J. Am. Chem. Soc. 1994, 116, 2466–2470

Radiative Association Reactions of Silicon and Transition-Metal Cations with the PAH Compounds Benzene, Naphthalene, and Anthracene

Robert C. Dunbar,[*,†] Guy T. Uechi,[†] and Bruce Asamoto[‡]

Contribution from the Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106, and BP Research, 4440 Warrensville Road, Cleveland, Ohio 44128

Received June 28, 1993[●]

Abstract: Using the ion cyclotron resonance ion trap, reactions of Si^+ with benzene, naphthalene, and anthracene were studied under low-pressure conditions of interest in interstellar modeling. Radiative association was efficient with all three hydrocarbons, occurring on roughly one-quarter of collisions. Association competed with charge transfer and/or condensation reactions in all three cases. In the naphthalene case it was inferred from collision-induced dissociation evidence and from reaction behavior that the association product ion at low pressure rearranges to a σ complex or other intimately bonded structure, in contrast to the π complex assigned under the high-pressure conditions in the SIFT. Reactions of the transition-metal ions Fe^+, Cr^+, and Mn^+ with naphthalene were studied for comparison. Radiative association was also efficient for these ions. Association of the transition metal–naphthalene adducts with a further naphthalene molecule to yield the "sandwich" complex was also observed, although this type of complex was not formed for Si^+ reacting with naphthalene.

Introduction

Much study of gas-phase ion chemistry has been motivated by the demands of astrochemistry. Experimental and computational information about the ion–molecule reactions of small molecules has given essential input to the detailed models of chemical evolution in interstellar clouds which are now highly developed.[1–6] Opportunities for similar interstellar modeling applications of the ion chemistry of larger systems are becoming apparent, inspired for instance by suggestions that polyaromatic hydrocarbons (PAH) are important in the chemistry of such clouds.[7–11] Modeling the chemistry of large systems like PAH molecules raises some rather different questions from those addressed with atoms or small molecules. For instance, a large molecule has extended and varying surface topography, so attacking reagents may attach or react at different sites, forming different or isomeric products. Also, larger molecules have increasingly important ability to accommodate energy internally and function as effective internal heat baths with well-defined temperatures. Such differences inspire our ongoing exploration of the particular nature of the heating, cooling, association, dissociation, and reaction processes of larger ionic systems under conditions, particularly the conditions of low pressure, relevant to interstellar chemical evolution.

The ion chemistry of PAH molecules needed for such modeling has not yet been fully studied in the laboratory. Bohme and others have worked effectively at relatively high pressures in the selected-ion flow tube (SIFT), and this productive approach is responsible for most of the laboratory results used in interstellar modeling.[12–16] SIFT studies are preeminent in giving laboratory rate values for bimolecular ion–neutral reactions of thermalized reactants. However, there are some reactions for which the high-pressure conditions (0.35 Torr of helium buffer gas) in a SIFT are not directly comparable to the low-pressure conditions of the interstellar medium. In particular, SIFT studies do not give directly useful information about interestellar kinetics involving reactions which are enhanced (e.g., termolecular association) or suppressed (e.g., slow unimolecular dissociation) by collisions. The low-pressure conditions conveniently available in a Fourier transform ion cyclotron resonance (FT-ICR) ion trap spectrometer (10^{-9}–10^{-7} Torr, or around 10^8 molecules cm^{-3}) are better suited to studying interstellar chemistry in cases where such reactions play a role. These low-pressure conditions mimic those found in interstellar clouds, in the sense that in both environments the collision rate is low compared with most of the relevant processes.

In the interstellar environment, H_2 is the molecule of highest density, at approximately[1,2,17] 10^4 cm^{-3}; at this density the rate of collisions experienced by ions of the order of one per day. In the ICR ion trap operated at typical low pressures, collision rates are of the order of one per second.

The abundance of silicon is substantial in interstellar clouds. SiO is easily detected,[18] and at least one model containing 300 gas-phase reactions[6] has been developed to account for the neutral and ionic silicon chemistry in these clouds. Si^+ densities of the order of 10^{-7} cm^{-3} have been estimated in modeling.[1,2] To investigate the low-pressure chemistry between silicon ions and PAH molecules, we studied the gas-phase reactions between silicon

---

[†] Case Western Reserve University.

[‡] BP Research.

[●] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) Hasegawa, T. I.; Herbst, E. *Mon. Not. R. Astronom. Soc.* **1993**, *261*, 83.

(2) Hasegawa, T. I.; Herbst, E. *Astrophys. j. Suppl.* **1992**, *82*, 167.

(3) Heck, E. L.; Flower, D. R.; LeBourlot, J.; Pineau des Forets, G.; Roeff, E. *Mon. Not. R. Astronom. Soc.* **1992**, *258*, 377.

(4) *Astrochemistry* of Cosmic Phenomena; International Astronomical Society Symposium 150; Kluwer: Dordrecht, 1992.

(5) Herbst, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 595.

(6) Herbst, E.; Millar, T. J.; Wlodek, S.; Bohme, D. K. *Astron. Astrophys.* **1989**, *222*, 205.

(7) Millar, T. J. *Mon. Not. R. Astronom. Soc.* **1992**, *259*, 35P.

(8) Bohme, D. K.; Wlodek, S.; Wincel, H. *Astrophys. J.* **1989**, *342*, L91.

(9) Allamandola, L. J.; Tielens, A. G. G. M.; Barker, J. R. *Astrophys. J. Suppl.* **1989**, *71*, 733.

(10) Lepp, S.; Dalgarno, A.; van Dishoeck, E. F.; Black, J. H. *Astrophys. J.* **1988**, *329*, 418.

(11) Lepp, S.; Dalgarno, A. *Astrophys. J.* **1988**, *324*, 553.

(12) Bohme, D. K.; Wlodek, S.; Wincel, H. *J. Am. Chem. Soc.* **1991**, *113*, 6396.

(13) Wlodek, S.; Fox, A.; Bohme, D. K. *J. Am. Chem. Soc.* **1991**, *113*, 4461.

(14) Wlodek, S.; Bohme, D. K. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1643.

(15) Wlodek, S.; Rodriguez, C. F.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Chem. Phys. Lett.* **1988**, *143*, 385.

(16) Wlodek, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2396.

(17) Geuzel, R.; Stutzki, J. *Annu. Rev. Astron. Astrophys.* **1989**, *27*, 41.

(18) Ziurys, L. M.; Friberg, P.; Irvine, W. M. *Astrophys. J.* **1989**, *343*, 201.

0002-7863/94/1516-2466$04.50/0

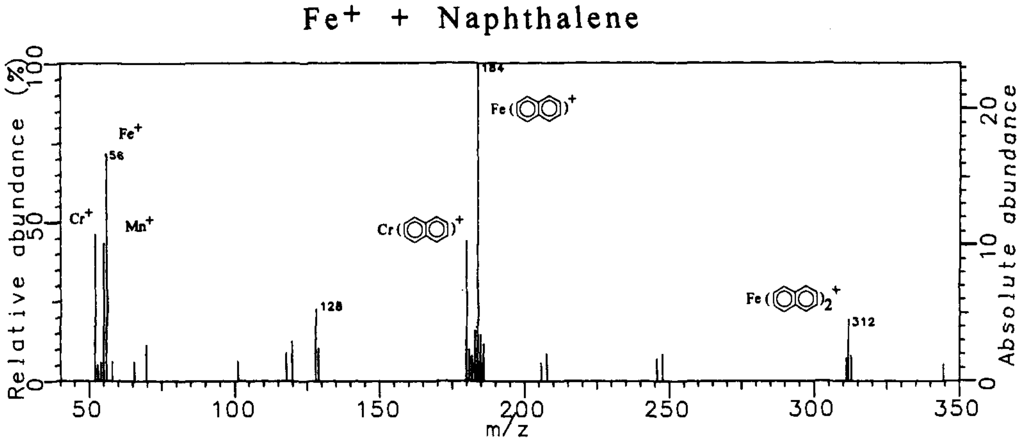
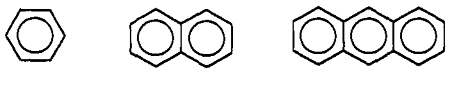


Figure 1. Transition-metal ions with naphthalene at 4 × 10^{-8} Torr and 1.3-s reaction time. The principal reaction product ions are labeled. The naphthalene ion at *m/z* 128 is not involved in this chemistry.

ions and benzene, naphthalene, and anthracene. For comparison,



PAH Substrates

we also looked at the chemistry of naphthalene with Fe^+, whose interstellar abundance has been modeled[1,2] to be in the vicinity of 10^{-4} cm^{-3}, and two other transition-metal ions, Mn^+ and Cr^+.

Pioneering study of the chemistry of Si^+ with the smallest PAH molecules, benzene and naphthalene, was carried out by Bohme et al. under the higher pressure conditions of the SIFT.[12] Efficient collisional association was observed in both cases, and they speculated that radiative association could be viable in interstellar conditions. The present work takes up these speculations and investigates the low-pressure chemistry of these two molecules, as well as anthracene, with Si^+.

Experimental Section

The experiments were performed in the Nicolet/Extrel FTMS 2000 FT-ICR spectrometer.[19] The techniques were quite similar to previously described work with atomic–ion reactions in this instrument.[20,21] A pulsed TEA-CO_2 laser was focused on a silicon wafer attached to the tip of the sample autoprobe to produce singly charged silicon ions by laser desorption/ionization. Silicon ions were easily and reproducibly produced at low laser energies of 5–10 mJ/pulse after the silicon surface was "cleaned" by repetitive CO_2 laser irradiation at higher energies to remove K^+ ions. Ground-state $Si^+(^2P)$ ions were assured since no reaction was observed with deuterium, which has been reported to scavenge metastable $Si^+(^4P)$ ions.[22] The transition-metal ions were produced by striking the stainless steel tip of the probe with the laser.

Ions were trapped in the source region of the dual cell in the Extrel FT/MS 200 at 0.4–0.6 V trapping voltage for periods ranging from 25 ms to 8 s. The reactions were studied by observing the time-dependent atomic ion depletion and product ion formation. As an illustration, Figure 1 shows a typical spectrum of Fe^+ with naphthalene, taken after a substantial reaction time (1.3 s). Benzene and naphthalene were introduced into the mass spectrometer through the sample batch inlet. A constant pressure of neutral reagent molecules was achieved by maintaining constant pressure in the batch inlet. Anthracene was introduced into the cell by placing a sample adjacent to the silicon wafer on the tip of the sample autoprobe, without probe heating.

The pressure readings from the ion gauge were found to correlate in acceptably linear fashion with the observed reaction rates, but there was considerable uncertainty about the absolute calibration, especially for the low-volatility naphthalene and anthracene samples, since the ion gauge is located remote to the cell. For naphthalene, an indication of the calibration was obtained by measuring the proton-transfer rate between protonated water ions and naphthalene. Assuming this reaction to proceed near the collision rate, as is typical of proton transfer, the ion gauge pressure was found to correspond fairly well to the true naphthalene pressure. Benzene and naphthalene pressures were normally in the range (1.5–3) × 10^{-8} Torr, ranging up to 8 × 10^{-8} Torr in a few runs. The chemistry did not change in any obvious way with these variations in pressure. The gauge readings (about 1.5 × 10^{-8} Torr) were clearly lower than the true pressure for anthracene. We have limited confidence in the accuracy of the absolute pressure calibrations, and the absolute rate constants reported below should undoubtedly be considered uncertain to perhaps a factor of 2, although the relative rates for various reactions with the same neutral molecule should be accurate to better than 20%.

Collision-induced dissociation (CID) experiments were done on the product ions to probe their structures. After the silicon ions were allowed to react, the product ion of interest was isolated by selective ejection of all other ions. Argon gas was introduced into the cell by a pulsed valve and was used as a collision gas. These isolated product ions were excited to higher kinetic energies and allowed to collide with the argon gas to induce dissociation.

Since the silicon ions and the silicon-containing product ions were reactive to water, precautions were taken to ensure that the argon gas was sufficiently dry in the CID experiments. A liquid nitrogen trap was placed in the argon supply line to the sample batch inlet. A simple electron impact spectrum of the argon gas did not show the presence of any water vapor. However, water could always be observed by exposing Si^+ ions to the argon and detecting the $SiOH^+$ ions produced. Although completely dry argon gas was never achieved, conditions were obtained where less than 10% of the Si^+ ions reacted with water.

Results

Association Reactions. Ground-state silicon ions were found to be highly reactive with neutral benzene, naphthalene, and anthracene. At low pressure, the observed reactions of Si^+ with an aromatic hydrocarbon RH are encompassed by the following scheme:

$$Si^+ + RH \rightarrow SiRH^{*+} \rightarrow SiRH^+ + h\nu \qquad \text{(i)}$$

$$\rightarrow SiR^+ + H \qquad \text{(ii)}$$

$$\rightarrow RH^+ + Si \qquad \text{(iii)}$$

The three reaction types are (i) radiative association, (ii) condensation with H-atom elimination, and (iii) charge transfer. Figure 2 shows the evolution of the naphthalene system, and Figure 3 shows the anthracene system. The major primary

---

[19] See, for instance: *Analytical Applications of FT-ICR Mass Spectrometry*; Asamoto, B., Ed.; VCH: New York, 1991.

[20] Dunbar, R. C.; Solooki, D.; Tessier, C. A.; Youngs, W. J.; Asamoto, B. *Organometallics* **1991**, *10*, 52.

[21] Dunbar, R. C.; Uechi, G. T.; Solooki, D.; Tessier, C. A.; Youngs, W. J.; Asamoto, B. *J. Am. Chem. Soc.* **1993**, *115*, 12477.

[22] Stewart, G. W.; Henis, J. M. S.; Gaspar, P. P. *J. Chem. Phys.* **1972**, *57*, 1990.

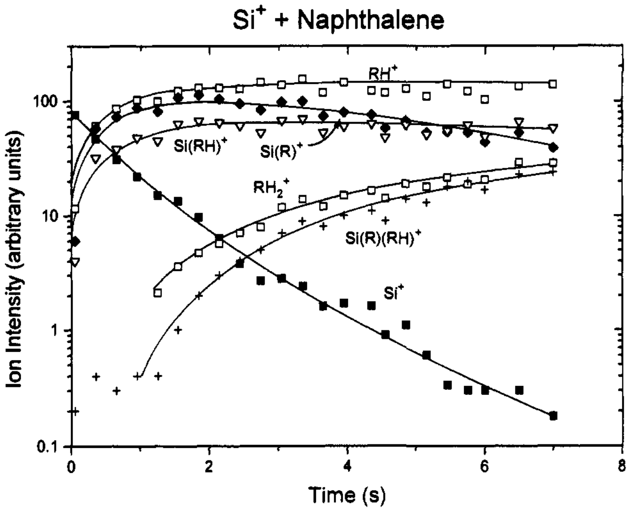


Figure 2. Reaction of Si^+ with naphthalene at 3×10^{-8} Torr. RH is naphthalene, $C_{10}H_8$. The solid lines are only to guide the eye.

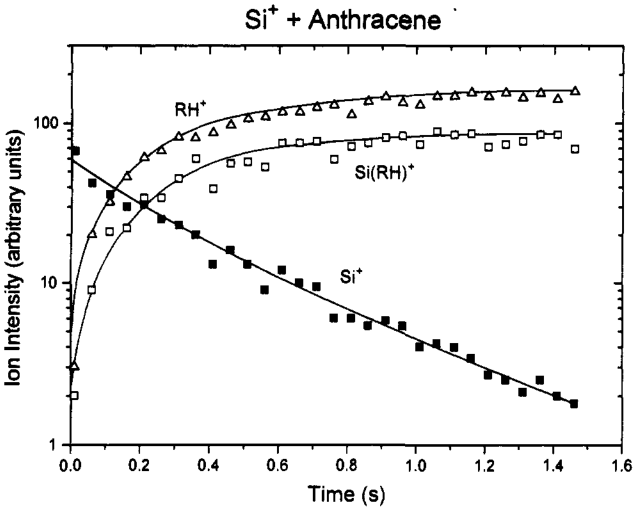


Figure 3. Reaction of Si^+ with anthracene at 1.6×10^{-8} Torr. RH is anthracene, $C_{14}H_{10}$. The solid lines are only to guide the eye.

reaction product ions with their relative abundances were as follows:

$$Si^+ + C_6H_6 \xrightarrow{(i)} SiC_6H_6^+\ (m/z\ 106) \qquad 15\% \qquad (1)$$

$$\xrightarrow{(ii)} SiC_6H_5^+\ (m/z\ 105) + H \qquad 85\% \qquad (2)$$

$$Si^+ + C_{10}H_8 \xrightarrow{(i)} SiC_{10}H_8^+\ (m/z\ 156) \qquad 20\% \qquad (3)$$

$$\xrightarrow{(ii)} SiC_{10}H_7^+\ (m/z\ 155) + H \qquad 37\% \qquad (4)$$

$$\xrightarrow{(iii)} C_{10}H_8^+\ (m/z\ 128) + Si \qquad 43\% \qquad (5)$$

$$Si^+ + C_{14}H_{10} \xrightarrow{(i)} SiC_{14}H_{10}^+\ (m/z\ 206) \qquad 35\% \qquad (6)$$

$$\xrightarrow{(iii)} C_{14}H_{10}^+\ (m/z\ 178) + Si \qquad 65\% \qquad (7)$$

Minor peaks were seen for anthracene condensation products with both loss of H and loss of H_2, giving the ions $SiC_{14}H_9^+$ (*m/z* 205) and $SiC_{14}H_8^+$ (*m/z* 204).

Secondary Reactions. The primary condensation products underwent some subsequent chemistry, reacting both with the parent hydrocarbon and also with background water (and possibly other contaminants). As suggested by the curves in Figure 2, the naphthalene condensation product ion $SiC_{10}H_7^+$ (*m/z* 155) reacted slowly to give two secondary product ions, $Si(C_{10}H_7)(C_{10}H_8)^+$ (*m/z* 283) and $C_{10}H_9^+$ (*m/z* 129).

Small peaks were seen in the anthracene system for $Si(C_{14}H_9)(C_{14}H_{10})^+$ (*m/z* 383) and $Si(C_{14}H_8)(C_{14}H_{10})^+$ (*m/z* 382). These are presumably direct attachment products from the minor ions at *m/z* 205 and 204.

No secondary chemistry was observed in the benzene system. None of the adducts $Si(RH)^+$ were observed to undergo further chemistry, and in particular the "sandwich" complex $Si(RH)_2^+$ was not observed in any case.

Argon CID was successful in bringing about informative fragmentations of the ions in the naphthalene case. The reactions observed were

$$SiC_{10}H_8^+\ (m/z\ 156) \xrightarrow{Ar} SiC_{10}H_7^+\ (m/z\ 155) + H \qquad (8)$$

$$SiC_{10}H_7^+\ (m/z\ 155) \xrightarrow{Ar} SiC_8H_5^+\ (m/z\ 129) + C_2H_2 \qquad (9)$$

$$Si(C_{10}H_7)(C_{10}H_8)^+\ (m/z\ 283) \xrightarrow{Ar} SiC_{10}H_7^+\ (m/z\ 155) + C_{10}H_8 \qquad (10)$$

Transition-Metal Ions. The transition-metal ions Fe^+ and Cr^+ reacted rapidly with naphthalene, while Mn^+ also reacted, but more slowly. Association was the only major reaction observed for the atomic ions, as suggested by Figure 1. Some charge-transfer product ($C_{10}H_8^+$) was observed (from undetermined precursors), but this was not a major channel. The total amount of $C_{10}H_8^+$ produced from all sources was typically less than 20% of the $Fe(C_{10}H_8)^+$ ion abundance. The observation of little or no charge transfer from the metal ions was expected, since all of these metal atoms have lower ionization energies than naphthalene. For iron, the reactions observed were

$$Fe^+ \xrightarrow{C_{10}H_8} Fe(C_{10}H_8)^+\ (m/z\ 184) \qquad (11)$$

$$Fe(C_{10}H_8)^+ \xrightarrow{C_{10}H_8} Fe(C_{10}H_8)_2^+\ (m/z\ 312) \qquad (12)$$

For chromium, the association reaction analogous to (11) was observed, with similar rate constant. The corresponding reaction analogous to (12) forming (presumably) a sandwich complex was observed for chromium, with a rate constant noticeably lower than that for (12) by perhaps a factor of 3. Sandwich complex formation for manganese was observed but with small abundance and a rate constant significantly slower than that for chromium.

Rate Constants. (All given in units of $cm^3\ molecule^{-1}\ s^{-1}$). Subject to the absolute pressure uncertainty noted in the Experimental Section, we can estimate that the rate of Si^+ disappearance in all three systems was of the order of the collision rate ($(1-2) \times 10^{-9}$). This leads to estimates of absolute rate constants of 1×10^{-9} for the charge-transfer and condensation reactions (2), (4), and (5) and (7); 3×10^{-10} for the associations (1), (3), (6), and (11); and 5×10^{-11} for the secondary associations such as (12).

Discussion

Our primary interest in this study was to characterize the radiative association reactions between ground-state Si^+ ions and neutral aromatic hydrocarbons. All three aromatic molecules formed the association product ions $SiRH^+$ (where RH is the neutral aromatic hydrocarbon molecule) as a significant fraction of their reaction products. Most of this chemistry was observed at pressures of the order of 3×10^{-8} Torr, at which ion–neutral collisions occur at about one per second.

At these pressures we can rule out any significant contribution of collisionally stabilized association. For systems where quantitative results have been reported,[23] the lowest pressures at which collisional association is significant in comparison with radiative stabilization are in the mid 10^{-7} Torr region. This is in accord with expectations from measured rates of infrared radiative emission:[24] even the most inefficient IR-radiating ions with excess internal energies greater than 1 eV have photon radiation rates faster than 10 s^{-1}, so collision rates less than 10 s^{-1} will not compete with radiative stabilization. In fact, the benzene ion is known to be an exceptionally efficient infrared radiator,[25] and by analogy we would expect the unstabilized complexes in this study to radiate photons faster than 100 s^{-1}. Thus the IR radiation rates are at least 1 and probably 2 orders of magnitude faster than the collision rates in these experiments. Infrared radiative stabilization is the only reasonable mechanism for the association reaction.

Radiative association reactions in general fall into one of two kinetic regimes. In the inefficient stabilization regime, redissociation to reactants competes with complex stabilization, and only a small fraction of collisions result in a stable complex. In the saturated regime, complex stabilization is faster than redissociation, and essentially every collision results in stabilized complex. (Both of these regimes can be complicated by the presence of competing exothermic reactions, as is the case in all three of the systems considered here). It is clear from the large association rate constants that all three of these systems lie in or near the saturated regime.

The large Si^+ disappearance rate with all three reactants shows that roughly every collision of Si^+ with any of these substrates results in some reaction. Nonproductive collisions which revert to reactants are not dominant in any case. This being true for even the smallest PAH (benzene) at room temperature, it will be all the more true at the typically lower temperatures of interstellar chemical synthesis and for larger PAH molecules.

Thermochemistry. The binding energies of Si^+ to these molecules are not experimentally known. The π complex of Si^+ with benzene was calculated to have a binding energy of 1.92 eV, and a silicon insertion complex was calculated at 1.68 eV.[26] Values for larger PAHs are unknown. An interesting approach to estimating the binding energies, described in recent theoretical considerations of radiative association in hydrocarbon systems,[27,28] is based on the strong sensitivity of radiative association efficiency to the binding energy. The fact that the association complexes are formed with reasonable efficiency in all three of these systems places approximate *lower bounds* on their binding energies.[29] These lower bounds are given in Table 1. From these estimates, the Si^+–PAH complexes are quite strongly bound. The lower limit estimated for benzene is actually a bit higher than the upper limit of 1.89 eV determined by reactivity by Bohme et al.[12] and similarly higher than the calculated 1.92 eV,[26] although these differences are easily within the uncertainty of the generic estimation scheme used here.

Table 1

ion	lower-limit binding energy (eV)
$SiC_6H_6^+$	≥2.2
$SiC_{10}H_8^+$	≥1.8
$FeC_{10}H_8^+$	≥1.8
$SiC_{14}H_{10}^+$	≥1.5

The Nature of $SiC_{10}H_8^+$. The high-pressure SIFT study of Bohme et al.[12] observed the collisional association complex $SiC_{10}H_8^+$ as the exclusive reaction product (other than charge transfer) for naphthalene. On the basis of its patterns of reactivity with various molecules, they concluded that this ion was a complex (presumably a π complex) of Si^+ with an intact naphthalene molecule. Two lines of reasoning suggest that the stabilized complexes observed at low pressure in the ICR ion trap do not have such a structure but rather incorporate the Si into more intimate bonding.

One argument is from the CID evidence. It would be confidently expected that the fragmentation of the π complex would yield Si^+, $C_{10}H_8^+$, or most likely a mixture of these. In fact, neither of these was formed by CID, but only the H-loss product $SiC_{10}H_7^+$. Loss of hydrogen is a high-energy process for either naphthalene (4.5 eV) or naphthalene ion (4.4 eV), so this dissociation path would seem unlikely in preference to breaking the weaker Si–aromatic bond of the π complex but would be reasonable for a more intimately bonded Si complex.

A second argument is from the fact that the sandwich complex $Si(C_{10}H_8)_2^+$ is not formed with an observable rate. A study of formation of sandwich complexes with the planar, delocalized hydrocarbon tribenzocyclyne[21] found Si^+ to be one of the very best atomic ions for sandwich complex binding with that ligand. Taking the view that naphthalene is an analogous ligand, we would expect ready formation of the radiatively stabilized sandwich complex in this system. Indeed, all three transition metals observed here did form such a complex, and in the Fe^+ and Cr^+ cases, the efficiency of formation was at least as high as for formation of complexes with the tribenzocyclyne ligand.[20,21] Thus the unwillingness of $SiC_{10}H_8^+$ to attach a second naphthalene molecule seems significant and suggests that in this complex the Si atom is not accessible as it would be in a π complex structure.

The anthracene adduct was not characterized in an equally satisfactory way. A useful CID analysis of the m/z 206 ion was not obtained. The absence of a sandwich complex at m/z 384 is one indication that in this case also the silicon atom may be incorporated into intimate binding.

Charge-Transfer Reaction Channel. Charge transfer was observed in competition with radiative association for silicon ions with naphthalene and anthracene. Two aspects of this are unexpected and notable. One is that the charge-transfer channel in the naphthalene case has similar order-of-magnitude probability at low pressure (43%) and at high pressure (12%).[12] The other is that association is observed to be competitive with the highly exothermic charge transfer in the anthracene case.

Charge transfer to naphthalene (IE = 8.14 eV) is essentially thermoneutral for silicon ion (IE = 8.15 eV). Once the collision complex is formed, there is no energy advantage to proceeding on to charge-transfer products in preference to redissociating to reactants. Thus successful collisional or radiative stabilization of the complex in competition with charge transfer is not surprising. However, a dramatic difference in stabilization rate would surely be expected between the ICR and SIFT experiments. The similar order of magnitude for the ratio of these channels at high and low pressure can be understood only if charge transfer is not in kinetic competition with complex stabilization. One might suppose that charge transfer occurs in nonintimate or grazing collisions where no tight collision complex is formed, while those collisions which result in a strongly bound complex are radiatively or collisionally stabilized with high probability.

---

(23) Reviewed by Dunbar: Dunbar, R. C. In *Current Topics in Ion Chemistry and Physics, Vol. 2*; Ng, C. Y., Ed.; Wiley, in press.

(24) Dunbar, R. C. *Mass Spectrom. Rev.* **1992**, *11*, 309.

(25) Ahmed, M. S.; So, H. Y.; Dunbar, R. C. *Chem. Phys. Lett.* **1988**, *151*, 128.

(26) Srinivas, R.; Hrusak, J.; Sulzle, D.; Bohme, D. K.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2802.

(27) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423.

(28) Herbst, E.; Dunbar, R. C. *Mon. Not. R. Astronom. Soc.* **1991**, *253*, 341.

(29) The generic modeling approach of ref 27 was applied to obtain these estimates, assuming that 10% or more of collisions result in stabilized complexes. Since benzene ion is known to radiate IR photons an order of magnitude faster than typical hydrocarbon ions (ref 25), an adjustment was made in its radiative rate, giving a modest lowering (0.3 eV) of the estimated energy. The uncertainty in absolute rate constants noted in the Experimental Section is insignificant compared with other uncertainties in this modeling approach.

The IE of anthracene is 7.5 eV, which makes charge transfer with silicon ions 0.65 eV exothermic. Since the presence of a substantially exothermic, barrierless product channel is unfavorable to radiative association in smaller molecules,[28] it is surprising that the two channels are competitive in this case.[30] Collision-stabilized C_{60} association with Si^+ is faster than charge transfer, which is similarly surprising.[31] Viggiano and Paulson recently concluded that modeling such a competition in smaller systems (eight atoms) as a kinetic competition within the complex is possible only by assuming nearly thermoneutral charge transfer.[32] The ability of complex stabilization to compete with exothermic charge transfer in our much larger complex may be an illustration of the effect of the heat capacity of the large anthracene molecule, which can accommodate the extra 0.65 eV of energy relative to the charge-transfer exit channel in its many internal degrees of freedom. Modeling suggests that a strongly bound Si^+–anthracene complex can be successfully stabilized in competition with charge transfer if the binding energy is of the order of 3 eV (rather than the 1.5 eV suggested in Table 1).

An alternative (or supplementary) line of explanation for the observation of association in competition with charge transfer was suggested as a way of rationalizing similar observations in the association of some atomic ions with tribenzocyclyne.[21] This suggests that charge transfer may be inhibited or a barrier may be created by a curve-crossing mechanism in the situation where an atomic ion associates with a large, highly polarizable neutral molecule.

ICR vs SIFT. A clear picture emerges of the difference between high- and low-pressure regimes for this chemistry. One major difference between these ICR experiments and the SIFT experiments of Bohme et al.[12] is the pressure. Unimolecular reactions of the energetic collision complex which occur slower than a microsecond are likely to be suppressed by collisional quenching in the SIFT experiment, while in the ICR ion trap milliseconds are available for reactions before radiative cooling of the energetic complex. The condensation reactions (2) and (4) apparently fall into the range of rates such that they compete with radiative stabilization in the low-pressure regime but are suppressed by collisional stabilization at high pressure. This situation apparently also holds for the rearrangement of the Si^+–naphthalene π complex observed in the SIFT to the more intimately bound complex inferred from the ICR results.

The other difference in the two experiments is that in the ICR ion trap at very low pressure, the laser-desorbed ions may retain unrelaxed kinetic energy in both the cyclotron and the axial degrees of freedom. This kinetic energy is dissipated after the first few ion–neutral collisions, but in the present cases few or no collisions precede reaction, so this unrelaxed kinetic energy may play a role in the differences in chemistry observed in the two instruments. Ions are rapidly and completely thermalized by collisions under SIFT conditions. If excess kinetic energy is present and adds energy to the collision complex under ICR conditions, it makes all the stronger the major conclusion of the present work, that radiative association at low pressure is highly efficient for these systems.

Conclusions

Radiative association of Si^+ to these three simplest PAH molecules occurs with reasonable efficiency, estimated to be a quarter of the collision rate. However, at least one other fast reaction channel is in significant competition with the simple association at low pressure in all three cases. From the point of view of interstellar molecule building, the competing condensation reactions (2) and (4) in the benzene and naphthalene cases are as productive as simple association, since they also combine silicon with a large molecule. We might regard the charge transfer (7) with anthracene as a retrograde event, replacing the highly reactive Si^+ with the less reactive hydrocarbon ion.

We can follow the trends of the present results to anticipate the situation for Si^+ reacting with larger PAH substrates. Assuming that the Si^+–PAH binding energy levels off to a reasonably constant value, radiative stabilization should increasingly dominate over charge transfer and other exothermic reactions as the PAH becomes larger. The lower temperature of interstellar chemistry should not affect this conclusion, raising the already high radiative association efficiencies toward unity. This study gives additional evidence suggesting that Si^+ is a highly reactive species toward PAH substrates. While confirming and extending the SIFT conclusion that simple association is an important reaction channel, it also suggests that the reaction chemistry is richer at the low pressures of interstellar conditions than in the high-pressure flow tube. The efficient radiative association of Fe^+ with one and two naphthalene molecules is also notable, since this is one of the most abundant heavy ions in interstellar chemical models.[1,2]

Acknowledgment. This work benefited by encouragement from and discussion with Prof. Diethard Bohme. The support of the National Science Foundation and of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The authors are grateful to BP for permitting use for this purpose of the FT-ICR instrument. G.T.U. acknowledges with gratitude the support of a fellowship from BP.

---

(30) Some of the charge transfer in this case may occur in noncompetitive grazing collisions, similar to the suggestion for the naphthalene case. Regardless of this possibility, we still need to explain the existence of efficient radiative association in a situation where the substantially exothermic charge-transfer channel is available.

(31) Bohme, D. K. *Chem. Rev.* **1992**, *92*, 1487. Petrie, S.; Jahavery, G.; Bohme, D. K. *Astron. Astrophys.* **1993**, *271*, 662.

(32) Viggiano, A. A.; Paulson, J. P. *J. Phys. Chem.* **1991**, *95*, 10719.