

A study on the reaction of hydroselenyl (HSe^\cdot) and selenenic (HSeO^\cdot) radicals

Mauricio Vega-Tejido, Martina Kieninger, Oscar N. Ventura.

Computational Chemistry and Biology Group (CCBG), CCBG-DETEMA, Facultad de Química, UdelaR-Isidoro de Maria 1614 – 11400, Montevideo, Uruguay.
mauryvg@fq.edu.uy

Abstract: Selenium presents some similarities with de sulfur reactivity and has been described in diverse biological systems. The selenocystein (Sec) residue is the one which characterizes the selenoproteins.^[1] These proteins has been asociated with many cellular mechanisms, for intance, redox signalling and oxydative stress.^[1] In biology, selenium compounds such as selenocystine (Sec-Sec) were associated with the role of free-radicals scavenger.^[2]

Selenium species formed in these processes involve neutral and radical intermediaries such hydroselenyl (HSe^\cdot) and selenelic (HSeO^\cdot) moieties. Recently, Borji et al. (2016)^[3] reported a study of the hydrosulfinyl and mercapto radicals reaction. Here we compare the selenium analogs in order to have an approximation to the behavior of these species in the biological systems.

All the structures were initially optimized by means gaussian 09 program with B3LYP/6-311++G(3df,3pd) using "Ahlrichs coulomb fitting" basis set with electronic core potential (ECP) for both Se atoms. Same method was used for the electronic density calculation. After that, the structures were re-optimized using M06-2X, M06-GD3 and B3LYP functionals with 6-311++G(3df,3pd) basis set for all the atoms. The minima in the PES were confirmed by IR frequencies calculations.

In this work is presented a profile of the reaction mechanism of the mentioned Se-radicals showing possible products, intermediates and transition state structures. The process can be described with the initial formation of the CR adduct that derives in INT (through TS2), and then derives in cis-HSeSeOH passing through two possible transition states: TS21 or TS22. The way passing by TS1, that connects directly CR with cis-HSeSeOH, is the one with the highest barrier and positive values in the relative energy. TS31 and TS32 correspond to the cis-trans rotation of the neutral compound HSeSeOH. In figura 1 can be seen the changes in the electronic density that surrounds Se atoms. While CR presents one Se with 1 LP (lone pair) and the other with 2 LP, in INT both presents 2 LP. In INT one of the LP is located between both Se favoring the interaction, in parallel, is observed that the Se-Se bond is shorter in INT (2.2Å) than in CR (2.4Å).

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Table of free energies (kcal/mol) relative to the free reactants				
Species	B3LYP	M062x	M06-GD3	$\Delta\Delta G^a$
HSe+HSeO	0	0	0	0
CR	-31.8	-31.9	-34.9	-
INT	-43.9	-49.0	-45.9	-
Cis-HSeSeOH	-62.3	-67.6	-64.1	-
Trans-HSeSeOH	-62.5	-67.8	-64.3	-
TS1	1.7	2.2	2.1	37.0
TS2	-14.5	-17.6	-17.7	17.2
TS21	-	-4.5	-10.9	34.9
TS22	-	-33.2	-29.2	16.7
TS31	-	-58.2	-54.8	9.2
TS32	-	-59.2	-55.9	8.2

^a The barriers correspond to the M06-GD3 calculations.

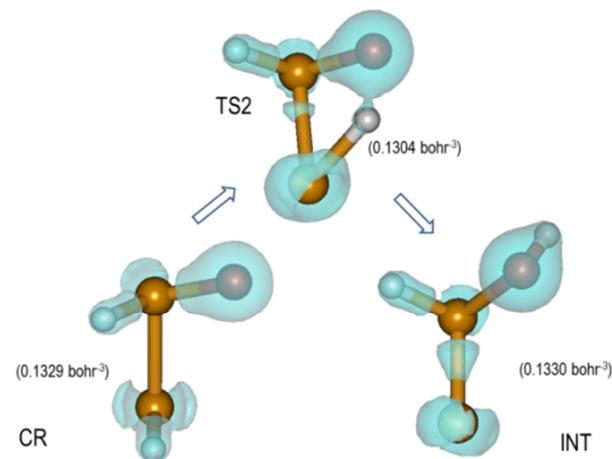


Figure 1.- Electronic density in the conversion of CR in INT (TS2). Is observed changes in the lone pairs of both Se.

Key-words: M06, selenium radicals, electronic density

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