Carbon Chain Ion Reaction with D_2: Differences between Cation and Anion

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Due to flexible balance of s and p orbitals, carbon species are found in many different geometrical forms: linear chains, planar graphene, and three dimensional fullerene. Due to interest in astrophysics and combustion communities, many studies were performed on carbon clusters with focus on the effect of geometric structure towards the reactivity. In this paper we concentrated on the small ionic species and studied the difference/similarities of reactivities of linear $C_n^{+/-}$ (n = 4–9) and D_2.

In the first part I present results on linear C_n^+ (n = 4–9) and D_2, studied using ion mobility mass spectrometry techniques and quantum chemical calculations. Only linear C_nD^+ product was observed for the odd (n=5, 7, 9) linear clusters, while $C_nD_2^+$ was the main product for the even clusters. As for the reaction rate constants determined for these two channels, we have 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 for these reactions. This is opposed to the previous interpretations 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 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.

In the latter half, I will present results on the reaction of linear C_n^- (n = 4–9) and D_2. Our simulations showed very small reactivity, $<10^{-17}$ cm^3 sec^{-1}, and this is consistent with the fact that it was not possible to detect the reaction in the room temeprature experiments. Analysis concerngin the difference in the cation and anion reaction will also be discussed.

References

[1] K. Koyasu, T. Ohtaki, K.Takahashi, and F. Misaizu Phys., Chem. Chem. Phys, 17, 24810-24819 (2015).