Molecular growth induced by ions and electron: from linear 1,3-butadiene clusters towards 6-member ring compounds

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Synopsis The formation of many-member ring structures from neutral, linear 1,3-butadiene (C_4H_6) loosely bonded clusters is observed in the gas-phase experiments with collisions of low energy ions as well as electrons and identified with quantum chemistry calculations. The observations of key cyclic 6-membered ring formations explain the most intense "magic-number" peaks in both experiments. Interestingly, the accessibility of those peaks is higher for Ar^+ collision, which is correlated with the reaction barrier/exit channel energy.

Molecules embedded into clusters present an explicit environmental effect on encapsulated target molecules, especially when their reactivity is induced with e.g. highly-charged ions. The interaction of ions with clusters of fullerenes, polycyclic aromatic hydrocarbons (PAHs), or molecules of biological interest, is stabilized with a protective effect due to the presence of an environment around the one excited molecule [1]. This is explained by a redistribution of energy and charge between the different residues in the cluster. In addition, the presence of an environment can induce an additional reactivity within the cluster itself, such as hydrogen transfers [2] or molecular growth processes [3], that is not observed in the individual molecule fragmentation.

Based on *ab initio* molecular dynamics and potential energy surface calculations we postulate that cosmic radiation can induce Diels-Alder (**DA**) reaction in the outer space (gas-phase), transforming the clusters of small linear unsaturated hydrocarbons into more stable, long-lived cyclic species. Some of the peaks observed by us e.g. m/z=68^+ and m/z=79^+ have been previously proposed as PAHs precursors, cyclic or bicyclic singly charged species, that have been observed in outer-space. [4]

The production of a long-live cyclic structure from an initial linear 1,3-butadiene cluster has been accounted for the **DA**-like mechanism, allowing to easily form 4-vinylcyclohexene radical cation.

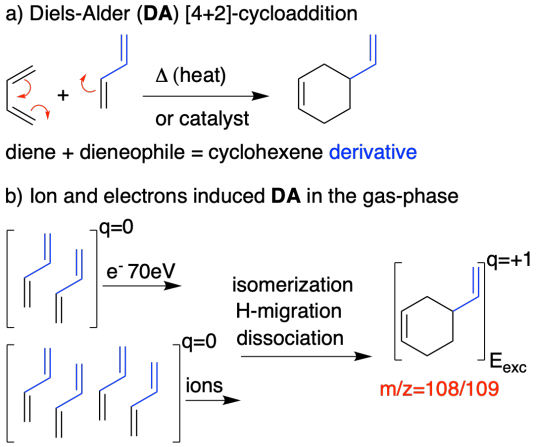

Figure 1. a) general scheme of Diels-Alder mechanism and b) our approach.

References

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