Bypassing the Multi-reference Character of Singlet Molecular Oxygen. Part 2: Ene-reaction

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Abstract

Theoretical calculations involving singlet molecular oxygen (O2(1g)) are challeng- ing due to their inherent multi-reference character. We have tested the quality of re- stricted and unrestricted DFT geometries obtained for the reaction between singlet oxy- gen and a series of alkenes (propene, 2-methylpropene, trans-butene, 2-methylbutene and 2,3-dimethylbutene) which are able to follow the ene-reaction. The electronic en- ergy of the obtained geometries are rened using 3 dierent methods which account for the multi-reference character of singlet oxygen. The results show that the mechanism for the ene-reaction is qualitatively dierent when either one or two allylic-hydrogen groups are available for the reaction. When one allylic-hydrogen group is available the UDFT calculations predict a stepwise addition forming a biradical intermediate, while, the RDFT calculations predict a concerted reaction where both hydrogen abstrac- tion and oxygen addition occur simultaneously. When two allylic-hydrogen groups are available for the reaction then UDFT and RDFT predict the same reaction mechanism, namely that the reaction occurs as a stepwise addition without a stable intermediate between the two transition states. The calculated rate constants are in reasonable agreement with experimental data, except for trans-butene where the calculated rate constant is three orders of magnitude lower than the experimental one. In conclusion we nd that the simple bypassing scheme tested in this paper is a robust approach for calculations of reaction involving singlet oxygen in the limit that the transition state processes low multi-reference character. 2

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