94.7, 94.8, 105.6, 111.5, 127.3, 145.5, 152.8, 157.8, 196.6, 198.5. MS, m/z ($I_{\rm rel}$ (%)): 266 (92), 265 (100), 223 (52).

2,3-Epoxy-2,3-dihydro-2,3,5,6,8-pentahydroxy-7-propyl-1,4-naphthoquinone (7b), m.p. 152—156 °C (decomp.). IR (dioxane), ν/cm^{-1}: 3298 b (O—H); 1666 sh.s, 1656 v.s (C=O); 1602 s, 1598 s (C=C). ^{1}H NMR (CDCl$_3$), δ: 0.99 (t, 3 H, CH$_3$, J = 7.5 Hz); 1.63 (m, 2 H, CH$_2$); 2.77 (t, 2 H, CH$_2$, J = 7.5 Hz); 4.35 and 4.43 (both br.s, 1 H, OH); 6.59 (br.s, 1 H, β-OH); 11.09 and 11.60 (both s, 1 H, α-OH). ^{1}H NMR (CD$_3$CN), δ: 1.03 (t, 3 H, CH$_3$, J = 7.5 Hz); 1.64 (m, 2 H, CH$_2$); 2.75 (t, 2 H, CH$_2$, J = 7.5 Hz); 5.07 (br.s, 2 H, 2 OH); 7.98 (br.s, 1 H, β-OH); 11.13 and 11.77 (both s, 1 H, α-OH). MS, m/z ($I_{\rm rel}$ (%)): 280 (63), 279 (100), 252 (15), 251 (28), 250 (22), 224 (18), 223 (77), 222 (67).

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Laser study of photooxidation of chloranyl-sensitized 1,2,3,4-tetrachlorodibenzo-*p*-dioxine

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The kinetics of quenching of the triplet state of chloranyl (CA) by 1,2,3,4-tetrachlorodibenzo-*p*-dioxine (TCD) in benzene and acetonitrile was studied by nanosecond laser flash photolysis. The reaction proceeds *via* electron transfer (ET) with the rate constants of $1.5 \cdot 10^9$ and $3.7 \cdot 10^9$ L mol^{-1} s^{-1}, respectively. In benzene ET results in the formation of short-lived triplet radical ion pairs (lifetime 100 ns). In acetonitrile relatively long-lived (lifetime ≥10 μs) radical anion CA$^{\cdot -}$ and radical cation TCD$^{\cdot -}$ are formed and decay due to bimolecular reactions in the bulk of the solvent accompanied by the consumption of TCD.

Key words: laser photolysis, *p*-chloranyl, 1,2,3,4-tetrachlorodibenzo-*p*-dioxine, electron transfer, radical ion, triplet radical ion pair.

Investigation of the kinetics and mechanism of photochemical reactions involving polychlorinated dibenzo-*p*-dioxines is urgent because of the high toxicity of these organic compounds formed as admixtures in several important industrial processes.[1,2] Dye-sensitized photodestruction of dioxines can be a promising method for their demolition because it allows one to perform the process under irradiation with visible light. In this work,

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we studied the kinetics and mechanism of the interaction of the triplet state of chloranyl (CA) with 1,2,3,4-tetrachlorodibenzo-*p*-dioxine (TCD) in benzene and acetonitrile. Chloranyl in the triplet electron-excited state (^{3}CA) can remove an electron even from such weak electron donors as hydroxybenzenes.[3—7] It can be expected that the electron transfer (ET) also occurs when TCD is used as the electron donor.

Experimental

Absorption spectra of solutions were recorded on a Specord UV—VIS spectrophotometer. Differential absorption spectra and the kinetics of decay of intermediates were studied on a laser photolysis setup using a dye laser (390 nm, 1 ns, 0.2 mJ) with pumping with an N_2 laser.[3] The registration system contained an analog-to-digital converter (100 MHz) with the storage (Biomation 6500, USA) connected with a Pentium-200 computer. Kinetic curves were averaged using 16—128 laser pulses.

Chloranyl was sublimed *in vacuo*, and TCD was recrystallized from acetonitrile. Benzene and acetonitrile "for spectroscopy" grade were used. The air oxygen was removed from samples by argon bubbling. All measurements were carried out at 15 °C.

Results and Discussion

Under our experimental conditions, pulse photoexcitation of solutions of CA in benzene and acetonitrile ($5 \cdot 10^{-4}$—$1 \cdot 10^{-3}$ mol L^{-1}) results in the formation of ^{3}CA characterized[3—5] by the known absorption spectrum with a maximum at ~500 nm (Fig. 1) and a lifetime > 10 μs. The introduction of TCD is accompanied by the acceleration of ^{3}CA decay. TCD virtually does not absorb in the region of wavelengths longer than 360 nm (the longest-wave absorption band of TCD is characterized by a maximum at ~320 nm and an extinction coefficient of $1.2 \cdot 10^3$ L mol^{-1} cm^{-1}), which allows selective photoexcitation of CA only that possesses (in the solution) a sufficiently broad long-wave absorption band with a maximum at ~380 nm. The dependence of the rate constant of ^{3}CA decay on the TCD concentration is described by a linear law with a slope corresponding to a high value of the quenching rate constant ($1.5 \cdot 10^9$ and $3.7 \cdot 10^9$ L mol^{-1} s^{-1} in benzene and acetonitrile, respectively) close to the diffusion limit.

Interaction of ^{3}CA with TCD in acetonitrile results in the formation of two new relatively long-lived intermediates with absorption spectra with maxima at 445 and 735 nm (see Fig. 1). The spectrum of the induced absorption in the wavelength region of 400—500 nm almost coincides with the known[3—6] absorption spectrum of the $CA^{\cdot -}$ radical anion. It follows from this that the process involves ET and the absorption in the 600—800 nm region is due to the $TCD^{\cdot +}$ radical cation.

The kinetics of radical ion decay is independent of the presence of dioxygen in the system and is satisfactorily described by the second-order law if the recombination of the radical cations and anions between each other (Fig. 2) is taken into account along with the cross recombination (inverse ET with regeneration of the initial reagents) which is characteristic of similar systems.[4—7] In this process, $TCD^{\cdot +}$ disappears faster than $CA^{\cdot -}$ due to the high rate constant of recombination of $TCD^{\cdot +}$ with each other (this constant is comparable to that of cross recombination (see Fig. 2)). It can be assumed that the recombination of $TCD^{\cdot +}$ finally results in the consumption of TCD. Thus, photochemical destruction of

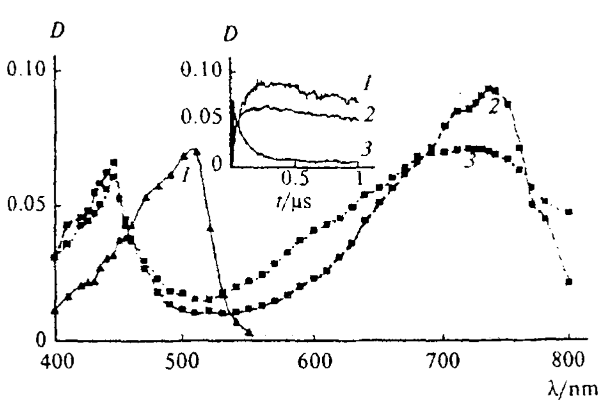

Fig. 1. Differential absorption spectra of intermediate products obtained by laser photolysis of CA ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of TCD ($2 \cdot 10^{-3}$ mol L^{-1}) in acetonitrile at the initial moment (*1*) and 0.5 μs after the laser pulse (*2*). *3*, Differential absorption spectrum of intermediate products obtained by laser photolysis of CA ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of TCD (0.1 mol L^{-1}) in benzene immediately after the laser pulse. Insertion: kinetic curves of formation and decay of intermediates in MeCN measured in different spectral ranges: λ = 735 (*1*), 445 (*2*), and 510 nm (*3*).

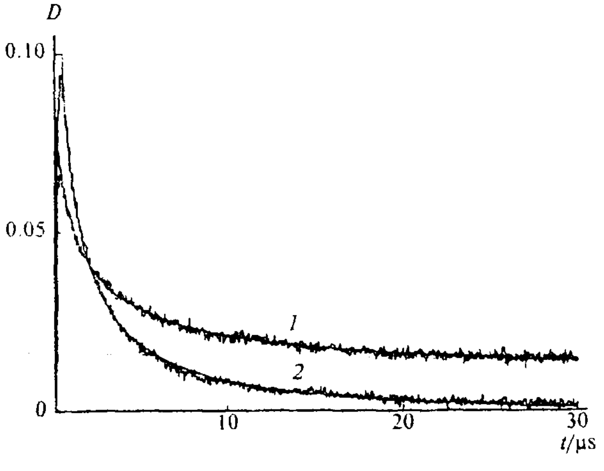

Fig. 2. Kinetic curves of disappearance of laser pulse-induced absorption in an acetonitrile solution of CA ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of TCD ($2 \cdot 10^{-3}$ mol L^{-1}) at 445 (*1*) and 735 nm (*2*). Lines correspond to the approximation of the second-order kinetic equation for the ratios of the rate constants of recombination of the radical anions and radical cations between each other and the rate constant of cross recombination of 1.8 and 12, respectively.

dioxines under visible light irradiation is possible in the CA—dioxine system in polar solvents.

Interaction of ^{3}CA with TCD in benzene results in the formation of a short-lived intermediate characterized by an absorption spectrum close to a superposition of the spectra of $CA^{\cdot -}$ and $TCD^{\cdot +}$; however, the corresponding bands are noticeably broadened as compared to similar absorption bands in acetonitrile (see Fig. 1). The decay kinetics of the intermediate is described by the first-order law with a rate constant of $8.2 \cdot 10^6$ s^{-1}, which is independent of the wavelength of observation, but increases to $11 \cdot 10^6$ s^{-1} when dioxygen is added to the system. The listed regularities are typical of triplet radical ion pairs appearing during ET from aromatic electron donors to triplet states of quinones in low-polar solvents.[3—7] Thus, in the photochemical reaction with *p*-chloranyl, chlorinated dibenzo-*p*-dioxines act as an electron donor. The reaction affords the corresponding radical cations, which allows the oxidation of dioxines under visible light.

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Decomposition of 2-[4-(2-chloro-1,1-dimethylethyl)phenyl]-propan-2-yl hydroperoxide catalyzed by sulfuric acid

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The decomposition of 2-[4-(2-chloro-1,1-dimethylethyl)phenyl]propan-2-yl hydroperoxide in acetone catalyzed by H_2SO_4 affords 4-(2-chloro-1,1-dimethylethyl)phenol. The kinetics of this reaction at 56°C was studied.

Key words: 4-(2-chloro-1,1-dimethylethyl)phenol, 2-[4-(2-chloro-1,1-dimethylethyl)phenyl]propan-2-yl hydroperoxide, acid-catalyzed decomposition.

Ethopheneprox, a synthetic pyrethroid, is an efficient insecticide which holds promise in agricultural and household applications.[1] A key intermediate in the synthesis of ethopheneprox is 4-(2-chloro-1,1-dimethylethyl)phenol (**1**), obtained from 2-[4-(2-chloro-1,1-dimethylethyl)phenyl]propan-2-yl hydroperoxide (**2**), whose synthesis was described by us earlier.[2]

The present work deals with the synthesis of phenol **1** by acid-catalyzed decomposition of hydroperoxide **2**. The reaction kinetics was studied to optimize this process.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument in $CDCl_3$ with Me_4Si as the internal standard. Decomposition of hydroperoxide **2** catalyzed by sulfuric acid was studied in acetone at 56 °C.

Hydroperoxide **2** was synthesized according to the known procedure.[2]

4-(2-Chloro-1,1-dimethylethyl)phenol (1). Compound **2** (45 g, 0.185 mol) and acetone (870 g) were placed in a 2-L

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