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Addition of Me$_2{}^\bullet$CCN, Me$_2{}^\bullet$CPh, and CCl$_3$CH$_2{}^\bullet$CHPh radicals to fullerene C$_{60}$

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The rate constants for addition of the Me$_2{}^\bullet$CCN, Me$_2{}^\bullet$CPh, and CCl$_3$CH$_2{}^\bullet$CHPh radicals to fullerene C$_{60}$ at 22 °C were determined by ESR spectroscopy using spin trapping technique.

Key words: ESR spectroscopy, spin trapping technique, addition rate constants, fullerene, free radicals.

Processes involving free radicals are being used in recent years to synthesize various fullerene derivatives, including their copolymers with unsaturated compounds (M).[1—5] The fullerene derivatives contain both radicals from initiators (R) and telomer-radicals $(M)_nC_{60}R$.

The rate constants for addition of free radicals to fullerene need to be known for the purposeful use of radical reactions in the synthesis of fullerene derivatives. The rate constants of interaction of fullerene with some carbon-centered radicals have recently been determined.[5,6] These values differ by at least an order of magnitude from those of addition of free radicals to fullerene determined previously.[7,8] The rate constants for the addition of benzyl radicals to fullerene C$_{60}$ found in these works differ by two orders.

In this work, the rate constants for addition of radicals Me$_2{}^\bullet$CCN ($^\bullet$R^1), Me$_2{}^\bullet$CPh ($^\bullet$R^2), and CCl$_3$CH$_2{}^\bullet$CHPh ($^\bullet$R^3) to fullerene C$_{60}$ were determined by ESR.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Degassed reaction solutions in glass tubes were irradiated by a DRSh-1000 lamp in the resonator of the spectrometer at 22 °C. The band with a maximum at $\lambda \approx 366$ nm was separated using a glass light filter. The required amount of nitrosodurene (ND) was diluted with a minor amount of CH$_2$Cl$_2$ before addition of liquid solvents.

2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO, Aldrich) was used as reference for calculation of concentrations of nitroxyl radicals ($[\text{TEMPO}]_0 = 3 \cdot 10^{-3}$ mol L^{-1}). AIBN was crystallized from EtOH. Azocumene was prepared by a known procedure.[9]

The $^\bullet$R^1 and $^\bullet$R^2 radicals were generated by the photochemical decomposition of AIBN and azocumene, respectively, and $^\bullet$R^3 was produced by the elimination of the Br atom from the CCl$_3$CH$_2$CHBrPh molecule by the $^\bullet$Re(CO)$_5$ radicals formed in photolysis of Re$_2$(CO)$_{10}$.[10]

Results and Discussion

The method of competitive kinetics was applied to determine the rate constants for addition of the $^\bullet$R^i radicals ($^\bullet$R^i = $^\bullet$R^1—$^\bullet$R^3) to fullerene (reaction (1)). The addition of the $^\bullet$R^i radicals to ND resulting in the formation of the spin-adducts of $^\bullet$R^i with the spin trap was used as a competing reaction

$$^\bullet R^i + C_{60} \xrightarrow{k_1} {}^\bullet C_{60}R^i, \qquad (1)$$

$$^\bullet R^i + ND \xrightarrow{k_2} \underset{\mathbf{A}}{R^iN(O^\bullet)Ar}, \qquad (2)$$

Ar = 2,3,5,6-Me$_4$C$_6$H.

The k_1 rate constants were determined from the expression

$$d[\mathbf{A}]/d[^\bullet C_{60}R^i] = k_2[ND]_0/k_1[C_{60}]_0, \qquad (3)$$

where $[ND]_0$ and $[C_{60}]_0$ are the initial concentrations of the spin trap and fullerene C$_{60}$, respectively; $d[\mathbf{A}]$ and $d[^\bullet C_{60}R^i]$ are the changes in the intensities of signals from nitroxyl radicals **A** and spin-adducts of the $^\bullet$R^i radicals with fullerene C$_{60}$. As can be seen in Eq. (3), to determine k_1, one has to know k_2, which are[11,12] $5 \cdot 10^6$ and $1.0 \cdot 10^7$ L mol^{-1} s^{-1} for the interaction of the $^\bullet$R^2 and $^\bullet$R^3 radicals, respectively, with ND at 22 °C.

When solutions of ND and AIBN in CH$_2$Cl$_2$ are irradiated, the ESR spectra exhibit[13] a triplet with a_N = 12.92 G attributed to spin-adducts of the $^\bullet$R^1 radicals with the trap. The intensity of the signal increases with an increase in the initial concentration of AIBN at the un-

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changed concentration of ND. The formation of these radicals can be described by the following scheme:

$$R^1{-}N{=}N{-}R^1 \longrightarrow 2\,{}^{\bullet}R^1,$$

$${}^{\bullet}R^1 + ND \xrightarrow{k_2} \mathbf{A},$$

$${}^{\bullet}R^1 + \mathbf{A} \xrightarrow{k_0} \text{Stable products},$$

$$2\,\mathbf{A} \longrightarrow \text{Stable products.}$$

The k_2 rate constant for the ${}^{\bullet}R^1$ radicals was determined using a known procedure**14** from the function of [**A**] ($R^i = R^1$) *vs.* $[ND]_0$

$$k_2 = k_0(d[\mathbf{A}]/d[ND]_0), \qquad (4)$$

$[ND]_0 \rightarrow 0$.

Based on the dependence of [**A**] ($R^i = R^1$) on the concentration of ND (Fig. 1) and accepting that $k_0 = 2 \cdot 10^8$ L mol^{-1} s^{-1},**10** we determined the addition rate constant for the ${}^{\bullet}R^1$ radicals to ND ($k_2 = 2.0 \cdot 10^7$ L mol^{-1} s^{-1}) at 22 °C.

Irradiation of toluene solutions containing fullerene C_{60}, ND, and AIBN results in the appearance in the ESR spectra of signals from spin-adducts of the ${}^{\bullet}R^1$ radicals with fullerene (${}^{\bullet}C_{60}R^1$) (Fig. 2, *a*, singlet **1**) and ND (**A**, $R^i = R^1$) (Fig. 2, *a*, triplet **2**). The same spectrum was obtained by irradiation of toluene solutions containing fullerene C_{60}, ND, and azocumene. Data on changes in time of the intensities of signals from the spin-adducts of the ${}^{\bullet}R^1$ and ${}^{\bullet}R^2$ radicals with fullerene C_{60} and ND (Fig. 2, *b*) were processed using the least-squares method (correlation coefficients 0.95 and 0.96). The addition rate constants (k_1) for the ${}^{\bullet}R^1$ and ${}^{\bullet}R^2$ radicals to fullerene C_{60} were determined using Eq. (3). At 22 °C they are $3.0 \cdot 10^6$ and $8.1 \cdot 10^5$ L mol^{-1} s^{-1}, respectively.

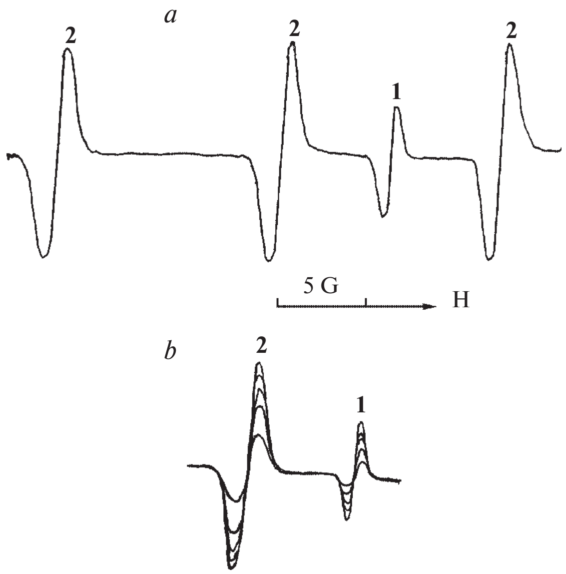

Fig. 2. *a.* ESR spectrum of radicals ${}^{\bullet}C_{60}C(CN)Me_2$ (**1**) and nitroxyl radicals $Me_2C(CN)N(O^{\bullet})Ar$ (Ar = 2,3,5,6-Me_4C_6H) (**2**) obtained under irradiation of a toluene solution containing nitrosodurene ($[ND]_0 = 1.0 \cdot 10^{-3}$ mol L^{-1}) and fullerene C_{60} ($[C_{60}]_0 = 1.0 \cdot 10^{-3}$ mol L^{-1}). *b.* Change in time of the intensity of signals from **1** and **2** (recording of spectra at an interval of 40 s).

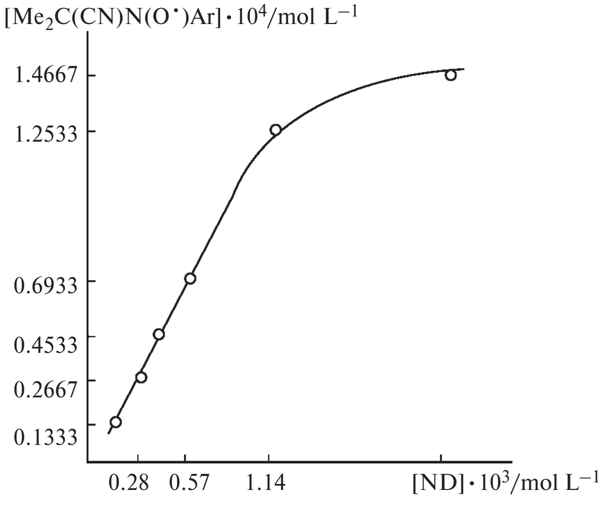

Fig. 1. Plot of the yield of nitroxyl radicals $(Me_2CCN)N(O^{\bullet})Ar$ (Ar = 2,3,5,6-Me_4C_6H) *vs.* concentration of nitrosodurene ([ND]).

For the photochemical decomposition of AIBN in a CH_2Cl_2 solution containing ND and styrene (ST), the ESR spectra contain a triplet with a_N =12.8 G and a triplet of doublets with a_N = 13.8 G and $a_{\beta\text{-H}}$ = 3.8 G, which characterize the spin-adducts of the ${}^{\bullet}R^1$ and $R^1CH_2{}^{\bullet}CHPh$ (${}^{\bullet}R^4$) radicals with ND.**15** Measuring the rates of formation of the spin-adducts of the ${}^{\bullet}R^1$ and ${}^{\bullet}R^4$ radicals with ND in the linear region of changes in the intensity of signals in the ESR spectra and using the expression

$$d[R^1N(O^{\bullet})Ar]/d[R^4N(O^{\bullet})Ar] = k_2[ND]_0/k_3[ST]_0, \qquad (5)$$

$$k_2 = 2 \cdot 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$$

we determined the rate constant k_3 for addition of the ${}^{\bullet}R^1$ radicals to ST, which is $7.5 \cdot 10^3$ L mol^{-1} s^{-1}.

$${}^{\bullet}R^1 + CH_2{=}CHPh \xrightarrow{k_3} R^1CH_2{}^{\bullet}CHPh$$

The rate constants determined for the addition of the ${}^{\bullet}R^1$ radicals to fullerene C_{60} and ST make it possible to compare them with the results of preparative experiments published previously,**4** which show that for the AIBN-initiated copolymerization of fullerene C_{60} with ST the ratio of the yields of the products $R^1{-}(CH_2CHPh{-})_n$: $C_{60}R^1$ = 2.5, and in the case with methyl methacrylate,

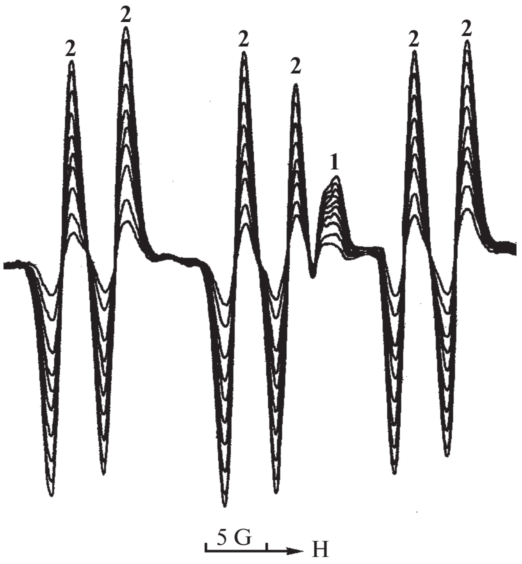

Fig. 3. Change in time of the intensities of signals in the ESR spectra of radicals $^{\bullet}C_{60}(Ph)CHCH_2CCl_3$ (**1**) and nitroxyl radicals $CCl_3CH_2CH(Ph)N(O^{\bullet})Ar$ (Ar = 2,3,5,6-Me_4C_6H) (**2**) obtained by irradiation of a toluene solution containing $CCl_3CH_2CHBrPh$, $Re_2(CO)_{10}$, nitrosodurene ($[ND]_0 = 1.31 \cdot 10^{-3}$ mol L^{-1}), and fullerene C_{60} ($[C_{60}] = 1.0 \cdot 10^{-3}$ mol L^{-1}). Recording of spectra at an interval of 40 s.

R^1—$(CH_2CMeCO_2Me—)_n$: $C_{60}R^1$ = 1.6 at the ratio monomer : fullerene = 700 : 1. Taking into account the k_1 and k_3 constants, we obtain that the ratio of formation rate of R^1—$(CH_2CHPh—)_n$ to $C_{60}R^1$ should be 1.8, which is rather close to 2.5. Since the reactivities of methyl methacrylate and ST toward carbon-centered radicals slightly differ,[15] we can assume that the ratio of formation rates R^1—$(CH_2CMeCO_2Me—)_n$: $C_{60}R^1$ should be 1.8, which agrees well with known data.[4]

The ESR spectrum of the radicals obtained by irradiation of a toluene solution containing ND, fullerene C_{60}, $Re_2(CO)_{10}$, and $CCl_3CH_2CHBrPh$ is presented in Fig. 3. It exhibits signals from spin-adducts of the $^{\bullet}R^3$ radicals with fullerene (see Fig. 3, **1**) and ND, *viz.*, a doublet of triplets (other six signals, **2**). Processing changes in time of the intensity of these signals by the least-squares method (correlation coefficients 0.96 and 0.97) and accepting the addition rate constant for the $^{\bullet}R_3$ radicals to ND to be equal to $1.0 \cdot 10^7$ L mol^{-1} s^{-1},[12] we determined the rate constant (k_1) for addition of the $^{\bullet}R^3$ radicals to fullerene C_{60} as $8.5 \cdot 10^5$ L mol^{-1} s^{-1} at 22 °C. This value is close to a similar one for addition of benzyl radicals to fullerenes C_{60}.[6]

These results indicate the possibility of using fullerene C_{60} as a trapping agent of growing radicals in the polymerization and copolymerization of unsaturated compounds for the preparation of practically important "living" polymers and copolymers.[16]

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