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Reactions of Titanium−Carbon Cluster Cations with Acetone: New Evidence for the Stability of the Met-Cars

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Abstract: Reactivities of titanium−carbon clusters with acetone are investigated using a triple quadrupole mass spectrometer coupled with a laser vaporization source. Unlike the Met-Car $Ti_8C_{12}^+$, the other titanium−carbon clusters studied here show some degree of chemical reactivity toward acetone. In addition to reacting via association channels, the carbon-poor cluster $Ti_8C_{11}^+$ is able to break the chemical bonds of acetone. It is also observed that the carbon-rich clusters $Ti_8C_{13}^+$ and $Ti_8C_{14}^+$ can undergo reactive loss of carbon, leading to the $Ti_8C_{12}^+$ species (Met-Car) upon interaction with the acetone reactant. These studies provide new insight into the reactivities of transition metal−carbon clusters and further evidence for the stability of Met-Cars.

Introduction

In early 1992, we reported the discovery of a new class of molecular clusters referred to as Metallo-Carbohedrenes, or Met-Cars.[1] This discovery has stimulated a number of investigations to elucidate the physical and chemical stability of this new class of clusters. For example, our group and others have utilized metastable decay, collision-induced dissociation, and photodissociation techniques to probe the bonding and dissociation patterns of Met-Cars.[2−6] It appears that the Met-Car $Ti_8C_{12}^+$ is physically more stable than other neighboring titanium−carbon clusters.[4] However, in terms of the dissociation patterns, it was observed that the fragmentation behavior of this Met-Car was similar to that of other titanium−carbon clusters. We have also reported the results of the reactivity of $Ti_8C_{12}^+$ toward a variety of small molecules.[7] It was found that $Ti_8C_{12}^+$ reacts mainly via an association mechanism with molecules such as H_2O, NH_3, CH_3OH, and C_6H_6, for example.

A question arises concerning the reaction patterns of other titanium−carbon clusters. Are their reactions similar to that of $Ti_8C_{12}^+$? Are Met-Cars chemically more stable than the proximate non Met-Car clusters? To address these issues, we have conducted a series of experiments to examine reactions of titanium−carbon clusters with acetone. This molecule was chosen for two reasons. First, it can, in principle, exhibit both bimolecular and association reactions. Second, because of our knowledge of its reaction behavior with various niobium-containing Met-Cars, we are able to gain further insight into the nature of reactions for species proximate to the Met-Cars. Therefore, our studies are concentrated on determining the multiple reaction products of $Ti_8C_{11}^+$, $Ti_8C_{13}^+$, and $Ti_8C_{14}^+$ with acetone so that we can determine whether $Ti_8C_{12}^+$ has unique chemical stability as it does physical stability, in accordance with the findings reported in the above-referenced investigations. We found that indeed, the reactivity of other titanium−carbon clusters is quite different from that of $Ti_8C_{12}^+$ and that $Ti_8C_{12}^+$ is chemically more stable than other clusters of proximate size. Reporting these new findings is the subject of this paper.

Experimental Section

The experiments were conducted with a triple quadrupole mass spectrometer (TQMS) coupled with a laser vaporization source, which has already been discussed in a previous paper.[4] Briefly, the 532 nm second harmonic beam of a Nd:YAG laser is focused onto a rotating titanium rod or disk. The plasma reaction occurs when the titanium vapor becomes entrained into pulses of a 15% to 20% mixture of methane seeded in helium. As a result, various titanium−carbon cluster ions are formed and undergo supersonic expansion as they exit the laser vaporization (LAVA) source region. After passing through a 5 mm skimmer and several focusing lenses and deflectors, the $Ti_xC_y^+$ cluster ions enter the first quadrupole mass spectrometer. In the present study, the first mass spectrometer is utilized to select a specific titanium−carbon cluster from the cluster beam in order to investigate its reactions. The selected $Ti_xC_y^+$ cluster ions are then focused by another set of lenses and deflectors before entering the second quadrupole. The second quadrupole mass spectrometer functions as a reaction cell, in which reactions between the selected cluster and reactants occur. Upon exiting the second quadrupole, the reaction products are analyzed by a third quadrupole mass spectrometer coupled with a channeltron electron multiplier. In these experiments, a small positive electrical potential is biased on the rods of the second quadrupole (collision cell) in order to reduce the translational energy of the selected cluster acquired from supersonic expansion. Consequently, we were able to study the desired reactions under essential thermal energy conditions.

Results and Discussion

As reported earlier,[8] $Ti_8C_{12}^+$ reacts with acetone through association mechanisms, and no bond breaking is observed in either the Met-Car or the reactant acetone. These observations indicate that the Met-Cars are collisionally cooled upon exiting the source. Interestingly, unlike $Ti_8C_{12}^+$, the reaction scheme of $Ti_8C_{11}^+$ with acetone involves not only association of acetone molecules onto $Ti_8C_{11}^+$ but also the breakage of the chemical

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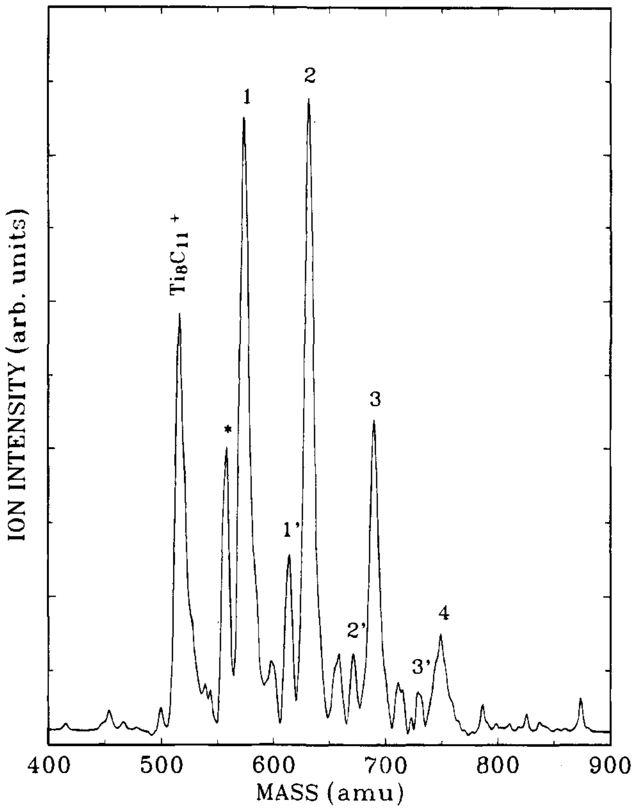

Figure 1. Product distribution arising from multistep reactions of $Ti_8C_{11}^+$ with 0.44 mTorr of acetone. The peak labeled by 1 represents addition of an acetone molecule to $Ti_8C_{11}^+$ via an association reaction. The peak marked by * is the chemical reaction product $Ti_8C_{11}^+(COCH_3)$. The sequential association products onto the peaks marked 1 and * are labeled n and n′, respectively.

bonds of acetone upon reaction with this cluster. Its reaction product distribution is exhibited in Figure 1. The peak labeled by 1 corresponds to the association product, and the peak labeled by * corresponds to the product arising from the chemical reaction in which bond breaking/formation has occurred. Other remaining peaks correspond to the sequential products arising from further acetone association to products 1 and *. The association reaction of $Ti_8C_{11}^+$ proceeds as follows:

$$Ti_8C_{11}^+ + \text{acetone} \rightarrow Ti_8C_{11}^+(\text{acetone}) \qquad (1)$$

while the destructive bimolecular chemical reaction of $Ti_8C_{11}^+$ proceeds via the following:

$$Ti_8C_{11}^+ + \text{acetone} \rightarrow Ti_8C_{11}^+(COCH_3) + CH_3 \qquad (2)$$

The most striking result from the reaction of $Ti_8C_{11}^+$ with acetone is its chemical reaction pattern shown in eq 2. It appears that this cluster is capable of breaking bonds in acetone and incorporating part of the molecule as a result of the interaction. This result can be rationalized in light of the closed-cage structure proposed for Met-Cars. $Ti_8C_{11}^+$ has one less carbon atom than the Met-Car $Ti_8C_{12}^+$, and the vacancy left by the missing carbon atom might lead to an opening in the cage. It may be speculated that when this cluster reacts with acetone, bond breakage of the reactant molecule occurs. The $COCH_3$ unit from the acetone may serve to fill the hole left by the missing carbon atom in the cage, so that the cage can be closed. One of the carbon atoms of the fragment $COCH_3$ could be able to break away from the arest of the atoms and complete the cage structure to form the Met-Car $Ti_8C_{12}^+$. At the same time, the remaining OCH_3 group might undergo rearrangement to bond onto this Met-Car.

The bond breaking of acetone induced by $Ti_8C_{11}^+$ may be compared to similar reactions of acetone with the binary Met-Car $Ti_7NbC_{12}^+$, which has been reported in a related paper.[8] Each of these ionic species break the chemical bonds of acetone in addition to reacting via association reactions; however, $Ti_7NbC_{12}^+$ is observed to break the C=O bonds of acetone. Since the C=O bonds are stronger than the C−C bonds of acetone (179 versus 80 kcal/mol[9]), we predict that the binary metal Met-Car $Ti_7NbC_{12}^+$ exhibits chemical reactivity due to the change in its electronic structure (i.e. substitution of one titanium atom with one niobium atom). In the case of $Ti_8C_{11}^+$, however, the structure may be visualized as an incomplete cage containing three reactive sites. In this model, two titanium atoms and one niobium atom would be left "dangling" due to the vacancy left by the missing carbon atom; hence, this vacancy is very likely to be the reactive site in this incomplete cage structure. Although this reaction mechanism appears to be quite complex, the abstraction of a methyl group rather than breakage of the carbonyl bond provides evidence that $Ti_8C_{11}^+$ is attempting to complete its cage structure.

In a separate work, we have found that $Ti_8C_{12}^+$ is capable of breaking a weak Me−I bond and bond to one iodine atom.[18] This result has been rationalized by the argument that $Ti_8C_{12}^+$ might have one unpaired electron (because it has a total of 79 electrons) and it could tend to bond onto one iodine atom which also has one unpaired electron. As a result, the unpaired electrons in both $Ti_8C_{12}^+$ and the iodine atom are paired and $Ti_8C_{12}^+(I)$ could therefore have a closed electronic shell in terms of electron pairing. Hence, in the present case, the remaining OCH_3 group, which has one unpaired electron as well, could bond to $Ti_8C_{12}^+$. Consequently, the unpaired electrons in both $Ti_8C_{12}^+$ and OCH_3 become paired and the $Ti_8C_{12}(OCH_3)^+$ which is formed could have a closed-shell structure.

More surprisingly, as shown in Figure 2, there are three possible channels for reactions of $Ti_8C_{13}^+$ with acetone. One is the typical association channel, (A), through which an acetone molecule associates onto this cluster. Another pathway, (B), appears to be more dominant, in which $Ti_8C_{13}^+$ fragments to the Met-Car $Ti_8C_{12}^+$. This reaction channel is described by the following equation:

$$Ti_8C_{13}^+ + \text{acetone} \rightarrow Ti_8C_{12}^+ + \text{products} \qquad (3)$$

A third reaction channel, (C), may be a replacement reaction, for which the carbon atom may be "switched" with an acetone molecule. The first step in mechanisms (B) and (C) applies only to an isomer of $Ti_8C_{13}^+$ where the extra carbon is bound externally to the cage.

As shown in Figure 3, reaction pathways of $Ti_8C_{14}^+$ with acetone are quite similar to those of $Ti_8C_{13}^+$. One is the association pathway, (A), by which an acetone molecule attaches to a Ti atom at a site distant from the extra carbon atoms (presumably on the outside of the cage structure). Another reaction channel, (B), involves the fragmentation of $Ti_8C_{14}^+$ to $Ti_8C_{12}^+$ by loss of two carbon atoms upon reaction with acetone. This chemical reaction is described by the following mechanism:

$$Ti_8C_{14}^+ + \text{acetone} \rightarrow Ti_8C_{12}^+ + \text{products} \qquad (4)$$

The other reaction channel, (C), may also be a replacement reaction, involving "switching" of the two carbon atoms by an

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(9) *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1986.

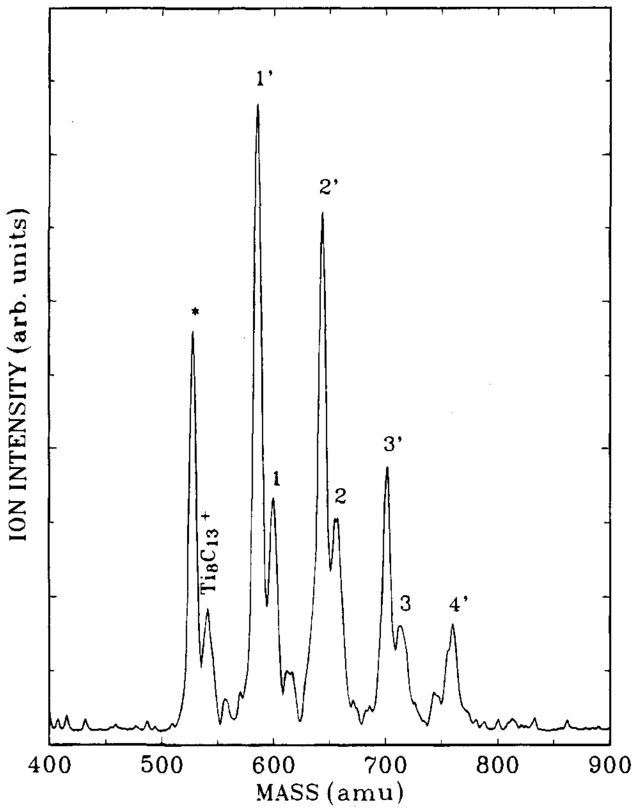

Figure 2. Product distribution arising from multistep reactions of $Ti_8C_{13}^+$ with 0.47 mTorr of acetone. The peak labeled by 1 corresponds to an association product onto $Ti_8C_{13}^+$. An ∗ denotes the chemical reaction product $Ti_8C_{12}^+$. Other peaks marked by n and n′ correspond to association products onto $Ti_8C_{13}^+$ and its product $Ti_8C_{12}^+$, respectively.

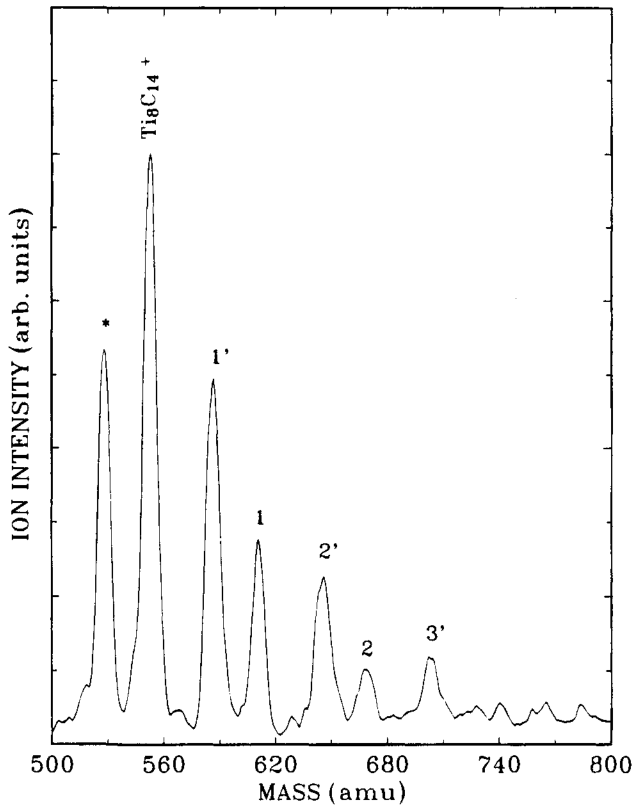

Figure 3. Product distribution arising from multistep reactions of $Ti_8C_{14}^+$ with 0.44 mTorr of acetone. The peaks marked 1 and 2 represent acetone molecules associating onto $Ti_8C_{14}^+$. The peak marked by ∗ corresponds to the chemical reaction product $Ti_8C_{12}^+$. The remaining peaks labeled by n′ are association products coordinating onto the $Ti_8C_{12}^+$ product.

acetone molecule, which results from attack of the extra carbons by the reactant at that site. From these results, we are sure that two carbon atoms are lost at the same time since no $Ti_8C_{13}^+$ was observed. Furthermore, as will be discussed later, we have conducted experiments with non-reactive gases over a wide range of pressures and collision energies to show that no concomitant collision-induced dissociation or metastable decay is taking place. As a result, we have determined that "real" chemical reactions are responsible for the observations.

As noted above, although both $Ti_8C_{13}^+$ and $Ti_8C_{14}^+$ can also undergo (bond rearrangement) chemical reactions with acetone, their chemical reaction pattern is completely different from that of $Ti_8C_{11}^+$. The two hyperstoichiometric clusters, $Ti_8C_{13}^+$ and $Ti_8C_{14}^+$, tend to fragment to the Met-Car $Ti_8C_{12}^+$ by the loss of one or two carbon atoms, respectively, upon interaction with acetone. This difference could also be explained in terms of the proposed closed-cage structure of Met-Cars. Unlike $Ti_8C_{11}^+$, both $Ti_8C_{13}^+$ and $Ti_8C_{14}^+$ may be viewed as carbon-rich clusters since there might be extra carbon atom(s) outside the cage of the Met-Car. As shown in Figures 2 and 3, when these carbon-rich clusters interact with acetone, they can fragment via the loss of the extra carbon(s) to form a naked closed-edge structure which is regarded as the most stable structure for Met-Cars.

In light of these results, we must differentiate between these titanium–carbon clusters in terms of their chemical reactivity and their physical stability, which has been shown previously in our collision-induced dissociation (CID) studies.[4] We have observed the loss of a neutral titanium atom in the primary dissociation process from all the above-mentioned titanium–carbon clusters. These observations were made through interacting the mass selected clusters with krypton collision gas at collision energies above 60 eV. In the present work, however, we are certain that collision-induced dissociation plays no role in the reaction patterns. First, our collision energy in the second quadrupole (reaction cell) is kept between 0 and +2 eV. In fact, the small positive value represents a retarding potential, which also serves to reduce the velocity of the beam and thereby lower its kinetic energy. Second, we have conducted experiments at reactant gas pressures between 0.1 and 0.15 mTorr, which show the "single collision" or primary reaction products. At these low pressures, we observe the same reaction pathways for all three clusters of interest, and the only difference observed when varying the pressure is that of relative signal intensity. Indeed, we do not see any new products formed from these titanium–carbon clusters upon addition of higher concentrations (pressures) of acetone, with the exception of more association products. Furthermore, we observe no metal loss from the selected titanium–carbon clusters, even at pressures greater than 0.6 mTorr. Under these "multiple-collision" conditions, in studies dominated by CID we would normally observe multiple metal loss; however, the collision energy is so low in the present reaction experiments that the pressures of reactants employed cannot yield collision-induced dissociation channel. For these reasons, we can predict that the Met-Car $Ti_8C_{12}^+$ is far less reactive than its neighboring titanium–carbon clusters due to its inherent larger stability.

Very recently, we have been able to produce $Ti_8C_{12}(L)^+$ (L = CH_3OH, C_6H_6) directly from our laser vaporization source. Upon selecting $Ti_8C_{12}(L)^+$ for determination of its CID product(s), we have observed fragmentation to $Ti_8C_{12}^+$ under various collision conditions. Since no fragmentation of either $Ti_8C_{12}^+$ or the reactant ligand itself was observed, this new finding provides further supporting evidence of the considerable chemical inertness of the Met-Car, $Ti_8C_{12}^+$, toward these ligands.

Moreover, this shows that the ligands attack by simple association and not via an insertion mechanism. All evidence suggests that the same observations would be found for acetone as well, but due to mass overlap in selecting the ligated cluster, we are unable to definitively prove this point.

Finally, we briefly consider the association reactions. Generally speaking, when a cluster ion undergoes reactions with a polar molecule, there are two potential reaction pathways. One is a three-body association, while the other is a bimolecular chemical reaction (if this pathway is possible). Hence, the observation of both association and chemical reaction products could be interpreted as reflecting the existence of competing processes between association and chemical reactions. Certainly, it is also likely that this observation might be due in part to the coexistence of several isomeric structures, especially in the case of $Ti_8C_{13}^+$. One is chemically more reactive, which tends to undergo "real" chemical reactions. The other is less reactive, which then displays predominantly association reactions. There have been some suggestions that $Ti_8C_{13}^+$ is a carbon-doped Met-Car.[2,10] If this is true, the present work suggests that the 8–13 species which undergo association reactions might be carbon-doped Met-Car isomers, while those which yield products involving bond-breaking are mainly due to the more reactive isomer of $Ti_8C_{13}^+$.

In conclusion, non Met-Car (both carbon-poor and -rich) titanium–carbon clusters display quite different chemistry from that of the Met-Car $Ti_8C_{12}^+$. Besides normal association reactions, those clusters can also undergo real bond disruption chemical reactions with acetone. The carbon-poor $Ti_8C_{11}^+$ cluster tends to break acetone and incorporate part of the acetone molecule to complete the cage of the Met-Car, while the carbon-rich clusters give rise to the loss of the extra carbons upon reaction with acetone and form Met-Cars. These experiments show that neighboring titanium–carbon clusters are more chemically reactive than the Met-Car $Ti_8C_{12}^+$. Importantly, the observed chemical reaction patterns of those clusters provide new evidence supporting the argument that Met-Cars are very stable molecular clusters. Indeed, the lack of observable reactivity with acetone is consistent with a closed-shell, thermodynamically stable molecular cluster.

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