_ CHEMICAL KINETICS _____ AND CATALYSIS _____

Quantum Chemical Study of the Rearrangement of Phenoxyl-Hydroxyphenyl Radicals

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Abstract—The absorption spectra and decomposition kinetics of intermediates formed upon the photolysis of p-iodophenol are studied via flash photolysis. The extinction coefficient of the p-iodophenoxyl radical is calculated. It is found that p-iodophenol acts as an inhibitor of light-independent liquid-phase oxidation reactions.

Keywords: phenyl and phenoxyl radicals, iodophenol, absorption spectra, kinetics of radical decay **DOI:** 10.1134/S0036024417030220

INTRODUCTION

Direct Photolysis of p-Iodophenol

Phenyl radicals Ph[•] are the simplest representatives of aromatic radicals and, like phenol radicals, are present as intermediates in many chemical, biological, and photochemical systems. The study of reactivities of phenyl and phenoxyl radicals is for this reason an important problem in the physical kinetics of radical reactions [1-7].

p-Iodophenol can serve as a convenient source of phenoxyl and phenyl radicals upon photolysis: the formation of *p*-iodophenoxyl and hydrophenoxyl radicals upon its photolysis is possible in principle. The absorption spectra and decay kinetics of intermediates formed upon the photolysis of *p*-iodophenol at 20° C have been studied via flash photolysis.

The flash photoexcitation ($\lambda > 280$ nm) of an oxygen-free solution of *p*-iodophenol in benzene (10⁻² M) results in the emergence of intermediate products whose absorption spectrum is shown in Fig. 1. According to experiments on flash photolysis of an iodine solution in benzene, and to the data obtained in this work (Fig. 1), the absorption band at 495 nm is due to complexation between atomic iodine and benzene. The initial photolysis event is thus a homolytic cleavage of the carbon—iodine bond:

$$HOC_6H_4J + hv \to HOC_6H_4 + J^{\prime}.$$
 (1)

The detached iodine atom participates in complexation with the solvent:

$$J^{\bullet} + C_6 H_6 \leftrightarrow C_6 H_6 J^{\bullet}.$$
 (2)

The band at 350 nm in the absorption spectrum of intermediate products (Fig. 1) is due to the formation of p-hydroxyphenyliodohydroxycyclohexadienyl radicals during the reaction between the solvated hydroxyphenyl radical and the initial phenol:

$$OHC_6H_4^{\bullet} + JC_6H_4OH \to R^{\bullet}.$$
 (3)

The absence of absorption at 350 nm in the spectrum of intermediates upon the flash photolysis of solutions containing *p*-iodophenol at low concentrations of 10^{-5} M (Fig. 1) suggests reaction (3) occurs. Other evidence for the formation of the R radical via reaction (3) is experiments on the photolysis of aqueous solutions of *p*-iodophenol. Figure 1d shows the absorption spectrum ($\lambda_{max} = 370$ nm) for the R[•] radical formed by reaction (3) upon the flash photoexcitation ($\lambda > 200$ nm) of an aqueous solution of *p*-iodophenol (10^{-2} M). The occurrence of such processes in aqueous solutions has been shown via pulse radiolysis, ESR, and the analysis of products. The shift in the absorption maximum and the slight change in the shape of the absorption band of the R[•] radical are due to differences in the solvating properties of water and benzene.

The decay kinetics of the iodine–benzene complexes and the R^{\bullet} radicals (measured at 495 and 350 nm, respectively) are governed by the secondorder law

$$2C_6H_6J^{\bullet} \to J_2 + C_6H_6, \qquad (4)$$

$$2R \rightarrow \text{products},$$
 (5)

and $k/\epsilon_{350} = 1.3 \times 10^5$ cm s⁻¹.



Fig. 1. Absorption spectra for intermediates at 5×10^5 s, obtained upon the flash photolysis of *p*-iodophenol in benzene: (*I*) *p*-iodophenol in benzene (10^{-2} M), (*2*) *p*-iodophenol in benzene (2×10^{-4} M), (*3*) *p*-iodophenol in benzene (2×10^{-5} M), and (*4*) *p*-iodophenol in water (10^{-2} M).

The quantum yield of reaction (1) upon steadystate irradiation using light with $\lambda = 300$ nm is 0.12.

At low concentrations of *p*-iodophenol (about 10^{-5} M), the recombination of hydroxyphenyl radicals,

$$2\text{HOC}_6\text{H}_4^{\bullet} \rightarrow \text{products}$$
 (6)

can compete with reaction (3), and the absorption spectrum of intermediates displays only absorption at 495 nm. In the condensed phase, the hydroxyphenyl radical absorbs in a farther UV region ($\lambda < 300$ nm). In accordance with reaction (4), one of final products of the photolysis of iodophenol was molecular iodine. The amount of the liberated iodine was determined via spectrophotometry using a calibration curve. This allowed us to obtain the concentration of iodine atoms

after a flash and thus the equal concentration of R[•] and the extinction coefficient of R[•] $\varepsilon_{350} = 1.2 \times 10^2 \,\mathrm{M^{-1} \, cm^{-1}}$. The rate of reaction (5) was $K_5 =$

 $1.5 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1}$.

The equilibrium constant for process (2) was obtained using the equation

$$K_{2} = \frac{[C_{6}H_{4}J^{\bullet}]}{[C_{6}H_{4}][J^{\bullet}]} = 3 \times 10^{-3} \text{ M}^{-1}.$$
 (7)

The resulting equilibrium constant was considerably lower than the one for complexation between atomic iodine and mesitylene, due likely to the lower basicity of the benzene ring.

Sensibilized Photooxidation of p-Iodophenol

The 2,6-disulfoanthraquinone-sensibilized photooxidation of phenyls is one way of preparing phenoxyl radicals. Photoexcitation through an UVS-6 filter ($\lambda =$ 320–360 nm) of an aqueous oxygen-free solution of 2,6-disulfoanthraquinone (5 × 10^{-5} M) in the presence of *p*-iodophenol (5 × 10^{-3} M) results in the formation of *p*-iodophenoxyl and anthrasemiquinone radicals (Fig. 2):

$$A_0 + hv \to A_S^* \to A_T^*; \tag{8}$$

$$A_{T}^{*} + HOC_{6}H_{4}J \rightarrow A^{-} + H^{+} + JC_{6}H_{4}O^{\bullet}.$$
 (9)

Introducing oxygen into a solution results in the reaction

$$\mathbf{A}^{\underline{\bullet}} + \mathbf{O}_2 \to \mathbf{A}_0 + \mathbf{O}_2^{\underline{\bullet}},\tag{10}$$

becoming the main pathway for the decay of anthrasemiquinone radicals. In accordance with reaction (10),

anthrasemiquinone radicals are replaced by O_2^{\bullet} in a period of 3×10^{-5} s in the presence of oxygen. The absorption in the range under study is due only to the phenoxyl radical (Fig. 2).

The extinction coefficient of the *p*-iodophenoxyl radical at the absorption peak at 420 nm was calculated to be $\varepsilon = 2.8 \times 10^3$ L M⁻¹ cm⁻¹. The decay of *p*-iodophenoxyl radicals in air-saturated solutions is governed by the second-order law

$$2JC_6H_4O^{\bullet} \to \text{products},$$

 $K_{11} = 5.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}.$
(11)

p-Iodophenol can liberate hydrogen atoms to form phenoxyl radicals with the same spectral and kinetic properties as the phenoxyl radicals of phenol and cresols. This means that *p*-iodophenol should act as an inhibitor of light-independent liquid-phase oxidation reactions. Under illumination *p*-iodophenol decomposes to form very reactive hydroxyphenyl radicals and should act as the catalyst of chain processes. It appears



Fig. 2. Absorption spectra for intermediates at 5×10^5 s, obtained upon the flash photolysis of aqueous solutions (pH 9) of *p*-iodophenol (5×10^{-3} M) and 2,6-disulfoanthraquinone (5×10^{-5} M): (*1*) oxygen-free solution and (*2*) air-saturated solution.

that the study of oxidizing systems containing *p*-iodophenol at certain concentrations will allow us to control the oxidation chain reaction using light.

The authors of [2] studied the oxidation of phenol and proposed the prototropic rearrangement of the phenoxyl-hydroxyl radical.

The PM-3 semiempirical method was used to calculate the activation barriers of the intramolecular rearrangement of phenoxyl radicals into hydroxyphenyl radicals [8]. The radicals listed below were considered.





Hydroxyl Radicals

The studied reactions are endothermic. The energy profile of the reaction is shown in Fig. 3.

Reaction heats ΔH for the structures under consideration are almost identical (96.3–104.7 kJ/mol). The saddle point lies in the output reaction channel. The transition state corresponds to the position of the hydrogen atom above the ring plane near the oxygen atom. The dipole moment of the phenoxyl radical diminishes in the order I–III–II (Fig. 3), while that of the hydroxyphenyl radical increases in the same order (calculations were performed using both the PM-3 semiempirical method and the Hartree–Fock– Roothan method in the 3-21d basis set, allowing for electron correlation according to the MP-2 perturbation theory). For structures I, II, and III, the dipole moment of the phenoxyl radical is considerably higher (by 150–400%) than that of the hydroxyphenyl radical.

Our flash photolysis study did not confirm the prototropic rearrangement. The decay of phenoxyl radicals in oxygen-free solutions is strictly governed by a second-order law. Upon the photolysis and radiolysis of *p*-halophenols, one of primary products is the hydroxyphenyl radical; however, no decay of the phenoxyl radicals was observed during our chromatographic analysis of the reaction products.

We also studied whether rearrangement can proceed through the motion of the hydrogen atom in the ring plane or at a certain angle to it; optimizing the geometry of such systems produced a value of $\Delta H^* > 100$ kcal/mol. When studying radical reactions in the liquid phase, we must consider solvation. Since the dipole moment of the transition state is higher than that of the phenoxyl radical, we would expect



Fig. 3. Potential energy surface cross section along the reaction coordinate (angle φ): (a) phenoxyl radical, (b) transition state, and (c) hydroxyphenyl radical.

some decrease in the activation energy when considering rearrangement in polar solvents. The energy of solvation of the phenoxyl radical and the transition state in water was estimated using the Kirkwood formula. Assuming that equilibrium with the orientational and electronic components of the medium polarization is established in the transition state, the drop in the activation energy is only 3 cal/mol. Rearrangement thus has an extremely high activation energy, compared to that of the recombination of phenoxyl radicals. At room temperature, this rearrangement proceeds with the π radical transforming into the σ radical; it is likely to be symmetry-forbidden.

CONCLUSIONS

The direct photolysis of *p*-iodophenol in benzene and water was studied. The absorption spectra of the atomic iodine–benzene complex and the *p*-hydroxy-

phenyliodohydroxycyclohexadienyl radical R^{\bullet} were recorded.

The decay of atomic iodine–benzene complexes and R_x^{\bullet} radicals (5) is governed by a second-order law: $K_5 = 1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in benzene at 20°C.

The quantum yield of the photolysis of p-iodophenol according to reaction (1) upon steady-state irradiation with a light of 310 nm is 0.12.

The absorption spectrum was recorded, and the magnitude of the rate constant for the decay of the *p*-iodophenoxyl radical by the second-order law was obtained in experiments on the sensitized photooxidation of *p*-iodophenol.

The experimentally observed absence of rearrangement of phenoxyl radicals into hydroxyphenyl radicals agrees with the high activation energy of this process (>100 kcal/mol) calculated according to the PM-3 and Hartree–Fock–Roothan methods.

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