Sequential Capture of O(^{3}P) and Alkenes by Helium Nanodroplets: Infrared Spectroscopy and Ab Initio Computations of the Triplet Biradical Intermediates

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ABSTRACT

Catalytic thermal cracking of O_2 is employed to dope helium droplets with O(^{3}P) atoms.[1] Mass spectrometry of the doped droplet beam reveals an O_2 dissociation efficiency larger than 60%; approximately 26% of the droplet ensemble is doped with single oxygen atoms. Sequential capture of O(^{3}P) and HCN leads to the production of a hydrogen-bound O−HCN complex in a $^3\Sigma$ electronic state, as determined *via* comparisons of experimental and theoretical rovibrational Stark spectroscopy. *Ab initio* computations of the three lowest lying intermolecular potential energy surfaces reveal two isomers, the hydrogen-bound ($^3\Sigma$) O−HCN complex and a nitrogen-bound ($^3\Pi$) HCN−O complex, lying 323 cm^{-1} higher in energy. The non-relativistic HCN−O to O−HCN interconversion barrier is predicted to be only 42 cm^{-1}. Moreover, the barrier is reduced upon explicit consideration of spin-orbit coupling. Consistent with the prediction of a relatively small interconversion barrier, there is no experimental evidence for the production of the nitrogen-bound species upon sequential capture of O(^{3}P) and HCN.

According to Smith *et al.*,[2] for molecule + radical reactions, the energetic difference between the molecule's ionization energy (IE) and the radical's electron affinity (EA) can provide insight into the nature of the reaction barrier, either *above* or *below* the reactant asymptote. They propose that a difference (IE − EA) greater than 8.75 eV indicates a real barrier above the asymptotic limit, whereas a value below 8.75 eV indicates a submerged barrier. Indeed, this difference for the O(^{3}P) + HCN system is 12.2 eV. Accordingly, the barrier to oxygen insertion into the CN π system is ~10 kcal/mol above the reactant asymptote, and a van der Waals complex is observed when these species are brought together in a 0.4 K helium nanodroplet. However, O(^{3}P) reactions with *alkenes* are predicted to cross the postulated 8.75 eV threshold as the alkene substitution pattern evolves from ethene (no substitution) to propene (methyl group substitution) to butene (dimethyl substitution, of which there are four different isomers), and this trend was tested by Sabbah *et al.*.[3] Their findings corroborated the behaviour predicted by Smith *et al.*.[2] The HCN + O(^{3}P) results presented here demonstrate the feasibility for analogous alkene + O(^{3}P) spectroscopic studies, in which O(^{3}P) and alkenes of varying substitution are combined in helium droplets *via* the sequential capture scheme. As the *real* reaction barrier (*i.e.* for the ethene and propene reactions) evolves to being *submerged* below the asymptotic limit (*i.e.* for the butene reactions), one might expect that strongly bound reaction intermediates, such as triplet biradicals, will be observed in helium droplets, rather than van der Waals complexes. Given the fact that a 10,000 atom helium droplet can dissipate 140 kcal/mol, it should be possible to quench the internal energy of these reaction intermediates and probe them for the first time spectroscopically.

REFERENCES

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