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PAH and Fullerene Ions and Ion/Molecule Reactions in Interstellar and Circumstellar Chemistry

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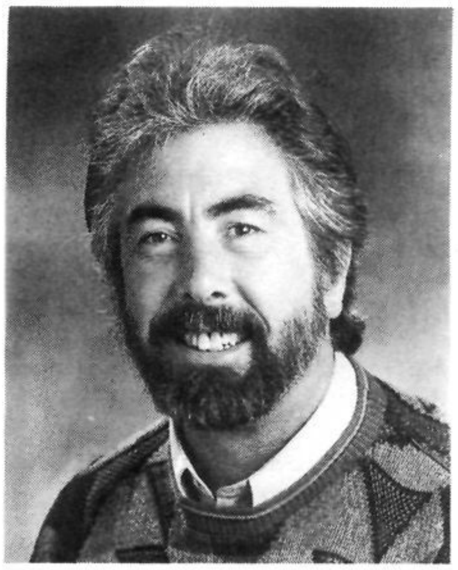
I. Introduction

Although it is well known that polycyclic aromatic hydrocarbons (PAHs, or polynuclear aromatic hydrocarbons) are widespread in the earth's environment, the likely presence of PAH-molecules and ions beyond the earth's atmosphere in space is still somewhat of a novelty for many chemists. Even though they have not yet been unequivocally identified, aromatic and polycyclic aromatic hydrocarbon molecules and ions are now generally accepted by the astrophysics community to be present in interstellar and circumstellar environments. Some have even argued for the presence of nonplanar PAHs and of hollow cages of carbon atoms known as fullerene molecules.

The hypothesis that PAHs are present in interstellar and circumstellar environments already has a substantial historical record[1] which began with the visionary suggestion[2] in 1956 that related carbonaceous species are responsible for visible diffuse absorption bands and crystallized with the discovery[3] that some astronomical objects emit a broad infrared emission band which peaks at 3050 cm^{-1} and other emission features[4] which peak in the region between 1610 and 890 cm^{-1}. Astronomical objects which emit these features include regions associated with individual stars such as H-II regions and reflection nebulae, as well as interstellar clouds such as the IR Cirrus, both in our own and other galaxies.[5] Soon after, these infrared emission features were attributed to infrared fluorescence from molecular-sized emitters excited by the absorption of ultraviolet and visible photons.[6] The idea that the fluorescence originated from vibrations of chemical groups attached to aromatic constituents of amorphous carbon particles[7] led to the proposal that individual PAH molecules are responsible for the infrared emission based on their stability against photodissociation and the resemblance of laboratory infrared fluorescence data of such species with the astrophysical spectra.[8] PAH molecules have also been proposed to be carriers of visible diffuse interstellar bands.[9] Nowadays the PAHs responsible for the infrared features are thought to be more abundant (~17% of the cosmic carbon) than all of the other known gaseous interstellar organic molecules combined.[10]



Diethard Kurt Bohme received his early education in Germany and Canada. He first specialized in chemistry at McGill University where he received his Ph.D. in Physical Chemistry in 1965. After postdoctoral fellowships in the Physics Department at University College, London, and the Aeronomy Laboratory at the Environmental Science Services Administration in Boulder, CO, he joined York University where he is now Professor of Chemistry. His early research interests included ionospheric chemistry, the physical–organic chemistry of ions including fundamental aspects of proton-transfer and nucleophilic displacement reactions, and flame–ion chemistry. Currently his research is directed to general aspects of the growth of ions and molecules by ion/molecule reactions in the gas phase (particularly as it relates to interstellar and circumstellar ion chemistry), ion-induced polymerization, and the ion chemistry of fullerene molecules.

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Current models of interstellar and circumstellar chemistry have emphasized planar PAHs with arrangements of hexagonal rings which are more or less compact ("catacondensed") with the general formula $C_{6p^2}H_{6p}$ such as coronene, $C_{24}H_{12}$, or elongated polyacenes with the general formula $C_{4n+2}H_{2n+4}$ such as naphthalene, anthracene, and tetracene.[1a] PAHs with loose arrangements of hexagonal rings, such as PAHs bound by single C–C bonds, have been neglected, as have aromatic molecules beyond hydrocarbons containing elements in addition to H and C. Neutral and positively-charged fused-ring molecules such as pyrene, coronene, and ovaline, either completely or partially hydrogenated, have been invoked to account for both the observed broad IR emission features in nebulae[8] and the observed diffuse interstellar absorption bands.[9] The very recent detection of additional sharp emission features[11] has led to the proposal that much simpler linear fused-ring molecules such as naphthalene, anthracene, and tetracene are responsible for the infrared emission and that benzene may also be present in these environments.[12] For example, anthracene has been suggested as the most abundant of these linear polyacenes in the Orion Ridge.[12]

The possibility that the fullerene molecule C_{60} might be widely distributed in the universe, particularly in the outflows of carbon stars, was suggested at the time of the original discovery of its stability.[13] Also, there have been indications that C_{60}, or a derivative, might be responsible for such features as the diffuse interstellar bands.[13] So far spectroscopic searches for C_{60} in space have led to negative results, and it seems clear now that neutral C_{60} is not responsible for the diffuse interstellar bands.[14] As a consequence, attention has been directed to the possible astrophysical importance of ionized C_{60} and other ionized fullerene molecules, as well as their derivatives such as, for example, endohedral (intracage) and exohedral (extracage) complexes involving alkali, alkali earth, or other elements such as He and O.[15] Very recently a theory has been proposed which makes a strong case for the contribution of fulleranes (hydrides of fullerenes) to the diffuse interstellar bands and the far-ultraviolet extinction.[16]

For astrophysicists and astrochemists, the proposition that polycyclic and other aromatic hydrocarbon (PAH) molecules and ions, and possibly larger fullerene molecules and ions, are present in interstellar and circumstellar environments has raised fascinating new questions about very fundamental aspects of reactions of ions with molecules. For example, it has become important to ask how atomic and molecular ions react with PAH and fullerene molecules and how PAH and fullerene ions react with neutral atoms and molecules. The energetics and gas-phase kinetics of these processes need to be determined for a variety of physical conditions. Can PAH and fullerene molecules be fragmented, and thus, be destroyed in reactions with atomic ions? Can dications of PAH and fullerene molecules be produced by chemical reactions and what is the chemistry of these dications? Can ion/molecule reactions lead to the formation of PAH and fullerene molecules and ions and ultimately to the ionic growth of large carbonaceous (dust) particles, and what is the mechanism of such growth? Can PAH and fullerene molecules and ions serve as molecular "surfaces" or even "cages" in promoting chemical reactions in the gas phase? Many such intriguing questions are now being addressed by laboratory ion chemists and chemical theoreticians worldwide. They have also captured the interest of the author and provided the motivation to write this review.

The remainder of this article is organized as follows: First, in section II, available knowledge is presented on the energetics of several fundamental processes involving PAH and fullerene ions and molecules: the capture of protons by the neutral molecules, the capture of electrons and H atoms by their cations, and the capture of electrons by their dications. Section III documents known reactions of atomic and molecular ions with PAH and fullerene molecules with a view to the role of such molecules as sinks for ions, their possible destruction by ion/molecule reactions, their ability to bond chemically with ions, and, in the case of the fullerene molecules, their ability to form endohedral (intracage) molecules. Section IV describes reactions of ionized PAH and fullerene molecules with atoms and molecules. Special attention is given to recombination reactions with electrons and negative ions, the hydrogenation of fullerene ions, ion-catalyzed recombination of H atoms, and reactions involving charge transfer, condensation, and adduct formation (including the formation of endohedral adducts). Reactions of benzene dimer ions and fullerene dications are also highlighted in this section. Section V draws together results described in sections III and IV in a discussion of the synthesis of PAH and fullerene ions and molecules by ion/molecule reactions. The condensation of carbon-chain molecules to form ring molecules is considered first, as a basis for an ensuing discussion of the growth of polyhedral carbon ions. Section V culminates in a review of current proposals for the growth of closed-shell polyhedral carbon ions such as fullerene ions. Section VI enters the realm of surface chemistry in which PAH and fullerene ions and molecules are viewed in terms of their potential role as surfaces in the occurrence of heterogeneous chemical change. Fundamental thermochemical aspects of the formation of adducts between ions and PAH or fullerene molecules are treated first, together with the structure of these adducts and the nature of the bonding. This section concludes with a survey of the kinds of neutralization and chemical reactions (together with some specific examples) which have been proposed for such adduct ions and which can lead to molecular synthesis by "surface chemistry" in the gas phase.

II. Thermochemical Properties of PAH and Fullerene Ions

A. Recombination Energies

The recombination energy of any cation is equal to the ionization energy of the corresponding neutral molecule. Vertical ionization energies are distinguished from adiabatic ionization energies on the basis of whether or not the removal of the electron occurs via a vertical Franck–Condon transition and will be significantly different if the equilibrium geometries of the ion and neutral are significantly different. For molecules of the size and structure of PAHs and fullerenes, such differences are expected to be small so that vertical and adiabatic ionization energies can be expected to be similar. The most extensive compilation of ionization energies of PAHs, including PAHs with up to 54 carbon atoms, is that of Lias et al. which covers the literature through the middle of 1986 and also contains critically evaluated data on heats of formation of positive and negative aromatic ions.[17] A survey of experimental techniques employed in the measurement of ionization energies is also provided in this compilation. Adiabatic ionization energies are most readily accessible from equilibrium constant measurements for charge-transfer reactions with the assumption that $\Delta IE_{adiabatic} \sim \Delta H^\circ_{ct} \sim \Delta G^\circ_{ct}$ where ct designates charge transfer. For example, in one extensive study of charge-transfer equilibria, with azulene (IE = 7.42 eV) and naphthalene (IE = 8.14 eV) as reference, the adiabatic ionization energies of PAH molecules were found to have values in the range from 7.26 (1,12-benzoperylene) to 7.63 (chrysene) and 8.48 eV (1,2,3,4-tetrahydronaphthalene).[18]

A characteristic ionization energy of 6.8 eV has been adopted for large PAH molecules in models of interstellar chemistry.[19]

The adiabatic ionization energies of large carbon clusters of the type C_n including C_{60} and C_{70} have been systematically investigated with Fourier-transform ion cyclotron resonance (FTICR) mass-spectrometric charge-transfer bracketing experiments.[20] The carbon-cluster ions were generated by the direct laser vaporization of graphite and allowed to thermalize before undergoing charge transfer. The IEs of C_{60} and C_{70} were bracketed by the same two charge-transfer compounds to have a common value of 7.61 ± 0.11 eV. These values agree favorably with the vertical ionization energy range from 6.42–7.87 eV obtained with photoionization bracketing experiments[21] and a gas-phase photoelectron study of C_{60} which has led to a value of 7.61 ± 0.02 eV for the vertical ionization energy.[22] A number of theoretical studies have predicted very similar ionization energies for these two molecules with values for IE between 7.5 and 7.9 eV.[23]

The appearance energies of doubly- and multiply-charged PAH and fullerene ions are not so well characterized. A survey of appearance energies for doubly-charged PAH ions, A^{2+}(PAH), which have been determined with electron-impact and photoionization measurements is available.[24] The appearance energies have been correlated with the recombination energies of the singly-charged PAH ions by the rule of thumb that A^{2+}(PAH)/IE(PAH) = 2.8 ± 0.1.[24] Actual values for A^{2+} range from 26.4 (benzene) to 22.7 (naphthalene) and 19.6 eV (pentacene). The ionization energy of $C_{60}^{\bullet+}$ has been established recently to be 11.39 ± 0.05 eV from a measurement of $A^{2+}(C_{60})$, 19.00 ± 0.03 eV, using synchrotron radiation and from IE(C_{60}) = 7.61 ± 0.02.[25] Other measurements involving charge-stripping of $C_{60}^{\bullet+}$,[26] photoelectron spectroscopy[27] and appearance-potential measurements[28] have led to similarly high values for IE($C_{60}^{\bullet+}$). Charge-transfer bracketing measurements have led to anomalously low values around 9.5 to 9.7 eV,[29,30] but these have now been rationalized in terms of the presence of an activation energy arising from Coulomb repulsion.[30] Also a theoretical value of 11.2 eV has recently been reported.[31]

Knowledge of the adiabatic ionization energies and standard enthalpies of formation of the PAH or fullerene molecules allows a determination of the standard enthalpy of formation of their ions. The enthalpies of formation of PAH molecules can be found in standard compilations.[17] The enthalpy of formation of C_{60} has been determined experimentally from the combustion of pure C_{60} to be 545 and 635 ± 6 kcal mol^{-1} while calculated values have ranged from 286 to 973 kcal mol^{-1}.[32,33] For example, the enthalpy of formation of C_{60} has been calculated to be 672 kcal mol^{-1} from its ab initio 6-31G* SCF total energy with a group equivalent method[34] previously applied successfully to obtain accurate enthalpies of formation of planar and nonplanar benzenoid aromatics.[35] The 545 kcal mol^{-1} is equivalent to 9.1 kcal (mol C)$^{-1}$ which is significantly larger than that of graphite (zero) and a graphitic monolayer, 1.5 kcal (mol C)$^{-1}$,[36] but smaller than the enthalpy of formation, ≈30 kcal (mol C)$^{-1}$, of the more highly-strained $C_{24}(O_h)$ cluster.[37] Adoption of 545 kcal mol^{-1} for the standard enthalpy of formation of C_{60}, $IE_{adiabatic}$ (C_{60}) = 7.61 eV and the stationary electron convention[17] leads to a standard enthalpy of formation for C_{60}^+ of 720 kcal mol^{-1} (12.0 per C), much larger than typical values for planar aromatic molecules, e.g. 233.2 (38.9 per C), 223.6 (22.4 per C), and 245 kcal mol^{-1} (11.1 per C) for the ions of benzene, naphthalene, and coronene respectively, but not out of line on a per C atom basis.

B. Proton Affinities

The proton affinity of an aromatic molecule is defined by the standard enthalpy required to remove the proton from the protonated aromatic molecule. Thus for PAHs, PA(PAH) = ΔH° for reaction 1, and for the fullerenes, PA(fullerene) = ΔH° for reaction 2. Experimentally determined values for PA(PAH) can be found in the extensive 1984 tabulation of Lias et al. which includes PAH molecules with up to 24 C atoms.[38] This compilation also provides a survey of the experimental techniques employed in the measurement of proton affinities. A particularly powerful technique for obtaining differences in PA for PAHs has been the measurement of equilibrium constants for proton-transfer reactions between PAH molecules. For example, PAs for a large number of PAH molecules have been determined with this technique to within ±1 kcal mol^{-1} and were found to have values (related to PA(NH_3) = 204 kcal mol^{-1})[38] in the range from 190.2 (naphthalene) to 204.0 (coronene) and 218.0 (azulene).[18] The experimental proton affinities determined in this study were correlated with localization energies[39] and CNDO/2 proton affinities.[40] The results show that, although the simple Huckel molecular-orbital method gives good results, the more advanced CNDO/2 method leads to considerable improvement in the predictive power of theory. However, the absolute CNDO/2 values are significantly higher (by ca. 100 kcal mol^{-1}) than the experimental values and the slope of the correlation line is much larger than unity.

$$(\mathrm{PAH})\mathrm{H}^+ \rightarrow \mathrm{PAH} + \mathrm{H}^+ \quad (1)$$

$$(\mathrm{fullerene})\mathrm{H}^+ \rightarrow \mathrm{fullerene} + \mathrm{H}^+ \quad (2)$$

A characteristic value of PA(PAH) = 207 kcal mol^{-1} (9 eV) has been suggested for models of interstellar chemistry.[1a]

The protonation of the fullerenes molecules C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} has been observed with triple quadrupole and Fourier transform mass spectrometry (FT-MS).[41] The proton affinities of C_{60} and C_{70} have been bracketed by proton-transfer reactions of type 3 and 4 for $n = 60$ and 70. They have been found to lie between

$$MH^+ + C_n \rightarrow C_nH^+ + M \quad (3)$$

$$C_nH^+ + M \rightarrow MH^+ + C_n \quad (4)$$

the proton affinities of ammonia (PA = 204 kcal mol^{-1})[38] and hexamethylbenzene (PA = 207 kcal mol^{-1})[38] with PA(C_{60}) being closer to PA(NH_3). Further FTMS studies have revealed the proton-transfer reaction between $C_{60}H^+$ and C_{70}, indicating that PA(C_{70}) > PA(C_{60}). Results of collision-induced dissociation (CID) experiments suggest that the charge of a protonated fullerene molecule is delocalized over the entire fullerene cage.[41]

C. Hydrogen-Atom Affinities

The hydrogen-atom affinity (HA) of a PAH cation is defined as the standard enthalpy change for reaction 5. It is related to the proton affinity and ionization

$$(PAH)H^+ \rightarrow PAH^+ + H \quad (5)$$

enthalpy of the neutral PAH molecule by eq 6. Typical

$$HA(PAH^+) = PA(PAH) + \Delta H^\circ_i(PAH) - \Delta H^\circ_i(H) \quad (6)$$

values for HA(PAH^+) computed according to eq 6 range from 85 to 64 kcal mol^{-1}, decreasing with increasing size until reaching a constant value of 64 ± 1 kcal mol^{-1} which is the H-atom affinity of such PAH molecules as perylene, 1,12-benzoperylene, and coronene.[18] Since the ionization energy is expected to decrease with increasing size faster than the proton affinity increases because of the increasing delocalization of the spin density of the radical ions, eq 6 predicts that HA(PAH^+) will decrease with increasingly conjugated π systems. Thus cyclic dienes have HAs of 80–84 kcal mol^{-1}, alkylbenzenes have HAs of 76–82 kcal mol^{-1}, and polycyclic aromatics have HAs of only 64–70 kcal mol^{-1}.[18] The characteristic trend in the decrease in HA with increasing size is particularly evident within a particular polycyclic series as, for example, the series phenanthrene–chrysene–picene and naphthalene–anthracene–tetracene. These trends suggest that a further increase in molecular size, even up to graphite, will not further reduce the H-atom affinity. A further increase in molecular size should not be accompanied by a further excess stabilization of the radical ion. The HA of a singly-ionized graphite monolayer can therefore be estimated to be 64 ± 1 kcal mol^{-1}.[18] The ionization energy of graphite, IE = 4.38 eV,[42] then leads to a proton affinity of 278 kcal mol^{-1} for a monolayer of graphite.[18] It has been suggested that the values of PA and HA for the monolayer should also apply to a graphite crystal since interlayer ion–neutral interactions should be negligible, but that these values should only be applicable if the edge carbons are hydrogenated as in the PAH series upon which they are based and for which protonation occurs on an sp^2 carbon atom bonded to hydrogen.[18]

The H-atom affinities of the fullerene cations can be similarly analyzed as is shown, for example, in eq 7 for C_{60}^+ and C_{70}^+. Values of 206 kcal mol^{-1} for the proton

$$HA(C_{60}^+,C_{70}^+) = PA(C_{60},C_{70}) + \Delta H^\circ_i(C_{60},C_{70}) - \Delta H^\circ_i(H) \quad (7)$$

affinity of the fullerene molecules and 7.61 eV (178 kcal mol^{-1}) for the ionization energy leads to a H-atom affinity of 63 kcal mol^{-1} for these two cations. This value is remarkably similar to that predicted for a singly-ionized graphite monolayer.[18]

III. Reactions of Ions with PAH and Fullerene Molecules

PAH molecules have been proposed to provide an important sink for atomic and molecular ions in interstellar clouds, particularly for atomic ions of low recombination energy since these recombine very slowly with electrons, react inefficiently with H_2, and generally are expected to be less reactive with other interstellar molecules. For example, it has been suggested that PAHs are probably by far the largest sink for Si^+ and atomic metal ions.[1a] Indeed, the abundance ratios of neutral atoms and their singly-charged ions have been proposed to provide the most sensitive probes of PAH chemistry in diffuse clouds.[19] Since the affinity of a carbonaceous surface for ions should not be very sensitive to curvature, interstellar fullerene molecules are expected to provide a sink for atomic and molecular ions as well. Furthermore, reactions between atomic ions with high recombination energies and PAH molecules, and perhaps fullerene molecules, conceivably could lead to the destruction of these molecules and so contribute to their loss in interstellar clouds.[1a] Still other reactions of PAH and fullerene molecules with ions may lead to chemical bonding and so, when accompanied by neutralization, would be important for the derivatization and growth of these molecules.

The known reactions of benzene, PAHs, and fullerene molecules with atomic ions are reviewed first and approximately in the order of increasing recombination energy of the atomic ion. The recombination energies of the atomic ions[43] are given in parentheses and we recall the ionization energies of benzene (9.25 eV), PAHs generally (6.8 eV), and C_{60} (7.61 eV). By far the most experimental measurements have involved benzene.

A. Reactions with Atomic Ions

Reactions of benzene and substituted benzenes with atomic ions have been of interest primarily with regard to solution chemistry, the chemistry of cluster ions and neutral clusters of benzene in the gas phase, and gas-phase organometallic ligand-switching reactions. The organometallic chemistry of aromatic compounds has been reviewed in this journal only very recently.[44] Quantitative kinetic information has been pursued less than data on relative stabilities and is rather sparse. Studies driven by interest in interstellar and circumstellar chemistry are more recent and have focused largely on the interactions of atomic ions with benzene, naphthalene, and fullerene molecules.

Sequential addition of up to four molecules of benzene to K^+ (4.341 eV) has been observed to occur in a high-pressure ion source in pure benzene vapor and 8.7% benzene/methane mixtures from about 250 to 525 K.[45] Rate constants were not measured but the kinetics were noted to be faster at lower temperatures. Similar measurements have also been reported for the direct addition of Na^+ (5.139 eV) and Pb^+ (7.146 eV) to benzene in He buffer gas at total pressures in the range 5.0–11 Torr.[46] The observation of adduct ions of benzene with Li^+ (5.392 eV) and Mn^+ (7.435 eV) has been reported as part of systematic studies of Li^+ and Mn^+ affinities of molecules with equilibrium-constant measurements of Li^+–L and Mn^+–L ligand (L)-switching reactions employing the trapped ICR technique.[47]

Reactions of Ni^+ (7.635 eV) with aromatic molecules have been investigated with a conventional ICR mass spectrometer.[48] No reactions were observed with benzene, toluene, chlorobenzene, phenol, aniline, and benzonitrile. Reactions did occur with other phenyl compounds, C_6H_5X, including those with X = Br, I, OCH_3, NO_2, CH_2Cl, CH_2Br, CH_2OH, CH_2NH_2, CH_2CH_3, $CH(OH)CH_3$, and $(CH_2)_3CH_3$. The phenyl group was observed to be largely unreactive and did not appear to prohibit the metal ion from interaction with other parts of these molecules. Products such as $NiC_6H_4^+$ and $NiC_5H_5^+$ were observed with X = Br, I, and NO_2. Ni^+ was seen to react with benzyl compounds by insertion into the $C_6H_5CH_2$–X bond, often followed by charge transfer to form $C_7H_7^+$ as a product. The reactions with X = OCH_3 and $CH(OH)CH_3$ are noteworthy in that they provide sources for $NiC_6H_6^+$ and $NiC_6H_5CH_3^+$, respectively, by losing CH_2O as is illustrated in reaction 8.

$$Ni^+ + C_6H_5OCH_3 \rightarrow NiC_6H_6^+ + CH_2O \qquad (8)$$

Ni^+ was also observed to decarbonylate the aromatic molecules $C_6H_5C(O)X$ with X = H, CH_3, OH, OCH_3, and C_6H_5. For example, for X = H reaction 9 produces the $NiC_6H_6^+$ ion.

$$Ni^+ + C_6H_5C(O)H \rightarrow NiC_6H_6^+ + CO \qquad (9)$$

The reactions of Fe^+ with aromatic molecules have been studied systematically using FTMS techniques and laser desorption to generate Fe^+.[49] The reactions of Fe^+ with benzene, toluene, styrene, and benzonitrile were found to be simple in that only adduct formation was observed and a second molecule (up to four in the case of benzonitrile) was added sequentially. In the reactions with ethylbenzene, cumene, benzyl chloride, benzyl alcohol, phenol, thiophenol, anisole, phenetole, benzaldehyde dimethyl acetal, benzaldehyde, acetophenone, methyl benzoate, benzoyl chloride, phenyl halides, aniline, methylaniline, nitrobenzene, and several pentafluorobenzene derivatives the phenyl group generally was not involved in the reaction, although the formation of the benzyne (C_6H_4) ligand was commonly observed. Only in the case of nitrobenzene was the benzene C_6 skeleton altered and $FeC_5H_5^+$ observed as a product. Fe^+ usually inserted into a bond to the most electronegative atom in the substituent group. Insertions into C–C and C–H were also observed, and hydrogen or methyl group shifts often preceded bond cleavage. As was the case with Ni^+, Fe^+ was observed to produce $FeC_6H_6^+$ in reactions of type 10

$$Fe^+ + C_6H_5OCH_3 \rightarrow FeC_6H_6^+ + CH_2O \qquad (10)$$

with $C_6H_5OCH_3$ and $C_6H_5OC_2H_5$ and in a decarbonylation reaction of type 11 with $C_6H_5C(O)H$. The

$$Fe^+ + C_6H_5CHO \rightarrow FeC_6H_6^+ + CO \qquad (11)$$

reaction of Fe^+ with $C_6H_5C(O)CH_3$ was observed to produce $FeC_6H_6^+$ with loss of both CO and CH_2O.

The metal–ion complexes of benzene with Al^+ (5.99 eV),[50a] of benzene and toluene with Ag^+ (7.58 eV),[50b] and of benzene with Bi^+ (7.29 eV), Mg^+ (7.65 eV), Cu^+ (7.73 eV), and Fe^+ (7.87 eV)[50c] have been produced in a laser vaporization/pulsed-nozzle cluster source. Complexes with more than one benzene molecule up to $Ag^+\cdot(C_6H_6)_3$ and complexes with more than one silver atom, $Ag_2^+\cdot(C_6H_6)_{1-3}$ and $Ag_3^+\cdot C_6H_6$, were also reported.[50b] Another extensive study using a laser ablation/molecular beam method has shown the formation of the benzene adducts with M^+ for the transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, and W and the metals Al, Zn, In, Sn, and Pb.[51] Pressure-dependent studies were able to show that collisional stabilization with benzene molecules was effective in stabilizing the adduct ions under these experimental operating conditions. The reaction of Nb^+ (6.88 eV) with benzene was an exception in that it led to the dehydrogenation reaction 12 which has been substantiated in independent FTMS experiments.[52] Reaction

$$Nb^+ + C_6H_6 \rightarrow NbC_6H_4^+ + H_2 \qquad (12)$$

12 is an interesting source for molecular hydrogen. A similar dehydrogenation reaction has been reported for Ta^+ (7.89 eV) which also eliminates C_2H_2 and C_2H_4 and so is an interesting source for these unsaturated hydrocarbon molecules.[53]

Metal–ion complexes of C_{60}, MC_{60}^+, in which the metal atom is bound on the outer surface of the fullerene molecule (exohedral complex) have been produced in systematic studies with a Fourier-transform mass spectrometer in which M^+ is generated from pure metal targets by laser desorption.[54] The atomic metal ions La^+ (5.58 eV), Rh^+ (7.46 eV), Ni^+ (7.635 eV), Cu^+ (7.726 eV), Co^+ (7.86 eV), and Fe^+ (7.87 eV) were observed to react with C_{60} to form MC_{60}^+ by direct attachment and varying amounts of C_{60}^+ by charge transfer. Fe^+ was observed to react predominantly by charge transfer but FeC_{60}^+ and FeC_{70}^+ could be generated from ligand-exchange reactions with $Fe(C_nH_{2n})^+$ (n = 2–5).[54a] A reaction sequence initiated by the direct attachment of Ni^+ to C_{60} was observed to form $Ni(C_{60})_2^+$.[54c] This result suggests the possibility of a family of "dumbbell" complexes including other metal ions and other fullerene molecules.

An "energy-rich" $SiC_6H_6^+$ complex has been observed to be formed in collisions of Si^+ (8.151 eV) with C_6H_6 at center-of-mass energies between 0.7 and 7 eV.[55] Decomposition of this complex was seen to lead to $C_6H_6^+$ + Si and $SiC_6H_5^+$ + H, and it could be stabilized by collision at ca. 5×10^{-3} Torr of benzene.[55] $SiC_6H_6^+$ was also observed in these experiments as a product of the reactions of SiH^+ and SiH_2^+ with benzene at 1 eV.

Subsequently, selective-ion flow tube (SIFT) experiments were able to show that the ground-state $Si^+(^2P)$ rapidly adds to C_6H_6 in helium carrier gas at 0.35 Torr and 296 ± 2 K with a rate constant $k = (1.5 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[56] The $Si^+{\cdot}C_6H_6$ adduct was found to be quite unreactive toward benzene, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}, but trace amounts of $Si^+{\cdot}(C_6H_6)_2$ were observed to be formed. Very recently $SiC_6H_6^+$ ions have been derived from a mixture of tetramethylsilane and benzene under CI conditions, from phenylsilane by electron impact at 70 eV, and by charge reversal of $C_6H_6Si^-$ with O_2 at 8 keV.[57] Since the recombination energy of the atomic silicon ion (8.152 eV) is slightly higher than the ionization energy of naphthalene (8.14 eV), charge transfer becomes exothermic in the reaction of $Si^+(^2P)$ with naphthalene. The reaction of $Si^+(^2P)$ with naphthalene has been investigated in a SIFT experiment with helium buffer gas at 0.35 Torr and 296 K.[56] It was observed to proceed both by adduct formation and charge transfer in a ratio of 7 to 1 as indicated in reaction 13. A rate constant

$$\begin{aligned} Si^+ + C_{10}H_8 &\rightarrow SiC_{10}H_8^+ \\ &\rightarrow C_{10}H_8^+ + Si \end{aligned} \qquad (13)$$

was not reported for this reaction. Similar measurements with C_{60} indicated the same product channels for this molecule as indicated in reaction 14 with adduct

$$\begin{aligned} Si^+ + C_{60} &\rightarrow C_{60}^+ + Si \\ &\rightarrow SiC_{60}^+ \end{aligned} \qquad (14)$$

formation being preferred in a ratio of about 2 to 1.[58a]

Reactions of Au^+ (9.225 eV) with aromatic molecules have been investigated using FTMS.[49] Both charge transfer (6%) and addition to form $AuC_6H_6^+$ (94%) were observed for the reaction of Au^+ with benzene. The charge-transfer channel in this case is thermoneutral or slightly endothermic within the uncertainty of IE(benzene). $AuC_6H_6^+$ added a second molecule of benzene to form $Au(C_6H_6)_2^+$. The reaction with toluene has an additional channel corresponding to hydride transfer (16%) to produce $C_7H_7^+$ + AuH and so is an interesting source for a metal hydride molecule. The reaction of Au^+ with ethylbenzene was still more complicated and exhibited three *additional* channels involving formation of $AuCH_3$ ($+C_7H_7^+$) (2%), $AuC_2H_4^+$ (8%), and $AuC_6H_6^+$ (5%). The mechanism of formation of the latter two product ions is interesting in that it may involve initial insertion across the ethyl–phenyl C–C bond, followed by a β-hydride transfer onto the gold with subsequent migration of hydrogen to the phenyl ring to form an activated complex, C_2H_4–Au^+–C_6H_6 which fragments to produce $AuC_2H_4^+$ and $AuC_6H_6^+$. An independent FTICR study observed charge transfer and addition channels for the reaction of Au^+ with C_6D_6.[60] No charge exchange was observed with Au_2^+ and Au_3^+.

The reaction of C^+ (11.260 eV) with benzene (9.247 eV) has been studied in low-pressure tandem mass spectrometer experiments over a range of translational energies of 0.1 to 12 eV[61] and in SIFT experiments at 296 K.[62] The reaction proceeds with a large rate constant at 296 K, $k = (2.4 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, and forms a variety of products as shown in eq 15 which also indicates the measured product distribution.

$$\begin{aligned} C^+ + C_6H_6 &\rightarrow C_6H_6^+ + C && 0.67 \\ &\rightarrow C_7H_5^+ + H && 0.10 \\ &\rightarrow C_5H_3^+ + (C_2H_2 + H) && 0.17 \\ &\rightarrow C_3H_3^+ + (C_4H_2 + H) && 0.06 \end{aligned} \qquad (15)$$

The neutral product molecules were not identified. Charge transfer is the predominant product at 296 K (67%) and more so at 0.1 eV (83%). The formation of $C_7H_5^+$ provides direct evidence for the formation of a C_7 intermediate species, $(C_7H_6^+)^*$, which may result from C^+ attack of the π-system of benzene.[62] The observation of the C_7 product is interesting as it represents a growth mechanism for carbonaceous species. Clearly there is a need to investigate the reactions of this ion with PAH and fullerene molecules to explore similar possibilities of growth with these species.

The reaction of C^+ with C_{60} has been studied with $^{13}C^+$ labeling under single-collision conditions over the energy range from 2 to 78 eV.[63] C_{61}^+ was observed to be formed with no activation energy and to survive for milliseconds at excess energies up to 10 eV. The $^{13}C^+$ projectile was observed to undergo exchange with C atoms in the C_{60} target. At collision energies above 20 eV, a series of C^+_{60-2n} products were observed for which their also was evidence for C-atom exchange.

Astrophysicists have proposed that the addition of H atoms on the periphery by reaction with H^+ (13.598 eV) can lead to the chemisputtering of PAHs with formation of CH_4 or H_2, although the competition with charge transfer may be self-limiting.[1a,64] Reactions with H^+ therefore may play a critical role in the destruction of PAH molecules. Very little experimental data is available to test this proposal. Preliminary results of SIFT measurements indicate that D^+ reacts rapidly with both benzene and naphthalene at 297 ± 2 K primarily by charge transfer, but fragmentation of the carbon skeletons into smaller hydrocarbon fragments also contributes.[58b] Little is known about the reactions of protons with fullerene molecules at thermal energies and below, although one might expect charge transfer to predominate on the basis of thermodynamics. Indeed, recent SIFT measurements at 297 ± 2 K have indicated that D^+ transfers a charge to C_{60}.[58c] At high collision energies protons can be expected to dissociate and possible to penetrate fullerene molecules in the manner shown for the interaction of Ne^+ with C_{60} as discussed below.

The reaction of Ne^+ (21.564 eV) with C_{60} has been studied in a SIFT apparatus at thermal energies and in mass spectrometer beam experiments at energies in the range from 2 to 212 eV (CM).[65] The SIFT experiments at 294 ± 2 K indicate that charge transfer and charge transfer accompanied by electron detachment produce C_{60}^+ and C_{60}^{2+} according to reaction 16.[58d] More than 5% of the reaction yields C_{60}^{2+} in what is an unprecedented reaction at thermal energies. There was no evidence for dissociative charge transfer at thermal

$$\mathrm{Ne^+ + C_{60} \rightarrow C_{60}^{\ +} + Ne}$$
$$\mathrm{\rightarrow C_{60}^{\ 2+} + Ne + e} \quad (16)$$

energies. A series of channels due to multiple C_2 loss from C_{60}^+ appear in the beam experiments as the ion collision energy is increased beyond 20 eV.[65] The formation of C^{2+}_{60-2n} was also reported.[65] The fragmentation pattern for C^+_{60-2n} which was observed at high energies is similar to those observed in high-energy collisions of C_{60}^+ with neutral targets, as well as in electron impact ionization, metastable decay, and other processes which produce excited C_{60}^+. Also, at collision energies between 20 and 30 eV $C_{58}Ne^+$ begins to appear and is replaced by a distribution of successively smaller $C_{60-2n}Ne^+$ products as the collision energy increases still further. The dominant mechanism for the production of $C_{60-2n}Ne^+$ has been proposed to be insertion into the cage of C_{60} to give $C_{60}Ne^+$ which then boils off variable numbers of C_2 units, depending on the collision energy.[65]

Reactions with He^+ (24.587 eV) have also been invoked by astrophysicists as efficient destruction processes for PAH molecules.[1a] Preliminary results of SIFT experiments indicate that He^+ reacts rapidly at 297 ± 2 K with benzene primarily by dissociative charge transfer and with naphthalene primarily by the charge-transfer electron-detachment process given in eq 17, which yields the doubly-charged naphthalene cation, and also by charge transfer and dissociative charge transfer.[58b] The possibility of generating doubly-

$$\mathrm{He^+ + C_{10}H_8 \rightarrow C_{10}H_8^{\ 2+} + He + e} \quad (17)$$

charged PAH ions *at thermal energies* is most intriguing. Reaction 17 also should be exothermic with PAH molecules larger than naphthalene and so could be an important source for such ions in the interstellar medium. Virtually nothing is known about the chemical reactivity of double-charged PAH ions at thermal energies, not even with molecular hydrogen. The fullerenes should also become singly- and doubly-ionized at thermal energies in reactions with He^+. Indeed, recent SIFT experiments indicate a reaction of He^+ with C_{60} at 294 ± 2 K which leads to single (<90%) and double ionization (>10%) as was observed for reaction 16 with Ne^+, and again without dissociation. At higher ion energies (in the kiloelectronvolt range) dissociation and penetration (with trapping) should occur as observed for Ne^+.[65]

Recently it has become possible to react atomic ions with neutral clusters of aromatic molecules. Ion/molecule reactions of metal ions with neutral benzene *clusters* recently have been investigated with a laser ablation/molecular beam method.[66] Complex ions $M(C_6H_6)_m^+$ were observed for the atomic metal ions Mg^+ and Al^+ up to $m = 4$, In^+ and Pb^+ up to $m = 2$, and the transition-metal ions Au^+, V^+, Cr^+, and Co^+ up to $m = 2$. These complex ions are proposed to be formed in ion/molecule reactions of type 18 in which benzene molecules are liberated by evaporation. The reactions

$$\mathrm{M^+ + (C_6H_6)_n \rightarrow M(C_6H_6)_m^{\ +} + (n - m)C_6H_6} \quad (n \geq 2) \quad (18)$$

of Y^+, Nb^+, and Ta^+ ions with benzene clusters indicate another feature of metal ion/benzene cluster ion chemistry. Two types of intracluster ion/molecule reactions have been proposed: hydrogen-molecule(s)-elimination reactions of type 19 and hydrocarbon-elimination reactions of type 20 to form ions of the type $M(C_6H_6)(C_xH_y)^+$ with $x = 2,4,6$ and $y = 0,2,4$.[66] Reactions 19

$$\mathrm{[M(C_6H_6)_2^{\ +}]^* \rightarrow M[(C_6H_6)_2 - \mathit{x}H_2]^+ + \mathit{x}H_2} \quad (x = 1,2,3) \quad (19)$$

$$\mathrm{[M(C_6H_6)_2^{\ +}]^* \rightarrow M[(C_6H_6)_2 - C_{2\mathit{y}}H_{2\mathit{z}}]^+ + C_{2\mathit{y}}H_{2\mathit{z}}} \quad (y = 1,2;\ z = 1,2,3) \quad (20)$$

and 20 involve cleavage of C–C and/or C–H bonds in one benzene moiety instead of the breakup of the weak van der Waals bond of the benzene dimer which occurs in reaction 18. Reactions of type 20 are interesting as sources for hydrocarbon molecules such as C_2H_2, C_2H_4, C_2H_6, C_4H_4, and C_4H_6.

B. Reactions with Molecular Ions

Current knowledge of the kinetics for reactions of PAH and fullerene molecules with molecular ions is restricted largely to reactions of benzene and some of naphthalene and C_{60}. There has been considerable interest in the reactions of benzene with hydrocarbon ions, particularly $C_3H_3^+$, in connection with flame ion chemistry and soot formation, and the chemistry of carbon–cluster ions.

The protonation of benzene with CH_5^+ has been reported in an ICR study of the formation of $C_6H_7^+$ ions.[67] The $C_6H_7^+$ produced in this fashion was reacted with the molecules CH_3OH, $CH_3C{\equiv}CH$, $CH_2{=}C{=}CH_2$, CH_3CHO, CH_3SH, PH_3, $HCOOCH_3$, CH_3OCH_3, $HCOO(n\text{-}C_4H_8)$, $i\text{-}C_4H_8$, CH_3COCH_3, and $CH_2{=}CHCH{=}CHCH{=}CH_2$. Rate constants near thermal energies were reported for all of these reactions. Their values range from 4.4×10^{-11} to 2.1×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. Proton transfer was observed in all cases except for the reaction of $C_6H_7^+$ with $CH_2{=}CHCH{=}CHCH{=}CH_2$ which was observed to proceed by condensation.

The propargyl isomer of $C_3H_3^+$ has been seen with the ICR technique to react with benzene to lead to the two channels shown in reaction 21 with $k = 1.4 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}.[68] At least 80% of the $C_7H_7^+$ product

$$\mathrm{CH_2CCH^+ + C_6H_6 \rightarrow C_9H_7^{\ +} + H_2}$$
$$\mathrm{\rightarrow C_7H_7^{\ +} + C_2H_2} \quad (21)$$

ions were formed with the benzyl structure, $C_6H_5CH_2^+$, indicating that a new C–C bond forms in this reaction. In contrast, the cyclopropenylium isomer was found to be unreactive. Later ICR mass-spectrometer studies at low pressure and near room temperature confirmed these results and provided additional kinetic data for reactions of both isomers of $C_3H_3^+$ with toluene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and indene.[69] The linear propargyl ion was seen to react fast, $k \geq 7 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, except for the reaction with 2-methylnaphthalene for which $k = 1.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The cyclic isomer was found to be much less reactive, $k \leq 4 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The predominant channels observed in these reactions were charge transfer and hydride transfer, although the reaction with indene showed channels analogous to those observed with benzene.

Benzene was observed to react rapidly with ionized diacetylene in a SIFT experiment conducted in helium at 0.35 Torr at 296 ± 2 K, $k = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[70] The predominant reaction channel was charge transfer and a possibility of up to 5% of proton transfer was reported. The $C_6H_6^+$ ion produced in this fashion was observed to react further with benzene to form the ionized dimer with an effective bimolecular rate constant, $k \geq 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Equilibrium studies of charge-transfer and proton-transfer reactions involving PAH molecules indirectly imply high reaction efficiencies for these processes. Actual determinations of rate constants indicate that such reactions proceed essentially at the collision rate. This has been established, for example, for the proton-transfer reactions of t-$C_3H_7^+$ with fluorene, naphthalene, and indene, and for the charge-transfer reactions of $C_6H_6^+$ with azulene, biphenylene, 9-methyl-anthracene, and 9,10-dihydroanthracene.[18] Indeed, current atmospheric pressure ionization techniques developed for the detection of ambient PAH in the atmosphere are based on the chemical-ionization reactions of electron transfer from PAHs to $C_6H_6^+$ and proton transfer from hydrated hydronium ions, $H_3O^+{\cdot}(H_2O)_n$ to PAH molecules.[71]

The gas-phase ionic alkylation and silylation of aromatic molecules has received considerable attention from experimentalists, albeit the focus has been primarily on thermodynamics, rather than kinetics. Radiolytic techniques have been applied at pressures from 10–760 Torr and temperatures in the range 273 to 400 K to investigate adduct formation between the electrophiles $(CH_3)_3C^+$, $C_4H_9^+$, and $(CH_3)_3Si^+$ and the aromatic molecules benzene and toluene.[72] High-pressure mass-spectrometric studies of similar systems have provided standard enthalpy and standard entropy changes for the addition reactions.[73,74] The experimental evidence appears to favor C–C and C–Si σ-bond formation in the adduct ions (known as arenium ions in the case of C–C bond formation) as opposed to the formation of a π-complex. Experimental evidence has been reported for the interconversion and coexistence of σ- and π-complexes in the protonation of arenes in the gas phase.[75] The interaction of SF_5^+ with benzene also has been investigated with high-pressure mass spectrometry.[76] SF_5^+ forms an adduct with benzene which disappears rapidly at 350 K by loss of HF to give $SF_4C_6H_5^+$ which does not react further with benzene. Almost 20% of the reaction proceeds by charge transfer and is followed by formation of the stable dimer $(C_6H_6)_2^+$. Toluene was observed to behave similarly with charge transfer becoming predominant. Indeed, the efficiency of charge transfer was found to increase systematically with decreasing ionization energy of the aromatic molecule.

Reactions of carbon-cluster ions (C_n^+, $11 \leq n \leq 23$) with various aromatic and polyaromatic hydrocarbons have been studied in a FTICR mass spectrometer.[77] The reactions were observed to proceed by one or more of three routes: charge transfer, condensation with H-atom elimination, and adduct formation stabilized by collision or the emission of radiation. The reactivity was found to alternate between adduct formation and condensation depending on whether the reacting cluster ion contained an even or odd number of carbon atoms. All reactions were found to have a significant dependence on the kinetic energy of the cluster ion and on the pressure of a bath gas. For example, for the reaction of C_{16}^+ with naphthalene, the ratio of adduct formation to charge transfer decreased as a function of increasing ion kinetic energy and increased as a function of argon pressure from 1×10^{-6} to 1×10^{-5} Torr. Collision-induced dissociation (CID) studies of the reaction products indicated that, rather than being loosely bound, the adduct and condensation products were tightly bound perhaps via multiple bonds with PAH-like conjugation. CID produced limited fragmentation: loss of H-atoms and $C_2H_{(1,2)}$ molecules from adducts formed with PAHs or styrene, loss of HCN(HNC) from aniline adducts, and loss of CH_3 from toluene adducts.

Energy-rich collision complexes have been observed to be formed in the reactions of SiH^+ and SiH_3^+ with benzene.[55] Tandem mass spectrometer experiments at a laboratory energy of 1.0 eV and a collision chamber pressure of 1.0×10^{-3} Torr showed the formation of the product ions given in eqs 22 and 23. Phenomenological

$$\begin{aligned} SiH^+ + C_6H_6 &\rightarrow C_6H_6^+ + SiH \\ &\rightarrow SiC_6H_7^+ \\ &\rightarrow SiC_6H_5^+ + H_2 \\ &\rightarrow SiC_4H_5^+ + C_2H_2 \\ &\rightarrow C_6H_7^+ + Si \\ &\rightarrow SiC_6H_6^+ + H \end{aligned} \tag{22}$$

$$\begin{aligned} SiH_3^+ + C_6H_6 &\rightarrow SiC_6H_9^+ \\ &\rightarrow SiC_6H_7^+ + H_2 \\ &\rightarrow C_6H_6^+ + SiH_3 \\ &\rightarrow SiC_4H_5^+ + C_2H_4 \\ &\rightarrow C_6H_7^+ + SiH_2 \\ &\rightarrow SiC_4H_7^+ + C_2H_2 \end{aligned} \tag{23}$$

rate constants of 8.9 and 10×10^{-10} cm^3 molecule^{-1} s^{-1} were reported for these two reactions, respectively, for 1 eV ions. Branching ratios are available in terms of cross sections for the formation of individual product ions which are 14, 6.7, 6.6, 3.6, 2.2, and 1.4 Å^2, respectively, for the products of reaction 22, and 18, 8.6, 8.0, 2.8, 1.5, and 1.0 Å^2, respectively, for reaction 23. Charge transfer is endothermic for both reactions and proton transfer is endothermic with SiH^+ and about thermoneutral with SiH_3^+. Measurements of the kinetic energy dependence of the cross sections indicated that all other channels are exothermic. Kinetic energy and pressure dependence studies provided insight into the mechanisms of these reactions. Both are proposed to proceed via the formation of energy-rich adduct ions which were estimated from their observance at the detector to have lifetimes of 7.5 and 8.9 μs for $(SiC_6H_7^+)^*$ and $(SiC_6H_9^+)^*$, respectively. Experiments with SiD_3^+ indicated that the SiD_3^+ retains to a very large extent its chemical identity in the complex and that very little exchange of deuterium with the hydrogen atoms of the benzene takes place. Simple rupture of the Si–C bond in a σ-bonded $(H_3SiC_6H_6^+)^*$ is proposed to lead to charge transfer, while a 1,2 molecular hydrogen elimination is proposed to form the phenylsilyl ion $C_6H_5SiH_2^+$ rather than a tropylium-like ion in which the Si is inserted into the ring. Experiments with SiD^+ indicated that the deuterium exchanges rather extensively with the ring hydrogens in benzene.

The reaction of SiH_2^+ with benzene has also been investigated in a tandem mass spectrometer at 1 eV ion energy, but in this case charge transfer and proton transfer are both exothermic and no adduct ion was detected. Charge transfer is the major reaction which is observed. Other products are listed in reaction 24. A phenomenological rate constant of 3.4×10^{-9} cm^3 molecule^{-1} s^{-1} has been reported for this set of reactions,

$$\begin{aligned} SiH_2^+ + C_6H_6 &\rightarrow C_6H_6^+ + SiH_2 \\ &\rightarrow SiC_6H_6^+ + H_2 \\ &\rightarrow SiC_6H_7^+ + H \\ &\rightarrow C_6H_7^+ + SiH \\ &\rightarrow SiC_6H_5^+ + H_2 + H \end{aligned} \tag{24}$$

and the cross sections for the individual reaction channels have been measured to be 75, 33, 18, 6.0, and 2.9 Å^2, respectively. All the observed reaction channels were suggested to be exothermic.

Reactions of $NiCO^+$, $NiPF_3^+$, and $NiC_5H_5^+$ with 24 substituted benzene molecules, C_6H_5X, were investigated using an ICR mass spectrometer as part of a study to explore the influence of ligands on the chemistry of the bare Ni^+ ion.[48] CO is largely a "spectator" in the chemistry of $NiCO^+$ which often reacts in a manner very similar to Ni^+ or experiences a ligand displacement as shown in reaction 25 for the formation of $NiC_6H_6^+$.

$$NiCO^+ + C_6H_6 \rightarrow NiC_6H_6^+ + CO \tag{25}$$

Ligand displacement was a channel also commonly observed in the reactions of $NiPH_3^+$ with C_6H_5X which in general follow closely the reactions of $NiCO^+$. The cyclopentadienyl ligand was found to influence the chemistry of Ni^+ much differently than the CO and PH_3 ligands as it appeared to be more strongly bound. For example HX elimination was observed instead of ligand displacement with several PhX molecules. In many cases the reactivity decreased as the size of the ligand increased, suggesting the importance of steric interactions even for these reactions with monoligated species.

Reactions of $FeCo^+$ with benzene and toluene have been observed in which Fe is displaced by the aromatic molecule to produce $CoC_6H_6^+$ and $CoC_7H_8^+$, respectively.[78] Equation 26 shows the reaction with benzene.

$$FeCo^+ + C_6H_6 \rightarrow CoC_6H_6^+ + Fe \tag{26}$$

An analogous reaction has been seen with the dimer ion Fe_2^+, reaction 27.[78]

$$Fe_2^+ + C_6H_6 \rightarrow FeC_6H_6^+ + Fe \tag{27}$$

Niobium cluster ions (Nb_x^+, x = 1–15) have been found to dehydrogenate benzene in the gas phase.[79] The observed product distributions exhibit a unique "duality": for $x \geq 4$, only $Nb_xC_6H_m^+$ with m = 0,6 are observed, while for x = 1–3, m = 0 is not observed but primarily the m = 4 and m = 6 species are formed. The minimum cluster size of four atoms which appears to be required to produce complete dehydrogenation to m = 0 may indicate the formation of a special type of "template" on the cluster surface whose electronic character is favorable for activation of the C–H bonds.[79] Complete dehydrogenation of benzene was also found to occur with niobium cluster oxide ions Nb_xO^+ containing 5–15 Nb atoms.[79]

Absolute rate constants for reactions of ions with C_{60} or other fullerene molecules are not available at this time. However, the experimental determinations of the ionization potential and proton affinity of C_{60} with bracketing reactions involving ions with known recombination energies and proton affinities have indicated that exothermic charge transfer and proton reactions with C_{60} occur close to the collision limit.[20,41] $C_6H_6^+$ has been used as a charge-transfer agent in the detection of fullerene molecules by chemical ionization.[60] The charge-transfer agents used in the ionization-energy determination are not particularly relevant to interstellar or circumstellar chemistry and there is a clear need to investigate charge-transfer reactions of the fullerene molecules with small ions of the type He^+, H_2^+, etc., at room temperature and below. The proton-affinity bracketing experiments provide evidence for the occurrence of proton transfer between CH_5^+, H_3O^+, $CH_3OH_2^+$, and NH_4^+ and the fullerene molecules C_{60} and C_{70}.[41] Even the transfer of a proton from $C_{60}H^+$ to C_{70} was observed.[41] Only the proton transfer reaction of NH_4^+ with C_{60} appeared to be slow, but this can be understood on the basis of a similarity in the proton affinity of NH_3 and C_{60}. Proton transfer between H_3^+ and C_{60} has not been investigated although this reaction would clearly be of interstellar interest. Charge transfer between $C_{60/70}H^+$ and C_{60} or C_{70} was not observed in the proton-affinity bracketing measurements.[41]

Observations of addition reactions of ions with fullerene molecules also have been reported. The ion $C_2H_5^+$ derived from the ionization of methane and the ions $C_3H_7^+$ and $C_4H_9^+$ derived from the ionization of isobutane have been reported to attach to C_{60} and C_{70} in the studies of the proton affinities of these fullerene molecules.[41] Related chemical-ionization experiments directed to the detection of fullerene molecules have shown the formation of adducts of C_{60} and C_{70} with tropylium ions $C_7H_7^+$ derived from the ionization of benzene.[60] VO^+, but not LaO^+, was observed to attach to C_{60} molecules in FTMS–laser metal desorption experiments.[54c]

IV. Reactions of PAH and Fullerene Ions

A. Recombination with Electrons and Negative Ions

The recombination of PAH cations with free electrons and, since it is likely that PAHs bear a significant fraction of the negative charge in molecular clouds,[1a] by mutual neutralization with negative ions as shown in eq 28 are deemed to be important ion loss processes in these clouds.[81] Of course the presence of fullerene molecules could lead to other important neutralization events such as those given in eqs 29 and 30. The excess energies in such processes are determined by the relative magnitudes of the ionization energy and electron affinity, $\Delta H \approx$ EA − IE. For PAHs, viz. reaction 29, this is of the order of 140 kcal mol^{-1} (6 eV) since the electron affinities of PAHs are typically in the range 0.5 to 1 eV. Because of the high EAs of fullerene molecules [EA(C_{60}) has been estimated to be 2.6–2.8 eV from photoelectron measurements],[82] the excess energy is considerably smaller for fullerene ion recombination, reaction 30, having a value of the order of 110 kcal mol^{-1} (4.7 eV). In principle, an energy up to the excess energy of the recombination is available for the internal excitation and/or fragmentation of the neutral products and it is of great interest to know how this energy is partitioned. Efficient fragmentation would make reactions 29 and 30 important loss processes for PAH and fullerene molecules in interstellar and circumstellar chemistry.

$$\mathrm{PAH^+ + PAH^- \rightarrow PAH + PAH} \qquad (28)$$

$$\mathrm{C_{60}{}^+ + PAH^- \rightarrow C_{60} + PAH} \qquad (29)$$

$$\mathrm{C_{60}{}^+ + C_{60}{}^- \rightarrow C_{60} + C_{60}} \qquad (30)$$

In electron–ion recombination reactions of type 31 and 32 the recombination energy of the cation is available for dissociation of the neutral products, viz. around 7 eV.

$$\mathrm{PAH^+ + e \rightarrow products} \qquad (31)$$

$$\mathrm{C_{60}{}^+ + e \rightarrow products} \qquad (32)$$

There appears to be no experimental or theoretical information available for the recombination of the cations of benzene, PAHs, and the fullerenes either with electrons or with negative ions. With regard to the efficiency of recombination, experience with smaller polyatomic ions investigated with the flowing afterglow Langmuir probe (FALP) technique suggests that the recombination coefficient, α, increases gradually with increasing complexity.[83] Also, the decay of hydrocarbon flame ions, $C_nH_x{}^+$, observed by mass spectrometric sampling as a function of flame height (time) indicates an increase in α from 1.6, 2.2, 3.6, 3.8, 5.1, and 4.9, to 5.8×10^{-7} cm^3 molecule^{-1} s^{-1} for n = 2–8.[84] A separate study of the recombination of $C_3H_3{}^+$ had yielded an estimate for $\alpha = 1 \times 10^{-7}$ cm^3 molecule^{-1} s^{-1}.[85] On this basis we might expect large electron/ion recombination coefficients for PAH ions but clearly there is a need to develop methods for the measurement of the neutralization efficiencies for both PAH and fullerene ions. The same can be said about the measurement of the nature and distributions of the products of these neutralization reactions which are still very much open to question.[86] It is interesting to note that the recombination energy of 7.61 eV for reaction 32 is much less than the apparent activation energy of 18 eV which exists[87] for the fragmentation of $C_{60}{}^+$ by loss of C_2 so that dissociative recombination of $C_{60}{}^+$ may not be efficient, at least not relative to radiative recombination which will be enhanced by the long lifetime expected from the many vibrational degrees of freedom of the complex $(C_{60})^*$.[88] On the other hand, dissociative recombination of $C_{60}{}^+$ derivatized with H or some other substituent(s) may well be more efficient because of the relatively low-binding energy of a substituent.[88] Similar comments apply to the recombination of $C_{60}{}^{2+}$ with electrons.[88]

B. Reactions with Atoms

Reactions with atomic hydrogen are of particular importance to the interstellar and circumstellar chemistry of PAH and fullerene ions. Collisional or radiative association reactions with H atoms will serve to hydrogenate these ions as is illustrated in reaction 33 for the $C_{60}{}^+$ fullerene ion. Neutralization can be achieved if reaction 33 is followed by proton transfer as in reaction 34. If a second reaction with H proceeds by H-atom abstraction instead, reaction 35, the net result is a fullerene ion-catalized recombination of hydrogen atoms. The reaction sequence 33 and 35 is thermodynamically allowed for PAH and fullerene ions so that the presence of these species in principle may contribute to the formation of molecular hydrogen in interstellar clouds which, currently, is attributed to surface recombination on interstellar dust grains.

$$\mathrm{C_{60}{}^+ + H \rightarrow C_{60}H^+} \qquad (33)$$

$$\mathrm{C_{60}H^+ + M \rightarrow C_{60} + MH^+} \qquad (34)$$

$$\mathrm{C_{60}H^+ + H \rightarrow C_{60}{}^+ + H_2} \qquad (35)$$

Experimental studies of reactions of PAH$^+$ ions with atoms have been very few. A very recent SIFT study has shown that H atoms attach readily at 297 ± 3 K and 0.35 Torr of helium to the ions derived from benzene and naphthalene in reactions of type 36 with second-order rate constants having values exceeding 5×10^{-11} cm^3 molecule^{-1} s^{-1}.[89] However, a further reaction with atomic hydrogen to release molecular hydrogen in reactions of type 37 were observed not to occur.

$$\mathrm{PAH^+ + H \rightarrow (PAH)H^+} \qquad (36)$$

$$\mathrm{(PAH)H^+ + H \rightarrow PAH^+ + H_2} \qquad (37)$$

Apparently PAH$^+$ ions of this type do not catalyze the recombination of hydrogen atoms under the operating conditions of the SIFT experiments.

Recent SIFT experiments have shown that the fullerene ions $C_{60}{}^+$, $C_{60}{}^{2+}$, $C_{70}{}^+$, and $C_{70}{}^{2+}$ all add atomic hydrogen or deuterium with remarkably high efficiency at 294 ± 2 K in helium at 0.40 Torr.[58e] The measured second-order rate constants for the reactions of $C_{60}{}^+$ and $C_{60}{}^{2+}$ with H atoms, for example, were reported to be larger than 1 and 3×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. Further H-atom addition reactions were observed to establish $C_{60}H_n{}^+$ with n up to 3 (a tentative identification of $C_{60}D_4{}^+$ was reported) and $C_{60}H_n{}^{2+}$ with n up to 4. These association reactions are presumed to occur by termolecular reactions under the experimental

SIFT conditions. The possibility of analogous radiative association reactions gives credence to the suggestions that fullerene ions may act as a sink for interstellar hydrogen atoms and that the spectral characteristics of multiply-hydrogenated fullerene ions and neutrals, also known as fulleranes, should be compared with currently unidentified interstellar absorption and emission features.[16,58e,88] The possibility of fullerene cation-catalyzed recombination of H atoms has not yet been ruled out by the experimental results.

Recent mass spectrometer beam experiments have shown that C_{60}^+ and C_{70}^+ can take up atoms and possibly molecules in keV collisions and so to form endohedral fullerene ions. He, Ne, and possibly Ar and H_2 have been seen to be incorporated into C_{60}^+ and C_{70}^+ at ion energies in the range from 2 to 8 keV.[90-92] A time-of-flight mass spectrometer experiment has shown that the incorporation of helium has a center-of-mass threshold energy at 6±2 eV with a maximum capture occurring at about 32 eV.[93] C_{70}^+ has been seen to take up two He atoms under multiple-collision conditions to form $C_{70}He_2^+$.[92] Also, doubly- and triply-charged cations of C_{60} have been seen to take up He in high-energy beam experiments.[94] Ab initio molecular orbital calculations of the energy barrier for the penetration of a benzene ring by a helium atom have been presented as model studies of the formation of endohedral $He@C_{60}^+$ by high-energy bimolecular reaction.[95] Molecular dynamics simulations have provided a detailed picture of the trapping process.[96] They predict that optimal endohedral complex formation in collisions between C_{60}^+ and He should occur at ion energies of 8 keV which is consistent with the experimental observation of optimal uptake at 5–6 keV.[90-92]

Finally, it has been suggested that cosmic ray interactions may also lead to the formation of endohedral complexes of atoms or atomic ions trapped within fullerene cages.[88] While a close model to cosmic ray trapping, a high-energy collision involving H^+ and C_{60}, has not yet been studied experimentally, it is anticipated that any small ion should be capable of intercalation within the fullerene cage in this manner. Since most cosmic rays are protons, deuterons, and α particles, the most likely candidates for formation of endohedral complexes in this manner are H, D, and He.

C. Reactions with Molecules

Reactions of $C_6H_6^+$ and $C_{10}H_8^+$ with various interstellar and other molecules have been measured in a complementary study performed with the SIFT and FTICR techniques.[70] The reactions observed and rate constants determined with the SIFT technique in helium buffer gas at a total pressure of 0.35 Torr and 296 ± 2 K are summarized in Table I. $C_6H_6^+$ was produced by the charge-transfer reaction between NO^+ and C_6H_6 which is exothermic by only 0.018 eV. $C_{10}H_8^+$ was derived either by electron-impact ionization of naphthalene or from the association reaction of ionized benzene with diacetylene. The observed failure to react with deuterium excludes both D-atom transfer and D-atom exchange as possible reaction channels. The association reaction of $C_6H_6^+$ with diacetylene was also investigated with the FTICR technique at about 10^{-6} Torr and was found to have a rate constant of about 1×10^{-10} cm^3 molecule^{-1} s^{-1} which is somewhat lower than the SIFT value measured at much higher pressures, but still quite large. This result may imply that the addition reaction proceeds by radiative association. Indeed, the Dunbar model for radiative association[97] predicts an efficiency of close to unity for this radiative association at 300 K. Another molecule of C_4H_2 was observed to add to $C_{10}H_8^+$ in the SIFT experiments but at a rate 500 times slower. The observation of this slow addition of diacetylene to $C_{10}H_8^+$ contrasts the failure to observe any addition with acetylene or styrene.

Table I. Summary of Rate Constants (in 10^{-9} cm^3 molecule^{-1} s^{-1}), Reaction Efficiencies, and Products Determined for Reactions of $C_6H_6^+$ Radical Cations Produced from Benzene by Chemical Ionization with NO^+ and for the Reactions of $C_{10}H_8^+$ Cations Derived (a) by Ionization of Naphthalene or (b) from the Association of Ionized Benzene with Diacetylene at 296 ± 2 K

	k_{exp}[b]		
reaction[a]	(a)	(b)	k_{exp}/k_c[c]
$C_6H_6^+ + D_2 \rightarrow$ no reaction	≤0.0002		≤0.0002
$C_8H_6^+ + C_2H_2 \rightarrow$ no reaction	≤0.0004		≤0.0004
$C_6H_6^+ + C_4H_2 \rightarrow C_{10}H_8^+$	0.5		0.5
$C_8H_6^+ + C_6H_6 \rightarrow C_{12}H_{12}^+$	>0.05		>0.04
$C_6H_6^+ + C_0H_8^+ \rightarrow C_0H_6^+ + C_6H_6$	0.78		0.5
$C_{10}H_8^+ + D_2 \rightarrow$ no reaction	≤0.0004	≤0.0004	≤0.0004
$C_{10}H_8^+ + C_2H_2 \rightarrow$ no reaction	≤0.001	≤0.001	≤0.001
$C_{10}H_8^+ + C_4H_2 \rightarrow C_{14}H_{10}^+$	≤0.001	≤0.001	≤0.001
$C_{10}H_8^+ + C_8H_8 \rightarrow$ no reaction	≤0.001	≤0.001	≤0.0007
$C_{10}H_8^+ +$ $(CH_3)_3N \rightarrow (CH_3)_3N^+ + C_{10}H_8$ 0.8 (0.7) $\rightarrow (CH_3)_3NH^+ + C_{10}H_7$ 0.2 (0.3)	1.1	1.0	1.0
$C_{10}H_8^+ + NO \rightarrow$ no reaction	≤0.0002	≤0.0002	≤0.0003

[a] C_6H_6 and C_8H_8 represent the vapors of benzene and styrene, respectively. The product distributions are rounded off to the nearest 5% and are estimated to be accurate to within ±30%. [b] The effective bimolecular rate constant is given at a total helium pressure of 0.35 Torr. The accuracy of the rate constants is estimated to be better than ±30%. [c] k_{exp}/k_c is a measure of the reaction efficiency. Collision rate constants, k_c, are derived from the combined variational transition state theory–classical trajectory study of T. Su and W. J. Chesnavich (*J. Chem. Phys.* 1982, *76*, 5183).

Chemical reactivity and photodissociation measurements were used to explore the identity of the $C_{10}H_8^+$ product ion in the association reaction of $C_6H_6^+$ with C_4H_2 and they suggest that it has the structure of ionized naphthalene.[70] The $C_{10}H_8^+$ ions produced in these two ways have been shown to have identical reactivities, within experimental error, with D_2, C_2H_2, C_4H_2, C_8H_8 (styrene), $(CH_3)_3N$, and NO under SIFT conditions, and with 1,2,4,5-tetramethylbenzene and *p*-methylaniline by charge transfer under FTICR conditions. In contrast, $C_{10}H_8^+$ ions produced by electron impact of azulene were unreactive with 1,2,4,5-tetramethylbenzene and reacted more slowly with methylaniline under FTICR conditions.

The reaction of silane with $C_6H_6^+$ produced by electron-impact ionization at 84 eV has been investigated at an ion energy of 1.0 eV in a tandem mass spectrometer.[55] The phenomenological rate constant was reported to be 7×10^{-11} cm^3 molecule^{-1} s^{-1} and products were observed with m/z = 31 (SiH_3^+), 39 ($C_3H_3^+$), and 52 (SiC_2^+ or $C_4H_4^+$) with cross sections of 3.8, 0.2, and 0.5 Å^2, respectively.

The formation of both radical dimer cations and protonated dimer cations of polycyclic aromatic molecules by association reactions of the type $B^+ + B \rightleftarrows B^+{\cdot}B$ and $BH^+ + B \rightleftarrows BH^+{\cdot}B$ has been reported in a pulsed-ionization high-pressure mass spectrometry study of their binding energies.[98] Radical dimer cations of the type $B^{+}\cdot B$ have been observed for B = benzene, 1,3,5-trimethylbenzene, naphthalene, azulene, acenaphthene, biphenylene, fluorene, anthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, phenanthrene, pyrene, chrysene, perylene, 1,12-benzoperylene, and coronene. The observation of protonated dimer cations of the type $BH^{+}\cdot B$ was also reported for these molecules with the exception of azulene and coronene. Furthermore, mixed adduct ions of the type $B^{+}\cdot A$ and $BH^{+}\cdot A$ were reported for B^{+} = biphenylene^{+} with acenaphthene, fluorene, naphthalene, and biphenyl, for B^{+} = azulene with biphenylene, fluorene and biphenyl, and for BH^{+} = (biphenylene)H^{+} with naphthalene. Relative third-order rate constants, mostly at 25 ± 2 °C, for the formation of $B^{+}\cdot B$ from B^{+} have been measured in a high-pressure photoionization source for a variety of aromatic molecules including benzene, toluene, xylenes, and halogenated benzene and toluene.[99] Furthermore, reagent ion monitoring has been used to the relative rates of reactions of the dimer $B^{+}\cdot B$ and the monomer B^{+} ions with a series of mainly aromatic molecules, A.[99] $C_6H_6^{+}$ reacts primarily by charge transfer with molecules of a lower ionization energy than C_6H_6. $(C_6H_6)_2^{+}$ reacts only by charge transfer if the ionization energy of A is more than 0.5 eV lower than that of benzene. When the difference is smaller, mixed adduct ions are observed to be formed probably by switching reactions of type 38. Absolute reaction rates have been reported for

$$(C_6H_6)_2^{+} + A \rightarrow (C_6H_6\cdot A)^{+} + C_6H_6 \qquad (38)$$

reactions 39 and 40 for which $k = (1.3 \pm 0.3) \times 10^{-9}$ and $(1.5 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, respectively.[98]

$$(C_6H_6)_2^{+} + \text{octahydroanthracene} \rightarrow \text{octahydroanthracene}^{+} + 2C_6H_6 \qquad (39)$$

$$(C_6H_6)_2^{+} + \text{naphthalene} \rightarrow \text{naphthalene}^{+} + 2C_6H_6 \qquad (40)$$

C_{60}^{+} has been found to be unreactive toward H_2, O_2, NO, and NH_3 and both C_{50}^{+} and C_{60}^{+} were found to be unreactive with diacetylene under FTICR conditions.[100,101]

Charge-transfer reactions of C_{60}^{+} and C_{70}^{+} were investigated as part of a larger bracketing study of the ionization energies of C_n cluster molecules.[20] The following molecules were used as reagents (the ionization energy of the molecule is given in parentheses in eV): durene (8.04), hexamethylbenzene (7.85), aniline (7.72), *m*-toluidine (7.50), azulene (7.41), *p*-toluidine (7.24), *N,N*-dimethylaniline (7.13), *N,N*-diethylaniline (7.00), *N,N*-dimethyl-*p*-toluidine (6.93), ferrocene (6.75), methylferrocene (6.45), and nickelocene (6.20). Charge transfer was observed with the molecules with IE ≤ 7.50 eV and not with molecules with IE ≥ 7.72 eV. There was no evidence for different isomeric species with significantly different reactivities. C_{60}^{+} and C_{70}^{+} were found to react at a somewhat slower rate (up to about 2 times slower) than the other carbon cluster ions with ferrocene, methylferrocene, and nickelocene and at a faster rate (from about 2 to 3 times faster) with *N,N*-diethylaniline. It has been suggested that the reduced reactivities with the metallocenes is due to poor electron-orbital overlap as has been described for self-electron-exchange reactions of metallocenes.[102]

Table II. Reactions of $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ with Various Neutral Molecules at 294 ± 3 K

neutral	products[a]	k_{60}[b]	k_{70}[c]	$k_{c,300}$[d]
NH_3	$C_{60}\cdot NH_3^{\cdot+}$	0.0005	<0.001	1.7
CH_3NH_2	$C_{60}\cdot CH_3NH_2^{\cdot+}$	0.09	<0.01	1.4
$(CH_3)_2NH$	$C_{60}\cdot (CH_3)_2NH^{\cdot+}$	2.0	obs[e]	1.2
$(CH_3)_3N$	$C_{60}\cdot (CH_3)_3N^{\cdot+}$	2.5	obs[e]	1.05
$CH_3CH_2NH_2$	$C_{60}\cdot CH_3CH_2NH_2^{\cdot+}$	0.7	obs[e]	1.3
c-C_5H_6	$C_{60}\cdot C_5H_6^{\cdot+}$	0.03	obs[e]	1.0

[a] Products shown are those for $C_{60}^{\cdot+}$ + X. In all cases, the product channels observed for $C_{70}^{\cdot+}$ + X were entirely analogous. [b] Observed effective bimolecular reaction rate coefficient for $C_{60}^{\cdot+}$ + X at 0.40 Torr in helium, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] Observed effective bimolecular reaction rate coefficient for $C_{70}^{\cdot+}$ + X at 0.40 Torr in helium, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [d] ADO collision rate coefficient (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}), calculated according to the method of T. Su and M. T. Bowers (*Int. J. Mass Spectrom. Ion Phys.* 1973, *12*, 347), for $C_{60}^{\cdot+}$ + X at 300 K. The difference in calculated collision rates for $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ are always less than 1%. [e] Reaction observed, but rate coefficient not determined.

C_{60}^{+} and C_{70}^{+} have been observed not to react under SIFT conditions in helium at 0.40 Torr with the molecules H_2, D_2, N_2, O_2, CO, NO, CO_2, COS, $(CH_3)_2O$, CH_4, C_2H_2, C_2H_4, C_2H_6, CH_3CCH, CH_2CCH_2, $CH_2CHCHCH_2$, C_6H_6, and $C_{10}H_8$ ($k \leq 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and with the molecules H_2O and $C_{10}H_8$ ($k \leq 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).[88,103] Ammonia and the amines, molecules of significant interstellar abundance, as well as cyclopentadiene, were observed to add to C_{60}^{+} and C_{70}^{+}. As indicated in Table II, the reaction with ammonia was observed to be very inefficient, but more highly substituted amines such as $(CH_3)_2NH$ and $(CH_3)_3N$ were observed to add extremely rapidly. This tendency has suggested that the amine and alkylammonium functionalization may be comparatively common for interstellar fullerenes.[88] There has been one interesting report of an FTMS study in which kinetically or internally excited C_{60}^{+} was observed to react with $Fe(CO)_5$ to form $Fe(CO)_4C_{60}^{+}$ and $Fe(CO)_3C_{60}^{+}$ (with the release of CO and 2CO, respectively) in about equal amounts.[104]

Charge-transfer reactions of C_{60}^{2+} and C_{70}^{2+} have been investigated as part of a bracketing study of IE(C_{60}^{+}) and IE(C_{70}^{+}). In an FTICR study at low pressures C_{60}^{2+} was observed to charge transfer to *m*-nitrotoluene (IE = 9.48 eV) and to molecules with lower IEs, but not to hexafluorobenzene (IE = 9.91 eV) or to compounds having higher IEs.[40] C_{70}^{+} was observed to charge transfer to *m*-dichlorobenzene (IE = 9.11) and to molecules with lower IEs, but not to fluorobenzene (IE = 9.20 eV) or to molecules with higher IEs. In a SIFT investigation in He at 0.40 Torr and 294 K charge transfer reactions with various neutrals occurred with measurable rates (see Table III).[41] Charge transfer was not observed for molecules with IE ≥ 9.69 eV (for C_{60}^{2+}) and IE ≥ 9.26 eV (for C_{70}^{2+}) in keeping with the FTICR results. Charge-transfer reactions have also been reported for these two fullerene dications reacting with benzene, naphthalene, anthracene, C_{60}, and C_{70} under SIFT conditions.[105] The failure to observe competing adduct formation under these conditions has been

Table III. Reactions of C_{60}^{2+} and C_{70}^{2+} with Various Neutral Molecules at 294 ± 3 K

neutral	products[a]		k_{60}[b]	k_{70}[c]	$k_{c,300}$[d]
NH_3	$C_{60}{\cdot}NH_3^{2+}$		1.2	0.7	3.4
CH_3NH_2	$C_{60}{\cdot}CH_3NH_2^{2+}$	[0.90]	2.4	obs[e]	2.9
	$C_{60}^{\cdot+} + CH_3NH_2^{\cdot+}$	[0.10]			
$(CH_3)_2NH$	$C_{60}{\cdot}(CH_3)_2NH^+$	[0.10]	7.0	obs[e]	2.4
	$C_{60}^{\cdot+} + (CH_3)_2NH^{\cdot+}$	[0.90]			
$(CH_3)_3N$	$C_{60}^{\cdot+} + (CH_3)_3N^{\cdot+}$		5.4	obs[e]	2.1
$CH_3CH_2NH_2$	$C_{60}{\cdot}CH_3CH_2NH_2^{2+}$	[0.70]	5.0	obs[e]	2.7
	$C_{60}^{\cdot+} + CH_3CH_2NH_2^{\cdot+}$	[0.30]			
C_2H_2	$C_{60}{\cdot}C_2H_2^{2+}$		<0.001	<0.001	1.8
C_2H_4	$C_{60}{\cdot}C_2H_4^{2+}$		<0.001	<0.001	1.9
CH_2CCH_2	$C_{60}{\cdot}C_3H_4^{2+}$		0.08	0.009	1.85
CH_3CCH	$C_{60}{\cdot}C_3H_4^{2+}$		0.5	0.03	2.3
CH_2CHCH_3	$C_{60}{\cdot}C_3H_8^{2+}$		1.3	>0.4	2.0
C_3H_8	$C_{60}H^+ + C_3H_7^+$		0.002	<0.001	1.9
$CH_2CHCHCH_2$	$C_{60}{\cdot}C_4H_8^{2+}$	[0.80]	1.0	1.0	1.9
	$C_{60}^+ + C_4H_6^{\cdot+}$	[0.20]			
c-C_6H_6	$C_{60}^{\cdot+} + C_6H_6^{\cdot+}$		fast[e]	fast[e]	1.9
C_6H_6	$C_{60}^{\cdot+} + C_8H_6^{\cdot+}$		2.3	0.14	1.8
$C_{10}H_8$	$C_{60}^{\cdot+} + C_{10}H_8^{\cdot+}$		9.0	10.0	1.9
$NO^{\cdot}$	$C_{60}^{\cdot+} + NO^+$		0.02	<0.001	1.2

[a] Products are those detected for C_{60}^{2+}. Unless otherwise indicated, the product channels detected for C_{70}^{2+} are entirely analogous. Where more than one product channel was detected, the branching ratio (for C_{60}^{2+}) is given in square brackets. [b] Observed effective bimolecular reaction rate coefficient for C_{60}^{2+} + X at 0.40 Torr in helium, in units of 10^{-9} cm³ molecule^{-1} s^{-1}. [c] Observed effective bimolecular reaction rate coefficient for C_{70}^{2+} + X at 0.40 Torr in helium, in units of 10^{-9} cm³ molecule^{-1} s^{-1}. [d] ADO collision rate coefficient (in units of 10^{-9} cm³ molecule^{-1} s^{-1}), calculated according to the method of T. Su and M. T. Bowers (*Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347), for C_{60}^{2+} + X at 300 K. The difference in calculated collision rates for C_{60}^{2+} and C_{70}^{2+} are always less than 1%. [e] Reaction observed, but rate coefficient not determined.

interpreted to imply that doubly-charged fullerene cations are unlikely to act as nuclei for the condensation of aromatic molecules or to initiate the formation of doubly-charged fullerene clusters or "strings of fullerene beads".[105]

Slow hydride transfer as indicated by eq 41 has been observed in SIFT experiments between C_{60}^{2+} and the saturated hydrocarbon molecules C_3H_8, n-C_4H_{10} and i-C_4H_{10}.[103] Otherwise adduct formation was commonly

$$C_{60}^{2+} + RH \rightarrow C_{60}H^+ + R^+ \qquad (41)$$

observed as with the following polar molecules and unsaturated hydrocarbons:[106,107] XH = NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, CH_3CN, CH_2CHCN, $CH_3CH_2CH_2CN$, CH_3OH, CH_3CH_2OH, CH_3COCH_3, $CH_3COC_2H_5$, HCOOH, $HCOOCH_3$, and CH_3COOH. No reactions were seen with H_2O, CH_3OCH_3, H_2CO, and CH_3CHO. The adduct ions showed interesting secondary reactions in that adduct formation was observed to compete with proton transfer as shown in eq 42:

$$C_{60}XH^{2+} + XH \rightarrow C_{60}(XH)_2^{2+} \qquad (42a)$$

$$\rightarrow C_{60}X^+ + XH_2^+ \qquad (42b)$$

The primary and secondary addition reactions have been ascribed to the formation of dative bonds between the carbon atoms bearing the positive charges in the fullerene shell and an atom (the electronegative atom in the case of the polar molecules listed above) of the reacting molecule. This proposed method of addition restricts the number of molecules added to the number of charges on the fullerene. Indeed, no more than two additions were seen in the reactions of C_{60}^{2+} which were investigated. Three examples of "winged" structures of the double adducts, $C_{60}(XH)_2^{2+}$, are given in Figure 1. Proton transfer, reaction 42b, was observed to compete with adduct formation, reaction 42a, in a number of cases,[106,107] as, for example, in the reaction with ammonia in which proton transfer dominates:[106]

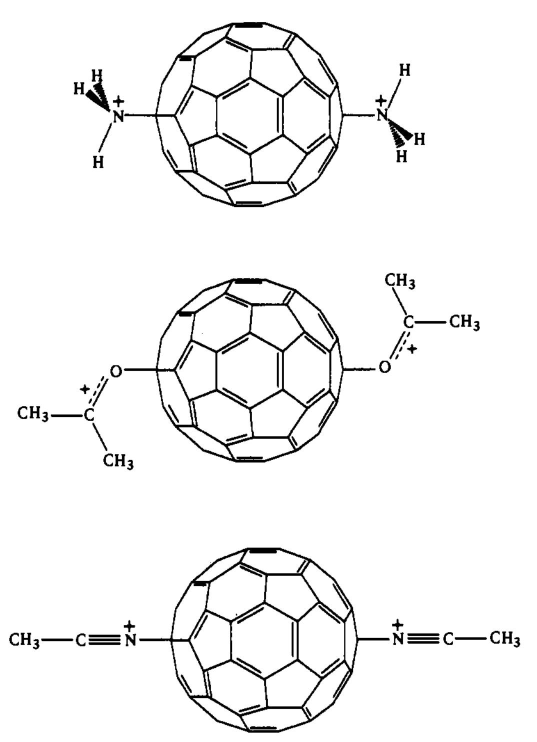


Figure 1. Three examples of proposed "winged" structures for double adducts of the type $C_{60}(XH)_2^{2+}$ where XH = NH_3, $(CH_3)_2CO$, and CH_3CN.

$$C_{60}NH_3^{2+} + NH_3 \rightarrow C_{60}NH_2^+ + NH_4^+ \qquad (43a)$$

$$\rightarrow C_{60}(NH_3)_2^{2+} \qquad (43b)$$

When coupled with neutralization by recombination with electrons or proton transfer, the formation of these fullerene adduct ions in this fashion provides interesting possibilities for the derivatization of neutral fullerene molecules by ion/molecule reactions.[88]

No reactions were observed under SIFT conditions between the doubly-charged fullerene ions C_{60}^{2+} and C_{70}^{2+} and the molecules H_2, D_2, N_2, O_2, CO, CO_2, COS, CH_4, and C_2H_6 ($k \leq 1 \times 10^{-12}$ cm³ molecule^{-1} s^{-1}) and H_2O ($k \leq 1.0 \times 10^{-11}$ cm³ molecule^{-1} s^{-1}).[103]

The observation[58c] of efficient association reactions of C_{60}^+ and C_{60}^{2+} with H suggests that other association reactions of these ions with radicals may also occur. While experimental studies of such reactions would be very difficult to perform, the associations of singly- and doubly-charged fullerene cations with radical species such as CH_3, OH, C_2H, CN, and C_2H_3 are likely to be efficient and would be well worth experimental investigation. The exceptional ability of neutral fullerenes to add, repeatedly, radicals such as CH_3 and C_6H_5 has already been reported.[108]

There has been one report of an FTICR study of the chemistry of the triply-charged fullerene cation C_{60}^{3+}.[40a]

Reactions were investigated between C_{60}^{3+} and Xe, C_2H_6, C_2H_2, CH_3NO_2, C_3H_8, CH_3OH, C_2H_4, C_6H_5F, and C_6H_6. Hydride abstraction was observed with C_3H_8, oxide abstraction with CH_3NO_2, adduct formation with C_2H_2, and charge transfer with CH_3OH, C_2H_4, C_6H_5F, and C_6H_6.[40a]

V. Synthesis of PAH and Fullerene Ions and Molecules by Ion/Molecule Reactions

Ionized and neutral carbon atoms are born in the interior of carbon stars, and it is in the atmospheres of such stars that their chemistry first springs to life. The astrochemist needs to ask how ensuing chemical reactions can lead to the formation of C–C bonds and the growth of ions and molecules as chains, rings, sheets, and spheres of C atoms which eventually may be transformed into small carbonaceous grains.[109] Can PAH and fullerene ions and molecules be expected to be important products of such growth and can they, in turn, act as intermediates in, or promote, further growth? Current opinions on the production and loss of interstellar PAHs have recently been reviewed by Turner who indicates that PAHs are probably formed mostly in the hot, dense envelopes of evolved stars from which they are ejected into the interstellar medium.[1c] Indeed, it has been argued recently that there is sufficient evidence in observational data and theoretical modeling to show that (asymptotic giant branch) carbon stars are a primary source of PAHs.[110] The mixing of PAHs from mass-loss winds of carbon stars into the interstellar medium has also been discussed and it has been shown that if the PAHs have a long lifetime in the interstellar medium (ca. 10^8 years), then the known numbers of the most extreme mass-losing carbon stars are able to produce PAHs in sufficient quantities to maintain the inferred interstellar abundance.[110]

Chemical models have been proposed for the gas-phase formation of large-chain molecules and PAHs in circumstellar envelopes[111] as well as in dense interstellar clouds where similar growth and further processing may take place.[112] It is interesting to note that the chemistry of soot formation in hydrocarbon flames has proven to be a useful basis for some of these models.[111d] Even though such models often are limited because of the lack of information about rate constants, particularly for reactions involving larger molecular ions and molecules, it is clear from these models that gas-phase ion chemistry plays a significant role in the buildup of PAHs in circumstellar and interstellar environments.

The gas-phase synthesis of PAH molecules and ions by ion/molecule reactions has been suggested to be possible in at least two ways: either directly by cross-bonding initiated by the side-on approach of extended chainlike hydrocarbon ions and molecules such as cumulenes or polyacetylenes, or through the successive formation of hexagonal rings beginning with benzene as the embryo.[109] These shall be treated first, before turning to the formation of fullerene ions and molecules.

A. Condensation of Carbon Chains

Laboratory studies have now demonstrated the feasibility of synthesizing benzene with ion/molecule reactions involving acyclic three-carbon units.[113] The bimolecular reactions 44 and 45 occur in ionized allene and propyne, respectively, and lead to the formation of the benzenium ion. Collisional activation and chemical reactivity studies have shown that 70% of the $C_6H_7^+$ ions produced in allene and 44% of the $C_6H_7^+$ ions produced in propyne have the benzenium structure.[113a] The benzenium ion may be neutralized to benzene by proton transfer to a molecule M or recombination with electrons according to reaction 46. Interestingly, the structures of the remaining $C_6H_7^+$ ions formed in reactions 44 and 45 appear to correspond to protonated fulvenes or protonated dimethylenecyclobutenes.[113a]

$$H_2C{=}C{=}CH_2^+ + H_2C{=}C{=}CH_2 \rightarrow C_6H_7^+ + H \quad (44)$$

$$HC{\equiv}C{-}CH_3^+ + HC{\equiv}C{-}CH_3 \rightarrow C_6H_7^+ + H \quad (45)$$

$$C_6H_7^+ + M,e \rightarrow C_6H_6 + MH^+,H \quad (46)$$

Other, analogous combinations of larger chainlike carbon units have been envisaged to lead directly to larger fused-ring structures.[109] For example, the possibility of the growth of graphite-like molecules through the side-on cross-bonding cumulenes or polyacetylenes, where one of the reactants may be ionic, is intriguing. It corresponds to the inverse of the mechanism proposed for the transformation of graphite at high temperatures.[114] When reactions 44 and 45 are regarded as the lowest members of a series of such reactions, the next members would be the reactions of ionized $H_2C{=}C{=}C{=}C{=}CH_2$ and ionized 1,3-pentadiyne with their neutral parent molecules to form ionized naphthalene.[109]

The feasibility of producing benzene with ion chemistry involving only two-carbon units has also been discussed, but it is less certain.[109] Although $C_2H_2^+$ and $C_2H_3^+$ are known to add sequentially two molecules of acetylene to form $C_6H_6^+$ and $C_6H_7^+$ respectively, albeit with a decreasing rate, the structures of the $C_6H_n^+$ ions have not been elucidated.[109,115] However, studies of the ionization of 1,5-hexadiyne by electron impact and by charge-transfer reactions indicate that 1,5-hexadiyne ions isomerize to the benzene ion structure or dissociate to produce $C_6H_5^+$ having the phenylium ion structure, depending on internal energy.[116] The formation of the dimeric intermediates $C_4H_4^+$ and $C_4H_5^+$ ions in the acetylene chemistry is also of interest if they correspond to ionized and protonated cyclobutadiene, respectively. In analogy with proposed neutral chemistry,[117] they could then add methylacetylene, vinylacetylene, and diacetylene to form ionized and protonated toluene, styrene, and phenylacetylene. Similar processes could lead to the formation of the fused-ring ions of indene and naphthalene from a combination of acetylene, methylacetylene, and vinylacetylene in the case of indene, and a combination of either acetylene and two vinylacetylene molecules, or acetylene, methylacetylene, and methyldiacetylene in the case of naphthalene.

It is also of interest to know whether non-carbonaceous ions can act to catalyze the formation of benzene from smaller carbon units. Recent neutralization–reionization mass spectrometry (NRMS) experiments have demonstrated that the oligomerization of acetylene ($xC_2H_2 \rightarrow C_{2x}H_{2x}$; x = 2–4) can be mediated by Fe^+ in the gas phase.[118] It was shown that the preferred structure is $Fe^+{\cdot}(C_2H_2)_2$ for $x = 2$; isomerization to $Fe^+{\cdot}c\text{-}C_4H_4$ or the formation of the ferracyclopentadiene ion were both negligible. When a third molecule of acetylene is added a substantial fraction of the trimer $Fe^+{\cdot}(C_2H_2)_3$ isomerizes to $Fe^+{\cdot}C_6H_6$. Addition of a further molecule of C_2H_2 showed no evidence for the formation of a $Fe^+{\cdot}c\text{-}C_8H_8$ complex; the barrier to the isomerization $Fe^+{\cdot}C_6H_6{\cdot}C_2H_2 \rightarrow Fe^+{\cdot}C_8H_8$ is apparently too high. Charge transfer studies with 1,5-hexadiyne suggest an ion-assisted isomerization reaction of type 47, where M^+ may be an atomic ion.[116k]

$$M^+ + HC{\equiv}CCH_2CH_2C{\equiv}CH_2 \rightarrow [M{\cdot}HC{\equiv}CCH_2CH_2C{\equiv}CH]^+ \rightarrow [M{\cdot}\text{benzene}]^+ \rightarrow M + \text{benzene}^+ \quad (47)$$

B. Growth of Polyhedral Carbon Ions

1. Ring Formation in One Step

Growth of PAH molecules has also been envisaged to proceed by the evolution of additional aromatic rings, for example through the development of a side chain which ultimately closes by the sequential addition of a combination of 1,2, and 3 carbon units or in one step through a condensation reaction with a polycarbon species.[109] The latter mechanism has been proposed for the high-temperature polymerization of PAHs[119] and is a basis for the perceived growth of the large aromatic ions which are believed to be precursors in the ionic formation of soot[120,121] in hydrocarbon flames.

Details of the kinetics and mechanism of such growth have not yet been characterized in the laboratory, although some results have recently become available for the first few steps. SIFT and FTICR experiments have shown that diacetylene adds efficiently to $C_6H_6^+$ in helium buffer gas at 0.35 Torr and 296 ± 2 K according to reaction 48.[70] With regard to the further growth of

$$C_6H_6^+ + C_4H_2 \rightarrow C_{10}H_8^+ \quad (48)$$

the naphthalene ion, it is interesting to note that some addition of diacetylene to the naphthalene cation was observed in the SIFT experiments but at a rate more than 500 times slower than the addition to the benzene cation. These results imply that formation of anthracene or phenanthrene cations may be possible at room temperature, but with a much reduced rate. However, higher-order addition reactions of this type may be much more facile in hot circumstellar envelopes. In this connection it is interesting to note that the appearance of PAH^+ in fuel-rich flames ($C/O \geq 0.6$) is associated with an increase in the concentration of diacetylene.[121]

Condensation reactions of type 48 have been suggested for the growth of PAH^+ ions and oxo-PAH^+ ions in benzene/oxygen flames. For example, the very exothermic (80 kcal mol^{-1}) condensation reaction of ring-protonated phenol with diacetylene has been proposed as a source of ring-protonated naphthol.[122]

2. Ring Formation in Several Steps

An alternative to growth of aromatic rings in one step is the growth of side chains in multiple steps with eventual cyclization. Such a method of growth is more versatile, in principle, since rings may be formed which are not necessarily hexagonal and may contain 4, 5, 7, etc. C atoms. The most elementary version of such growth with the successive addition of single-carbon units has been proposed for growth of side chains on aromatic molecules in interstellar gas clouds in which C or C^+ are relatively abundant.[1a] Other building blocks in these environments might be CH_3^+, $C_2H_2^+$, $C_2H_3^+$, and $C_3H_3^+$.[109]

The laboratory measurements for the reaction of C^+ with benzene indicate that, aside from charge transfer, both condensation and destruction reactions proceeding through a $(C_7H_6^+)^*$ intermediate complex are important. For naphthalene and larger PAH molecules similar exothermic channels exist. It has been proposed that the intermediate complex might stabilize by IR emission in the interstellar medium and do so with a much larger probability for the analogous reactions with naphthalene and larger PAH molecules.[1a]

The counter reactions of ionized aromatic molecules with neutral building-block molecules such as methane, acetylene, and methylacetylene also should be considered in the chemistry of formation of PAH ions and molecules. For example, a two-step synthesis of $C_{10}H_8^+$ with acetylene, perhaps with ionized ethynylbenzene or ionized ethenylbenzene as intermediates, is thermodynamically favorable.[70] However, interestingly, acetylene was observed not to add to $C_6H_6^+$ at room temperature so that this mechanism is not favorable and no other examples are known.[70]

3. Coagulation of PAHs

Coagulation of PAH molecules in the gas phase has been proposed to contribute, but probably in a relatively minor fashion, to the evolution of PAHs in dense interstellar clouds.[1a] Condensation reactions of this type with one of the PAH molecules carrying a positive charge are now well characterized in the laboratory, particularly when they proceed in a buffer gas at moderate pressures as described in section IV.C. Little is known about the efficiency of "coagulation" at the low pressures of interstellar clouds where such processes would have to occur by radiative stabilization.

4. Chemi-ionization

Chemi-ionization reactions of type 49 also have been proposed as a possible source for larger PAH species.[122]

$$\text{PAH} + \text{PAH} \rightarrow \text{poly-PAH}^+ + e \quad (49)$$

However, there are no known examples of such reactions. They are unlikely to be exothermic at room temperature since the energy gained in the bonding of the poly-PAH^+ ion would have to exceed its recombination energy.

C. Growth of Closed-Shell Polyhedral Carbon Ions

Direct laser vaporization of graphite experiments using photoionization time-of-flight mass spectrometry (PITOFMS),[123] direct TOFMS,[124] FTICRMS,[125] and double-focusing MS[126] have provided a wealth of data on the production of high-mass cluster ions having more than 30 C atoms. Laser TOF mass spectra of the PAHs chrysene, pyrene, and anthracene have been reported, showing even-numbered carbon clusters up to C_{584}^+.[127]

Laser-desorption FTMS experiments with benzene soot samples have led to the observation of PAH ions below m/z 1000 and even-numbered carbon-cluster ions extending above m/z 7200![128] The formation of fullerene ions from graphite has been attributed to ion/molecule reactions that occur in the laser-induced plasma which is generated in the small channel which is drilled into the sample a longer irradiation times, rather, than the result of the detachment of large graphitic sheets.[123b,125,129]

Simple kinetic mechanisms for carbon-cluster growth have been discussed and developed to explain features of ionic carbon clusters that have been observed by laser vaporization mass spectrometry.[129] The mechanisms are based on stepwise addition of small carbon species (C to C_3) followed by collisional quenching or unimolecular decomposition. A model has been presented which examines the variation of cluster-size distributions with plasma density, the formation of cluster ions with "magic numbers", the formation of predominantly even clusters, the loss of hydrogen from clusters formed in a hydrogen-containing plasma, and the effect of isomerization of large clusters ($n > 31$) on the high-mass distribution.[129a] Remarkable agreement is found between experimental observations and the gas-phase kinetic model.

A large number of different polyhedral carbon ions with supposedly closed-shell structures have been detected in sooting acetylene and benzene/oxygen flames.[130] Considerations of the measured profiles for these ions and the influence of C/O ratio and the unburned gas velocity support a mechanism of formation from small soot particles rather than by growth from smaller building blocks. No correlation is observed between the growth of the PAH and the appearance of the fullerene ions.[131] Oxidation and pyrolysis at the outer carbon layers of the particles is proposed to lead to the removal of C and H atoms from an outer six-membered ring to form the necessary five-membered rings. The fullerenes form subsequently as the curved-particle layers dissociate. A related, but more detailed, proposal has been advanced for the growth of fullerene molecules in benzene/oxygen flames.[122] Two large PAH species oriented face-to-face are viewed to condense via a radical-zipper mechanism which involves the formation of radical sites by H_2 elimination followed by C–C bond formation. The tension created by the five-membered rings formed along the seam is minimized by isomerization.[132] This mechanism is remarkably versatile in that several different-sized patches of PAH can be zippered together to produce a particular fullerene molecule and can account for the appearance of fullerene ions before PAHs have had a chance to build up to an equivalent carbon content by sequential reactions.

A theoretical nucleation mechanism in which the efficient formation of fullerene molecules is reduced to a purely geometric problem has been developed to track various nucleation pathways toward large fullerene molecules.[133] The model draws attention to the possible formation of various structural isomers, the intramolecular rearrangement of isomers, the role of cumulative chains and single cumulative rings in early stages of nucleation, and the role of the naphthaleno octyl radical, C_{10}, as the essential monomer for fullerene nucleation.

Table IV. Thermochemical Data Obtained from Equilibrium Constant Measurements for Benzene Addition Reactions of the Type $M^+{\cdot}B_n + B \rightleftarrows M^+{\cdot}B_{n+1}$

reactant ion	$-\Delta H°$ (kcal mol^{-1})	$-\Delta S°$ (cal mol^{-1} K^{-1})	$-\Delta G°$ (kcal mol^{-1})
Na^+	28.0 ± 0.1	31.2 ± 0.2	18.7
Pb^+	26.2 ± 0.4	21.6 ± 0.6	19.8
K^+	19.2	24.6	11.9
$K^+{\cdot}B$	18.8	33.9	8.8
$K^+{\cdot}B_2$	14.5	32.7	4.7
$K^+{\cdot}B_3$	12.6	41.4	0.3

An overview of mechanisms of formation or "self-assembly" of fullerene molecules, particularly those which relate to fullerene formation induced by laser ablation or resistive heating of graphite has appeared very recently.[134] The point is made that "there must be hundreds of mechanisms whereby a fullerene like C_{60} can form". None of these are as yet fully resolved.

VI. Gas-Phase Surface Chemistry with PAH and Fullerene Ions and Molecules

PAH and fullerene molecules, either free or embedded in grains, have been proposed as important sites for the chemistry and catalysis of interstellar and circumstellar reactions.[13,135] Furthermore, as a consequence of their large number of carbon atoms, PAH and fullerene molecules might be expected to share several basic properties with carbonaceous solids such as graphite, the end member of the PAH series, so that the interaction of an ion with a free PAH or fullerene molecule, as well as the chemistry of the resulting adduct ion, is likely to be similar to the interaction of an ion with larger carbonaceous interstellar grains and its surface chemistry.[1a,c,135] The adduct ions which are of interest in this connection are those in which the bonding is not strongly chemical, viz. where the ion (or atom) is free to react with incoming molecules while weakly "tethered", perhaps electrostatically, to the molecular (or ionic) substrate. Nothing is known about the spectroscopy of such adduct ions so that a telescopic search for their presence in the interstellar or circumstellar gas has not been possible yet.

A. Thermochemistry of Adduct Ions

So far in time, experimental measurements of the thermochemistry of the interaction of ions with PAH or fullerene molecules are not extensive. They have been restricted primarily to interactions with benzene, naphthalene, and C_{60}.

Experimental insight into the energetics of the interaction of atomic ions with benzene has come primarily from gas-phase equilibrium constant measurements. The gas-phase equilibria given in eq 50, where B represents benzene, have been investigated for $n = 1$ to $n = 4$ with measurements of the temperature dependence of the equilibrium constants $K_{n-1,n}$ in a high-pressure ion source.[45] The thermodynamic data derived

$$K^+{\cdot}B_{n-1} + B \rightleftarrows K^+{\cdot}B_n \qquad (50)$$

from these measurements is presented in Table IV. Other equilibrium constant measurements as a function of temperature have provided thermochemical properties for the association reactions 51 and 52 and these are also included in Table IV.[46]

$$Na^+ + C_6H_6 \rightleftarrows Na^+{\cdot}C_6H_6 \qquad (51)$$

$$Pb^+ + C_6H_6 \rightleftarrows Pb^+{\cdot}C_6H_6 \qquad (52)$$

The observation of ligand-switching reactions at room temperature can provide information about relative binding energies and collision-induced dissociation experiments provide insight into the nature of the bonding. An FTMS study of displacement reactions has led to a binding energy 71 ± 3 kcal mol^{-1} > $D°(Co^+–C_6H_6)$ > 61 ± 4 kcal mol^{-1} and $D°(Co^+–C_6H_6) > D°(Fe^+–C_6H_6)$.[78a] The binding energy of Mn^+ to benzene has been placed relative to that with nonaromatic organic molecules with measurements of ligand-exchange reactions.[47b] Other ligand-exchange reactions which have been observed include reactions 53[59] and 54.[49] The

$$AuC_6H_6{}^+ + CH_3CH{=\!=}CH_2 \rightarrow AuC_3H_6{}^+ + C_6H_6 \qquad (53)$$

$$FeC_6H_6{}^+ + C_6H_5OCH_3 \rightarrow FeC_6H_5OCH_3{}^+ + C_6H_6 \qquad (54)$$

naphthalene adduct ion with Si^+ was observed in SIFT experiments at room temperature to be completely unreactive toward benzene, $k < 6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[56] Not even trace amounts of the $Si^+{\cdot}C_6H_6$ adduct ion which might arise from a ligand-switching reaction were observed to be formed. This result implies that $D°(Si^+{\cdot}C_{10}H_8) > D°(Si^+{\cdot}C_6H_6)$.

M^+ (M = V, Fe, Co) is formed exclusively in the collision-induced dissociation and photodissociation of $MC_6H_6{}^+$ produced in reactions with cyclohexene.[136] Bond energies (in kcal mol^{-1}) deduced from photodissociation have been reported for $V^+–C_6H_6$ (62 ± 5), $VC_6H_6{}^+–C_6H_6$ (57), $Co^+–C_6H_6$ (68 ± 5), and $Fe^+–C_6H_6$ (55 ± 5).

Results of FTMS studies of ligand-switching reactions with $FeC_{60}{}^+$ imply that $D°(Fe^+–C_{60}) > D°(Fe^+–C_nH_{2n}) \simeq 40$ kcal mol^{-1}.[54a] Collision-induced dissociation of the $FeC_{60}{}^+$ ions with Ar at center-of-mass energies from 0.6 to 11.8 eV showed $C_{60}{}^+$ as the sole product. This result indicates that charge has been transferred to C_{60} in the $FeC_{60}{}^+$ which is consistent with relative ionization energy of Fe (IE = 7.870 eV) and C_{60} (IE = 7.61 ± 0.02 eV). The collision-induced dissociation of fullerene adducts with molecular ions also has been observed to be consistent with known relative ionization energies as well as relative proton affinities.[41] For example, the adduct of C_{60} and $C_4H_9{}^+$ dissociates to yield $C_{60}H^+$ at low energies (50 eV) under single-collision conditions and the $C_{60}H^+/C_4H_9{}^+$ ratio is greater than 1 which is consistent with the known proton affinities of C_{60} and C_4H_8, $PA(C_{60}) > PA(C_4H_8)$. The fragmentation product is mainly $C_{60}{}^+$ at higher collision energies with multiple collisions and must occur either by sequential loss of C_4H_8 and H or by the loss of C_4H_9 which has an ionization energy higher than that of C_{60}.

B. Structures and Bonding

Information about the structure of ionic adducts of atoms and aromatic molecules has come primarily from theory, and the calculations have been restricted primarily to interactions of ions with benzene. STO-3G calculations for $Na^+{\cdot}C_6H_6$ predict that the structure with C_{6v} symmetry is the most stable.[45,46] The sigma complex was found to be nonbonding. The sodium ion lies 2.13 Å above the center of the benzene ring and does not change the structure and bonding of the benzene very much. A Mulliken population analysis indicates that the sodium carries 86% of the charge and it appears that the bonding is largely electrostatic. A detailed calculation has been performed to gain insight into the nature of the bonding in the related adduct $K^+{\cdot}C_6H_6$. The binding energy was calculated as the sum of the energies due to electrostatic interaction (ion–quadrupole), induction (ion-induced dipole), dispersion and electronic repulsion. The ion–quadrupole and ion-induced dipole energies were found to be nearly equal and to provide the two major contributions to the bonding, but the dispersion interaction was also found to be significant. Ab initio SCF calculations predict a stabilization energy of −12.4 kcal mol^{-1} for the axial structure. The much lower value than that determined experimentally, $\Delta H°(K^+{\cdot}C_6H_6) = 18.8$ kcal mol^{-1}, has been attributed to the failure of the theory to account for London dispersion energies. With regard to the observation of the $K^+{\cdot}(C_6H_6)_4$ complex, the suggestion has been made that four benzene molecules can be accomodated in a tetrahedral arrangement around the K^+ ion, but the resulting structure is very tightly packed. The addition of a fifth molecule of benzene which will have to be far removed from K^+ and so be very weakly bound was not observed. The bonding between Pb^+ and benzene also has been discussed in terms of electrostatic repulsion and Pauli attraction.[46]

SCF-based ab initio calculations have shown that the optimal structure of the $Mg^+{\cdot}C_6H_6$ adduct ion has C_{6v} symmetry with the Mg^+ 4.78 Å above the plane of the benzene.[137] The bonding is electrostatic in origin, principally charge induced dipole, and there is only a small change in the C_6H_6 symmetry. The SCF computed binding energy D_0 has a value of 30.4 kcal mol^{-1}.

Theoretical studies have been reported for the bonding of benzene to the first-row transition-metal ions Sc^+, Ti^+, V^+, Cr^+, Mn^+, Fe^+, Co^+, Ni^+, and Cu^+, and the second-row transition-metal ions Y^+, Nb^+, Ru^+, and Ag^+.[138] Geometrical parameters for selected systems were optimized at the SCF level. The bonding was found to be predominantly electrostatic but a significant enhancement to the bonding arose from metal donation into the π^* orbitals of benzene. Binding energies were computed to an estimated accuracy of ±5 kcal mol^{-1}. Overall there is reasonable agreement between the theoretical and experimental $M^+–C_6H_6$ binding energies, especially for Sc^+, Fe^+, Cu^+, and Ag^+. For the other systems, excluding Ti^+ for which there is only a lower bound, the experimental binding energies are larger than the theoretical values.

Ab initio MO calculations at the MP2/6-31G**//UHF/3-21G* level have predicted the stability order π-complex > C–H insertion complex > ring insertion complex for the adduct of Si^+ with benzene.[57] NRMS experiments have provided experimental evidence for the stabilities of the π-complex $Si^+{\cdot}C_6H_6$ and the C–H insertion complex $C_6H_5SiH^+$.[57]

Recent theoretical studies have considered the structures and bonding of endohedral complexes of C_{60} with H^+, Li^+ and the ten-electron species F^-, Ne, Na^+, Mg^{2+} and Mg^{3+}.[139] The results of the ab initio calculations indicate that placing the ions at the center of the cage results in net stabilization and screening of the charges. The ionic guests either decrease (F^-) or increase (Na^+, Mg^{2+}, Al^{3+}) the cage radius. Calculations have also been presented[139b,c] for the exohedral complexes of Li^+ and Na^+ with C_{60}. The bond-length patterns of the exohedral and endohedral complexes were found to be quite different. Na^+ was found to "hover" 2.571 Å above a five-membered ring and 2.088 Å in the case of Li^+. The recombination energies of the exohedral and endohedral complexes also were found to be quite different: 10.90 vs 10.19 eV (LiC_{60}^+) and 10.95 vs 9.99 eV (NaC_{60}^+) for the endohedral and exohedral complexes, respectively.

C. Reactivities of Adduct Ions

1. Neutralization Reactions

The attachment of electrons to PAH molecules has been proposed to promote the neutralization of atomic ions which recombine slowly with electrons and react inefficiently with hydrogen molecules in diffuse interstellar clouds.[19] The nature of this promotion is shown in reaction 55 where the PAH molecule acts as a catalyst for the atomic ion/electron recombination. An analogous catalysis can be initiated by the attachment of atomic ions to PAH molecules as is illustrated in eq 56 and analogous schemes are feasible with fullerene molecules. There is a serious lack of experimental and theoretical investigations of these two novel routes for PAH- and fullerene-catalyzed atomic ion/electron recombination.

$$\begin{array}{l} e + PAH \rightarrow PAH^- \\ \underline{X^+ + PAH^- \rightarrow PAH} \\ e + X^+ \rightarrow X \end{array} \qquad (55)$$

$$\begin{array}{l} X^+ + PAH \rightarrow (XPAH)^+ \\ \underline{e + (XPAH)^+ \rightarrow X + PAH} \\ X^+ + e \rightarrow X \end{array} \qquad (56)$$

2. Chemical Reactions

In analogy with the neutralization routes, novel routes have been proposed for ion/molecule reactions catalyzed or assisted by PAH molecules.[135] They apply to the fullerene molecules as well. For example, reaction 57 can lead to the catalytic association of the species X^+ and Y. In this sequence the positive charge is associated with X in the adduct $(XPAH)^+$ as it reacts with Y (in a manner other than mere displacement, viz. the interchange of Y and the PAH molecule). The reaction may be viewed to occur in the vicinity and above the surface of the neutral PAH or fullerene molecule.

$$\begin{array}{l} X^+ + PAH \rightarrow (X^+\cdots PAH) \\ \underline{(X^+\cdots PAH) + Y \rightarrow XY^+ + PAH} \\ X^+ + Y \rightarrow XY^+ \end{array} \qquad (57)$$

Table V. Kinetic Data Obtained for Reactions of $SiC_6H_6^+$ and $SiC_{10}H_8^+$ at 296 ± 2 K in Helium Buffer Gas at 0.35 Torr[a]

	$SiC_6H_6^+$			$SiC_{10}H_8^+$		
molecule	reaction	BR	*k*	reaction	BR	*k*
D_2	no reaction		<0.003	no reaction		<0.0035
CO	no reaction		<0.0009	no reaction		<0.0031
N_2	no reaction		<0.002	no reaction		<0.004
O_2	$C_6H_6^+ + SiO_2$	0.9	0.03	$C_{10}H_8^+ + SiO_2$	1.0	0.0037
	$C_6H_6O^+ + SiO$	0.1				
H_2O	$SiC_6H_6^+{\cdot}H_2O$	0.4[b]	2.0	$C_{10}H_8^+ + SiOH_2$	1.0	0.055
	$C_6H_6^+ + SiOH_2$	0.35[b]				
	$C_0H_7^+ + SiOH$	0.25[b]				
NH_3	$SiC_6H_6^+{\cdot}NH_3$	1.0	3.9	$SiC_{10}H_8^+{\cdot}NH_3$	1.0	4.1
C_2H_2	$SiC_0H_6^+$	0.6	0.6	$C_{10}H_8^+ + SiC_2H_2$	0.9	0.63
	$SiC_0H_7^+ + H$	0.4		$SiC_{12}H_{10}^+$	0.1	
C_4H_2	$SiC_4H_2^+ + C_6H_6$	>0.3	7.0	$C_{10}H_8^+ + SiC_4H_2$	1.0	10
	$SiC_6H_8^+{\cdot}C_4H_2$	<0.7				

[a] BR is the branching ratio with an estimated accuracy of ±30%. The rate constant, *k*, is given in units of 10^{-10} cm^3 molecule^{-1} s^{-1} and also has an estimated accuracy of ±30%. [b] Product distribution for the completely deuteriated reaction.

A derivative scheme in which the charge on the X^+ is transferred to the PAH or fullerene molecule in the first step and a neutral reaction occurs in the second step in the vicinity and above the surface of the charged PAH (or fullerene molecule) is shown in reaction 58.

$$\begin{array}{l} X^+ + PAH \rightarrow (X^+\cdots PAH) \\ \underline{(X^+\cdots PAH^+) + Y \rightarrow XY + PAH^+} \\ X^+ + Y \rightarrow PAH \rightarrow XY + PAH^+ \end{array} \qquad (58)$$

This scheme is not catalytic since the PAH (or fullerene) molecule is not regenerated as a neutral molecule. But, from a point of view of molecular synthesis, it has the attractive feature that it leads directly to the formation of a bonded neutral molecule and it does so without requiring a separate neutralization step. The positive charge ends up on the departing PAH molecule.

In both reactions 57 and 58 the reaction of the adduct ion is critical to the occurrence of the overall reaction. Known examples of such reactions are few. They have been investigated in the greatest detail for adducts of Si^+ with benzene and naphthalene. One isolated example which is related is the reaction of the $FeC_6H_6^+$ adduct ion with benzaldehyde which has been reported to proceed both by elimination of CO, reaction 59, and by adduct formation.[49] However, benzene (or ionized benzene) is not regenerated in reaction 59. Nevertheless, the $FeC_6H_6^+$ reacts in the same manner as the isolated Fe^+ ion[49] which is consistent with a structure for the adduct in which Fe^+ is tethered to the benzene molecule. The excess energy of reaction 59 appears to be insufficient to release the $FeC_6H_6^+$ from the benzene surface.

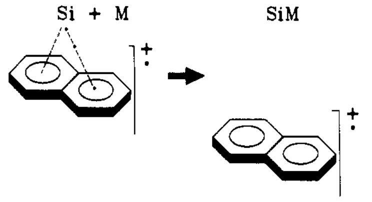
$$FeC_6H_6^+ + C_6H_5CHO \rightarrow Fe(C_6H_6)_2^+ + CO \qquad (59)$$

Results of SIFT experiments have been reported for the reactions of the adduct ions of Si^+ and both benzene and naphthalene with the molecules D_2, CO, N_2, O_2, H_2O, NH_3, C_2H_2, and C_4H_2 at 296 ± 2 K and these are summarized in Table V.[56] A wide range in reactivity was observed with both aromatic adduct ions, and while some common features were apparent in this chemistry, significant differences in reactivity also were seen, particularly for the reactions with C_2H_2 and C_4H_2. The reactions occurring in the presence of benzene appear to involve a π-complex in which the atomic silicon ion is poised above the aromatic ring ready for reaction with an incoming molecule. In contrast, the reactions occurring in the presence of naphthalene seem to proceed with a neutral silicon atom perched above the (charged) aromatic surface.

The availability of kinetic data for reactions of bare silicon ions occurring under similar experimental conditions has allowed an evaluation of the influence of the presence of benzene or naphthalene on the reaction kinetics and product formation.[140] For example, dramatic changes in the rate as well as in the mode of reaction were observed in the reactions with O_2 and H_2O. In the case of reaction with O_2, with which Si^+ reacts slowly to produce SiO_2^+, addition of naphthalene to the atomic silicon ion *increases* the rate of reaction by more than a factor of 3 and forms ionized naphthalene as the only ionic product. Addition of benzene to the atomic silicon ion, rather than naphthalene, enhances the rate by more than a factor of 30 and leads to the formation of two product ions, $C_6H_6^+$, and what could be the phenol cation, $C_6H_5OH^+$. The intrinsic reaction of H_2O with Si^+ leads exclusively to H-atom elimination with the formation of $SiOH^+$ (and not $HSiO^+$).[140a] In this case addition of a naphthalene molecule to Si^+ *reduces* the reaction rate by about a factor of 40, but again the product ion changes and again it is ionized naphthalene. The benzene adduct ion reacts with H_2O at a rate about equal to that of its reaction with the atomic ion and so about 4 times faster than the naphthalene adduct ion. In contrast, the reaction of acetylene with the benzene adduct $SiC_6H_6^+$ resembles that observed with Si^+ in that adduct formation and H-atom elimination are the observed products, but it is 5 times slower. Also, and quite remarkably so, the product distribution is the same within experimental error. Diacetylene, on the other hand, reacts quite differently with Si^+ in the presence and absence of benzene. The bare atomic silicon ion reacts with diacetylene simply by hydride transfer. Diacetylene reacts with the benzene adduct of Si^+ to displace the benzene molecule from $SiC_6H_6^+$ to form $SiC_4H_2^+$.

The products observed for the reactions of the $SiC_6H_6^+$ adduct are consistent with a mechanism initiated by the interaction of the Si^+ with the incoming molecule and followed by further transformations before separation into products. For example, the reaction of $SiC_6H_6^+$ with O_2 has been viewed to be initiated by the interaction of the oxygen molecule with the Si^+ sitting above the benzene ring to form the chemically-bonded ion SiO_2^+. Then charge transfer between SiO_2^+ and benzene can yield $C_6H_6^+$ which can appear as a final product if the products separate. Further intramolecular O-atom insertion into the C–H bond of $C_6H_6^+$ can explain the formation of the observed $C_6H_6O^+$ product ion if it is assumed to be the phenol cation $C_6H_5OH^+$. The reaction products with H_2O can be similarly understood in terms of sequential transformations within the intermediate complex. The water molecule interacts with the Si^+ attached to the benzene ring initially to form $Si^+\cdots OH_2$ and then $HSiOH^+$. Apparently the further reaction to form $SiOH^+$ and H which is observed for the bare Si^+ ion is not sufficiently exothermic in the presence of benzene for these two products to leave the benzene molecule. If the intermediate $HSiOH^+$ then transfers a charge or a proton to the benzene molecule, the proposed neutral molecules HSiOH and SiOH and the observed ions $C_6H_6^+$ and $C_6H_7^+$ are produced, respectively.

The SIFT measurements indicate that the chemistry of the $SiC_{10}H_8^+$ adduct ion (with the exception of its reaction with ammonia) is dominated by the elimination of ionized naphthalene in reactions of type 60. This



(60)

observation, together with the observation of a small charge-transfer channel competing with the formation of the adduct ion, strongly suggests that charge is transferred from Si^+ to naphthalene as the adduct is formed and that the adduct $SiC_{10}H_8^+$ is a π-complex of a neutral silicon atom interacting with a positive naphthalene ion. The charge transfer to naphthalene is exothermic by only 0.01 eV, but if the charge resides mostly on the naphthalene, reaction 60 may be viewed as a "surface" reaction in the sense that a neutral Si atom would interact with the incoming molecule M while perched above the plane of the charged naphthalene molecule. The identity of the neutral products of such a "surface" reaction of the naphthalene adduct is intriguing. If SiM leaves as a bound molecule, reactions of type 60 provide a novel route for molecular synthesis. SiO, SiO_2, SiOH, t-HSiOH and c-SiC_2H_2 have been postulated as the likely neutral products in the reactions of the $SiC_{10}H_8^+$ with O_2, H_2O, and C_2H_2, respectively.

Apparently higher-order reactions occur with analogous mechanisms. For example, the secondary reaction 61 of the water adduct of the benzene adduct of Si^+ has been reported.[56] The rate constant for this

$$SiC_6H_6^+{\cdot}H_2O + H_2O \rightarrow C_6H_8^+ + (SiH_2O_2) \qquad (61a)$$

$$\rightarrow C_6H_7^+ + (SiH_3O_2) \qquad (61b)$$

reaction was determined to be $(1.5 \pm 1.0) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} in a SIFT apparatus.[56] Again this reaction is of interest with regard to molecular synthesis. Possible neutral products are silanoic acid HSi(O)OH and the dihydroxy radical HSi·(OH)$_2$ for channels 8a and 8b, respectively, which occur in a ratio of 3 to 2 (but the relative exothermicities for other connectivities or for the formation of neutral fragments are not known). The adduct ions of $SiC_6H_6^+$ and $SiC_{10}H_8^+$ with ammonia have been reported to again react rapidly with ammonia to form $Si(NH_3)_2^+$ according to the interesting bimolecular reactions 62 and 63. A case has been made

$$SiC_6H_6^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2^+ + C_6H_6 \qquad (62)$$

$$SiC_{10}H_8^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2^+ + C_{10}H_8 \qquad (63)$$

for a mechanism involving adduct ions with the connectivities $HSiNH_2^+{\cdot}C_6H_6$ and $HSiNH_2{\cdot}C_{10}H_8^+$ in which reactions between $HSiNH_2^+$ and ammonia occur above benzene and naphthalene, respectively, perhaps to form the covalently bound ion of diaminosilane, $H_2Si(NH_2)_2^+$. In the case of the reaction in the presence of naphthalene, this reaction would be preceded by the transfer of the charge on naphthalene to the $HSiNH_2$ molecule. It is interesting to note that benzene (B) and naphthalene (N) catalyze the formation of $Si(NH_3)_2^+$ according to the reaction sequence 64 which

$$\begin{array}{l} Si^+ + B,N \rightarrow SiB^+,SiN^+ \qquad (64) \\ SiB^+,SiN^+ + NH_3 \rightarrow SiB^+{\cdot}NH_3,SiN^+{\cdot}NH_3 \\ \underline{SiB^+{\cdot}NH_3,SiN^+{\cdot}NH_3 + NH_3 \rightarrow Si(NH_3)_2^+ + B,N} \\ Si^+ + 2NH_3 \rightarrow Si(NH_3)_2^+ \end{array}$$

is written without any inferences being made about structure or mechanism. The sequential reactions of Si^+ with ammonia which occur in the absence of these aromatic molecules are given by reactions 65 and 66.

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \qquad (65)$$

$$SiNH_2^+ + NH_3 \rightarrow NH_4^+ + SiNH \qquad (66)$$

They do not form an ion with composition $Si(NH_3)_2^+$, but lead to protonated ammonia instead.

The nonreactivity of the $SiC_6H_6^+$ and $SiC_{10}H_8^+$ adduct ions toward D_2 and CO means that these adduct ions will persist in interstellar and circumstellar regions rich in H_2 and CO and be available for chemical reaction with other, less abundant molecules.

In principle, the adduct ion $(XPAH)^+$, where X is any atom, may be formed either by the capture of the atomic X^+ by the PAH molecule or by the capture of the neutral atom X by a positively-charged PAH ion. The ionization energies of the interstellar atoms S (10.360 eV), Zn (9.394 eV), Fe (7.870 eV), and Mg (7.646 eV) are all larger than that typical for the larger PAH molecules (6.8 eV), as is the case for the relative ionization energy of Si and naphthalene. In contrast, the ionization energies of Ca (6.113 eV) and Al (5.986 eV) are both smaller, as is the case for the relative ionization energy of Si and benzene. The ions of Ca, Al, and Si are therefore likely to form $(XPAH)^+$ adduct ions in interstellar regions of low density in a radiative association reaction of type 67, and the reactions of

$$X^+ + PAH \rightarrow X^+{\cdot}PAH + h\nu \qquad (67)$$

these adduct ions should mimic the behavior observed for the $Si^+{\cdot}C_6H_6$ adduct, e.g. form CaO/CaO_2 and AlO/AlO_2 from O_2 and AlOH and CaOH from H_2O. Because of the likelihood of charge transfer between the ions of the other atoms and PAH molecules, the corresponding adduct in this case must be formed by the radiative association of the neutral atom and the cation of the PAH molecule according to reaction 68. The reactions

$$X + PAH^+ \rightarrow X{\cdot}PAH^+ + h\nu \qquad (68)$$

of these adduct ions should mimic those observed in this study for $SiC_{10}H_8^+$, viz. reactions of type 69.

$$XPAH^+ + M \rightarrow PAH^+ + (XM) \qquad (69)$$

A cautionary remark about the possible influence of the size of the PAH molecule on the reaction mechanism of reactions of type 69 is noteworthy. With larger PAH's the incoming molecule M will have a larger opportunity to stick to the PAH rather than to interact directly with X^+/X. Surface mobility would then be required, as in the surface chemistry on macroscopic objects, to allow the interaction of M with X^+/X.

The FTMS study of the formation of the FeC_{60}^+ and FeC_{70}^+ adduct ions indicated that these did not react further with background pentane.[54a] This is an interesting result in that the adduct ions do not mimic the reactivity of isolated Fe^+ ions which have been observed to react with pentane to eliminate a variety of neutral molecules.[141] Indeed, this would not be expected if the charge is located primarily on the fullerene molecules as suggested by the CID studies[54a] and the relative recombination energy of Fe^+ (7.7870 eV) and C_{60}^+ (7.61 eV). So it appears that the Fe^+ adduct ions with fullerene molecules present a neutral Fe atom "tethered" to an ionized fullerene molecule to an incoming reactant molecule.

The opposite situation appears to apply for the adduct formed between Y^+ and C_{60}. Y^+ has a recombination energy (6.22 eV) considerably lower than that of C_{60}^+ so that the charge is not expected to transfer to C_{60} in the adduct ion. Indeed, the reaction of YC_{60}^+ with N_2O has been reported to produce $YO^+ + [C_{60} + N_2]$ rather than $C_{60}^+ + [YO + N_2]$.[142]

Atoms or molecules trapped inside endohedral cluster ions are not expected to react rapidly with other atoms or molecules at room temperatures because of the high barrier for the transport from inside the cage to the outside. The reactivity of such cluster ions in the gas phase is likely to be determined by the charged carbonaceous shell. For example, they might react by charge transfer in the manner established for the pure fullerene ions.[20] Aside from one report of the nonreactivity of endohedral $C_{60}La^+$ ions toward H_2, O_2, NO, and NH_3 which mimics the observed nonreactivity of C_{60}^+,[20] nothing is known at this time about the reactivity of endohedral cluster ions.[100]

Truly "endohedral chemistry" in which chemical reactions actually take place inside the carbon cage of a charged fullerene molecule has not yet been achieved in the laboratory, although two helium atoms apparently have been inserted into C_{60}^+ and much larger fullerene ions and molecules with a much larger internal volume now are known.[92,143]

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