Imprint of Electronic Structure on the Reactivity of Linear Carbon Chain Cations

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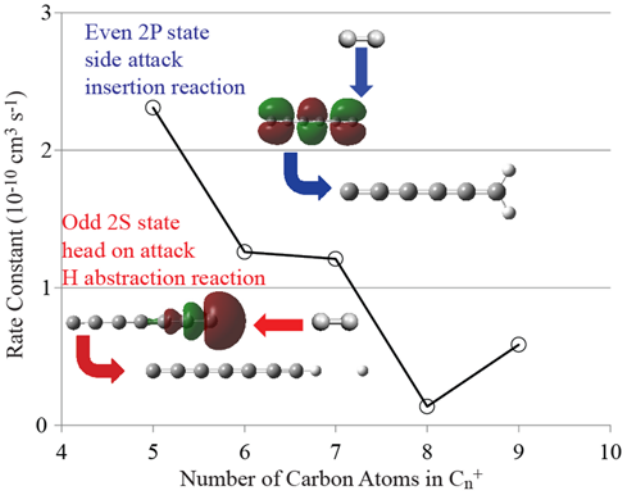
Due to the flexible balance of s and p orbitals, carbon species are found in many different geometrical forms: linear chains, planar graphene, and three dimensional fullerenes. Furthermore, in the astrophysics and combustion communities, many studies have been performed on carbon clusters with a focus on the effect of geometric structure towards the reactivity. Although there have been a lot of studies on these clusters, an understanding of their fairly complex electronic states is still lacking. Here we thus investigate the reactions of size and isomer selected carbon cations C_n^+ (n = 4–9) and D_2 with an emphasis on the imprint of electronic structure on reactivity.

Only linear C_nD^+ products were observed for the odd (n = 5, 7, 9) linear clusters, while $C_nD_2^+$ was the main product for the even clusters. For the reaction rate constants determined for these two channels, we obtained the following two features: (1) the rate constant decreases with the size n, and (2) even-sized clusters have lower rate constants than neighboring odd-sized clusters. In the theoretical calculations using the CCSD(T) and B3LYP methods with the cc-pVTZ basis, we found that a low lying $^2\Sigma$ state in odd clusters may play an important role in these reactions. This opposes the previous interpretation that the $^2\Pi_{g/u}$ state is the dominant electronic state for linear C_n^+ (n = 4–9) clusters. We showed that a barrierless radical abstraction forming C_nD^+ occurs through a direct head on approach for the $^2\Sigma$ state C_n^+. In contrast, a carbene-like insertion forming $C_nD_2^+$ occurs through a sideways approach for the $^2\Pi_{g/u}$ state C_n^+. We have concluded that the higher rate constants for the odd clusters come from the existence of symmetry broken $^2\Sigma$ states which are absent in even linear clusters.



References:
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