$M_4C_9^+$ (M = Ti, V): New gas phase clusters

R SELVAN, L GOWRISHANKAR and T PRADEEP*
Regional Sophisticated Instrumentation Centre, and Department of
Chemistry, Indian Institute of Technology, Chennai 600 036, India
e-mail: pradeep@iitm.ac.in

Abstract. New metal–carbon clusters, $M_4C_9^+$ (M = Ti, V), generated using a combined thermal arc discharge evaporation set-up, have been studied with quadrupole mass spectrometry. Reactivities of these clusters have been investigated by means of association reactions with H_2O. Metal–carbon clusters of other compositions have also been studied. We speculate on the mechanism of formation of larger metal–carbon clusters.

Keywords. Metal–carbon clusters; gas phase clusters.

1. Introduction

In Castleman's first report on metcars (metallocarbohedranes)[1], cationic Ti–C clusters were produced in the laser vaporisation source. Charge on the clusters decides the relative importance of the metcar peak with respect to the other species in the mass spectrum[1]. In most of the experiments, cationic metal–carbon clusters show the same magic numbers. The neutral species selected show different mass spectra with enhanced contributions from smaller non metcar clusters. Wei *et al*[2] obtained the mass spectra of neutral Ti–C and V–C clusters at fixed ionisation laser energy, which show peaks due to (1,2), (2,4), (3,6), (4,8), (5,10), (6,12) and (7,13) clusters along with the magic peak, Ti_8C_{12} ((n, m) corresponds to Ti_nC_m). From this it was confirmed that MC_2 serves as the main building unit in the formation of metcars[2]. According to Brock and Duncan[3], the spectra of Wei *et al*[2] arise due to the photofragmentation processes and do not correspond to the nascent distribution. The mass spectrum reported by Brock and Duncan[3] does not favour any specific building block. Sakurai and Castleman[4] have shown that the relative abundance of neutral Ti_8C_{12} depends upon the experimental conditions and on the laser power. Wang *et al*[5] developed a procedure to detect metal–carbon cluster anions[5]. The mass spectrum was obtained by the vaporisation of pure titanium target with helium carrier gas containing 5% CH_4. In this experiment, Wang *et al*[6] observed peaks corresponding to $Ti_xC_y^-$ at (x, y) = (3,8), (4,8), (6,13), (7,13) and (9,15). Many theoretical calculations have been performed on small metal–carbon clusters such as Ti_2C_2, Ti_2C_3, TiC_x ($x = 1–4$) as well as smaller molybdenum carbide species[7–15].

It is in this context that we decided to try to investigate the mechanism of formation of these metal–carbon clusters using the cluster mass spectrometry apparatus. Since we have already developed a methodology to synthesize metal–carbon clusters in the solid state[16], it was decided to look at the small metal–carbon clusters existing in the gas

*For correspondence

phase *in situ*. For this purpose we coupled a quadrupole mass spectrometer to an already fabricated arc-discharge evaporation set-up. While we were performing Ti–C evaporation, a new metal–carbon cluster ion, $Ti_4C_9^+$, was observed in the gas phase. Photodetachment spectrum of Wang *et al*[6] shows $Ti_4C_8^-$ along with other clusters. Wang *et al*[6] have proposed cage-like structures for Ti_4C_8 belonging to D_{4h} and D_{2d} point groups on the basis of theoretical studies. The D_{2d} structure (four C_2 units bonded at the 4 faces of the tetrahedral Ti_4 cluster) was found to be 2·67 eV more favourable compared to the D_{4h} structure. Munoz *et al*[13] proposed a structure in which two C_4 chains of butadiene type are connected to four metal atoms, overall point group being D_{2d}. Munoz *et al*[13] reoptimized the D_{2d} structure proposed by Wang *et al*[6] and Ge *et al*[15] and found that they are stabilized at 70·94 and 72·35 eV respectively. From theoretical studies it is clear that the D_{2d} structure is the most stable structure for neutral Ti_4C_8. The structure of $Ti_4C_9^+$ can be understood in this background.

2. Experimental details

We fabricated a combined thermal arc-discharge set-up, which consists of two water-cooled copper rods housed in a vacuum chamber through which a high current of 100–200 A (20 V AC) can be passed. This set-up is similar to the Kratschmer–Huffman arrangement for the synthesis of fullerenes[17]. The metal–carbon composite electrodes were prepared in the arc-discharge evaporation set-up itself. To prepare the electrodes, a rectangular graphite rod with a boat-like depression was taken and connected to both the ends of the electrode[16]. A titanium rod was kept over the depression and was melted by resistive heating at a current of ~100 A. The depression was filled with Ti and it formed a coating over the graphite. The details of the set-up used to prepare metal–carbon composite electrodes have been presented earlier[16]. The Ti–C composite electrode thus prepared had a Ti:C weight ratio of 1:1·5 and was evaporated by resistive heating under a constant flow of helium. The flow rate of helium was not directly measured. The system was pumped using a 150 l/min mechanical pump and the dynamic helium pressure was maintained at 5 torr. Under lower pressures of helium, the clusters reported in this paper were not observed. The metal–carbon clusters formed were detected immediately. After the evaporation was complete, water vapour was continuously admitted into the differential chamber and the spectra were recorded. The gas phase clusters pass through the water vapour in the differential pumping region and then to the quadrupole mass spectrometer for analysis. The mass spectrometer consisted of an analyser supplied by a commercial vendor and home-built electronics. A small disc with 0·5 mm diameter hole was inserted between the arc evaporation chamber and the differential pumping region. There was another such disc kept before the mass spectrometer chamber. The clusters were ionised by 70 eV electron impact. The differential pumping region has a solvent inlet through which solvent vapours can be admitted into the chamber to undergo reaction with the clusters formed in the gas phase. The pressure of the admitted solvents was measured using a gauge mounted on the pumping line. The resolution of the quadrupole was 2 amu. Graphite, titanium and solvents used for the reaction were of the highest purity (99% pure) available from commercial sources.

3. Results and discussion

3.1 *Ti$_4$C$_9^+$, a new gas phase cluster ion*

Graphite evaporation by resistive heating under 5 torr of flowing helium resulted in the formation of only elemental carbon. The arc was operated only for a short interval. It is likely that the neutral clusters do not survive our long (50 cm) differential pumping region, as a result of which carbon distribution is not observed. When a metal–carbon composite electrode was evaporated in a dynamic helium atmosphere, an intense peak was observed at 300 amu (figure 1). To find the metal–carbon composition of this peak the following tests were performed. (1) A vanadium carbon composite electrode was prepared and this was evaporated under the same experimental conditions to identify the peak shift. (2) The formed clusters were allowed to react with water and the addition products were analysed. Ions, if produced in the arc, did not contribute to the mass spectrum as there were no peaks when the ion source filament was turned off.

The formed cluster at *m/z* 300 was allowed to react with water and the reaction products were studied at various intervals of time. Note that reactions were performed prior to ionization. The cluster ion peak is stable only for a short time (about 2 min) after evaporation while the addition products persist for a long time. Instability of this peak is very clear from figures 2a and b. Ti$_4$C$_9$ is highly reactive, as a result it undergoes an association reaction with water and the addition product seems to build up in the analysis chamber and thus there is a time effect on the Ti$_4$C$_9$ cation. Four water molecule additions are observed (figure 2a). All the addition products are separated by 18 amu. As time proceeds, the peak at 300 amu decreased in intensity and the water adducts gained in intensity (figure 2b). The distribution of adducts confirms that the peak at 300 amu consists of four metal atoms. Most probable composition of this peak could be Ti$_4$C$_9$ as there are no other elements used in the synthesis. The intensities of the formed addition products are not even. The peaks corresponding to Ti$_4$C$_8$(H$_2$O)$_2$ and Ti$_4$C$_8$(H$_2$O)$_3$ are intense and similar in intensity compared to the peaks
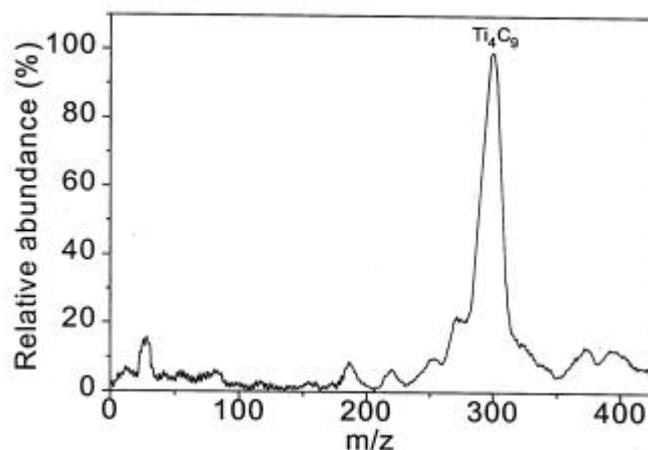

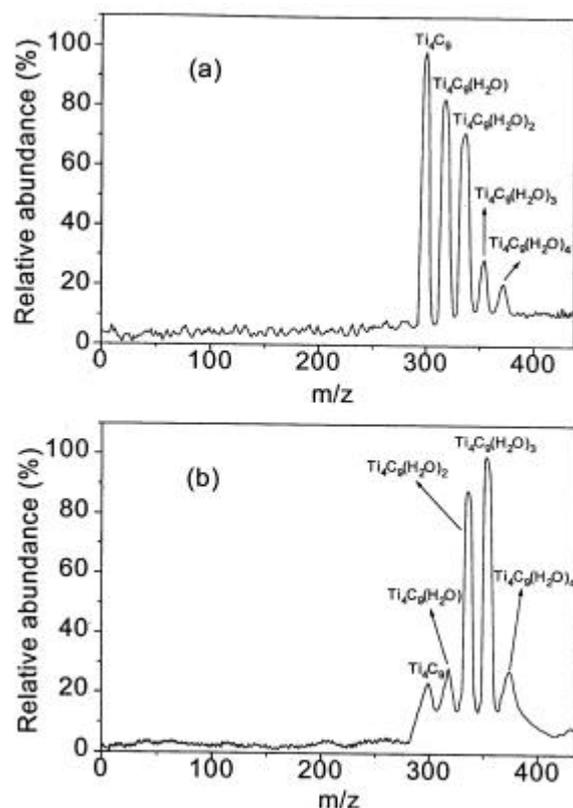**Figure 1.** The mass spectrum of Ti$_4$C$_9$ obtained by the evaporation of a Ti–C composite electrode.

Figure 2. (**a**) Mass spectrum of the Ti_4C_9 after a minute of the exposure of water vapour. (**b**) Mass spectrum recorded after two minutes.

due to $Ti_4C_8(H_2O)$ and $Ti_4C_8(H_2O)_4$. After two minutes, the peak due to Ti_4C_9 disappears whereas the remaining peaks continue to manifest (figure 3a). After three minutes, only the peaks due to $Ti_4C_9(H_2O)_3$ and $Ti_4C_9(H_2O)_4$ are observed (figure 3b). The product distribution truncates at $Ti_4C_9(H_2O)_4$ and there is no further addition confirming the presence of four metal atoms. Intensity pattern of these water adducts (figure 2b) suggests that there could be coexistence of different isomeric structures.

3.2 *Vanadium carbon clusters*

A similar experiment done with vanadium under the same conditions gave a peak at 312 amu. This is due to V_4C_9 (figure 4). On changing the metal atom, there is a corresponding shift in the mass number suggesting the presence of four metal atoms. The instrument resolution was inadequate to resolve the isotope distribution of both the metals. In addition to the peak at m/z 312, peaks are observed at m/z 237 and m/z 387 corresponding to $V_3C_9^+$ and $V_5C_{11}^+$ respectively. All the three peaks are separated by 75 amu which is due to VC_2 addition. A peak observed at 363 amu is due to $V_5C_9^+$, the loss of two carbon atoms from $V_5C_{11}^+$. From this experiment it is clear that the structure of $V_4C_9^+$ would be similar to that of $Ti_4C_9^+$. From $V_4C_9^+$ there is no carbon
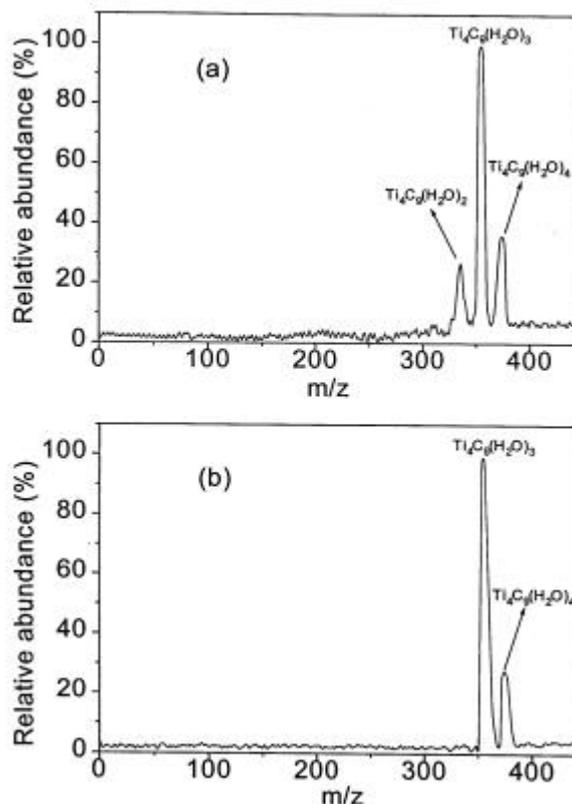
Figure 3. (**a**) Mass spectrum of the same reaction after three minutes showing the absence of $Ti_4C_9^+$. (**b**) Mass spectrum after four minutes showing only the presence of $Ti_4C_9(H_2O)_3^+$ and $Ti_4C_9(H_2O)_4^+$.

loss to give $V_4C_8^+$ suggesting that the extra carbon atom could be in the endohedral position. After a minute, the peaks at *m/z* 237, 312 and 387 disappear and the peak at *m/z* 75 appears and finally an intense peak at *m/z* 432 remains. The peak at *m/z* 75 is due to VC_2 (figure 4b). In all these experiments, after the disappearance of the peaks due to metal–carbon clusters this intense peak at *m/z* 432 survives. This peak persists for several hours after the evaporation. We believe this to be due to the newly discovered fullerene, C_{36}[18]. Other fullerenes do not form under these conditions; due to experimental limitations we have not been able to observe higher mass number fullerenes.

3.3 *Structure of M_4C_9*

New metal–carbon cluster $Ti_4C_9^+$ could be Ti_4C_8 with an endohedral carbon atom. This extra carbon present inside the cage can be bonded to four metal atoms thereby increasing its stability. In the D_{2d} structure optimised by Wang *et al*[6] the distance between the diagonally opposite titanium and carbon is 3·70 Å, which suggests that the extra carbon atom can be located inside the cage. Similarly in the D_{2d} structure
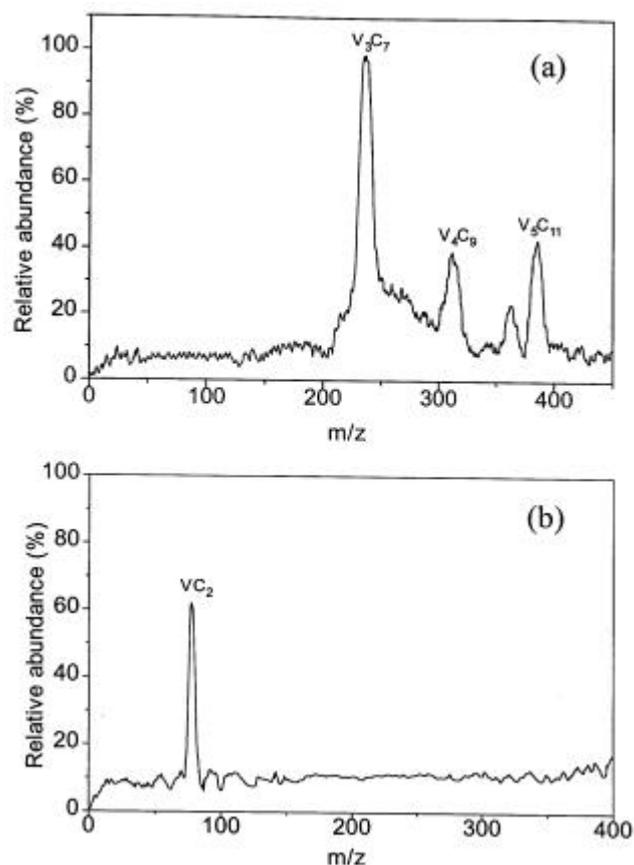
Figure 4. (**a**) The mass spectrum of V–C clusters obtained by the evaporation of a V–C composite electrode. (**b**) Mass spectrum showing the formation of VC_2.

optimised by Munoz *et al*[13] the diagonally opposite titanium and carbon in the cage are $3.66 \, \text{Å}$ apart, which again confirms the same. If the extra carbon is in the exohedral position, it can hinder the addition of water molecules, which is not observed. In both experiments, with titanium as well as with vanadium, we have not observed the peaks due to $Ti_4C_8^+$ and $V_4C_8^+$ suggesting that the loss of this extra carbon is not favoured. Reaction of water with vanadium carbon clusters cannot be performed in the present set-up since they are highly unstable.

From the theoretical studies[13], it is known that Ti_4C_8 can exist in three different types of structures with D_{2d} symmetry which are almost equal in their stabilisation energies. The variation in the intensity of the water adduct peaks could be due to the coexistence of these structures in the gas phase.

3.4 *Small titanium–carbon clusters other than* $Ti_4C_9^+$

During the arc-discharge evaporation of the Ti–C composite electrode, we observed only peaks due to $Ti_4C_9^+$, $V_4C_9^+$, VC_2^+ and their water adducts. Most of the other small
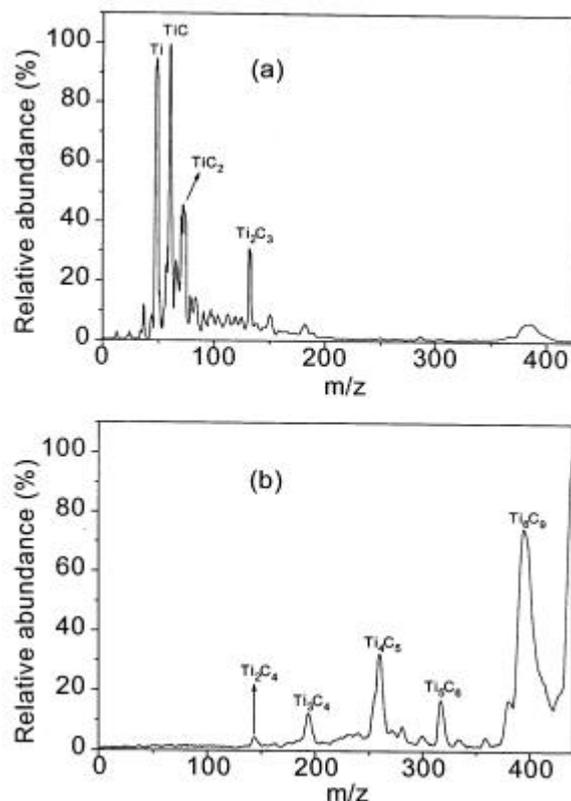
Figure 5. (**a**) Mass spectrum obtained immediately after evaporation when the transfer line was under baking condition. (**b**) Mass spectrum of the same system after a minute of evaporation.

metal–carbon clusters were lost in the flight region. To avoid this, arc-discharge evaporation was done when the flight region was baked. Under these conditions, the spectrum (figure 5a) recorded shows a peak at m/z 48 due to titanium. There is a peak at 60 amu due to TiC$^+$, the peak at m/z 72 is due to TiC$_2$$^+$. The peak at m/z 84 amu is due to TiC$_3$$^+$. In Castleman's metastable dissociation experiment, all these smaller fragments were observed [19]. The peak observed at m/z 132 is due to Ti$_2$C$_3$$^+$. A few scans after evaporation all these low mass number peaks disappear and a peak at m/z 144 appears which is due to the Ti$_2$C$_4$$^+$ fragment (figure 5b). From m/z 144, at 60 amu separation, a peak appears at m/z 180 attributed to the addition of a TiC unit to Ti$_2$C$_2$$^+$ and there is another 48 amu addition leading to Ti$_3$C$_2$$^+$. The absence of peaks at m/z 48, 60 and 72 in this spectrum (figure 5b) indicates that these are getting converted to high mass number metal–carbon clusters. This suggests that the formed metal atoms as well as smaller units like TiC$_2$, TiC$_3$ etc. can react with one another to form larger metal–carbon clusters.

4. Conclusions

Arc evaporation coupled mass spectrometer is useful in identifying new gas phase clusters. We have observed a new gas phase cluster $M_4C_9^+$ (M = Ti, V) in the gas phase. Reaction of Ti_4C_9 with water shows four successive additions. Vanadium–carbon clusters with different compositions were also observed. Experiments also indicate that smaller metal–carbon clusters formed in the plasma are the building units for the formation of larger clusters. Metal atoms formed in the plasma get converted to metal–carbon clusters and therefore the composition of the Ti–C composite electrode is important in the generation of these metal–carbon clusters.

References

1. Guo B C, Kerns K P and Castleman A W Jr 1992 *Science* **255** 1411
2. Wei S, Guo B C, Purnell J, Buzza S and Castleman A W Jr 1992 *J. Phys. Chem.* **96** 4166
3. Brock L R and Duncan M A 1996 *J. Phys. Chem.* **100** 5654
4. Sakurai H and Castleman A W Jr 1997 *J. Phys. Chem.* **A101** 7695
5. Wang L S, Li S and Wu H 1996 *J. Phys. Chem.* **100** 19211
6. Wang L S, Wang X B, Wu H and Cheng H 1998 *J. Am. Chem. Soc.* **120** 6556
7. Sumathi R and Hendrikx M 1998 *J. Phys. Chem.* **A102** 4883
8. Sumathi R and Hendrikx M 1998 *J. Phys. Chem.* **A102** 7308
9. Wei P and Yang W 1995 *Phys. Rev.* **B51** 7224
10. Wang L S and Cheng H 1997 *Phys. Rev. Lett.* **78**, 2893
11. Yeh C S, Byun Y G, Afzaal S, Kan S Z, Lee S, Freiser B S and Hay P J 1995 *J. Am. Chem. Soc.* **117** 4042
12. Yang J, Toigo F and Wang K 1994 *Chem. Phys. Lett.* **228**, 279
13. Munoz J, Rohmer M M, Benard M and Poblet J M 1999 *J. Phys. Chem.* **A103** 4762
14. Rohmer M M, Benard M and Poblet J M 2000 *Chem. Rev.* **100** 495
15. Ge M, Feng J, Yang C, Li Z and Sun C 1999 *Int. J. Quantum Chem.* **71** 313
16. Selvan R and Pradeep T 1999 *Chem. Phys. Lett.* **309** 149
17. Kratschmer W, Lamb L D, Fostiropoulos K and Huffman D L 1990 *Nature (London)* **347** 354
18. Piskoti S, Yarger J and Zettl A 1998 *Nature (London)* **393** 771
19. Wei S, Guo B C, Purnell J, Buzza S A and Castleman A W Jr 1993 *J. Phys. Chem.* 9**7** 9559