Influence of excitation conditions on photolysis of phenols

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Photolysis of aqueous solutions of phenol and *n*-chlorophenol at excitation by laser radiation with different wavelength and output density is studied. It is found that the mechanism of photolysis of aqueous solutions of phenols at excitation by high-power radiation of KrCl laser (222 nm, 30 MW/cm^2) has some peculiarities as compared to their phototransformations at excitation by low-intensity radiation at a long-wave absorption band. This is connected with nonlinear excitation of the solvent by high-power UV laser radiation.

Introduction

Pollution of natural media with various toxicants requires thorough study of the processes of their photodecomposition under exposure to UV irradiation both in nature and at artificial purification of water. Phenol and some its derivatives, for example, chlorophenols[1,2] are widespread organic pollutants. Toxicity of the latter is higher than that of phenol itself, and it increases with the increasing number of chlorine substitutions.

The process of photolysis of organic molecules is extremely complex and consists of a great number of elementary photophysical and photochemical processes.[3] Laser sources of radiation are now widely used for studying the mechanisms of photolysis.[4,5] The study of interaction of laser UV radiation of different power with phenol aqueous solutions is interesting from the viewpoint of development of new methods for analysis and detection of ecotoxicants.

Laser sources emit in a narrow spectral range. This increases the selectivity of action on the object of study and simplifies the study of photolysis. Some change in an excitation wavelength can cause a change in the efficiency and ways of photolysis of a molecule. Due to its high directivity, radiation can be conveyed easily and with minimum loss to any point of a reactor. Besides the excitation wavelength, a change in other radiation parameters, e.g., intensity and coherence, can affect the photolysis. Thus, the increase in the power density of the exciting radiation in a narrow spectral region can lead to nonlinear interaction of radiation with matter. For example, two-photon effects begin to show themselves already at the power density about 0.1 MW/cm^2 (Ref. 6).

This paper presents the results of research into photolysis of aqueous solutions of phenol (P) and *n*-chlorophenol (*n*-CP) at excitation by laser radiation of different power and wavelength. The influence of excitation parameters on the efficiency of photolysis is under study. Possible influence of nonlinear processes on photolysis of P and *n*-CP is considered.

Technique

We have studied photolysis of P and *n*-CP aqueous solutions in the concentration of 10^{-3} mol/l. The parameters of the excitation sources are given in the Table. At excitation by the fourth harmonic of the Nd−YAG laser the radiation has power density no higher than 1 kW/cm^2 per pulse. This is several orders of magnitude lower than the power density of radiation emitted by the excimer KrCl, XeCl, and nitrogen gas-discharge lasers. At excitation by gas-discharge lasers, the radiation was focused by the crossed long-focus cylindrical lenses. As a result, the power density was as high as 250 MW/cm^2. In all the cases, the same dose of energy, equal to 1−1.2 J/cm^3, was absorbed by a unit volume of the solution (at excitation by the fourth harmonic of the Nd−YAG laser for comparison of the efficiency of phototransformations, the absorbed dose in some cases reached 25 J/cm^3).

Table. Parameters of excitation sources

Source	Parameters			Objects of study
	Wavelength, nm	Frequency, Hz/pulse length, ns	Peak power density, MW/cm^2	
4th harmonic of Nd−YAG laser	266	3×10^3/200	$\leq 10^{-3}$	Photolysis, spectral-luminescent characteristics of irradiated solutions, spectra and intensity of laser-induced fluorescence
KrCl laser	222	1/7	1−50	
XeCl laser	308	1/15	1−250	
N$_2$ laser	337	1/7	1−20	

Spectral-luminescent characteristics of solutions were measured before and after irradiation with the use of a Specord M40 spectrophotometer and Hitachi 850 spectrofluorimeter. During irradiation, phototransformations were monitored by changes in the spectra of the laser-induced fluorescence (LIF). To record LIF spectra in the case of excitation by the fourth harmonic of the Nd−YAG laser, the recording system "MDR−2 monochromator − FEU−140 PMT − amplifier − IBM PC" was used. The personal computer controlled the monochromator and the laser. In other cases, LIF spectra were recorded by the system "MDR− 23 monochromator − FOTON photodetector − pulse amplifier" and were plotted by an N−306 plotter.

Results and discussion

Photolysis of phenol and chlorophenol at excitation by radiation of Nd−YAG and KrCl lasers

We consider photolysis at excitation by the fourth harmonic of a Nd−YAG laser. The radiation wavelength (266 nm) in this case corresponds to the long-wave part of the absorption spectrum of P and n-CP. The absorption spectra of solutions of P and n-CP before and after irradiation are shown in Fig. 1. As is noted above, the solution absorbs the energy of (1.2 ± 0.2) J/cm^3. The most probable channel of P and n-CP decomposition under exposure to the fourth harmonic of the Nd−YAG laser irradiation is transformations in lower electronic excited states. Due to low intensity of exciting radiation, population of high electronic levels by reabsorption is improbable.

As is seen from the absorption (Fig. 1) and fluorescence (Fig. 2) spectra, several photoproducts are generated at irradiation. Absorption spectra of these photoproducts overlap the spectra of initial compounds, therefore extra absorption all over the spectrum arises after irradiation.[7] This complicates spectral estimation of quantum yield of the photodecomposition. Spectral luminescent analysis allows one to identify some final photoproducts, for example, n-quinone and hydroquinone. The ionic forms of P and n-CP are present as intermediate products. A sophisticated treatment of the nature of photoproducts at excitation to the lower electronic state is beyond the scope of this paper; it can be found, for example, in Refs. 8 and 9.

Let us now consider photolysis at excitation by radiation of excimer KrCl laser. The radiation at the wavelength of 222 nm (45000 cm^{-1}) excites P and n-CP to the state higher than S_1 (see Fig. 1). Besides, the power density of the KrCl laser radiation is three to four orders of magnitude higher than that of the fourth harmonic of a Nd−YAG laser. This increases significantly the probability of nonlinear population of highly excited states of phenols. The absorption spectra of solutions irradiated by this source are shown in Fig. 1 as curves 3 and 4 (the deposited energy is

$(1-1.2 \pm 0.1)$ J/cm^3, as in the case of irradiation by the fourth harmonic of a Nd−YAG laser). As is seen from the comparison of curves 2 and 4 for P (Fig. 1a) and curves 2 and 4 for n-CP (Fig. 1b), photolysis is much more efficient at excitation by a KrCl laser radiation than at irradiation by a Nd−YAG laser, although the generated photoproducts are the same in the both cases.
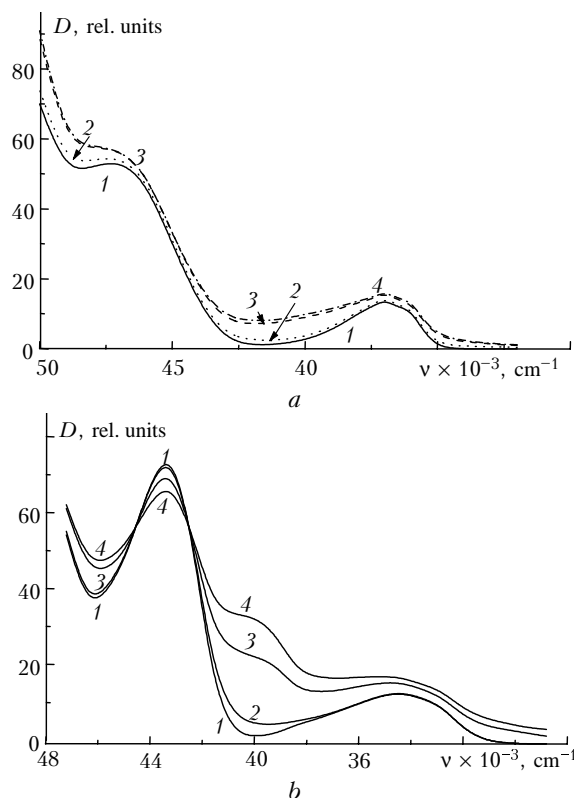

Fig. 1. Absorption spectra of phenol (a) and n-chlorophenol (b) before irradiation (curves 1), after irradiation: by Nd−YAG laser with power density $\leq 10^{-3}$ MW/cm^2 (curves 2), KrCl laser with power density of 30 MW/cm^2 (curves 3) and 1 MW/cm^2 (curves 4).
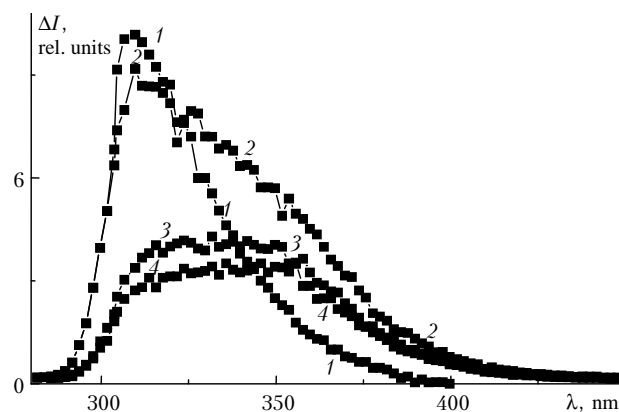

Fig. 2. Fluorescence spectra of n-chlorophenol $C = 10^{-3}$ mol/l in water: radiation-free solution at stationary excitation (1); spectra of laser-induced fluorescence at irradiation by the fourth harmonic of Nd−YAG laser ($2 - 4$): the solution has absorbed 1.2 (curve 2), 7.1 (3), and 25 J/cm^3 (4).

Thus, for example, curves *4* (see Fig. 1) illustrate the changes that correspond to the deposited energy about (20 ± 5) J/cm^3 at irradiation by the fourth harmonic of a Nd–YAG laser. There can exist several causes for more than an order of magnitude increase in the photolysis efficiency at excitation by KrCl laser radiation: first, harder irradiating quantum and, second, higher power density. Excitation by high-energy UV quanta (222 nm) can lead to direct population of higher photodissociative states. Higher states are also populated with the increase of excitation power density, because in this case the probability of two-photon and stepwise absorption increases. However, the study of transmission of KrCl laser radiation by phenol solutions showed that some clearing-up of phenol solutions is observed at the power density values under study, i.e., no additional absorption (comparable with the linear one) is observed (Fig. 3). This means that the efficiency of two-photon and stepwise processes in phenols at excitation by KrCl laser radiation is lower than that of linear ones.
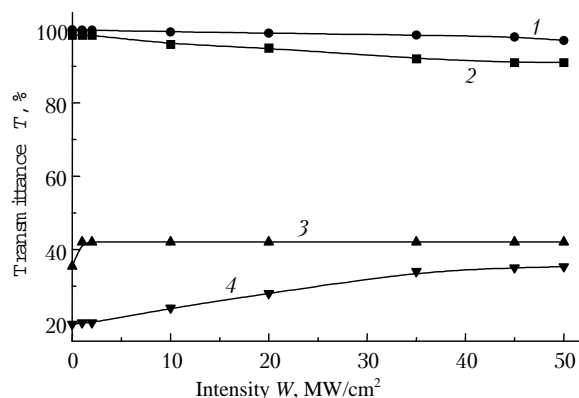

Fig. 3. Transmittance of solutions as a function of power density of pump radiation: XeCl laser (curve *1*) and KrCl laser (curves *2–4*); water (*1, 2*), phenol (*3*), and *n*-chlorophenol (*4*); 1-cm thick cell (*1*) and 1-mm thick cell (*2–4*).

On the other hand, besides direct interaction of radiation with molecules of the substance under study, excitation of molecules of the solvent is also possible. Studying the transmittance of the distilled water at stationary excitation with the Specord M40 spectrophotometer, we observed insignificant absorption at 222 nm ($T = 0.98$ at $l = 0.1$ cm). At excitation by KrCl laser radiation ($W = 30$ MW/cm^2), transmittance of water decreases (see Fig. 3, curve *2*). Two-photon absorption of XeCl and KrCl laser radiation leads to excitation of water in the region from 110 to 150 nm. As follows from Ref. 10, this causes generation of hydroxyl (OH) radicals. Thus, one more probable channel of decomposition of P and *n*-CP molecules arises, namely, reaction between an unexcited molecule of the substance under study and a solvent radical.[11–13]

To confirm this assumption, solutions of P and *n*-CP were irradiated by XeCl (308 nm, 32 470 cm^{-1}) and N$_2$ (337 nm, 29 670 cm^{-1}) lasers with the power density

of output radiation more than 1 MW/cm^2. As is seen from Fig. 1, the irradiated substances at ordinary low-intensity excitation do not absorb radiation of these wavelengths. Changes in the phenol absorption and emission spectra, observed by us at laser excitation, indicate that two-photon processes influence transformation of phenols and have qualitatively the same character as in the case of excitation by KrCl laser radiation. Study of transmission of XeCl laser radiation by distilled water also revealed some blacking-out with the increase of the radiation power density. In the optical layer of 1 cm thick, the transmittance was less than 90% at the power density of 250 MW/cm^2 (see Fig. 3, curve *1*), i.e., OH-radicals can be generated at two-photon absorption of the XeCl laser radiation by water as well.

These results allow us to explain the peculiarities in photolysis of phenols at excitation by the KrCl laser.

Influence of power density of radiation on photolysis of phenol and п-chlorophenol at excitation by KrCl laser

Photolysis of P and *n*-CP was observed at excitation by the KrCl laser radiation with two power density values: 1 and 30 MW/cm^2. Experiments showed that the solution of P cleared up already at the power density about 1 MW/cm^2. In that case, the transmittance T at 1 and 30 MW/cm^2 was 0.42. This value is higher than that measured by the spectrophotometer in the case of linear absorption $T_0 = 0.35$ (see Fig. 3). Clearing-up of *n*-CP begins at higher power density, since at 1 MW/cm^2 it coincides with the linear one $T_0 = 0.20$, and at 30 MW/cm^2 it is far higher ($T = 0.33$). This means that at excitation by KrCl laser radiation, the pulse-average population of the ground state S_0 decreases due to transition of some molecules to the excited state (for P at the power density about 1 MW/cm^2, and for *n*-CP at 30 MW/cm^2).

The efficiency of phototransformations of P under the exposure to radiation with the power density of 1 and 30 MW/cm^2 differs insignificantly (see Fig. 1*a*, curves *3* and *4*); the difference is within the measurement error. In the case of *n*-CF, the photolysis is more efficient at the power density of 1 MW/cm^2 than at 30 MW/cm^2 (see Fig. 1*b*, curves *3* and *4*). It follows herefrom that the decrease of the efficiency of *n*-CP photolysis is connected with the increase of the concentration of excited molecules and the decrease of the population of the ground state as the power density increases up to 30 MW/cm^2.

These results together with nonlinear effects in the solvent indicate that at high-power excitation (in contrast to low-power one) of phenol solutions by radiation of KrCl and XeCl lasers ($W \geq 1$ MW/cm^2), the main channel of phenol transformation is interaction of the molecule in the ground state with the OH radical generated at two-photon excitation of

water. This channel dominates over the channel of transformation of P and n-CP molecules from the excited state, since the concentration of molecules in the ground state is far higher than that in the excited state, even at clearing-up. Such a point of view is confirmed by the significant increase of the rate of phenol phototransformation at intense irradiation due to additions, which sensitize OH-radicals.[13] The concentration of molecules in the ground state decreases during a laser pulse life for n-CF at 30 MW/cm^2, whereas at 1 MW/cm^2 it remains equal to the total concentration of molecules in solution. This decrease must lead to the decrease in the efficiency of n-CP phototransformation at the power density of 30 MW/cm^2. Just this is observed in the experiment (see Fig. 1b), and this fact confirms the proposed mechanism.

Conclusion

Thus, the use of laser sources with different power density and spectral composition of radiation has allowed us to reveal the mechanism of phototransformations of phenols at high-power excitation. It has been shown that the higher efficiency of photolysis of P and n-PC at excitation by a KrCl laser as compared to excitation by the fourth harmonic of a Nd−YAG laser can be caused by the additional reaction between the solvent radicals generated under the effect of high-power UV radiation and the unexcited molecule of P or n-CP.

Acknowledgments

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