Determination of the rate constants of addition of $^{\cdot}P(O)(OPr^i)_2$ radicals to fullerenes C_{60} and C_{70}

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The rate constants of the addition of phosphoryl radicals to fullerenes C_{60} and C_{70} were determined by the method of competitive reactions. The phosphoryl radicals were shown to be 1.5—3 orders of magnitude more reactive than the carbon-centered radicals.

Key words: fullerenes, ESR spectroscopy, phosphoryl radicals, competitive reactions, rate constant.

The addition products (AP) of phosphoryl radicals $^{\cdot}R$ to fullerenes C_{60} and C_{70} have previously[1—3] been observed by the ESR method. Unlike the AP of carbon-centered radicals (*cf.* Ref. 4) to fullerenes, the phosphoryl-fullerenyl radicals $^{\cdot}C_{60}P(O)R_2$ and $^{\cdot}C_{70}P(O)R_2$ (R = OMe, $OCHMe_2$, *etc.*) are characterized by higher hyperfine coupling (HFC) constants of an unpaired electron with the P atom nucleus (a doublet at 50—70 G). These properties of the AP of the phosphoryl radicals to fullerenes make it possible to distinguish them, using the ESR spectra, from the AP of the carbon-centered radicals to fullerenes (a singlet line) when they are simultaneously present in the reaction mixture.

In this work, the rate constants of the addition of the $^{\cdot}P(O)(OPr^i)_2(R^1)$ radicals to fullerenes C_{60} and C_{70} were determined by the method of competitive reactions.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Samples in calibrated glass tubes were degassed by several "freezing—evacuation—defrosting" cycles. UV irradiation was performed in the cavity of the spectrometer with a DRSh-1000 lamp.

Toluene and 1-octene were distilled in an Ar atmosphere immediately before experiments.

$Hg[P(O)(OPr^i)_2]_2$ was synthesized by analogy to the previously described method.[5] Crystallosolvate $C_{70}(MeC_6H_5)_n$ ($n \approx 1$) with 98% content of fullerene C_{70} was used.

Results and Discussion

Radicals R^1 were generated by the known procedure[1—3] by the photochemical decomposition of $Hg[P(O)(OPr^i)_2]_2$

$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} 2\ ^{\cdot}P(O)(OPr^i)_2(R^1) + Hg, \quad (1)$$

$$R^1 + C_n \xrightarrow{k_1} C_nR^1 \ \ \mathbf{(A)} \ \ (n = 60, 70). \quad (2)$$

The addition of the R^1 radicals to 1-octene (M) was chosen as the reaction competitive with stage (2):

$$R^1 + CH_2{=}CHC_6H_{13}\ (M) \xrightarrow{k_2} R^1CH_2{-}^{\cdot}CHC_6H_{13}(R^2), \quad (3)$$

$$R^2 + C_n \longrightarrow R^2C^{\cdot}_n.$$

The following expression[6] is valid for reactions (1)—(3)

$$dA^1/dA^2 = 1 + k_2[M]_0/(k_1[C_n]_0), \quad (4)$$

where dA^1/dA^2 is the ratio of the rates of AP formation of the R^1 radicals to fullerenes C_n in the absence and presence of 1-octene, respectively. It follows from Eq. (4) that the rate constant of the addition of the R^1 radical to fullerene can be determined by the method of competitive reactions if the rate constant of the addition of the R^1 radicals to 1-octene is known.

The ESR spectra of the phosphoryl-fullerenyl radicals produced by UV irradiation of toluene solutions containing C_{60} or C_{70} and $Hg[P(O)(OPr^i)_2]_2$ exhibit signals with the following HFC constants with the phosphorus atom nucleus: $^{\cdot}C_{60}R^1$ — a_P = 63.7 G (doublet)[2]; $^{\cdot}C_{70}R^1$ — a_P = 70.5 G (doublet), g = 2.0031 (**1**); a_P = 66.5 G (doublet), g = 2.0027 (**2**); a_P = 55.2 G (doublet), g = 2.0080 (**3**) (these signals are attributed to three of five possible $^{\cdot}C_{70}R^1$ regioisomers).[4] In the presence of 1-octene, the ESR spectra exhibit, along with the above marked signals, a singlet assigned to the AP of the R^2 radicals to fullerenes (Fig. 1, *a*: **4**). The yields of these radicals increase with an increase in the concentration of 1-octene.

The dA^1/dA^2 ratios, which linearly depend, according to Eq. (4), on $[M]_0/[C_n]_0$, are presented in Table 1. These values were obtained by the least-squares approximation of the changes in the intensity of the signals from

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radicals A (Fig. 1, *b*) at different concentrations of octene.

The rate constant of the addition of the $^{\bullet}P(O)(OPr^i)_2$ radicals to 1-hexene, which is equal to k_2 = 2.9 · 10^5 L mol^{-1} s^{-1} at room temperature, has been determined previously.[7] From the dependence of dA^1/dA^2 on [M] we found $k_2/(k_1[C_{60}])$ = 0.4257, $k_2/(k_1[C_{70}])$ = 1.4914, 1.2968, and 1.1861 for regioisomers **1**, **2**, and **3**, respectively. The rate constants of the addition of the R^1 radicals to fullerenes were determined from the obtained values under the assumption of k_2 = 2.9 · 10^5 L mol^{-1} s^{-1} (see Table 1).

The ESR spectrum obtained under UV irradiation of a toluene solution containing equal amounts of C_{60} and C_{70} (1 · 10^{-3} mol L^{-1} each) and 8.23 · 10^{-3} mol L^{-1} of $Hg[P(O)(OPr^i)_2]_2$ is presented in Fig. 2. It follows from the data in Table 1 and Fig. 2 that k_2 for C_{60} is several times higher than the corresponding rate constants of the addition of the radicals to the nonequivalent carbon atoms of C_{70}. The reactivity of the carbon atoms in fullerenes is determined by the surface curvature at the carbon atom, which is attacked by the radicals, the number of the reaction sites to which the radicals can add, and the energy gain due to the delocalization of an unpaired electron.[8,9] The k_2 constant for C_{60} is higher due to 60 equivalent vertices in this fullerene, whereas in C_{70} the ratio of the nonequivalent carbon atoms to which the R^1 radicals add is equal to 10 : 20 : 20 (vertices B (A), C, and D[4] (Fig. 3)).

Table 1. Rate constants of the addition of the $^{\bullet}P(O)(OPr^i)_2$ radicals to fullerenes C_n* at 295 K

Fullerene	$k_2 \cdot 10^{-8}$ /L mol^{-1} s^{-1}	$[M]_0$ /mol L^{-1}	dA^1/dA^2
C_{60}	6.8	0.1296	1.0345
		0.2592	1.0909
		0.5185	1.2245
		0.7778	1.3043
			$dA^1/dA^2 = 1 + 0.4257[M]_0$ (R^2 = 0.97)
C_{70}	1.9 (isomer **1**)		1.3203
			2.1080
			2.4778
			3.6623
			$dA^1/dA^2 = 1 + 1.4914[M]$ (R^2 = 0.98)
	2.2 (isomer **2**)	0.2592	1.0698
		0.5185	1.6731
		1.0368	2.0886
		1.8144	3.2519
			$dA^1/dA^2 = 1 + 1.2968[M]$ (R^2 = 0.97)
	2.4 (isomer **3**)		1.0074
			1.7030
			2.5450
			3.2805
			$dA^1/dA^2 = 1 + 1.1861[M]$ (R^2 = 0.98)

* $[C_n]_0$ = 1 · 10^{-3} mol L^{-1}.

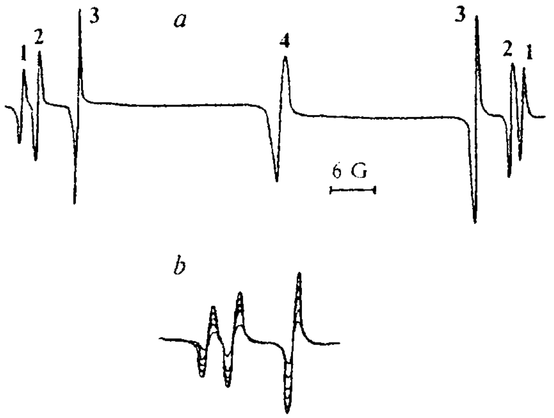

Fig. 1. *a*. ESR spectrum of the addition products of $^{\bullet}P(O)(OPr^i)_2$ to C_{70} (**1**—**3**) obtained by UV irradiation of a toluene solution containing C_{70} (1 · 10^{-3} mol L^{-1}), $Hg[P(O)(OPr^i)_2]_2$ (8.23 · 10^{-3} mol L^{-1}), and $CH_2=CHC_6H_{13}$ (1.81 mol L^{-1}). Signal **4** was attributed to the AP of $P(O)(OPr^i)_2-CH_2-{}^{\bullet}CHC_6H_{13}$ to C_{70}. *b*. Change in the intensity of the first three lines in time (the spectra were recorded at an interval of 40 s).

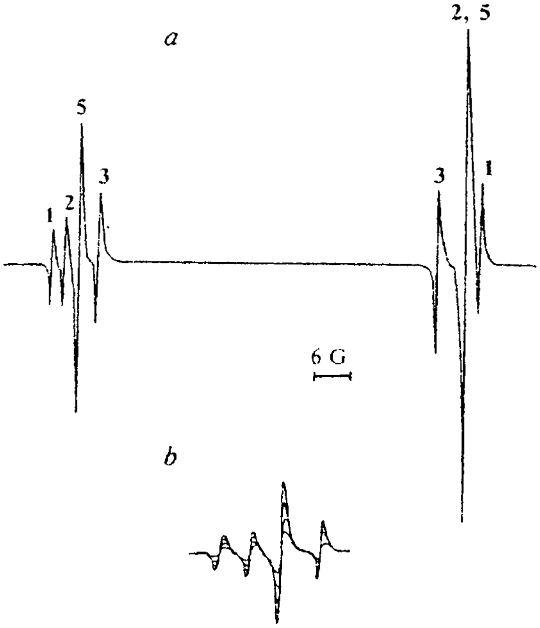

Fig. 2. *a*. ESR spectrum of the AP of $^{\bullet}P(O)(OPr^i)_2$ to C_{70} (**1**—**3**) and C_{60} (**5**) obtained by UV irradiation of a toluene solution containing C_{60} (1 · 10^{-3} mol L^{-1}), C_{70} (1 · 10^{-3} mol L^{-1}), and $Hg[P(O)(OPr^i)_2]_2$ (8.23 · 10^{-3} mol L^{-1}). *b*. Change in the intensity of the first three lines in time (the spectra were recorded at an interval of 40 s).

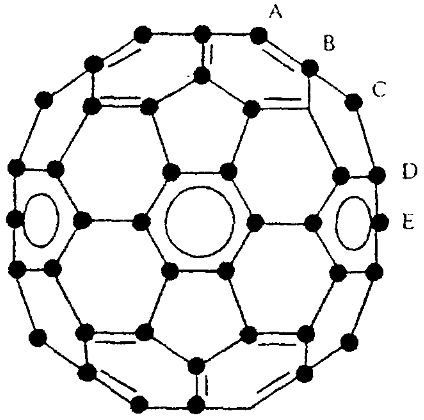

Fig. 3. Fullerenes C_{70}. A—E are the groups of nonequivalent carbon atoms.

Comparison of the rate constants of the addition of the carbon-centered[10,11] and R^1 radicals to fullerenes shows that the latter are by 1.5—3 orders of magnitude more active in this reaction than the first radicals.

The results of this work indicate new possibilities of the use of fullerenes as spin traps for obtaining quantitative data on particular stages of chemical processes involving phosphoryl radicals. They manifest a higher reactivity in addition to unsaturated compounds,[12] abstraction of halogen from halogen-containing compounds,[12,13] and other processes.

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