Titanium−Carbon Clusters: New Evidence for High Stability of Neutral Met-Cars

H. Sakurai and A. W. Castleman, Jr.*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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The objective of the present study is to establish whether the *neutral* titanium metallocarbohedrene cluster (Met-Car), Ti_8C_{12}, has a high stability as does its cation counterpart. In this investigation, neutral titanium−carbon clusters were studied by mass spectrometry following near-threshold photoionization. We found that copious quantities of the *neutral* Met-Cars are produced under certain conditions where the power of the vaporization laser for cluster formation is sufficiently high. Under these conditions, a prominent peak corresponding to Ti_8C_{12} is detected even at very low fluences of the ionization laser employed to acquire single-photon ionization conditions. The present study provides clear evidence to lay to rest the question raised by Brock and Duncan in their recent paper (*J. Phys. Chem.* **1996**, *100*, 5654), whether the *neutral* Met-Cars are stable or not.

Introduction

Ever since the discovery in our group of metallo-carbohedrenes[1−3] (or Met-Cars for short), which are early transition metal−carbon clusters of the stoichiometry M_8C_{12} (M = Ti, V, Hf, Nb, Zr), there has been intense interest in their properties, structure, and stability. Experimentally, predominant signal intensities in the mass spectra recorded for both charged (cations and anions) and neutral clusters have been taken as evidence of the high stability of Met-Cars. For charged clusters, interpretation of the mass spectra obtained without any form of postionization is straightforward. Therefore, the dominant stability of *positively charged* Met-Cars among proximate clusters of the same charge state is clearly established according to the obtained mass spectra.[1−4] For the *negatively charged* clusters, mass spectra have been reported that evidence the high stability of the vanadium Met-Car anion,[5] and a low electron affinity has been reported for the titanium Met-Car;[6] however, the stability of Met-Car anions is still uncertain, and further investigation is required.

As for the *neutral* Met-Cars, early photoionization-mass spectrometry studies were conducted in our group of titanium− and vanadium−carbon clusters,[7] revealing intense peaks of Ti_8C_{12} and V_8C_{12}. However, these experiments were done under high fluences of the ionization laser (0.01−1000 J cm^{-2}) and probably involved multiphoton ionization. While neither the fluence nor the wavelength (266, 355, 532, or 1064 nm) of the ionization laser was found to appreciably affect the mass distribution, multiphoton absorption and some concomitant fragmentation of clusters larger than Met-Cars could not be totally ruled out under the ionization conditions employed.

Recently, Brock and Duncan reported experimental data of neutral titanium−carbon clusters studied by near-threshold photoionization mass spectrometry.[8] In their experiment, ionization of the titanium−carbon clusters was accomplished at fluences of the ionization laser in the range of about 0.005−1 mJ cm^{-2}, considerably lower than that employed in our aforementioned study. Power dependence studies carried out at selected wavelengths established that the ionization was accomplished under single-photon absorption conditions. The most puzzling result reported in their paper was that the Ti_8C_{12} clusters were generally seen as species of only minor abundance. From this, they raised the question whether *neutral* Met-Cars are really stable compared to the other neutrals of different metal−carbon stoichiometry.

Prompted by this apparently contradictory finding to our early work, we conducted a similar experimental study of neutral titanium−carbon clusters, i.e., under single-photon ionization conditions, but with careful attention to the conditions of Met-Car formation. The new findings reveal that the Ti_8C_{12} peak intensity in the mass spectra depends strongly on the conditions of cluster production and, more importantly, that the Met-Car peak dominates when the power of the vaporization laser is sufficiently high. Further experimental studies confirmed that the observed mass distribution is not an artifact but instead implies that the *neutral* titanium Met-Cars possess extremely high stability. We should emphasize, to avoid any confusion, that it is not the purpose of this paper to refute the data presented by Brock and Duncan.[8] Our focus herein is to prove that the *neutral* titanium Met-Cars are very stable, a point questioned by Brock and Duncan, and to demonstrate that they can be produced in abundant amounts if appropriate conditions are employed.

Experimental Section

The apparatus used in this work was a time-of-flight (TOF) mass spectrometer coupled with a laser-induced plasma reactor as a cluster source and a dye laser for photoionization; complete descriptions will be given elsewhere.[9] Briefly, a plasma reaction was induced by impinging a strong laser beam onto a titanium rod in the presence of a gas jet ejected from a pulsed valve. The plasma reaction was initiated with focused 532-nm light from a Nd:YAG laser. The vaporization laser power employed in the present experiments was set at selected values in the range from 2 to 15 mJ $pulse^{-1}$ depending on the desired cluster mass distribution; the details are described in the following section. The pulsed gas jet was comprised of a mixture of methane and helium at an absolute backing pressure of about 700 kPa. The concentration of methane was typically 15 vol %, although a range of conditions was investigated. The clusters of both neutrals and ions were ejected from the source through a conical nozzle, resulting in a supersonic cluster beam expansion in vacuum. To focus solely on neutral clusters, an electric potential was applied to a metal rod located parallel to the cluster beam, which served to deflect all initially charged species. The neutral

* Corresponding author. Email address: awc@psu.edu.

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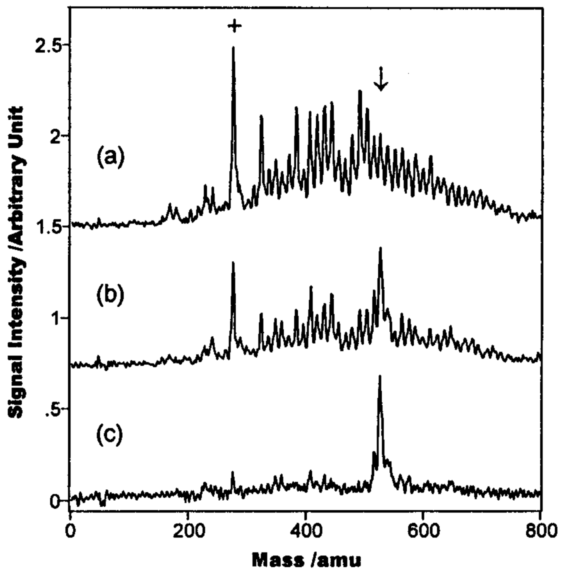

Figure 1. Photoionization mass spectra of neutral titanium−carbon clusters produced with different vaporization laser powers at a constant photoionization condition. All spectra are plotted on the same scale. The arrow (↓) marks the peaks of the Ti_8C_{12} cluster. The intense peak marked by the plus (+) is located at 276 amu, and we have not identified it as yet. (According to Brock and Duncan,[8] it is Ti_5C_3.) The ionization photon energy and laser fluence were 4.86 eV (255 nm) and 0.6 mJ cm^{-2}, respectively. The data were smoothed without losing primary features.

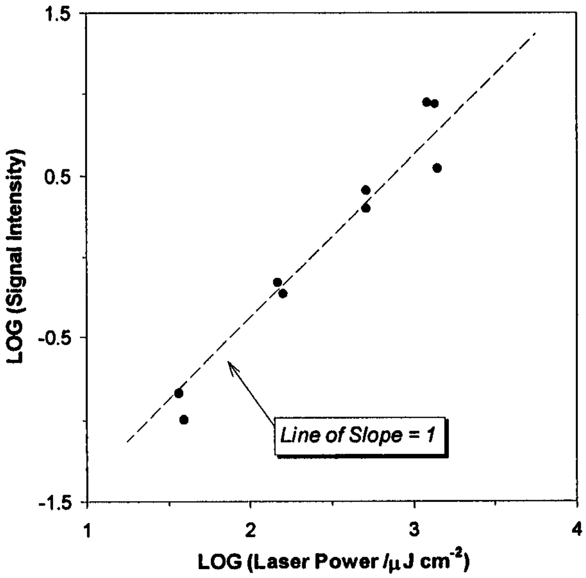

Figure 2. Photoionization laser power dependence of the Ti_8C_{12} cluster at a photon energy of 5.64 eV (220 nm). The dashed line represents the slope for a single-photon ionization condition.

clusters then entered the second vacuum chamber after passing through a skimmer. Ionization of the neutral clusters was accomplished by irradiation of ultraviolet light from a dye laser in the TOF lens using an arrangement where the electric field was perpendicular to the cluster beam. The photon energies employed in the present study were in the range between 4.77 and 5.64 eV, which corresponds to 260 and 220 nm in wavelength, respectively. The ionized clusters were analyzed by the TOF mass spectrometer equipped with a reflectron electrostatic mirror, followed by Chevron microchannel plates for ion detection. Typically, each spectrum was obtained through data accumulated for 5000 laser shots in a constant experimental setting.

Results and Discussion

The mass spectra of the titanium−carbon clusters obtained under three different cluster source conditions are shown in Figure 1. The photoionization condition was kept constant: the fluence of the ionization laser was about 0.6 mJ cm^{-2}, and the photon energy was 4.86 eV (255 nm), which was about the ionization potential (4.9 ± 0.2 eV) measured by Brock and Duncan.[8] Also, all other experimental conditions were maintained constant, except the vaporization laser power for cluster formation, which was selected as a variable quantity; the vaporization laser power was 3.1, 4.3, and 6.5 mJ pulse^{-1} for (a), (b), and (c), respectively. In (a), at the lowest vaporization laser power in Figure 1, the Ti_8C_{12} peak (↓) is not very intense and many clusters are seen to display peaks of comparable intensity. Indeed, because of many possible mass overlaps, we are not even certain whether Ti_8C_{12} exists at all under these conditions. In (b), at a medium vaporization laser power, the peak for Ti_8C_{12} becomes more intense while other peaks lose their intensity, which makes the Ti_8C_{12} peak rather prominent. In trace (c), the vaporization laser power is further increased. As a result, the dominant Ti_8C_{12} peak gains more intensity while other peaks have almost totally disappeared. It seems, from these data, that the vaporization laser power significantly affects the cluster formation and that, under the condition employed in (c), Met-Car is the only species existing in the *neutral* cluster beam in the mass range studied.

To confirm that this observation was made under a “soft” ionization condition and that the Met-Car peak does not arise solely due to fragmentation, we carried out a number of additional experiments including an investigation of the ionization laser power dependence of the intensity of the dominant Ti_8C_{12} peak. The results with 220 nm light (5.64 eV) are plotted in Figure 2. In the power range employed here, which corresponds to 0.040−1.4 mJ cm^{-2}, the mass distribution does not change with the laser power. Within limits of error, the slope is unity, which establishes that photoionization in the power range studied was accomplished by a single-photon process. We also investigated the power dependence with photon energies of 4.77, 4.86, 4.96, 5.17, and 5.39 eV (ranging from 260 to 230 nm) and found the slope to be unity in all cases. In addition, it should be noted that, within the range of the photon energies studied herein, under single-photon ionization conditions the Ti_8C_{12} peak is always dominant when the vaporization laser power is sufficiently high. This result establishes that the intense Ti_8C_{12} peak is not due to difference in photoionization cross section between the Met-Car and the other species.

Reconsidering Figure 1, it is quite surprising that the peaks other than those of the Met-Car have almost totally disappeared. A question that must be addressed next is whether fragmentation upon laser irradiation is so significant even under *single*-photon absorption conditions that it might cause the prominent Ti_8C_{12} peak by creating more Met-Cars at the expense of larger cluster species. Therefore, we conducted further experimental studies to answer this question. First, mass spectra were sequentially recorded with the cluster source and ionization laser conditions kept unchanged, but scanning the difference in the time delay between firing the ionization laser and the laser used in the cluster formation. After clusters are produced and ejected from the source, they fly at velocities with magnitudes determined at the exit nozzle of the cluster source by mass-dependent velocity slippage effects; this enforces mass separation on the clusters before they are irradiated by the laser. Hence, study of variations in the mass distributions with the time delay provides a method suitable to investigate fragmentation effects upon photon absorption.[10]

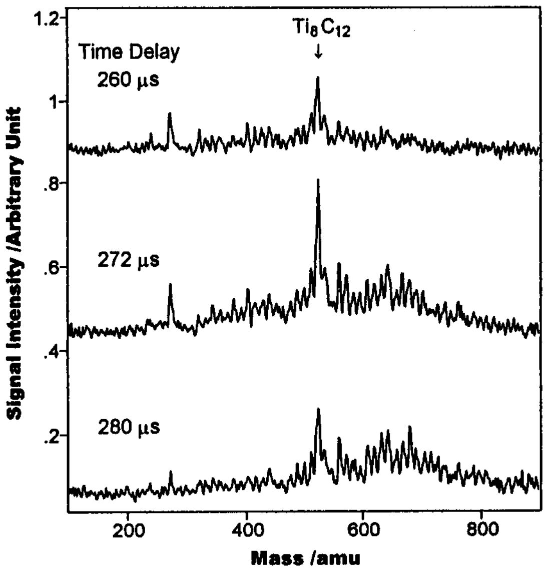

Figure 3. Mass spectra recorded at different timings of firing the ionization laser with respect to the timing of the vaporization laser used in cluster formation. All other conditions are kept unchanged. The vaporization laser power was 4 mJ pulse^{-1}, and the ionization photon energy and laser fluence were 4.86 eV (255 nm) and 0.3 mJ cm^{-2}, respectively. Note that the same intensity scale was used in recording all these traces.

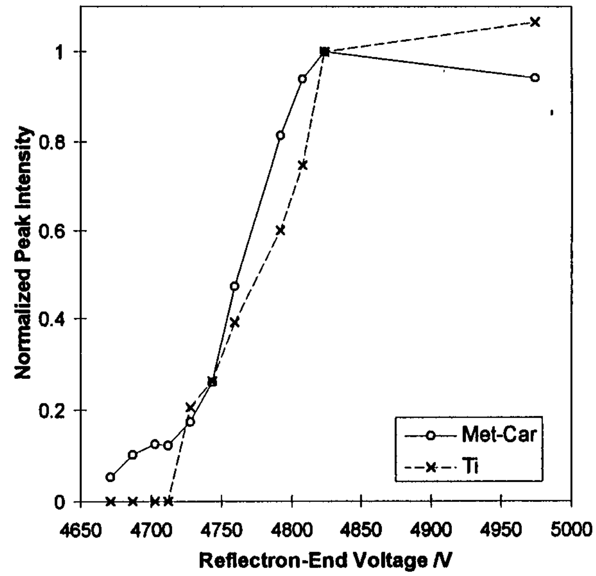

Figure 4. Plots of peak intensities of the Met-Car with different voltages applied to the reflectron-end mesh. As a reference, peak intensities of atomic Ti are also presented. The Ti peaks were seen but were quite weak as a result of the required multiphoton ionization by the low-power ionization laser. The peak intensities of both species are normalized by the intensities obtained at 4820 V.

The results of the present study are shown in Figure 3. In these experiments, the vaporization laser power was set at a medium value (~5 mJ pulse^{-1}) such that both the prominent Ti_8C_{12} peak and other peaks were visible in the mass spectra. The top trace was recorded at the shortest interval (260 μs), which gave more emphasis to the detection of small clusters; the interval was elongated by 12 and 20 μs in the middle and bottom traces, respectively. The most important outcome from this study is that the peak intensity change of the Met-Car does not correlate with those of the larger clusters. For example, while the Met-Car peak has the highest intensity in the middle trace, the peaks for the larger ones keep their intensity almost unchanged in both the middle and the bottom traces. Moreover, comparing the top and the bottom spectra, it is seen that while the Met-Car peaks have a comparable intensity in both traces, the intensities for the larger species are substantially different. This study strongly supports the conclusion that the fragmentation of the large clusters upon photon absorption is not the source of the intense Met-Car peak.

Next, we studied the change in the mass distribution resulting when the ionization laser power was sufficiently high to enable the clusters to absorb more than one photon. In our study, this was accomplished by increasing the ionization laser power to 1.5 mJ cm^{-2} or above. These conditions were easily found because, as the ionization laser power exceeds this limit, the mass distribution starts to become significantly distorted, and the Ti_8C_{12} peak is intensified with the laser power dependence being greater than unity. Importantly, this observation is accompanied by the findings of a decrease of the relative peak intensities of clusters larger than the Met-Car. This result indicates that fragmentation of the larger clusters can affect the further production of the Ti_8C_{12} cations, but our findings show that this occurs *only* under conditions where the clusters undergo multiphoton excitation by the ionization laser. In other words, when the ionization laser fluence is below the multiphoton absorption limit, in which the data in Figure 1 were recorded, fragmentation is not very appreciable.

Third, we conducted a "cutoff" experiment[11,12] to investigate if metastable fragmentation following photoionization contributes to the intense Met-Car peak at all. We did this experiment because, in general, we expect some metastability of the fragmenting clusters, assuming that the fragmentation is due to a small amount of excess internal energy left in the clusters after single-photon excitation−ionization. The experiment in the present study was done with 255-nm light (4.86 eV) for ionization under a high vaporization laser power condition such that the Met-Car peak dominated the mass distribution.[13] The time window open to metastable dissociation for the apparatus used was up to about 30 μs for clusters as heavy as Ti_8C_{12}.

The results of the study are shown in Figure 4. Most importantly, when the reflectron-end voltage is decreased and the peak of Ti, which is taken as a reference, completely disappears, the Met-Car peak also fades out. From this, it is concluded that metastable fragmentation does not have a significant effect. It should be noted that a weak but nonvanishing peak of Ti_8C_{12} was observed below the cutoff potential of Ti, which is seen as a small step in the lower left corner of Figure 4. We investigated this steplike feature carefully, and concluded that a small amount of Ti_8C_{12}, about 10−15%, was produced by fragmentation. However, we do not believe that this is due to metastability of the clusters for two reasons. First, if we assume that the species of low cutoff potential are the products of metastable dissociation *in* the field-free drift region, the calculated parentage for the observed voltage cutoff would correspond to species whose mass is only about 5 amu greater than the mass of the Met-Car; this is too small for the titanium−carbon system, and therefore, the metastable fragmentation in the field-free region is ruled out. Second, if the fragmentation takes place before the clusters exit the TOF lens, the steplike shape, especially the level plateau region, cannot be explained by the general assumption that the time profile of the metastable dissociation rate is represented by an exponential function. Instead, we think it is due to a small effect occurring in the TOF lens assembly, perhaps due to collision with one of the mesh grids. Therefore, although we do not know clearly what the fragmentation mechanism is, the contribution of *metastable* dissociation is ruled out. Summarizing the results discussed above, we conclude that fragmentation is not a dominant process upon single-photon absorption and that, although under some conditions fragmentation occurs to a small extent, it is by far insufficient to eliminate all the clusters other than the Met-Car from the mass spectra. Hence, it cannot be a significant source of Met-Cars.

One of the reasons why we observe a significant difference in the mass distribution of metal−carbon clusters with laser power as is shown in Figure 1 is thought to be the same as what we proposed in a previous paper[3] and was also theoretically predicted by Reddy and Khanna;[14] the relative concentrations of titanium and carbon atoms in the plasma of the cluster source determine the cluster growth mechanisms, leading to either cubes or Met-Cars. Clear-cut evidence of this effect has been acquired through our experimental studies showing the switching from cubes to Met-Cars in the niobium system.[3,9] When the vaporization laser power is low, the plasma is not sufficiently energetic to effect an efficient dehydrogenation process. Therefore, insufficient carbon atoms are available for cluster growth, and the reactions terminate at a high Ti/C ratio, in which the clusters end in either a rock-salt structure or as random assemblies of carbon, titanium, and perhaps some hydrogen atoms. On the other hand, when the vaporization laser power is high, more carbon atoms without any attached hydrogen become available,[15] and the clusters grow to Met-Cars. Although this does not provide an explanation why clusters other than the Met-Car are not efficiently formed at higher vaporization laser powers, it explains why Met-Cars are produced more intensively under these source conditions.

Following our study presented herein, another important question arises about the relative stability between the *neutral* and *cation* Met-Cars: will we observe a similar mass distribution change as in Figure 1 if we study the cation clusters under the same cluster source conditions? Similar questions had been discussed in the studies of the stability of C_{60} as cations and anions,[16−18] where it was finally proven experimentally that, depending on the charge state, the cluster source has different optimum conditions for abundant production of C_{60}.[18] Based on this intriguing result for C_{60}, studies to answer related questions for Met-Cars are to be conducted next.

In addition, knowledge about the stability of the neutral Met-Cars of other metal systems is of interest, but this may be a hard question to address based on the comparatively high IP measurement of the M_8C_{12} clusters by Brock and Duncan.[8] The IP's of vanadium, zirconium, and niobium Met-Cars were determined to be greater than 5.76 eV, which require higher photon energies than those available with our present dye laser setup.

In summary, we have established that *neutral* titanium Met-Cars are predominantly produced under cluster source conditions where the vaporization laser power for cluster formation is sufficiently high. We conclude, from this result, that the *neutral* titanium Met-Car has quite high stability, in keeping with our observation of its formation in the condensed state[19] and our finding that it alone in the mass distribution of titanium−carbon clusters undergoes delayed ionization.[20,21]

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