ON THE OUTCOME OF THE REACTIONS BETWEEN HYDROCARBON RADICALS AND O_2 IN HELIUM NANODROPLETS

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Helium nanodroplet isolation and infrared laser spectroscopy are used to investigate the CH_3 + O_2 and C_3H_3 (propargyl) + O_2 reactions. The hydrocarbon radicals are generated in an effusive pyrolysis source located upstream from a differentially pumped O_2 gas pick-up cell. In this experimental configuration, the reaction occurs between sequentially picked-up and presumably cold fragments. The CH_3 + O_2 reaction leads barrierlessly to the methyl-peroxy radical, and despite having to dissipate an energy of approximately 30 kcal/mol, the infrared spectra reveal a large abundance of droplets containing the cold CH_3O_2 radical. Theoretical studies have predicted an approximately 2-4 kcal/mol barrier in the entrance channel of the C_3H_3 + O_2 reaction. Therefore, we initially expected to see a weakly bound entrance channel C_3H_3–O_2 van-der-Waals complex, given the rapid cooling provided by the dissipative helium environment. However, only the trans-acetylenic isomer of the propargyl-peroxy radical is observed. The dipole moment of this species is measured with infrared laser Stark spectroscopy.