INTERMEDIATE COMPOUNDS AT LOW TEMPERATURE OXIDATION OF C_{60} BY OXYGEN. QUANTUM-CHEMICAL MODELING

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Introduction

Recently the ability of fullerene lattice to bind small foreign molecules in interstitial cavities was directly observed [1]. For chemically active guest species there is an interesting question about their possible reactions with the host molecules. It is well known the addition of radicals to double C=C bonds of C_{60} is rather easy reaction. So one could expect similar reactions for biradical O_2. To understand the situation first of all it is necessary to know the thermodynamics of possible primary reactions of C_{60} with O_2. For elucidation the picture of O_2 interaction with C_{60} quantum-chemical calculations were carried by the PBE density functional method out in SBK basis using the program PRIRODA [2].

Results and discussion

Is was found that addition of an oxygen molecule to the C=C bond of fullerene with formation of dioxetane cycle (See Fig.1) leads to stable molecular structure. The lengths of O-O, C-O and C-C bonds in a cycle C_2O_2 are equal to 1.502 1.460 and 1.572 A accordingly. The estimation of an equilibrium constant of the adduct formation from interstitial oxygen gives the value close to unit.

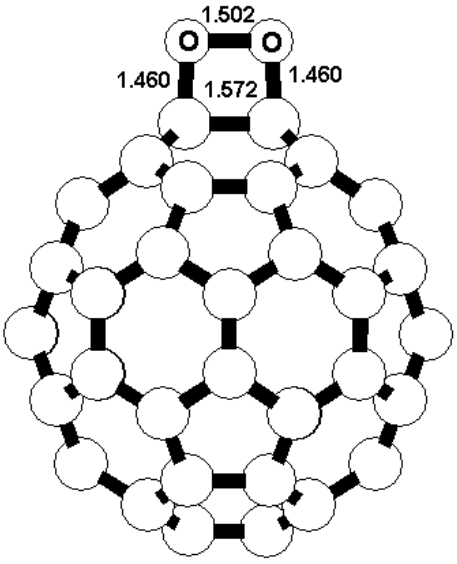

Fig.1. The structure of $C_{60}O_2$ adduct in the ground singlet state

At linkage of the O_2 molecule there is also the appreciable reduction of the O-O vibration frequencies with 1542 cm^{-1} (the experimental value 1580 cm^{-1}) up to 870 cm^{-1}. However the intensity of this vibration, 3.0 km/mol, (the effective mass 15.9) is much less than for the symmetric C-O vibration (95.8 km/mol) with the frequency of 1019 cm^{-1} and the effective mass of 12.6. The asymmetric C-O vibration with the frequency 936 cm^{-1} has essentially smaller intensity of 0.23 km/mol (the effective mass 12.7) in comparison with the symmetric one. Thus, in view of small percentage of oxygen in a lattice of fulleren it is possible to expect only observation of the symmetric C-O vibration of 1019 sm^{-1}.

The addition of O_2 appreciably reduces a position of lower triplet level. So, the energy of vertical singlet-triplet transition in $C_{60}O_2$ makes 15 kcal/mol that is almost twice lower than in C_{60}. The structures of the $C_{60}O_2$ molecule in the triplet singlet states differ negligibly and the spin density is spread outside of OO fragment. As the energy barrier of O_2 addition to C_{60} is determined by the field of crossing of singlet and triplet potential energy surfaces for the C_{60} + O_2 system, in view of the above-mentioned singlet-triplet splitting values a small activation barrier of O_2 addition to C_{60} can be expected.

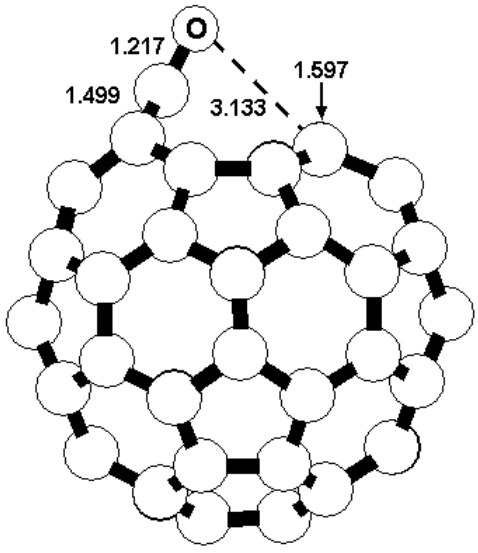

Fig.2. The structure of $C_{59}O$ product (after elimination of CO)

It is interesting that the O_2 addition to formally single C-C of bond (between 5 and 6-memeber cycles) is possible. This structure is only 15.4 kcal/mol above on energy and has close values of bond lengths in the dioxetane

cycle: 1.511 1.464 and 1.598 A. In the both cases the lengths of bonds, adjacent to the semi cleaved C-C bond, are elongated on 0.07-0.09 A, and other C-C bonds in C_{60} remain constant, in limits of 0.01 A.

Elimination of CO molecule with formation of sphere like structure of $C_{59}O$ (with three almost equal C-O bonds of 1.520, 1.548 and 1.520 A) is the endothermal process with expenses of 18.3 kcal/mol. However the isomer form of $C_{59}O$ with isolated carbonyl group (See Fig.2) is more stable on 6.3 kcal/mol. Just this structure has the greatest similarity to an initial molecule $C_{60}O_2$, and taking into account entropy increase at eliberation of CO molecule its formation gives the free energy change in this process close to zero. Elimination of the subsequent CO molecule requires more significant energy expenses of 43 kcal/mol. However if this process is connected to addition of O_2 molecule, the energy gain of 39.4 kcal/mol is present. In almost spherical $C_{58}O_2$ structure formed there are two nonplane C_4O cycles so deformed that the oxygen atoms were removed on the 2.251 A distance of nonvalent interactions. If the O_2 molecule binds to $C_{59}O$ without eliberation of CO then the $C_{59}O_3$ molecule with three carbonyl groups " framing" a small orifice in C_{60} is formed with 97.8 kcal/mol energy release.

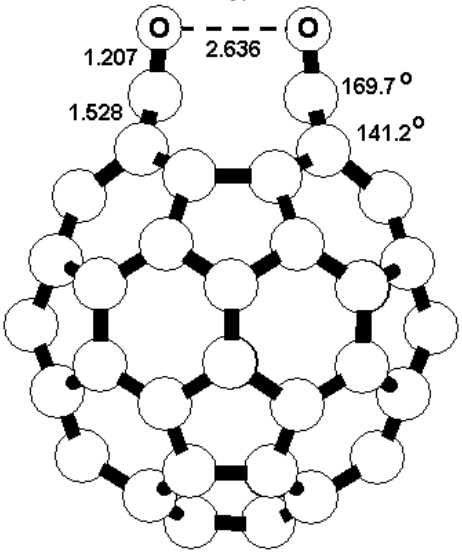

Fig.3. The structure of the lower energy isomer of $C_{60}O_2$.

Simultaneous break of O-O and C-C bonds in $C_{60}O_2$ adduct results in its transformation to the structure with two isolated carbonyl groups (See Fig.3) with energy gain of 33.5 kcal/mol. From sterical hindrance for two C=O groups they have to leave planes of conjugated C_5 of cycles (the angles between C-O and C_3 plane and between C_3 and C_4 planes are 169.7 and 141.2 respectively) and take almost parallel positions. In result the C-C(O) bonds appear to be weaken (Confer Fig. 2 and 3), and an oxygen molecule binding to one of these bonds results in the energy gain of 28.8 kcal/mol. The product formed contains OO peroxo group in the structure of -OOC(O)- fragment, which replace one carbonyl group in the initial $C_{60}O_2$ molecule. Its destruction with eliberation of CO_2 molecule results in the significant energy release of 79.4 kcal/mol. In the formed $C_{59}O_2$ molecule (See Fig.4) in comparison with $C_{59}O$ one the additional oxygen atom enters the structure of nonplane C_4O cycle.

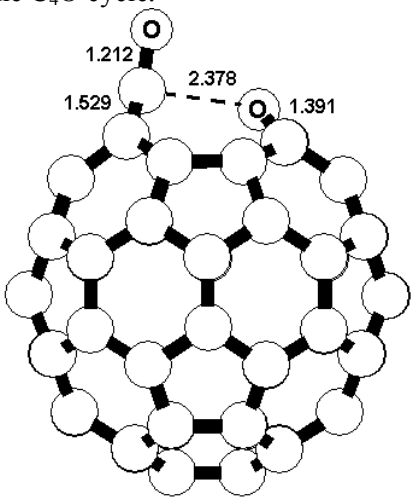

Fig.4. The structure of the $C_{59}O_2$ (after O_2 addition of and CO_2 elimination).

The similar reactions with O_2 leading to the carbon skeleton dectruction, apparently occur in carbon hemispheres at heating of closed carbontubes in oxygen.

Conclusions

The quantum-chemical calculation fulfilled point out an opportunity of primary interaction C_{60} fullerene with molecular oxygen in mild conditions with formation of products incomplete (CO) and deep (CO_2) oxidation.

References

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2. D.N. Laikov. Fast evaluation of density functional exchange-correlation terms using the expansion of the electron density in auxiliary basis sets. Chem. Phys. Lett. 1997; v. 281. p. 1