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Reactions of platinum cluster ions with benzene

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In this work, the cation and anion products of the reactions between platinum clusters produced by laser ablation and the benzene molecules seeded in argon have been studied using a high-resolution reflectron time-of-flight mass spectrometer (RTOFMS). The dominant cation products are $[C_{6n}H_{6n-k}]^+$ and $[Pt_m(C_6H_6)_n]^+$ complexes, while the dominant anion products are dehydrogenated species, $[C_6H_5PtH]^-$, $[PtC_{12}H_k]^-$ and $[Pt_mC_6H_4\cdots(C_6H_6)_n]^-$, etc. Some important intermediate structures ($[PtC_6H_6]^+$, $[Pt(C_6H_6)_2]^+$, $[Pt_2(C_6H_6)_3]^+$, $[C_6H_5PtH]^-$, $[Pt_2C_6H_4]^-$, $[Pt_3C_6H_4]^-$ and $[Pt_4C_6H_4]^-$) have been analyzed using density functional theory (DFT) calculations. Different reaction mechanisms are proposed for platinum cluster cations and anions with benzene, respectively. Copyright © 2006 John Wiley & Sons, Ltd.

Studies of the chemical interactions between metal clusters and organic molecules can provide useful information which leads to a deeper understanding of some of the important heterogeneous catalytic processes in organometallic chemistry.[1] As a fundamental chemical issue in both theoretical studies and industrial applications, the adsorption and dissociation of benzene on the surfaces of metal clusters has been a topic of some interest for many years.[2–8] The structure and properties of metal-aromatic molecule complexes have been studied extensively. For example, Duncan and co-workers[9,10] have investigated the dissociation processes of metal cation-benzene complexes in the gas phase and discussed the dissociative charge-transfer process in detail. Kaya and co-workers[11–13] have synthesized neutral 3d transition-metal–benzene complexes through the reactions between metal clusters and benzene in the gas phase. They studied the mass distribution, the reactivity, and the ionization energy of these complexes and presented two different structures: (1) a sandwich structure (for Sc, Ti, V, etc.), in which the metal atom was separated by benzene molecules one by one, and (2) a rice-ball structure (for Fe, Co, Ni, etc.), in which the metal clusters were surrounded by benzene molecules. In our previous work,[14,15] we reported the generation of $[M_m\text{–phenyl}]^-$ ($M = Mn\text{–}Cu$) complexes and the reactions between cation and anion lead clusters with benzene, and proposed the reaction mechanism of the anion metal clusters inducing a selective benzene C–H cleavage.

Platinum is one of the most important metal catalysts with applications including hydrogenation, dehydrogenation, and cracking of various hydrocarbons. Considering the importance of these processes, it comes as no surprise that many of the corresponding reactions have been studied using platinum clusters as model systems.[16–22] Prior analyses of platinum cluster reactions with benzene have mainly concentrated on neutral and cationic clusters. Kaldor and co-workers[5] studied neutral platinum cluster reactions with benzene by photoionization time-of-flight mass spectrometry, and they observed platinum cluster chemisorbed benzene ($Pt_m(C_6H_6)_n$), and for $Pt_m(C_6H_6)_n$ ($m \geq 3$) the benzene adducts begin to dehydrogenate. Jackson and co-workers[23] studied small platinum cluster cations reacted with benzene using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, and they found Pt_n^+ ($n = 1\text{–}4$) cluster ions could dehydrogenate benzene after the reaction was completed (30 s). *Ab initio* calculations have been carried out recently for small benzene–platinum complexes by Balasubramanian and co-workers,[24,25] and they suggested neutral $Pt_m(C_6H_6)_n$ complexes had a staircase structure, while the $PtC_6H_6^+$ complex had a C_{6v} structure (platinum atom above the benzene molecule centre). However, the small anionic platinum cluster reaction with benzene has rarely been reported, except by Eberhardt and co-workers,[26] who studied $Pt_2(C_6H_6)^-$ ions by photoelectron detachment spectroscopy. The reactions of negative and positive atomic platinum ions with benzene have been studied in detail by El-Nakat and co-workers,[27] who did not observe products of the reaction of the Pt^- ion with benzene.

In the study reported here, the reactions between platinum cluster ions and benzene molecules were carried out using laser ablation and a buffer gas in the ion source. The products were analyzed using a high-resolution reflectron time-of-flight mass spectrometer (RTOFMS). In particular, the reactions of platinum cluster anions with benzene have been studied in detail, as those had not been reported previously. Through comparison with previous experimental results, different reaction processes and bonding patterns were observed for the platinum cluster cations and anions

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with benzene. The proposed mechanisms involved in these reactions are discussed in detail.

EXPERIMENTAL

The reactions of platinum clusters with benzene were performed using a home-made high-resolution RTOFMS (similar to that of Mamyrin and Scmikk[28]) coupled with a Smalley-type[29] laser vaporization source. A detailed description of the apparatus has been given elsewhere,[30,31] and only an outline is given here.

The pure platinum disk targets were ablated by a pulsed laser beam (532 nm Nd:YAG laser, 10 mJ/pulse) and the targets were rotated during the experiment. The laser-induced plasma was mixed with benzene (analytical reagent) in a channel and the benzene was seeded in argon (purity 99.99%) carrier gas delivered by a pulsed valve at a backing pressure of about 400 kPa. The volume ratio of benzene in the mixed gas was about 0.2%. The clustering processes and the reactions with benzene are completed near the nozzle exit.[32] The products are cooled by supersonic expansion into vacuum. After passing a skimmer, all products enter into the accelerating area. The pulsed electric field is operated in two polarity modes to detect either cationic or anionic products. The products are then extracted perpendicularly from the collimated cluster beam for size analysis by the RTOFMS. The resolution (M/ΔM) of the mass spectrometer is about 2000, so it is easy to resolve the number of hydrogen atoms in the products.

RESULTS AND DISCUSSION

Reaction of platinum cluster cations with benzene

Figure 1 shows a typical mass spectrum of cationic products from the reaction of platinum cluster cations with benzene. Pt_n^+ ions are very weak among the abundant cationic species in the spectrum shown Fig. 1 and only Pt^+ and Pt_2^+ ions are observed. Tian and co-workers[33,34] investigated lead (Pb) cluster reactions with some small organic molecules, and found seeding of the reaction gas (i.e., acetone) in the carrier gas (argon) promoted the growth of Pb_k^+ clusters. However, this phenomenon is not apparent in the experiments reported here. The dominant reaction channel in our experimental results is association of the cation with benzene, forming $[Pt_m(C_6H_6)_n]^+$ (m = 1–4, n = 1–5) complexes. The increased width of $[Pt_m(C_6H_6)_n]^+$ complex peaks is due to the large isotope distribution of Pt_m. Additionally, several hydrocarbon cations, e.g. $C_{10}H_{10}^+$ and $[(C_6H_6)_n]^+$ (n = 1–4), are also observed. In the experimental apparatus used here, the reactions occurred at about 200–270 K in the tube reactor, and the products are cooled to about 150 K by supersonic expansion into the vacuum (simulation results using the 3D-hydro program).[35] Under these experimental conditions, benzene molecules should be adsorbed on platinum cluster cations through chemical interaction in the complexes formed.

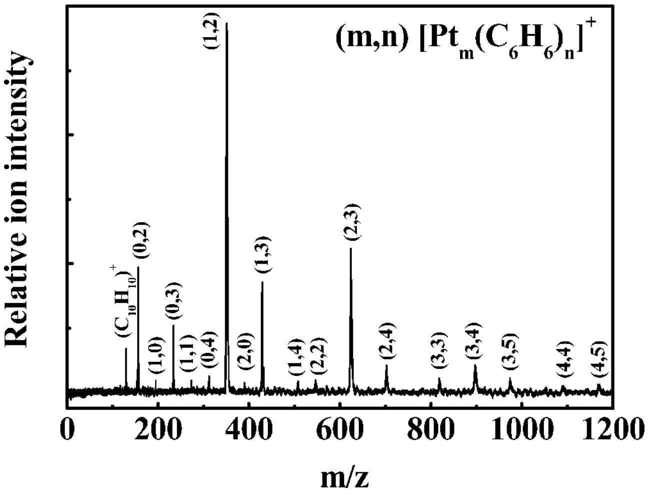

Figure 1. Typical mass spectrum of the cation products by laser vaporization/ionization of platinum into a mixture of argon and benzene (0.2% benzene in 400 kPa mixed gas).

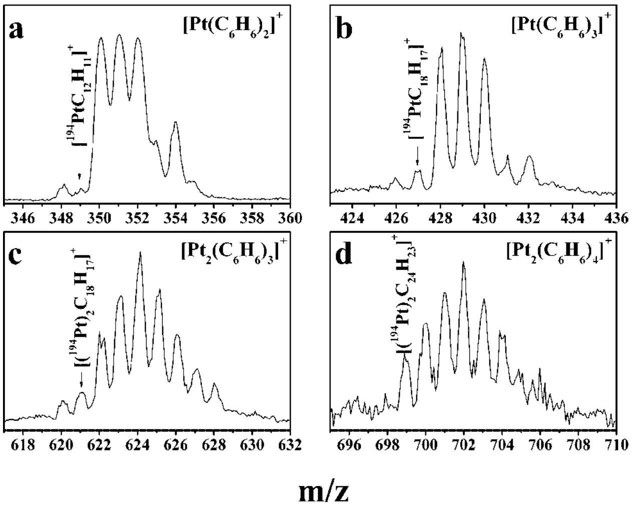

Figure 2. The enlarged mass spectrum of several typical Pt/benzene cation product peak profiles: (a) $[Pt(C_6H_6)_2]^+$, (b) $[Pt(C_6H_6)_3]^+$, (c) $[Pt_2(C_6H_6)_3]^+$, and (d) $[Pt_2(C_6H_6)_4]^+$.

Several typical enlarged peaks from $[Pt_m(C_6H_6)_n]^+$ complexes are shown in Fig. 2. Here we should note that in Fig. 2(a) the $[Pt(C_6H_6)_2]^+$ ion abundance is so strong that its ion signal has saturated. Nonetheless, the isotopic peak distributions are still clear. In Fig. 2(a), the intensity distribution of the ions at *m/z* of 350, 351, 352 and 354 are in agreement with a single Pt species. This can only be explained as the benzene product $[Pt(C_6H_6)_2]^+$. The phenyl addition product $[PtC_{12}H_{11}]^+$ is unambiguously evident as minor products because of the presence of the low intensity ion of $[^{194}PtC_{12}H_{11}]^+$ at *m/z* 349 (here we also have taken into account the contribution of $[^{192}Pt^{13}CC_{11}H_{12}]^+$, with a contribution to the ion intensity less than 20%). Thus the peaks at *m/z* 350 and 351 are from more than one ion, e.g. *m/z* 350 is a mixture of $[^{194}Pt(C_6H_6)_2]^+$ and $[^{195}PtC_{12}H_{11}]^+$. The ions in the spectra shown in Figs. 2(b)–2(d) can be identified in a similar way to that in Fig. 2(a). Hence analyzing the ion distributions, we find that the $[Pt_m(C_6H_6)_n]^+$ complexes are the major products, and the minor products $[Pt_mC_{6n}H_{6n-1}]^+$ are also observed. For the other $[Pt_m(C_6H_6)_n]^+$ complex

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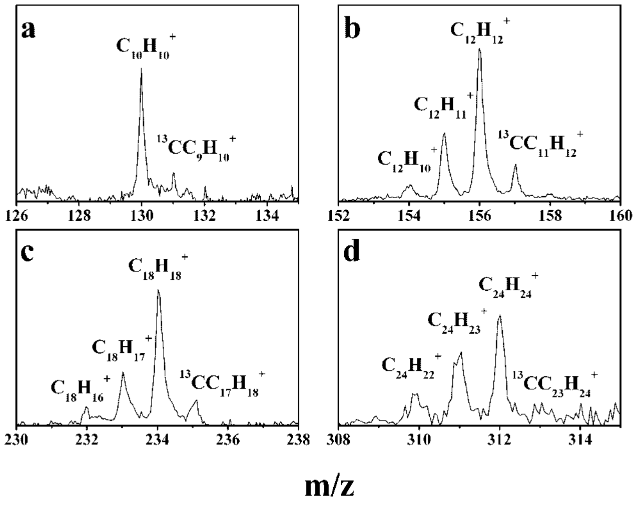


Figure 3. The enlarged mass spectrum of several typical hydrocarbon cation product peak profiles: (a) $[C_{10}H_{10}]^+$, (b) $[C_{12}H_{12-k}]^+$, (c) $[C_{18}H_{18-k}]^+$, and (d) $[C_{24}H_{24-k}]^+$ ($k = 0$–2).

peaks, their minor dehydrogenated products cannot be clearly distinguished owing to their weak signals.

Figure 3 shows those hydrocarbon ion products in detail. The $[C_{10}H_{10}]^+$ ion is shown in Fig. 3(a). All the other peaks from $[(C_6H_6)_n]^+$ ions in Figs. 3(b)–3(d) exhibit the dehydrogenated products such as $[C_{12}H_{11}]^+$, $[C_{12}H_{10}^+]$, $[C_{18}H_{17}]^+$, $[C_{18}H_{16}^+]$ and $[C_{24}H_{23}^+]$, etc. The order of ion intensity is $[C_{6n}H_{6n}]^+ > [C_{6n}H_{6n-1}]^+ > [C_{6n}H_{6n-2}]^+$.

In our experiments the cation products are different to those from a previous publication of Jackson and co-workers,[23] who observed Pt_m^+ ($m = 1$–4) dehydrogenated benzene. They also observed final products that lost at least one H_2, and no hydrocarbon cation products were observed. A possible reason for this is that the concentration of the reagent benzene is different between this work (benzene at 0.2% of a mixed gas is several orders of magnitude greater than that of FTICR) and that of the Pt ions studied by Jackson and co-workers.[23] The platinum clusters formed in our reactor do not have sufficient time to be cooled down, and the carrier gas plays a very important role in stabilizing the products. It has been reported that the association products form easily at low collision energies and under multiple-collision conditions.[36] The excited $[Pt_m(C_6H_6)_n]^{+*}$ and $[Pt_mC_{6n}H_{6n-k}]^{+*}$ could be stabilized by collisions with the carrier gas or dissociated to platinum clusters and hydrocarbon ions. Thus, we conclude that the formation of the cation products occurs via Eqns. (1), (2), (3) and (4), with the major processes those shown in Eqns. (1) and (2).

$$Pt_m^+ + (C_6H_6)_n \rightarrow [Pt_m(C_6H_6)_n]^{+*} \xrightarrow{Ar} [Pt_m(C_6H_6)_n]^+ \tag{1}$$

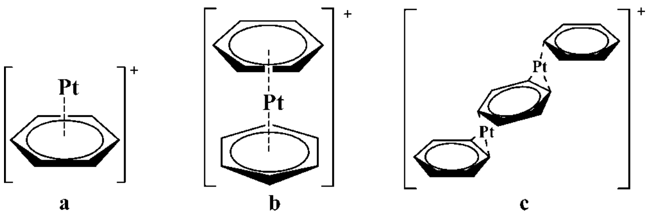
$$[Pt_m(C_6H_6)_n]^{+*} \rightarrow Pt_m + [(C_6H_6)_n]^+ \tag{2}$$

$$\begin{aligned} Pt_m^+ + (C_6H_6)_n &\rightarrow [Pt_mC_{6n}H_{6n-k}]^{+*} + k[H] \\ &\xrightarrow{Ar} [Pt_mC_{6n}H_{6n-k}]^+ \end{aligned} \tag{3}$$

$$[Pt_mC_{6n}H_{6n-k}]^{+*} \rightarrow Pt_m + [C_{6n}H_{6n-k}]^+ \tag{4}$$

The distribution of the $[Pt_m(C_6H_6)_n]^+$ series in Fig. 1 has two characteristics. One is that the number of adsorbed benzene molecules is no less than the number of Pt atoms. Another is that the $[Pt_m(C_6H_6)_{m+1}]^+$ ions show apparently enhanced intensity among the cationic species, while the intensities of the $[Pt_m(C_6H_6)_m]^+$ ions are very weak. This characteristic is different from that of the reactions between Pb_m^+ and benzene,[15] for which no apparent 'magic number' of peaks appeared in the product series. However, our results are similar to reports of the reactions between vanadium and benzene,[11] for which a similar 'magic number' of peaks of $[V_m(C_6H_6)_{m+1}]^+$ ions was observed, and their structure was confirmed as a sandwich.

In order to determine the possible structures for these products, density functional theory (DFT) calculations have been performed on $[PtC_6H_6]^+$, $[Pt(C_6H_6)_2]^+$ and $[Pt_2(C_6H_6)_3]^+$ using Amsterdam density functional (ADF) programs.[37] Full geometric optimization for all the cluster structures is performed with relativistic DFT calculations at the level of the generalized gradient approach using a Perdew-Wang exchange-correlation functional.[38] The zero-order regular approximation Hamiltonian is used to account for the scalar (mass velocity and Darwin) relativistic effects.[39] The standard Slater-type orbital basis sets of the triple-zeta plus two polarization functions (TZ2P) are used for the orbitals of Pt, C and H atoms and the frozen core ($1s^2$–$4f^{14}$) approximation is used for Pt. It has been shown previously that these theoretical methods are suitable for studying transition-metal clusters.[40,41] The optimized lowest energy structures are shown in Scheme 1. For the $[PtC_6H_6]^+$ ion (Scheme 1, **a**), the platinum atom is situated on the sixfold axis of the benzene molecule with a C_{6v} structure. For the $[Pt(C_6H_6)_2]^+$ ion (Scheme 1, **b**), the lowest energy structure is a sandwich structure. However, the $[Pt_2(C_6H_6)_3]^+$ ion (Scheme 1, **c**) prefers a low-symmetry equilibrium staircase structure, which is similar to the neutral $[Pt_2(C_6H_6)_3]$ complex reported by Balasubramanian and co-workers.[24] According to the above analysis, we suggest all the larger $[Pt_m(C_6H_6)_{m+1}]^+$ ions are most likely similar to the neutral cases, i.e. having a staircase structure. The staircase structures do not fit for the $[Pt_m(C_6H_6)_{m+2}]^+$ complexes, for which the rice-ball structure appears to be more reasonable.[12]



Scheme 1. Proposed structures with the lowest energy optimized by DFT calculations: (a) $[PtC_6H_6]^+$, (b) $[Pt(C_6H_6)_2]^+$ and (c) $[Pt_2(C_6H_6)_3]^+$.

Reaction of platinum cluster anions with benzene

In comparison with the cations, the reactions between anionic platinum clusters and benzene are very different. A

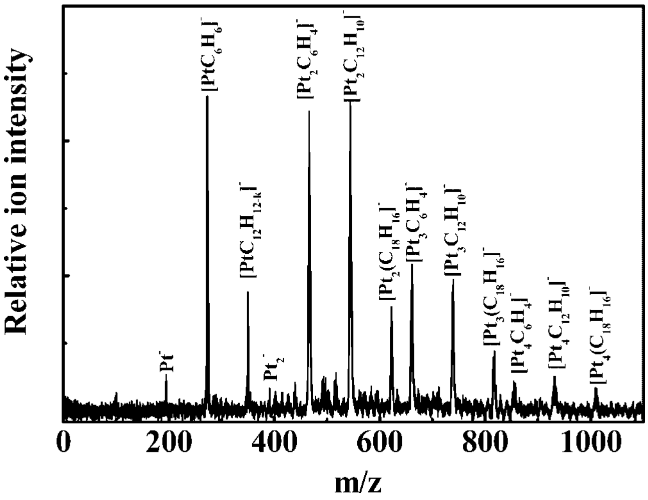


Figure 4. Typical mass spectrum of the anion products by laser vaporization/ionization of platinum into a mixture of argon and benzene (0.2% benzene in 400 kPa mixed gas).

typical time-of-flight (TOF) mass spectrum of the anionic products is shown in Fig. 4. Several typical reaction product peaks have been enlarged in Fig. 5, which shows the isotopic distributions and resolves the number of hydrogen atoms in the products easily.

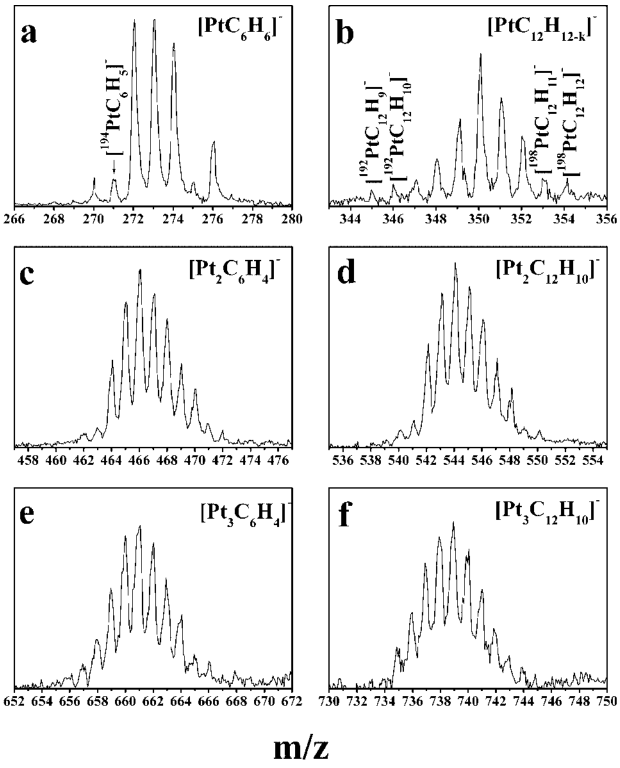
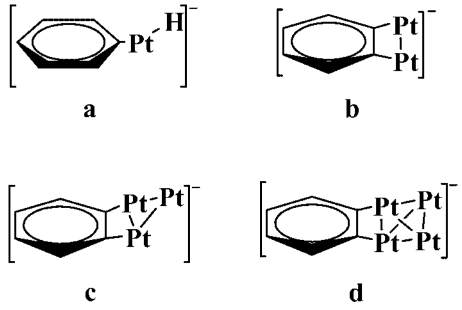


Figure 5. The enlarged mass spectrum of several typical Pt/benzene anion product peak profiles: (a) $[PtC_6H_6]^-$, (b) $[PtC_{12}H_{12-k}]^-$, (c) $[Pt_2C_6H_4]^-$, (d) $[Pt_2C_{12}H_{10}]^+$, (e) $[Pt_3C_6H_4]^-$, and (f) $[Pt_3C_{12}H_{10}]^+$.



Scheme 2. Proposed structures with the lowest energy optimized by DFT calculations: (a) $[C_6H_5PtH]^-$, (b) $[Pt_2C_6H_4]^-$, (c) $[Pt_3C_6H_4]^-$, and (d) $[Pt_4C_6H_4]^-$.

As shown in Fig. 4, the pure Pt_m^- clusters are very weak and only $Pt^-$and Pt_2^- ions are observed, which is similar to the case of the cationic reactions. The dominant products are $[PtC_6H_6]^-$, $[PtC_{12}H_k]^-$ (k = 9–12) and $[Pt_mC_{6n}H_{6n-2}]^-$ (m = 2–4, n = 1–3). Figure 5(a) is an enlargement of the $[PtC_6H_6]^-$ ion peaks, from which the existence of the minor dehydrogenated $[PtC_6H_5]^-$ ions can be deduced from the isotopic distribution. It can be estimated from ion abundance calculations that the $[PtC_6H_5]^-$ ion abundance is less than 10% of the $[PtC_6H_6]^-$ ion. In Fig. 5(b), the ions at *m/z* of 345, 346, 353 and 354 can only be from $[^{192}PtC_{12}H_9]^-$, $[^{192}PtC_{12}H_{10}]^-$, $[^{198}PtC_{12}H_{11}]^-$ and $[^{198}PtC_{12}H_{12}]^-$, successively again. Through ion abundance calculations we can determine the approximate percentages of each product. These are 10% $[PtC_{12}H_9]^-$, 26% $[PtC_{12}H_{10}]^-$, 17% $[PtC_{12}H_{11}]^-$ and 47% $[PtC_{12}H_{12}]^-$. Except for the products of the negative platinum ion reaction with benzene, all the other products (i.e. $[Pt_mC_{6n}H_{6n-2}]^-$ (m = 2–4, n = 1–3)) have lost one H_2 from the benzene ligands. As an example, several typical products of those complexes can be seen clearly in Figs. 5(c)–5(f). These show that platinum cluster anions dehydrogenate benzene in the gas phase.

The results from DFT calculations for $[PtC_6H_6]^-$ are shown in Scheme 2 and the insertion structure of the $[PtC_6H_6]^-$ ion (Scheme 2, **a**) has the lowest energy, which is about 1.74 eV lower than the second energy minimum C_{6v} structure (like the case of the $[PtC_6H_6]^+$ product **a** in Scheme 1, where the Pt atom is above the benzene molecule centre). So we suggest in our experiments that the Pt^- inserts into the C–H bond forming $[C_6H_5–PtH]^{-*}$, which can be stabilized through collision with argon. A fraction of the $[C_6H_5–PtH]^{-*}$ ions lose the hydrogen atom producing $[C_6H_5–Pt]^-$. The $[C_6H_5–PtH]^{-*}$ also can react with another benzene producing $[PtC_{12}H_{12-k}]^-$. The mechanisms of negative platinum ion reactions with benzene are summarized in Eqns. (5)–(7).

$$Pt^- + C_6H_6 \rightarrow [C_6H_6 - PtH]^{-*} \xrightarrow{Ar} [C_6H_5 - PtH]^- \quad (5)$$

$$[C_6H_6 - PtH]^{-*} \xrightarrow{Ar} [C_6H_5 - Pt]^- + [H] \quad (6)$$

$$[C_6H_6 - PtH]^{-*} + C_6H_6 \rightarrow [PtC_{12}H_{12-k}]^{-*} + k[H] \xrightarrow{Ar} [PtC_{12}H_{12-k}]^- \quad (7)$$

According to the number of adsorbed benzene molecules, $[Pt_mC_{6n}H_{6n-2}]^-$ products can be divided into three series. First, the single benzene loses one H_2 forming the benzyne products, $[Pt_mC_6H_4]^-$ (m = 2–4). This is different from our previous results with other reactions of metal cluster anions with benzene, which generated the $[M_m\text{-phenyl}]^-$ (M = Mn–Cu, and Pb) complexes, and the phenyl groups bond on the metal surfaces using the metal–carbon σ bond.[14,15] Obviously, the most likely reaction mechanism is that two adjacent hydrogen atoms of benzene are displaced by Pt_m^- and then one H_2 is eliminated forming the benzyne complexes $[Pt_mC_6H_4]^-$. The optimized structures of the lowest energy are listed in Scheme 2 (**b**–**d**), and all show the Pt_m combined to benzyne through two σ bonds. $[PtC_6H_4]^+$ has been observed by El-Nakat and co-workers,[27] and benzyne complexes are given more attention in organometallic chemistry.[42] The second series is where only one H_2 is lost to form $[Pt_mC_{12}H_{10}]^-$ complexes. If we analyze the bonding patterns separately in these anion products, they should be expressed as $[Pt_m\text{–}(C_6H_5)_2]^-$, the phenyl groups should bind with the metal cluster using the metal–carbon σ bond. But in view of the presence of the first series of $[Pt_mC_6H_4]^-$ complexes, we prefer the explanation that it is the $[Pt_mC_6H_4]^-$ adsorbing another benzene molecule, forming a $[Pt_mC_6H_4\cdots C_6H_6]^-$ species, in which two possible bond patterns (metal–carbon σ bond and metal surfaces/π-orbital of benzene interaction) exist. Using this stepwise adsorbing process provides a more reasonable explanation of the $[Pt_mC_{18}H_{16}]^-$ complexes also being formed by $[Pt_mC_6H_4]^-$ adsorbing two benzene molecules. So the last product series should be expressed as $[Pt_mC_6H_4\cdots(C_6H_6)_2]^-$. The above process is similar to the case of $[M_m\text{–phenyl}]^-$ (M =(Mn–Cu) complexes adsorbing benzene.[14] When $[Pt_mC_6H_4]^-$ is formed, the negative charge in the metal can partially delocalize to the benzene group through the metal–carbon bond, and therefore another benzene molecule can possibly be adsorbed onto the metal. Then in turn the $[Pt_mC_6H_4\cdots C_6H_6]^-$ can adsorb the third benzene molecule forming $[Pt_mC_6H_4\cdots(C_6H_6)_2]^-$; however, adding one benzene on $[Pt_mC_6H_4\cdots C_6H_6]^-$ is harder than on $[Pt_mC_6H_4]^-$ owing to the first benzene having a steric effect. As can be seen in Fig. 4, the ion intensities of $[Pt_mC_6H_4\cdots(C_6H_6)_2]^-$ are much lower compared with the $[Pt_mC_6H_4]^-$ and $[Pt_mC_6H_4\cdots C_6H_6]^-$ ions. In summary, the anion reaction products and the proposed formation mechanisms are expressed in Eqns. (8)–(10).

$$Pt_m^- + C_6H_6 \rightarrow [Pt_m\cdots(C_6H_6)]^{-*} \rightarrow [Pt_mC_6H_4]^- + H_2 \quad (8)$$

$$[Pt_mC_6H_4]^- + C_6H_6 \rightarrow [Pt_mC_6H_4\cdots C_6H_6]^{-*} \xrightarrow{Ar} [Pt_mC_6H_4\cdots C_6H_6]^- \quad (9)$$

$$[Pt_mC_6H_4\cdots C_6H_6]^- + C_6H_6 \rightarrow [Pt_mC_6H_4\cdots(C_6H_6)_2]^{-*} \xrightarrow{Ar} [Pt_mC_6H_4\cdots(C_6H_6)_2]^- \quad (10)$$

Publications reporting reactions of the platinum anion have been relatively few; only Ervin and co-workers have carried out work on the reactions of small platinum cluster anions.[21,22] The resulting clusters, Pt_nO^-, react with CO, yielding Pt_n^- and CO_2, thus providing an example of a complete catalytic cycle in the gas phase.[43] In recent research, photoelectron spectroscopy (PES) of $Pt_2\text{–}C_6H_6^-$ anions has been reported by Eberhardt and co-workers,[26] and Pt–benzene anion complexes have been produced using a similar cluster ion source, in which no dehydrogenated products were observed. However, based on the high resolution of the RTOFMS, the platinum cluster anion dehydrogenated benzene products are unambiguously observed in our experiments. We suggest a more reasonable mechanism and bonding pattern of anion products through analyzing the observed mass spectra; however, mass spectra alone do not allow a complete understanding of the reaction mechanism and structures for the products. There may be other possible product structures, e.g. the $[Pt_mC_6H_4\cdots C_6H_6]^-$ ions may exist as another isomer structure of the phenyl group products $[Pt_m\text{–}(C_6H_5)_2]^-$. A further experimental study on the details of the reaction mechanism and structures for the products will be carried out to explore these alternate possibilities.

CONCLUSIONS

The reactivity of platinum cluster ions with benzene has been studied using a RTOFMS with a laser ablation argon buffer gas ion source. Based on the high resolution of the RTOFMS the isotopic distributions of many peaks have been analyzed in detail. The dominant cation products are $[Pt_m(C_6H_6)_n]^+$ complexes, which are mixed with minor amounts of the products with one less hydrogen atom, i.e. $[Pt_mC_{6n}H_{6n-1}]^+$. The results from DFT calculations indicate that larger $[Pt_m(C_6H_6)_n]^+$ complexes prefer low-symmetry staircase structures. Several hydrocarbon ions such as $[C_{10}H_{10}]^+$ and $[C_{6n}H_{6n-k}]^+$ (n = 2–4, k = 0–2) have been observed.

In the case of anions, the products of negative platinum ion reactions with benzene are $[C_6H_5PtH]^-$ and $[PtC_{12}H_{12-k}]^-$ (k = 0–3). The calculated platinum atom insertion structure of $[C_6H_5PtH]^-$ has the lowest energy, and this result is different from the case of the $[PtC_6H_6]^+$ cations, for which the lowest energy structure has the platinum above the benzene molecule centre. The products of the Pt_m^- (m = 2–4) reaction with benzene are $[Pt_mC_6H_4\cdots(C_6H_6)_n]^-$ (n = 0–2) complexes. The reaction mechanisms are proposed to involve platinum cluster anions dehydrogenating benzene followed by a stepped adsorption of benzene, which is a rare case in chemistry. Verifying these structures and properties is therefore essential for developing a microscopic level description of these important organic reactions. A combination of the PES[44] and *ab initio* calculations for these anion products is now underway.

Acknowledgements

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