

Addition of phosphoryl radicals to [76]fullerene gives six stable regioisomeric spin-adducts: MNDO/PM3 calculations of spin densities

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The addition of photochemically generated phosphoryl radicals [$\text{P}(\text{O})(\text{OPr}^t)_2$] to [76]fullerene has been studied by EPR and seven out of the nineteen possible RC_{76}^\bullet regioisomers are obtained, six of which are stable. This compares with the previously observed addition of phosphoryl radicals to [70]fullerene which afforded three of the five expected RC_{70}^\bullet regioisomers (only one being stable). Semi-empirical MNDO/PM3 calculations of the energies of all nineteen HC_{76}^\bullet models and the unpaired electron distributions within them, were carried out in order to aid the assignment of the observed spectra to specific $\text{P}(\text{O})(\text{OPr}^t)_2\text{C}_{76}^\bullet$ regioisomers.

Introduction

A considerable amount of information concerning the addition of the radicals of different chemical structure to [60]- and [70]-fullerenes has been obtained previously.¹ The concentration of a given fullerenyl radical might be expected to reflect the ease of attachment of the attacking radical to a given bond and hence the π -bond order of the latter (kinetic effect), or it could reflect the stability of the derived radical (thermodynamic effect). The kinetic effect requires that regions of a fullerene where electron delocalisation is considerable should be less susceptible to attack. Where delocalisation in the product is poor, the spin density of the radical will be concentrated largely on the adjacent (β) carbon, but in regions where there is higher aromaticity, the spin densities will be spread more widely. A notable feature of fullerenyl radicals is that some dimerise readily upon lowering the temperature or upon removing UV irradiation; steric considerations dictate that dimerisation most probably involves inter-fullerene bonding between positions *para* to the added moiety, or conceivably but less probably, at a more remote location. Dimerisation should be less favourable, the larger the radical addend, and where the spin density is more delocalised.

For [70]fullerene, there are five types of non-equivalent carbons, yielding in principle five isomeric radicals RC_{70}^\bullet , differing in both EPR parameters and their reactivity. However all five adducts are obtained only in the reaction between [70]fullerene and either aryl, methoxyl or trifluoroalkyl radicals.^{2,3} Four are formed (one of which is stable) on reaction with perfluoroalkyl radicals,⁴ and three each with thiomethyl,² alkyl,³ *m*-carboranyl,⁵ trichloromethyl,⁶ phosphoryl [$(\text{MeO})_2\text{OP}^\bullet$, $(\text{Pr}^t\text{O})_2\text{OP}^\bullet$] and hydrogen⁸ radicals. A higher number of products may equate with higher nucleophilicity of the radicals, because the aromatic region (see below) is more easily attacked by them. The identification of each type of radical adduct has been attempted by comparison of the experimental results with semi-empirical calculations.^{3,8} Thus the calculated (MNDO/PM3) relative values of $\Delta(\Delta H^\circ_f)$ for the five HC_{70}^\bullet isomers indicated that the E-isomer is thermodynamically much less stable than isomers A–D, of which the C- and D-isomers are the most stable.^{3,8} (A–E is the notation for the carbon locations in [70]fullerene.⁹) Kinetic effects, by contrast, lead to the expectation of preferential reactivity at the high order A–B and C–C bonds.

Both [70]- and [76]fullerenes have some similar features, namely an elongated shape, highly curved polar regions and a more planar and aromatic equatorial region, which in the case of [76]fullerene has varying curvature in two orthogonal planes parallel to the long axis. [70]Fullerene has two bonds of high π -bond order in the polar region leading to the probability of the ready formation of three radicals (the 5- and 6-positions are equivalent), confirmed by the foregoing literature data. [76]-Fullerene has four bonds of high π -bond order in the polar region (the 1,6-, 2,3-, 4,5-, and 14,15-bonds)¹⁰ and this leads to the expectation of the ready formation of seven radical adducts (the 1- and 6-positions are equivalent). In these polar regions the spin densities adjacent to the addend will be high and hence the probability of dimerisation should be low.

Previously there have been no experimental studies of the radical reactions of the higher fullerenes.¹¹ For [76]fullerene the few other reactions concern osmylation,¹² cycloaddition,¹³ hydrogenation,¹⁴ and the formation of methylene derivatives;¹⁵ only in cycloaddition has it been possible to characterise the products. We now describe radical phosphorylation of [76]fullerene, and compare the results with both those obtained previously for [70]fullerene and with semi-empirical calculations. Just as the five non-identical carbons for [70]fullerene (C-2, C-1, C-5, C-7, C-21) are labelled A–E respectively, so the nineteen different carbons for [76]fullerene (C-1, C-2, C-3, C-4, C-5, C-11, C-12, C-13, C-14, C-15, C-16, C-17, C-18, C-19, C-29, C-30, C-31, C-32, C-33, Fig. 1) are labelled A–S respectively.

Experimental

The saturated solutions of [76]fullerene in toluene containing 1.6×10^3 mol of $\text{Hg}[\text{P}(\text{O})(\text{OPr}^t)_2]$ and 0.1×10^{-3} mol of $(\text{CF}_3)_3\text{COH}$ were irradiated with the focused light of a DRSh-1000 high-pressure mercury lamp (1 kW). EPR spectra were recorded on a Varian E-12A spectrometer. The GAMESS program,¹⁶ running on a DEC 3000 Alpha AXP 400X workstation was employed.

To aid location of the sites of the addition of the phosphoryl radicals, calculations of ΔH°_f for HC_{76}^\bullet species (Table 1), and spin-density distributions for all possible 19 isomeric model spin-adducts with H-atoms (Table 2) were carried out using the MNDO/PM3 method¹⁷ at the ROHF level. The sums of the

Table 1 Semi-empirical calculations of the model isomeric spin-adducts of HC_{76}^{\cdot} , arranged in order of decreasing (calculated) stability

Isomer	H addition site	$\Delta(\Delta H_f^\circ)/$ kcal mol ⁻¹	Convexity (360° – sum of the carbon valency angles)
I	14	0	13.5
J	15	0.01	13.25
C	3	1.93	13.6
B	2	2.11	13.5
D	4	2.11	11.4
A	1	3.01	13.5
E	5	3.38	11.3
F	11	4.17	8.7
K	16	4.19	8.5
R	32	4.39	10.4
P	30	4.40	8.7
L	17	5.11	10.4
Q	31	5.42	7.9
G	12	8.47	11.7
H	13	8.72	11.4
O	29	14.33	4.1
N	19	14.35	5.0
S	33	16.40	6.9
M	18	20.99	5.1

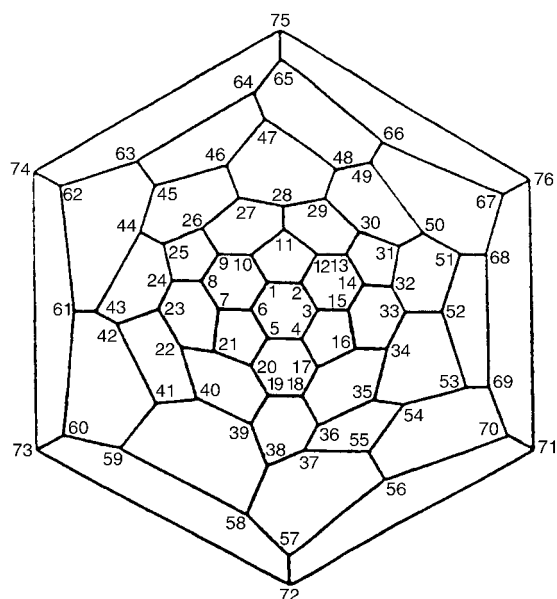
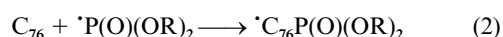
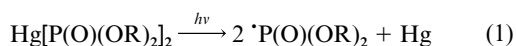


Fig. 1 Schlegel diagram for [76]fullerene showing the numbering.

valence angles at each non-equivalent carbon of [76]fullerene were also optimised by MM+ calculations (carried out using the "HyperChem 5.0" program) in order to determine the "convexity degree" of the carbon centre in the fullerene framework (Table 1). The greater the difference between angle sum and 360°, the more convex is the framework in the vicinity of this carbon, and the greater the possibility of the radical addition to the local double bond since the latter will be less delocalised (higher π -bond order). Moreover, less distortion of the framework will be produced on conversion of the carbon hybridisation from sp^2 to sp^3 upon addition.

Results and discussion

With the primary purpose of obtaining mono-adducts, the reaction [eqns. (1), (2), $R = \text{Pr}^\cdot$] was carried out in the presence



of $(\text{CF}_3)_3\text{COH}$.¹⁸ This led to the appearance of seven groups of

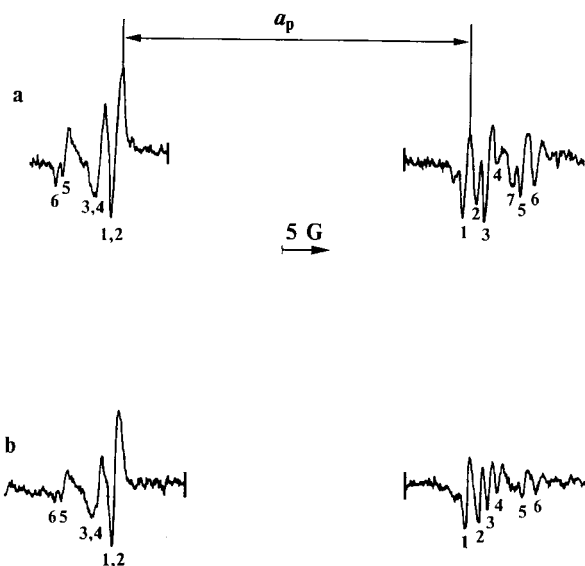


Fig. 2 The EPR spectrum of the spin-adducts of reaction of phosphoryl radicals with [76]fullerene at 300 K. (a) Under UV-irradiation; (b) without UV-irradiation.

signals in the EPR-spectrum differing in hyperfine coupling constants and g -factors (**1**: $a = 40.2$ G, $g = 2.0032$; **2**: $a = 42.25$ G, $g = 2.0028$; **3**: $a = 44.5$ G, $g = 2.0028$; **4**: $a = 45.75$ G, $g = 2.0025$; **5**: $a = 52.5$ G, $g = 2.0029$; **6**: $a = 55.0$ G, $g = 2.0017$) (Fig. 2a).

On removing the light there remained signals from only six isomers (Fig. 2b), the seventh one disappearing because of dimerisation.

Before analysing the data for [76]fullerene we recognise that the regiochemistry of radical addition to [70]fullerene is not yet well understood.³ For example, assuming correct assignments, the relative yields in various additions follow the order (carbon): $D > C > B > A > E$. This analysis is based in part on the calculated thermodynamic stabilities of the HC_{70}^{\cdot} radical, but the order is counter to the observations in most other additions to [70]fullerene (*e.g.* hydrogenation, cycloadditions and addition of organometallic reagents) in which the positional reactivity order is $A, B > C$ (kinetic order); the only additions at the D,D positions occur in chlorination (1,4)¹⁹ and with benzyne (1,2) (where it is a minor component of the overall reaction).²⁰ Moreover, the spin densities are calculated to be most delocalised for addition to D and E, since these are the most aromatic regions of the molecule. By contrast for addition to A, B, and C, the spin density is localised mainly on the β -carbon. These latter radicals should therefore be the most stable, due to shielding by the addend. Since the *opposite* is true, then either the assignments are incorrect or one must seek an additional factor, which could be the greater curvature of the [70]fullerene surface at the poles. This will allow closer approach between two addended polar regions of the cage than between two addended equatorial regions.

As noted above, the four bonds in [76]fullerene having the highest (and similar) calculated π -bond orders are the 14,15-, 4,5-, 1,6- and 2,3-bonds. There is an appreciable gap in bond order to the next group *viz.*, the 29,30-, 11,28- and 12,13-bonds (which as a group also have similar bond orders) and then further gaps to other groups of bonds.¹⁰ Since the 1- and 6-positions are identical, then on the basis of kinetic stability seven radical adducts could be expected (the number observed), with addition to carbons C-14, C-15, C-4, C-5, C-1, C-2, C-3. However, in view of the foregoing conflicting data for [70]fullerene addition, it is necessary first to consider the calculated thermodynamic stabilities (Table 1). These also indicate that hydrogen should add (in order of increasing ΔH_f°) to the following: C-14, C-15, C-3, C-2, C-4, C-1, C-5 *i.e.*, $I > J > C > B > D > A > E$. The fragments of the framework, containing

Table 2 Calculated spin density distributions for the nineteen isomers of HC_{76}^{\cdot}

Isomer	Added site	Principal spin density and location	Type	Spin densities (>0.03) at other sites
A	C-1	0.705 (C-6)	β	0.066 (C-4), 0.065 (C-8)
B	C-2	0.701 (C-3)	β	0.071 (C-14), 0.069 (C-5)
C	C-3	0.713 (C-2)	β	0.062 (C-6), 0.045 (C-13)
D	C-4	0.711 (C-5)	β	0.059 (C-1), 0.048 (C-19)
E	C-5	0.685 (C-4)	β	0.068 (C-2), 0.051 (C-16), 0.03 (C-18)
F	C-11	0.527 (C-30)	δ	0.063 (C-12), 0.059 (C-32)
G	C-12	0.656 (C-13)	β	0.086 (C-29), 0.079 (C-15)
H	C-13	0.678 (C-12)	β	0.073 (C-28), 0.06 (C-3)
I	C-14	0.698 (C-15)	β	0.066 (C-2), 0.048 (C-17), 0.031 (C-34)
J	C-15	0.696 (C-14)	β	0.058 (C-31), 0.051 (C-12)
K	C-16	0.500 (C-36)	δ	0.145 (C-17), 0.051 (C-38)
L	C-17	0.462 (C-35)	δ	0.18 (C-16), 0.08 (C-18), 0.075 (C-53)
M	C-18	0.665 (C-36)	β	0.056 (C-38), 0.071 (C-34), 0.032 (C-17) C-36?
N	C-19	0.699 (C-20)	β	0.061 (C-4), 0.058 (C-22)
O	C-29	0.679 (C-30)	β	0.065 (C-12), 0.0535 (C-32)
P	C-30	0.514 (C-11)	δ	0.155 (C-29), 0.060 (C-9), 0.057 (C-13)
Q	C-31	0.473 (C-52)	δ	0.173 (C-32), 0.066 (C-50), 0.071 (C-54)
R	C-32	0.514 (C-31)	β	0.166 (C-51), 0.061 (C-29), 0.035 (C-33)
S	C-33	0.678 (C-52)	β	0.068 (C-54), 0.067 (C-50), 0.03 (C15)

these atoms, also comprise seven of the nine atoms having the greatest convexity. Addition to C-11, C-16, C-32, C-30, C-17 and C-31 is also thermodynamically reasonably favourable but these sites are calculated to be more planar, thereby lowering the probability of addition. The remaining sites are predicted to have either low stability or low convexity, or both.

The question then arises as to why one of the radicals is less stable than the others. Since, in contrast to the case of [70]fullerene, there is no conflict between the kinetic and thermodynamic orders, it is reasonable to suppose that either: (a) only these seven sites are involved, but one of them, due to greater curvature of the fullerene surface, is able to dimerise as appears to be the case in [70]fullerene, or (b) one of the favoured radicals is not formed and addition takes place elsewhere in the molecule where there is greater delocalisation of the single electron. In [70]fullerene chlorination occurs around the waist of the molecule (at the D-carbons) in a sequential 1,4-pattern¹⁹ as this overcomes the unfavourable location of double bonds that arises when double bonds are placed exocyclic to pentagons,²¹ the most stable arrangement.²² In [76]fullerene a similar unfavourable arrangement occurs in the ring comprised of the carbons 16 (= 36), 17 (= 35), 18 (= 34) (there are three other equivalent rings). Consequently there should be strong *para* delocalisation of the spin density to C-36 for addition to C-16, and to C-35 for addition to C-17, and this is confirmed by the calculations in Table 2. Addition/delocalisation involving C-18/C-34 will, by contrast, be strongly disfavoured by the unfavourable convexity, *i.e.* the strain that will result on forming an sp^3 carbon at the junction of three hexagons, confirmed by the low calculated stability (Table 1). Both the addition and delocalisation site involve a three-hexagon junction.

Four different carbons are located at three-hexagon junctions, *viz.* C-18 (\equiv C-27, 50, 59), C-19 (\equiv C-28, 49, 58), C-29 (\equiv C-38, 39, 48) and C-33 (\equiv C-34, 43, 44). Delocalisation of radicals to these from adjacent addition sites will also be unfavourable, and this accounts for the δ delocalisation found for addition to C-11, C-16, C-17, C-30, and C-31. Overall, taking into account all of the stability and convexity factors, and the calculated spin density at the δ carbon, if the unstable isomer is one involving δ delocalisation, the most likely candidate is isomer F.

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