



# Ozone addition to C<sub>60</sub> and C<sub>70</sub> fullerenes: A DFT study

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## ABSTRACT

Three modes of synchronous ozone addition ([6,6]-, [5,6]-, and 1,4-addition) to C<sub>60</sub> fullerene and three modes of ozone addition to C<sub>70</sub> (*ab*-, *cc*-, and *de*-addition) have been studied using density functional theory calculations. Comparison of activation enthalpies shows that in the case of C<sub>60</sub>, [6,6]-addition of ozone is the most favorable energetically and occurs without a barrier. In the case of the C<sub>70</sub> fullerene, additions to *ab*- and *cc*-bonds are the most favorable. The initial step of interaction between a C<sub>60</sub>/C<sub>70</sub> and O<sub>3</sub> is the formation of a molecular complex, which then converts into a primary ozonide. The calculated rate constant of the [6,6]-addition to the C<sub>60</sub> fullerene according to the proposed scheme is  $3.90 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , which corresponds well to the experimental value.

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## 1. Introduction

Interaction with ozone is one of the first reactions of fullerenes that attracted investigators with an opportunity of oxygen functionalization of the carbon framework. Heymann et al. [1] have detected the primary ozonide (PO) C<sub>60</sub>O<sub>3</sub> as a product of initial ozone addition, which has been isolated with low-temperature high-performance liquid chromatography. A study of its decomposition with UV–visible spectroscopy and luminescent methods has shown that C<sub>60</sub>O<sub>3</sub> eliminates O<sub>2</sub> molecule, producing the fullerene epoxide C<sub>60</sub>O [1] (other investigations have shown that the carbonyl derivatives are also produced during the PO conversion [2,3]). Those experimental data were sufficient to determine PO's empirical formula while its structural peculiarities have not been clear. Similarly to alkene primary ozonides, the 1,2,3-trioxalane functionality of a 6.6 fullerene bond has been declared for this matter. In the case of C<sub>70</sub>, two POs have been detected [4]. Analyzing structures of the epoxides produced by oxygen elimination from the initial POs of C<sub>70</sub>, the authors [4] proposed that ozone reacts with the tops of the ellipsoidal molecule of C<sub>70</sub>, generating two products (*ab*-C<sub>70</sub>O<sub>3</sub> and *cc*-C<sub>70</sub>O<sub>3</sub> presumably). Prolonged ozonolysis of C<sub>60</sub> and C<sub>70</sub> produces water-soluble polymeric structures containing peroxide and secondary ozonide functionalities on the transformed fullerene framework [5–7].

In spite of the great success in identification and purification of the products of ozonolysis, its mechanism has been insufficiently known

till now. So, using the theoretical methods of quantum chemistry becomes expedient. Quantum chemical investigation of interaction between C<sub>60</sub> and ozone has been performed in [8,9]. However, those works have not paid attention to the steps of interaction between the C<sub>60</sub> fullerene and ozone, which forego the PO formation. Moreover, these calculations have been performed with semiempirical AM1 method, which does not allow correct description of polar molecules, such as ozone and products of its addition [10].

In the present study Perdew–Burke–Ernzerhof (PBE) density functional theory method has been used to investigate the several ways of ozone addition to C<sub>60</sub> and C<sub>70</sub>.

## 2. Calculation details

Structures of fullerenes are similar to polycyclic hydrocarbons. So, they can be described with sufficient precision by semiempirical methods (MNDO, AM1, PM3) which yield reliable results for their geometries [11]. But as we have noted before, AM1 and PM3 methods overestimate enthalpies of formation for fullerenes [7].

Ozone and trioxides are molecules, which demand high-level theory methods to determine their structure and energetic properties. The ground state of ozone cannot be reliably described with only one electronic configuration. The best approach is a superposition of several resonance (biradical and zwitterionic) electronic structures using multi-configuration self-consistent field methods or Møller–Plesset theory methods [12]. However, these are not suitable for the optimization of fullerene-containing structures due to excessive need of computational resources. The density functional theory (DFT) methods have received a good reputation as applied to different classes of organic substances.

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**Table 1**

Calculated by PBE/3z geometric and energetic properties in comparison with experimental data

Value	Ozone		$I_h$ -C <sub>60</sub>	
	PBE/3z	Experimental data [10]	PBE/3z	Experimental data [16]
Geometry	$L_{O1-O2} = 1.282 \text{ \AA}$ $\varphi_{OOO} = 118.06^\circ$	$1.2780 \pm 003 \text{ \AA}$ $116.83 \pm 0.5^\circ$	$L_{5-6} = 1.453 \text{ \AA}$ $L_{6-6} = 1.399 \text{ \AA}$	$1.458 \text{ \AA}$ $1.401 \text{ \AA}$ (electron diffraction)
Dipole moment $\mu$ (D)	0.60	$0.58 \pm 0.05$	0.00	0.00
Polarizability ( $\text{\AA}^3$ )	2.4	$\sim 2.8$	82.7	$\sim 80$
IR spectrum ( $\text{cm}^{-1}$ )	702	705	526	527
	1041	1043	576	576
	1171	1110	1179	1183
$S_f^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	239.0	238.9 (gas)	1432	1429
			549.1	544.0 (gas)

The PBE approach [13] with original 3z basis [14] (Priroda 2.02 + program package [15]) has been selected, because it correctly reproduces experimental data of structure, IR spectra and energetic properties of reactants (See Table 1).

Geometries of reactants and products have been completely optimized. The type of each stationary point on the potential energy surface (PES) has been determined by vibration modes solving: the number of negative eigenvalues in the diagonalized Hessian  $N_{\text{neg}} = 0$  for minima on the PES, and  $N_{\text{neg}} = 1$  if a stationary point is a transition state (TS). Transition state of each elementary process has been confirmed by intrinsic reaction coordinate (IRC) calculations.

Enthalpies of elementary processes have been calculated with the following difference:

$$\Delta H_r^\circ(298 \text{ K}) = \sum_{\text{products}} (E_{\text{tot}} + \varepsilon_{\text{ZPV}} + H_{\text{corr}}) - \sum_{\text{reactants}} (E_{\text{tot}} + \varepsilon_{\text{ZPV}} + H_{\text{corr}}) \quad (1)$$

where  $E_{\text{tot}}$  is total energies,  $\varepsilon_{\text{ZPV}}$  is zero point vibration energies, and  $H_{\text{corr}}$  is thermal corrections to enthalpy.

Analyzing the structure of initial fullerenes and trioxides being formed, we use a supplementary geometric characteristic: the spatial angle  $\psi_{C_1C_2C_3}$  with  $C_0$  vertex has been calculated as [17]:

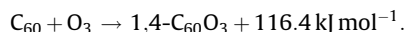
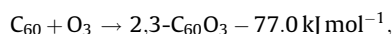
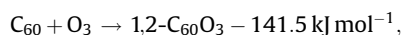
$$\cos \psi_{C_1C_2C_3} = \frac{\cos \phi_{C_1C_0C_3} - \cos \phi_{C_1C_0C_2} \cos \phi_{C_2C_0C_3}}{\sin \phi_{C_1C_0C_2} \sin \phi_{C_2C_0C_3}}, \quad (2)$$

where  $\phi_i$  are angles, formed by  $C_0$ , and  $C_1$ ,  $C_2$ ,  $C_3$  carbon atoms which are the nearest to  $C_0$ .

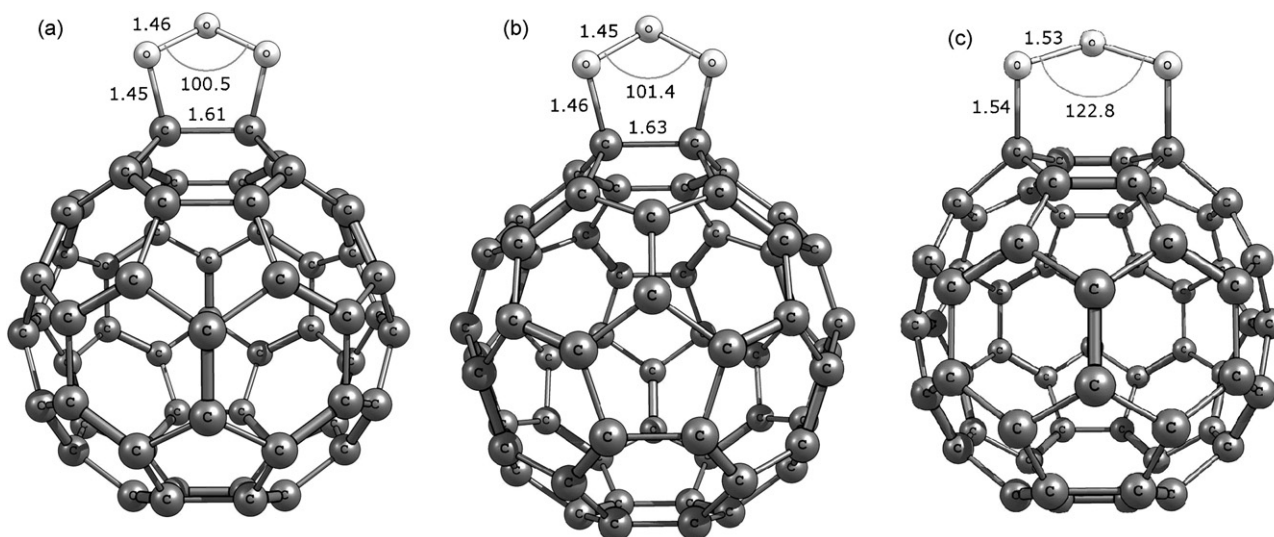
### 3. Results and discussion

#### 3.1. Ways of ozone addition to C<sub>60</sub>

There are two types of bonds (shorter 6.6 and longer 5.6 bonds) in the structure of  $I_h$ -C<sub>60</sub>. So, we proposed three ways of addition, which form [6,6]-, [5,6]-, and 1,4-adducts (see Fig. 1). 1,4-Addition should lead to a transannular adduct similar to the behavior of polycyclic aromatic hydrocarbons [10]. Moreover, 1,4-adducts have been detected among products of the other reactions of addition to the C<sub>60</sub> fullerene [18]. The enthalpies of different modes are below:



We can rule out 1,4-addition due to its calculated endothermic effect. Analyzing the structure of 1,4-adduct, having  $C_5$  symmetry, we should note that its formation requires intense deformation of molecules of reagents. The carbon atoms that are being functionalized should significantly stick out of the pristine carbon surface. It is clearly demonstrated with spatial angles of a fullerene cage: in the initial C<sub>60</sub> cage all of them are equal to  $142.6^\circ$ , and in the formed transannular adduct spatial angles corresponding to the functionalized carbon atoms are  $109.6^\circ$ . In case of [6,6]- and [5,6]-adducts, these angles are closer to initial value, being  $124.7^\circ$  and  $116.3^\circ$ , respectively. The internuclear distance between the



**Fig. 1.** Proposed structures for products of ozone addition to 6.6 fullerene bond (a), to 5.6 fullerene bond (b), and product of 1,4-addition (c). Bond lengths in Angstroms, angles in degrees.

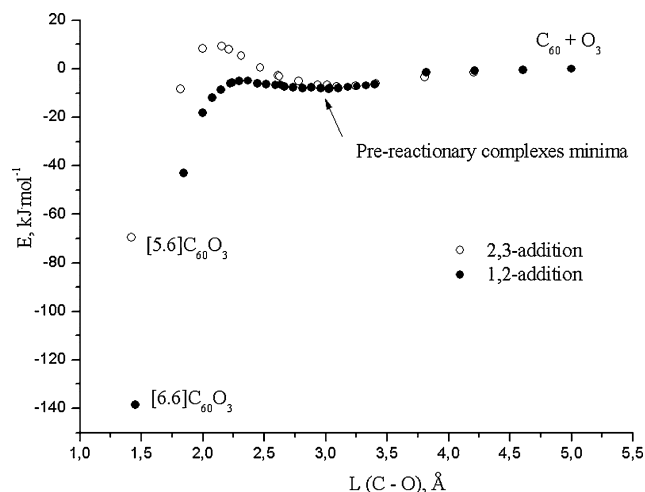
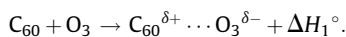


Fig. 2. The PES relaxed scanning of exothermic pathways of the ozone addition to  $C_{60}$ .

terminal oxygen atoms in ozone is 2.198 Å, but it must stretch to 2.691 Å in the transannular ozonide. For these two reasons, formation of the transannular ozonide is unfavorable.

The PES scanning of exothermic reaction paths has shown a decrease in total energy  $E_{\text{tot}}$  upon approach of the reactants. It should be interpreted as a pre-reactionary complex (PRC) formation (Fig. 2):



In the case of [6.6]-PRC, the internuclear distances C...O between fullerene carbons and terminal oxygen atoms of ozone, aligned toward the 6.6 bond, is 2.92 Å (see Fig. 3;  $C_2H_4 \cdots O_3$  complex is characterized with  $L_{C \cdots O} = 2.75$  Å, obtained with B3LYP/6-311+G\*\* calculations [19]). Heat effect of [6.6]-PRC formation makes up  $-9.6 \text{ kJ mol}^{-1}$  (Table 2). It is comparable with experimental enthalpies of the arene  $\cdots O_3$  complexes formation, which located in the range  $-6.3 \dots -12.6 \text{ kJ mol}^{-1}$  [20]. Charge transfer  $\delta$  in [6.6]-PRC is 0.11e (Mullikan population analysis).

Table 2  
Energetic properties of  $C_{60} \cdots O_3$  complexes

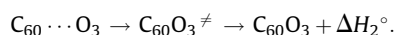
Complex	$\delta$ (e)	$\Delta H_1^\circ$ (kJ mol $^{-1}$ )	$\Delta S_1^\circ$ (J mol $^{-1}$ K $^{-1}$ )
[6.6] $C_{60} \cdots O_3$ ; $C_5$ symmetry	0.11	-9.6	-75.8
[5.6] $C_{60} \cdots O_3$ ; asymmetric	0.09	-7.1	-67.4

Table 3  
Energetic characteristics of [6.6]- and [5.6]-addition

Mode of addition	$\Delta H_2^\circ$ (kJ mol $^{-1}$ )	$\Delta S_2^\circ$ (J mol $^{-1}$ K $^{-1}$ )	$\Delta H^\ddagger$ (kJ mol $^{-1}$ )	$\Delta S^\ddagger$ (J mol $^{-1}$ K $^{-1}$ )
[6.6]-addition	-131.9	-89.2	0.0	-55.7
[5.6]-addition	-69.9	-92.2	8.4	-66.2

In generating a PRC as the initial step of interaction with ozone, the  $C_{60}$  fullerene has been found to be similar to unsaturated hydrocarbons. A PRC is analogous to  $\pi$ -complexes of arenes and alkenes, where hydrocarbon is a donor and ozone is an acceptor of electrons.

The next step of interaction between  $C_{60}$  and ozone is conversion of a PRC into a PO:



Thermodynamic and activation parameters of these processes are described in Table 3. Structures of TSs are shown in Fig. 4. The IRC calculations for [6.6]-TS and [5.6]-TS (Fig. 5) have shown a decrease in total energy and resulted in the formation of the suggested reactants and products. It confirmed that found TSs are correct. Comparison of the calculated activation enthalpies (Table 3) makes clear that 1,2-addition is more favorable energetically and occurs without a barrier. This is in accordance with the experimental identification of [6.6] closed epoxide  $C_{60}O$  among the products of the further primary ozone adduct decomposition [1,2].

[6.6]-TS has a  $C_5$  symmetry structure that is typical for symmetric alkenes (Fig. 4). The favor of 1,2-addition correlates with bond orders in the  $C_{60}$  molecule: calculated in the present work by PBE/3z, the 6.6 bond order equals to 1.44, and it is 1.23 for

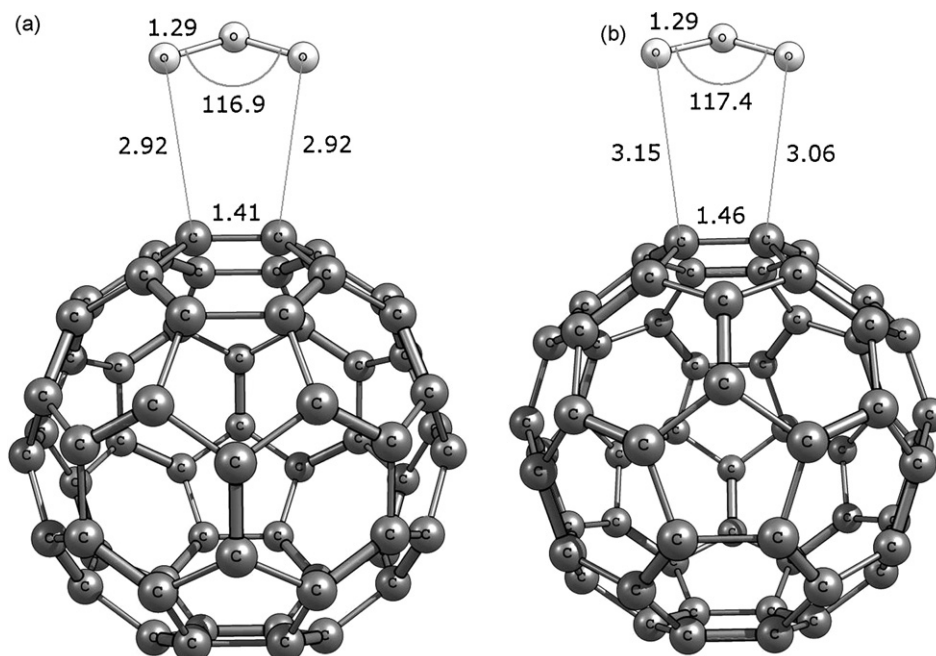
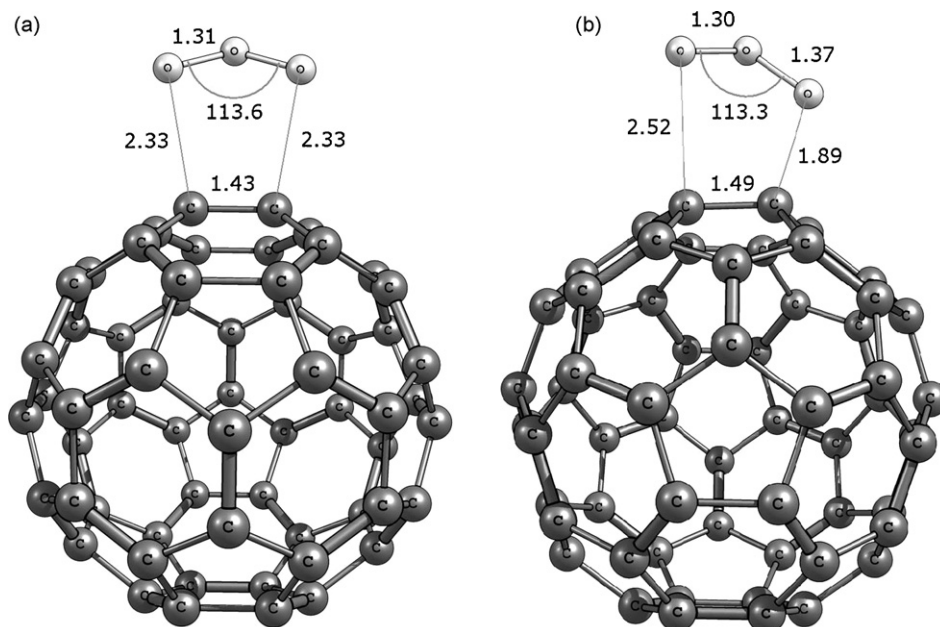
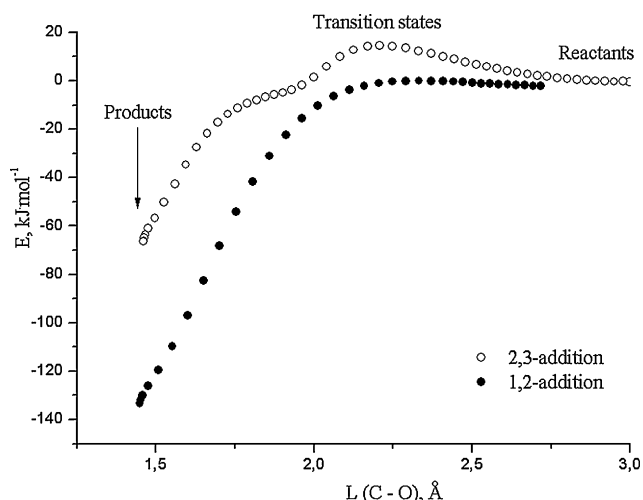


Fig. 3. Structures of [6.6]-PRC (a) and [5.6]-PRC (b) of ozone addition to  $C_{60}$ . Bond lengths in Angstroms, angles in degrees.



**Fig. 4.** Transition states of ozone addition to  $C_{60}$  (a) [6,6]-TS (imaginary frequency is  $96.1i\text{ cm}^{-1}$ ) and (b) [5,6]-TS (imaginary frequency is  $234.6i\text{ cm}^{-1}$ ). Bond lengths in Angstroms, angles in degrees.



**Fig. 5.** The IRC calculations of the ozone addition to 6.6 and 5.6 bonds of  $C_{60}$ .  $L(\text{C}-\text{O})$ , Å, average distance between terminal oxygen atoms of  $\text{O}_3$  and reaction sites on the fullerene skeleton.

the 5.6 bond. The orders of C–C bonds in some model compounds optimized with the same method are: ethylene, 1.97; butadiene-1,3, 1.77 and 1.11; benzene, 1.40. While the 6.6 bond order is greater than the 5.6 bond order, the ozone attack is oriented to 6.6 bonds.

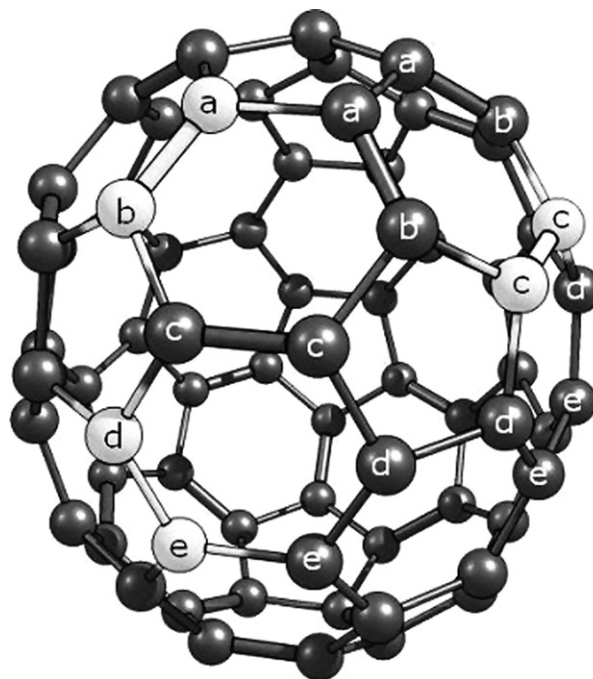
### 3.2. Ozone addition to $C_{70}$

The molecule of  $D_{5h}$ - $C_{70}$  has atoms of five types that are usually marked as *a*, *b*, *c*, *d*, *e* (Fig. 6). There are eight types of bonds in the  $C_{70}$  molecule. Calculated lengths and bond orders each of them are shown in Table 4. The *ab*, *cc*, *de* bonds can be considered as probable modes of ozone addition because they are characterized with maximal values of bond orders.

The PES scanning for these modes (Fig. 7) shows that the first step of  $C_{70} + \text{O}_3$  interaction is the formation of molecular complexes as in the case of  $C_{60}$ . Optimized structures of molecular complexes are shown in Fig. 8. Enthalpies of stabilization of *ab*-

$C_{70} \cdots \text{O}_3$ , *cc*- $C_{70} \cdots \text{O}_3$ , *de*- $C_{70} \cdots \text{O}_3$  are  $-8.2$ ,  $-10.7$ ,  $-10.0\text{ kJ mol}^{-1}$ , respectively.

Transition states of conversion of the PRCs into the POs are shown in Fig. 9. The IRC calculations for *ab*- $C_{70}\text{O}_3^\ddagger$ , *cc*- $C_{70}\text{O}_3^\ddagger$ , *de*- $C_{70}\text{O}_3^\ddagger$  (Fig. 10) have confirmed that these TSs are correct. The structure of *cc*- $C_{70}\text{O}_3^\ddagger$  has  $C_s$  symmetry, and TSs of other pathways of addition are asymmetric. Experimental observation of only two POs of  $C_{70}$  [4] allows us to conclude that the most probable ways of  $C_{70} + \text{O}_3$  interaction are ozone attacks of the *ab* and *cc* bonds, which occur with low activation barriers ( $0.3$  and  $5.0\text{ kJ mol}^{-1}$ , respectively) (see Table 5).



**Fig. 6.** Schematic representation of the  $C_{70}$  structure. The proposed reaction sites marked by white.



**Table 4**  
Bond orders (b.o.) and lengths in the molecule of  $D_{5h}$ - $C_{70}$

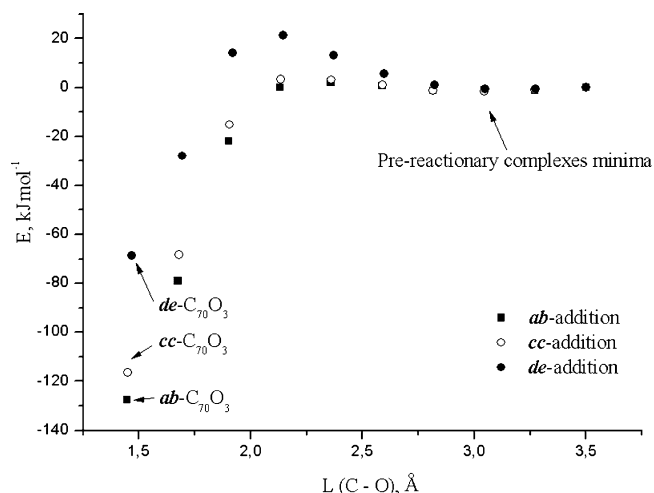
Bond	Type of bond	b.o.	Length (Å)
aa	5.6	1.23	1.45
ab	6.6	1.45	1.40
bc	5.6	1.21	1.45
cc	6.6	1.41	1.39
cd	5.6	1.23	1.45
dd	5.6	1.29	1.44
de	6.6	1.34	1.42
ee	6.6	1.23	1.47

**Table 5**  
Energetic characteristics of different modes of ozone addition to the  $C_{70}$  fullerene

Energetic characteristic	Way of addition		
	ab bond	cc bond	de bond
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	-128.0	-115.1	-69.1
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	0.3	5.2	13.8

**Table 6**  
Properties of fullerene primary ozonides in comparison with those of hydrocarbon analogs

Primary ozonide	Symmetry	Properties of functionalized C-C bond		Dipole moment (D)
		Length (Å)	Bond order	
Fullerene primary ozonides				
[6.6]-C <sub>60</sub> O <sub>3</sub>	C <sub>5</sub>	1.61	0.82	2.47
ab-C <sub>70</sub> O <sub>3</sub>	C <sub>1</sub>	1.61	0.81	2.31
cc-C <sub>70</sub> O <sub>3</sub>	C <sub>5</sub>	1.59	0.75	2.41
Hydrocarbon primary ozonides				
Ethylene primary ozonide	C <sub>5</sub>	1.56	0.99	3.36
Benzene primary ozonide	C <sub>5</sub>	1.57	1.09	3.61
Butadiene-1,3 primary ozonide	C <sub>1</sub>	1.56	0.92	3.37



**Fig. 7.** The PES relaxed scanning of different modes of the ozone addition to  $C_{70}$ .

### 3.3. Peculiarities of [6.6]- $C_{60}O_3$ , ab- $C_{70}O_3$ , cc- $C_{70}O_3$ primary ozonides

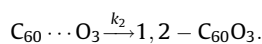
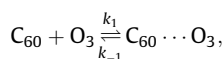
Introduction of a trioxide fragment into the fullerene molecules reduces the initial molecular symmetry to  $C_5$  (in the case of [6.6]- $C_{60}O_3$  and cc- $C_{70}O_3$ ) and  $C_1$  (in the case of ab- $C_{70}O_3$ ) symmetry group (see Figs. 1a and 11). All of the POs are characterized with weak C–C bond of a 1,2,3-trioxalane ring: its length is  $\sim 1.6$  Å; and its bond order is  $\sim 0.8$  (Table 6). The ozone adducts are polar structures. Their dipole moments are greater than 2.00 D (Table 6).

The trioxalane ring disturbs the symmetric  $\pi$ -electronic system of the pristine  $C_{60}$  fullerene, and 6.6 bonds in  $C_{60}O_3$  become unequivalent. It could be illustrated with the bond orders of the bonds located in a hexagon adjacent to the trioxide fragment: the order of 6.6 bond increases to 1.52 (from 1.44), and the order of 5.6 bond decreases to 1.08 (from 1.23). Bond orders in the other rings of a fullerene skeleton change insignificantly. The disappearance of

conjugation leads the next molecule of ozone to the functionalized hexagon of  $C_{60}O_3$ .

### 3.4. Rate constant of ozone [6.6]-addition to the $C_{60}$ fullerene

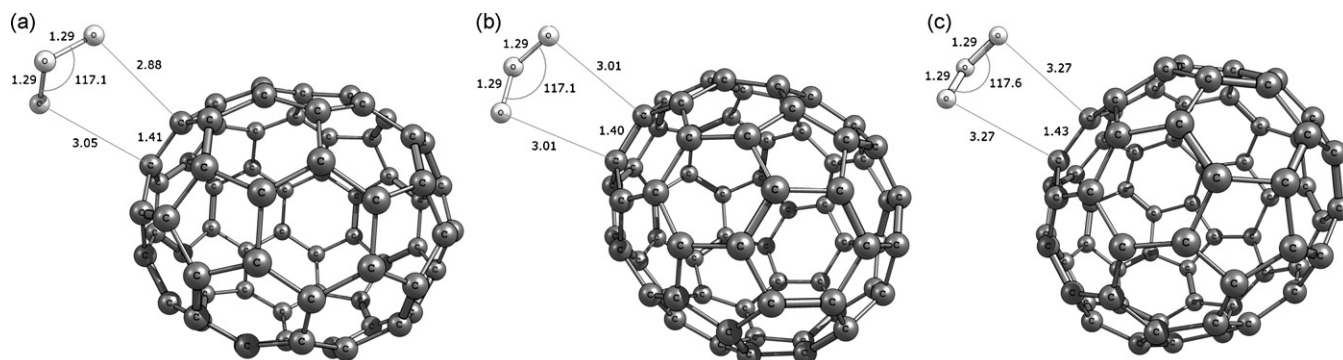
Summarizing the previous considerations, we can propose the following kinetic scheme of  $C_{60} + O_3$  interaction with two elementary steps:



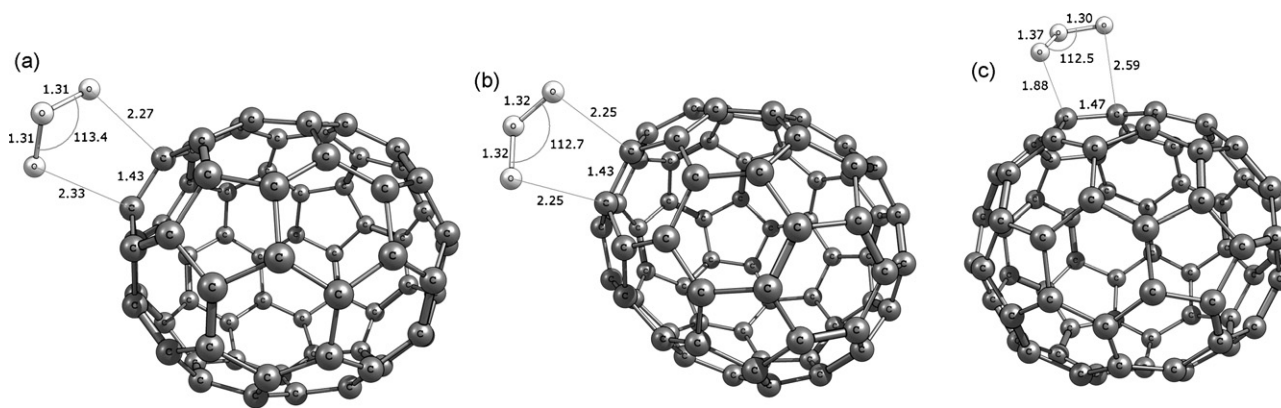
The effective rate constant corresponding to this scheme is:

$$k_{\text{ef}} = \frac{k_1 k_2}{k_{-1} + k_2}. \quad (3)$$

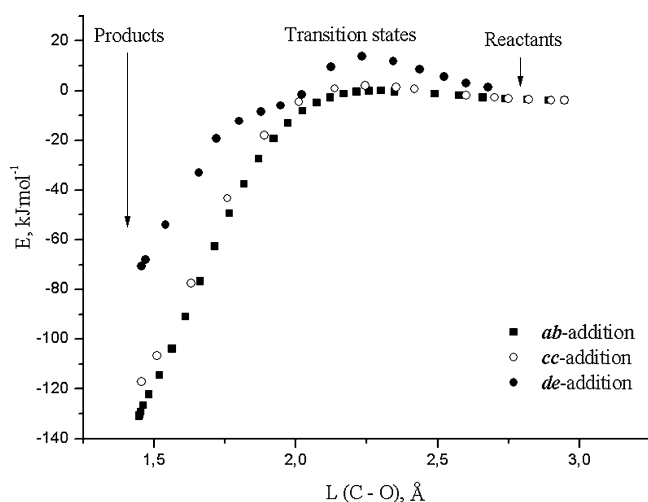
Calculated values of  $\Delta H_1^\circ$ ,  $\Delta S_1^\circ$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  allow estimating the rate constant of each step in terms of transition state theory



**Fig. 8.** Structures of ab-PRC (a) cc-PRC (b) and de-PRC (c) of ozone addition to  $C_{70}$ . Bond lengths in Angstroms, angles in degrees.



**Fig. 9.** Transition states of ozone addition to  $C_{70}$  (a) *ab*-TS (imaginary frequency is  $109.2i\text{ cm}^{-1}$ ) and (b) *cc*-TS (imaginary frequency is  $131.2i\text{ cm}^{-1}$ ), *de*-TS (imaginary frequency is  $259.8i\text{ cm}^{-1}$ ). Bond lengths in Angstroms, angles in degrees.



**Fig. 10.** The IRC calculations of three modes of the ozone addition to the  $C_{70}$  molecule.  $L(\text{C}-\text{O})$ , Å, average distance between terminal oxygen atoms of  $\text{O}_3$  and reaction sites on the fullerene skeleton.

equations [21]:

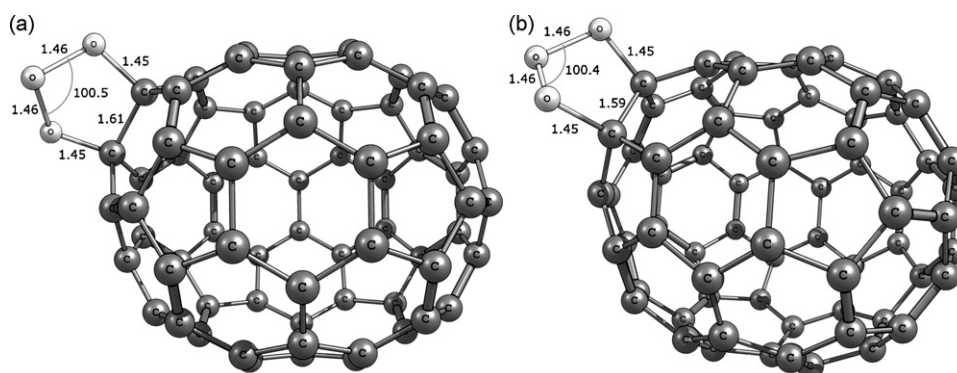
$$k_1 = \kappa \frac{k_B T}{h} \frac{RT}{p} \exp \frac{\Delta S_1^\ddagger}{R} \exp \left( -\frac{\Delta H_1^\ddagger}{RT} \right), \quad (4)$$

$$k_{-1} = \kappa \frac{k_B T}{h} \exp \left( -\frac{\Delta S_1^\ddagger}{R} \right) \exp \frac{\Delta H_1^\ddagger}{RT}, \quad (5)$$

$$k_2 = \kappa \frac{k_B T}{h} \exp \frac{\Delta S^\ddagger}{R} \exp \left( -\frac{\Delta H^\ddagger}{RT} \right), \quad (6)$$

where  $\kappa$  is a transmission coefficient. Considering  $\kappa = 1$ , the values of rate constants at standard conditions ( $T = 298.15\text{ K}$ ,  $p = 101325\text{ Pa}$ ) are:  $k_1 = 6.42 \times 10^{11}\text{ L mol}^{-1}\text{ s}^{-1}$ ,  $k_{-1} = 1.26 \times 10^{18}\text{ s}^{-1}$  and  $k_2 = 7.65 \times 10^{12}\text{ s}^{-1}$ . Thus, the effective rate constant, calculated by Eq. (3), equals to  $3.90 \times 10^6\text{ L mol}^{-1}\text{ s}^{-1}$ . Usually, values of rate constants of unsaturated hydrocarbon ozonolysis are of the order  $10^2$  to  $10^7\text{ L mol}^{-1}\text{ s}^{-1}$  [10,22]. So, the rate constant calculated above is comparable with those, but it should be compared with experimental data of the  $C_{60}$  fullerene ozonolysis.

In a study of the temperature effect on the reaction kinetics, the activation energy and pre-exponential Arrhenius factor for  $C_{60} + \text{O}_3$  interaction (standard conditions, solvent –  $\text{CCl}_4$ ) have been measured and equal to  $10.0\text{--}10.9\text{ kJ mol}^{-1}$  and  $(1.20\text{--}1.80) \times 10^7\text{ L mol}^{-1}\text{ s}^{-1}$ , respectively [23]. Using average experimental values for Arrhenius equation, we have found the experimental rate constant, which is  $\sim 2.05 \times 10^5\text{ L mol}^{-1}\text{ s}^{-1}$ . The experimental and the calculated rate constants differ by one order of magnitude, but it should be noted that there are some difficulties in measurement of the experimental rate constants if a reaction has a low activation barrier ( $<40\text{ kJ mol}^{-1}$ ), and estimation of Arrhenius factor can be in the range of 1–3 orders [10,22]. Also the present quantum chemical investigation does not include the solvent effect on the kinetics. So, we can conclude that the experimental and calculated effective rate constants are in good agreement.



**Fig. 11.** The most probable structures of ozone adducts to  $C_{70}$  (a) *ab*- $C_{70}\text{O}_3$  and (b) *cc*- $C_{70}\text{O}_3$ . Bond lengths in Angstroms, angles in degrees.

#### 4. Conclusion

Density functional theory calculations PBE/3z have shown that the most favorable ways of ozone attack are the 6.6 bonds of the  $C_{60}$  fullerene and the *ab* and *cc* bonds of the  $C_{70}$  fullerene. These modes are the most exothermic pathways and occur with negligibly low (in the case of formation of  $[6.6]-C_{60}O_3$  and *ab*- $C_{70}O_3$ ) or low activation barriers (in the case of *cc*- $C_{70}O_3$  formation). This favored pathways correlate with the bond orders in the initial structures of fullerenes. Formation of ozone adducts occurs through the formation of a molecular complex which is typical of unsaturated hydrocarbons.

The structures of the PO are characterized with weak C–C bond that has been functionalized. Attachment of a trioxalane fragment on the fullerene framework distorts the pristine  $\pi$ -electronic system. It makes the double bonds that are nearest to trioxalane ring closer to those of alkenes, which is also reflected on the bond orders in POs.

1,4-Addition of ozone is an endothermic process, because the formation of a transannular adduct requires significant deformation of a fullerene cage and ozone molecule.

The proposed mechanism of the initial steps of  $C_{60} + O_3$  interaction is in a good agreement with experimental data: the calculated effective rate constant  $3.90 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  corresponds to its experimental value  $\sim 2.05 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ .

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