

# Identification of the transition state for fast reactions: The trapping of hydroxyl and methyl radicals by DMPO - A DFT approach

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Up to date, attempts to locate the transition state (TS) for the trapping reaction between  $\cdot\text{OH}$  and  $\cdot\text{DMPO}$  have been unsuccessful, and the lack of molecular mechanisms by which  $\cdot\text{OH}$  binds to the spin-trap constitutes a question still unsolved. Herein, we have taken a step forward on this task by describing the theoretical TS for the trapping of  $\cdot\text{OH}$  and  $\cdot\text{CH}_3$  by DMPO and the intrinsic reaction coordinates. This work aims to provide new understandings on the molecular orbital (MO) interactions that rule these reaction paths. Besides we assessed the degree of involvement of weak interactions and the charge transfer (CT) phenomenon involved in such interactions. Regarding the trapping of  $\cdot\text{OH}$ , the beginning of the reaction would be ruled by weak interactions to then give way to stronger MO interactions conducive to the formation of the TS. For  $\cdot\text{CH}_3$ , the reaction is, instead, early ruled by significant MO interactions, and a relatively small contribution in the weak interactions range. At the T