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Photolytic Transformations of Aluminum, Gallium, and Indium Tris(3,6-di-*tert*-butyl-1,2-semiquinolates)

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Abstract—The quantum yields of photolytic transformations of aluminum, gallium, and indium tris(3,6-di-*tert*-butyl-1,2-semiquinolates) in solutions of saturated hydrocarbons were determined. The final products of photodecomposition formed upon irradiation of the compounds with the light of wavelength 313 nm were identified. The kinetic scheme for decomposition of the metal *o*-semiquinone complexes upon irradiation is suggested.

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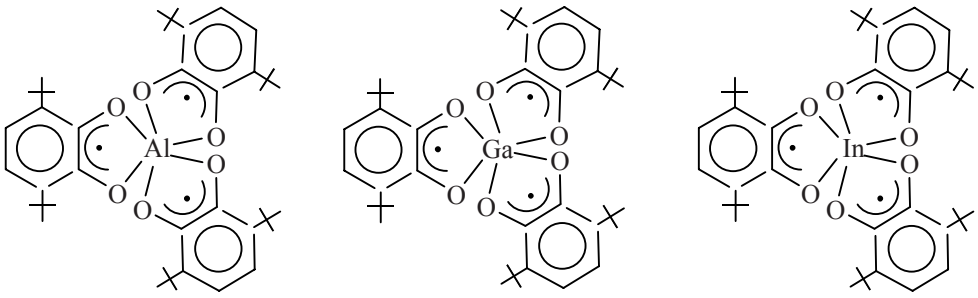
The solutions of aluminum **I**, gallium **II**, and indium **III** tris(3,6-di-*tert*-butyl^{-1},2-semiquinolates) with concentration of ca. 10^{-5}–10^{-4} mol l^{-1}) were subjected to photolysis with the light of wavelength 313 nm (Scheme 1).

The synthesis of the products of phototransformations **I–III** was performed by prolonged irradiation of more concentrated solutions (10^{-4} mol l^{-1}) in hexane. Upon irradiation, the color of the solutions turned from green to yellow-brown.

The quantum yields of photolysis of aluminum **I**, gallium **II**, and indium **III** tris(3,6-di-*tert*-butyl–1,2-semiquinolates) do not depend on the initial concentration of the substrates in the range (3–20)×10^{-5} mol l^{-1} or on intensity of the absorbed irradiation in the range (3–15)×10^{17} quanta s^{-1} l^{-1} and are equal to (2.2±0.3)×10^{-3}, (3.0±0.6)×10^{-3}, and (1.8±0.3)×10^{-4}, respectively.

The variation of the optical density of the reaction mixtures in the course of photolysis of the complexes at the wavelength of 300 nm has the shape of kinetic curves of the zero order. At the same time, the consumption of the *o*-semiquinolate groups upon irradiation of the solutions of Al and Ga complexes monitored by the ESR method obeys the kinetic equation of the first order (Fig. 1). The contribution of

Scheme 1.



I **II** **III**

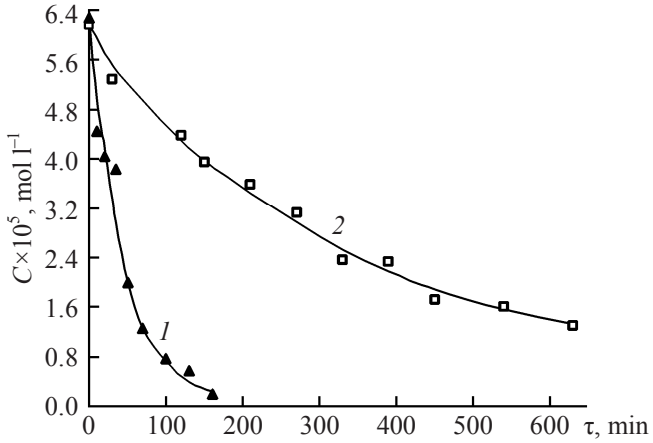


Fig. 1. Variation of concentrations of compounds **I** and **II** etermined by ESR spectroscopy. λ_{phot} = 313 nm, T = 298 K, l = 0.41 cm. (*1*) $C_{\mathbf{I}} = 6.3\times10^{-5}$ mol l^{-1}and (*2*) $C_{\mathbf{II}} = 6.16\times10^{-5}$ mol l^{-1}.

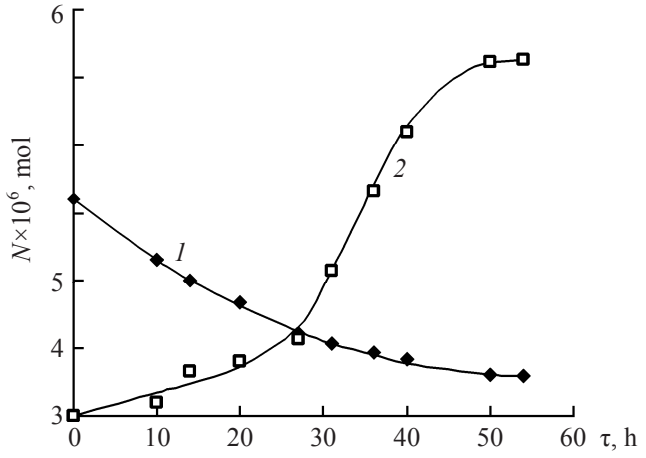


Fig. 2. Consumption of complex (*1*) **I** and (*2*) accumulation of carbon monoxide in the course of photolysis. C_0 = 5.25×10^{-5} mol l^{-1}, λ_{phot} = 313 nm, T = 298 K.

the primary products of transformations into the optical density of the reaction mixture at wavelength of 300 nm can compensate the decrease of optical density of the reaction mixture, which in the absence of the reaction products must follow the first order kinetic equation. This is confirmed by the measurements of optical density at wavelength of 366 nm during the photolysis (Fig. 2). The photolysis rate constant for **I** for the intensity of the absorbed irradiation of 1.8×10^{18} quanta s^{-1} l^{-1} is equal to (3.5±0.5)×10^{-4} s^{-1}. On going from **I** to **III** a regular decrease in the rate constants of photodecomposition of the starting compounds is observed in the order 20:4.5:1.

Upon photolysis of solutions of the investigated metal tris-*o*-semiquinolates in normal hydrocarbons evolution of carbon monoxide is observed in the yield of ca. 1.5 mol to 1 mol of the converted complex. The kinetic curves for accumulation of CO are characterized by the presence of induction period (Fig. 2). Besides, in the final products of irradiation of **I–II** in solutions in aliphatic hydrocarbons 2,5-di-*tert*-butylcyclopentadienone and its dimer as well as the corresponding insoluble metal catecholates were found in close to quantitative yield. By the example of the products of phototransformation of **I** and **II** it was found that due to acidic hydrolysis the solid phase formed during the reaction was converted into catechol and acidic aluminum or gallium salt [1–3] in the ratio of 3:2. In the IR spectra of the solid products the absorption bands are observed in the range of 480–530 and 1260–1270 cm^{-1} characteristic of the M–O and C–O bonds, respectively.

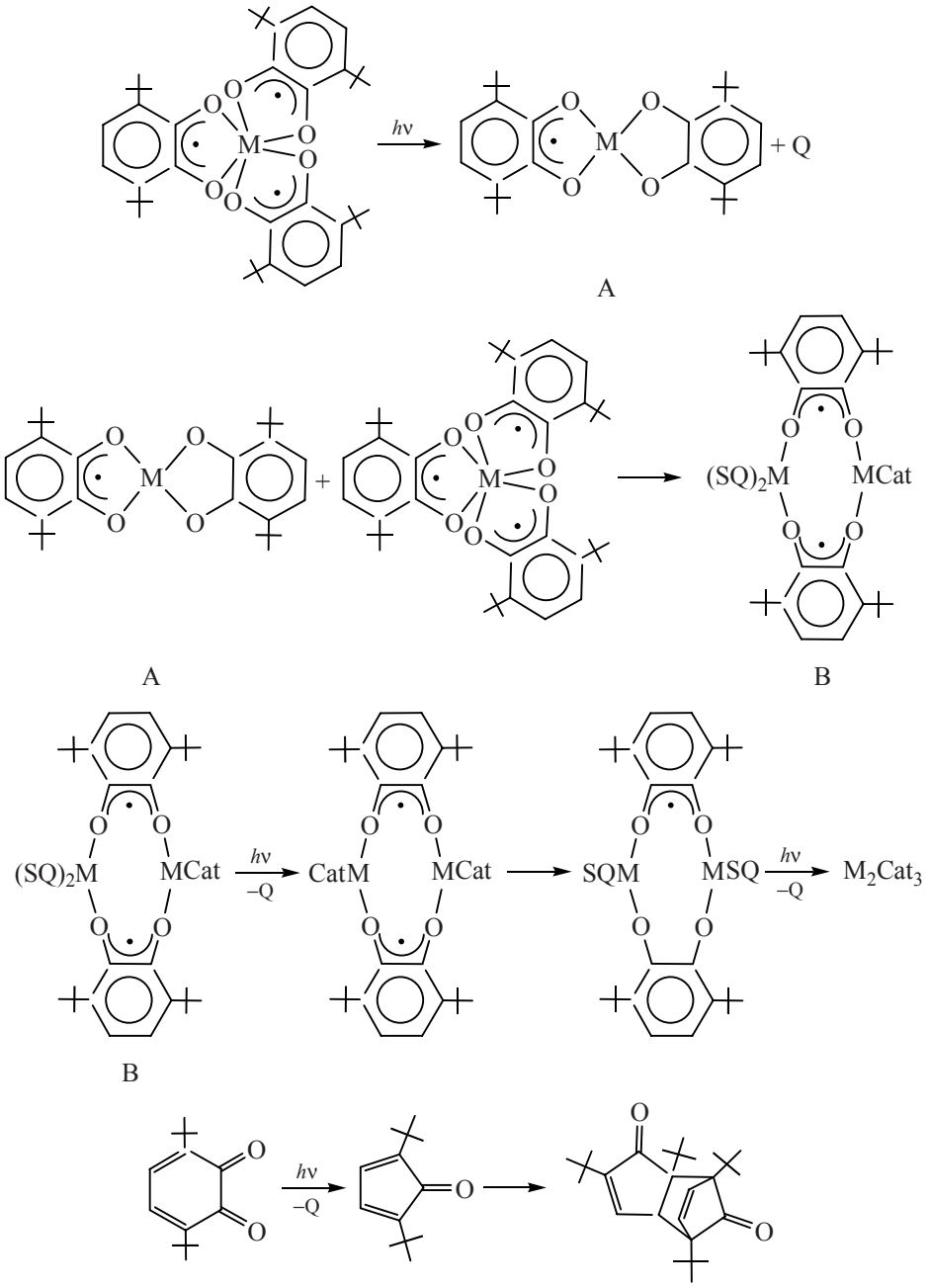
Transformations occurring upon photolysis of the initial metal complexes can be described as follows. First, upon irradiation of **I–III** in nonane, decomposition of the starting compound with the formation of the metal 3,6-di-*tert*-butyl–1,2-semiquinolato-3,6-di-*tert*-butylcatecholate (A) and 3,6-di-*tert*-butyl-*o*-benzoquinone (Q) occurs. The latter under the action of light is decomposed to carbon monoxide and 2,5-di-*tert*-butylcyclopentadienone [4]. According to the results obtained in [5], 2,5-di-*tert*-butylcyclopentadienone can form the dimer upon irradiation. This fact provides a realistic understanding of the presence of an induction period on the kinetic curve of accumulation of CO upon photolysis of solution of **I** in nonane (Fig. 2). The reaction of compound (A) with the molecule of the initial complex can give rise to associate (B) whose decomposition may yield the metal catecholate and lead to the evolution of another two molecules of quinone (see Scheme 2).

Aluminum, gallium, and indium alkoxides are known to exist in solutions as associates [6, 7]. According to [8], aluminum alkoxides in nonane are practically fully dimerized at concentration of 3×10^{-2} mol l^{-1}. It is presumable that at the concentrations used in this work some percent of dimers is present in solutions along with the monomers.

EXPERIMENTAL

Compounds **I–III** were synthesized according to the procedure described in [9]. Hexane and nonane of "chemically pure" grade were dried according to

Scheme 2.



the standard procedures [10] and distilled collecting the fractions boiling at 68.6–69.0°C and 150–151°C, respectively.

The photolytic equipment and technique for measuring the intensity of the incident irradiation are described in [4].

The amount of carbon monoxide was determined chromatographically on a Tsvet-104 instrument with glass column 1500×2.5 mm filled with activated charcoal "CTK" with grains of 0.2–0.4 mm, temperature of columns and detector 70°C, catharometer bridge current 250 mA; rate of gas-carrier (helium) 25 ml min^{-1}.

ESR spectra were registered on an AE-4700 radiospectrometer, Mn^{+2} ions in the crystal lattice of MgO were used as a standard for calibration of the magnetic field.

A specimen of the solid precipitate was refluxed in the presence of equal volumes of benzene and 0.1 N sulfuric acid for several hours. The organic phase was analyzed for the content of catechol, water phase , for aluminum, according to standard procedures [1–3].

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

NMR spectra were obtained on a Bruker DPX-200 instrument with working frequency 200 MHz with TMS as an internal standard.

NMR spectra of **2,5-di-*tert*-butylcyclopentadienone** and **1,4,6,8-tetra-*tert*-butylbicyclo-[5.2.1.0^{2,6}]-deca-4,8-dien-3,10-dione** (dimer of **2,5-di-*tert*-butylcyclopentadienone**) coincide with the earlier published data [4, 5].

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