1582 Russian Chemical Bulletin, Vol. 43, No. 9, September, 1994

Conformational isomerism of phosphorus-containing fullerenyl radicals

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ESR spectra of phosphorus-containing fullerenyl radicals $^{\cdot}C_{60}—P(O)(OPr^i)_2$ and $^{\cdot}C_{60}—P(O)(OEt)Ph$ were studied at low temperatures (193—273 K). A decrease in the rate of rotation of organophosphorus group around the C—P bond results first in line broadening and then in the appearance of two doublets due to two "extreme" conformations, which have different *g*-factors and hyperfine coupling constants (HCC) of the unpaired electron with the ^{31}P nucleus. The kinetic and thermodynamic parameters of the conformational isomerism were calculated.

Key words: fullerene, phosphorus-containing fullerenyl radicals; conformational isomerism; ESR.

It is known that dialkoxyphosphoryl* radicals interact with the C=C double bonds of branched alkenes to form spin-adducts, which can be detected by ESR.[1—4] Earlier we investigated the structure and reactivity of fullerenylphosphonate radicals formed by the addition of dialkoxyphosphoryl radicals to fullerene-60.[5,6] The ESR spectra of $^{\cdot}C_{60}—P(O)(OR)_2$ radicals (R = Me, Et, Pr^i) are characterized by a single value of HCC with the ^{31}P nucleus (a_P = 63.5 G) and a *g*-factor equal to 2.0023. The radical structure implies the presence of the eclipsed conformation. In this conformation the best conditions of overlap between the $2p_z$-orbital of the unpaired electron and the $C^{\beta}—P$ bond, which is formed by sp^3- and spd-hybridized orbitals of C and P atoms, are realized. When one discusses the influence of temperature on the ESR spectra of spin-adducts of organophosphorus radicals and alkenes one must acknowledge that there are two possible types of rotation around the $^{\cdot}C^{\alpha}—C^{\beta}$ and $C^{\beta}—P$ bonds (*cf.* Ref. 7). In the case of fullerene C_{60} rotation around the C—C bond is not possible and all effects may be attributed to restricted rotation around $C^{\beta}—P$ bonds.

Radicals **1** and **2** were obtained[5,6] by photolysis of the corresponding mercury compounds in a saturated toluene solution of C_{60} in the resonator of an ESR spectrometer.

$$Hg[P(O)XY]_2 \xrightarrow{h\nu} 2\ ^{\cdot}P(O)XY + Hg$$

$$C_{60} + {}^{\cdot}P(O)XY \longrightarrow {}^{\cdot}C_{60}—P(O)XY$$

1, 2

1: X = Y = OPr^i
2: X = Ph, Y = OEt

As phosphorus-containing fullerenyl radicals dimerize after the cessation of UV-radiation forming weak C—C bonds,[6] in order to have a stationary pattern we used a special two-stage technique, which eliminated changes in the ESR spectrum due to either multiple additions of phosphorus-centered radicals or photodecomposition of **1** and **2**. At the first stage, a toluene solution containing equimolar quantities of fullerene C_{60} and $Hg[P(O)XY]_2$ was irradiated by UV light for the purpose of accumulating $XY(O)PC_{60}—C_{60}P(O)XY$ dimers (the measurement of the concentration of radical **1** made it possible to determine the concentration of the dimers; it was found to be ~5—10 % of the amount of C_{60} present in the solution). At the second stage of the ESR study, samples were irradiated by filtered light (λ = 620 to 680 nm), the action of which did not cause photodecomposition of the organomercuryphosphorus compound but resulted in dissociation of the dimers.

$$XY(O)PC_{60}—C_{60}P(O)XY \xrightarrow{h\nu} 2\ {}^{\cdot}C_{60}P(O)XY$$

When the samples being analyzed were cooled, the ESR pattern of radical **1** underwent considerable changes. As can be seen in Fig. 1, which illustrates the evolution of the low-field component of the phosphorus doublet, if the temperature drops from 273 to 243 K the lines become much broader. One of the reasons for this line broadening might be the restricted rotation of the phosphoryl group between the positions characterized by the different HCC of the unpaired electron with the ^{31}P nucleus. In fact, with a further drop in temperature (<243 K) "the freezing out" of two conformers (Fig. 2), characterized by the following parameters: **1a**, a_P = 62.1 G, *g* = 2.0022; **1b**, a_P = 65.0 G, *g* = 2.0020, begins. The equilibrium constants (*K*) at different tem-

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* The widely used appellation of such radicals as dialkoxyphosphonyl ones does not correspond to the IUPAC nomenclature.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1671—1673, September, 1994.

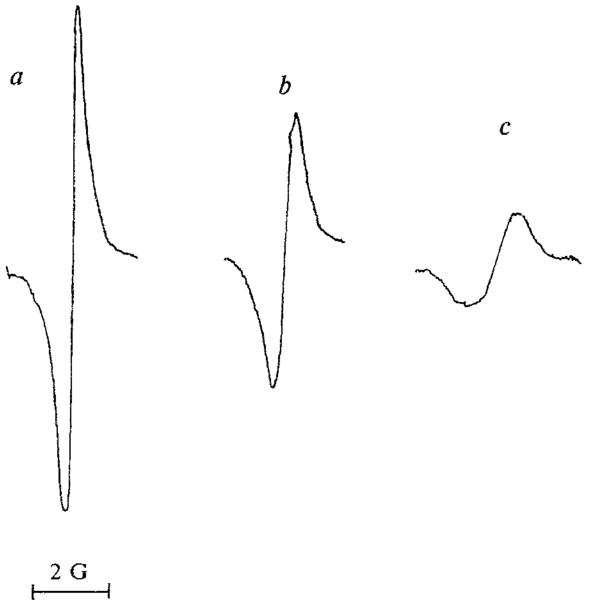

Fig. 1. ESR spectrum of the low-field component of the phosphoryl doublet of the radical $^{\cdot}C_{60}{-}P(O)(OPr^i)_2$ at 273 K (*a*), 263 K (*b*), and 243 K (*c*).

peratures were determined using the relative intensity of the spectral lines of radicals **1a** and **1b**.

T/K	230	220	210	200
K	0.55	0.66	0.85	1

The difference in the enthalpies (ΔH) of the two conformers was found from the $\ln K{-}T^{-1}$ relationship: ΔH = 1.8 kcal mol^{-1}.

The spectral and thermodynamic data obtained made it possible to evaluate the rate constants (k_1 and k_{-1}) of the transition between the two conformations in the temperature range 270—240 K using the relationship[8] $\Delta T_2^{-1} = [\alpha(1-\alpha)\gamma e(\Delta a)^2]/(k_1+k_{-1})$, where α and $(1-\alpha)$ are mole fractions of the two conformers, and Δa/G is the distance between the exchanging lines. This expression is true when the line widths of the radical in the two conformations are equal. As K is related to the rate constants ($K = k_1/k_{-1}$), it is possible to derive the equation for one of the rate constants:

$$Kk_{-1} + k_{-1} = \frac{\alpha(1-\alpha)\gamma e(\Delta a)^2}{\Delta T_2^{-1}}$$

and calculate the kinetic parameters of the restricted rotation of the phosphoryl group. Below are given the values of k_{-1} at various temperatures.

T/K	270	260	250	240
k_{-1}/s^{-1}	$5 \cdot 10^7$	$3.8 \cdot 10^7$	$2.7 \cdot 10^7$	$1.1 \cdot 10^7$

The activation energy of this process was determined to be E_a = 4.8 kcal mol^{-1}. The value of k_1 at 270 K is $4 \cdot 10^6$ s^{-1}.

Fig. 2. ESR spectrum of the radical $^{\cdot}C_{60}{-}P(O)(OPr^i)_2$ at 300 K (*a*), 233 K (*b*), and 200 K (*c*).

The HCC with the P nucleus for radical **2** is less than that for **1**: a_P = 55.3 G (g = 2.0023). When the temperature is decreased the lines of ESR spectrum broaden and two conformers are "frozen out"; they are characterized by the following parameters: **2a**, a_P = 56.7 G, g = 2.0022; **2b**, a_P = 54.2 G, g = 2.0023. In the case of radical **2** the value of the activation energy of transfer between the two conformations is 0.6 kcal mol^{-1}, and the equilibrium constant at 193 K is 0.3. It is not possible to detect the "extreme" conformations for the radical $^{\cdot}C_{60}{-}P(O)(OMe)_2$.

An increase in the g-factor in the conformers is accompanied by a decrease in the HCC with the P nucleus. The observed changes may be related to the different orientation of the P=O group with respect to the unpaired electron cloud. We believe that the disposition of the P=O bond with respect to the $2p_z$-orbital of the unpaired electron results in the appearance of spin density on the O atom, which exhibits more spin-orbital interaction than C atoms (*cf.* Ref. 9). If the spin density from the O atom is transferred to the P atom by the mechanism of spin polarization, then a decrease in the HCC value, whose main contribution comes from hyperconjugation,[9] might occur.

Similar spectral patterns were observed for spin-adducts of phosphoryl radicals with C_{70}. The details of this study will be reported elsewhere.

We wish to acknowledge V. I. Sokolov and A. I. Prokof'ev for their participation in discussions of results obtained.

Experimental

ESR spectra were recorded on a Varian-E12A radiospectrometer. The solutions under investigation were placed in quartz tubes which were carefully degassed and filled with argon. The irradiation was performed with the focused light of a DRSh-1000 lamp. A Unipan-660 regulator was used for maintaining constant sample temperature in the spectrometer resonator. Organomercuryphosphorus compounds were synthesized in a way similar to the methods described earlier.[10]

This work was supported by the Russian Foundation for Basic Research (Projects No. 93-03-18725 and 93-03-4101).

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Received March 9, 1994;
in revised form May 20, 1994

Synthesis of alkyl (3-pyridyl)hydroxymethylphosphonates and their IR spectra

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The reaction of dialkyl H-phosphonates with pyridine-3-carbaldehyde gives alkyl (3-pyridyl)hydroxymethylphosphonates. In liquid systems, the hydrogen atom is localized at the oxygen atom of the hydroxyl group; in crystals, the existence of a zwitter-ionic form could not be excluded. In $CHCl_3$ solutions, isolated molecules and cyclic dimeric H-complexes exist in an equilibrium.

Key words: alkyl (3-pyridyl)hydroxymethylphosphonates, H-bond; IR spectra.

The interaction of pyridine-3-carbaldehyde with dialkyl H-phosphonates has been studied. In the presence of MeONa, the reaction proceeds exothermically with the formation of alkyl (3-pyridyl)hydroxymethylphosphonates **1**—**4** (Scheme 1). The IR spectra of ethyl (3-pyridyl)hydroxymethylphosphonate (**2**) and ethyl α-hydroxybenzylphosphonate (**5**)[1] (Fig. 1) contain characteristic absorption bands (ν/cm^{-1}): 2600—3300 (AH), 1230—1260 (P=O), 1010—1070 (PO—C), as well as ~3000 and 1600 (CH and $C\overset{---}{=}C$, respectively).[2]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1674—1676, September, 1994.