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Reactions between M^+ (M = Si, Ge, Sn and Pb) and benzene in the gas phase

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Using a laser ablation/inert buffer gas ion source coupled with a reflectron time-of-flight mass spectrometer, the gas-phase reactions between the IVA group element ions M^+ (M = Si, Ge, Sn and Pb) and benzene seeded in argon gas were studied. In addition to the association reaction pathway (forming $[M(C_6H_6)_x]^+$, x = 1, 2, etc.), benzene was dissociated to form complex ions $[M(C_5H_5)]^+$, $[M(C_7H_5)]^+$ and $[M(C_9H_x)]^+$ (x = 5, 7 and 9), etc. DFT theoretical calculations indicated that, in the association products $[M(C_6H_6)]^+$, the M atom is close to one carbon atom of benzene, while in most of the dissociation complexes, pentagonal structures (M/cyclopentadienyl derivatives) were formed, with the M atom situated near the fivefold axis of the five-membered ring. The bond patterns in these complexes are discussed. Copyright © 2003 John Wiley & Sons, Ltd.

The reactions of gas-phase atoms or clusters with organic molecules, for example, transition metals and aromatic systems, have been studied extensively.[1–17] The resulting complexes have bonding interactions representative of those in many organometallic systems. The laser vaporization and molecular beam technique is an effective method in these studies. For example, Duncan and co-workers[2–4] have investigated dissociation processes of metal atom-benzene cations in the gas phase, and discussed the dissociative charge-transfer process in detail. Kaya and co-workers[5–7] have synthesized all neutral 3d transition metal-benzene complexes by reaction of metal species with benzene in the gas phase, and two different structures, namely, sandwich complexes for Sc, Ti and V, etc., and rice-ball complexes for Fe, Co and Ni, etc., were suggested. Theoretical investigations directed at understanding the structures and properties of these metal-benzene association complexes were recently conducted by Pandey *et al.*[8] using density functional theory with the generalized gradient approximation (DFT-GGA). Besides these association reactions, benzene can be dehydrogenated by cations such as Sc^+,[9] Nb^+,[10,11] and Ta^+,[12,13] etc., and Ta^+ affords loss of C_2H_2 and C_2H_4 fragments as well. Benzene clusters can also be dissociated by Y^+, Nb^+ and Ta^+, etc., forming fragment ions $[M(C_6H_6)(C_xH_y)]^+$ in the gas phase.[14] The dehydrogenation or dissociation of benzene molecules on gas-phase metal clusters, for example, those of V,[15] Pt,[16] Nb,[17] and Rh,[17] has also been observed. In all these reactions (including those of metal cations or clusters), the dehydrogenation and dissociation processes of benzene molecules only involved losses of H_2 molecules or C_2 fragments (such as C_2H_2, C_2H_4, etc.).

Group IVA elements (including Si, Ge, Sn and Pb) play an important role in organic or organometallic chemistry.[18,19] However, gas-phase reactions involving these elements have been less studied than the other metal species detailed above. The special electronic structure of these elements (ns^2np^2, with unfilled shells or unpaired electrons in p orbitals) may lead to special metal-ligand interactions. In the present experiment, the gas-phase reactions of Si, Ge, Sn and Pb cations with benzene molecules were studied using a laser ablation/argon buffer gas ion source, and the products were examined using a high-resolution reflectron time-of-flight mass spectrometer (RTOFMS). Density functional theory (DFT) calculations were performed to illuminate the structures of the dominant products. The results indicated that these four elements formed pentagonal structures with most of the dissociated fragments of benzene.

EXPERIMENTAL

Reactions of laser-ablated species with benzene were studied using a home-built reflectron time-of-flight mass spectrometer coupled with a Smalley-type laser vaporization source.[20] A detailed description of the apparatus has been given elsewhere,[21,22] and only an outline is given here.

The focused second harmonic output of a Nb:YAG laser (10 mJ/pulse, 10 Hz, beam spot size on the target 1 mm in diameter) was used to ablate the sample target. Pulses of a mixture of benzene seeded in argon were injected by a pulsed nozzle, and directed to cross the laser-generated metal ions to form the reaction gas flux. The central point of the crossing region of the benzene beam and the metal ion beam was 10 mm from the pulsed nozzle and 2.5 mm from the surface of

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the sample target. The reaction gas flow was then temporarily encaged in a reaction channel (3 mm diameter × 10 mm length), where reactions of these ions with benzene were completed. The reaction products were cooled by expansion into vacuum through a 0.75 mm diameter orifice opening into a 5° (half angle) conical nozzle. The expansion was carried by the pulsed argon flow through a conical skimmer (throat diameter of 2.5 mm) positioned about 30 mm downstream from the nozzle, and entered the pulsed ion extraction region in the flight tube. The cationic products were then extracted and accelerated through about 1.2 kV perpendicularly to the direction of the cluster beam. They experienced two sets of einzel electrostatic lenses to guide and focus the ion beam and then were reflected by the reflector. Finally, they reached the space focus of the mass spectrometer and were detected using a dual microchannel plate (MCP). The output signal from the MCP was amplified in an oscilloscope with a 60 MHz sampling rate (Aron), recorded by a 100 MHz transient recorder (USTC, China), and stored by a PC. The timing sequence of the system (including valve opening, laser firing, ion acceleration pulse, and spectra recording) was controlled by a delay pulse generator (Stanford Research DG535). The final digitized TOF mass spectra were typically averaged over 300 laser pulses.

The source chamber, the flight tube and the reflectron region were all differentially pumped with mechanical and turbomolecular pumps. The corresponding operating pressures were 10^{-4}, 10^{-6}, and 10^{-7} Torr, respectively.

The best mass resolution (M/ΔM) of the mass spectrometer can reach 2000, which enabled the apparatus to resolve product ions differing by one hydrogen atom.

RESULTS AND DISCUSSION

Product analysis using the mass spectrometer

Figures 1(A)–1(C) show the reaction products between laser-vaporized M^+ (M = Si, Ge or Sn) species and benzene molecules. The reaction products of lead cation species with benzene are shown in Fig. 2. From these spectra it can be seen that, apart from the M-benzene association products, benzene molecules could be dissociated in the reactions, and many M-hydrocarbon fragment complexes were formed. Based on the mass numbers of the peaks and the isotopic distributions, these products could be assigned unambiguously.

In Fig. 1(A), the products observed contain only one silicon atom. The silicon-benzene association products were $[Si(C_6H_6)_x]^+$, x = 1 and 2; however, several peaks which corresponded to addition or elimination of hydrogen atoms from these adduct ions were also observed. The silicon-hydrocarbon fragment complexes included $[Si(C_5H_5)]^+$, $[Si(C_7H_5)]^+$ and $[Si(C_9H_x)]^+$ (x = 5, 7 and 9). Additionally, several hydrocarbon ions, e.g. $[(C_6H_6)]^+$ and $[(C_6H_6)_2 \pm H_x]^+$, were also observed. The peaks near *m/z* 117 were assigned as $[SiOH(C_6H_6)]^+$; the oxygen probably was derived from trace impurities in the silicon sample. Several peaks near *m/z* 130, which could not be assigned, were possibly hydrocarbon fragment cations derived from dissociation of benzene in the plasma.

The products observed in the germanium system also contained mainly one Ge atom, as shown in Fig. 1(B). The germanium-benzene association products were $[Ge(C_6H_6)_x]^+$ (x = 1, 2, etc.), and species originating from addition or elimination of hydrogen atoms were also observed. The

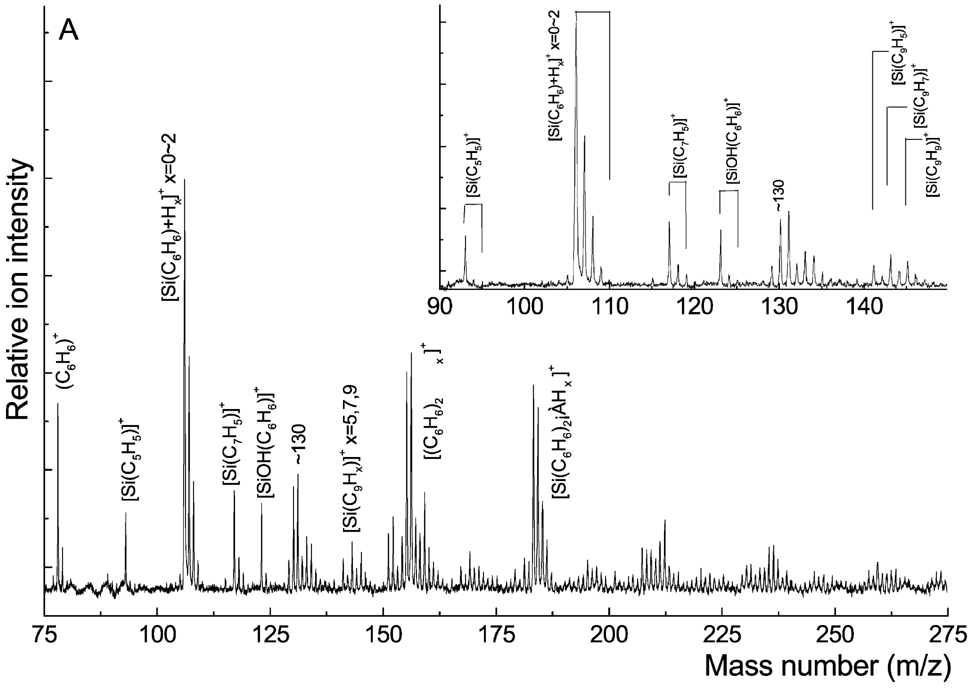


Figure 1. Typical TOF mass spectra for cationic products which were obtained from the Nd: YAG laser (532 nm, 10 mJ/pulse) ablation on the tablets of (A) Si, (B) Ge, (C) Sn in the benzene/argon (~1.25% benzene) mixed carrier gas (the insert in each mass spectra is the enlarged part of the low mass region).

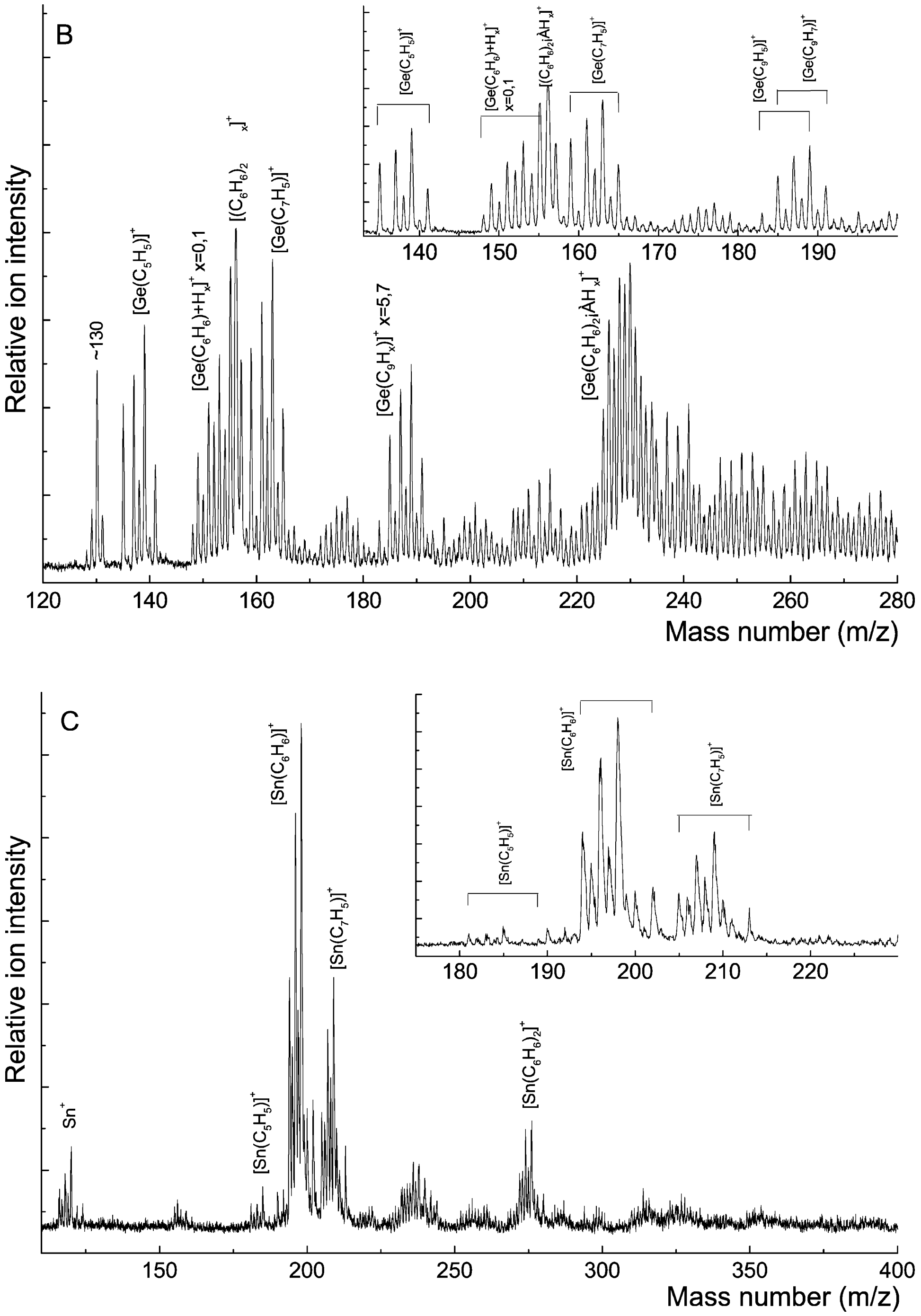


Figure 1. Continued

germanium-hydrocarbon fragment complexes were $[Ge(C_5H_5)]^+$, $[Ge(C_7H_5)]^+$ and $[Ge(C_9H_x)]^+$ (x = 5 and 7); $[(C_6H_6)_2 \pm H_x]^+$ species and unassigned peaks near *m/z* 130 were also present. In Fig. 1(C), the products for the tin reaction system include Sn-benzene association complexes $[Sn(C_6H_6)_x]^+$ (x = 1 and 2), and the Sn-hydrocarbon fragment complexes $[Sn(C_5H_5)]^+$ and $[Sn(C_7H_5)]^+$.

Figure 2(A) shows the products observed in the reactions between lead cation species (including atomic cations and clusters) and benzene molecules. In contrast to the other three elements, lead could form metal cluster ions containing up to tens of atoms under the present conditions (similar to our earlier studies[22,23]). These cluster cations could adsorb up to four benzene molecules, and no dissociation products of benzene were observed on them (not even on the dimer Pb_2^+). In order to compare the products of benzene with the Si, Ge and Sn cation species, the low-mass region (the products containing mainly one lead atom) is enlarged in Fig. 2(B). Apart from the lead-benzene association products $[Pb(C_6H_6)_x]^+$ (x = 1–4), the observed Pb-hydrocarbon fragment complexes in the spectra were $[Pb(C_5H_5)]^+$, $[Pb(C_7H_5)]^+$ and $[Pb(C_9H_x)]^+$ (x = 5, 7 and 9). Additionally, these dissociation products could adsorb other benzene molecules, forming $[Pb(C_5H_5)(C_6H_6)_x]^+$, $[Pb(C_7H_5)(C_6H_6)_x]^+$ and $[Pb(C_9H_x)(C_6H_6)_x]^+$, etc. species (x = 1, 2). The products listed above show that the Pb-hydrocarbon fragment

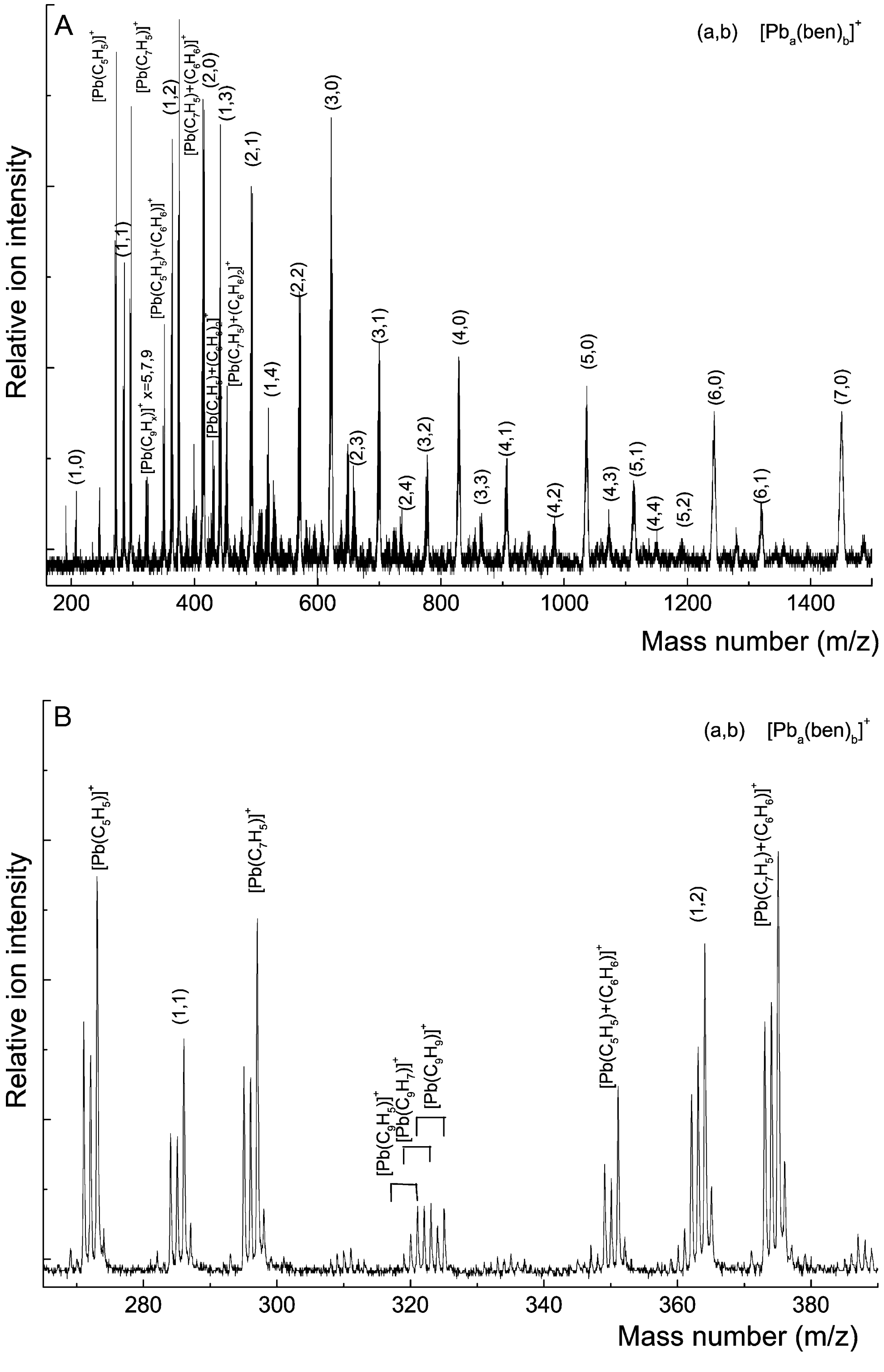


Figure 2. Typical TOF mass spectra for cationic products which were obtained from the Nd: YAG laser (532 nm, 10 mJ/pulse) ablation on the lead tablet in the benzene/argon (~1.25% benzene) mixed carrier gas. (A) is the total spectra while (B) shows the enlarged part of the low mass region.

complexes could only form in the reactions between lead atomic cations and benzene, while lead clusters were not involved in forming such reaction products.

In summary, although the properties of bulk Si, Ge, Sn and Pb change from those of semiconductors to typical metals, the reactions of their cations with benzene in the gas phase yielded similar products. The common products for these four elements included the association species $[M(C_6H_6)_x]^+$ ($x = 1, 2$, etc.) and the dissociation species $[M(C_5H_5)]^+$ and $[M(C_7H_5)]^+$, etc. The products $[M(C_9H_x)]^+$ ($x = 5$, 7 and 9) could be distinguished clearly in the Si and Pb systems, while only $[M(C_9H_x)]^+$ ($x = 5$ and 7) were observed in Ge system and very low abundance $[M(C_9H_x)]^+$ ($x = 5$, 7 and 9) complexes could be distinguished in the Sn reaction products. The main reaction channel involved in the reactions of these four elements can be described by

Eqns. (1) and (2):

$$M^+ + (C_6H_6)_x \rightarrow [M(C_6H_6)_x]^+ \qquad (x \leq 4) \qquad (1)$$

$$M^+ + (C_6H_6)_x \rightarrow [M(C_5H_5)]^+, [M(C_7H_5)]^+, [M(C_9H_x)]^+ \\ (x = 5, 7 \text{ and } 9), \text{ etc.} + \text{hydrocarbon fragments} \qquad (2)$$

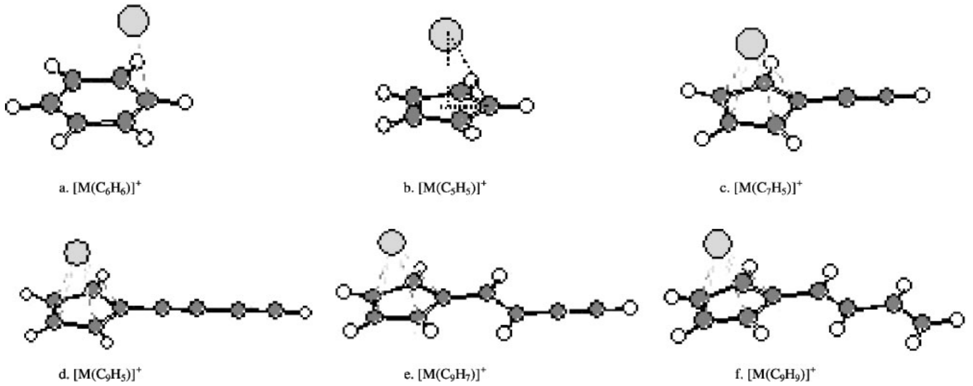
In reaction path (1), benzene molecules or clusters could be adsorbed by M^+ due to attractive electrostatic interactions, and the complexes thus formed were stabilized by collisions with the argon gas. Reaction path (2) clearly involves C–C dissociation and hydrogen migration processes. The excitation energy needed could be derived from the high-temperature laser ablation plasma. One common characteristic of the dissociation products in reaction (2) was that they contained only odd numbers of carbon atoms or hydrogen atoms. This was in contrast to the dissociation or dehydrogenation of benzene on other metal species, such as Sc^+,[9] Nb^+,[10,11] Ta^+,[12,13] etc., where the products contained mainly even numbers of carbon atoms or hydrogen atoms through losses of H_2 molecules or C_2H_2, C_2H_4, etc. The compositions of these complexes for Si, Ge, Sn and Pb imply that certain special structures could be possibly formed. This will be discussed in detail in the following section.

Structural analysis based on DFT calculations

Typically, the valence of these four elements in organic compounds is IV and the geometries in their tetravalent compounds are tetrahedral.[18,19] The only well-defined examples of M(II) compounds are bis(cyclopentadienyl) M(II) and their derivatives, and they show bent-sandwich structures in the gas phase.[24] In the present experiments the structures of the observed complexes could not be hypothesized reasonably based on the usual valence rules. In this section we will analyze their possible structures based on theoretical calculations. The products considered include $[M(C_6H_6)]^+$, $[M(C_5H_5)]^+$, $[M(C_7H_5)]^+$ and $[M(C_9H_x)]^+$ ($x = 5$, 7 and 9; M = Si, Ge, Sn and Pb). Although $[Ge(C_9H_9)]^+$ and $[Sn(C_9H_x)]^+$ ($x = 5$, 7 and 9) were not distinguished clearly in the mass spectra, their structures were also optimized in order to compare with the results for $[M(C_9H_x)]^+$ ($x = 5$, 7 and 9; M = Si and Pb).

All studies were conducted using the Gaussian 98 program.[25] The theory level used was B3LYP (Becke's three-parameter hybrid density functional method with the Lee-Yang-Parr correlation functional method[26]). All group IV atoms (Si, Ge, Sn and Pb) were described using the lanl2dz basis, while the C and H atoms were described using the 6-31G* basis. It was found that, based on the calculated results, similar composition complexes for Si, Ge, Sn and Pb have similar structures at their energy minima. Numerous local-minimum energy structures were found (e.g. forming different carbon skeletons or hydrogen adding to different sites, etc.), and only the most stable structure for each complex is shown in Scheme 1.

For $[M(C_6H_6)]^+$ (M = Si, Ge, Sn and Pb), the predicted structures are shown in Scheme 1(a). It can be seen that the M atom lies close to one carbon atom of the benzene molecule. This is in contrast to most of the transition metal-benzene complexes, where the transition metal atom is situated on the sixfold axis of the benzene molecule.[8] This difference is due to the different bond patterns involved. In transition metal-benzene complexes, d orbitals of transition metals interact with π orbitals of the benzene molecules, while, in complexes of group IVA elements with benzene, p orbitals of M (M = Si, Ge, Sn and Pb) and π orbitals of benzene are mainly involved.



a. $[M(C_6H_6)]^+$ b. $[M(C_5H_5)]^+$ c. $[M(C_7H_5)]^+$

d. $[M(C_9H_5)]^+$ e. $[M(C_9H_7)]^+$ f. $[M(C_9H_9)]^+$

Scheme 1. The structures of the most stable structures for (a) $[M(C_6H_6)]^+$, (b) $[M(C_5H_5)]^+$, (c) $[M(C_7H_5)]^+$, (d) $[M(C_9H_5)]^+$, (e) $[M(C_9H_7)]^+$ and (f) $[M(C_9H_9)]^+$. (M = Si, Ge, Sn and Pb, M: ○, C: ●, H: ○).

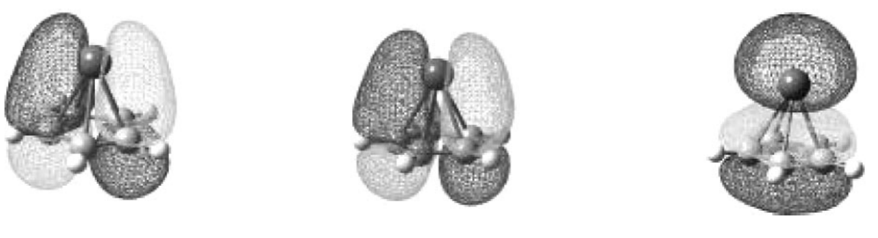


Figure 3. The HOMO(e_1), HOMO-1(e_1) and HOMO-2(a_1) orbitals in the stable structure of $[PbC_5H_5]^+$. (Plotted based on the DFT calculation results).

The lower-lying structures for all dissociation products were found to be pentagonal structures in which the M atom is situated on the fivefold axis of a five-membered ring. The main bond pattern between the M atom and the five-membered ring should be that one p electron of each of the five carbon atoms is part of the large π system, which also includes the unpaired p electron of the M cation. The planarity, and delocalized-ring π system, including six electrons of the five-membered-ring, indicate its aromatic character. This was confirmed by an examination of the molecular orbitals of these complexes. As an example, the shapes of the HOMO(e_1), HOMO-1(e_1) and HOMO-2(a_1) orbitals of $[Pb(C_5H_5)]^+$ were plotted (Fig. 3), based on the calculation results. They were very similar to those of the two e_1 ''orbitals and one a_2'' orbital in the free aromatic $(C_5H_5)^-$ group, respectively.[27]

CONCLUSIONS

Reactions between M^+ (M = Si, Ge, Sn and Pb) and benzene in the gas phase were studied using a laser ablation/inert buffer gas ion source coupled with a reflectron time-of-flight mass spectrometer. Two kinds of reactions were observed: (1) an association reaction pathway and (2) a dissociation reaction pathway. DFT calculations were performed on the possible structures of the dominant products. The results showed that in the association products $[M(C_6H_6)]^+$, M is close to one carbon atom of benzene, while in the dissociation complexes $[M(C_5H_5)]^+$, $[M(C_7H_5)]^+$ and $[M(C_9H_x)]^+$ (x = 5, 7, 9), etc., M was situated on the fivefold axis of a five-membered ring structure (M/cyclopentadienyl derivatives), in which an aromatic π system was formed.

Acknowledgements

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REFERENCES

1. Eller K, Schwarz H. *Chem. Rev.* 1991; **91**: 1121.
2. Willy KF, Chen PY, Bishop MB, Duncan MA. *J. Am. Chem. Soc.* 1991; **113**: 4721.
3. Willy KF, Yeh CS, Robbins DL, Duncan MA. *J. Phys. Chem.* 1992; **96**: 9106.
4. Yeh CS, Willy KF, Robbins DL, Duncan MA. *Int. J. Mass Spectrom. Ion Processes* 1994; **131**: 307.
5. Hosshino K, Kurikawa T, Takeda H, Nakajima A, Kaya K. *J. Phys. Chem.* 1995; **99**: 3053.
6. Kurikawa T, Hirano M, Takeda H, Yagi K, Hoshino K, Nakajima A, Kaya K. *J. Phys. Chem.* 1995; **99**: 16248.
7. Kurkawa T, Takeda H, Hiranok M, Judai K, Arita T, Nagao S, Nakajima A, Kaya K. *Organometallics* 1999; **18**: 1430.
8. Pandey R, Rao BK, Jena P, Blanco MA. *J. Am. Chem. Soc.* 2001; **123**: 3799.
9. Freiser BS. *Bonding Energetics in Organometallic Compounds.* ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990; 55.
10. Buckner SW, Macmahon TJ, Byrd GD, Frieser BS. *Inorg. Chem.* 1989; **28**: 3511.
11. Higashide H, Oka T, Kasatani K, Shinohara H, Sato H. *Chem. Phys. Lett.* 1989; **163**: 485.
12. Wise MB, Jacobson DB, Freiser BS. *J. Am. Chem. Soc.* 1985; **107**: 1590.
13. Wise MB, Jacobson DB, Freiser BS. *J. Am. Chem. Soc.* 1985; **107**: 6744.
14. Higashide H, Kaya T, Kobayash M, Shinohara H, Sato H. *Chem. Phys. Lett.* 1990; **171**: 297.
15. Judai K, Hirano M, Kawamata H, Yabushita S, Nakajima A, Kaya K. *Chem. Phys. Lett.* 1997, **270**, 23.
16. Jackson GS, White FM, Hammill CL, Clark RJ, Marshall AG. *J. Am. Chem. Soc.* 1997; **119**: 7567.
17. Berg C, Beyer M, Achatz U, Joos S, Niedner-Schatteburg G, Bondybey VE. *J. Chem. Phys.* 1998; **108**: 5398.
18. Rochow EG, Abel EW. *The Chemistry of Ge, Tin and Lead.* Pergamon Press: Oxford, 1975.
19. Harrison PG. *Organometallic Compounds of Ge, Tin and Lead.* Chapman and Hall Ltd: London, 1985.
20. Maruyama S, Anderson LR, Smalley RE. *Rev. Sci. Instrum.* 1990; **61**: 3686.
21. Xing XP, Tian ZX, Liu P, Gao Z, Zhu QH, Tang ZC. *Chin. J. Chem. Phys.* 2002; **15**: 83.
22. Tian ZX, Xing XP, Tang ZC. *Rapid Commun. Mass Spectrom.* 2003; **17**: 17.
23. Tian ZX, Xing XP, Tang ZC. *Rapid Commun. Mass Spectrom.* 2002; **16**: 1515.
24. Smith JD, Hanusa TP. *Organometallics* 2001; **20**: 3056.
25. Frisch MJ, *et al.* Gaussian, Inc., Pittsburgh PA, 1998.
26. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648.
27. Thomas AA, Jeremy KB, Myung-hwan W. *Orbital Interactions in Chemistry.* Wiley-Interscience: New York, 1984; 214.