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Features of Photolytic Transformations of Di-*o*-quinones Containing Sulfide Fragments

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Abstract—Quantum yields and products of photolytic transformation of bis(2,5-di-*tert*-butylcyclohexadiene-1,5-dion-3,4-yl)sulfide and 1,4,7,10-tetra-*tert*-butyl-5,6,11,12-tetrathia-dibenzo-cyclooctene-2,3,8,9-tetraone dissolved in saturated hydrocarbon at the action of irradiation with wavelength 436 and 313 nm, respectively. Possible mechanism of these photo reactions is proposed.

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The principal directions of *o*-quinone transformations in a paraffin solution under the action of UV and visible irradiation are reactions of decarbonylation and photoreduction [1]. Contribution of certain transformation pathway to the whole process is defined by the nature of substituents at the quinoid ring [2].

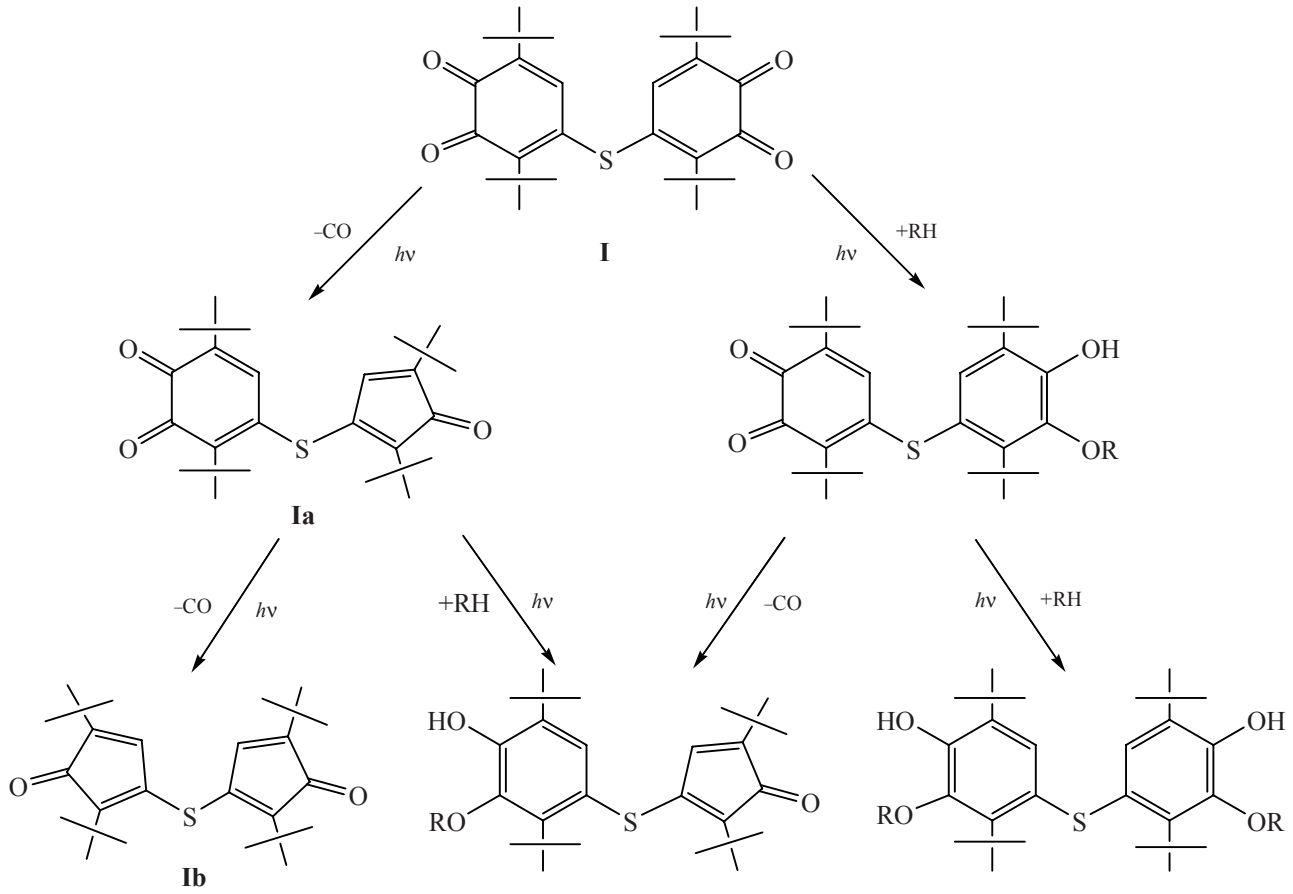
The electron spectrum of bis(2,5-di-*tert*-butylcyclohexadiene-1,5-dion-3,4-yl)sulfide (**I**) has absorption maxima in the regions of 340 and 480 nm. The absorption maxima of 1,4,7,10-tetra-*tert*-butyl-5,6,11,12-tetrathia-dibenzo-cyclooctene-2,3,8,9-tetraone (**II**) are at 270 and 530 nm. We subjected to photolysis by the light at the wavelenghts 436 and 313 nm for **I** and **II** respectively the solutions of these quinones in nonane at the concentration 10^{-4}–10^{-5} mol l^{-1}. Synthesis of the products of phototransformation was carried out at prolonged irradiation of more concentrated solutions of these quinones in hexane (10^{-3} mol l^{-1}). At irradiation, the reaction mixture color changed from yellow to cherry-red (**I**) and from violet to pale yellow (**II**). The value of quantum yield of decomposition of compound **I** in the range of initial concentrations (1–2.5)×10^{-4} mol l^{-1} and intensity of absorbed irradiation (0.43–2.21)×10^{18} quant l^{-1} s^{-1} is (3.18±0.13)×10^{-2}.

The dominating direction of transformation of **I** at the action of irradiation at wavelength 436 nm is decarbonylation. Yield of carbon monoxide in this case is 1.95±0.08 mol per mol of parent substance. The first step is spliting off one molecule of molecule of carbon monooxide with formation of primary photolysis product **Ia** (Scheme 1) that under irradiation is decomposed with ejection of second CO group. The main final product of photodecomposition of **I** is bis-(2,4-di-*tert*-butylcyclopentadiene-1,4-on-3-yl)sulfide (**Ib**).

Compound **Ib** is separated and analyzed with the methods of UV, IR and NMR spectroscopy and chromatomass spectrometry. From spectral characteristics of components of **I** and **Ib** in UV and visible spectral regions concentrations of these components in the reaction mixture at the photolysis are measured with 2-3% accuracy and curves of their decomposition and accumulation are constructed (see figure, curves *1* and *2*). But the sum of actual concentrations of compounds **I** and **Ib** in nonane in the course of irradiation is not equal to initial concentration of compound **I**. Obviously the system contains a third component, namely, the product of decarbonylation of the parent quinone at one quinoid ring **Ia**. From these experimental observations was drawn the plot of current concentration of compound **Ia** in the course of photolysis (see figure, curve *3*).

The second possible pathway of transformation of the studied compound **I** in a paraffin is its photo-

Scheme 1.

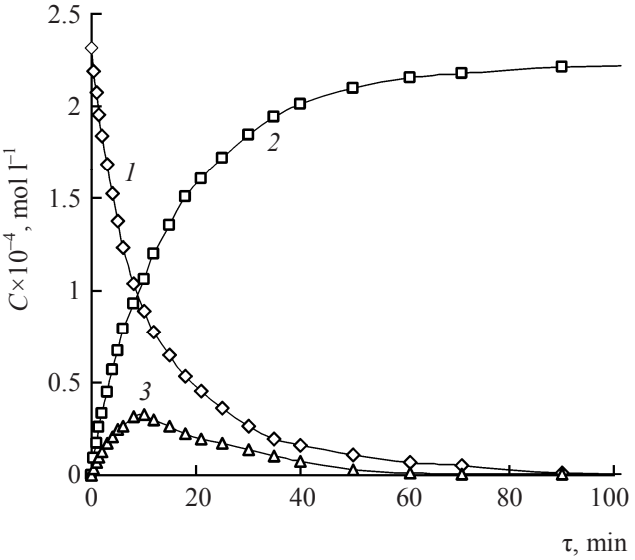


reduction to the respective phenol ethers. Yield of the products at this direction does not exceed 3–5%.

From the experimental data we calculated rate constant of phototransformation of **I** along the both these pathways, which found equal to $(8.1\pm0.3)\times10^{-4}$ s^{-1}. Omitting reactions of reduction of parent substance and compound **Ia**, from the equation of secular equilibrium for two consecutive reactions [3] **I** → **Ia** → **Ib** we calculated the rate of consumption of **Ia**. It found equal to $(7.3\pm0.3)\times10^{-4}$ s^{-1}.

Quantum yield of transformation of **II** in a paraffin solution does not depend on the initial concentration of substrate in the range of $(3–8)\times10^{-5}$ mol l^{-1} at the intensity of absorbed irradiation $(5.75–13.05)\times10^{17}$ quant l^{-1} s^{-1} and equals to $(8.9\pm0.5)\times10^{-3}$.

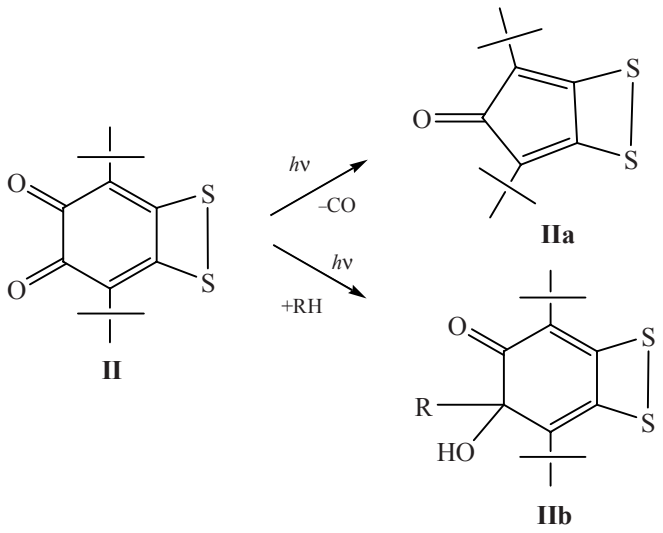
The published data on the photolysis of compounds containing disulfide fragments and experiments on electrochemical reduction and oxidation of compound **II** by the method of cyclic voltammetry (CVA) show that the primary act of this process is homolytic cleavage of S–S bond with formation of a biradical.



Photolysis of compound **I**. $C_0 = 2.32\times10^{-4}$ mol l^{-1}, λ_{phot} = 436 nm, $I_{0,sp} = 5.6\times10^{18}$ quant s^{-1} l^{-1}, $T = 298$ K. (*1*) consumption of **I,** (*2*) accumulation of **Ib,** and (*3*) ac-cumulation of **Ia.**

The appearing biradical can transform by three possible pathwatys: recombination of the radicals into the parent molecule, splitting of hydrogen atom off from the solvent molecule and stabilization of the system via transformation into compound **IIa** containing S–S bond. As far as NMR spectra of the compound **II** photolysis products do not display signal that could be assigned to S–H, we suggest that contribution of second pathway is insignificant. The attack of sulfur-centered radical on the second S–S bond should lead to formation of two molecules of a bicyclic compound containing, besides the quinoid fragment, a sulfur-containing four-membered ring **IIa** (Scheme 2).

Scheme 2.



After the monomolecular decomposition of compound **II** at S–S bonds with formation of two molecules **IIa**, their further transformation at the irradiation develop in two directions. The first pathway is elimination of CO in 30% yield. The second pathway is photoreduction of intermediate compound **IIa**. The final products of photolysis of **II** do not absorb in the studied region of electronic spectra and initial concentration of **II** in the photolysis experiments provide first order for this reaction. However, change in optical density of reaction mixture at the wavelength 270 nm at the photolysis of **II** does not obey first order kinetics on the current concentration (Fig. 2). The primary product of transformation of **II** contains quinoid fragment and for it is characteristic the presence of absorption bands at 230–250, 400, and 600 nm [1]. The first one contributes substantially to the measured value of optical density (*D*). As far as current concentrations of compound **II** at its photolysis in nonane could not be measured, the study of transformation of this quinone at irradiation is restricted to the analysis of final reaction products.

EXPERIMENTAL

Compounds **I** (mp 202.0°C) and **II** (mp 134°C) are courteously provided by researchers of Razuvaev Institute of Organometallic Chemistry. Hexane and nonane of "chemically pure" grade were treated for removing water by the common procedures [4] and then distilled with collecting the fractions, respectively, 68.6–69.0°C and 150–151°C.

The device for photolytic experiments, procedures for measuring of intensity of incoming beam and for analysis of the products of transformation by TLC have been described in [2].

Amount of carbon monooxide was determined by chromatograpy on a Tsvet-104 instrument: glass column 1500×2.5 mm filled with active carbon STK with granules 0.2–0.4 mm, the temperature of the column thermostat and of detector 70°C, the catharometer bridge current 250 μA; the carrier gas (helium) rate 25 ml min^{-1}.

For IR and NMR analysis, the products of photolysis of the reaction mixture was initially separated preparatively in thin layer [5]. The zones with separate spots on the silica gel plates after eluting were explored separately. The adsorbed substances were extracted with ethyl acetate. The solutions formed at the treatment of similar spots were joined together. The residue after careful removing of solvent were analyzed.

IR spectra of the products of photolysis were recorded on a Shimadzu IR Prestige-21 instrument from KBr pellets.

The NMR spectra were registered in the Analytical Center of Razuvaev Institute on a Bruker DPX-200 instrument (200 MHz) with internal TMS.

The chromato-mass spectrometric analysis was carried out on a Trance GC Ultra/DSQ II instrument, capillary column TR 5, length 60 m, diameter 0.25 mm, sample volume 0.01 μl, injector temperature 300°C, carier gas (helium M 60) flow rate 1 ml min^{-1}, column temperature was varied in the range 50 to 300°C, the range of mass numbers 29 to 700.

Measuring of red-ox potential was conducted by the method of cyclic voltammetry (CVA) in a three-electrode cell using a PI-50.1 potentiostat, under inert atmosphere (argon). Work electrode is stationary platinum (Pt) 2 mm diameter, auxillary electrode is platinum plate (S = 18 mm^2), reference electrode (Ag/AgCl/KCl) with water tight diafragm. Potential sweep rate 0.5 V s^{-1}. Background electrolyte 0.1M Bu_4NClO_4 (99%, "Acros") twice recrystallized from aqueous EtOH and dried in a vacuum for 48 h at 50°C. Dichloromethane and acetonitrile were dried and purified by the known procedures. Concentrations of the studied compounds 0.003 mol l^{-1}.

Bis(2,5-di-*tert*-butylcyclohexadien-1,5-dion-3,4-yl)sulfide (I). The IR spectrum (ν_{CO}, cm^{-1}: 1680, 1650). Found, %: C 70.97; H 8.35; S 6.93. $C_{28}H_{38}O_4S$. Calculated, %: C 71.49; H 8.08; S 6.81; O 13.62.

Bis(2,4-di-*tert*-butylcyclopentadien-1,4-on-3-yl)-sulfide (Ib). The UV spectrum [nonane, λ_{max}, nm (ε_λ, l mol^{-1} cm^{-1})]: 290 (4850±330), 490 (2150±180). The IR spectrum (ν_{CO}, cm^{-1}: 1700). The ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.15, 1.32 s (18H, $C^{2,4}$-*t*-Bu), 6.2 s (1H, C^5H). The ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 29.2 and 30.4 [both $C(CH_3)_3$]; 31.8 and 34.0 (both CMe_3); 135.4, 136.8, 140.8, 143.8 ($C^{1,2,4,5}$); 199.5 (C=O).

2,5-Di-*tert*-butyl-7,8-dithiabicyclo[4.2.0]-octa-1,5-dien-3,4-dione (II). The IR spectrum (ν_{CO}, cm^{-1}: 1655, 1665, 1643, 1620). Found, %: C 60.37; H 6.73; S 23.12. $C_{28}H_{36}O_4S_4$. Calculated, %: C 61.22; H 6.12; S 21.77; O 10.88. The mass-spectrum, m/z: 564 (M^+, 25), 507 (50), 450 (20), 400 (60), 383 (80).

2,4-Di-*tert*-butyl-6,7-dithiabicyclo[3.2.0]-hepta-1,4-dien-3-one (IIa). The ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.37 s [$C(CH_3)$]. The ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 29.3 [$C(CH_3)$], 35.4 [$C(CH_3)$], 141.9 ($C^{2,5}$), 151.6 ($C^{3,4}$), 189.9 (C=O).

2,5-Di-*tert*-butyl-4-hydroxy-7,8-dithiabicyclo-[4.2.0]octa-1,5-dien-3-one (IIb). The IR spectrum (ν_{CO}, cm^{-1}: 1695, 1685, 1640, 1620). The ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.35 s [$C(CH_3)$], 7.6 d (C_6H_{13}). The ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 29.8 [$C(CH_3)$], 31.1 s and 32.9 s [$C(CH_3)$], 132.9 ($C^{2,5}$), 154.5 ($C^{3,4}$), 207.2 (C=O).

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REFERENCES

1. El'tsov, A.V., Studzinskii, O.P., and Grebenkina, V.M., *Usp. Khim*., 1977, vol. 46, no. 2, p. 185.
2. Klement'eva, S.V., Mishchenko, O.G., Maslennikov, S.V., and Spirina, I.V., *Zh. Obshch. Khim*., 2007, vol. 77, no. 4, p. 649.
3. Kalvert, J. and Pitts, J., *Fotokhimiya* (Photochemistry), Moscow: Mir, 1968.
4. *Spravochnik khimika* (Chemist's Handbook), Moscow: Khimicheskaya Literatura, 1951, vol 2.
5. Akhrem, A.A. and Kuznetsova, A.I., *Tonkosloinaya khromatografiya* (Thin-Layer Chromatography), Moscow: Mir, 1964.