

Energetic diagrams and structural properties of monohaloacetylenes $\text{HC}\equiv\text{CX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)

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Highly correlated electronic wavefunctions within the Multi Reference Configuration Interaction (MRCI) approach are used to study the stability and the formation processes of the monohaloacetylenes HCCX and monohalovinylidenes C_2HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$). These tetra-atomic can be formed through the reaction of triatomic fragments C_2F , C_2Cl , C_2Br with an hydrogen atom or of C_2H with halogen atoms via barrierless reactions whereas the reactions between the diatomics $[\text{C}_2 + \text{HX}]$ need to overcome barriers of 1.70 eV, 0.89 eV and 0.58 eV for $\text{X} = \text{F}, \text{Cl}, \text{Br}$ respectively. It is found that the linear HCCX isomers, in singlet symmetry, are more stable than the singlet C_2HX iso-forms by 46.0 kcal/mol, 48.0 kcal/mol and 45.2 kcal/mol for $\text{X} = \text{F}, \text{Cl}, \text{Br}$ respectively. The very small isomerization barriers from iso to linear forms are calculated 1.54 kcal/mol, 1.01 kcal/mol and 2.30 kcal/mol for F, Cl and Br systems respectively. The dissociation energies of the HCCX systems (without ZPE corrections), resulting from the breaking of the CX bond, are calculated to be 130.24 kcal/mol, 108.17 kcal/mol and 95.23 kcal/mol for $\text{X} = \text{F}, \text{Cl}, \text{Br}$ respectively. At the equilibrium geometry of the $\text{X}^1\Sigma^+$ state of HCCX , the vertical excitation energies in singlet and triplet symmetries are all larger than the dissociation energies. Stable excited states are found only as $^3\text{A}'$, $^3\text{A}''$ and $^1\text{A}''$ monohalovinylidene structures.

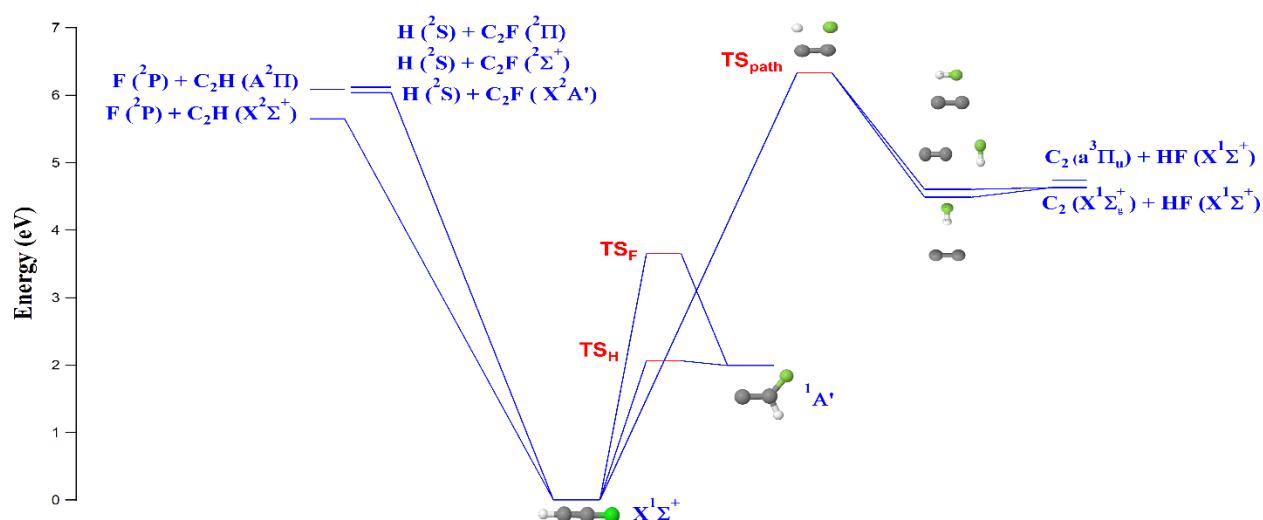


Figure 1 : Energetic diagram of the $[\text{C}_2\text{HF}]$ system