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Reactivities of Metallocarbohedrenes: FTICR Studies of $V_8C_{12}^+$ in the Gas Phase

C. S. Yeh, S. Afzaal, S. A. Lee, Y. G. Byun, and
Ben S. Freiser*

H. C. Brown Laboratory of Chemistry
Purdue University, West Lafayette, Indiana 47907

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A new class of transition metal-carbon clusters named "metallocarbohedrenes" or "met-cars" with the stoichiometry M_8C_{12} (M = Ti, V, Zr, and Hf)[1-5] has become the focus of intense investigation. These species, discovered by Castleman and co-workers, have been mainly observed as "supermagic" peaks in mass spectra obtained from supersonic metal cluster sources in which the He expansion gas is seeded with a hydrocarbon. Like the fullerenes, the metallocarbohedrenes are of both fundamental interest and hold promise as important new materials. Duncan and co-workers have reported the observation of chromium, iron, and molybdenum met-cars and the decomposition mechanisms from the photodissociation of the met-car species.[6,7] In addition, higher order magic number metal-carbon clusters,[3,8] and mixed-metal met-cars have also been observed.[9]

Although a pentagonal dodecahedron cage structure with T_h symmetry was originally proposed to account for the stability of M_8C_{12},[10-16] more recently D_{2d} and T_d structural isomers have been calculated to be substantially more stable.[17-20] One calculation indicates that the T_d structure is somewhat lower in energy than the D_{2d} structure.[19] In the T_d structure the six C_2 units are accommodated in a tetracapped tetrahedron formed by the eight transition metals in a butterfly topology. While all eight metal sites are equivalent in the T_h structure, two types of coordination sites exist in the D_{2d} and T_d structures. This may provide a criterion by which to distinguish the T_h isomer from these other two possible structures experimentally. For example, Castleman and co-workers have shown that $Ti_8C_{12}^+$ and $V_8C_{12}^+$ react with polar molecules such as ammonia to coordinate up to eight ligands. These results are consistent with the T_h structure. For the π-bonding ligand benzene, however, a maximum of four molecules are seen to attach to $Ti_8C_{12}^+$,[21] which might be due to steric hindrance. In addition, $Ti_8C_{12}^+$ is essentially unreactive with oxygen, except for a small amount of addition products observed. These results are provocative and provide the impetus for additional chemical studies. Of particular interest will be the effect of electronic structure on reactivity as the metal centers are varied. In this communication, we report preliminary results on the reactivity of $V_8C_{12}^+$ with O_2 and provide evidence for the existence of two different metal atom sites consistent with the D_{2d} or T_d structures.

All of the experiments were performed on an Extrel FTMS-2000 dual-cell Fourier transform ion cyclotron resonance (FTICR) mass spectrometer[22,23] combined with a compact supersonic source developed by Smalley and co-workers.[24] The laser vaporization technique is used to generate metal-carbon clusters in a manner similar to that of Castleman and co-workers by seeding the He expansion gas with ~1% CH_4.[25,26] Reagents are either introduced at a static pressure (~10^{-8}–10^{-6} Torr) using Varian leak valves or, alternatively, pulsed into the chamber using General Valve Corporation Series 9 solenoid pulsed valves.[27] Ar is used as the collision gas at a static pressure of 10^{-6} Torr. Ion isolation[22] and collision-induced dissociation[28] are accomplished either by using standard FTICR radio-frequency pulses of variable frequency and power or by using SWIFT excitation.[29] For the rate constant measurement, the O_2 pressure was measured using standard procedures for calibrating the ion gauge for the sensitivity toward O_2.[30] The error in the pressure measurement is conservatively estimated at ±50% and is the biggest source of error in the rate constant measurement.

$V_8C_{12}^+$ reacts readily with a static background pressure of oxygen at ~10^{-8} Torr via reaction 1 to generate $V_8C_{10}^+$ and, presumably, two CO molecules (Figure 1). $V_8C_{10}^+$ in turn reacts further with oxygen to form additional metal-carbon clusters, $V_8C_N^+$ (N = even), and oxidation products, $V_8C_MO^+$ (M = odd), by reactions 1 and 2, respectively. A small fraction of metal-carbon cluster ions of the form $V_8C_N^+$ (N = odd) are also observed, which, presumably, arise from the loss of CO_2. However, no $V_XC_N^+$ ($X < 8$) ions, arising from the loss of vanadium containing neutrals, are observed. Pseudo-first-order kinetics are observed for the reaction of $V_8C_{12}^+$ with O_2 over 2 half-lives, indicating, but not unequivocally, that the ion population is cooled and consists predominantly of a single isomeric structure. From the data, a rate constant of $2.75 \pm 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is estimated. Taking the ratio of this value to the calculated Langevin collision rate[31] yields a reaction efficiency of 51%, indicative of an exothermic reaction. The difference in reactivity with O_2 between $Ti_8C_{12}^+$, which is relatively inert, and $V_8C_{12}^+$ is consistent with the prediction that $Ti_8C_{12}^+$ is nearly closed shell, while $V_8C_{12}^+$ has a number of unpaired electrons in antibonding orbitals.[20] Formation of two CO from C_2 and O_2 is ~10 eV exothermic,

$$V_8C_N^+ + O_2 \rightarrow V_8C_{N-2}^+ + 2CO \tag{1}$$

$$V_8C_N^+ + O_2 \rightarrow V_8C_{N-1}O^+ + CO \tag{2}$$

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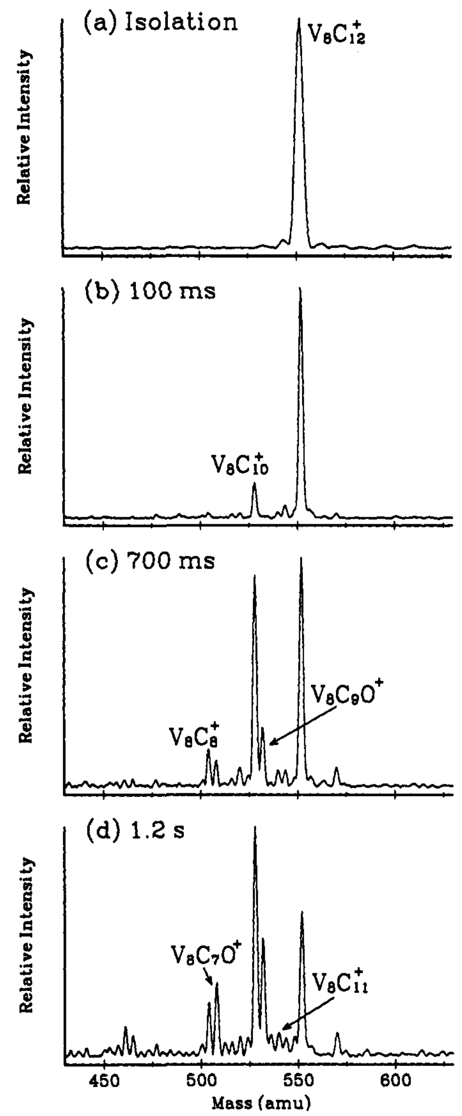

Figure 1. Reaction of $V_8C_{12}^+$ with O_2 (~1.12 × 10^{-7} Torr) at various times: (a) isolated $V_8C_{12}^+$; (b) 100 ms reaction time; (c) 700 ms reaction time; (d) 1.2 s reaction time.

while generation of CO_2 from C and O_2 is ~11.5 eV exothermic,[32] placing upper limits on the energy required to extract C_2 or C from $V_8C_{12}^+$, respectively. This can be compared to the average binding energy per atom calculated for V_8C_{12} of around 6 eV.[12,17]

$V_8C_{12}^+$ was found to be quite rugged in an inert atmosphere, requiring the use of multiple excitation collisional activation (MECA)[33] to promote fragmentation. The predominant process observed is the sequential loss of V (up to three under the experimental conditions used), which is in accordance with both photodissociation and metastable results.[6,34] In the presence of trace amounts of O_2 (e.g., 1.6 – 3.4 × 10^{-8} Torr), however, C_2 loss is observed above the background at low energies prior to the onset of the first V loss. This product remains relatively small, however, and decreases at higher energies. Under these same conditions, products corresponding to losses of VC and VC_2 can be seen at higher energies together with the predominant V loss products.

In order to study the coordination chemistry of $V_8C_{12}^+$, the reagents CH_3CN, benzene, and H_2O were chosen to be tested.

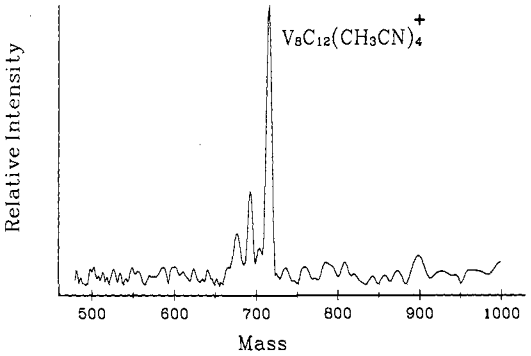

Figure 2. Reaction of $V_8C_{12}^+$ with CH_3CN (~2.2 × 10^{-6} Torr) for 2 s. Minor peaks in the mass spectrum arise, due to residual water in the ICR cell. For example, the peak at mass 697 corresponds to $V_8C_{12}(CH_3CN)_3(H_2O)^+$.

CH_3CN and benzene undergo sequential association reactions, exclusively, yielding mass spectra that truncate sharply at $M_8C_{12}X_4^+$, reaction 3. This is exemplified for CH_3CN in Figure 2. While a saturation limit of 4 may be due in part to the relatively

$$V_8C_{12}X_N^+ + X \rightarrow V_8C_{12}X_{N+1}^+ \qquad (3)$$

$$N = 0\text{–}3,\ X = CH_3CN,\ C_6H_6$$

low reagent pressures used in the FTICR experiment,[35] the coordination of only four benzenes was also noted in the previous high pressure work.[21] Since we observe acetonitrile to add more rapidly than benzene, some addition of at least a fifth acetonitrile would be expected if similar coordination sites were in fact available. Thus, these results obtained under low-pressure conditions are consistent with either a D_{2d} or T_d structure which, on the basis of theoretical calculations, should preferentially bind the first four ligands more strongly than the subsequent ligands.[17-20]

$V_8C_{12}^+$ reacts readily with leaked in H_2O to form $V_8C_{12}(H_2O)^+$. This process is highly favorable and is observed even with trace background moisture in the ICR cell when $V_8C_{12}^+$ is trapped for more than ~100 ms. Surprisingly, $V_8C_{12}(H_2O)^+$ reacts with a second molecule of water by dehydrogenation to form $V_8C_{12}(H_2O)O^+$. This reaction was confirmed using $H_2{}^{18}O$. With longer reaction times and higher pressures of water, $V_8C_{12}(H_2O)_2O^+$ and $V_8C_{12}(H_2O)_3O^+$ are also observed. Once again truncation occurs at four attachments, as all of the ion intensity eventually shifts to $V_8C_{12}(H_2O)_3O^+$. Finally, $V_8C_{12}^+$ sequentially abstracts chlorine atoms when reacted with chloroform and methylene chloride. Further work with these and various other halogenated compounds is currently underway.

The results presented here represent the first evidence of the high combustibility of $V_8C_{12}^+$ in the presence of oxygen and lend further support to the T_d or D_{2d} structure predicted by theory. The reactivity observed is also consistent with the predicted electronic structure indicating that $V_8C_{12}^+$ is a high-spin species. We are extending our work to the reactivities and CID behavior of other met-cars and to the larger metal–carbon clusters, such as $M_{14}C_{13}^+$,[8] which can be produced in our instrument.

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