DFT STUDY OF RADICAL MECHANISM FOR THE REACTION OF DIHYDROXIFUMARIC ACID WITH THE STABLE RADICAL DPPH$^{\bullet}$

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Many organic compounds with enol or phenol groups are effective antioxidants which transform various free radicals into their diamagnetic derivatives [1]. From the literature it is known that dihydroxyfumaric acid (DHFA) is a very powerful antioxidant [2], having inhibitory properties pronounced against free radicals. In the work [3] we have proposed and studied the ionic mechanism describing interaction between dihydroxyfumaric acid (DHFA) and the stable radical DPPH. It was shown that this interaction begins with protonation of DPPH and formation of the radical-cation [DPPH-H]$^{*+}$. The latter forms the charge-transfer complex with the anion of DHFA. Herein we present the computational results (DFT PBE cc-pVDZ [4]) concerning the radical mechanism of the reaction

$$A\text{-}H_2 + 2R^{\bullet} = A + 2RH$$

which includes the two following stages (see the Figure 1).

(**i**) $A\text{-}H_2 + DPPH^{\bullet} = TSi = A\text{-}H^{\bullet} + RH$ and (**ii**) $A\text{-}H^{\bullet} + DPPH^{\bullet} = TSii = A + RH$

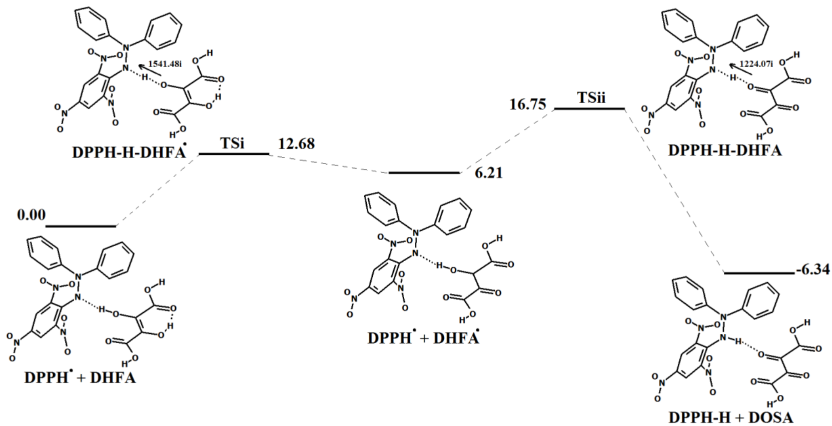

Fig. 1. The energy profile of the entire reaction

The transition states **TSi and TSii** connected with the intermolecular hydrogen transfer were localized. This result was confirmed by the presence of one imaginary frequency in each transition state (1541.48i cm^{-1} and 1224.07i cm^{-1}, respectively). The calculated activation energies are: 12.68 kcal/mol for the step (**i**) and 10.54 kcal/mol for (**ii**). The whole process is exothermic one; it is accompanied with the calculated energy release of 6.34 kcal/mol.

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