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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Direct Photolysis of Chlorophenols in Aqueous Solutions by UV Radiation from Excilamps

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Abstract—Direct photolysis of 2- and 4-chlorophenol and 2,4-dichlorophenol in aqueous solutions by UV radiation from XeBr (282 nm) and KrCl (222 nm) excilamps at various pH values was subjected to a comparative study.

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It is known that chlorophenols (CPs) are widely used in syntheses of herbicides, dyes, medicinal agents and can serve as antiseptics and preservatives for wood, leather, and fabrics. These compounds are formed as by-products in chlorine bleaching of cellulose and chlorination of residual phenols in disinfection of potable water. Chlorophenols are highly toxic for the aqueous biota and belong to priority aquatic toxicants [1, 2]. They decompose in aqueous solutions both under treatment with UV radiation (direct photolysis) and in combined treatment, e.g., with UV radiation in the presence of oxidizing agents or photocatalysts [3]. As UV radiation sources commonly serve low- and medium-pressure mercury lamps having a broad emission spectrum. In this case, the kinetics of CP photolysis is, as a rule, characterized by comparatively low decomposition rate constants and long half-decomposition periods. A promising way to intensify destruction processes of ecotoxicants of this kind is to use modern UV radiation sources, excilamps emitting light in a narrow spectral range [4, 5].

Previously, studies of spectral-luminescent properties have shown the efficiency of photolysis of methylated phenols in water with KrCl (222 nm), XeBr (283 nm) and XeCl (308 nm) excilamps [6] and of phenol, 4-chlorophenol, and 4-bromophenol with KrCl and XeBr exilamps [7, 8]. It has been found that direct photolysis of a herbicide, 2,4-dichlorophenoxyacetic acid, whose main decomposition product is 2,4-dichlorophenol, occurs more effectively with KrCl and XeBr exilamps, compared with photolysis with a mercury or XeCl excilamp [9]. For the initial pH values of a 4-chlorophenol solution, the kinetic of photolysis with a KrCl excilamp has been calculated [10] and a higher efficiency of the photolytic decomposition of 4-chlorophenol, compared with enzymatic destruction, has been revealed [11].

The goal of our study was to make a comparative analysis of the direct photolysis of chlorophenols in aqueous solutions under exposure to light of KrCl and XeBr excilamps at varied pH of the medium.

EXPERIMENTAL

Our experiments were performed with 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), and 2,4-dichlorophenol (2,4-DCP) (Merck, >98% purity). As a source of UV radiation served a XeBr or KrCl excilamp with barrier-discharge excitation (Institute of High-Current Electronics, Siberian Branch, Russian Academy of Sciences, Tomsk). Aqueous solutions of the CP objects of study (volume 20 cm^3, initial concentration 20 mg l^{-1}) were irradiated in a reactor (d = 5 cm, h = 3.2 cm) mounted under the exit window of an excilamp at room temperature (23 ± 2°C) under permanent agitation with a magnetic rabble. The energy absorbed by a solution upon irradiation for 1 to 20 min was 0.1–7.9 J cm^{-3}.

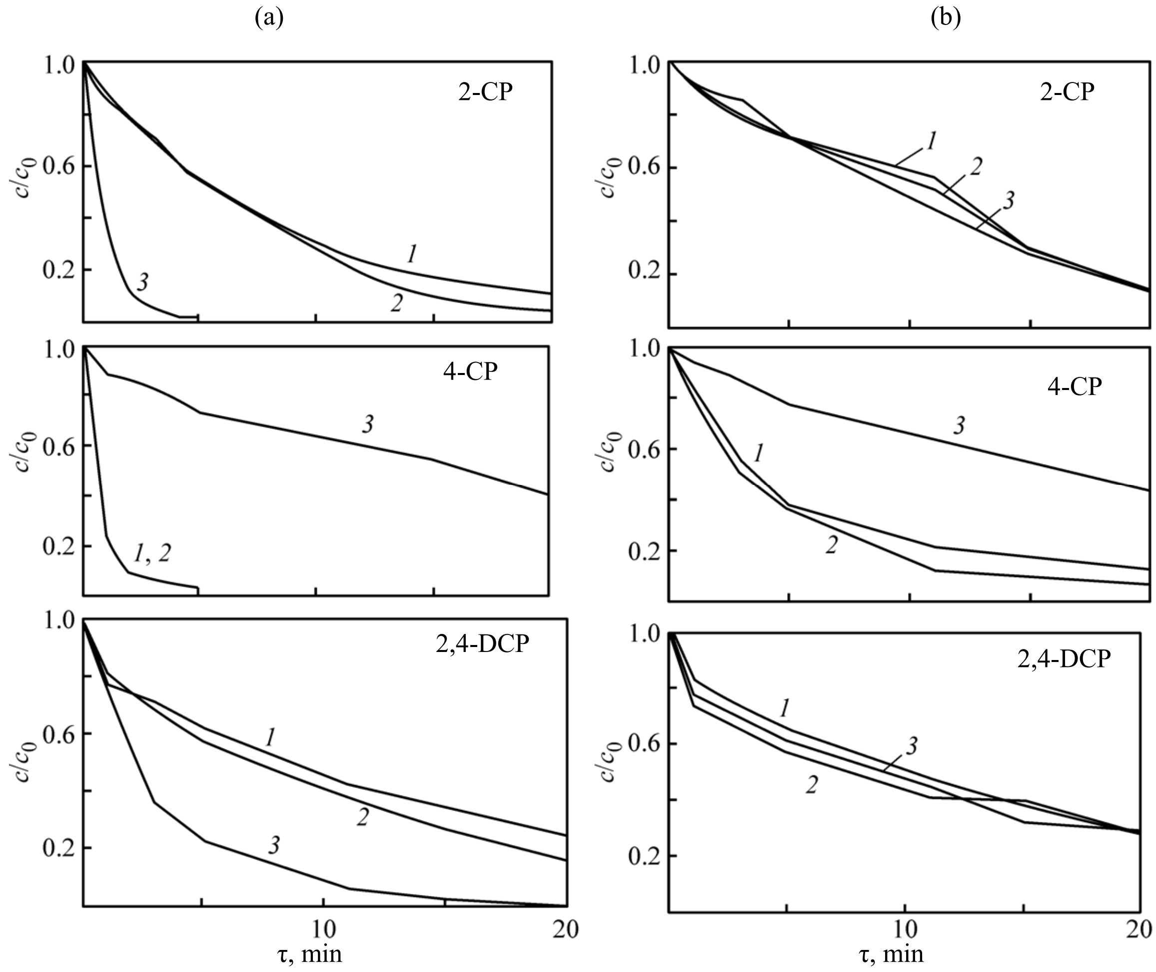

Fig. 1. c/c_0 vs. the duration τ of photolysis of chlorophenols (c = 20 mg l^{-1}) by light from (a) XeBr and (b) KrCl excilamps. pH value: (*1*) 2, (*2*) 5.4–5.7, and (*3*) 11.

The residual concentration of 2- and 4-CP in the course of irradiation was determined colorimetrically by using the reaction with 4-aminoantipyrine [12]. The concentration of of 2,4-DCP was determined by HPLC on a Milikhrom A-02 liquid chromatograph with a UV detector. We used a ProntoSIL-120-5-C18 column (2 × 75 mm), 1 : 1 acetonitrile–water mixture as eluent, and elution rate of 150 μl min^{-1}. The initial solution pH was brought to 2 or 11 by introduction of a solution of H_2SO_4 (4.6×10^{-3} M) or NaOH (2.5×10^{-4} M) and was monitored with an I-16 ion meter (Gomel plant of measuring instruments, Belarus). Electronic absorption spectra of CP solutions were recorded with an Agilent 3843 UV-VIS spectrophotometer (United States).

Figure 1 shows how the ratio between the residual concentration c and the initial concentration c_0 of CP depends on the solution exposure duration at pH 5.4–5.7 (initial solution pH) and 2 and 11.

It is known that CPs in an aqueous solution are mostly in the molecular form at pH < pK_a and in the dissociated form at pH > pK_a, with the dissociated forms (anions) considered to be more reactive than those in the molecular state [13]. It can be seen in Table 1 that, at pH 11, UV absorption spectra of CPs show a bathochromic shift of band peaks in the medium- and long-wavelength regions, which is characteristic of the formation of anionic forms. The maximum photolysis rates and minimum half-decomposition periods were observed in the case of irradiation with a XeBr excilamp (282 nm) for 2-CP and 2,4-DCP at pH 11, and for 4-CP at pH 2 and at the initial pH value (5.7) (Fig. 1, Table 2). A possible reason is that light with a wavelength λ = 282 nm is

Table 1. Spectral characteristics of chlorophenols in aqueous solutions

Chlorophenol	λ_{max}, nm	pH_{in}	Form	$\varepsilon_{\lambda max}$, M^{-1} cm^{-1}
2-CP	223	2 and 5.6	Molecular	3788
	274	2 and 5.6	The same	1958
	237	11	Anionic	8242
	293	11	The same	3733
4-CP	225	2 and 5.7	Molecular	8599
	280	2 and 5.7	The same	1609
	244	11	Anionic	12056
	298	11	The same	2599
2,4-DCP	225	2 and 5.4	Molecular	6099
	284	2 and 5.4	The same	2062
	245	11	Anionic	9726
	305	11	The same	3654

Table 2. Pseudofirst-order rate constants *k*, half-decomposition periods $t_{1/2}$, and quantum efficiencies φ of photolysis in irradiation of chlorophenol solutions at various pH of the medium with XeBr (282 nm) and KrCl (222 nm) excilamps

Chlorophenol	pH_{in}	λ, nm	ε_λ, M^{-1} cm^{-1}	k, min^{-1}	$t_{1/2}$, min	φ
2-CP	2	222	4288	8.5×10^{-2}	8.1	0.034
	5.6	222	4253	8.5×10^{-2}	8.2	0.034
	11	222	4860	8.7×10^{-2}	7.9	0.031
	2	282	1519	1.1×10^{-1}	6.1	0.036
	5.6	282	1498	1.5×10^{-1}	4.5	0.049
	11	282	2440	9.0×10^{-1}	0.8	0.174
4-CP	2	222	7662	1.5×10^{-1}	4.6	0.034
	5.7	222	8185	1.9×10^{-1}	3.6	0.041
	11	222	4739	4.0×10^{-2}	17.0	0.015
	2	282	1436	8.0×10^{-1}	0.9	0.264
	5.7	282	1545	7.9×10^{-1}	0.9	0.241
	11	282	1458	4.3×10^{-2}	16.1	0.014
2,4-DCP	2	222	6575	6.6×10^{-2}	10.4	0.017
	5.4	222	6293	6.8×10^{-2}	10.2	0.019
	11	222	4677	6.9×10^{-2}	10.0	0.026
	2	282	2091	6.7×10^{-2}	10.4	0.015
	5.4	282	1979	9.1×10^{-2}	7.6	0.022
	11	282	1114	1.8×10^{-1}	3.8	0.077

effectively absorbed by low-energy electronically excited states of 4-CP molecules and 2-CP and 2,4-DCP anions. This leads to rupture of C–Cl, O–H, and C–C bonds. To compare our results with published data on the CP photolysis by UV light at other wavelengths and intensities, we estimated the quantum efficiencies of photolysis. The first-order quantum efficiency of photolysis of a substance, φ, can be calculated by the formula [14, 15]:

$$\varphi = \frac{k}{2.303 I_\lambda \varepsilon_\lambda l},$$

where k is the pseudofirst-order rate constant (min^{-1}); I_λ, light intensity at a wavelength λ (einstein l^{-1} min^{-1}); ε_λ, molar absorption coefficient at a wavelength λ (M^{-1} cm^{-1}); and l, optical path length in the cuvette (cm).

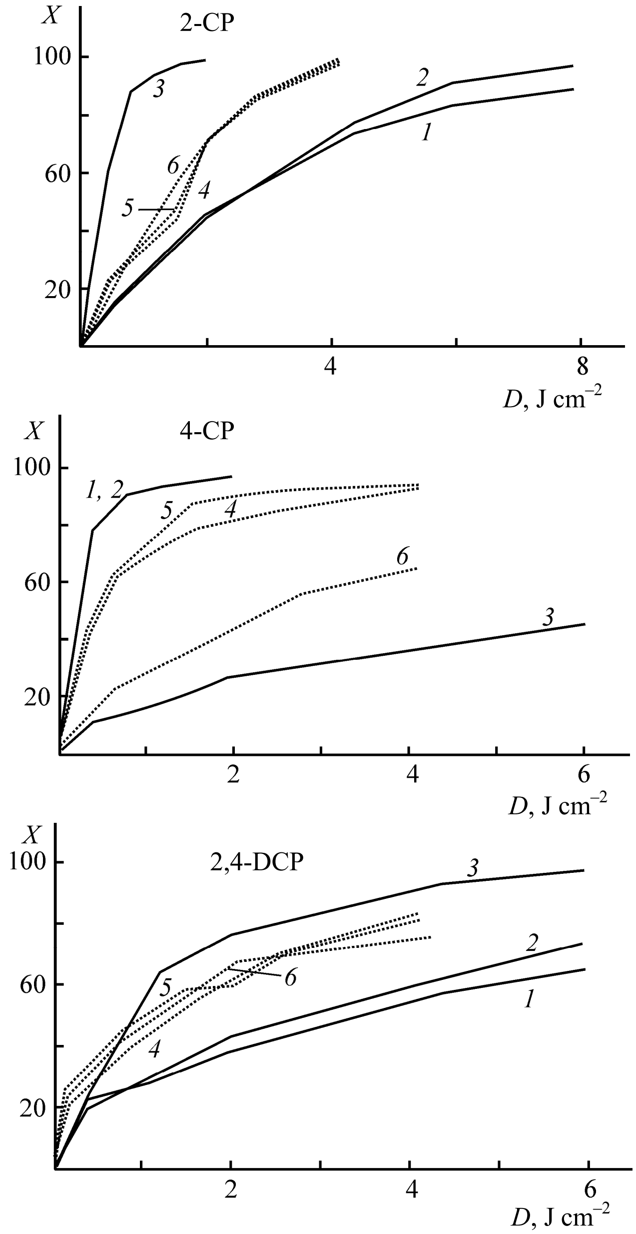

Fig. 2. Photolysis efficiency *X* of chlorophenols vs. the UV irradiation dose *D* from (*1–3*) XeBr and (*4–6*) KrCl excilamps. pH value (*1, 4*) 2, (*2, 5*) 5.4–5.7, and (*3, 6*) 11. *X*, % relative to the initial concentration.

This equation is applicable to the excilamps we used because the halfwidth of the emission band does not exceed 1 nm.

It can be seen in Table 2 that the values of φ for 2-CP anions and 4-CP molecules at λ = 282 nm substantially exceed (φ_{282}) those for 2-CP molecules and 4-CP anions. The values of φ_{282} for 2,4-DCP anions also exceeded those for molecules. This is in agreement with published data on photolysis at 296 nm for 2-CP (φ = 0.03–0.04 for molecules and 0.20–0.30 for anions) [16–18], and also for 2,4-DCP (φ = 0.01–0.02 for molecules and 0.10 for anions) [19, 20].

The average quantum efficiency of CP-4 photolysis is 0.25 in the pH range 1–13 under irradiation at λ = 254 or 296 nm (medium- and high-pressure mercury lamp) [16]. As follows from the data in Table 2, the value of φ_{282} for 4-CP molecules is comparable with the above value, whereas φ_{222} is an order of magnitude smaller and is comparable with the value of φ (0.017), previously found in photolysis of 4-CP molecules with a high-pressure mercury lamp, which emits light in a broad spectral range 238–579 nm with peaks at 254, 313, and 366 nm [21]. At the same time, the photolysis of 4-CP anions is characterized by the smallest values of φ, with $\varphi_{282} \approx \varphi_{222}$, which is indicated by the corresponding values of the rate constants. The wavelength of 282 nm nearly corresponds to the long-wavelength absorption peak of 4-CP molecules (280 nm), which is due to the electron transition from the ground state S_0 to $S_2(\pi\sigma^*)$ partly localized on the C–Cl bond [22]. Therefore, we assume that, upon irradiation of a 4-CP molecule at λ = 282 nm, a chloride atom is easily abstracted to give the main intermediates, hydroquinone and *para*-benzoquinone, which is indicated by the yellow coloration of a solution and has been additionally confirmed previously by a chromato-mass-spectrometric analysis [23]. 2-CP and 2,4-DCP molecules more difficultly undergo photolysis, compared with 4-CP molecules, because of the formation of intermolecular hydrogen bonds between a Cl atom in an *ortho* position and a hydrogen atom of the OH group of another molecule. Also possible is formation of intramolecular hydrogen bonds and bonds with water molecules [18].

The photolysis of 2-CP anions and 4-CP molecules by light at λ = 222 nm was characterized by a substantially lower quantum efficiency, compared with the respective values of φ_{282}. Despite that the light from KrCl excilamp falls within the range in which short-wavelength absorption peaks lie, transitions from high-energy excited electronic states probably do not lead to bond rupture, being involved in other effects, e.g., nonradiative processes [24].

A comparison of the CP photolysis efficiencies at various UV irradiation doses demonstrated that in the strongly acidic medium and at initial pH values of solution the maximum decomposition efficiency of 2-CP and 2,4-DCP molecules at the lowest expended dose was achieved with the KrCl excilamp (Fig. 2). This agrees with the results of photolysis of 4-CP solutions [25]. Nevertheless, full decomposition of 2-CP and 2,4-CP anions at pH 11 required smaller UV radiation doses with the XeBr excilamp, which was also observed in photolysis of 4-CP molecules at pH 2 and 5.7.

CONCLUSIONS

(1) Under the experimental conditions, the rate of direct photolysis of chlorophenols by light of XeBr and KrCl excilamps increased in the order 2,4-dichlorophenol < 2-chlorophenol < 4-chlorophenol for molecules (pH 2 and 5.4–5.7) and 4-chlorophenol < 2,4-dichlorophenol < 2-chlorophenol for anions (pH 11). The maximum photolysis rates were observed with the XeBr excilamp (282 nm) for 4-chlorophenol molecules and 2-chlorophenol and 2,4-dichlorophenol anions.

(2) The maximum photolysis efficiency of 2-chlorophenol and 2,4-dichlorophenol molecules with the smallest absorbed energy dose was achieved with the KrCl excilamp (222 nm), whereas photolysis of 2-chlorophenol and 2,4-dichlorophenol required smaller irradiation doses for the XeBr excilamp (282 nm). The opposite dependence was observed for 4-chlorophenol molecules and anions.

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