 4).

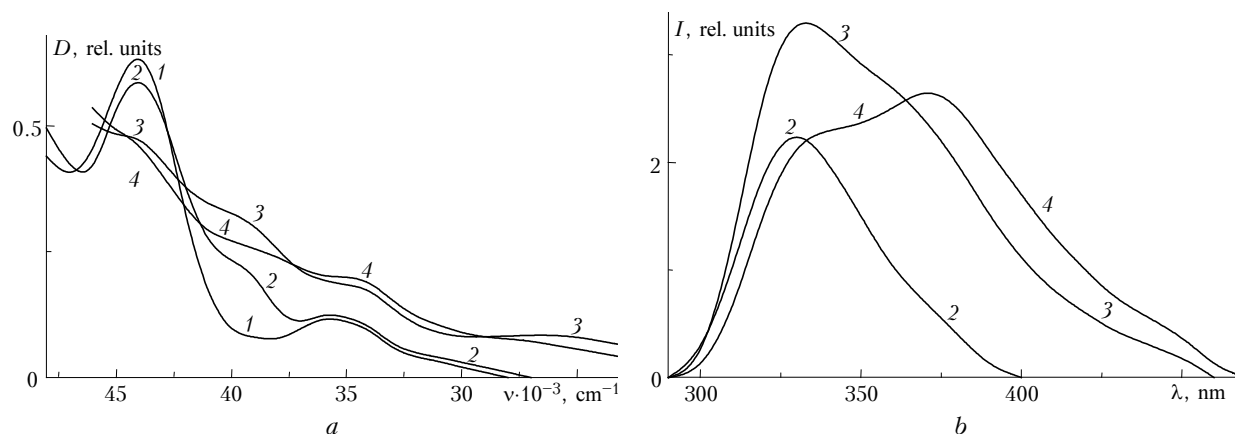


Fig. 2. Absorption (a) and fluorescence (b) spectra of aqueous solution of 4-bromphenol before (1) and after the exposure to radiation of XeBr (2, 3) and KrCl (4) lamps: $E_{\text{pump}} = 0.6$ (2) and 6 J/cm^3 (3, 4).

Table 1. Spectral-luminescent properties of ionic forms of 4-chlorophenol and 4-bromphenol

Compound	pH	Absorption (in parenthesis $\epsilon_{\text{max}}, \text{l}/(\text{mol}\cdot\text{cm})$)		Fluorescence
		λ_1, nm	λ_2, nm	$\lambda_{\text{max}}, \text{nm}$
Phenol in water	6.3	210 (7200)	270 (1720)	296
Phenol + 10^{-1} M KOH	12.5	230 (12800)	290 (5000)	$\lambda_{\text{exc}} = 270 \text{ nm}$ 345
Phenol + 20% H_2SO_4	-0.5	240 (11000)	300 (1000)	$\lambda_{\text{exc}} = 300 \text{ nm}$ 415
4-chlorophenol in water	6.5	230 (9900)	280 (2000)	$\lambda_{\text{exc}} = 300 \text{ nm}$ 310
4-chlorophenol + 10^{-1} M KOH	13	240 (9800)	305 (2400)	$\lambda_{\text{exc}} = 280 \text{ nm}$ 355
4-chlorophenol + 20% H_2SO_4	-0.9	230 (8800)	275 (1760)	$\lambda_{\text{exc}} = 300 \text{ nm}$ 425
4-bromphenol in water	6	225 (7000)	280 (1400)	No fluorescence
4-bromphenol + 10^{-1} M KOH	12.8	245 (8400)	300 (1800)	No fluorescence
4-bromphenol + 20% H_2SO_4	-1	220 (9400)	330 (600)	No fluorescence

Note. λ_{exc} is the fluorescence excitation wavelength; ϵ_{max} is the molecular extinction coefficient at the maximum of the absorption band.

Table 2. Calculated spectra of electronic excited states of phenol and its substituted molecules

Compound	State	Calculation			Experiment	
		E, cm^{-1}	f	P	E, cm^{-1}	$\epsilon \cdot 10^{-3}$
Phenol	$S_1(\pi\pi^*)$	36749	0.020	Y	37037	2.0
	$S_2(\pi\pi^*)$	45394	0.100	X	47393	6.5
	$S_3(\pi\sigma^*)$	47737	0.002	Z		
4-chlorophenol	$S_1(\pi\pi^*)$	36265	0.050	Y	35700	2.0
	$S_2(\pi\sigma^*)$	37200	0.006	Z		
	$S_3(\pi\pi^*)$	42941	0.210	X	41400	9.0
4-bromphenol	$S_1(\pi\pi^*)$	35662	0.060	Y	35000	2.3
	$S_2(\pi\sigma^*)$	37692	0.008	Z		
	$S_3(\pi\pi^*)$	42193	0.232	X	40000	9.0

Note. E , f , and P are, respectively, the energy, oscillator strength, and polarization of electronic transition.

According to the calculations, the low quantum yield of phenol fluorescence is caused by intercombination ($S-T$) conversion which is more efficient than the radiation decay of the state S_1 ($k_r = 3 \cdot 10^7 \text{ s}^{-1}$, $k_{ST} = 10^8 \text{ s}^{-1}$). Substitutions increase the efficiency of

this radiationless channel of the fluorescent state deactivation, decrease the quantum yield in 4-chlorophenol as compared with phenol fluorescence quenching in 4-bromphenol ($\gamma_{\text{Ph}} = 0.23$, $\gamma_{\text{Cl-Ph}} = 0.09$, $\gamma_{\text{Br-Ph}} = 10^{-4}$) (Fig. 3).

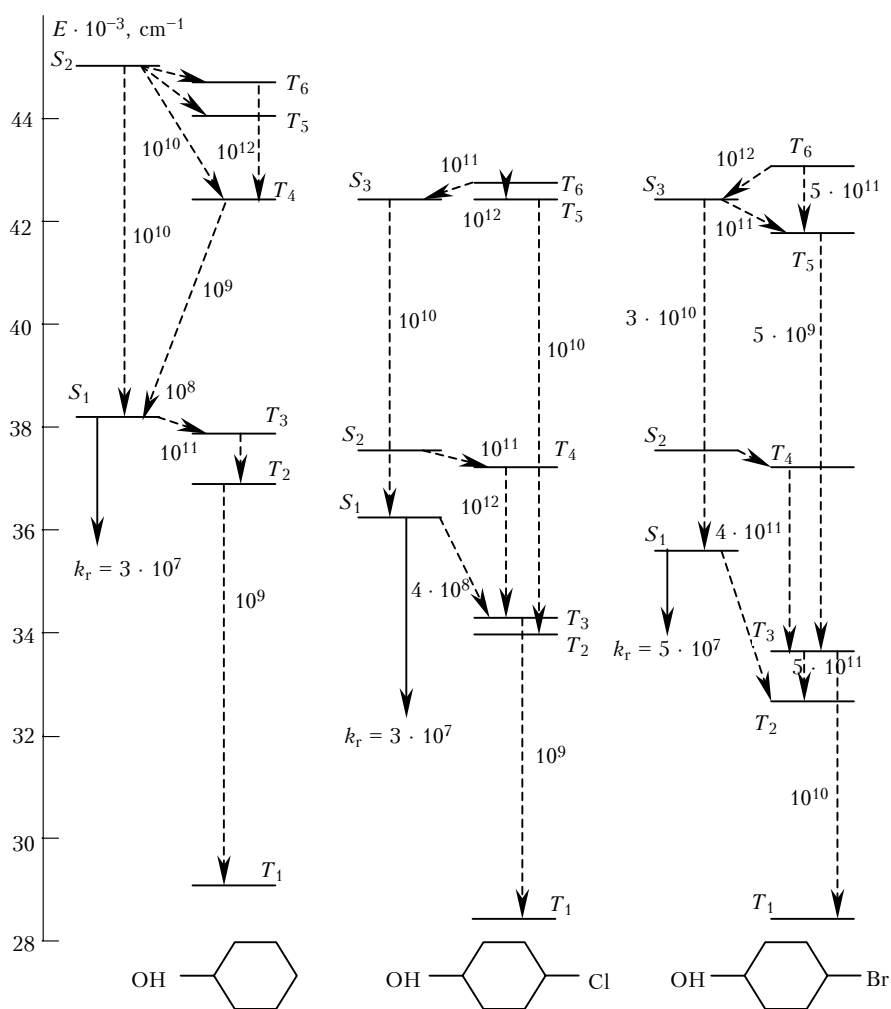


Fig. 3. Diagram of electronic excited states of phenol and its halogen-substituted molecules (k_r is the rate constant of radiation decay of the fluorescent state, s^{-1} ; the rates of radiationless photophysical processes, in s^{-1} , are shown nearby the dashed lines).

Photolysis

After the exposure to the lamp radiation, the diffuse absorption increases all over the spectrum of the studied molecules due to phototransformations. However, these changes are small in the case of phenol, but much more pronounced in the spectra of its substituted molecules (Figs. 1a and 2a). This fact evidences production of several photoproducts. Photochemical decomposition of the phenol molecule proceeds through a break of the O–H bond. For the halogen-substituted molecules this process goes through break of the O–H and C–Hal bonds. Therefore, the appearance of absorption bands in the region of 245–255 nm is characteristic of production of quinone-type structures.⁶ Spectra of the photoproducts are depicted in Figs. 4 and 5.

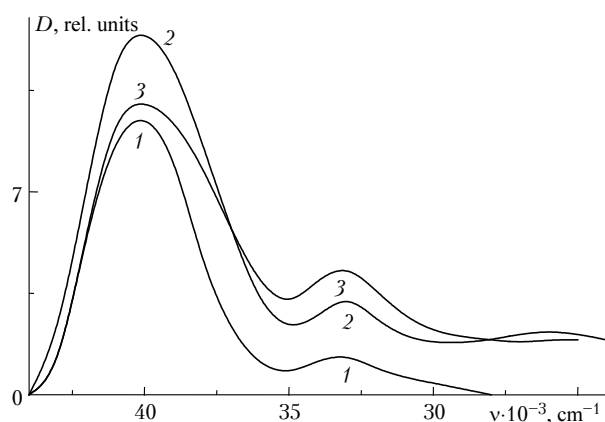


Fig. 4. Absorption spectra of products of 4-chlorophenol photolysis under the exposure to radiation of KrCl (3) and XeBr (1, 2) lamps: $E_{\text{pump}} = 0.6$ (1) and 6 J/cm^3 (2, 3).

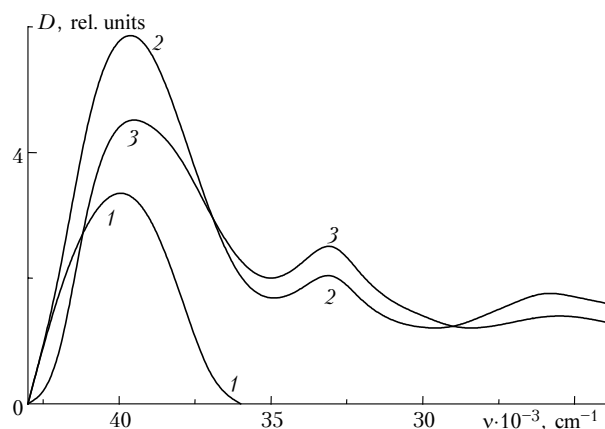


Fig. 5. Absorption spectra of products of 4-bromophenol photolysis under the exposure to radiation of KrCl (3) and XeBr (1, 2) lamps: $E_{\text{pump}} = 0.6$ (1) and 6 J/cm^3 (2, 3).

The results of quantum-chemical study of the phenol O–H bond photobreak depending on substitution and the energy of the exciting radiation show the following. The break of the O–H bond in phenol follows the pre-dissociation mechanism in the electronic excited states of the $\pi\sigma_{\text{OH}}^*$ -type.⁷ Table 3 presents the rate constants

of transition of excited molecules into the photodissociation singlet and triplet states through the internal or singlet-triplet conversion.

Table 3. Rate constants of transition into photodissociation states $S_D \equiv S(\pi\sigma_{\text{OH}}^*)$ and $T_D \equiv T(\pi\sigma_{\text{OH}}^*)$

Compound	$K(S_1 \rightarrow S_D)$	$K(S_1 \rightarrow T_D)$	$K(S_3 \rightarrow S_D)$	$K(S_3 \rightarrow T_D)$
Phenol	10^{-4}	$6 \cdot 10^9$	10^{-3}	$8 \cdot 10^{10}$
4-chlorophenol	10^{-1}	$3 \cdot 10^9$	10^{-6}	$7 \cdot 10^{10}$
4-bromophenol	10^{-5}	10^{10}	10^{-5}	$2 \cdot 10^{11}$

In isolated molecules the triplet photodissociation state is populated. Therefore, in phenol and its substituted molecules we can expect the highest efficiency of photobreak of the O–H bond in the triplet states. The efficiency of break of the O–H bond for the studied molecular structures increases at excitation in the medium part of the spectrum as compared with the longwave part. The heavy atom substitution almost does not affect the above regularities of the O–H bond photobreak. The calculations show that the C–Hal bond in the studied molecules breaks predominantly in the triplet state of the $\pi\sigma^*$ -type localized at this bond. Photobreak of the C–Hal bond in the singlet state of the similar type (S2) is inefficient, since the oscillator strength of the transition $S_0 \rightarrow S_2$ is low, and this state is not populated through intramolecular photophysical processes (see Fig. 3).

Under irradiation of the aqueous solution of 4-chlorophenol, we observed the decrease in the fluorescence intensity in the fundamental band ($\lambda^{\text{max}} = 310 \text{ nm}$) belonging to the molecule of 4-chlorophenol. Simultaneously a photoproduct band with the maximum nearby 330 nm arose. This band was assigned to fluorescence of hydroquinone as a primary product of photodecomposition of 4-chlorophenol.⁸ With the increase of the energy pumped into the solution (up to 6 J/cm^3), we observed the decrease in the intensity of the hydroquinone 330-nm fluorescence band (Fig. 1b) and weak unidentified radiation in the region of 370 nm. The decrease in the intensity of the hydroquinone fluorescence band was likely connected with its oxidation into *n*-benzoquinone, which was the final product of phototransformation of 4-chlorophenol in this study.

The mechanism of decomposition of the bromine-substituted phenol is similar to the mechanism of photolysis of 4-chlorophenol, since after irradiation the fluorescence of its photoproducts was observed in the spectrum at 330 and 370 nm (Fig. 2b). The study of the fluorescence spectra of substituted phenols after the exposure to the radiation of exciplex lamps shows the following. Regardless of the substituent nature, photoproducts produced after irradiation fluoresce in the region of 330 and 370 nm. It should be noted that at the exposure of the aqueous solutions of substituted phenols to the KrCl lamp radiation (medium part of the absorption spectrum) the photoproducts fluorescing

in the region $\lambda > 370$ nm are predominantly produced (see Figs. 1*b* and 2*b*). The photoproducts fluorescing in the shortwave region ($330 < \lambda < 370$ nm) are produced under the exposure of the halogen-substituted phenols to the XeBr lamp radiation (longwave absorption band).

The efficiency of phototransformations of the substituted phenols is roughly the same, but, as compared with phenol, the efficiency of photolysis of 4-chlorophenol and 4-bromophenol under the exposure to UV radiation increases sharply. However, no increase in the photolysis efficiency was observed at the transition from 4-chlorophenol to 4-bromophenol, although the quantum yield of fluorescence in the bromine-substituted phenol drops down to almost zero. Consequently, in this case the bromine atoms affect markedly photophysical processes, rather than photochemical ones.

Thus, the obtained results show that the exposure of mono-halogen-substituted phenols to UV radiation leads to their efficient decomposition.

Acknowledgments

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