Generalized theoretical approach to the estimation of fullerenes reactivity in the reactions of addition based on curvature indices

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Earlier we have worked out the theoretical approach to estimation of fullerenes reactivity towards ozone and diazomethane with the use of curvature indices [1] and then applied it to some C_{60} derivatives.

In the present paper, to determine the general regularities of the addition to fullerenes we have analyzed parameters of correlation equations for reactions of [2+*n*]-cycloaddition and radical addition. In the framework of the approach, a linear equation (See the Table)

$$\Delta H_r^\circ = B + Ak$$

has been assigned for each reaction. Here ΔH_r° is a heat of reaction calculated by PBE/3z density functional method; k is a curvature index of reaction site calculated as $k = 2\sin\theta / a$, (a – average internuclear distance between reaction site of the fullerene molecule and its neighboring atoms, θ – pyramidalization angle). Parameters B can be interpreted as heats of addition of molecules (radicals) to hypothetic reaction site with zero curvature. Parameters A determine the slope of linear correlations and lie in the intervals which are characteristic for the reactions of each type. Important to note that these correlations unite reactions of fullerenes with both isolated (C_{60}, C_{70}, C_{76}) and shared pentagons (C_{20}, C_{24}, C_{30}, C_{36}, C_{40}). So, they could be considered as common features of carbon clusters.

Table. Correlations $\Delta H_r^\circ = B + Ak$ for reactions $C_n + Y \rightarrow C_nY$.

Y	A, kJ E mol^{-1}	B, kJ mol^{-1}	*r*
[2+1]-Cycloaddition			
:CH_2	−528.6	253.8	0.91
:NH	−518.3	326.4	0.92
[2+3]-Cycloaddition			
HN_3	−910.1	262.9	0.80
$CH_2{=}N^+{-}CH_2{}^-$	−959.5	120.0	0.87
O_3	−946.4	142.4	0.96
CH_2N_2	−904.3	216.0	0.97
Radical addition [2]			
H•	−772.9	68.2	0.96
F•	−746.4	35.7	0.95

The same slopes (parameters A) of the correlations of reactions pertaining to one type allow formulating the following rule. If reactions of C_n fullerene with reactants Y_1 and Y_2 have the same mechanism and it is known that C_n shows a higher reactivity towards Y_1, than towards Y_2, then other members of the fullerenes family are more reactive towards Y_1.

So, the approach takes into account all features of the addition reactions, *i.e.* peculiarities of reaction site in a fullerene molecule (*k* index), type of added reactant (parameter B) and type of reaction (parameter A).

[1] Sabirov D.Sh., Khursan S.L., Bulgakov R.G., *Russ. Chem. Bull., Int. Ed.* **57**, 2520 (2008).
[2] Sabirov D.Sh., Bulgakov R.G., *Comput. Theor. Chem.*. **963**, 185 (2011).