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Features of Photolytic Transformation of [4-(2-Methyl-5-t-butyl-cyclohexadiene-1,5-dion-3,4-yl)-3-methyl-6-*tert*-butyl-catecholato]triphenylantimony(V)

E. V. Ilyakina[a], **O. G. Mishchenko**[a], **A. I. Poddel'skii**[b],
S. V. Maslennikov[a], **and I. V. Spirina**[a]

[a] *Chemical Research Institute, Lobachevskii Nizhnii Novgorogd State University*
pr. Gagarina, 23, korp. 5, Nizhnii Novgorod, 603950 Russia
e-mail: spirina@ichem.unn.ru

[b] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii Novgorod, Russia*

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Abstract—Photolysis of [4-(2-methyl-5-*tert*-butyl-cyclohexadiene-1,5-dion-3,4-yl)-3-methyl-6-t-butyl-catecholato]triphenylantimony(V) in toluene by irradiation with the light of wavelength 546 nm leads to excitation of the molecule of parent compound which reacts with a molecule of $Ph_3SbCatQ$ affording 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) and 4,4'-di[(3-methyl-6-*tert*-butyl-catecholato)triphenylantimony(V)]. The formed compounds react with each other returning the system into the initial state. Action of light of wavelength 313 and 405 nm on the initial reaction mixture leads to the formation of carbon monoxide, $Ph_3SbCatCatSbPh_3$ and the products of photolytic transformation of 4,4'-di(3-methyl-6-*tert*-butyl-*o*-benzoquinone).

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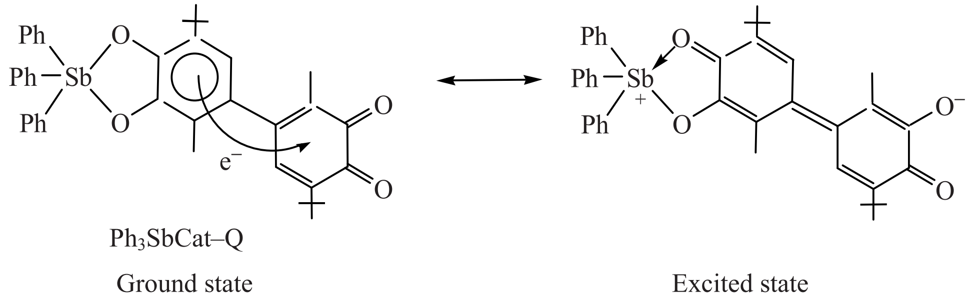
Among the methods of synthesis of [4-(2-methyl-5-*tert*-butyl-cyclohexadiene-1,5-dion-3,4-yl)-3-methyl-6-*tert*-butyl-catecholato]triphenylantimony(V) (Ph_3SbCat–Q) there is a reaction between 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) (Q–Q) and 4,4'-di-[(3-methyl-6-*tert*-butyl-catecholato)triphenylantimony(V)] (Ph_3SbCat–$CatSbPh_3$) [1]:

$$Ph_3SbCat\text{–}CatSbPh_3 + Q\text{–}Q \rightarrow 2\,Ph_3SbCat\text{–}Q. \quad (1)$$

Electron absorption spectra of equimolar mixture of Q–Q and Ph_3SbCat–$CatSbPh_3$ registered in the course of the reaction process are characterized by the presence of an isobestic point at the λ = 350 nm and undergo changes with the appearance of absorption bands at 410 and 505 nm (Fig. 1a). The first maximum corresponds to π–π* transition in the carbonyl group of the quinone fragment [2]. The second corresponds to the charge transfer complex [1]:



Ph_3SbCat–Q

Ground state

Excited state

In the course of the photolysis of Ph_3SbCat–Q the electron absorption spectra have an isobestic point at the wavelength 350 nm, and the changes in the optical density are just opposite to the observed in the course of the reaction (1). Upon irradiation of the initial compound in toluene by the light of wavelength 546 nm the optical density of the reaction mixture at 505 nm decreases by no more than 30–40% of its initial value

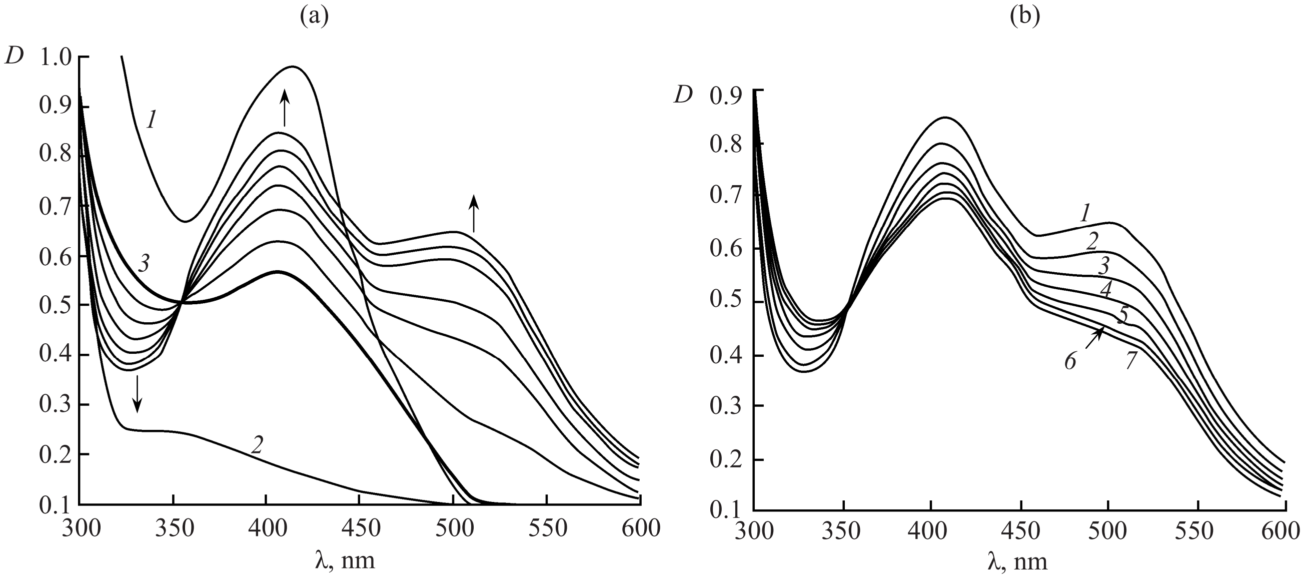


Fig. 1. (a) Electron absorption spectra of compounds (*1*) Q–Q and (*2*) $Ph_3SbCat–CatSbPh_3$, and (*3*) changes in the spectra of their equimolar reaction mixture in the process of the synthesis of $Ph_3SbCat–Q$, recorded each 3 min. $C(Q–Q) = C(Ph_3SbCat–CatSbPh_3) = 2\times10^{-4}$ mol l^{-1}, $T = 298$ K; (b) The spectra of reaction mixture at the photolysis of $Ph_3SbCat–Q$ in toluene with the light of $\lambda = 546$ nm. $C(CPh_3SbCat–Q) = 2.3\times10^{-4}$ mol l^{-1}, $I_{0,spec} = 9.8\times10^{17}$ quant s^{-1} l^{-1}, $T = 298$ K, $l = 0.71$cm. (*1*) 0; (*2*) 2.5; (*3*) 5; (*4*) 9; (*5*) 15; (*6*) 25; and (*7*) 50 min.

(Fig.1b). By the method of TLC compounds Q–Q and Ph_3SbCat-$CatSbPh_3$ were detected in the reaction mixture obtained at the photolysis of $Ph_3SbCat–Q$. In the course of the photolysis no formation of carbon monoxide was observed.

The scope of these observations allows an assumption that photolytic transformation of $Ph_3SbCat–Q$ can proceed along the following scheme:

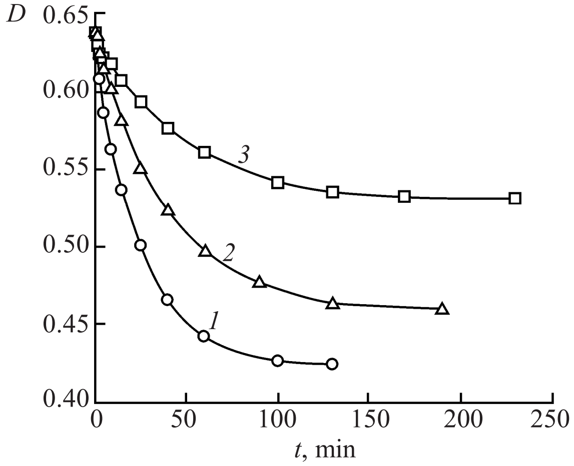


Fig. 2. Changes in the optical density in the course of photolysis of $Ph_3SbCat–Q$ in toluene at $\lambda = 505$ nm at varied intensity of incident illumination. $C(Ph_3SbCat–Q) = 2.3\times10^{-4}$ mol l^{-1}, $\lambda_{phot} = 546$ nm, $T = 298$ K. (*1*) 9.8×10^{17}, (*2*) 7.8×10^{17}, and (*3*) 2×10^{17} quant s^{-1} l^{-1}.

$$Ph_3SbCat–Q + h\nu \rightarrow Ph_3SbCat–Q^*, \tag{2}$$

$$Ph_3SbCat–Q^* + Ph_3SbCat–Q \rightarrow Ph_3SbCat–CatSbPh_3 + Q–Q. \tag{3}$$

As far as the decrease in the optical density at the photolysis of $Ph_3SbCat–Q$ by the light with the wavelength 546 nm is only 40% or less, and compounds Q–Q and $Ph_3SbCat–CatSbPh_3$ do not absorb the initiating irradiation, the most probable pathway of transformation of the products formed in reaction (3) is the reaction between these compounds along Eq. (1). In this case the optical density at the wavelength 505 nm should fall to the limit when the rate of photolysis of $Ph_3SbCat–Q$ is the same as the rate of reaction between Q–Q and $Ph_3SbCat–CatSbPh_3$. Therewith, the concentrations of the system components correspond to the steady state. As a consequence, both the positions of absorption bands and the optical densities at the band maxima in the spectra of the reaction mixture in UV and visible regions remain unchanged.

A complementary evidence of this hypothesis is given by the following two sets of experiments. At the illumination of $Ph_3SbCat–Q$ in toluene by the light $\lambda = 546$ nm of different intensity occurs a change in the initial rate constant of the photolytic transformation of this compound. Moreover, the lesser intensity of the

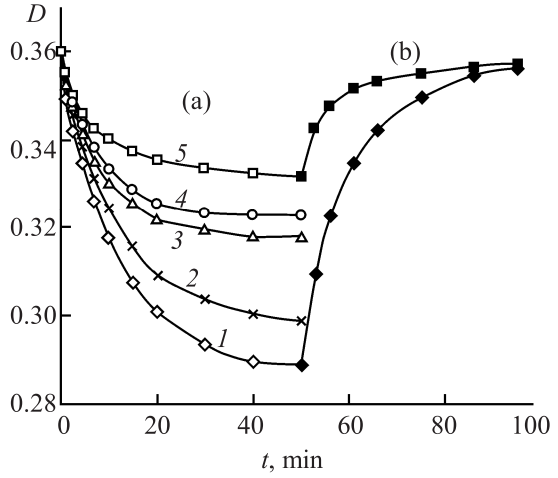


Fig. 3. (a) Effect of $Ph_3SbCat–CatSbPh_3$ additive on the rate of photo-transformation of $Ph_3SbCat–Q$ at $\lambda = 546$ nm in toluene. $C(Ph_3SbCat–Q) = 1.85\times10^{-4}$ mol l^{-1}, $I_{0,spec} = 9.8\times10^{17}$ quant s^{-1} l^{-1}, $T = 298$ K. Concentration of $Ph_3SbCat–CatSbPh_3$ in the reaction mixture before the photolysis: (*1*) 0, (*2*) 1.28×10^{-5}, (*3*) 5.28×10^{-5}, (*4*) 1.06×10^{-4}, and (*5*) 1.74×10^{-4} mol l^{-1}; (b) Restoration of optical density of the reaction mixtures at the wavelength 505 nm after ceasing illumination.

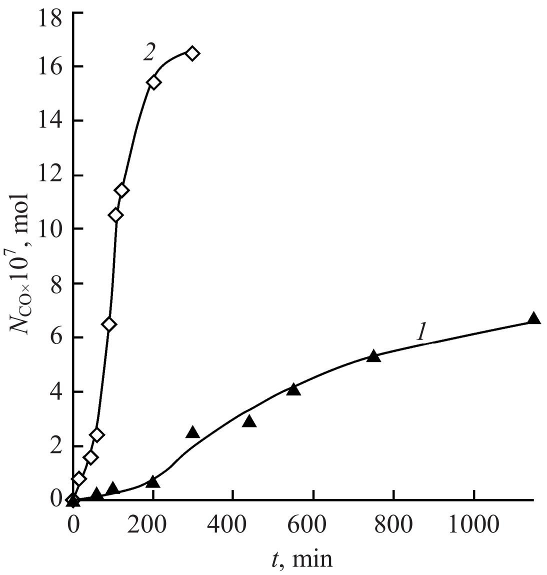


Fig. 4. Accumulation of carbon monoxide in the course of photolysis of $Ph_3SbCat–Q$ in toluene. $T = 298$ K, $C(Ph_3SbCat–Q) = 2.30\times10^{-4}$ mol l^{-1}. (*1*) l = 313 nm, $I_{0,spec} = 2.25\times10^{17}$ quant s^{-1} l^{-1}, (*2*) 405 nm, $I_{0,spec} = 5.10\times10^{18}$ quant s^{-1} l^{-1}.

light consumed by the reaction system, the lesser conversion is required for attaining the steady state by the system. The steady state is characterized by a plateau on the kinetic curve of the change in optical density (Fig. 2). In the second set of the experiments the initial concentration of $Ph_3SbCat–Q$ and intensity of the absorbed light were kept constant, but prior to the photolysis $Ph_3SbCat–CatSbPh_3$ was added to the reaction mixture to various concentrations. The higher was the concentration of the added $Ph_3SbCat–CatSbPh_3$ component, the faster was achieved the steady state (Fig. 3a). After ceasing the light action on the system, the optical density of the latter on the wavelength 505 nm returned to its initial value (Fig. 3b).

Illumination of $Ph_3SbCat–Q$ solution in toluene with the light of shorter wavelengths destroys the steady state of the system and leads to complete expenditure of the initial compound. One product of the photolytic decomposition of $Ph_3SbCat–Q$ dissolved in a hydrocarbon by the light of λ 313 or 405 nm is carbon monoxide, its yield is, respectively, 0.5 and 1 mole of CO per one mole of transformed compound (Fig. 4). The kinetic curves of CO accumulation include induction period that points to the gas formation in the secondary processes. The 4,4'-di(3-methyl-6-*tert*-butyl-*o*-benzoquinone) appearing at the photolysis of $Ph_3SbCat–Q$ by the data of [3] undergoes decomposition at the action of light of the wavelength λ 313 and 405 nm, that proceeds with liberation of carbon monoxide. Eventually, in the reaction mixture after the photoplysis of $Ph_3SbCat–Q$ were detected by TLC $Ph_3SbCat-CatSbPh_3$, 6-*tert*-butyl-4-(4'-*tert*-butyl-2'-methyl-3'-oxocyclopenta-1',4'-dienyl)-3-methyl-1,2-pyrocatechol, 3,3'-di(2-methyl-5-*tert*-butylcyclopenta-2,4-dienone) and 5,5'-di-*tert*-butyl-3,3'-dihydroxy-2,2'-dimethylbicyclohexylidene-2,5,2',5'-tetraene-4,4'-dione.

EXPERIMENTAL

The compounds $Ph_3SbCat–Q$ and $Ph_3SbCat-CatSbPh_3$ were synthesized along the procedure in [1]. Hexane and nonane of “chemicaly pure” grade were dried according to commonly used procedures [4] and then were distilled collecting the fractions 68.6–69.0°C and 150–151°C respectively.

The construction of photolytic installation and procedures for measuring intensity of incident beam have been described in [5].

The amount of carbon monoxide was measured by chromatography on a Tsvet-104 instrument, glass column 1500×2.5 mm filled with active charcoal STK with granule size 0.2–0.4 mm, temperature of the oven and detector 70°C, katharometer bridge current 250 mA, carrier gas (helium) flow rate 25 ml min^{-1}.

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

The TLC analysis of the products of photolysis [4] was carried out on silica gel plates Silufol UV 254, a mixture of hexane–diethyl ether (4:1) was used as eluent. The elution was carried out in a closed chamber, under the atmosphere saturated with the eluent vapor.

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