Interaction of the iridium(III) trihydridophosphine complex with fullerene C_{60} under thermal and photochemical excitation

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The interaction of the PPh_3-stabilized iridium trihydrido complex $H_3Ir(PPh_3)_3$ with fullerene C_{60} under thermal and photochemical excitation was studied under anaerobic conditions. Heating (100 °C) or photolysis by the visible light of the $H_3Ir(PPh_3)_3$—C_{60} mixture (~1 : 1) in toluene leads to the appearance of new absorption bands at 435, 600, and 650 nm, which are characteristic of the η^2-coordinated C_{60} in several fullerene-containing metal complexes. The kinetic behavior of the $H_3Ir(PPh_3)_3$—C_{60} system in benzonitrile was investigated using a Nd^{3+}—YAG laser (λ = 532 nm). The quenching rate constant determined from the dependence of the effective first-order quenching constant of $C_{60}(T)$ on the concentration of $H_3Ir(PPh_3)_3$ is equal to $1.1 \cdot 10^9$ L mol^{-1} s^{-1}. The quenching of $C_{60}(T)$ by the iridium hydridophosphine complex follows the reductive mechanism to form a C_{60} monoanion. The ESR signal with g = 2.0000 and ΔH = 0.17 mT (at room temperature) and characteristic absorption bands in the near-IR region at 940, 1004, and 1076 nm support the formation of the C_{60} monoanion during the interaction of the triplet-excited C_{60} with $H_3Ir(PPh_3)_3$.

Key words: fullerene C_{60}, laser photolysis, quenching rate constant, ESR spectroscopy, near-IR spectroscopy, iridium trihydrido complexes.

The discovery of fullerenes, a new allotropic modification of carbon, resulted in the intense study of their chemical properties,[1] including their interaction with nucleophiles[2—4] and metal complexes.[5—8] The ability of a C_{60} molecule to form different types of coordination compounds[1] suggests the possibility of using fullerenes as a polyfunctional ligand in metal complexes, which is capable, for example, of changing the type of coordination at different oxidation states of the metal, and of functioning as an electron and/or hydrogen acceptor, *etc.*

In this work, we studied the interaction in the $H_3Ir(PPh_3)_3$—C_{60} system under thermal and photochemical excitation.

Results and Discussion

Toluene solutions of C_{60} containing the iridium(III) hydridophosphine complex for a long time undergo no visible changes in the dark, under anaerobic conditions at room temperature. Heating or irradiation of these solutions by light with wavelength $\lambda > 400$ nm or light of the second harmonic of a Nd^{3+}—YAG laser (532 nm) results in substantial changes in the absorption spectrum of C_{60}.

When a $H_3Ir(PPh_3)_3$—C_{60} (1 : 1) mixture in toluene in a sealed ampule is heated at 100 °C, the color of the solution changes from violet to intense-green. New absorption bands (Fig. 1) at 435, 602, and 650 nm, which are characteristic of fullerene-containing low-valence rhodium, iridium, and palladium complexes (see, *e.g.*, Refs. 7 and 8), appear in the visible region of the absorption spectrum. The values of the molar absorption coefficient ($\varepsilon_{435} \approx 4800$, $\varepsilon_{602} \approx 2300$, $\varepsilon_{650} \approx 1800$ L mol^{-1} cm^{-1}) for the η^2-fullerene complexes formed in this system differ noticeably from the ε values for the known fullerene-containing complexes, for example, $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$ [7] ($\varepsilon_{435} \approx 8000$ L mol^{-1} cm^{-1}). No hydrogen is evolved at the stage of formation of the complex (green solution). The addition of oxygen results in fast decolorization of the solution and the appearance of free fullerene (TLC, Silufol-254, benzene—hexane, 1 : 10), which indicates that the iridium hydridophosphine complex with fullerene formed is unstable.

Changes similar to those observed under the thermal treatment (see Fig. 1) are observed when a $H_3Ir(PPh_3)_3$—C_{60} (3 : 1) mixture in toluene is irradiated by light with $\lambda > 400$ nm under anaerobic conditions, *i.e.*, when the photoexcited fullerene ($^3C_{60}$) and/or the complex are generated. It is noteworthy that when the $H_3Ir(PPh_3)_3$—C_{60} mixture in toluene is either heated or irradiated by visible light, the absorption at 1076 nm in the near-IR region and the ESR signal from the $C_{60}^{\cdot -}$ radical anion do not appear.[3] The fact that C_{60} in toluene is not

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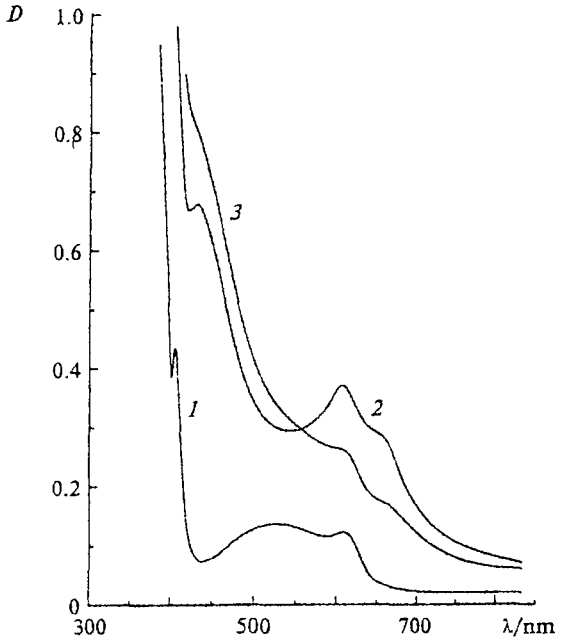


Fig. 1. Absorption spectra of the $H_3Ir(PPh_3)_3$—C_{60} mixture ([Ir] ≈ [C_{60}] = $1.4 \cdot 10^{-4}$ mol L^{-1}) in toluene before the reaction (*1*); after heating (100 °C, 0.5 h) in a sealed cell (*2*); after photolysis (λ > 400 nm, 0.5 h), [Ir] = $5.03 \cdot 10^{-4}$ mol L^{-1}, [C_{60}] = $1.4 \cdot 10^{-4}$ mol L^{-1} (*3*).

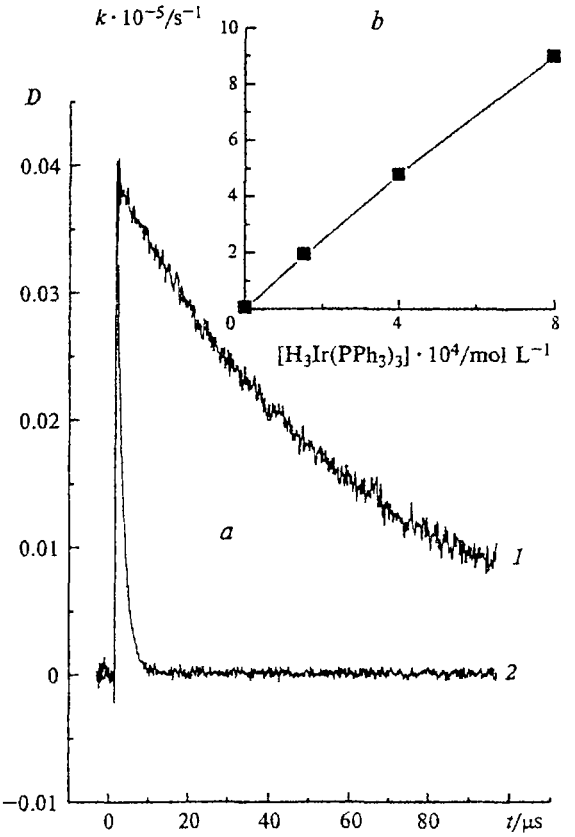


Fig. 2. *a*. Changes in the optical density at λ = 750 nm in time for triplet-excited C_{60} in benzonitrile ([C_{60}] = $8.7 \cdot 10^{-5}$ mol L^{-1}, λ_{exc} = 532 nm) for [$H_3Ir(PPh_3)_3$] = 0 (*1*) and $8 \cdot 10^{-4}$ mol L^{-1} (*2*). *b*. Dependence of the inverse lifetime of $^3C_{60}$ (*k*) on the concentration of $H_3Ir(PPh_3)_3$ (benzonitrile as the solvent).

reduced by such strong reducing agents as Cr^{II} and Sn^{II} can be related to a very weak coordinating ability of the $C_{60}^{\cdot-}$ radical anion, but the addition of a polar solvent (THF, MeCN) results in the reduction of C_{60} in both systems.[9]

The kinetic behavior of the $H_3Ir(PPh_3)_3$—C_{60} (1 : 1—10 : 1) system in benzonitrile in the absence of oxygen was studied by laser pulse photolysis using excitation by the second harmonic of a Nd^{3+}—YAG laser (λ = 532 nm). The differential absorption spectrum after a laser pulse corresponds to the T—T-absorption of the triplet C_{60}. The spectrum exhibits a characteristic band with maximum at 750 nm. A decrease in the lifetimes of the excited states at 750 nm (absorption maximum of the triplet state of C_{60}) indicates that $^3C_{60}$ is quenched by the iridium hydridophosphine complex (Fig. 2, *a*). The quenching rate constant determined from the dependence of the effective first-order quenching constant of $^3C_{60}$ on the concentration of $H_3Ir(PPh_3)_3$ is equal to $1.1 \cdot 10^9$ L mol^{-1} s^{-1} (Fig. 2, *b*), *i.e.*, it is close to the diffusion limit by an order of magnitude. An increase in the optical density with the characteristic time coinciding with the lifetime of $^3C_{60}$ is observed at 950 nm, which corresponds to the absorption of $C_{60}^{\cdot-}$ (T—T-absorption of $^3C_{60}$ is absent). This fact indicates that the absorption at λ = 950 nm appears due to the product of quenching of $^3C_{60}$. Thus, the triplet-excited fullerene is quenched by the $H_3Ir(PPh_3)_3$ complex *via* the reductive mechanism. The quantum yield of the formation of $C_{60}^{\cdot-}$ (φ ≈ 7%) was estimated from the ratio of the optical density of $^3C_{60}$ (λ = 750 nm) at the moment t = 0 to the optical density of $C_{60}^{\cdot-}$ (λ = 950 nm) up to the moment of complete quenching of $^3C_{60}$.

Figure 3 presents the absorption spectrum of the $H_3Ir(PPh_3)_3$—C_{60} (10 : 1) system in benzonitrile in the visible (Fig. 3, *a*) and near-IR (Fig. 3, *b*) regions after photolysis. Absorption bands at λ = 940, 1004, and 1076 nm appear in the near-IR region of the spectrum of the reaction mixture after steady-state photolysis (30 min) under anaerobic conditions, which indicates, according to previously published data,[3,4,10] that the $C_{60}^{\cdot-}$ radical anion is present in the solution. In the near-IR region, the absorption spectrum of the evacuated sample remains unchanged for a long time, but the absorption bands disappear immediately after exposure of the solution to air, which is also typical of the fullerene radical anion.[3] According to the data of spectrophotometry, the reaction of $^3C_{60}$ with the iridium(III) hydridophosphine complex results in the reduction of ~10—20% fullerene to $C_{60}^{\cdot-}$ (ε_{1076} = 1.2—$2.0 \cdot 10^4$ L mol^{-1} cm^{-1})[10].

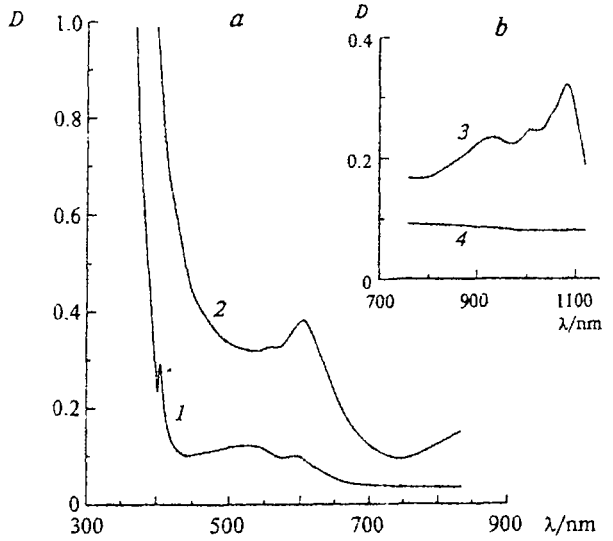


Fig. 3. *a*. Absorption spectra of the $H_3Ir(PPh_3)_3$—C_{60} mixture ($[H_3Ir(PPh_3)_3] = 8 \cdot 10^{-4}$ mol L^{-1}, $[C_{60}] = 8.7 \cdot 10^{-5}$ mol L^{-1}) in benzonitrile before (*1*) and after laser photolysis (*2*) (Nd^{3+}—YAG laser, $\lambda = 532$ nm). *b*. Absorption spectrum of the sample in the near-IR region after photolysis ($\lambda = 532$ nm) in vacuum (*3*) and after exposure in air (*4*).

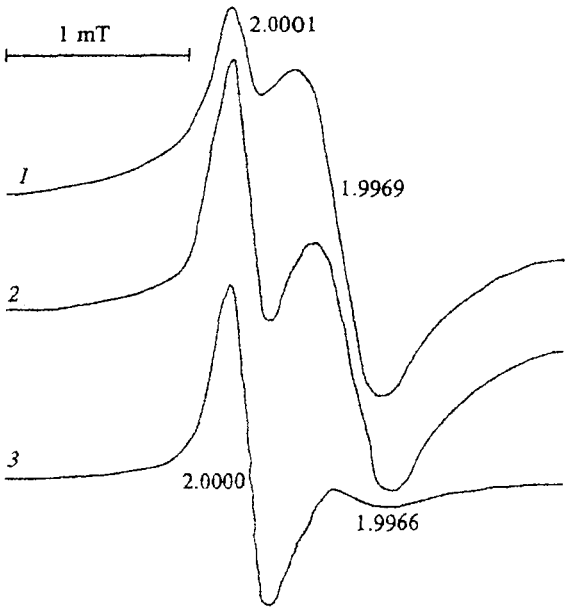


Fig. 4. ESR spectra of the $H_3Ir(PPh_3)_3$—C_{60} system ($[H_3Ir(PPh_3)_3] = 8 \cdot 10^{-4}$ mol L^{-1}, $[C_{60}] = 8.7 \cdot 10^{-5}$ mol L^{-1}) in benzonitrile at 77 K after photolysis (*1*), after storage at −20 °C for 1 (*2*) and 2 months (*3*).

The formation of the radical anion of C_{60} when the $H_3Ir(PPh_3)_3$—C_{60} system in benzonitrile is irradiated by visible light is also confirmed by the appearance of the ESR signal. The ESR spectrum of the sample studied, which was recorded at 77 K immediately after the irradiation was completed, consists of two lines: an intense line with $g = 1.9969$ and $\Delta H = 0.47$ mT and a weak line with $g = 2.0001$ and $\Delta H = 0.24$ mT (Fig. 4). Only one line with $g = 2.0000$ and $\Delta H = 0.17$ mT is observed at −20 °C. Storage of the sample at −20 °C is accompanied by slow changes in the ESR spectrum monitored at 77 K: the intensity of the line with $g = 1.9969$ decreases, while the intensity of the line with $g = 2.0001$ increases, and 2 months later only the line with $g = 2.0001$ remains in the spectrum. The second integral of the ESR spectrum remains unchanged, *i.e.*, the number of paramagnetic centers does not change. The comparison of the second integrals of the ESR spectra of the sample studied and the standard solution of the nitroxyl radical shows that the sample contains $3 \cdot 10^{-6}$ mol L^{-1} paramagnetic centers. This value agrees by an order of magnitude with the concentration of $C_{60}^{\cdot -}$ determined from the optical spectra. The width and amplitude of the ESR spectrum of the sample studied remain unchanged during storage at −20 °C. It is mentioned in Ref. 4 that the Bu_4N^+ counterion affects noticeably the stabilization of $C_{60}^{\cdot -}$ formed due to the photoinduced transfer of an electron between R_3N and C_{60}.

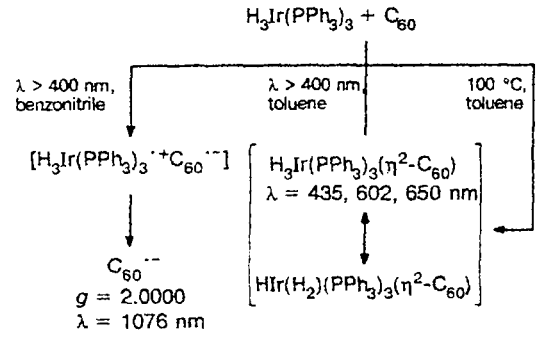
The ESR spectrum of the sample recorded at 77 K immediately after irradiation resembles[11] the ESR spectrum of the $C_{60}^{\cdot -}$ monoanion at the temperature of liquid helium. However, as the temperature increases to 77 K, the spectrum is transformed due to averaging of the Jahn—Teller distortion by thermal oscillations of the $C_{60}^{\cdot -}$ molecule. Perhaps in this case, associates of the $C_{60}^{\cdot -}$ molecules are formed, in which averaging of the Jahn—Teller distortion is difficult at 77 K. The slow change in the ESR spectra during storage can likely be explained by the slow deaggregation of these associates. At −20 °C the spectrum exhibits only one line with $g = 2.0000$ typical of the free $C_{60}^{\cdot -}$. Apparently, at −20 °C the associate—free $C_{60}^{\cdot -}$ equilibrium is shifted toward the free $C_{60}^{\cdot -}$. The nature of these associates and the reason for their slow deaggregation are presently unknown.

When the mixture is irradiated by the full light of a xenon lamp, no ESR signals appear probably due to the fact that transformations occurring in the $H_3Ir(PPh_3)_3$—C_{60} system are more pronounced. We failed to identify an active iridium-containing species in this system. It should be noted that no spectral proofs for the formation of iridium(IV) were obtained by studying the electrochemical or chemical oxidation of the iridium(III) hydridophosphine complexes.[12]

The formation of the η^2-fullerene complexes in the $H_3Ir(PPh_3)_3$—C_{60} system on heating in toluene probably occurs through the stage of formation of the iridium dihydrogen complex, which is the real intermediate in reactions of iridium trihydrido complexes with electro-

philes, for example, H^+.[13] The oxidation of iridium and generation of $C_{60}^{\cdot -}$ become possible in benzonitrile due to the photoinduced transfer of an electron from $H_3Ir(PPh_3)_3$ (oxidation potential +0.55 V)[12] to C_{60} involving the triplet-excited state of C_{60} (oxidation potential +1.14 V). An increase in the polarity of the medium facilitates the charge separation. The effect of the donor—acceptor properties of solvents on the stabilization of $C_{60}^{\cdot -}$ has been mentioned previously.[4,9]

Scheme 1



Thus, the interaction in the $H_3Ir(PPh_3)_3$—C_{60} system (toluene or benzonitrile as the solvents) under anaerobic conditions was established (Scheme 1) to occur *via* different routes in the dark and under irradiation: on heating (100 °C) in toluene to form η^2-iridium complexes with C_{60} and under irradiation of the system in benzonitrile with the oxidation of iridium by the triplet-excited C_{60} (Nd^{3+}—YAG laser, λ = 532 nm). The photochemical reaction in benzonitrile results in the appearance of the absorption band in the near-IR region and the ESR signal (λ = 1076 nm and g = 2.0000, respectively) for the $C_{60}^{\cdot -}$ radical anion.

Experimental

Toluene and benzonitrile were purified by standard procedures.[14] The $H_3Ir(PPh_3)_3$ complex was obtained by a known method,[15] IR (Vaseline oil), ν(Ir—H)/cm^{-1}: 1740, 2130.

Steady-state photolysis (λ > 400 nm) of the $H_3Ir(PPh_3)_3$—C_{60} mixture was carried out at ~20 °C under anaerobic conditions (1-cm quartz cell) using a Xe lamp (100 W) with a system of thermal and light filters. Laser photolysis of the $H_3Ir(PPh_3)_3$—C_{60} system was carried out by the second harmonic of a Nd^{3+}—YAG laser (λ = 532 nm, pulse duration 12 ns, pulse energy ~10 mJ). The detection system has been described in detail previously.[16]

Absorption spectra were recorded on Specord M-40 and SF-8 spectrophotometers in 1-cm quartz cells.

ESR spectra were obtained on a Radiopan SE/X-2544 radiospectrometer with a modulation of 0.125 mT and a microwave power of ~3 mW at ~20 °C and 77 K.

Solutions of $H_3Ir(PPh_3)_3$ and C_{60} ($H_3Ir(PPh_3)_3$—C_{60}, 1 : 1) in toluene were heated at 100 °C for 0.5 h in a sealed ampule until the solution attained a stable green color. Heating of this mixture with argon bubbling does not result in similar changes.

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References

1. V. I. Sokolov and I. V. Stankevich, *Usp. Khim.*, 1993, **62**, 455 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
2. A. Hirsch, Q. Li, and F. Wudl, *Angew. Chem. Int. Ed.*, 1991, **30**, 1309.
3. N. F. Gol'dshleger, A. S. Lobach, A. S. Astakhova, M. G. Kaplunov, A. V. Kulikov, A. P. Moravskii, O. S. Roshchupkina, and Yu. M. Shul'ga, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1143 [*Russ. Chem. Bull.*, 1994, **43**, 1081 (Engl. Transl.)].
4. V. Brezová, A. Staško, P. Rapta, G. Domschke, A. Bartl, and L. Dunsch, *J. Phys. Chem.*, 1995, **99**, 16234.
5. A. V. Usatov, K. N. Kudin, E. V. Vorontsov, L. E. Vinogradova, and Yu. N. Novikov, *J. Organomet. Chem.*, 1996, **522**, 147.
6. A. L. Balch, J. W. Lee, B. C. Noll, and M. M. Olmstead, *Inorg. Chem.*, 1993, **32**, 3577.
7. R. S. Koefod, M. F. Hudgens, and J. R. Shapley, *J. Am. Chem. Soc.*, 1991, **113**, 8957.
8. N. N. Denisov, A. S. Lobach, and V. A. Nadtochenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1163 [*Russ. Chem. Bull.*, 1996, **45**, 1103 (Engl. Transl.)].
9. J. Stinchcombe, A. Pénicaud, P. Bhyrappa, P. D. W. Boyd, and C. A. Rud, *J. Am. Chem. Soc.*, 1993, **115**, 5212.
10. M. M. Khaled, R. T. Carlin, P. C. Trulone, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, 1994, **116**, 3465.
11. A. S. Lobach, N. F. Goldshleger, M. G. Kaplunov, and A. V. Kulikov, *Chem. Phys. Lett.*, 1995, **243**, 22.
12. D. E. Westerberg, L. F. Rhodes, J. Edwin, W. E. Geiger, and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 1107.
13. E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein, and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 855.
14. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents*, Wiley, New York, 1955.
15. J. J. Levison and S. D. Robinson, *J. Chem. Soc., A*, 1970, 2947.
16. V. A. Nadtochenko, N. N. Denisov, I. V. Rubtsov, A. S. Lobach, and A. P. Moravskii, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1228 [*Russ. Chem. Bull.*, 1993, **42**, 1171 (Engl. Transl.)].

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