are \( f_1 = 52.9\% \) and \( f_2 = 18.2\% \) while they are 49.6\% and 16.9\%, respectively, for the rapidly quenched glass. It therefore appears that the structure of the annealed glass differs significantly from the quenched glass in that a larger number of neighbors have reoriented resulting in a larger number of groups in the first peak region (see Figure 2). Rearrangement involving translational degrees of freedom does not appear to be significant. Densities of the annealed and quenched glassy phases were practically the same even though the two states differ in their intermolecular energies. This is understandable since reorientation is the main structural difference between these two glassy phases.

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**Registry No.** Isopentane, 78-78-4.

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### The Electronic and Geometric Structures of the Transition-Metal Carbyne Cations Sc\(^{+}\), Ti\(^{+}\), V\(^{+}\), and Cr\(^{+}\)

**A. Mavridis, A. E. Alvarado-Swaisgood, and J. F. Harrison**

**Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322**

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The electronic and geometric structures of several transition-metal carbyne cations have been studied by ab initio methods (MCSCF and MCSCF+1+2). \( \text{Cr}^{+}(^2\Sigma) \), \( \text{V}^{+}(^2\Delta) \), and \( \text{TIC}^{+}(^2\Pi) \) are all characterized by a metal–carbon triple bond of remarkably similar length (1.772, 1.745, and 1.758 \( \text{Å} \), respectively). Relative to the spin allowed dissociation products (the metal ion in its ground state and \( \text{C} \) in the excited \( ^2\Sigma^+ \) state) the metal–carbon bond energies are calculated (in kcal/mol) to be \( \text{Cr}^{+} \) (70.8), \( \text{V}^{+} \) (108.0), and \( \text{TIC}^{+} \) (113.0). Relative to the \( ^2\Pi \) ground state of \( \text{CH} \) these bond energies become 53.7, 90.8, and 95.9 kcal/mol. The experimental VC bond energy in \( \text{V}^{+} \) is 115 kcal/mol, approximately 24 kcal/mol higher than our calculated value of 90.8. Analysis of the exchange energy loss of the metal ion upon bond formation suggests that there is an intrinsic metal–carbon bond energy for these species given by the sum of the exchange energy loss and the calculated bond energy. The \( ^2\Pi \) state of \( \text{Cr}^{+} \) is characterized by a double bond between Sc and C, with a bond length of 1.940 \( \text{Å} \) and \( D_0 \) of 96.3/79.2 kcal/mol relative to the \( ^2\Sigma^+/^2\Pi \) state of \( \text{CH} \). The electron distribution in the metal–carbon bond is analyzed for each of the titled molecules.

**TABLE I: Energies of Asymptotic Fragments Used in This Study**

<table>
<thead>
<tr>
<th>System</th>
<th>SCF Energy, au</th>
<th>SCF+1+2 Energy, au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(^{+})(D)</td>
<td>-759.52848</td>
<td>-759.52906</td>
</tr>
<tr>
<td>Ti(^{+})(F)</td>
<td>-648.18946</td>
<td>-848.19309</td>
</tr>
<tr>
<td>V(^{+})(F)</td>
<td>-942.65997</td>
<td>-942.66979</td>
</tr>
<tr>
<td>V(^{+})(D)</td>
<td>-942.64975</td>
<td>-942.67443</td>
</tr>
<tr>
<td>Cr(^{+})(S)</td>
<td>-1043.11354</td>
<td>-1043.15458</td>
</tr>
<tr>
<td>CH(^{+})(S(^2))</td>
<td>-38.28348</td>
<td>-38.30018</td>
</tr>
</tbody>
</table>

\(^+\)The SCF+1+2 energies for the TM ions allows only valence (4s, 3d) excitations while for the CH only the three unpaired electrons on carbon are correlated.

H basis sets were contracted to 3s2p1d and 2s1p as recommended by Raffenetti.\(^6\) The energies calculated for the transition-metal ions and the CH fragment are collected in Table I, while in Table II we collect the energies calculated for the various molecules to be discussed.

All calculations were done in a **PES-164** jointly supported by the Michigan State University Chemistry Department and the Office of the Provost using the Argonne National Laboratory collection of QUEST-164 codes. In particular, the integrals were calculated using the program ARGOS written by Pitzer;\(^10\) the SCF and MCSCF calculations used the **GVB164** programs by Bair;\(^11\) and the **UEXP** program and related utility codes written by Shepard.\(^12\) The configuration interaction calculations were done with the program UCI (and its related utility codes) written by Lischka, Shepard, Brown, and Shavitt.\(^13\)

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\( ^{4} \) Dunning, Jr., T. J., private communication.


\( ^{7} \) Duijneveldt, F. B. IBM Research Laboratory, San Jose, CA, 1971; IBM Technical Report Report No. RJ-945.


\( ^{10} \) The ARGOS integral program was developed by R. M. Pitzer (Ohio State University).

\( ^{11} \) The **GVB164** program was written by R. Bair (Argonne National Laboratory).

TABLE II: Total Molecular Energies (kcal/mol), Bond Lengths (Å), and M=CH Bond Energies (kcal/mol) for the Carbynes Studied

<table>
<thead>
<tr>
<th></th>
<th>ScCH+ ((2\Sigma^+))</th>
<th>TiCH+ ((2\Pi^+))</th>
<th>VCH+ ((2\Delta))</th>
<th>CrCH+ ((2\Sigma^+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(equilb)</td>
<td>-797.91880</td>
<td>-797.98268</td>
<td>-981.0754</td>
<td>-1081.4834</td>
</tr>
<tr>
<td>E(R=20 au)</td>
<td>-797.81241</td>
<td>-797.89229</td>
<td>-980.94286</td>
<td>-1081.3974</td>
</tr>
<tr>
<td>R(M-C)</td>
<td>1.973</td>
<td>1.940</td>
<td>1.745</td>
<td>1.761</td>
</tr>
<tr>
<td>R(C-H)</td>
<td>1.082</td>
<td>1.082</td>
<td>1.092</td>
<td>1.082</td>
</tr>
<tr>
<td>D1((\Sigma^+))</td>
<td>60.8</td>
<td>96.3</td>
<td>87.5</td>
<td>91.0</td>
</tr>
<tr>
<td>D2((\Sigma^+))</td>
<td>49.7</td>
<td>79.2</td>
<td>70.4</td>
<td>90.9</td>
</tr>
<tr>
<td>E(sd4)</td>
<td>549.7</td>
<td>79.2</td>
<td>96.3</td>
<td>36.7</td>
</tr>
<tr>
<td>E(sd3)</td>
<td>512.0</td>
<td>79.2</td>
<td>96.3</td>
<td>36.7</td>
</tr>
<tr>
<td>E(sd2)</td>
<td>549.7</td>
<td>79.2</td>
<td>96.3</td>
<td>36.7</td>
</tr>
</tbody>
</table>

* The \(\Delta_u\) and \(\Delta_d\) orbitals were kept singly occupied. Relative to the \(3\Sigma^+\) state, this bond length was obtained by optimizing the CH(\(\Sigma^+\)) bond length at the SCF level of calculation.

Expectations

Our recently predicted structure\(^1\) for CrCH\(^+\) in the \(2\Sigma^+\) state has the schematic representation

\[
\begin{align*}
\Delta_u & \quad \text{Cr} \quad \text{CH}^+ \\
\Delta_d & \quad \text{V} \quad \text{HC}^+ \\
\text{Ti} & \quad \text{CH}^+ \\
\end{align*}
\]

Note that we label the 3d\(_{\pi,\sigma}\) and 3d\(_{\pi}\) orbitals on the TM as \(\Delta_u\) and \(\Delta_d\) with the 3d\(_{\pi,\sigma}\), 3d\(_{\pi}\), and 3d\(_{\pi}\) represented as \(d_\pi, d_\sigma\), and \(d_\pi\), respectively. Since VCH\(^+\) and TiCH\(^+\) will have one and two fewer electrons, respectively, we anticipate they will have the Lewis structures

\[
\begin{align*}
\mathbf{\Delta_u} & \quad \text{V} \quad \text{C} \quad \text{H}^+ \\
\mathbf{\Delta_d} & \quad \text{Ti} \quad \text{C} \quad \text{H}^+ \\
\text{Sc} & \quad \text{C} \quad \text{H}^+ \\
\end{align*}
\]

Wave Functions and Computational Details

a. The Fragments. As one goes from Sc\(^+\) to Cr\(^+\) the ground state of the ion changes from that associated with the sd\(^o\) configuration to a state associated with the d\(^{N+}\) configuration. This is illustrated in Figure 1 where we plot the experimental\(^1\) energy difference \(E(d^{N+}) - E(sd^o)\) with the corresponding SCF and MCSCF (d-d correlation) approximations. Note that although experimentally the d\(^{0}\) configuration of V\(^+\) lies below the sd\(^{2}\) (by 2.1 kcal/mol) the SCF theory has the ground state being sd\(^{2}\) (by 5.8 kcal/mol). The SCF+1+2 (Table I) predicts the correct order and places the d\(^{4}\) 4.6 kcal/mol below the sd\(^{2}\). V\(^+\) is the only early transition element ion where the ground-state configuration is incorrectly predicted at the SCF level. Consequently since the VCH\(^+\) MCSCF wave function is designed to separate to the SCF products it will separate to the sd\(^{2}\) configuration on V\(^+\).

The CH fragment has two low-lying states\(^1\) (\(\Sigma^+\) and \(\Sigma^+\)) that correlate with the ground states of C and H. The \(\Sigma^+\) is the ground state, and has the schematic representation

\[
\begin{align*}
\mathbf{\Delta_u} & \quad \text{C} \quad \text{H}^+ \\
\mathbf{\Delta_d} & \quad \text{H} \quad \text{C}^+ \\
\text{Cr} & \quad \text{H} \quad \text{C}^+ \\
\end{align*}
\]

while the \(\Sigma^+\) is 17 kcal/mol higher and has the structure

\[
\begin{align*}
\Delta_u & \quad \text{H} \quad \text{C}^+ \\
\Delta_d & \quad \text{H} \quad \text{C}^+ \\
\text{Sc} & \quad \text{H} \quad \text{C}^+ \\
\text{Cr} & \quad \text{H} \quad \text{C}^+ \\
\end{align*}
\]

b. The Carbynes. Consider first the CrCH\(^+\) molecule. The asymptotic form of the \(\Sigma^+\) wave functions is

\[
\begin{align*}
\Sigma^+ & \sim (d_{\pi} + p_{\alpha})(d_{\pi}p_{\alpha} + p_{d_x})d_{d_x}d_{d_y}d_{d_z}d_{d_x} \\
\end{align*}
\]

where the singly occupied d orbitals have \(\alpha\) spin. In this and in subsequent discussions we will suppress the Ar core on the transition metal, the 1s orbital on C and the CH bonding orbitals. These are of course included in the calculation. As the Cr\(^+\) and CH approach one another the atomic orbitals evolve into those

\[
\begin{align*}
\Delta_u & \quad \text{H} \quad \text{C}^+ \\
\Delta_d & \quad \text{H} \quad \text{C}^+ \\
\text{Sc} & \quad \text{H} \quad \text{C}^+ \\
\text{Cr} & \quad \text{H} \quad \text{C}^+ \\
\end{align*}
\]

appropriate for the molecular environment. In particular the $\sigma$ orbital on Cr$^+$ evolves from a pure $d_z$ to a mixture of $d_z$ and $4s$. An MCSCF wave function of the above form which separates to the SCF products ($^6S + ^4\Sigma$) consists of 126 CSF's (in $C_{6v}$ symmetry) and was constructed as a function of the Cr-C separation (at a fixed CH distance of 1.082 Å). A CI consisting of all single and double excitations from this 126 CSF reference space consists of 249 208 CSF's and was not attempted. Instead we restricted the CI to always have the two triplet coupled d electrons singly occupied and thus reduced the number of CSF's in the CI to 107 216. The resulting potential energy curves are shown in Figure 2. The forms of the wave functions for VCH$^+ (\Delta)$ and TiCH$^+ (\Sigma^\pm)$ are obtained from that which is used for CrCH$^+ (\Sigma^\pm)$ by removing first one and then both $d_z$ electrons. The resulting MCSCF wave functions contain (in $C_{6v}$ symmetry) 76 and 37 CSF's, respectively, and separate to the proper SCF products. Note that in the case of VCH$^+$ this means the excited $(s^2 t^{-1})$ configuration. The singles and doubles CI's from these reference spaces consist of 95 590 and 25 483 CSF's, respectively. The resulting potential energy curves are shown in Figures 3 and 4.

The wave function for the $^3\Pi$ state of ScCH$^+$ has the asymptotic form

$$^3\Pi_e \sim (\sigma p_x + p_{e\sigma})(d_{x^2}p_y + p_{d_{xy}})p_x$$

The MCSCF wave function and corresponding SDCI consists of 17 and 12 099 CSF's, respectively. The resulting potential energy curves are shown in Figure 5.

Discussion

a. Structural Predictions. The similarity of the bonding in CrCH$^+$, VCH$^+$, and TiCH$^+$ is vividly reflected in the near constancy ($\sim 1.76$ Å) of the metal–carbon bond length (Table II). The Sc–C bond length is significantly larger ($\sim 1.98$ Å) reflecting the change in the bonding from a $M=\text{C}$ to a $M=\text{C}$ linkage. Interestingly this double bond length is essentially the same as that found$^1$ for Cr=CH$^+\text{ in the } ^4\Pi_1\text{ state (1.92 Å). These results suggest, at least for the earlier transition elements, that there is a characteristic metal–carbon triple (and perhaps a metal–carbon double) bond length.}

b. Electron Distribution. In Figures 6–8 we display the electron population of several valence orbitals in CrCH$^+$, VCH$^+$, and TiCH$^+$ as a function of internuclear separation. These populations were constructed from the MCSCF wave functions using the Mulliken$^{17}$ prescription. Note that at large $M=\text{C}$ separation Ti$^+$ and V$^+$ have the configurations $4s^23d^3\Delta^1$ and $4s^23d^43d^1\Delta^1$, respectively, while at equilibrium the occupancies have evolved into $4s^0.084p_{e\sigma}^2d_{xy}^2d_{xz}^2$ for Ti$^+$ and the same occupancy plus $\Delta^1$ for V$^+$. While Cr$^{++}$ at large $M=\text{C}$ separations

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Figure 5. Potential energy curves for the lowest $^2\Pi$ state of ScCH$^+$. 

Figure 6. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 76 CF MCSCF wave function for $^2\Sigma^+$ VCH$^+$. 

Figure 7. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 76 CF MCSCF wave function for $^2\Delta$ VCH$^+$. 

Figure 8. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 76 CF MCSCF wave function for $^1\Sigma^+$ TiCH$^+$.

The experimental value of $D_e$ for VCH$^+$ is 115 kcal/mol relative to the $^2\Pi$ state of CH and our calculated value of 91 kcal/mol is in reasonable agreement with this result. Note that the constancy of the bond lengths in Ti, V, and Cr carbynes is not borne out by a similar trend in the calculated bond energies.

Insight into the reasons why the various metal–carbon bonds have the relative energies shown in Table II may be obtained by considering the variation of the intraatomic exchange energy associated with the d electrons on the metal. Consider, for example, the Cr$^+$(S) state. The exchange energy associated with the d electrons in the free Cr$^+$ ion ($d^5$ configuration) is given by

$$K(S) = \sum_i K_{ij}$$

i.e., the sum of 10 interactions between the five singly occupied

corollary being that there is an intrinsic exchange energy loss (upon triple bond formation) of 44 and 20 kcal/mol, respectively. This suggests that when a metal bonds to the CH fragment the calculated bond energy is the stabilization energy relative to the + state of CH. For example, the exchange energy loss suffered by the metal ion in anticipation of bond formation and the calculated bond energy. Relative to the + state of CH this is 148, 152, and 139 kcal/mol for CrCH', VCH', and TiCH', respectively.

The exchange energy loss when Sc' (3D) forms two bonds (to CH, for example) is only ~3 kcal/mol and so the calculated bond energy of 96 kcal/mol is close to the calculated intrinsic Sc=CH bond strength, ~100 kcal/mol. Note that if we calculate the bond energy relative to the + state of Sc' the exchange energy loss would be ~7 kcal/mol which when added to the 3D-(sd)–3F(d) excitation energy of 18 kcal/mol results in an intrinsic bond energy of (96 + 7 + 18) or 121 kcal/mol. Interestingly, although the calculated Sc=CH' bond strength is stronger than Cr=CH' and comparable to both V=CH' and Ti=CH', the "intrinsic" bond strengths are in the intuitively anticipated order, i.e., the triple bond (were it not for the inevitable exchange energy loss) would be much stronger than the double bond.

d. Size Consistency. From Tables I and II we see that every calculation reported is size consistent not only at the MCSCF level but also at the MCSCF+1+2 level. This is an important characteristic of these calculations and suggests that the D_j's calculated from the MCSCF+1+2 wave functions are lower bounds.

Conclusions

1. CrCH'+ (3Σ), VCH'+ (3Δ), and TiCH'+ (1Σ) are all characterized by a metal–carbon triple bond of similar length (1.772, 1.745, and 1.758 Å, respectively).

2. The calculated M=CH bond strengths for Cr, V, and Ti are 70.8, 108.0, and 113.0 kcal/mol relative to the 3Σ state of CH and 53.7, 90.8, and 95.9 kcal/mol relative to the 3Π state. (We use the experimental 3Σ–3Σ separation of 17 kcal/mol rather than our calculated splitting of 11 kcal/mol.)

3. There seems to be an approximate intrinsic metal–carbon bond energy for these species given by the sum of the exchange energy loss suffered by the metal ion in anticipation of bond formation and the calculated bond energy. Relative to the 3Σ state of CH this is 148, 152, and 139 kcal/mol for CrCH', VCH', and TiCH' for an average of 146 kcal/mol.

4. The 3Π state of ScCH' is characterized by a double bond between Sc and C with a bond length of 1.940 Å and a bond energy of 96.3 kcal/mol relative to the 1Π state of CH. This is remarkable similar. The 3d orbital on the metal contains ~0.5 electrons while each d orbital hosts ~1.1 electrons with the 4s, 4p, occupancy varying from 0.1 to 0.2 electrons.

6. The MCSCF+1+2 calculations used to determine D_j's are size consistent.

Acknowledgment. A.M. thanks the Council for International Exchange of Scholars for the award of a Fulbright grant while A.E.A.S. thanks the Dow Chemical Co. for the award of a Summer (1985) Fellowship. We thank the Argonne Theoretical Chemistry Group for providing the QUEST codes.

Registry No. CrCH', 96212-02-1; VCH', 101653-82-1; TiCH', 101653-83-2; ScCH', 101653-84-3.

(19) We use the ab initio values for the relevant exchange integrals obtained from SCF calculations on the appropriate state of the transition-metal ion in question.

(20) The exchange energy loss model, as used by us, is a SCF based concept which neglects intermolecular contributions.