

Carbon chemistry in helium droplets

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Synopsis A very high abundance of atomic carbon in the interstellar medium (ISM), and a high reactivity of these species rise a question about the outcome of collisions of carbon atoms with common ISM molecules. To test it, we performed a set of laboratory and computational studies of the reactions of PAHs, C₆₀, and H₂ with atomic carbon. The reactions were investigated in liquid helium droplets at $T = 0.37$ K and by quantum chemical computations. It was found that in the case of PAHs and H₂ molecules, C atoms are inserted into existing chemical bonds, while they are added on the top of CC bonds of C₆₀ molecule, providing its higher chemical reactivity.

Despite the fact that the temperature of the interstellar medium (ISM) could be as low as 1 K, the rich chemistry occurs in this environment. The reactions inside superfluid helium droplets closely simulate the reactions occurring on the surfaces of the cold dust particles present in the ISM. Moreover, the combination of the experiential and computational results allows the prediction of the outcomes and the rates of gas-phase reactions. Therefore, the helium droplet technique is nicely suited for investigations of low-temperature reactions important for astrophysics.

In our studies we adopt this technique to study the reactions of common ISM molecules (C₆₀, PAHs, and H₂) with atomic carbon. Molecules are added into He droplets (ca. 10⁶ He atoms) where they can aggregate and be cooled to the droplet temperature of 0.37 K. Carbon atoms are then added and allowed to react with the molecular aggregates. Low-energy carbon atoms are produced with a purity >99% from a heated, sealed tantalum tube containing carbon [1]. The accomplishments of the reactions are studied either by mass spectrometry [2] or by mass spectrometry in combination with calorimetry technique [3,4].

The low-temperature reaction $C + H_2 + M \rightarrow HCH + M$ was found to be barrierless [4]. Therefore, the reaction $C + H_2 \rightarrow CH + H$ and the reverse one $CH + H \rightarrow C + H_2$ are predicted to have no energy barrier. The ionization process introduces large amount of energy to the formed cations. This fact was used to test the stability of cations, which is expected to correlate with abundancies of the species in the ISM. In the case of hydrocarbon clusters, the ion-molecule reactions followed by an electron-

impact ionization lead to the dominant formation of CH₅⁺. This implies the high abundance of this cation in the ISM [4].

In the reaction of C₆₀, addition of up to at least five single C atoms that form carbenes of the type C₆₀(C:)_n, with $n = 1-5$, was observed [2]. Our results show that C-atom additions can transform the chemically inert C₆₀ into reactive carbenes C₆₀(C:)_n. Carbenes should play an important role in interstellar chemistry. Our experiments demonstrate the chemical reactivity of C₆₀(C:)_n toward H₂ and H₂O and the formation of the extremely stable bridged dumbbell structure C₆₀=C=C₆₀. We expect similar reactivity toward many other molecules leading to a generation of a new class of fullerene derivatives.

In contrast to C₆₀, where carbon atoms are added on the top of CC bonds, in the case of PAHs, the reaction proceeds via an addition of the carbon atom to form an initial intermediate complex followed by a ring opening and the formation of a seven-membered ring [3]. All small and all large cata-condensed PAHs react barrierlessly with atomic carbon, and therefore should be efficiently destroyed by such reactions in a broad temperature range. At the same time, large compact pericondensed PAHs should be more inert toward such a reaction.

References

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