METAL-CARBON CLUSTERS: NEW EVIDENCE FOR HIGH STABILITY OF NEUTRAL METALLOCARBOHEDRENES

H. Sakurai and A. W. Castleman, Jr.
Department of Chemistry
The Pennsylvania State University, University Park, PA 16802

Introduction

Ever since the discovery in our group of early transition metal-carbon clusters of the stoichiometry of M_8C_{12}, termed metallocarbohedrenes (Met-Cars) [1-3], their stability, as well as their properties and structure, has been intensively studied. It has been experimentally established that *cationic* Met-cars, $M_8C_{12}^+$ where M = Ti, V, Cr, Fe, Zr, Nb, Mo, and Hf, are predominantly stable among proximate clusters of the same charge state [1-4]. As for *neutral* Met-Cars, early photoionization-mass spectrometry studies were conducted in our group of the Ti/C and V/C clusters [5], revealing intense peaks of Ti_8C_{12} and V_8C_{12}. However, these experiments were done with high fluence ionization laser and undoubtedly involved multi-photon ionization. Thus, ambiguity in interpreting the mass spectra could not be totally ruled out.

Recently, Brock and Duncan reported experimental data of neutral Ti/C clusters studied by near-threshold photoionization mass spectrometry [6]. In the experiment, ionization of Ti_8C_{12} was accomplished under single-photon ionization conditions which was considerably 'softer' than that employed in our aforementioned study. The most puzzling result in their paper was that the Ti_8C_{12} clusters were seen as species of only minor abundance. From this, they raised the question whether *neutral* Met-Cars are really stable.

Prompted by this apparently contradictory finding to our early work, we conducted a similar experimental study of neutral Ti/C clusters, but with careful attention to the conditions of Met-Car formation. Reporting and discussing the proof of the high stability of *neutral* titanium Met-Cars is the subject of the present paper.

Experimental

The experimental set up has been reported in detail elsewhere [7], and only a brief description is given herein. The apparatus used in this work was a time-of-flight (TOF) mass spectrometer with a laser-induced plasma reactor in vacuum as a cluster source and a dye laser for photoionization. A plasma reaction was induced by impinging a strong laser beam onto a metal rod in the presence of a gas jet comprised of a mixture of methane and helium. In the plasma, the ablated metal atoms and the gas were mixed and plasma-induced dehydrogenation of methane molecules, followed by formation of the metal-carbon clusters, took place. The clusters of both neutrals and ions were ejected through a nozzle, resulting in a supersonic cluster beam expansion. After separation from their ionized counter parts via an electric field, only neutral clusters then entered the second vacuum chamber. Ionization of the neutral clusters was accomplished by irradiation of ultraviolet light from a dye laser system. The ionized clusters were then mass-analyzed by the TOF mass spectrometer and detected.

Results and Discussion

The mass spectra of the Ti/C clusters obtained under two different cluster source conditions are shown in Figure 1. In both traces, the photoionization condition was kept constant; the photon energy of the ionization laser was 5.17 eV (240 nm), which was above the ionization potential (4.9 ± 0.2 eV) of Ti_8C_{12} [6]. Also, all other experimental conditions were maintained constant, except the vaporization laser power for cluster formation; it was ~ 4 mJ/pulse in the upper trace and ~ 15 mJ/pulse in the lower. We found that the mass distribution can be

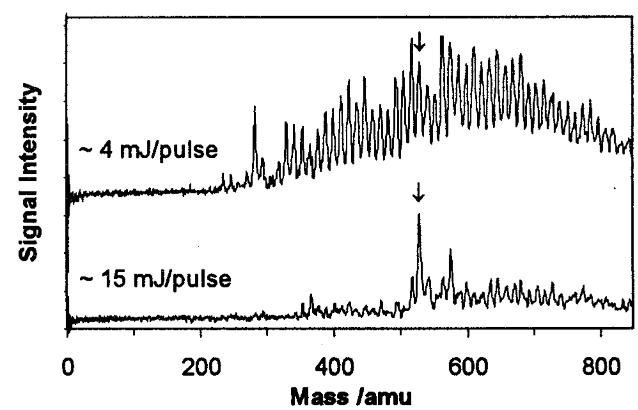

Figure 1. Photoionization mass spectra of neutral Ti/C clusters produced with two different vaporization laser powers at a constant photoionization condition. The peaks corresponding to Ti_8C_{12} are marked by arrows (↓).

totally altered; in the upper trace, the Ti_8C_{12} peak (↓) was not intense compared to neighboring clusters and many clusters display peaks of comparable intensity. Because of possible mass overlaps, we were even not sure whether Ti_8C_{12} existed at all. Strikingly, on the other hand, in the lower trace, the Ti_8C_{12} peak is the most dominant species, and most of the other peaks have disappeared.

To confirm that this observation was done under a soft ionization condition and that fragmentation was not the source of the intense Ti_8C_{12} peak, we investigated the ionization laser power dependence of the peak intensity of Ti_8C_{12}. Within limits of error, the slope of the dependence is unity, which establishes that photoionization was accomplished by a single photon.

One of the reasons for the significant difference in the mass distribution with laser power is thought to be the same as what was proposed in our previous paper [3] and also theoretically predicted by Reddy and Khanna [8]; the relative concentrations of Ti and C atoms in the plasma of the cluster source determine the cluster structure, leading to either cubes or Met-Cars. When the vaporization laser power is low, the plasma is not energetic enough to effect an efficient dehydrogenation process. Therefore, not many pure carbon species 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 with some hydrogen atoms. On the other hand, when the laser power is high, more pure carbon species become available, and the clusters grow to Met-Cars. Our experiments conducted with lower methane concentration also supported this mechanism; with a gas containing less methane, a strong Met-Car peak was not observed even when the vaporization laser power was higher than 15 mJ/pulse,.

Study of the niobium-carbon system under two different vaporization laser power conditions gave further evidence to the proposed mechanism (see Figure 2). The Nb/C ratio shift between them is apparently seen because mass overlaps are taken away in contrast to the Ti/C system. In the upper trace, when the vaporization laser power is lower, the average Nb/C ratio is approximately equal to unity; on the other hand, in the lower trace, when the power is higher, the Nb/C ratio is significantly below unity, i.e. more carbon atoms are contained in clusters of the same number of niobium atoms.

Another possible reason for the change in the mass distribution is the effect of the plasma temperature during cluster formation; it is likely that, at relatively high temperature due to high vaporization laser powers, only the most stable species can survive while relatively less stable species are eliminated before exiting the cluster source. On the other hand, species of moderate stability can grow when the temperature is lower, and these can then be seen in the mass spectra. This mechanism explains why species except Met-Cars *disappear* in the mass spectra, rather than keep their intensity unchanged.

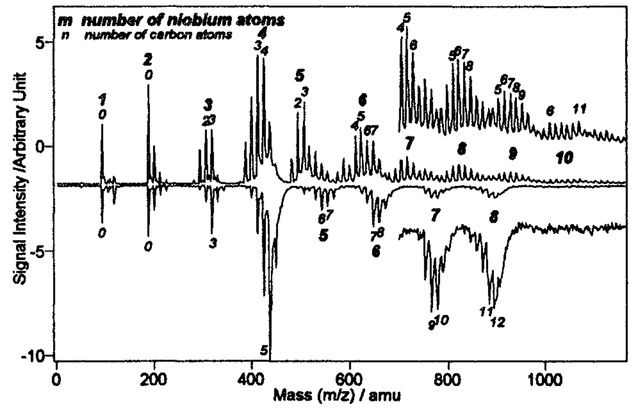

Figure 2. Photoionization mass spectra of neutral Nb/C clusters produced with two different vaporization laser powers at a constant photoionization condition. The vaporization laser power was ~ 4 mJ/pulse in the top and ~ 15 mJ/pulse in the lower. The lower trace was plotted upside down to guide eye.

In summary, we have found that *neutral* titanium Met-Cars are produced superdominantly in a certain cluster source condition. We conclude, from this result, that the *neutral* titanium Met-Car has quite high stability.

Acknowledgment

Funding by the Air Force Office of Scientific Research, Grant No. F49620-94-1-0162, is gratefully acknowledged.

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