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

*F. Z. Galin,[a] N. M. Andriyashina,[a] T. V. Le,[b] Yu. V. Tomilov,[b] and V. V. Shereshovets[a]**

[a]Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 6390. E-mail: tom@cacr.ioc.ac.ru

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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glass reactor equipped with a stirrer and a calcium chloride tube. Then, 96% H_2SO_4 (0.98 g, 0.01 mol) in acetone (284 g) was carefully added with vigorous stirring. The reaction mixture was stirred at 56 °C for 2—2.5 h, cooled to 20 °C, and neutralized with stirring with an excess of $NaHCO_3$ (0.2 g). Stirring was continued for 1 h, the crystals of Na_2SO_4 that formed were filtered off, and the acetone was evaporated. The residue was recrystallized from hexane to give phenol **1** (94.4%), m.p. 69—70 °C (from hexane). Found (%): C, 64.81; H, 7.37; Cl, 18.60 $C_{10}H_{13}ClO$. Calculated (%): C, 65.04; H, 7.05; Cl, 19.24. ^{1}H NMR ($CDCl_3$), δ: 7.20 and 6.81 (both br.d, 2×2 H, C_6H_4, J = 7.0 Hz); 5.42 (br.s, 1 H, OH); 3.62 (s, 2 H, CH_2); 1.40 (s, 6 H, 2 Me). ^{13}C NMR ($CDCl_3$), δ: 26.43 (CH_2); 39.12 (C_{quat}); 56.53 (2 Me); 115.08 (C-3, C-5); 127.19 (C-2, C-6); 138.36 (C-4); 153.73 (C—OH).

In the study of the kinetics of consumption of hydroperoxide **2**, samples were withdrawn from the reaction mixture after definite intervals and analyzed by iodometry.[3] The quantities of hydroperoxide and H_2SO_4 were varied from 9 to 185 mmol and from 0.51 to 10 mmol, respectively.

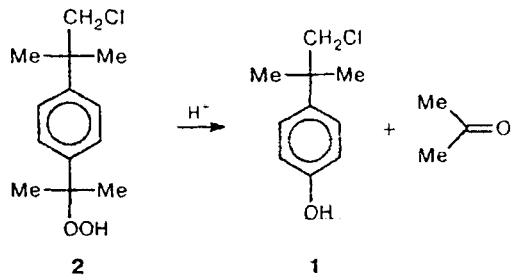
Results and Discussion

The study of the kinetics of H_2SO_4-catalyzed decomposition of hydroperoxide **2** in acetone at 56 °C showed that the process is a pseudofirst-order reaction.

$$-d[ROOH]/dt = k_{eff}[ROOH],$$

where k_{eff} is the effective first-order rate constant.

The typical kinetic curve of consumption of hydroperoxide **2** and its semilogarithmic anamorphosis are depicted in Fig. 1. According to the data obtained, k_{eff} is equal to $5.09 \cdot 10^{-4}$ s^{-1} at a catalyst (H_2SO_4) concentration of $6.8 \cdot 10^{-3}$ mol L^{-1}. For comparison, k_{eff} for H_2SO_4-catalyzed decomposition of cumyl hydroperoxide ([H_2SO_4] = $6.8 \cdot 10^{-3}$ mol L^{-1}, 1 : 6.5 phenol—acetone as the solvent, 20 °C) is equal to $4.33 \cdot 10^{-3}$ s^{-1}.[4] In this case, the higher k_{eff} value is due to the presence of phenol, whose accelerating action on the acid-catalyzed decomposition of cumyl hydroperoxide was noted earlier.[5]



2 **1**

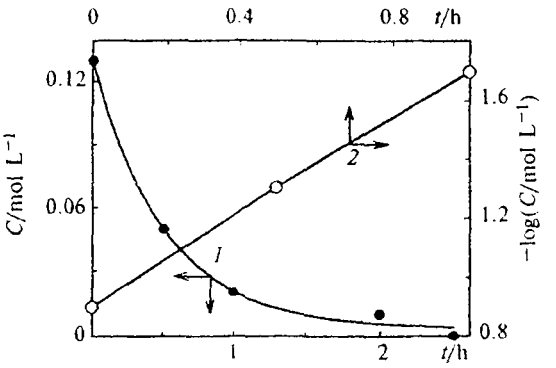


Fig. 1. A typical kinetic curve (*1*) and its anamorphosis (*2*) for H_2SO_4-catalyzed decomposition of 2-[4-(2-chloro-1,1-dimethylethyl)phenyl]propan-2-yl hydroperoxide (**2**) in acetone at 56 °C.

The structure of phenol **1** was established by IR and ^{1}H NMR spectroscopy. The IR spectrum exhibits an intense broad band of the OH stretching vibrations at 3240 cm^{-1} and a more intense band of the phenol C—O stretching vibrations at 1250 cm^{-1}. The character of substitution in the benzene ring is determined from absorption bands at 1615 cm^{-1} (s), 1512 cm^{-1} (v.s), and 840 cm^{-1} (s). The ^{1}H NMR spectrum shows two doublets from four aromatic protons at δ 6.81 and 7.20 characteristic of *para*-substituted benzenes.

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