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Bond-Forming Reactions of Molecular Dications as a New Route to Polyaromatic Hydrocarbons

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Since Pauling's seminal paper about He_2^{2+},[1] molecular dications have fascinated physicists and chemists.[2,3] Bimolecular reactions of dications with neutral molecules are, however, often dominated by mere electron transfer. The few known bond-forming reactions of molecular dications[4,5] are by and large limited to processes with concomitant electron transfer.[6]

Bond-forming reactions which maintain the charge of the dication are so far limited to species which have recombination energies low enough to prevent the occurrence of electron transfer, such as metal compounds[7] or fullerenes.[8] Bond-forming reactions of small- or medium-sized organic dications under maintenance of the 2-fold charge so far are unknown.[9,10] Fragmentation reactions of some arene dications[11−13] suggest, however, that medium-sized organic dications may react with neutral compounds, such as acetylene, without the occurrence of electron transfer.[14]

To investigate this conjecture, mass-selected $C_mH_n^{2+}$ dications generated by electron ionization of several aromatic precursors were allowed to react with neutral acetylene. Figure 1 demonstrates that the hypothesis of a bond-forming process does indeed hold true. Thus, mass-selected $C_7H_6^{2+}$, generated by ionization of toluene, reacts with acetylene to yield $C_9H_n^{2+}$ dications (eq 1).

$$C_7H_6^{2+} + C_2H_2 \rightarrow C_9H_7^{2+} + H \qquad (1a)$$

$$\rightarrow C_9H_6^{2+} + H_2 \qquad (1b)$$

Figure 1 shows the occurrence of several additional processes, such as Coulomb explosion of the dication to afford $C_5H_3^+ + C_2H_3^+$, proton transfer to yield $C_7H_5^+ + C_2H_3^+$, as well as a trace of direct electron transfer leading to the couple $C_7H_6^+ + C_2H_2^+$. Part of these reactions can be attributed to excess internal energy of the dications generated upon electron ionization, and part of these processes can be ascribed to reactions with the neutral acetylene. Given the clearly resolved dication signals in Figure 1, the occurrence of bond-forming reactions according to eq 1 is beyond any doubt, however. Moreover, high-resolution measurements using Fourier transform ion-cyclotron resonance (FTICR) mass spectrometry establish the identity of the designated products within less than ±0.001 mass units. Last but not least, the energy behavior of the product channels further supports the suggested scenario of a thermal ion/molecule reaction in that the $C_9H_n^{2+}$ products are only observed at low collision energies (left-hand inset in Figure 1). Further, the reaction of $C_7D_6^{2+}$ with C_2H_2 reveals H/D scrambling in the $C_9H_nD_o^{2+}$ products (right-hand inset in Figure 1), which implies both formation of a long-lived collision complex as well as occurrence of extensive rearrangements prior to dehydrogenation, and hence the exploration of various dication structures.[11,12]

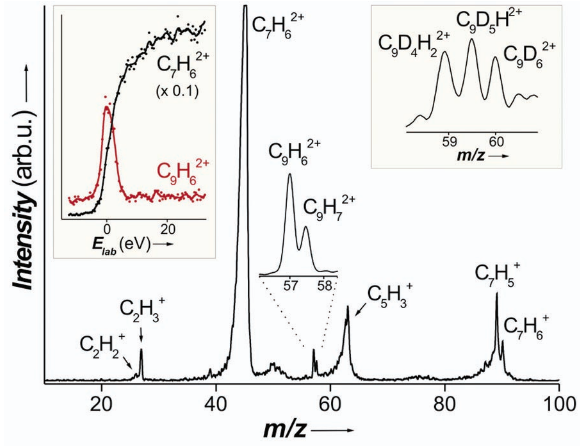

Figure 1. Reaction of mass-selected $C_7H_6^{2+}$ (off scale) with neutral acetylene. Aside charge separation yielding monocations, the occurrence of bond-forming reactions to afford $C_9H_n^{2+}$ dications is obvious (see expansion in the center). The left-hand inset shows the collision-energy dependence (E_{Lab} in eV) of the $C_7H_6^{2+}$ precursor and of the $C_9H_6^{2+}$ coupling product. The right-hand inset shows H/D scrambling in the $C_9H_nD_o^{2+}$ coupling products formed in the reaction of $C_7D_6^{2+}$ with C_2H_2.

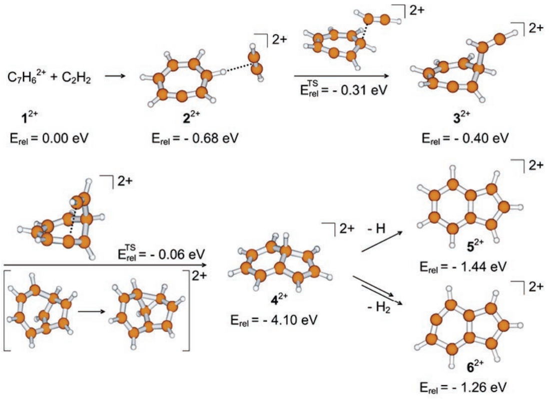

Figure 2. Pathway for the coupling reaction of $C_7H_6^{2+}$ (**1**$^{2+}$) with C_2H_2 according to B3LYP calculations (relative energies in eV). The structures in square brackets indicate the rearrangement to the indene skeleton along the associated intrinsic reaction coordinate.

According to density functional theory (B3LYP/6-311+G(2d,p)), the most stable isomer of $C_7H_6^{2+}$ accessible upon dissociative double ionization of toluene is the cycloheptatrienylidene dication **1**$^{2+}$.[15] The reaction of **1**$^{2+}$ with acetylene initially leads to the encounter complex **2**$^{2+}$ and provides 0.68 eV, which is hence available for bond activation (Figure 2). This amount of energy is indeed sufficient to overcome the barrier associated with a complex C−C coupling sequence to the indene skeleton (**2**$^{2+}$ → **3**$^{2+}$ → **4**$^{2+}$), in which hydrogen migration can be anticipated to be rather facile.[15,16] While the energy demand associated with the transition

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structure TS $\mathbf{3}^{2+}/\mathbf{4}^{2+}$ (−0.06 eV) is close to that of the entrance channel, the overall coupling is considerably exothermic, thereby enabling the competing losses of atomic as well as molecular hydrogen. Among several accessible structures, our computations suggest the indenyl dication $\mathbf{5}^{2+}$ and the dehydrogenation product $\mathbf{6}^{2+}$ as the most stable ones. The computed energetics thus fully supports the proposed scenario of bond-forming reactions of $C_mH_n^{2+}$ dications with acetylene to proceed below the energy of the entrance channel as required for a thermal ion/molecule reaction.

Independent confirmation of this conjecture evolves from a different experimental approach in which the unimolecular dissociations of mass-selected metastable $C_9H_8^{2+}$ dications are investigated. Losses of atomic as well as molecular hydrogen are observed in comparable amounts as the only unimolecular fragmentation pathways of $C_9H_8^{2+}$ generated by electron ionization of neutral indene. Hence, neither charge-separation reactions nor acetylene loss can kinetically compete with dehydrogenation.

To explore whether the bond-forming reactions can be continued to larger entities, mass-selected $C_9H_6^{2+}$ (generated from indene) was allowed to interact with acetylene. Again, coupling reactions concomitant with dehydrogenation are observed (reaction 2) with loss of molecular hydrogen as the major route ($-H^{\bullet}:-H_2 = 43:57$).

$$C_9H_6^{2+} + C_2H_2 \rightarrow C_{11}H_7^{2+} + H \tag{2a}$$

$$\rightarrow C_{11}H_6^{2+} + H_2 \tag{2b}$$

Similar dehydrogenation processes are observed for several $C_mH_n^{2+}$ dications generated from benzene ($m = 6$; $n = 4-6$), naphthalene ($m = 8, 10$; $n = 6, 8$), as well as phenanthrene ($m = 12, 14$; $n = 8, 10$), and once more deuterium labeling strongly supports the occurrence of bond-forming reactions. Accordingly, the coupling reaction with acetylene reported above is by no means an exceptional case for $C_7H_6^{2+}$, but appears as a general property of medium-sized $C_mH_n^{2+}$ dications.

Furthermore, the reaction kinetics is addressed briefly; note that the internal energy content of the $C_mH_n^{2+}$ dications so far was neglected here. Using the rate constant of the reaction of N_2^+ with acetylene as a reference,[17] the coupling of $C_7H_6^{2+}$ and acetylene (reaction 1) occurs with a rate constant of $(4 \pm 2) \times 10^{-11}$ cm^3 s^{-1}. The low rate constant is fully consistent with the computational finding that the rate-determining barrier of the C−C coupling reaction (TS $\mathbf{3}^{2+}/\mathbf{4}^{2+}$, Figure 2) is situated close to the energy of the reactants. The neutral reagent furthermore induces charge separation of the dication and serves also as a proton acceptor, where both processes act at the expense of the yield of dicationic reaction products. As expected, however, coupling of the slightly larger dication $C_9H_6^{2+}$ with acetylene (reaction 2) is considerably faster, $(2 \pm 1) \times 10^{-10}$ cm^3 s^{-1}. In a parallel approach, the rate constant of reaction 2 was determined as $(3 \pm 1) \times 10^{-10}$ cm^3 s^{-1} using FTICR mass spectrometry. In addition to the independent confirmation of the rate constant, the ICR experiments conducted at a pressure of ca. 10^{-8} mbar also prove the occurrence of the coupling reaction in the ultrahigh vacuum. Under these conditions, the corresponding monocations $C_mH_n^+$ are orders of magnitude less reactive toward acetylene, and most of them do not react at all ($k < 10^{-13}$ cm^3 s^{-1}). The monocation $C_9H_7^+$ derived from indene, for example, slowly reacts with acetylene at a rate constant of $(2.5 \pm 1.5) \times 10^{-12}$ cm^3 s^{-1} and thus about 100 times slower than the dication, and the molecular ion $C_9H_8^+$ does not react at all ($<10^{-13}$ cm^3 s^{-1}).

The present results provide the first unambiguous case of bond-forming reactions of medium-sized organic dications with maintenance of the 2-fold charge. In addition, they propose a new route for the gas-phase synthesis of polyaromatic hydrocarbons (PAH) in the extremely cold and dilute conditions of interstellar matter, where generation of PAHs imposes a problem for chemical reactivity.[14] Thus, starting with acetylene and related unsaturated carbon molecules, reactions of neutral or monocationic species accomplish the first steps of acetylene oligomerization up to C_7 compounds, but further growth is then suspended.[18] However, these hydrocarbon units are already sufficiently large and thus stable enough to eventually undergo photoionization to dications by interstellar VUV radiation;[14,19] also an alternative route to PAH dications via charge transfer with He^+ is feasible.[20] The resulting $C_mH_n^{2+}$ dications can then continue to react with acetylene to afford larger, hydrogen-depleted $C_mH_n^{2+}$ species. Electron recombination or proton transfer with appropriate dipolar molecules[6] can then afford first monocationic and then possibly also neutral PAH molecules.

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Supporting Information Available: Short description of experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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