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.

The Electronic and Geometric Structures of the Transition-Metal Carbyne Cations $ScCH^+$, $TiCH^+$, VCH^+, and $CrCH^+$

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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). $CrCH^+(^3\Sigma^-)$, $VCH^+(^2\Delta)$, and $TiCH^+(^1\Sigma^+)$ are all characterized by a metal–carbon triple bond of remarkably similar length (1.772, 1.745, and 1.758 Å, respectively). Relative to the spin allowed dissociation products (the metal ion in its ground state and CH in the excited $^4\Sigma^-$ state) the metal–carbon bond energies are calculated (in kcal/mol) to be $CrCH^+$ (70.8), VCH^+ (108.0), and $TiCH^+$ (113.0). Relative to the $^2\Pi$ ground state of CH these bond energies become 53.7, 90.8, and 95.9 kcal/mol. The experimental VC bond energy in VCH^+ 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 $ScCH^+$ is characterized by a double bond between Sc and C, with a bond length of 1.940 Å and D_e of 96.3/79.2 kcal/mol relative to the $^4\Sigma^-/^2\Pi$ state of CH. The electron distribution in the metal–carbon bond is analyzed for each of the titled molecules.

Introduction

Recently we reported[1] the electronic and geometric structure of $CrCH^+$ in the $^3\Sigma^-$ electronic state, noting that the CH fragment is bonded to Cr via a triple bond with the two triplet coupled electrons localized on Cr in orbitals which are essentially $3d_{\Delta_+}$ and $3d_{\Delta_-}$. In addition we observed that because of the metal–carbon triple bond the CH fragment must separate to the excited $^4\Sigma^-$ state rather than the ground $^2\Pi$. In this study we continue to investigate the nature of the metal–carbon multiple bond by studying the sequence $ScCH^+$, $TiCH^+$, and VCH^+ with a uniformly accurate level of calculation. In addition the experimental estimate of the Aristov and Armentrout[2] of the V–C bond energy in VCH^+ provides an excellent opportunity for us to assess the absolute accuracy of our calculations.

Basis Sets, Molecular Codes, and Total Energies. The basis set used for Sc, Ti, V, and Cr consists of 14s11p6d functions constructed by augmenting Wachters[3] 14s9p5d basis with two additional diffuse p functions[4] (to represent the 4p orbital) and an extra d as recommended by Hay.[5] This basis was contracted to 5s4p3d following Raffenetti.[6] The basis for carbon was a 9s5p1d set consisting of Duijneveldt's[7] 9s5p basis augmented by a d set with the exponent 0.85 as recommended by Dunning and Hay.[8] The hydrogen basis was 4s1p set consisting of Huzinaga's[9] set augmented by a p set with an exponent of 1.0. The C and 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.

TABLE I: Energies of Asymptotic Fragments Used in This Study[a]

system	energy, au	
	SCF	SCF+1+2
$Sc^+(^3D)$	−759.528 48	−759.529 06
$Ti^+(^4F)$	−848.189 46	−848.193 09
$V^+(^5F)$	−942.658 97	−942.669 79
$V^+(^5D)$	−942.649 75	−942.674 43
$Cr^+(^6S)$	−1043.113 54	−1043.154 58
$CH(^4\Sigma^+)$	−38.283 48	−38.300 18

[a] 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.

All calculations were done in a FPS-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 by 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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(1) Alvarado-Swaisgood, A. E.; Allison, J.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 2517.

(2) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.

(3) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(4) Dunning, Jr., T. J., private communication.

(5) Hay, P. J. *Chem. Phys.* **1977**, *66*, 4377.

(6) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.

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

(8) Dunning, Jr., T. J.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, III, H. F., Ed.; Plenum: New York, 1977; Vol. 3.

(9) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(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).

(12) A description of the UEXP program is given in: Shepard, R.; Simons, J.; Shavitt, I. *J. Chem. Phys.* **1982**, *76*, 543.

0022-3654/86/2090-2584$01.50/0

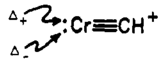
TABLE II: Total Molecular Energies (kcal/mol), Bond Lengths (Å), and M≡C Bond Energies (kcal/mol) for the Carbynes Studied

	$ScCH^+$ ($^2\Pi$)		$TiCH^+$ ($^1\Sigma^+$)		VCH^+ ($^2\Delta$)		$CrCH^+$ ($^3\Sigma^-$)	
	MCSCF	MCSCF+1+2[a]	MCSCF	MCSCF+1+2[a]	MCSCF	MCSCF+1+2[a]	MCSCF	MCSCF+1+2[a]
E(equilib)	−797.91880	−797.98268	−886.6124	−886.67225	−981.0754	−981.14695	−1081.4834	−1081.5425
E(R=20 au)	−797.81241	−797.82924	−886.46196	−886.49115	−980.94286	−980.97021	−1081.3974	−1081.4293
R(M–C)	1.973	1.940	1.763	1.758	1.745	1.745	1.761	1.772
R(C–H)	1.082[c]	1.082[c]	1.091	1.092	1.092	1.091	1.082[c]	1.082[c]
$D_e(^4\Sigma^-)$	66.8	96.3	87.5	113.0	83.4	108.0[b]	53.8	70.8
$D_e(^2\Pi)$	49.7	79.2	70.4	95.9	66.3	90.9	36.7	53.7

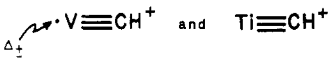
[a] The Δ_+ and Δ_- orbitals were kept singly occupied. [b] Relative to the ^5D state of V^+. [c] This bond length was obtained by optimizing the CH($^4\Sigma^-$) bond length at the SCF level of calculation.

Expectations

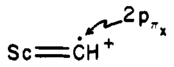
Our recently predicted structure[1] for $CrCH^+$ in the $^3\Sigma^-$ state has the schematic representation



Note that we label the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals on the TM as Δ_+ and Δ_- with the $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ represented as d_σ, d_{π_x}, and d_{π_y}, respectively. Since VCH^+ and $TiCH^+$ will have one and two fewer electrons, respectively, we anticipate they will have the Lewis structures

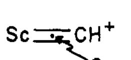


and will be of $^2\Delta$ and $^1\Sigma^+$ symmetry. Note that both of these electronic states correlates with the TM ion in its ground electronic state[14] [for V^+ (d^4) it is a ^5D while for Ti^+ (sd^2) it is a ^4F] and CH in its excited $^4\Sigma^-$ state. For $ScCH^+$ there are two a priori possibilities. If Sc^+ is in its ground state[14] (the ^3D arising from the sd configuration) and CH is in its $^4\Sigma^-$ state, then we could have



($^2\Pi$)

where the double bond consists of a σ component and a π_y component. The σ component would involve the 4s and d_σ on Sc and the p_σ on CH while the π component would involve the d_{π_y} on Sc and the $2p_{\pi_y}$ on CH. The other possibility would have the Sc^+ in the lowest state of the d^2 configuration (^3F) and CH in the $^4\Sigma^-$ state, resulting in



($^2\Sigma^+$)

where the double bond consists of two π components and the unpaired electron is in a p_σ orbital on CH.

Our calculations[15] rule out the $^2\Sigma^+$ and suggest strongly that the $^2\Pi$ is the ground state of $ScCH^+$. This will be discussed in detail in another publication.

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^N configuration to a state associated with the d^{N+1} configuration. This is illustrated in Figure 1 where we plot the experimental[14] energy difference $E(d^{N+1}) - E(sd^N)$ with the corresponding SCF and MCSCF (d–d correlation) approximations. Note that although experimentally the d^4 configuration of V^+ lies below the sd^3 (by 2.1 kcal/mol) the SCF theory has the ground state being sd^3 (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^3. 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^3 configuration on V^+.

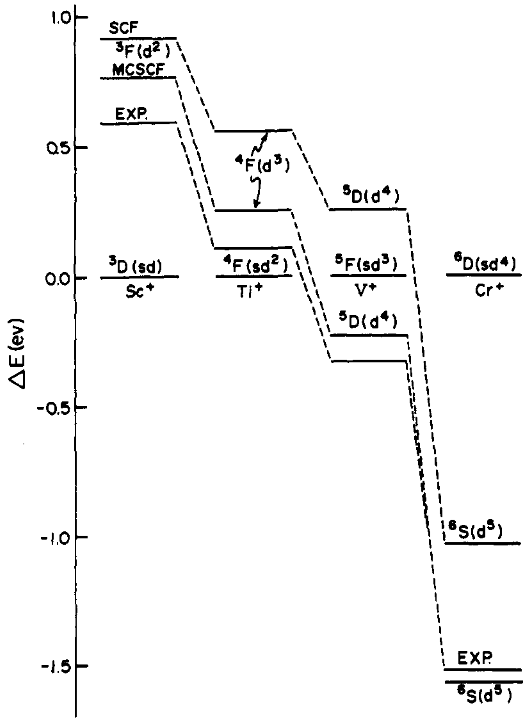
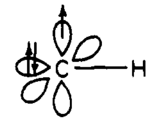
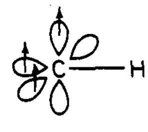


Figure 1. Comparison of experimental sd^N–d^{N+1} energy separation with SCF and MCSCF results.

The CH fragment has two low-lying states[16] ($^2\Pi$ and $^4\Sigma^-$) that correlate with the ground states of C and H. The $^2\Pi$ is the ground state and has the schematic representation



while the $^4\Sigma^-$ is 17 kcal/mol higher and has the structure



b. The Carbynes. Consider first the $CrCH^+$ molecule. The asymptotic form of the $^3\Sigma^+$ wave functions is

$$^3\Sigma^- \sim (\sigma p_\sigma + p_\sigma \sigma)(d_{\pi_x} p_x + p_x d_{\pi_x})(d_{\pi_y} p_y + p_y d_{\pi_y}) d_{\Delta_-} d_{\Delta_+}$$

where the singly occupied d orbitals have α 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

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(13) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. *Int. J. Quantum. Chem. Symp.* **1981**, *15*, 91.

(14) Moore, C. E. "Atomic Energy Levels"; *Natl. Stand. Ref. Data Ser.* NSRDS-NBS Circ. No. 35, Vol. 2.

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(16) Lie, G. C.; Hinze, J.; Liu, B. *J. Chem. Phys.* **1972**, *59*, 1872.

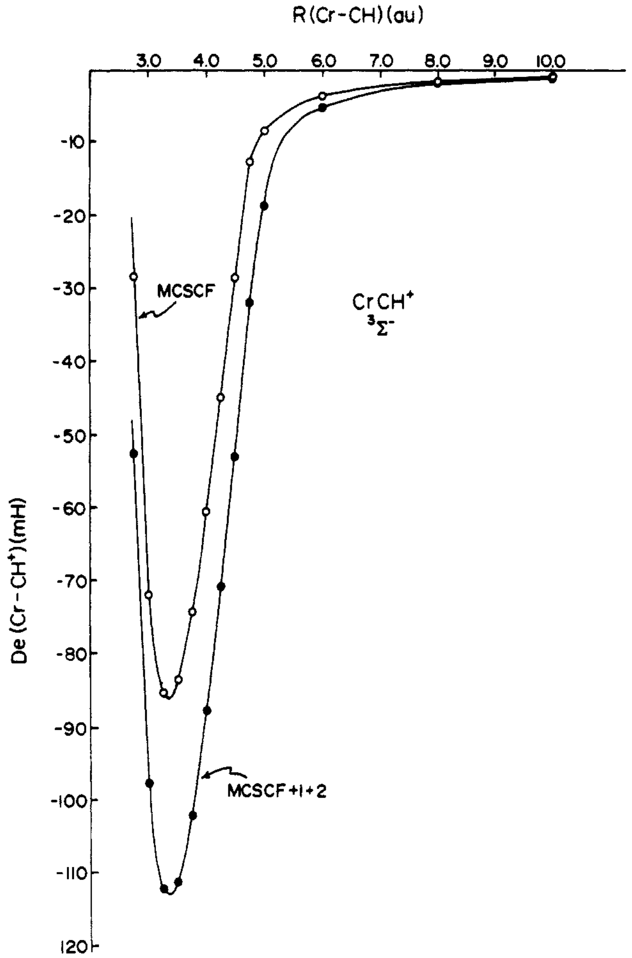

Figure 2. Potential energy curves for the lowest $^3\Sigma^-$ state of CrCH$^+$.

appropriate for the molecular environment. In particular the σ orbital on Cr$^+$ evolves from a pure d_σ to a mixture of d_σ 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_{2v} 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$^+$ ($^2\Delta$) and TiCH$^+$ ($^1\Sigma^+$) are obtained from that which is used for CrCH$^+$ ($^3\Sigma^-$) by removing first one and then both d_Δ electrons. The resulting MCSCF wave functions contain (in C_{2v} 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 sd^3 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 $^2\Pi$ state of ScCH$^+$ has the asymptotic form

$$^2\Pi_x \sim (\sigma p_\sigma + p_\sigma \sigma)(d_{\pi_y} p_y + p_y d_{\pi_y}) p_x$$

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 (~1.76 Å) of the metal–carbon bond length (Table II). The Sc–C bond length is significantly larger (~1.98 Å) reflecting the change in the bonding from a M≡C to a M=C linkage. Interestingly this double bond length is essentially the same as that found[1] for Cr=CH$_2^+$ in the $^4B_1$ 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–CH separation Ti$^+$ and V$^+$ have the configurations $4s^1 3d_{\pi_x}^1 3d_{\pi_y}^1$ and $4s^1 3d_{\pi_x}^1 3d_{\pi_y}^1 \Delta^1$, respectively, while at equilibrium the occupancies have evolved into $4s^{0.08} 4p_\sigma^{0.02} d_\sigma^{0.47} d_{\pi_x}^{1.08} d_{\pi_y}^{1.08}$ for Ti$^+$ and the same occupancy plus Δ_-^1 for V$^+$. While Cr$^+$ at large M–CH separations

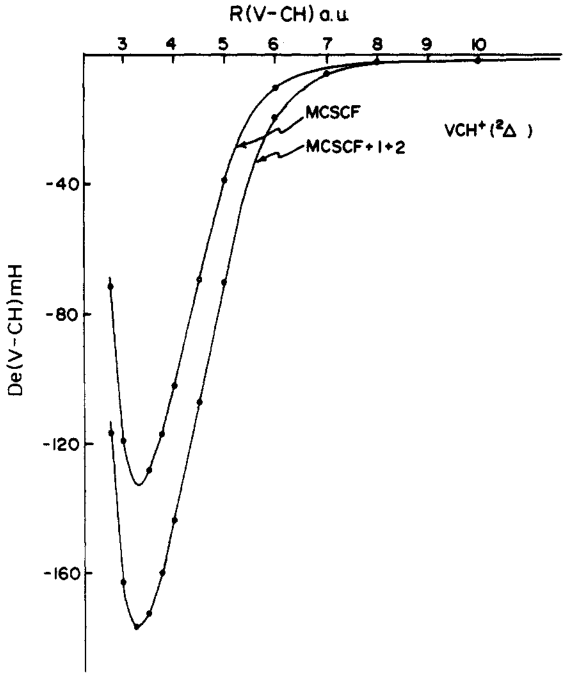

Figure 3. Potential energy curves for the lowest $^2\Delta$ state of VCH$^+$.

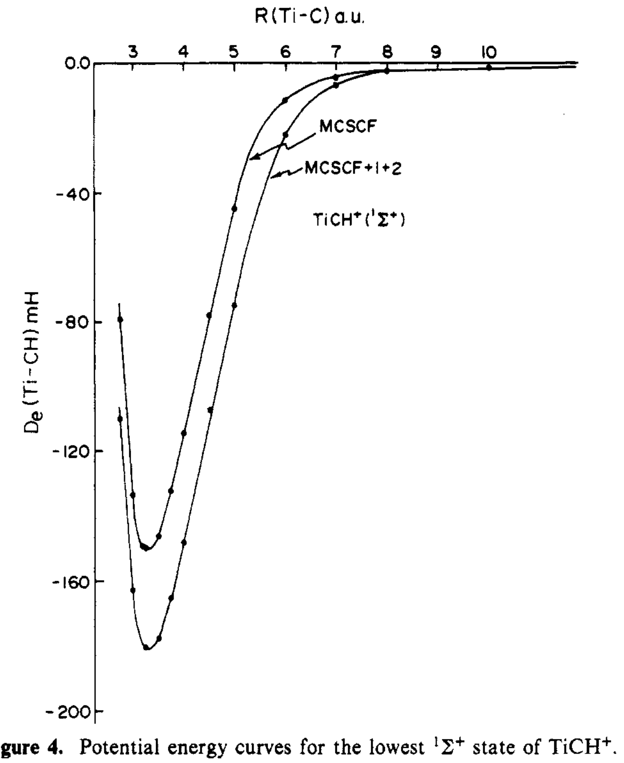

Figure 4. Potential energy curves for the lowest $^1\Sigma^+$ state of TiCH$^+$.

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[17] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343. For a critique see: Noell, J. O. *Inorg. Chem.* **1982**, *21*, 11.

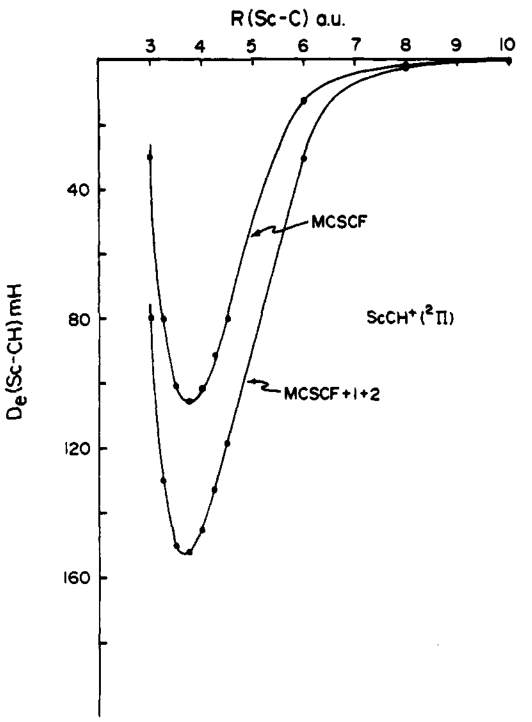

Figure 5. Potential energy curves for the lowest $^2\Pi$ state of $ScCH^+$.

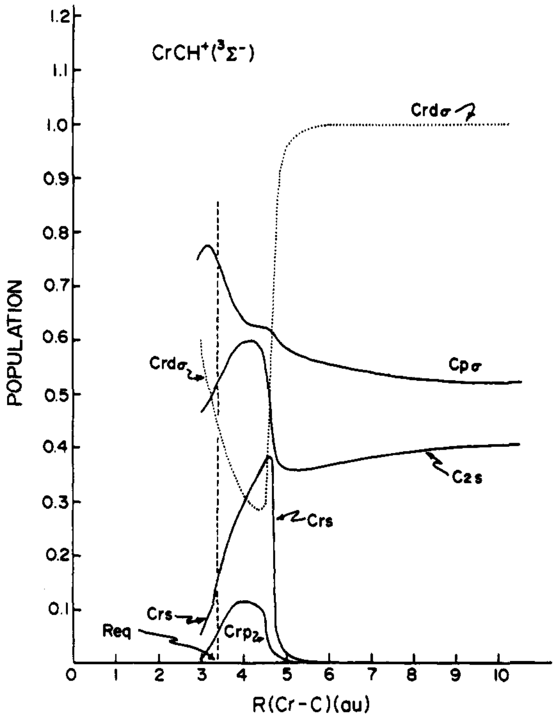

Figure 6. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 126 CF MCSCF wave function for $^3\Sigma^-$ $CrCH^+$.

has the configuration $d_\sigma^1 d_{\pi_x}^1 d_{\pi_y}^1 d_{\Delta_-}^1 d_{\Delta_+}^1$ it evolves into $4s^{0.15}4p_\sigma^{0.06}d_\sigma^{0.50}d_{\pi_x}^{1.11}d_{\pi_y}^{1.11}\Delta_+^1\Delta_-^1$, which is remarkably similar to the Ti^+ and V^+ distributions. It would appear that the optimal mixture of 4s, $4p_\sigma$, and $3d_\sigma$ is essentially metal-independent, an observation consistent with the invariance of the metal–carbon triple bond lengths. The evolution of the orbital occupancies in $ScCH^+$ is shown in Figure 9 and is similar to the Ti, V, and Cr distributions. The Sc^+ configuration evolves from $4s^1 3d_\pi^1$ to $4s^{0.15}4p_\sigma^{0.15}d_\sigma^{0.28}3d_\pi^{1.15}$, the enhanced sp occupancy and the diminished d_σ occupancy reflecting the substantially larger bond length.

c. Energetics. For each molecule we report the D_e relative to both the $^4\Sigma^-$ and $^2\Pi$ states of CH. In addition the D_e of VCH^+ is relative to the ^5F state at the SCF level and ^5D at the CI level.

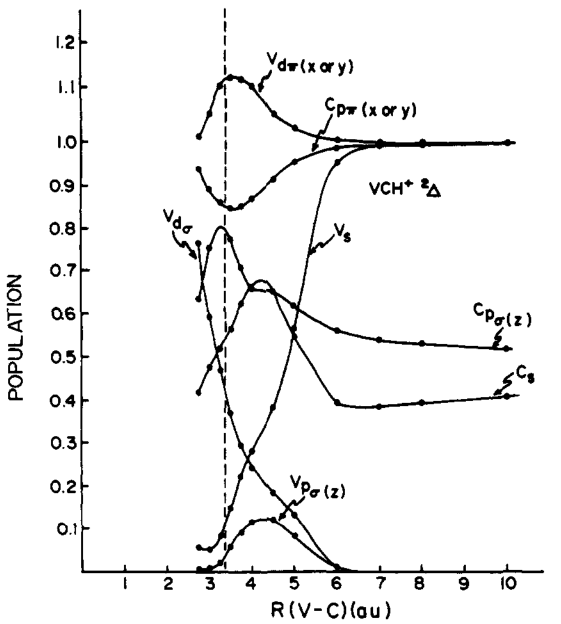

Figure 7. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 76 CF MCSCF wave function for $^2\Delta$ VCH^+.

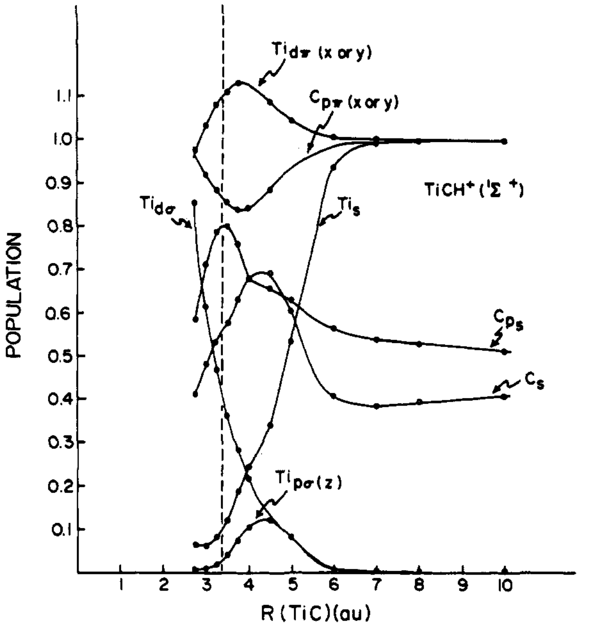

Figure 8. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 37 CF MCSCF wave functions for $^1\Sigma^+$ $TiCH^+$.

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.[18] Consider, for example, the $Cr^+(^6S)$ state. The exchange energy associated with the d electrons in the free Cr^+ ion (d^5 configuration) is given by

$$K(^6S) = \sum_{i>j}^{5} K_{ij}$$

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

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(18) See, for example: Carter, E. A.; Goddard, III, W. A. *J. Phys. Chem.* **1984**, *88*, 1485.

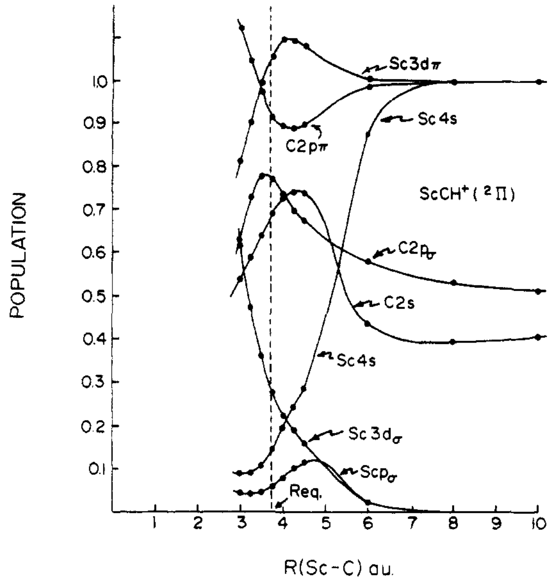

Figure 9. Electron population of selected atomic orbitals from the (valence) natural orbitals of the 17 CF MCSCF wave function for $^2\Pi$ ScCH$^+$.

d orbitals, d_σ, d_{π_x}, d_{π_y}, d_{Δ_+}, and d_{Δ_-}. When Cr$^+$ forms a triple bond with CH (for example) three of the five d electrons are encumbered. They no longer have α spin exclusively but statistically have 50% α and 50% β. This effectively reduces the contribution of the affected exchange intergrals in the above sum by $^1/_2$, raising the in situ exchange energy accordingly. The result[19] is that the in situ exchange energy is raised from −164 to −87 kcal/mol, resulting in an exchange energy loss of 77 kcal/mol. A similar analysis of V$^+$ (^{5}D from d^4) and Ti$^+$ (^{4}F from d^3) predicts an 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 which remains after this exchange energy debt is paid, the corollary being that there is an intrinsic M≡C bond strength given by the sum to the calculated D_e and the exchange energy loss. From the plots of the orbital occupancies vs. the metal–carbon bond length (Figures 6–9) we see that although the asymptotic electron configurations in Ti$^+$ and V$^+$ are sd^2 and sd^3 respectively, the in situ equilibrium configuration is closer to d^N for both ions. In view of this we will reference our intrinsic carbon–metal bond strength to the d^N configuration of the transition-metal ion. Relative to this asymptote our calculated bond energies become 108.0 and 118.8 kcal/mol for VCH$^+$ and TiCH$^+$. When these values are augmented by the calculated exchange energy loss the predicted intrinsic bond strengths are 148, 152, and 139 kcal/mol for CrCH$^+$, VCH$^+$, and TiCH$^+$, respectively, for an average of 148 kcal/mol. The approximate equality of these numbers is remarkable considering the approximations inherent in the exchange energy loss argument[20] and rather satisfying in light of the similarity between the metal carbon bond lengths and the electron distribution in this series.

The exchange energy loss when Sc$^+$ (^{3}D) 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═C bond strength, ~100 kcal/mol. Note that if we calculate the bond energy relative to the ^{3}F (d^2) state of Sc$^+$ the exchange energy loss would be ~7 kcal/mol which when added to the ^{3}D-(sd)–^{3}F(d^2) 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_e's calculated from the MCSCF+1+2 wave functions are lower bounds.

Conclusions

1. CrCH$^+$($^3\Sigma^-$), VCH$^+$($^2\Delta$), and TiCH$^+$($^1\Sigma^+$) 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≡C bond strengths for Cr, V, and Ti are 70.8, 108.0, and 113.0 kcal/mol relative to the $^4\Sigma^-$ state of CH and 53.7, 90.8, and 95.9 kcal/mol relative to the $^2\Pi$ state. (We use the experimental $^2\Pi$–$^4\Sigma^-$ 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 $^4\Sigma^-$ 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 $^2\Pi$ 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 96.3/79.2 kcal/mol relative to the $^4\Sigma^-$/$^2\Pi$ state of CH.

5. The electron distribution in CrCH$^+$, VCH$^+$, and TiCH$^+$ is remarkably similar. The 3d$_\sigma$ orbital on the metal contains ~0.5 electrons while each d$_\pi$ orbitals hosts ~1.10 electrons with the 4s,4p$_\sigma$ occupancy varying from 0.1 to 0.2 electrons.

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

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

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(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.