Addition of Me₂CCN, Me₂CPh, and CCl₃CH₂CHPh radicals to fullerene C₆₀

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The rate constants for addition of the Me₂CCN, Me₂CPh, and CCl₃CH₂CHPh radicals to fullerene C₆₀ 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)ₙC₆₀R.

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 C₆₀ found in these works differ by two orders.

In this work, the rate constants for addition of radicals Me₂•CCN (•R¹), Me₂•CPh (•R²), and CCl₃CH₂•CHPh (•R³) to fullerene C₆₀ 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 λ ≈ 366 nm was separated using a glass light filter. The required amount of nitrosodurene (ND) was diluted with a minor amount of CH₂Cl₂ 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 ([TEMPO]₀ = 3 × 10⁻³ mol L⁻¹). AIBN was crystallized from EtOH. Azocumene was prepared by a known procedure.9

The •R¹ and •R² radicals were generated by the photochemical decomposition of AIBN and azocumene, respectively, and •R³ was produced by the elimination of the Br atom from the CCl₃CH₂CHBrPh molecule by the •Re(CO)₅ radicals formed in photolysis of Re₂(CO)₁₀.10

Results and Discussion

The method of competitive kinetics was applied to determine the rate constants for addition of the •R radicals (•R = •R¹—•R³) to fullerene (reaction (1)). The addition of the •R radicals to ND resulting in the formation of the spin-adducts of •R with the spin trap was used as a competing reaction

\[ •R + C₆₀ \xrightarrow{k_1} •C₆₀R, \]

\[ •R + ND \xrightarrow{k_2} R\text{N(O\cdot)}\text{Ar}, \]

where \( k_1 \) and \( k_2 \) are the rate constants for addition of the •R radicals to fullerene C₆₀. As can be seen in Eq. (3), to determine \( k_1 \), one has to know \( k_2 \), which are 11.12 5 × 10⁶ and 1.0 × 10⁷ L mol⁻¹ s⁻¹ for the interaction of the •R² and •R³ radicals, respectively, with ND at 22 °C.

When solutions of ND and AIBN in CH₂Cl₂ are irradiated, the ESR spectra exhibit a triplet with \( a_N = 12.92 \) G attributed to spin-adducts of the •R¹ 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:

$$\text{R}^1 - \text{N} = \text{N} - \text{R}^1 \rightarrow 2 \cdot \text{R}^1,$$

$$\cdot \text{R}^1 + \text{ND} \rightarrow \text{A},$$

$$\cdot \text{R}^1 + \text{A} \rightarrow \text{Stable products},$$

$$2 \cdot \text{A} \rightarrow \text{Stable products}.$$

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

$$k_2 = k_0 \frac{d[A]}{d[ND]_0},$$

$[\text{ND}]_0 \rightarrow 0.$

Based on the dependence of $[\text{A}]$ ($R' = R^1$) on the concentration of ND (Fig. 1) and accepting that $k_0 = 2 \cdot 10^8 \text{L mol}^{-1} \text{s}^{-1},$ we determined the addition rate constant for the $\cdot \text{R}^1$ radicals to ND ($k_2 = 2.0 \cdot 10^7 \text{L mol}^{-1} \text{s}^{-1}$) 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 $\cdot \text{R}^1$ radicals with fullerene ($\cdot \text{C}_{60}\text{R}^1$) (Fig. 2, a, singlet 1) and ND ($\text{A}, R' = R^1$) (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 $\cdot \text{R}^1$ and $\cdot \text{R}^2$ 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 ($k_i$) for the $\cdot \text{R}^1$ and $\cdot \text{R}^2$ radicals to fullerene $C_{60}$ were determined using Eq. (3). At 22 °C they are $3.0 \cdot 10^6$ and $8.1 \cdot 10^5 \text{L mol}^{-1} \text{s}^{-1},$ respectively.

For the photochemical decomposition of AIBN in a CH$_2$Cl$_2$ solution containing ND and styrene (ST), the ESR spectra contain a triplet with $\alpha_N = 12.8 \text{ G}$ and a triplet of doublets with $\alpha_N = 13.8 \text{ G}$ and $\alpha_{\beta-H} = 3.8 \text{ G},$ which characterize the spin-adducts of the $\cdot \text{R}^1$ and $\cdot \text{CH}_2\text{CHPh}$ ($\cdot \text{R}^4$) radicals with ND. Measuring the rates of formation of the spin-adducts of the $\cdot \text{R}^1$ and $\cdot \text{R}^4$ radicals with ND in the linear region of changes in the intensity of signals in the ESR spectra and using the expression

$$\frac{d[R^1N(O^\cdot \text{Ar})]}{d[R^4N(O^\cdot \text{Ar})]} = k_3[\text{ND}]_0/k_1[\text{ST}]_0,$$

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

$$\cdot \text{R}^1 + \text{CH}_2=\text{CHPh} \rightarrow \text{R}^1\text{CH}_2\cdot \text{CHPh}$$

The rate constants determined for the addition of the $\cdot \text{R}^1$ radicals to fullerene $C_{60}$ and ST make it possible to compare them with the results of preparative experiments published previously, which show that for the AIBN-initiated copolymerization of fullerene $C_{60}$ with ST the ratio of the yields of the products $\text{R}^1-(\text{CH}_2\text{CHPh}-)_n : C_{60}\text{R}^1 = 2.5,$ and in the case with methyl methacrylate,