An ESR study of the products of multiple addition of diisopropoxyphosphoryl radicals to C_{60}

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The ESR spectra of the radicals resulting from the multiple addition of diisopropoxyphosphoryl radicals to C_{60} have been studied. The formation of six different types of radical adducts was detected. A structure for the stable product, characterized by hyperfine coupling of the unpaired electron with two phosphorus nuclei, was proposed. The unpaired electron in $C_{60}P(O)(OPr^i)_2$ is delocalized in the same way as in alkylfullerenyl radicals, *i.e.*, mainly over the two six-membered rings adjacent to the $C-CP(O)(OPr^i)_2$ bond.

Key words: fullerene, ESR, phosphoryl, multiple addition, electron delocalization.

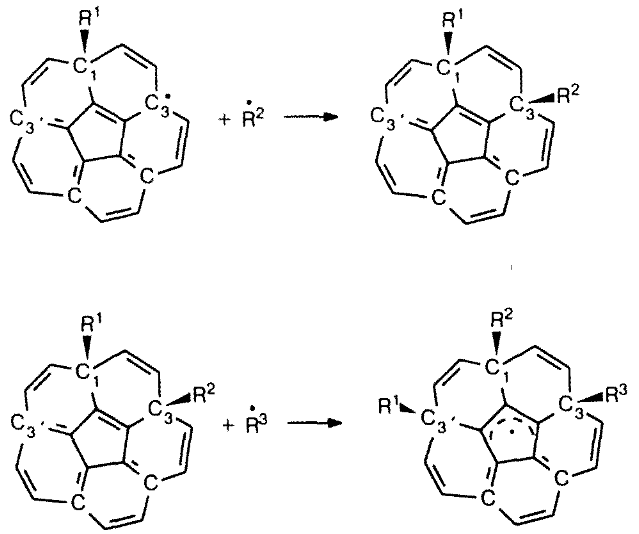
Fullerenes are able to add a large number of free radicals. The structures of the adducts thus formed can be determined based on the ESR spectra of fullerenyl radicals at various stages of the reaction. Previously we have observed the formation of allylic structures during the simultaneous generation of phosphoryl and carbon-centered radicals in a solution of C_{60} and have shown that the positions of the phosphoryl groups in the allyl system depend on the donor-acceptor properties of the carbon-centered radicals.[1,2] Whereas the products of multiple addition of benzyl radicals to C_{60} fullerene have structures similar to allyl or cyclopentadienyl radicals,[3] the multiple addition of phosphoryl radicals [$^{\cdot}P(O)(OMe)_2$] to fullerenes affords allylic structures only in the case of C_{70}.[4]

The data reported previously[3] indicate that the second radical undergoes recombination with position 3(3′) of the monoadduct, and the addition of the third radical leads to an allylic structure (Scheme 1).

However, no allyl type radicals are formed upon the multiple addition of phosphoryl radicals to fullerene.[5] This means that the third phosphoryl radical enters a position that is distant from the first two radicals, and the structure of the radical center thus formed differs basically from that of an allylic radical. The hyperfine coupling (HFC) of the unpaired electron with the ^{31}P nuclei of the R^1 and R^2 radicals added ($R^1 = R^2 = R^3 = R = {}^{\cdot}P(O)(OPr^i)_2$) that occurs in the ESR spectra of $^{\cdot}C_{60}(R^1R^2)R^3$ depends on the degree of delocalization of the unpaired electron in the phosphorylfullerenyl radicals.

In the present paper, we studied the ESR spectra of the products resulting from the multiple addition of phosphoryl radicals at various stages of photolysis and investigated the delocalization of the unpaired electron in the monophosphorylfullerenyl radical.

Scheme 1



Experimental

The solutions under consideration were irradiated by the unfiltered light from a high-pressure mercury lamp (DRSh-1000). The ESR spectra were recorded on a Varian E-12A spectrometer. The samples were thoroughly degassed and filled with argon.

Results and Discussion

To study the products of the multiple addition of $^{\cdot}P(O)(OPr^i)_2$ radicals to C_{60}, we prepared a saturated toluene solution of C_{60} containing a 15-fold molar excess of $Hg[P(O)(OPr^i)_2]_2$. The UV irradiation of this solution in the resonator of an ESR spectrometer re-

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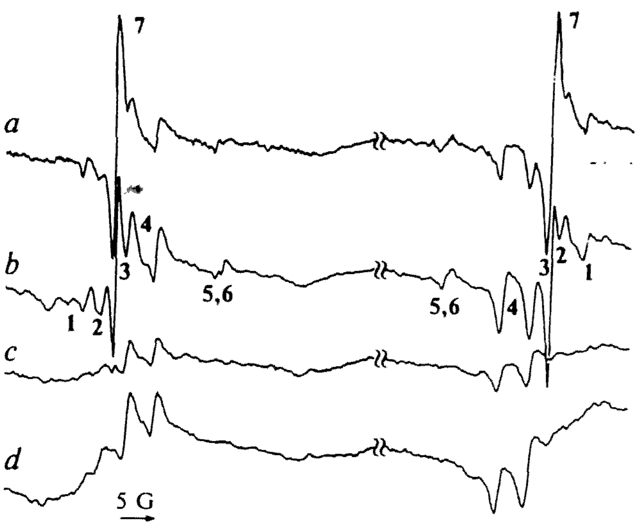


Fig. 1. ESR spectra of the products of multiple addition of phosphoryl radicals to C_{60} (**1**—**7**) at 20 °C during photolysis (irradiation with 620—680 nm visible light) for 8 (*a*), 16 (*b*), and 32 min (*c*), and after termination of irradiation carried out for 48 min (*d*).

sulted in the formation of radicals of six types (Fig. 1, *a*, *b*), characterized by the following constants of the HFC of the unpaired electron with the ^{31}P nucleus and by the following *g*-factors.

Radical	$a_P(1P)/G$	g
1	73.5	2.0019
2	66.75	2.0023
3	64.0	2.0023
4	4.25, 54.9	2.0025
5	33.5	2.0023
6	32.5	2.0023

The consecutive formation of the products of multiple addition can be described by the following scheme:

$$\mathrm{Hg[P(O)(OPr^i)_2]_2} \xrightarrow{h\nu} {}^{\cdot}\mathrm{HgP(O)(OPr^i)_2} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2},$$

$$\mathrm{C_{60}} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2} \longrightarrow {}^{\cdot}\mathrm{C_{60}P(O)(OPr^i)_2},$$

$${}^{\cdot}\mathrm{C_{60}P(O)(OPr^i)_2} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2} \longrightarrow \mathrm{C_{60}[P(O)(OPr^i)_2]_2},$$

$$\mathrm{C_{60}[P(O)(OPr^i)_2]_2} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2} \longrightarrow {}^{\cdot}\mathrm{C_{60}[P(O)(OPr^i)_2]_3},$$

$${}^{\cdot}\mathrm{C_{60}[P(O)(OPr^i)_2]_3} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2} \longrightarrow \mathrm{C_{60}[P(O)(OPr^i)_2]_4},$$

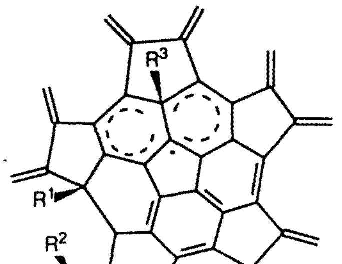
$$\mathrm{C_{60}[P(O)(OPr^i)_2]_{n-1}} + {}^{\cdot}\mathrm{P(O)(OPr^i)_2} \longrightarrow {}^{\cdot}\mathrm{C_{60}[P(O)(OPr^i)_2]_n},$$

$$n = 1, 3, 5, \mathit{etc.}$$

The parameters of radical **3** are close to those of monophosphorylfullerenyl radical **7**.[1] The other radical species result from multiple addition.

To determine the structures of adducts **1**, **2**, and **4**, it is necessary to consider the possible alternatives for the addition of phosphoryl radicals to $C_{60}[P(O)(OPr^i)_2]_2$.

The manifestation of the coupling of the unpaired electron with the ^{31}P nuclei in distant phosphoryl substituents in the ESR spectra depends on the degree of delocalization of the unpaired electron. Analysis of the spin coupling constants of the unpaired electron with ^{13}C in the $^{\cdot}C_{60}P(O)(OPr^i)_2$ radical (Fig. 2) and comparison of the results obtained with the results of the analysis of the spectra of alkylfullerenyl radicals[6] leads to the following values of $a_{^{13}C}$/G: 18.5 (1 C); 9.0 (4 C); 7.2 (3 C); 3.6 (6 C); ~2.0 (8 C) (manifested as a "shoulder" of the main signal at a small (0.05 G) amplitude of low-frequency modulation). This indicates that the unpaired electron in phosphorylfullerenyl radicals,



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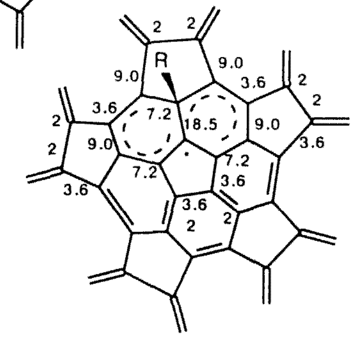

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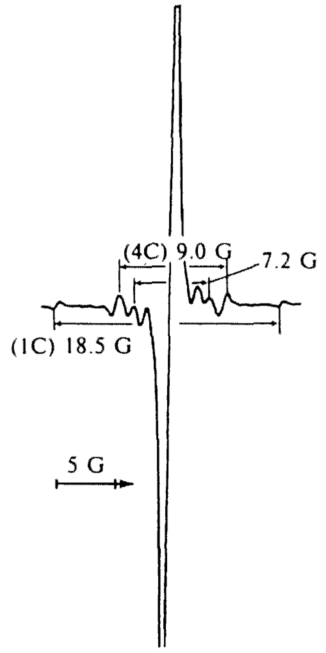

Fig. 2. ESR spectrum of the low-field component of the monophosphorylfullerenyl radical at 20 °C.

like that in alkylfullerenyl radicals, is mostly delocalized over the two six-membered rings adjacent to the $C-CP(O)(OR)_2$ bond.

The constants 3.6 and 2.0 G refer to those carbon atoms to which the R^1 and R^2 radicals in radical **4** are supposedly attached. It has been assumed that there is a quantitative correlation between the constants of HFC with the ^{13}C and ^{31}P nuclei in the related positions indicated for radicals **4** and 7. For example, if the constant of HFC with the ^{13}C nucleus of the carbon atom having the highest spin density is equal to 18.5 G, then the constant of 63.5 G for coupling with ^{31}P should be attributed to the nearest radical R^1. The addition of phosphoryl radicals to more distant six-membered rings should result in decreases in the constants of HFC with ^{31}P nuclei that are roughly proportional to the variation of the constants of HFC with the corresponding carbon atoms, for example, by factors of ~5 (18.5/3.6) and ~10 (18.5/2). The existence of a correlation between the constants of HFC with the ^{13}C nucleus in radical 7 and those with the ^{31}P nucleus in radical **4** has been assumed based on the similarity of their electronic structures.

The additional HFC with the ^{31}P nucleus (4.25 G) in radical **4** agrees with the above estimates and may be associated with a phosphoryl group attached to the adjacent six-membered ring.

When irradiation is terminated, the intensity of the spectrum of adduct **4** decreases by approximately one half over a period of 1 s (Fig. 1, *c*). Upon further irradiation of the solution with visible light (620—680 nm), the intensity of the ESR spectrum of adduct **4** is restored almost to the magnitude it attained during UV irradiation of the sample. This indicates that the HFC parameters of radical **4** correspond to adducts that contain three phosphorus atoms and are able to dimerize when irradiation is terminated, as well as to adducts that contain five or seven phosphoryl groups that stabilize the radical by shielding. Heating the sample from 290 to 330 K without irradiation results in a twofold increase in the steady-state concentration of radical **4**; however, at 350 K, adduct **4** is no longer detected.

In the case of radicals **1** and **2**, HFC with only one phosphorus atom is exhibited, and the constant of the HFC differs from the corresponding value for the monophosphorylfullerenyl radical. Apparently, these radicals are formed when a phosphoryl radical adds to a position that is far removed from the positions of the pair of phosphoryl groups added before. These facts can also be attributed to the formation of biradicals in which unpaired electrons interact only weakly with each other.[7] Apparently, the addition of phosphoryl radicals to fullerene has an effect on its geometry and electronic structure, and this causes the constant of HFC with the ^{31}P nucleus in the adduct radical to be different from that in the monofullerenyl radical. Similar effects were observed for the radical adducts of phosphoryl radicals with metal-containing complexes of C_{60}.[8]

When the irradiation is turned off, radicals **1** and **2** are destroyed over a period of 1 s (Fig. 1, *c*), which indicates that the shielding of the radical centers is weak.

Radicals **5** and **6** exhibit an unusually low constant of HFC with the ^{31}P nucleus, which is comparable with the constant for the HFC with the nucleus of the δ-phosphorus atom in the adduct of the platinum-centered radical $[^{\cdot}Pt(PPh_3)_2R]$ with C_{60}.[9] This may be due either to the fact that mercury-centered radicals add to C_{60} like platinum-centered radicals, or to a dramatic change in the character of the bond between the phosphoryl group and C_{60} (the formation of a C—O—P bond in place of the C—P bond).

The difference between the HFC constants of radicals **5** and **6** is probably due to the fact that the phosphorus-containing radicals are attached to different positions with respect to the phosphoryl substituents.

As noted above, increasing the time of photolysis to 15 min or more results in the formation of a stable radical whose ESR spectrum is a broad band caused by the superposition of the spectra of polyaddition products with different numbers of phosphoryl groups (Fig. 1, *d*). Our next task was to find out whether the addition of phosphoryl radicals to fullerene with heating is reversible, and whether migration over the fullerene surface is possible.

For this purpose a saturated solution of C_{60} and $Hg[P(O)(OPr^i)_2]_2$ in *tert*-butylbenzene was prepared. Signals similar to those described above were observed during the photolysis. After the formation of a stable radical, the solution was kept for 30 min at 430 K. During this period the intensity of the ESR signal decreased by approximately one half. Apparently, an equilibrium is established that is associated with the decomposition of the stable radical and the addition of new phosphoryl radicals due to the thermal decomposition of the mercury compound. In fact, heating a saturated solution of C_{60} and $Hg[P(O)(OPr^i)_2]_2$ in the resonator of a spectrometer to 430 K without irradiation results in the formation of the monoadduct $^{\cdot}C_{60}P(O)(OPr^i)_2$, whose steady-state concentration is approximately an order of magnitude lower than that in the case of the photochemical generation of phosphoryl radicals. This indicates that the addition to phosphoryl radicals to C_{60} is reversible.

The decrease in the intensity of the ESR signal of the stable radical is accompanied by the appearance and accumulation of a new stable radical (**8**), whose ESR spectrum is a triplet with the HFC constant a = 16.0 G and g = 2.0074 (the ratio of the line intensities is 1 : 1 : 1). The spectral parameters of **8** differ markedly from those of phosphoryl-containing allyl radicals,[2] and its *g*-factor differs sharply from the *g*-factor of a free electron. Radical **8** does not form when a saturated solution of fullerene and $Hg[P(O)(OPr^i)_2]_2$ is kept at 430 K. This implies that this new stable radical is formed from an adduct of multiple addition. At present, nothing definite can be said about the mechanism of its formation or its structure; however, the substantial shift of the *g*-factor indicates most likely that some oxygen-centered radicals have added to fullerene. The stability of radical **8** is due to its allylic structure, which is confirmed by the hyperfine coupling with two magnetic nuclei with spins of 1/2 (for example, with two equivalent δ-phosphorus atoms, located at the ends of an allylic system).

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