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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Spectral and GC–MS Analysis of Phototransformation of Herbicides in Water

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Abstract—The phototransformation of 2,4-dichlorophenoxyacetic and 2-methyl-4-chlorophenoxyacetic acids in water was studied using the $KrCl^*$ (λ_{rad} ~222 nm) and $XeBr^*$ (λ_{rad} ~283 nm) excilamps as UV radiation source.

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Among a variety of herbicides used now all over the world, 2,4-dichlorophenoxyacetic (2,4-D) and 2-methyl-4-chlorophenoxyacetic (MCPA) acids occupy the leading place in the production and application. After dispersion, herbicides remain on the soil surface, where they under degradation mainly by soil microorganisms or are sorbed by organic particles. By the literature data [1–5], 2,4-D may remain in the environment from 1 to 6 months.

Incorrect use, loss, and inappropriate storage and transportation of herbicides is dangerous, because their concentration in aqueous medium may attain several hundreds of ppm. Consequently, a necessary exists for the development of efficient methods of herbicide decomposition under various conditions.

Decomposition of 2,4-D was studied by means of chemical treatment with the H_2O_2/Fe^{2+} system, by photochemical treatment with the systems TiO_2/UV radiation/O_3, Fe^{2+}/UV radiation/O_3, UV radiation/Fe^{2+} oxidation, microwave radiation/UV radiation, TiO_2/solar radiation, TiO_2/UV radiation, TiO_2/active carbon/UV radiation, by means of photoelectrolytic treatment [6–12]. The use of ionizing radiation in oxidative decomposition of 2,4-D is also an efficient method, which, on the one hand, does not require addition of chemical reagents to aqueous solutions, but, on the other hand, requires a complex control measuring apparatus. As known, the use of catalysts and chemical reagents in combination with UV radiation may make reaction time shorter, however, these processes often require the additional stage of the separation, which increases the cost of the method.

Consequently, direct photodecomposition is a possible alternative method to the decomposition by ionizing radiation, because it uses simple apparatus, is cheap, and, apart from this, allows radiation intensity and wavelength to be easily controlled [13].

This study is concerned with the phototransformation of 2,4-dichlorophenoxyacetic and 2-methyl-4-chlorophenoxyacetic acids exposed to the UV radiation of exciplex lamps.

EXPERIMENTAL

We used in the study 2,4-D (98%, Aldrich) and MCPA (95%, Aldrich). Aqueous solutions of the compounds under study were prepared by dissolving a dry weighed portion. The dissolution of MCPA and 2,4-D to a 10^{-3}-M concentration was made complete by agitating a solution with an ultrasonic stirrer at 40°C for 15 min. The working concentration of herbicides was 10^{-4} M.

2,4-D and MCPA aqueous solutions were irradiated in a 10×10×45-mm quartz cell or in a glass beaker at room temperature. The irradiation time was from 1 to 60 min for both lamps. The distance from the

excilamps to the irradiated solution was 5 cm. During irradiation, a solution under study absorbed the energy $E = 0.5–3$ 1 J cm^{-3}. The installation was cooled with an air ventilator to protect the solution from overheating.

In photochemical study, unique excilamps, KrCl* (λ_{ra} ~222 nm) and XeBr* (λ_{rad} ~283 nm), with $\Delta\lambda = 5–10$ nm, $W_{peak} = 18$ mW cm^{-2}, $f = 200$ kHz, and a pulse length of 1 μs [14–17] were used as UV radiation sources.[1] These lamps were chosen because the UV radiation with λ_{rad}~222 nm is absorbed by higher-lying electronically excited states of molecules under study. From these states, a passage can occur into the photodissociative states participating in photocleavage of O–H, C–C, and C–Cl bonds. As a consequence, the efficiency of the molecular phototransformations increases [18–22]. The irradiation at λ_{rad} ~283 nm allows direct population of the photodissociaive state participating in photocleavage of C–Cl bond.

The spectral and luminescence characteristics of initial and irradiated 2,4-D and MCPA solutions were recorded with an UNICAM/Thermo Evolution 600 UV-Visible Spectrophotometer (USA) and a Varian Cary Eclipse spectrofluorimeter (Austria).

To determine the concentration of 2,4-D and MCPA after the photolysis, samples were preliminarily acidified with HCl to pH 1 and extracted with diethyl ether. Then, the extracts were evaporated in an airflow to a volume of 0.5 ml. The chromatography-mass spectrometry analysis of samples was done on a Finnigan Trace DSQ instrument (Thermo Electron Chromatography-Mass Spectrometry Division, USA). The conditions of the analysis were as follows: Trace TR-5MS column, 100°C (5 min), 10 deg min^{-1} to 180°C (5 min), 100 deg min^{-1} to 300°C (1 min), MS detector, carrier gas helium.

The toxicity of aqueous solutions was evaluated in biological test (lowest organisms, *Photobacterium phosphoreum* luminescent bacteria) [23]. We used in the analysis 10^9 bacterial cells ensuring the averaged statistically confident toxicity evaluation. The bioluminescence was measured on an "Angstrem" chemiluminometer equipped with a cooled photomultiplier, an amplifier, and a thermostatically controlled eight-position cell compartment. The total radiation intensity within 400–700 nm in the photon counting mode was measured. The toxicity of the solutions was estimated by the ratio BI = I/I_0 of the bioluminescence intensity of bacteria in a herbicide solution to that of the reference [23]. According to the world practice, solutions are ranked in the following order with respect to their toxicity: nontoxic ($I/I_0 = 1$), weakly toxic ($I/I_0 > 0.7$), medium-toxic ($I/I_0 = 0.5$), and extremely toxic ($I/I_0 < 0.3$).

Table 1. Spectral characterization of herbicides in water

Sample	Absorption, nm		Fluorescence, λ_{max}, nm
	λ^1_{max}	λ^2_{max}	
2,4-D	284	228	310
MPCA	278	226	310

The spectral characteristics of the studied molecules in water are given in Table 1. The 2,4-D and MCPA absorption spectra contain two characteristic bands. Noteworthy, the fluorescence intensity of 2,4-D is lower by a factor of 200 in comparison with MCPA.

The intensity decrease around 228 nm and the intensity increase in the region 240–260 nm were observed in the absorption spectra of 2,4-D exposed to KrCl* (λ_{rad} ~222 nm) or XeBr* (λ_{rad} ~283 nm) excilamp radiation. The above changes are due to the molecular phototransformations and formation of photoproducts. As the time of the UV irradiation increases to 60 min, the secondary photoproducts are observed in the absorption spectra at $\lambda > 350$ nm. Similar changes, occurring however after shorter irradiation time, were also found in the MPCA spectra (Fig. 1). Therefore, we may conclude that 2,4-D is more stable to photodegradation than MCPA. Yet, the data on the GC–MS analysis show that the degree of conversion of

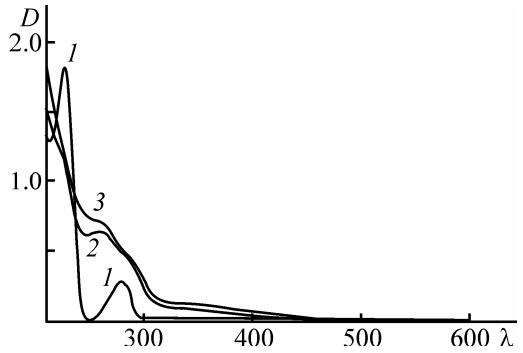


Fig. 1. Absorption spectra of MCPA in water ($c = 10^{-3}$ M) (*1*) before and (*2*) after 60 min of exposure to UV radiation of (*2*) XeBr* *and* (*3*) KrCl* excilamp; the same for Figs. 2–5. (*D*) Optical density (rel. units) and (λ) wavelength (nm).

[1] The lamps were developed under the supervision of V.F. Tarasenko at the High Current Electronics Institute, Russian Academy of Sciences, Siberian Branch, Tomsk, Russia).

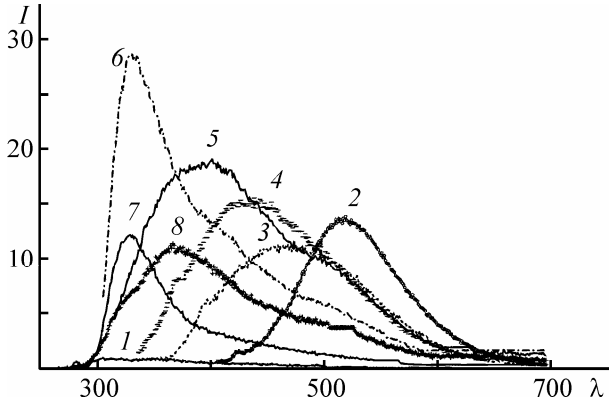


Fig. 2. Fluorescence spectra of 2,4-D aqueous solution (c = 10^{-3} M) (*1*) before and (*2*) after exposure to UV radiation of a KrCl* excilamp at different fluorescence excitation wavelengths. (*I*) Intensity (rel. units) and (λ) wavelength (nm); the same for Figs. 3–5. λ (nm): (*1*) 260, (*2*) 400, (*3*) 350, (*4*) 330, (*5*) 310, (*6*) 300, (*7*) 280, and (*8*) 260.

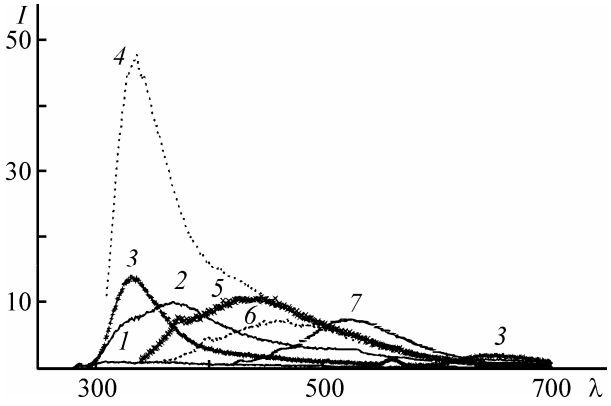
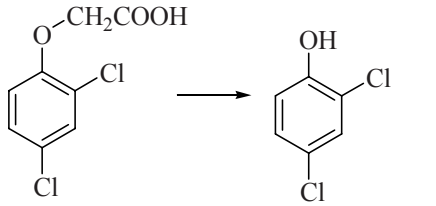


Fig. 3. Fluorescence spectra of 2,4-D aqueous solution (c = 10^{-3} M) (*1*) before and (*2*) after exposure to UV radiation of a XeBr* excilamp at different excitation wavelengths. λ (nm): (*1, 2*) 260, (*3*) 280, (*4*) 300, (*5*) 330, (*6*) 350, and (*7*) 400.

these molecules reaches 99% after 30 min of UV irradiation by these lamps.

The fluorescence analysis of 2,4-D subjected to UV irradiation revealed several fluorescent photoproducts (Figs. 2, 3). However, not all of them were detected by GC–MS method. When KrCl* excilamp is used for the irradiation, approximately six fluorescent products of 2,4-D photolysis appear. Their fluorescence in the regions peaking at 430, 475, and 525 nm coincides with the fluorescence of products formed after the XeBr* excilamp irradiation. No photolysis product emitting in the region 400 nm (Table 1) was recorded after the XeBr* excilamp irradiation, contrary to a KrCl irradiation. By the data of the chromatographic analysis, 2,4-D exposed to KrCl* (λ_{rad} ~222 nm, E = 1.92 J cm^{-3}) excilamp radiation is most probably converted to 2,4-dichlorophenol, in line with the literature data [24]:



2,4-D 2,4-Dichlorophenol

Table 2. Maxima of fluorescence bands of herbicides in water exposed to UV radiation of exciplex lamps

Fluorescence excitation wavelength, nm	λ_{max}, nm			
	KrCl*	XeBr*	KrCl*	XeBr*
	2,4-D		MPCA	
260	350	370	290	370
280	330	320	330	330
300	330	320	330	330
310	400	–	–	–
330	430	430	410	430
350	475	475	460	460
400	525	525	500	500

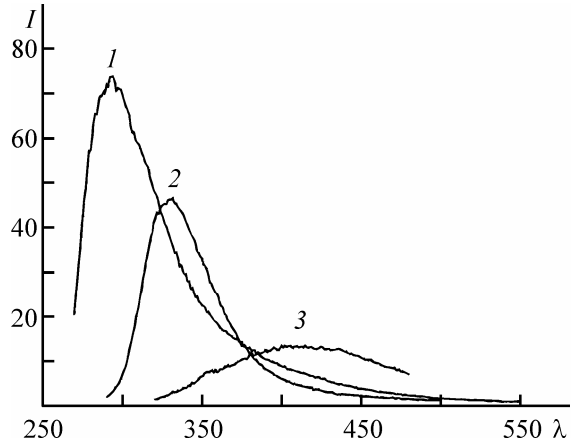


Fig. 4. Fluorescence spectra of MCPA aqueous solution (c = 10^{-3} M) (*1*) before and (*2*) after exposure to UV radiation of a KrCl* excilamp at different fluorescence excitation wavelengths. λ (nm): (*1*) 260, (*2*) 280, and (*3*) 330.

Scheme 1.

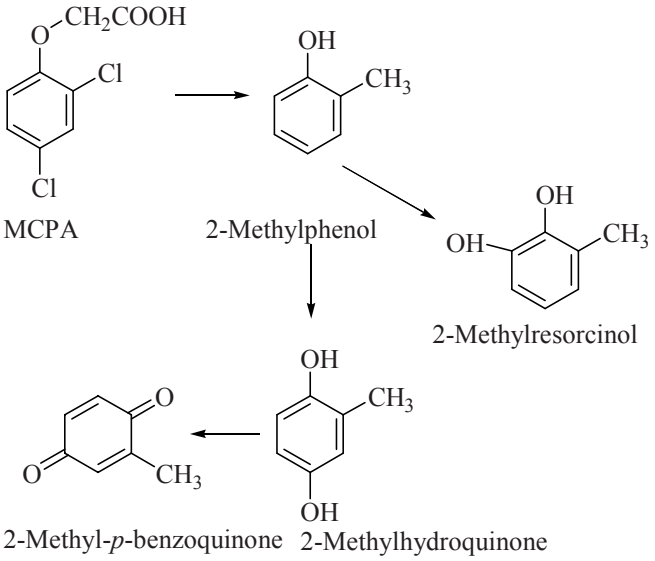
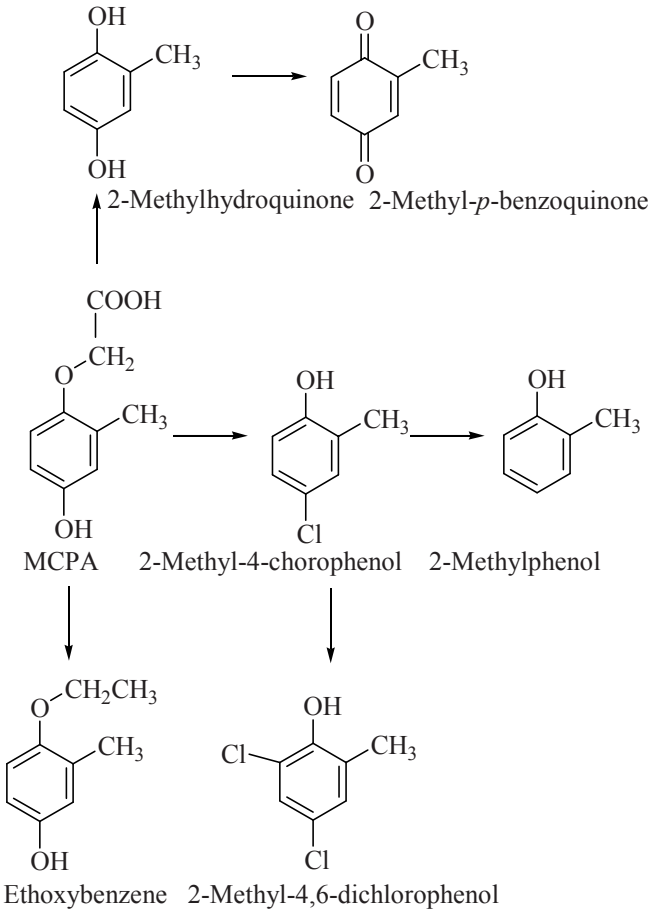


Table 3. Toxicity of 10^{-4} M aqueous solutions of MCPA and 2,4-D before and after UV irradiation

Test no.	Sample	Irradiation time, min, and energy, E, J cm^{-3}	Toxicity
1	MCPA	–	Medium
2	MCPA+KrCl*	15/1.5	″
3		30/3	″
4	MCPA+XeBr*	15/0.5	″
5		30/1	Extremal
6	2,4-D	–	Medium
7	2,4-D+KrCl*	15/1.5	″
8		30/3	″
9	2,4-D+XeBr*	15/0.7	″
10		30/1.44	″

Scheme 2.



The GC–MS analysis of 2,4-D aqueous solution exposed to a XeBr* radiation (λ_{rad} ~283 nm, E = 1.73 J cm^{-3}) revealed neither 2,4-D, nor products of its conversion. Apparently, to do this, sample preparation and conditions of the analysis should be changed. By the data of GC–MS, MCPA ($c = 2\times10^{-4}$ M) exposed to KrCl* excilamp radiation (E = 1.95 J cm^{-3}) decomposes by the Scheme 1.

According to the fluorescence analysis, three main photolysis products are present (Fig. 4). The fluorescent compounds in the regions 460 and 500 nm appear at longer irradiation times (Table 2). The transformation scheme for MCPA ($c = 2\times10^{-4}$ M) exposed to a XeBr* excilamp radiation (E = 1.6 J cm^{-3}) is given in Scheme 2.

Presence of different products was also confirmed by the fluorescence spectra (Fig. 5). As seen from these spectra, the mechanism of the MCPA photolysis is multichannel and involves breaking of both C–Cl and O–C bonds.

The toxicity of the 2,4-D and MCPA aqueous solution exposed to a KrCl* excilamp radiation does not exceed the medium value, i.e., no photolysis products increasing toxicity of the medium are formed (Table 3, tests nos. 2, 3, 7, 8). In the given case, the detoxication effect following the irradiation is not observed. The toxicity of the MCPA solutions exposed to a XeBr* excilamp radiation ranks as "extremely" toxic (Table 3, test no. 5). This may be due to

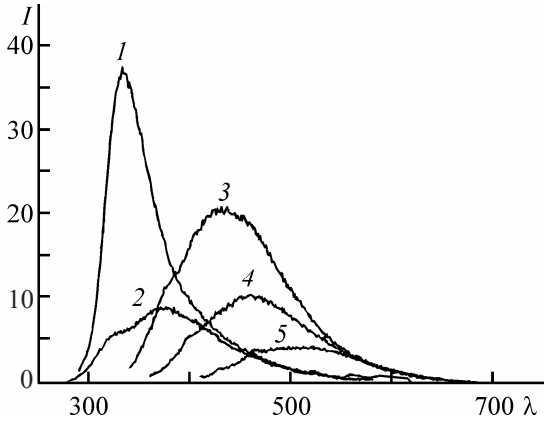


Fig. 5. Fluorescence spectra of MCPA aqueous solution ($c = 10^{-3}$ M) (*1*) before and (*2*) after exposure to UV radiation of a XeBr* excilamp at different fluorescence excitation wavelengths. λ (nm): (*1*) 280 and 300, (*2*) 260, (*3*) 330, (*4*) 350, and (*5*) 330.

formation of 2-methyl-4,6-dichlorophenol in the course of irradiation at this wavelength.

CONCLUSIONS

(1) It was found that the degradation of herbicides (2,4-dichlorophenoxyacetic and 2-methyl4-chlorophenoxyacetic acids) is the most efficient in the case of KrCl* and XeBr* excilamps, in contrast to the use of and XeCl lamps are used.

(2) The compositions of the photoproducts formed after the KrCl* and XeBr* excilamp irradiation are different. The main photolysis products of 2-methyl-4-chlorophenoxyacetic acid exposed to a XeBr* excilamp radiation are 2-methyl-4-chlorophenol, 2-methylphenol, 2-methylhydroquinone, 2-methyl-*p*-benzoquinone, 2-methyl-4,6-dichlorophenol, and ethoxybenzene; those formed upon the exposure to a KrCl* excilamp radiation are 2-mehylphenol, 2-methylresorcinol, 2-methyl-4-benzoquinone, and 2-methylhydroquinone. The conversion products of 2,4-dichlorophenoxyacetic acid exposed to a KrCl* excilamp radiation is 2,4-dichlorophenol. The degradation products of 2,4-dichlorophenoxyacetic acid exposed to irradiation by a XeBr* excilamp were not found.

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