C_{60} Fullerene, as ultraefficient quencher of singlet-excited adamantanone generated in photo- and chemiexcitation

R. G. Bulgakov and D. I. Galimov*

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Octyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

Quenching of the fluorescence of Ad=O and its singlet-exited state (^{1}Ad=O*) generated in chemiluminescent reaction of adamantylideneadamantane-1,2-dioxetane (AdOOAd) termolysis by C_{60} fullerene was detected and investigated. The "quenching efficiency—C_{60} concentration" plots obtained from the decrease in the fluorescence and chemiluminescence intensities obey the Stern—Volmer law. The bimolecular rate constants (k_{bim}) were determined and the overlap integrals of the Ad=O fluorescence spectra with the C_{60} absorption spectra ($\int_{Ov}$) were calculated. Based on the nonconstant $k_{bim}/\int_{Ov}$ ratios for different singlet-exited energy donors obtained for the ^{1}PAH*—C_{60} systems (PAH are polycyclic aromatic hydrocarbons) and ^{1}Ad=O*—C_{60}, a conclusion is drawn that quenching of ^{1}Ad=O* by C_{60} fullerene is a result of inductive-resonant singlet-singlet (major contribution) and exchange-resonant singlet-triplet (minor contribution) energy transfer.

Key words: C_{60} fullerene, quencher of exited states, adamantanone, fluorescence, adamantylideneadamantane-1,2-dioxetane, chemiluminescence.

Research on the deactivation of electronically excited states (EES) of various classes of compounds by C_{60} fullerene is of importance for understanding of the processes occurring upon photoirradiation of fullerene-containing systems promising for solar energy utilization, photodynamic therapy, optical switches, and for photochemical synthesis of C_{60} derivatives.[1—4] Earlier,[5,6] we have reported an unusually high efficiency of the quenching of EES of Ln^{3+}* ions and polycyclic aromatic hydrocarbons (^{1}PAH*) by C_{60} fullerene. In this work we detected and studied the quenching of ^{1}Ad=O* generated by photoexcitation and in chemiluminescent reaction of AdOOAd thermolysis by C_{60} fullerene.

Experimental

Experiments were carried out using commercially available C_{60} (purity 99.9%, synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod) and adamantanone ("chemically pure" grade). Toluene[7] and argon[8] were purified following the known procedures. Adamantylideneadamantane was synthesized by reduction of adamantanone with zinc dust in THF in the presence of $TiCl_4$ as catalyst.[9] Dioxetane AdOOAd was synthesized by photosensitized oxidation of adamantylideneadamantane.[10] Stock solutions of C_{60} (10^{-3} mol L^{-1}) and Ad=O ($4.8 \cdot 10^{-3}$ mol L^{-1}) were prepared by dissolving crystalline samples in toluene in the dark under argon atmosphere. In the fluorescence quenching studies, solutions of C_{60} fullerene were added to the Ad=O solutions and the fall-off of the intensity of Ad=O fluorescence maximum at 23260 cm^{-1} was measured at 293 K. Thermolysis of AdOOAd in toluene ($4.5 \cdot 10^{-3}$ mol L^{-1}, 343 K) was carried out in a Pyrex® cell with optically transparent bottom (diameter 35 mm). Chemiluminescence of AdOOAd was recorded using a FEU-114 photomultiplier. To study the effect of C_{60} fullerene on the chemiluminescence of AdOOAd, aliquots (0.2 mL) of a solution of C_{60} (10^{-3} mol L^{-1}, 293 K) were added to the reaction solution (10 mL). The change in the temperature measured by a copper-constantan thermocouple upon adding C_{60} was at most 0.5 K. The concentration of C_{60} in the solutions before and after excitation of fluorescence was monitored by HPLC.[11] The experimental setup and chemiluminescence measurement procedure were reported earlier.[8] The absorption spectra were recorded on a Specord M-40 spectrophotometer, the fluorescence spectra with a 2 nm resolution were recorded on an original spectrofluorimeter based on an MDR-23 monochromator. The overlap integrals of the Ad=O fluorescence spectra with the absorption spectrum of C_{60} were calculated as reported earlier.[5,12]

Results and Discussion

The addition of C_{60} to the Ad=O solution in toluene causes a decrease in the Ad=O fluorescence intensity, but the pattern of the fluorescence spectrum remains unchanged (λ_{max} = 430 nm). The absorption spectrum of C_{60} in the presence of Ad=O also shows no changes. The bimolecular rate constant for quenching (k_{bim}) was determined from the slope of the Stern—Volmer plot (Fig. 1)

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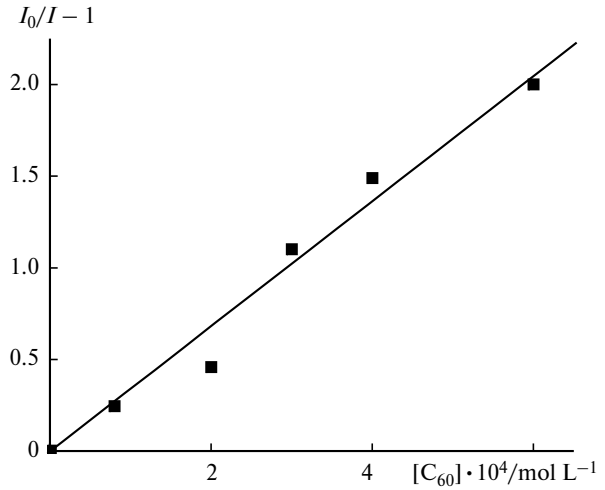

Fig. 1. Stern—Volmer plot of Ad=O fluorescence intensity *vs.* $[C_{60}]$ in toluene at 293 K; $[Ad{=}O] = 2.4 \cdot 10^{-3}$ mol L^{-1}, $\lambda_{exc} = 315$ nm; I_0 and I are the fluorescence intensities in the absence and in the presence of C_{60}.

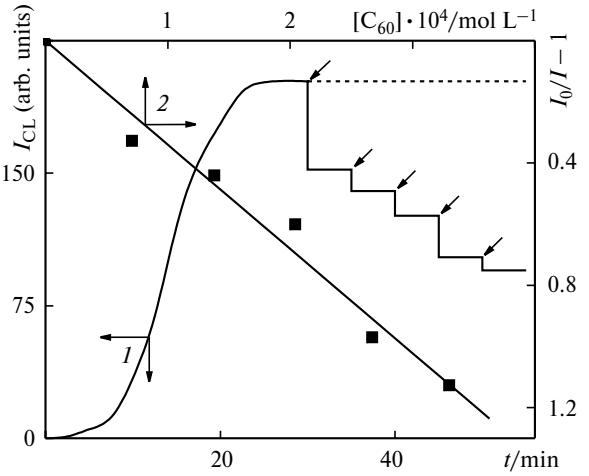

Fig. 2. Effect of additive (solution of C_{60}) on chemiluminescence intensity in thermolysis of AdOOAd in toluene (*1*), 343 K, $[AdOOAd]_0 = 4.5 \cdot 10^{-3}$ mol L^{-1}. The dashed line corresponds to the absence of C_{60}; chemiluminescence quenching efficiency ($I_0/I - 1$) plotted *vs.* $[C_{60}]$ (*2*); I_0 and I are the chemiluminescence intensities before and after adding C_{60} (horizontal levels).

for the fluorescence quenching efficiency (I_0/I, where I_0 and I are fluorescence intensities in the absence and in the presence of C_{60}) (Table 1). Using the known methods,[5,6] we calculated the overlap integral ($\int_{Ov}$) of the fluorescence spectrum of Ad=O with the absorption spectrum of C_{60} (see Table 1).

The chemiluminescence spectrum recorded in the AdOOAd thermolysis (spectrum is due to emission from ^{1}Ad=O* [13]) matches the fluorescence spectrum of Ad=O and the known[13] chemiluminescence spectrum of AdOOAd. The addition of a solution of C_{60} to the reaction solution causes the appearance of clearly seen stepwise chemiluminescence intensity fall-off regions (Fig. 2) followed by almost constant chemiluminescence intensity. The chemiluminescence spectrum retains its pattern. Using the Stern—Volmer dependence of the chemiluminescence quenching efficiency (ratio of the chemiluminescence intensity before (I_0) and after (I) adding C_{60}) on $[C_{60}]$ (see Fig. 2), we determined the k_{bim} value (see Table 1), which appeared to be equal, within the limits of experimental error, to the k_{bim} value determined from the fluorescence data.

Taking into account the results obtained and the absence[5,6] of absorption of Ad=O fluorescence by fullerene, we explain the quenching of ^{1}Ad=O* generated in photo- and chemiexcitation (reactions (1) and (2), respectively) by energy transfer to C_{60} (reaction (3)).

$$Ad{=}O + h\nu \longrightarrow {}^1Ad{=}O^* \quad (1)$$

$$AdOOAd \longrightarrow Ad{=}O + {}^1Ad{=}O^* \quad (2)$$

$$^1Ad{=}O^* + C_{60} \longrightarrow Ad{=}O + C_{60}^* \quad (3)$$

No sensitized luminescence of C_{60}* was detected (for the reasons for difficulties in recording the phenomenon, see Refs 5 and 6). Earlier,[6] we have shown that quenching of singlet excited states of PAH (^{1}PAH*) by C_{60} fullerene is also characterized by abnormally high values of the rate constant k_{bim} ($(0.18—6.78) \cdot 10^{12}$ L mol^{-1} s^{-1}). Based on the nonconstant $k_{bim}/\int_{Ov}$ ratios for different singlet-excited energy donors obtained for the systems (^{1}PAH—C_{60})[6] and (^{1}Ad=O*—C_{60}), it was concluded that the mechanism of quenching of ^{1}Ad=O* by fullerene is similar to that proposed earlier,[6] namely, the quenching is a result of inductive-resonance singlet-singlet (major contribution) and exchange singlet-triplet (minor contribution) energy transfer.

Table 1. Parameters of quenching of ^{1}Ad=O* by C_{60} fullerene in toluene

^{1}Ad=O* generation procedure	T/K	$[C_{60}] \cdot 10^4$/mol L^{-1}	τ_0/ns[a]	$k_{bim} \cdot 10^{-11}$/L mol^{-1} s^{-1}	$\int_{Ov} \cdot 10^{14}$
Photoexcitation[b]	293	0.08—6	9	3.79±0.02	0.18
Chemiexcitation[c]	343	0.7—3.3	9	3.71±0.03	—

[a] Lifetime of ^{1}Ad=O* in the absence of quencher.[12]
[b] $\lambda_{exc} = 315$ nm, $[Ad{=}O] = \text{const} = 2.4 \cdot 10^{-3}$ mol L^{-1}.
[c] $[AdOOAd]_0 = 4.5 \cdot 10^{-3}$ mol L^{-1}.

It should be emphasized that the rate constants for quenching of ^{1}Ad=O* by C_{60} fullerene obtained in this work are much higher than the k_{bim} values characterizing energy transfer from ^{1}Ad=O* to other energy acceptors, such as lanthanide ions[13] ($k_{bim} = 2.7 \cdot 10^9$ L mol^{-1} s^{-1}) and 9,10-diphenylanthracene[14] ($k_{bim} = 3.7 \cdot 10^{10}$ L mol^{-1} s^{-1}). They also much exceed the rate constants k_{bim} for quenching of ketone EES in other energy donor—quencher systems, namely, $^1CH_3COCH_3$*—9,10-phenylanthracene ($k_{bim} = 6 \cdot 10^{10}$ L mol^{-1} s^{-1}, S→S energy transfer),[15] $^3C_6H_5CH_2CHO$*—9,10-dibromoanthracene ($k_{bim} = 3.8 \cdot 10^8$ L mol^{-1} s^{-1}, T→S energy transfer),[16] and $^3C_6H_5CH_2CHO$*—naphthalene ($k_{bim} = 1.35 \cdot 10^{10}$ L mol^{-1} s^{-1}, T→T energy transfer).[17] Note that these examples illustrate the maximum efficiency of quenching. Based on these data and taking into account the fact that quenching of other energy donors (Ln^{3+}* ions[5] and ^{1}PAH* [6]) by C_{60} fullerene is also characterized by much higher k_{bim} compared to other quenchers, we can conclude that the unusually high efficiency of C_{60} as quencher of EES (energy acceptor) is due to an original electronic structure of this species, which includes an ensemble of 240 electrons. Probably, the C_{60} molecule is a more powerful inductor compared to other molecules and has a strong effect on the electronic structure of the energy donor molecules, thus inducing nonradiative deactivation of these species. As was shown earlier (see Refs 1, 5—8 cited in Ref. 5), characteristic of C_{60} fullerene is the quenching of fluorescence of different types of EES through electron transfer to C_{60} with the formation of a $C_{60}^{-\bullet}$ radical anion. In our recent studies[5,6] and in this work we first established that the quenching of EES of various classes of compounds by C_{60} fullerene occurs with record efficiency through energy transfer to C_{60}. Therefore, this type of EES deactivation can be treated as a new property of C_{60} fullerene.

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