

# Reactions of lead cluster ions with ethylene, propene, *trans*-butene, and *cis*-butene

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Reactions of lead cluster cations and anions with ethylene, propene, and *trans*- and *cis*-butene have been studied using a home-built reflectron time-of-flight mass spectrometer. Both the high- and low-energy pathway reactions were observed in the lead cluster reactions. For ethylene, only association products  $[\text{Pb}_k(\text{C}_2\text{H}_4)_n]^+$  were observed. For propene, both association products  $[\text{Pb}_k(\text{C}_3\text{H}_6)_n]^+$ , high-energy pathway products  $[\text{Pb}_k(\text{CH}_3)^+]$  and their further association products  $[\text{Pb}_k(\text{CH}_3)_m(\text{C}_3\text{H}_6)_n]^+$  were observed, while for butenes, besides the three kinds of products mentioned above,  $\text{Pb}_k(\text{C}_4\text{H}_8)_n^+$ ,  $\text{Pb}_k\text{CH}_3^+$  and  $\text{Pb}_k(\text{CH}_3)_m(\text{C}_4\text{H}_8)_n^+$ , low-energy pathway products  $[\text{Pb}_k\text{C}_4\text{H}_6^+]$ ,  $\text{Pb}_k\text{C}_3\text{H}_3^{(5)+}$ ,  $\text{Pb}_k\text{C}_3\text{H}_2^{(3)+}$  (for *cis*-butene only) and their further association products  $[\text{Pb}_k\text{C}_4\text{H}_6(\text{C}_4\text{H}_8)_n]^+$ ,  $\text{Pb}_k\text{C}_3\text{H}_3^{(5)}(\text{C}_4\text{H}_8)_n^+$ ,  $\text{Pb}_k\text{C}_3\text{H}_2^{(3)}(\text{C}_4\text{H}_8)_n^+$  (for *cis*-butene only) were also observed. Bond selectivity and effects of steric hindrance were observed in the low-energy pathway reactions of lead cluster cations with *trans*- and *cis*-butene. The same anionic products,  $\text{Pb}_k\text{C}_m^-$ , with nearly the same intensity distribution, were observed in the reactions of lead cluster anions with all four alkenes studied here. Some reaction mechanisms are proposed for these reactions. Copyright © 2002 John Wiley & Sons, Ltd.

Studies of gas-phase organometallic reactions can provide fruitful and meaningful information to further the understanding of corresponding condensed-phase reaction mechanisms or heterogeneous catalytic processes. It is well known that generalized organometallic reactions include the high-energy reaction pathway<sup>1</sup> and the low-energy reaction pathway<sup>2</sup>. Both reaction pathways have the same first step with adsorption of an atomic metal ion (usually cation) upon a ligand molecule followed by oxidative insertion of the metal ion into one bond of the ligand molecule. As for the following steps, migration of one or more atoms or groups of the ligand molecule to the metal ion and reductive elimination of a small molecule occur for the low-energy reaction pathway, provided the intermediates have sufficiently long lifetime to undergo rearrangement. Simple bond cleavage, which is usually not accessible at thermal energies, dominates the high-energy reaction pathway. These oxidative addition reactions (involving C–C and C–H bonds, etc.) provide a unique chance to study gas-phase oxidative addition dynamics.

Activation of C–H and C–C bonds is a very fundamental and important catalytic process in the chemical industry.

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Early studies on organometallic reactions were mainly concerned with alkanes for the huge potential of exploitation of natural gas and fuel feedstocks. However, quite a lot of work has been done on alkenes, which are involved in some fundamental reactions of industrial importance. As far as the metals are concerned, only reactions of atomic transition metal ions with alkenes have been studied, with only a few exceptions. Only association products were observed for the reactions of ethylene and propene with  $\text{Cr}^+$ ,<sup>3</sup>  $\text{Fe}^+$ ,<sup>4</sup>  $\text{Co}^+$ ,<sup>5</sup>  $\text{Ni}^+$ ,<sup>6</sup> and  $\text{Au}^+$ <sup>7</sup> in collision-induced decomposition experiments. The endothermic reactions of  $\text{V}^+$ ,<sup>8</sup>  $\text{Cr}^+$ ,<sup>9</sup>  $\text{Co}^+$ ,<sup>10</sup> and  $\text{Ni}^+$ <sup>11</sup> with ethylene followed a direct abstraction mechanism and gave metal-alkylidene and metal-hydrogen ions as products. Dehydrogenation of ethylene and propene occurred in reactions with  $\text{Sc}^+$ ,<sup>5,12</sup>  $\text{V}^+$ ,<sup>8</sup>  $\text{Nb}^+$ ,<sup>13</sup>  $\text{Ta}^+$ ,<sup>14</sup>  $\text{Os}^+$ ,<sup>15</sup> and  $\text{Pr}^+$ .<sup>16</sup> Butadiene complexes dominated the reaction of  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  with the three linear butene isomers.<sup>4,7,17–19</sup>  $\text{ScC}_4\text{H}_4^+$ , with a metallacyclopentadiene structure, was observed in the dehydrogenation reaction of *trans*- and *cis*-butene with  $\text{Sc}^+$ .<sup>12</sup> These reactions were usually studied using an ion-beam apparatus.

The study of metal cluster ions other than metal atomic ions in organometallic reactions will approach more closely the condensed-phase heterogeneous catalytic reactions and aid understanding the related structure-reactivity relationships; therefore, there is still much work required on the reactions of metal cluster ions. In addition, organometallic reactions of main-group metals rather than transition metals are seldom studied.

As a main group element, lead has a completely different

valence electronic structure to transition group elements, which may exert influence on bonding or reactions with other molecules. In industry, lead is involved in some important catalytic processes. Lead ruthenate has catalytic activity comparable with that of platinum in the catalytic decomposition of hydrogen peroxide in alkaline solution, and could be used as a second catalyst on the cathode side of fuel cells, which could in turn increase the electrode life and reduce the cathodic polarization.<sup>20</sup> Lead halides have been used to catalyze the allylation of diphenyl ether with allyl bromide and gave good functional selectivity.<sup>21</sup> Studying the behavior of lead in the gas phase may also contribute to atmospheric chemistry, since lead is among the heavy-metal ions in radioactive form as the progeny of radon and thoron present in the atmosphere, and eventually becomes incorporated into atmospheric aerosol particles.<sup>22</sup>

In addition to its practical implications, the study of lead cluster ions is also of fundamental interest. As early as 1972, Castleman *et al.*<sup>22</sup> studied the gas-phase hydration of the monovalent lead ion using high-pressure mass spectrometry; clusters of up to eight water molecules around a lead ion were observed. Later the same group reported the clustering reaction of benzene with lead ion.<sup>23</sup>

This paper reports work carried out by our research group on the cluster reactivity of a main-group metal, lead. The results reported here concern gas-phase organometallic reactions of lead cluster ions, other than lead atomic ion, with some common alkenes (including ethylene, propene, *trans*- and *cis*-butene), performed using our home-built reflectron time-of-flight mass spectrometers. A brief description of the experimental apparatus is given, and some conclusions are summarized in the final section.

## EXPERIMENTAL

The laser target was prepared by grinding lead (purity 99%) into a fine powder and pressing it into a tablet 12 mm in diameter and 5 mm in thickness. The reactant gas alkene (purity 99.9%) was seeded in argon (purity 99.9%) in a stainless steel vacuum bottle (about 1 L) to yield a total stagnation pressure of 4 atm; the volume ratio of the alkene in the mixed gas was 5%. All materials and chemical reagents were obtained commercially in high purity and used as supplied without any further purification.

Reactions of lead cluster cations and anions with alkenes were performed using a home-built reflectron TOF mass spectrometer (similar to that of Mamyrin<sup>24</sup>) coupled with a Smalley-type<sup>25</sup> laser vaporization source. A detailed description of the apparatus has been given elsewhere,<sup>26</sup> and only a outline is given here. The lead target was mounted 10 mm downstream from the nozzle (General Valve series 73, orifice diameter 0.8 mm) in the source chamber and ablated by the focused second harmonic output of a Nd:YAG laser (10 mJ/pulse, 10 Hz, beam spot size on the target 1 mm in diameter). The laser-vaporized metal plasma perpendicularly crossed an alkene supersonic beam and entered the "growth channel" (3 (in diameter)  $\times$  20 (in length) mm), where formation of lead cluster ions and reactions of these ions with alkenes occurred; the cluster formation of alkene was completed near the nozzle exit.<sup>27</sup> 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 pulsed electric field was operated in two polarity modes to detect either cationic or anionic products. The products were then extracted and accelerated to about 1.2 keV at right angle to the direction of the cluster beam. The product ions then experienced the first-order space focus in the first set of einzel electrostatic lenses to guide and focus the ion beam, then vertical and horizontal deflection plates, and the second-order space focus in the second set of einzel electrostatic lenses. Finally, the products were detected by a dual microchannel plate (MCP) in the reflectron region. 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 computer. The timing of valve opening, laser vaporization, pulse acceleration, and recording is optimized in a digital delay pulse generator (Stanford Research DG535). The final digitized TOF mass spectra were typically averaged over 1000 laser pulses.

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

The mass resolution of the mass spectrometer for this particular experiment was over 1000 below  $m/z$  1000, which enabled the apparatus to resolve hydrogen atoms coexisting in clusters (unit mass resolution).

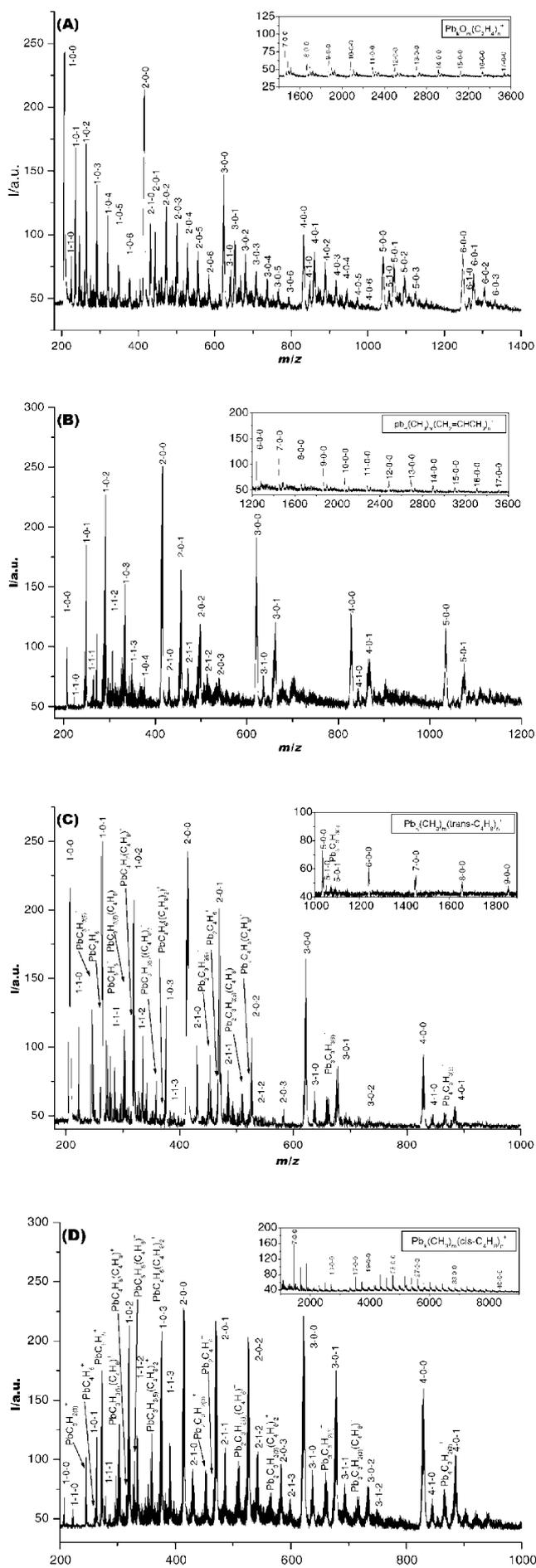
## RESULTS AND DISCUSSION

The reactions of lead cluster cations with four  $C_aH_{2a}$  ( $a = 2-4$ ) alkenes were investigated. The reaction channels observed in the reactions of  $Pb_k^+$  with ethylene, propene, and *trans*- and *cis*-butene under vaporization-expansion conditions included association of the alkene,  $Pb_kC_aH_{2a}^+$  ( $a = 2-4$ ), high-energy pathway dissociation,  $Pb_kCH_3^+$  ( $a = 3, 4$ ), and low-energy pathway dissociation,  $Pb_kC_4H_6^+$  ( $a = 4$ ),  $Pb_kC_3H_3^+$  ( $a = 4$ ), and  $Pb_kC_3H_2^+$  (*cis*-butene only). TOF mass spectra of cationic products from the reaction of lead cluster cations with supersonic ethylene, propene, and *trans*- and *cis*-butene beams are shown in Figs 1(A), 1(B), 1(C), and 1(D), respectively. In order to investigate the behavior of cluster anions, which have been seldom studied in organometallic reactions, the reactions of lead cluster anions with the four alkenes described above were also investigated. Interestingly, the same anionic products,  $Pb_kC_m^-$ , with nearly the same relative intensity distribution as  $k$  and  $m$  were varied, were obtained for all the alkenes; only one representative spectrum obtained from the reaction of lead cluster anions with ethylene is presented here (Fig. 3).

### Reactions of lead cluster cations

#### Lead cluster cations

Lead cluster cations were the dominant species in the four



mass spectra of Fig. 1. Rather wide  $Pb_k^+$  cluster distributions were observed here, especially those from interaction with *cis*-butene where  $Pb_k^+$  grew larger than  $Pb_{40}^+$ . Seeding of the reaction gas (i.e., alkene) in the carrier gas (Ar) promoted the growth of  $Pb_k^+$  clusters, since when only Ar was used, the intensity of  $Pb_k^+$  clusters was appreciably smaller and  $Pb_k^+$  could usually grow no larger than  $Pb^+$ . The underlying mechanism, we believe, involves the trace organic molecules effectively relaxing the internal energy (effective temperature) of the laser ablation plasma, which was advantageous for the formation of large-size clusters. We have observed the same phenomenon in the reaction of lead clusters with acetone.

### Association products

Among the secondary dominant species in Fig. 1 are the chemisorption species  $Pb_k(C_aH_{2a})_n^+$  ( $a = 2-4$ ) from the association channel, which occurred via reaction (1):



The reason that reaction (1) is believed not to be a physisorption channel is that the bond of the physisorbed species is too weak to survive sufficiently long enough to reach the detector. The intensity distribution of the association products  $Pb_k(C_aH_{2a})_n^+$  had several characteristics. First, for a given  $k$  value,  $Pb_k(C_aH_{2a})_n^+$  ( $a = 2-4$ ) had a nearly monotonically decreasing intensity distribution as  $n$  increased; second, the larger the alkene molecule, the fewer of them could be adsorbed on a given lead cationic cluster.

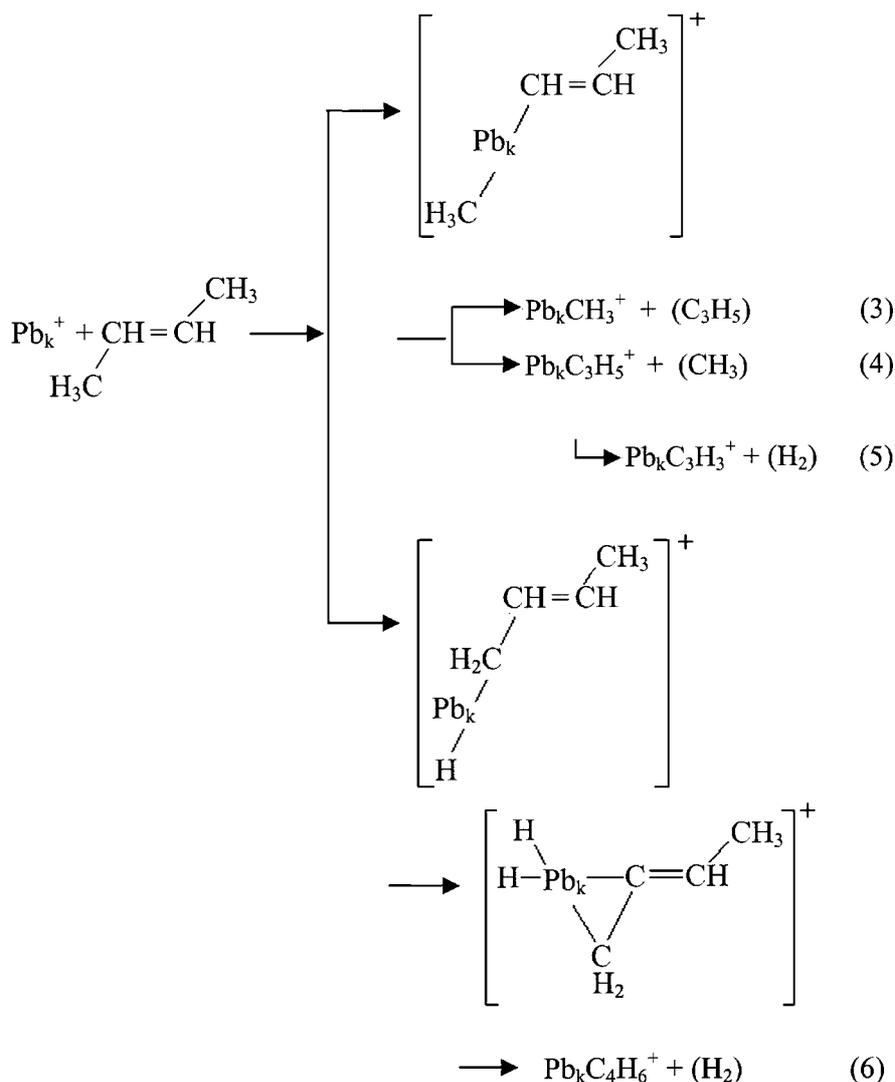
### High- and low-energy reaction pathway products

At sufficiently high energies derived from the high-temperature metal plasma, high-energy pathway reactions between lead cluster cations and alkenes occurred; such reaction processes often have favorable frequency factors.<sup>1</sup>

Ethylene was nonreactive with lead cluster cations, i.e., no high- (or low-) energy pathway reaction products were observed in the present work. This indicated that, under the present conditions, the lead cluster cations were not reactive enough, or possessed enough energy, to undergo an oxidative insertion into and finally break the carbon-carbon double bond or carbon-hydrogen bond.  $Pb_kO_m^+$  clusters were unexpectedly observed in Fig. 1(A); the oxygen probably came from free oxygen impurities in the ethylene, since these clusters were not observed in Figs 1(B), 1(C), or 1(D).

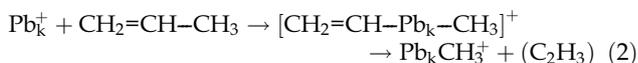
High-energy pathway reaction products  $Pb_kCH_3^+$  were observed for propene, and occurred via reaction (2) with an

**Figure 1.** Typical TOF mass spectra for cationic products which were obtained from the Nd:YAG laser (532 nm, 10 mJ/pulse) irradiation of a lead tablet in the ethylene (A), propene (B), *trans*-butene (C), *cis*-butene (D) + Ar (95%) mixed carrier gas. The inset (top right) in every mass spectrum was the high-mass region. The notation ' $Pb_kC_3H_3^+$ ' in (C) and (D) denotes the coexistence of  $Pb_kC_3H_3^+$  and  $Pb_kC_3H_5^+$ , while ' $Pb_kC_3H_{2(3)}^+$ ' denotes the coexistence of  $Pb_kC_3H_2^+$  and  $Pb_kC_3H_3^+$ .



**Scheme 1.** Reaction pathways for  $\text{Pb}_k^+$  cluster cations with *trans*-butene.

oxidative insertion of lead cluster cations into the allylic C–C bond:

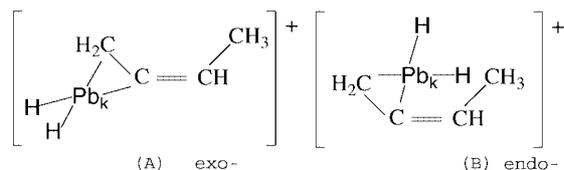


It should be noted that the neutral products (in parentheses) of these reactions could not be identified under the present experimental conditions. The preferred ionic product in reaction (2) was predicted to be the fragment having the lower ionization potential in accord with Stevenson's rule,<sup>28</sup> so the ionization potential of  $\text{Pb}_k(\text{CH}_3)$  is probably lower than that of the unobserved  $\text{Pb}_k(\text{CH}=\text{CH}_2)$ .

Both high- and low-energy pathways were important in reactions between lead cluster cations and *trans*-butene. The high-energy pathway reaction (oxidative insertion into a C–C bond) occurred with two parallel channels, as shown in reactions (3) and (4) (Scheme 1), which indicated that the ionization potential of  $\text{Pb}_k\text{C}_3\text{H}_5$  was near that of  $\text{Pb}_k\text{CH}_3$ . A low-energy pathway reaction also took place between lead cluster cations and *trans*-butene, as shown in reaction (6) (Scheme 1). The reaction mechanism involved first an

oxidative insertion of lead cluster cation into a C–H bond in the methyl group, then a  $\beta$ -H migration to the lead cluster cation, and finally expulsion of a hydrogen molecule. This reaction process also occurred for the high-energy pathway reaction products  $\text{Pb}_k\text{C}_3\text{H}_5^+$ , as shown in reaction (5). Reactions (3) and (4) have higher reaction probabilities than reactions (5) and (6), since the intensity of both  $\text{Pb}_k\text{CH}_3^+$  and  $\text{Pb}_k\text{C}_3\text{H}_5^+$  was appreciably larger than those of  $\text{Pb}_k\text{C}_3\text{H}_3^+$  and  $\text{Pb}_k\text{C}_4\text{H}_6^+$ .

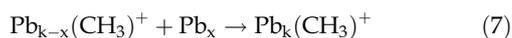
The same high- and low-energy pathway reaction products  $\text{Pb}_k\text{CH}_3^+$  and  $\text{Pb}_k\text{C}_4\text{H}_6^+$  as observed with *trans*-butene, shown in reactions (3) and 6, were obtained for *cis*-butene. In the case of reaction (6), when *trans*-butene was replaced by *cis*-butene, the second (high-energy) intermediate preferred to assume an exo configuration (see Fig. 2(A)) rather than an endo configuration (see Fig. 2(B)) in order to avoid steric hindrance. However, further dehydrogenation on the basis of reactions (4) and (5) occurred for *cis*-butene due to the effect of steric hindrance, so  $\text{Pb}_k\text{C}_3\text{H}_2^+$  ions instead of  $\text{Pb}_k\text{C}_3\text{H}_3^+$  were observed especially when  $k \geq 2$ , i.e., when  $k = 1$ , both  $\text{Pb}_k\text{C}_3\text{H}_2^+$  (denoting the coexistence of  $\text{Pb}_k\text{C}_3\text{H}_2^+$



**Figure 2.** Two possible intermediates for the low-energy pathway reaction of lead cluster cations  $Pb_k^+$  with *cis*-butene.

and  $Pb_kC_3H_3^+$  and  $Pb_kC_3H_3^{(5)+}$  (denoting the coexistence of  $Pb_kC_3H_3^+$  and  $Pb_kC_3H_3^{(5)+}$ ) were observed, but when  $k \geq 2$ , only  $Pb_kC_3H_2^{(3)+}$  was observed. These proposed reaction mechanisms for low-energy reaction pathways in reactions (5) and (6) for *trans*- or *cis*-butene need further experimental verification. Avery *et al.*<sup>29</sup> observed butyne ( $C_4H_6$ ) on Pt(111) upon the adsorption of *trans*- or *cis*-butene at 300 K.

It should be especially pointed out that  $Pb_k(CH_3)^+$  should not have mainly formed via the reaction mechanism shown in reaction (7) with neutral lead species  $Pb_x$  participating in the reaction, as otherwise we should have observed an obvious intensity change of  $Pb_k(CH_3)^+$  as the value of  $k$  increased in Figs 1(B), 1(C), or 1(D), in view of the effect of collision probabilities.



This consideration led us to make two conclusions: that reaction (7) made a minor contribution to the formation of  $Pb_k(CH_3)^+$ , and that oxidative insertion of metal cluster ions as well as of metal atomic ions in organometallic reactions was possible.

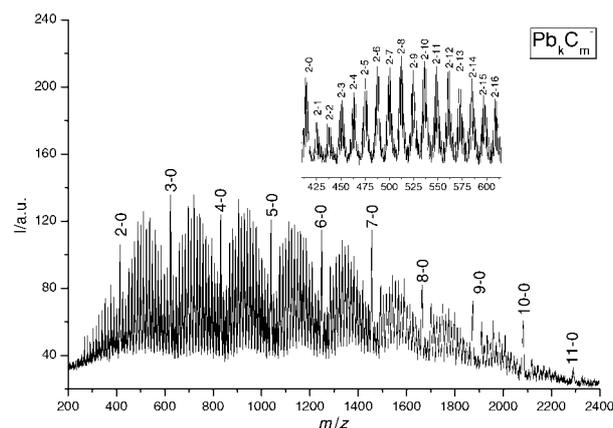
$Pb_kC_5H_5^+$  [and also  $Pb_kC_5H_5(C_4H_8)^+$  for *trans*-butene only] was also observed in Figs 1(C) and 1(D), and this product ion is also expected to arise from a low-energy reaction pathway of lead cluster cations with butenes; no detailed discussion of this reaction will be given here.

From the reactions of lead cluster cations with propene and butenes, it appears that the double bond directed the oxidation insertion of metal cluster cations into the allylic C–C bond; this kind of bond selectivity was also observed for  $Co^+$ .<sup>22</sup>

Carbide ions  $Ni_{n-1}C^+$  and  $Nb_nC_{2m}^+$  have been observed in the reaction of nickel cluster cations  $Ni_n^+$  with methanol,<sup>30</sup> and of niobium cluster cations  $Nb_n^+$  with ethylene.<sup>31</sup> In the present study, carbides were observed only in the reactions of lead cluster anions, which are discussed below.

### Reactions of lead cluster anions

In the reactions with lead cluster anions, all alkenes studied here were dehydrogenated, and the same anionic products  $Pb_kC_m^-$  with nearly the same intensity distribution were observed. Only one representative TOF mass spectrum, showing the dehydrogenation reaction of lead cluster anions with ethylene, is shown in Fig. 3. Since these dehydrogenated products were not dependent on the nature of the alkene, we could easily conclude that the growth process of  $Pb_kC_m^-$  was not appreciably influenced by the reactant alkene. This process was also observed previously for the



**Figure 3.** Typical TOF mass spectrum for anionic products which were obtained from the Nd:YAG laser (532 nm, 10 mJ/pulse) irradiation of a lead tablet in the ethylene + Ar (95%) mixed carrier gas. The inset (top right) has the mass scale expanded to show  $Pb_2C_m^-$ ,  $m = 0-16$ .

dehydrogenation of gaseous hydrocarbons in laser-induced plasma on a graphite or silicon rod, which was used to conveniently produce elemental and molecular clusters.<sup>32-34</sup> The underlying driving force for this process was considered to lie in the thermodynamics involved; the cluster formation and the following dehydrogenation process and carbide formation were all exothermic, and in the experiment the cluster was 'heated', which promoted the formation of molecular hydrogen and its 'evaporation' from the cluster.<sup>31,35,36</sup>

It can be seen from Fig. 3 that the  $Pb_kC_m^-$  ions ( $m = 1-16$ ) had the same composition of the  $C_m$  moiety, and nearly the same intensity distribution, with the variation of  $k$ ; therefore, a detailed assignment is given only for  $Pb_2C_m^-$  ( $m = 1-16$ ), as shown in the inset in Fig. 3. This fact suggests that the formation and structure of the  $C_m$  moiety in  $Pb_kC_m^-$  played a dominant role in the formation and structure of  $Pb_kC_m^-$ . It is believed that the  $C_m$  moiety formed first, and then as a whole associated with a  $Pb_k$  cluster. For a given  $k$  value, the intensity of  $Pb_kC_m^-$  had a nearly monotonic increase until  $m = 8$ , followed by a monotonic decrease to  $m = 16$ . This variation in intensity suggested analogous structures or similar structural stability<sup>37</sup> of  $Pb_kC_m^-$  even when  $m$  varied from 1 to 16 for a given  $k$  value. Although size-selected ultraviolet photoelectron spectroscopy (UPS) studies<sup>38</sup> of  $C_m^-$  have proven that  $C_m^-$  appeared to have linear chain structures when  $m < 10$  and ring structures when  $10 \leq m \leq 31$ , we did not observe a obvious intensity change at  $m = 10$ . A more detailed picture of the structures of the  $Pb_kC_m^-$  species observed here requires further theoretical or other experimental study. It should be noted that there was a significant extent of hydrogen-containing analogs of  $Pb_kC_m^-$  observed in Fig. 3, for which no detailed analysis is presented here.

### CONCLUSIONS

The reactions of lead cluster cations and anions with

ethylene, propene, and *trans*- and *cis*-butene seeded in argon carrier gas have been studied using a reflectron time-of-flight mass spectrometer. In the reactions of cations, only association products  $\text{Pb}_k(\text{C}_2\text{H}_4)_n^+$  were observed for ethylene. High-energy reaction pathway products  $\text{Pb}_k\text{CH}_3^+$ ,  $\text{Pb}_k\text{C}_3\text{H}_5^+$  (butenes only) were also observed for the remaining three alkenes besides association products  $\text{Pb}_k(\text{C}_a\text{H}_{2a})_n^+$  ( $a = 3-4$ ); in addition, butenes also yielded low-energy reaction pathway products  $\text{Pb}_k\text{C}_4\text{H}_6^+$ ,  $\text{Pb}_k\text{C}_3\text{H}_3^+$ , and  $\text{Pb}_k\text{C}_3\text{H}_2^+$  (*cis*-butene only). Because of the effect of steric hindrance, *trans*- and *cis*-butene gave different low-energy reaction pathway products; the larger the alkene molecule, the fewer molecules a single lead cluster could adsorb in the initial step. In the reactions of anions, the same anionic products  $\text{Pb}_k\text{C}_m^-$ , with nearly the same intensity distribution independent of alkene reactant, were observed. Relative branching ratios depending on the alkene pressure and ablation power for all above reactions will be reported elsewhere.

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