



# Thermodynamic selectivity of multicenter chemical reactions. A statistical quantification of a widespread intuitive approach and its application to reactions of fullerenes

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## ABSTRACT

Currently, there are many ways to estimate the selectivity of chemical reactions but none of them has the universal character. Therefore, novel approaches are introduced and developed. In the present study, we quantify a comparison of thermodynamic parameters of alternative reaction modes and propose the corresponding equation for thermodynamic selectivity describing the set of the one-type parallel reactions. It is defined as the ratio of the average difference in the  $\Delta H_r$  (or  $\Delta G_r$ ) values of the alternative reaction modes to the average  $\Delta H_r$  (or  $\Delta G_r$ ) value of the set. The application of this approach to addition reactions of fullerenes demonstrates good agreement with the relevant experimental data and general chemical notions.

## 1. Introduction

Assessing and tuning chemical reactions are one of the basic problems of chemistry. In this regard, methods for numerical description of selectivity and reactivity are developed [1–3]. Performing entirely experimental study, we just need to measure and compare the yields of the products formed in the parallel reactions. However, such empirical estimates are strongly influenced by the accuracy of experimental procedures (synthesis, extraction, separation, purification, and identification). Therefore, in a perfect case, such estimates must be compared with the corresponding theoretical predictions. The *a priori* estimates of probabilities of chemical reactions are generally based (i) on the structural and/or physicochemical parameters of reactants (bond lengths, hardness, electrophilicity indices, polarizability, pyramidal/curvature, atomic charges, etc.) or (ii) numerical parameters of chemical processes (rate constants, activation energies, enthalpies and Gibbs energies of reactions, etc.) [4]. Parameters from the two groups above are correlated in most cases.

Specific chemical studies often beg the question about the change in selectivity of the chemical reaction (or the set of the related reactions) under varying conditions (in the presence/absence of catalyst, in different solvents, in the case of electronic excitation, etc.). What do we do if we solve this question by means of computational chemistry? For example, if we deal with the reaction occurring *via* two reaction sites,

we are able to compare the difference between the enthalpy changes of the two reaction modes under the varying conditions. Further, this difference may be compared with the enthalpy changes themselves to reveal whether it is small or large relative to the overall exothermicity. If the number of reaction sites (or, that is the same, the number of reaction modes) is quite large, a comparison of their pairs becomes less informative or even uninformative.

Typical examples of the chemical systems with a large number of reaction sites may be found among fullerenes and their derivatives [5,6]. Only in the highly symmetric  $C_{60}$  ( $I_h$ ) molecule all the carbon atoms are equivalent. In the case of higher fullerenes [5,6] and fullerene adducts [7–13], the number of reaction sites rapidly grows. This is clearly evidenced from the distributions of the reaction sites over the types for the fullerenes nearest to buckminsterfullerene (number of atom types  $\times$  number of atoms):  $C_{70}$  ( $D_{5h}$ ) –  $3 \times 10 + 2 \times 20$ ;  $C_{76-2}$  ( $D_2$ ) –  $19 \times 4$ ;  $C_{78-1}$  ( $D_3$ ) –  $13 \times 6$ ;  $C_{84-22}$  ( $D_2$ ) –  $21 \times 4$ ; and  $C_{84-23}$  ( $D_{2d}$ ) –  $1 \times 4 + 10 \times 8$  [14–16]. The multicenter nature of fullerenes especially manifests in their radical addition reactions [17–30], polymerization processes at their presence [17,31–34], and inhibition of the oxidation of organic compounds by fullerenes and their derivatives [35–39]. Thus, numerical estimates of selectivity may provide valuable information for rationalization of the processes in the fullerene-containing systems.

In the present work, we lay a mathematical base under the approach

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used in computational chemistry to compare alternative reaction modes in a qualitative form and apply it to the addition reactions of fullerenes.

## 2. Algorithm for calculating selectivity

Under a qualitative comparison of the alternative reaction modes, their heat effects or activation energies are usually compared. Hereinafter, we focus on enthalpy changes in chemical reactions as they are more readily computable and in Section 4.4 we show that the approach is adaptable to the case of Gibbs energy changes. To formalize the abovementioned comparison and extrapolate it to the multicenter reactants, we consider the thermodynamic selectivity parameter  $q$  that is defined as the ratio of the average difference in the enthalpies of the alternative reaction modes  $\langle \Delta \Delta H_r^\circ \rangle$  to the average enthalpy change  $\langle \Delta H_r^\circ \rangle$  of the set of parallel reactions:

$$q = \frac{\langle \Delta \Delta H_r^\circ \rangle}{|\langle \Delta H_r^\circ \rangle|} \quad (1)$$

We consider such two-substrate reactions, in which one of the reactants has a number of reaction sites that may react with the second one. In each of these parallel reactions, the second reactant reacts only with one reaction site of the multicenter reactant. If the latter has two different reaction sites contesting the same chemical reaction, the thermodynamic selectivity of the set of parallel reactions is estimated as:

$$q = \frac{|\Delta H_{r_1}^\circ - \Delta H_{r_2}^\circ|}{1/2|\Delta H_{r_1}^\circ + \Delta H_{r_2}^\circ|} \quad (2)$$

Let consider two variants of the reaction occurring *via* two reaction sites, say in the first variant the average enthalpy change equals  $-50 \text{ kJ mol}^{-1}$  whereas it is  $-500 \text{ kJ mol}^{-1}$  in the second one (e.g., if the molecules react in the excited states). The difference in the enthalpy changes remains the same (due to Hess' law) and equals, e.g.,  $10 \text{ kJ mol}^{-1}$ . According to eq. (1), thermodynamic selectivity  $q$  is 10 times higher in the first reaction set:  $q^{(I)} = 0.2$  versus  $q^{(II)} = 0.02$ . Note that parameter  $q$  is dimensionless and may take values from 0 to  $+\infty$ . Its zero value means no selectivity and correspond to the case of identical reaction sites. Usually,  $\langle \Delta \Delta H_r^\circ \rangle < |\langle \Delta H_r^\circ \rangle|$ , so we should expect  $0 \leq q < 1$  with rare exceptions.

In the general case, the molecule has  $z_1$  sites of the 1st type,  $z_2$  sites of the 2nd type, ... and  $z_n$  sites of the  $n$ -th type (their total number is  $Z = \sum z_i$ ). The corresponding chemical reactions have enthalpy changes  $\Delta H_{r_1}^\circ, \Delta H_{r_2}^\circ, \dots, \Delta H_{r_n}^\circ$ . The average enthalpy change for this set and average difference in the enthalpies of the alternative reaction modes equal respectively:

$$\langle \Delta H_r^\circ \rangle = \frac{1}{Z} \sum_{i=1}^n z_i \Delta H_{r_i}^\circ \quad (3)$$

$$\langle \Delta \Delta H_r^\circ \rangle = \frac{1}{Q} \sum_{i=1}^{n-1} \sum_{j>i}^n z_i z_j |\Delta H_{r_i}^\circ - \Delta H_{r_j}^\circ| \quad (4)$$

where  $Q$  is the total number of differences under summation. It includes all combinations of the reaction sites (the first term in the expression below) except of the combinations of the identical sites (the second term):

$$Q = \frac{Z(Z-1)}{2} - \sum_{i=1}^n \frac{z_i(z_i-1)}{2} \quad (5)$$

or in more compact views:

$$Q = \sum_{i=1}^{n-1} \sum_{j>i}^n z_i z_j = \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n z_i z_j \quad (6)$$

After the substitution of eq. (3) and (4) in general formula (1), we obtain the final formula for thermodynamic selectivity of the reaction set:

$$q = \frac{\sum_{i=1}^n z_i}{\sum_{i=1}^{n-1} \sum_{j>i}^n z_i z_j} \times \frac{\sum_{i=1}^n \sum_{j>i}^n z_i z_j |\Delta H_{r_i}^\circ - \Delta H_{r_j}^\circ|}{|\sum_{i=1}^n z_i \Delta H_{r_i}^\circ|} \quad (7)$$

In the next sections, we demonstrate the usability of the approach for the analysis of the fullerene reactions with radicals and carbenes studied in our previous works with the PBE/3 $\zeta$  density functional theory method [33,41–43] and other reactions of the C<sub>70</sub> fullerene with radicals calculated in the present work.

## 3. Computational details

The PBE/3 $\zeta$  density functional theory method (Priroda program [43,44] was used for calculations as it accurately describes thermodynamic and kinetic parameters of fullerene reactions [4,29,32,40–42,45,46], spectral and physicochemical parameters of fullerene compounds [27–30,47].

The structures obtained by the standard DFT-optimizations were proved to correspond to the minima of the potential energy surfaces *via* the vibration modes solving (their Hessians contain no imaginary frequencies). Then the enthalpy changes in chemical reactions were calculated as the differences between the total energies  $E_{tot}$  of the resulting fullerene adduct and reactants, taking into account zero-point vibrational energy corrections  $\varepsilon_{ZPV}$  and the temperature corrections  $H_{corr}$  ( $T = 298 \text{ K}$ ):

$$\Delta H_r^\circ = (E_{tot} + \varepsilon_{ZPV} + H_{corr}) - \sum_{\text{reactants}} (E_{tot,i} + \varepsilon_{ZPV,i} + H_{corr,i}) \quad (8)$$

## 4. Results and discussion

### 4.1. Reaction of fullereryl radicals with O<sub>2</sub>

Before studying the reactions of the C<sub>70</sub> fullerene, we demonstrate the use of the algorithm on a simpler case of fullereryl radicals XC<sub>60</sub><sup>•</sup>, the intermediates of the radical addition reactions to C<sub>60</sub>. As is known [48,49], XC<sub>60</sub><sup>•</sup> very slowly interact with triplet dioxygen, the ground state of O<sub>2</sub>:



The use of singlet oxygen instead of the triplet was proposed to enhance this interaction [41] (Table 1). Thus, the selectivity of reaction (9) in the cases of <sup>3</sup>O<sub>2</sub> and <sup>1</sup>O<sub>2</sub> must differ. The unpaired electron in XC<sub>60</sub><sup>•</sup> is delocalized on the fullerene cage. The highest spin densities are typical for the reaction sites of two types ( $n = 2$ ): in positions 2 (one reaction site,  $z_1 = 1$ ) and 4 (two reaction sites,  $z_2 = 2$ ) relative to the position of addend X [4]. We use the previously calculated heat effects of 1,2- and 1,4-addition of O<sub>2</sub> to fullereryl radicals [41]. Note that reactions (9)

**Table 1**

Thermodynamic selectivity  $q$  of radical reactions XC<sub>60</sub><sup>•</sup> + O<sub>2</sub> → XC<sub>60</sub>OO<sup>•</sup> estimated with the enthalpy changes in the alternative reaction modes ( $\Delta H_{r_i}^\circ$ ) previously calculated with the PBE/3 $\zeta$  method [41].

Reactants	Enthalpy change (kJ mol <sup>-1</sup> )		$ \Delta H_{r_1}^\circ - \Delta H_{r_2}^\circ $ (kJ mol <sup>-1</sup> )	$\langle \Delta \Delta H_r^\circ \rangle$ (kJ mol <sup>-1</sup> )	$q$
	$\Delta H_{r_1}^\circ$	$\Delta H_{r_2}^\circ$			
<sup>t</sup> BuC <sub>60</sub> <sup>•</sup> + <sup>3</sup> O <sub>2</sub>	29.6	10.0	19.6	+16.5	1.19
<sup>t</sup> BuOOC <sub>60</sub> <sup>•</sup> + <sup>3</sup> O <sub>2</sub>	0.4	11.7	11.2	+7.9	1.42
Ph(CH <sub>3</sub> ) <sub>2</sub> CC <sub>60</sub> <sup>•</sup> + <sup>3</sup> O <sub>2</sub>	30.3	8.4	21.9	+15.7	1.40
Ph(CH <sub>3</sub> ) <sub>2</sub> COOC <sub>60</sub> <sup>•</sup> + <sup>3</sup> O <sub>2</sub>	2.6	10.4	7.8	+7.8	0.99
<sup>t</sup> BuC <sub>60</sub> <sup>•</sup> + <sup>1</sup> O <sub>2</sub>	-128.1	-147.7	19.6	-141.1	0.14
<sup>t</sup> BuOOC <sub>60</sub> <sup>•</sup> + <sup>1</sup> O <sub>2</sub>	-157.2	-146.0	11.2	-149.7	0.07
Ph(CH <sub>3</sub> ) <sub>2</sub> CC <sub>60</sub> <sup>•</sup> + <sup>1</sup> O <sub>2</sub>	-127.3	-149.3	21.9	-141.9	0.15
Ph(CH <sub>3</sub> ) <sub>2</sub> COOC <sub>60</sub> <sup>•</sup> + <sup>1</sup> O <sub>2</sub>	-155.0	-147.2	7.8	-149.8	0.05

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