

A Comparative Theoretical study of the Kinetics and Dynamics of the Reaction of H Atoms with Ground-state and Excited O₂

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The reaction of O₂ with H atoms is one of the most important reactions in combustion. Numerous studies are available on the reaction on the lowest potential energy surface (PES) involving ground-state, triplet O₂. Recently the possibility of presence of electronically excited O₂ in flames has been proposed. While the reactivity of singlet O₂ proves to be much lower, in particular, towards saturated compounds, it can react faster with radicals than ground-state O₂. As long as excited O₂ is really present in flames, it can influence the kinetics of O-atom and OH radical formation.

We have performed quasiclassical trajectory calculations on the O₂ + H → O + OH reaction using the PESs correlating with O₂(³Σ_g⁻) as well as with O₂(¹Δ_g), both developed by Guo and coworkers. The excited-state reaction is exothermic by about 0.43 eV in contrast to the ground-state reaction which is 0.53 eV endothermic. There is a deep well on both PESs which corresponds to ground-state and electronically excited HO₂; this well is less deep in the excited state (2 eV below O + OH) than in the ground state (2.85 eV). In the excited state there is a potential barrier of about 0.26 eV in the entrance channel, in contrast to the barrierless entrance channel of the ground-state reaction.

According to the trajectory calculations the excitation function for the reaction starting from excited-state O₂ rises above zero at about 0.3 eV and increases almost linearly, in good agreement with the exact quantum mechanical calculations by Guo. This reflects much larger reactivity than the ground-state cross sections having a threshold above 0.6 eV and remain much smaller than the excited-state data. For the reaction of excited O₂ the thermal rate coefficient is about 10⁻¹⁶ cm³molecule⁻¹s⁻¹ at room temperature and about 10⁻¹² cm³molecule⁻¹s⁻¹ at 1500 K, the latter is two orders of magnitude larger than the respective ground-state rate value.

Comparisons of the details of the dynamics will be presented.