desorbs from the surface at 175 K. Thus, ethylene desorption accounts for approximately 9% of the chemisorbed acetylene under these conditions. Furthermore, the coadsorption of H_2 and C_2D_2 shows that the desorbed ethylene consists entirely of mass 30, i.e., CHDCHD, implying that ethylene formation results from the reaction of two preadsorbed hydrogen adatoms with molecularly chemisorbed acetylene. Ethylene formation and desorption is observed only if the initial coverage of hydrogen adatoms exceeds approximately 70% of saturation (about 0.6 monolayer). No other hydrocarbons desorb from Ru(001) following hydrogen and acetylene coadsorption at 80 K (except for condensed multilayers of acetylene).

5. Electron energy loss spectra show that at 150 K the hydrocarbon adphase is a mixture of molecularly chemisorbed acetylene and a CH_2-containing species that is inferred to be $CHCH_2$ (for H_2 and C_2H_2 coadsorption). In addition to the ethylene desorption at 175 K, annealing the surface to 230 K causes the decomposition of chemisorbed acetylene. The two decomposition products, ethylidyne and acetylide, are the same as in the case of acetylene decomposition on the initially clean surface, although the ratio of ethylidyne to acetylide is increased.

Reaction of Scandium Ions with Ethane. First and Second Hydride–Scandium Ion Bond Energies

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Abstract: Reactions of atomic scandium ions with ethane (d_0, *1,1,1-d_3*, and d_6) are examined by using guided ion beam mass spectrometry. The present results for ethane-d_0 are in qualitative agreement with the previous work of Tolbert and Beauchamp.[1] Although the dominant reaction at low energies is exothermic dehydrogenation, this is inefficient. Strong inter- and intramolecular isotope effects suggest that this inefficiency results from the need for a triplet–singlet surface crossing. At low energies, dehydrogenation forms a Sc^+–ethene complex, while at higher energies, the product is Sc^+–ethylidene. Double dehydrogenation of ethane has two components: an exothermic one and an apparent endothermic one. Several possible explanations are discussed for this unusual result. The results are analyzed to yield both the first and second metal hydride bond energies, $D^\circ_{298}(Sc^+–H)$ = 56.2 ± 2 and $D^\circ_{298}(HSc^+H)$ = 59.3 ± 3.7 as well as $D^\circ_{298}(Sc^+–CH_3)$ = 59.0 ± 3 and $D^\circ_{298}(Sc^+–CH_2)$ ≥ 93.4 ± 2.5, all in kcal/mol.

Extensive progress in understanding the activation of carbon–hydrogen and carbon–carbon bonds by transition-metal system has been made recently. Studies not only include condensed phase chemistry but also investigations of such processes by atomic transition-metal ions in the gas phase.[2] While the relationship between these highly idealized systems and systems of true catalytic interest is unclear, gas-phase studies can provide quantitative thermochemistry as well as insight into the periodic trends of reactivity. Recently, Tolbert and Beauchamp published the first study of the reactions of Sc^+ with hydrocarbons.[1] They found that the electron deficiency of Sc^+ makes it one of the most reactive atomic metal ions studied. As a consequence, it behaves differently than any other first-row transition-metal ion. Most striking was the unprecedented observation of MR_2^+ species where M = Sc, R = H and alkyl radicals. A detailed knowledge of such species is extremely important to an understanding of oxidative addition–reductive elimination processes. Unfortunately, they were unable to obtain any thermodynamic data regarding these species although they did estimate such data.

Another aspect of Sc^+ chemistry which has taken on increasing importance since Tolbert and Beauchamp's study is as the focus for a number of ab initio theoretical calculations. The reason for this is clear: Sc^+, having only two valence electrons, is the simplest transition-metal ion. As such, electron correlation effects are at a minimum while there are still sufficient electrons to bind several ligands. Detailed calculations have now been performed for the monohydride ion, ScH^+,[3-5] the dihydride ion, ScH_2^+,[4,5] and $ScCH_x^+$, x = 1–3.[4] In addition, detailed potential energy surfaces for the activation of H_2 by Sc^+ have been calculated.[5] Such

calculations are of direct relevance to the similar processes of C–H and C–C bond activation.

In the present paper, we provide a detailed study of the reaction of Sc^+ with ethane. Ethane is of special interest because it is the simplest saturated hydrocarbon with both C–H and C–C bonds. It thus provides a model for more complex hydrocarbon chemistry while still being small enough to be tractable to detailed theoretical and experimental studies. Previous studies of the reaction of metal ions with ethane have been carried out under single collision conditions for Sc^+,[1] Ti^+,[6] V^+,[7,8] Cr^+,[9] Mn^+,[9] Fe^+,[6,10] Co^+,[10,11] and Ni^+[10] and under high-pressure conditions for the entire first transition series.[12] Here, the mechanism of the Sc^+–ethane

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(2) For a representative listing of papers from groups active in the field see ref 1–6 in Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 1806–1819.
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Table I. Electronic States of Sc^+

state	config	$E_{el}{}^a$	population[b]		
			1750 K	2250 K	2550 K
^3D	4s3d	0.013	0.933	0.880	0.848
^1D	4s3d	0.315	0.042	0.062	0.072
^3F	$3d^2$	0.608	0.025	0.057	0.079
^1D	$3d^2$	1.357	<<0.001	<0.001	0.001
^1S	$4s^2$	1.455			

[a] Energies are a statistical average over the J levels. Values are from Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1980**, *9*, 473–511. [b] Maxwell–Boltzmann distribution at the indicated filament temperature.

interaction is investigated by examination of the kinetic energy dependence of the reactions and by using selectively deuteriated ethane. The thermochemistry of a number of simple scandium ion–hydrocarbon species is determined by analysis of the threshold behavior of endothermic reactions. A determination of the heat of formation of ScH_2^+ is a focus of these analyses. The results are compared with the reactivity of other metal ions and with ab initio calculations of similar systems.

Experimental Section

A complete description of the apparatus and experimental procedures is given elsewhere.[13] Briefly, the apparatus comprises three differentially pumped vacuum chambers. In the first chamber, ions are produced as described below. The resulting ions are extracted, accelerated, and focused into a magnetic sector momentum analyzer[14] for mass analysis. In the second vacuum chamber, the mass-selected ions are decelerated to a desired kinetic energy and focused into an octopole ion guide.[15] Radio frequency electric fields in the guide create a radial potential well which traps ions over the mass range studied. The velocity of the ions parallel to the axis of the guide is unchanged. The octopole passes through a static cell into which a reactant gas can be introduced. Pressures of the gas are maintained at a sufficiently low level (less than 0.15 mtorr) so that multiple ion-molecule collisions are improbable. Product and unreacted beam ions are contained in the guide until they drift out of the gas cell. The ions are then extracted and focused into the third vacuum chamber which contains a quadrupole mass filter for product mass analysis. Ions are detected with a scintillation ion detector[16] and processed by pulse-counting techniques. The experiments are automated by use of a computer which collects the ion signals at different masses as it increments the incident ion energy.

Scandium ions are produced in a surface ionization source which has been described previously. Here, $ScCl_3\cdot 6H_2O$ (Aesar, 99.9% pure) is dehydrated and sublimed in an oven. The $ScCl_3$ vapor is directed at a rhenium filament that can be heated to temperatures up to 2600 K. There decomposition and ionization of the resultant scandium atoms take place. Most of the work in the present study uses a filament temperature of 2250 ± 50 K, as calibrated by optical pyrometry. Data for other ions suggests that a Maxwell–Boltzmann distribution at the filament temperature accurately describes the populations of the electronic states of the ions. Table I indicates the state populations of Sc^+ at several temperatures. Since all transitions between states in Table I are parity forbidden, the radiative lifetimes of the excited states[17] should be much greater than the flight time between the ionization and reaction regions (less than 1 ms). We thus assume that the distributions in Table I hold for the ions at the time of reaction.

Use of an octopole ion guide in the interaction region provides two major experimental advantages. The first is high collection efficiency. Product ion losses due to dynamic effects are small.[13] Increased product collection gives better sensitivity. This allows cross sections as small as 10^{-3} Å^2 to be measured and thus provides much better precision in the crucial threshold region for endothermic reactions as well as the ability to accurately monitor minor products. Raw ion intensities are converted to absolute cross sections as described previously. The accuracy of our absolute cross sections is estimated to be ±20%. Relative cross sections are more accurate. Uncertainties at low cross section values are generally about 10^{-3} Å^2, primarily because of random counting noise (typically 10 counts/s).
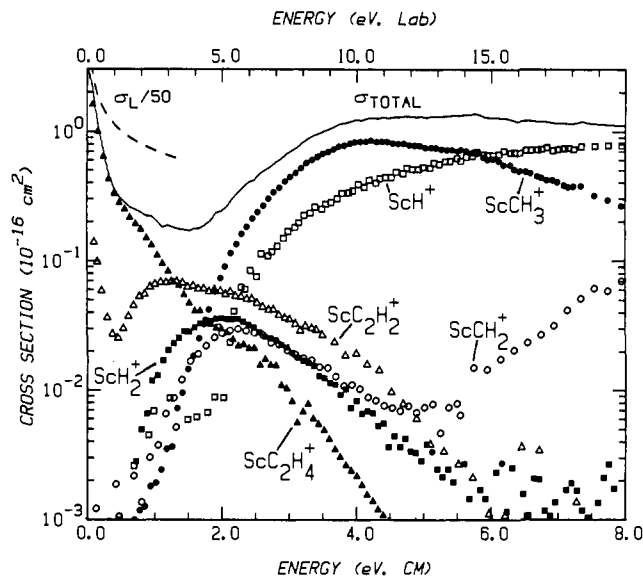

Figure 1. Variation of product cross sections with translational energy in the laboratory frame (upper axis) and the center-of-mass frame (lower axis) for the reaction of Sc^+ with C_2H_6. The dashed line is the LGS collision cross section, eq 2, divided by 50.

The second advantage of the octopole trap is that the absolute energy of the ions in the interaction region can be meaured easily by using the octopole as a retarding field analyzer (RFA). Because the retarding region is physically the same as the interaction region, this energy measurement has minimal uncertainties due to space charge, contact potentials, and focusing aberrations. By scanning through the nominal ion energy zero (where the potential in the ion source equals the DC potential on the octopole), an ion intensity cutoff curve is obtained. The differential of this curve is represented well by a Gaussian peak. The center of this peak is taken to be the true zero of the ion energy, and its width characterizes the kinetic energy distribution of the ion beam. The FWHM of the energy distribution is independent of energy and is generally around 0.3 eV in the center of mass (CM) frame of reference for these reactions. Uncertainties in the absolute energy scale are 0.10 eV in the lab frame. The behavior of the octopole as an RFA has been verified by time-of-flight measurements.[13]

Translational energies in the laboratory frame of reference are related to energies in the CM frame by eq 1, where M and m are the masses of

$$E_{CM} = E_{lab}m/(M + m) \qquad (1)$$

the incident ion and neutral reactant, respectively. At low energies (below ≈0.3 eV lab), the energies are corrected for truncation of the ion beam energy distribution as described previously.[13] The data obtained in this experiment are broadened by two effects: the ion energy spread (determined as discussed above) and thermal motion of the neutral gas.[18] The second effect, referred to as Doppler broadening, has a width in the CM frame of $0.42 E$ (eV)$^{1/2}$ for the reaction of Sc^+ with C_2H_6. When comparing model cross sections to experimental data, the calculated cross sections are convoluted with both sources of experimental energy broadening as described previously.[13]

CH_3CD_3 and C_2D_6 were obtained from Merck and Co., Inc./Isotopes. The stated purities are 98% and 99%, respectively.

Results and Discussion

Figure 1 shows the excitation functions for the various product channels in the reaction of ethane with Sc^+ under single collision conditions. The scandium ions are produced by surface ionization (SI) at 2250 K. These results are qualitatively in accord with the description provided by Tolbert and Beauchamp (TB),[1] who also used SI to produce Sc^+ (filament temperature ≈2500 K). They observe the dominant exothermic reaction, formation of $ScC_2H_4^+$, the primary endothermic reactions, production of ScH^+, $ScCH_3^+$, and also ScH_2^+ although the cross section for this latter product is too small for them to measure accurately. Some of the minor channels seen here ($ScC_2H_2^+$ and $ScCH_2^+$) were not observed by TB. A more detailed comparison than this cannot

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be made since TB show their experimental results only for the ScCH$_3^+$ product.

Unlike most first-row metals (except Ti$^+$),[6,19] Sc$^+$ is observed to dehydrogenate ethane at thermal energies to form ScC$_2$H$_4^+$. This is obviously an exothermic reaction as its cross section continues to increase as low in energy as we can go (<0.1 eV). Indeed, a second dehydrogenation to form ScC$_2$H$_2^+$ is also observed to occur. This latter process is somewhat unusual in that it has two components: an exothermic part and an apparently endothermic portion beginning about 0.5 eV. Despite the fact that both single and double dehydrogenation are exothermic, they apparently are not very efficient since their maximum cross section is comparable to that for formation of ScCH$_3^+$, the major product at high energies. This *endothermic* reaction is the dominant high-energy process observed with most atomic metal ions.[1,7,10,11,20] Other endothermic channels seen here, ScH$^+$ and ScCH$_2^+$, are also observed with other metals. The production of a metal dihydride ion ScH$_2^+$, however, is unique to Sc$^+$ among first-row metal ions. In the section below, the various reaction channels are described in more detail.

Reaction Efficiency. As noted above, the overall reaction of Sc$^+$ with ethane appears to be relatively inefficient at low energies. Usually, exothermic ion–molecule reactions are observed to have large cross sections near thermal energies which decrease monotonically with increasing energy. A simple model which often provides a reasonable accurate upper limit to such cross sections is the Langevin–Gioumousis–Stevenson (LGS) model.[21] When the long range interaction is an ion-induced dipole potential, $V = -\alpha e^2/2r^4$, this model predicts a cross section given by eq 2, where

$$\sigma_L = \pi e(2\alpha/E)^{1/2} \qquad (2)$$

e is the electronic charge, α is the polarizability of the neutral (4.4 Å^3 for ethane),[22] and E is the relative translational energy of the reactants. The result is σ_L (Å^2) = 35.3 E (eV)$^{-1/2}$ which is shown reduced by a factor of 50 in Figure 1. This comparison shows that the total, absolute cross section for the Sc$^+$–ethane reaction is approximately 0.017 ± 0.005 times the LGS cross section at 0.1 eV and less at higher energies. This is equivalent to a thermal rate constant of 2 ± 1 × 10^{-11} cm^3/s.[13] For comparison, Tonkyn and Weisshaar[12] have measured a thermal rate constant of 2 ± 0.4 × 10^{-11} cm^3/s for the total interaction rate between Sc$^+$ and ethane in a fast flow of He.

One possible reason for the small reaction efficiency is that only certain excited states of Sc$^+$ react with C$_2$H$_6$. Such a result is in fact observed for the reaction of ethane with V$^+$ produced by SI.[7] As seen in Table I, at 2250 K either of the first two excited states of Sc$^+$ have sufficient populations to account for the magnitude of the observed reaction. To test this possibility, the surface ionization filament temperature is varied, and the magnitude of the cross section is carefully measured. Within experimental error, no temperature dependence is seen over a range of 1750–2550 K. Assuming the Boltzmann distributions in Table I are valid, we should be able to see a change in cross section magnitude if excited states are predominantly responsible for the reaction. Changes comparable to those expected here were easily observed in our study of V$^+$ + ethane.[7] The failure to see such an effect indicates that *the observed reactivity is due primarily to the ^{3}D ground state of Sc$^+$.* We cannot rule out the possibility that excited states make small contributions to the reactions seen.

This conclusion is further reinforced by the agreement between the rate of reaction observed here and that measured by Tonkyn and Weisshaar.[12] These authors generate Sc$^+$ by a much different route, laser vaporization from a metal sample. The resultant ions are immediately entrained in a fast flow of He at about 1 torr. Collisions with He are expected to rapidly thermalize both the
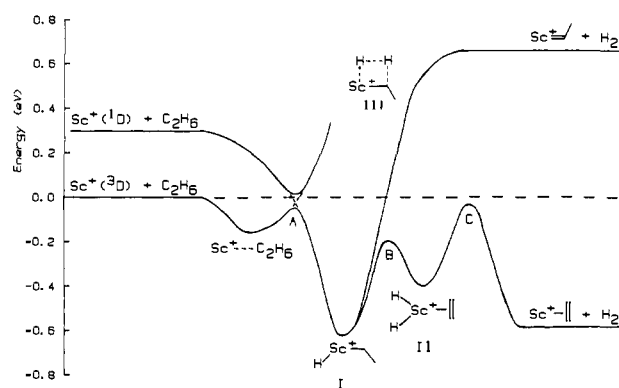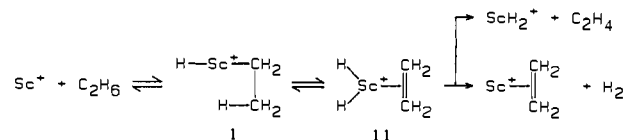

Figure 2. Semiquantitative potential energy surface for the dehydrogenation of C$_2$H$_6$ by Sc$^+$.

Scheme I

translational and electronic degrees of freedom such that only ground-state Sc$^+$ is present in these experiments. While this has not been experimentally verified for Sc$^+$, such collision-induced quenching of electronically excited transition-metal ions has been observed for Ti$^+$[12] and Fe$^+$.[23]

Further consideration of the inefficiency of the reaction of Sc$^+$ with ethane requires information regarding the mechanism of the reaction. The standard literature mechanism[11,24] for dehydrogenation of alkanes by transition-metal ions is shown in Scheme I. This involves an initial step of metal insertion into the C–H bond of ethane, followed by β-hydrogen transfer to the metal and reductive elimination of H$_2$. Note that intermediate I must be in a singlet state since both electrons on Sc$^+$ must be involved in the bonds to H and C$_2$H$_5$. Since the ground state of Sc$^+$ is a triplet, Table I, a triplet–singlet surface jump is necessary for insertion of Sc$^+$(^{3}D) into a C–H bond. To the degree that spin–orbit interactions come into play, this crossing can become avoided. This situation is shown schematically in Figure 2. Presumably, the energy of the crossing point must be below the energy of the reactants since no barrier is observed to the overall reaction.

In our studies of the analogous reactions between ethane and V$^+$,[7] we proposed a similar restriction to dehydrogenation based on spin conversion. In this system, a barrier of ≈0.3 eV is actually observed for the reaction with ground-state V$^+$. The failure to see a barrier here may be because the low-spin ^{1}D state of Sc$^+$ is only 0.3 eV above the ground-state Sc$^+$(^{3}D), Table I. In the vanadium system, the analogous low-spin state, V$^+$(^{3}F), is 1.1 eV above the V$^+$(^{5}D) ground state. Thus, the surface crossing shown in Figure 2 should be higher in energy in the vanadium system.

Theoretical studies of this type of surface crossing have been carried out by Upton and Rappe[5] for the case of H$_2$ activation by Sc$^+$. They find that insertion of Sc$^+$ into H$_2$ to form ScH$_2^+$ involves only 1 of the 15 spin–orbit components of the ^{3}D state. This fraction (0.067) can explain a large part of the reaction inefficiency observed here, although the loss of symmetry in going from H$_2$ to ethane could allow *more* spin–orbit components to react with ethane. The one component undergoes spin–orbit mixing with one component of the ^{1}D state such that an adiabatic pathway to ScH$_2^+$ is available although with an activation barrier of 0.82 eV (19 kcal/mol). Such a barrier is probably not observed in the case of ethane because the long-range interaction between Sc$^+$ and ethane (α = 4.4 Å^3) is substantially more attractive than

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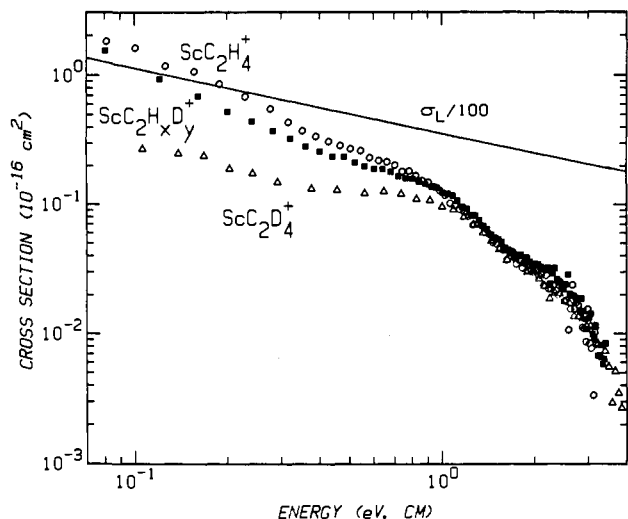
Figure 3. Variation of cross sections for reactions 3 (O), 5 (△), and the sum of 4a, 4b, and 4c (■) with translational energy in the center-of-mass frame. The solid line is the LGS collision cross section, eq 2, divided by 100.

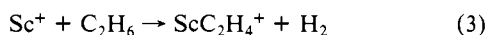**Table II.** Heats of Formation Used in Deriving Experimental Results[a]

neutral	$\Delta H°_{298}$, kcal/mol	neutral	$\Delta H°_{298}$, kcal/mol
H	52.1	HCCH	54.2 (0.2)
CH	142.3 (0.2)	CCH$_2$	94[c]
CH$_2$	93.4 (0.2)	H$_2$CCH$_2$	12.5 (0.2)
CH$_3$	35.1 (0.2)[b]	HCCH$_3$	88.5[d]
CH$_4$	−17.9 (0.2)	C$_2$H$_5$	28.3 (1.1)[e]
CCH	135 (1)[b]	C$_2$H$_6$	−20.2 (0.2)

[a] All values, except where noted, are from Wagman, D. D. et al. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement 2. Uncertainties when given are in parentheses. [b] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. [c] Osamura, Y.; Schaefer HF., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904–1907. [d] Frenking, G.; Schmidt, J. *Tetrahedron* **1984**, *40*, 2123–2132. [e] Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279–5283.

between Sc$^+$ and H$_2$ (α = 0.8 Å^3).[25] The remaining inefficiency of the ethane reaction can be explained either by assuming that the probability of the triplet–singlet surface hopping is low or by presuming that because of the barrier induced by the surface crossing, insertion is slow compared to dissociation of the ScC$_2$H$_6$$^+$ adduct back into reactants.

Reaction Mechanisms. ScC$_2$H$_4$$^+$. Intermolecular Isotope Effects. The dominant reaction ($\approx$90%) between Sc$^+$ and ethane at low energies is the exothermic dehydrogenation of ethane to form ScC$_2$H$_4$$^+$, reaction 3. This cross section is shown in Figure

$$Sc^+ + C_2H_6 \rightarrow ScC_2H_4^+ + H_2 \qquad (3)$$

1 and again in Figure 3. At low energies, the cross section falls off approximately as E^{-1}.[26] Beginning about 0.8 eV, the cross section begins to fall off more rapidly. A detailed examination of this behavior indicates that this decrease corresponds exactly with the increased cross section for ScC$_2$H$_2$$^+$. An alternative possibility, decomposition to Sc$^+$ + C$_2$H$_4$, cannot occur until 1.4 eV, Table II.

Figure 3 also shows results for processes 4 and 5, the analogues of process 3 in reactions of Sc$^+$ with isotopically labeled ethane. At low energies, the ratio of cross sections for reactions 3, 4, and

(25) At the calculated distance between the Sc$^+$ and the center of the H$_2$ bond (1.82 Å),[5] the ion-induced dipole potential between Sc$^+$ and H$_2$ is −0.5 eV. At the same distance, the potential between Sc$^+$ and C$_2$H$_6$ is −3 eV.

(26) This energy dependence is consistent with the Landau–Zener model (Landau, L. D. *Physik Zeitschr. Sowjetunion* **1932**, *2*, 46. Zener, C. *Proc. Roy. Soc. A* **1932**, *137*, 696.) for curve crossings in ion–neutral reactions in a low probability limit. In this model, the probability of making a curve crossing is proportional to $E^{-1/2}$, assuming that the potential energy of the crossing is close to the potential energy of the separate reactants. This in addition to the factor of $E^{-1/2}$ from eq 2 gives an E^{-1} energy dependence.

Table III. Zero-Point Energy Effects in Dehydrogenation Reactions of Isotopically Labeled Ethane[a]
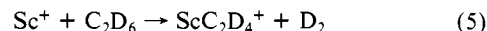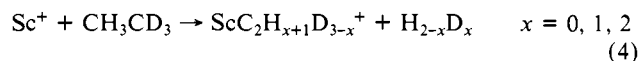
reaction	ΔH_r, eV $v = 0$	ΔH_r, eV $v = 1$	$\Delta\Delta H_r$[b]
C$_2$H$_6$ → C$_2$H$_4$ + H$_2$ (v)	1.42	1.96	0.54
C$_2$H$_6$ → C$_2$H$_2$ + H$_2$ (v) + H$_2$ (v = 0)	3.23	3.78	0.54
CH$_3$CD$_3$ → C$_2$H$_2$D$_2$ + HD (v)	1.46	1.93	0.47
CH$_3$CD$_3$ → C$_2$HD + HD (v) + HD (v = 0)	3.33	3.80	0.47
C$_2$D$_6$ → C$_2$D$_4$ + D$_2$ (v)	1.51	1.90	0.39
C$_2$D$_6$ → C$_2$D$_2$ + D$_2$ (v) + D$_2$ (v = 0)	3.42	3.81	0.39

[a] Calculated by using vibrational frequencies from Shimanouchi, T. *Natl. Stand. Ref. Data Sys., Natl. Bur. Stand.* **1972**, *39*, 1. Crawford, B. L., Jr.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1953**, *21*, 678–686 (CH$_2$CD$_2$). Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979 (H$_2$, HD, and D$_2$). Anharmonicities are included for H$_2$, HD, and D$_2$ only. [b] The difference in heats of reaction or equivalently, a vibrational quantum for the hydrogen molecule indicated.
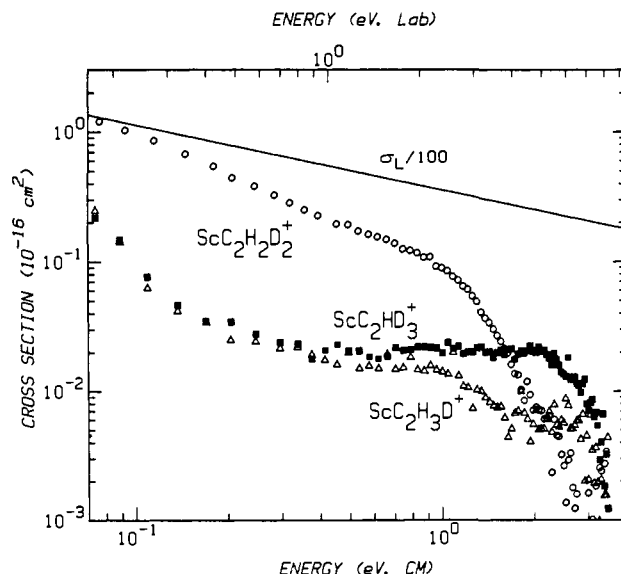
Figure 4. Variation of cross sections for reactions 4a (△), 4b (O), and 4c (■) with translational energy in the laboratory frame (upper axis) and the center-of-mass frame (lower axis). The solid line is the LGS collision cross section, eq 2, divided by 100.

5 is 1.0:0.75:0.20. At higher energies, the isotope effect is markedly reduced.
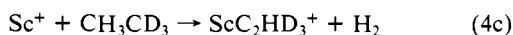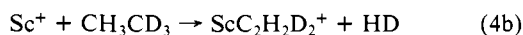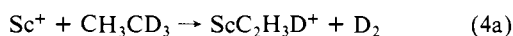
$$Sc^+ + CH_3CD_3 \rightarrow ScC_2H_{x+1}D_{3-x}^+ + H_{2-x}D_x \qquad x = 0, 1, 2 \qquad (4)$$

$$Sc^+ + C_2D_6 \rightarrow ScC_2D_4^+ + D_2 \qquad (5)$$

One possible explanation for this isotope effect returns to the idea that C–H bond insertion is restricted by the singlet–triplet surface crossing, as seen in Figure 2. The exact energy of the surface crossing may be dependent on the dissociation energy of the bond being activated. Since C–D bonds are stronger than C–H bonds by the difference in zero point energy, this could explain the relative efficiencies for reactions 3, 4, and 5.[27] The fact that the cross section for reaction 4 is closer to that of reaction 3 than to that of reaction 5 suggests a preference for activating the weaker C–H bond.

An alternate explanation for the intermolecular isotope effect makes the reasonable assumption that the β-hydrogen transfer step, I → II in Scheme I and Figure 2, is much slower if a D atom transfers rather than an H atom, i.e., the reaction bottleneck is at transition-state B rather than A. This could allow the decomposition of I back to reactants to compete more effectively with dehydrogenation, resulting in a lower cross section for

(27) An estimate of this effect indicates that the surface crossing for insertion into a C–H bond is about 0.03 eV lower than for a C–D bond.

deuteriated species. A third possibility contends that transition state C is the culprit, Figure 2. This supposes that reductive elimination of H_2 from II is more efficient than D_2 from II-d_6. Indeed, it does take more energy to dehydrogenate ethane-d_6 than ethane-d_3 which takes more than ethane-d_0, Table III. This assumes that the binding energy of ethene to Sc^+ is not sensitive to deuterium substitution, a reasonable postulate. All three of these explanations are consistent with the isotope effect observed and its smooth disappearance with increasing energy.

$ScC_2H_4^+$. Intramolecular Isotope Effects. Further insight into the validity of Scheme I can be obtained by studies of the reaction of Sc^+ with CH_3CD_3. The cross sections for reactions 4a, 4b, and 4c are shown in Figure 4. At 0.07 eV, the ratio of cross sections

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2H_3D^+ + D_2 \qquad (4a)$$

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2H_2D_2^+ + HD \qquad (4b)$$

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2HD_3^+ + H_2 \qquad (4c)$$

for reactions 4a:4b:4c is 1:5:1, while at 0.15 eV, the ratio is 1:17:1. At still higher energies, reactions 4a and 4c begin to dominate the reactivity. Some of the intensity for reactions 4a and 4c may come from impurities of the isotopic mixture used. The stated purity is 98 atom %, which, if exact, would yield an isotope ratio of about 1:23:1 for processes 4a:4b:4c. It is also possible that some of the cross section intensity observed for these minor processes is the result of incompletely resolved mass peaks in the analysis mass spectrometer. However, neither impurities nor mass resolution can explain the different energy dependences of reactions 4a, 4b, and 4c below 0.15 eV and above 0.4 eV.

The predominance of reaction 4b throughout the low-energy region indicates that 1,2-dihydrogen elimination is the main reaction. This observation verifies that the $ScC_2H_4^+$ species is an ethene complex at low energies and is consistent with the proposed mechanism, Scheme I. Processes 4a and 4c are due at least in part to isotopic scrambling which must occur via a reversible β-hydrogen transfer, I <=> II. The observation of scrambling is further evidence for the proposed mechanism, since it is difficult to reconcile scrambling if both I and II are not formed. Other dehydrogenation mechanisms, e.g., concerted H_2 elimination from I in a five-center transition state, therefore, seem very unlikely. The fact that at the lowest energies the cross sections for processes 4a and 4c fall off much faster than the cross section for process 4b indicates that the extent of scrambling is sensitive to the internal energy of the intermediates. This is presumably because the lifetimes of I and II decrease as the total available energy increases. At the lowest energies studied, the isotope ratio aproaches that characteristic of a purely statistical distribution of hydrogen lost, 1:3:1. Thus, the rate of scrambling is competitive with the dissociation rate of II to form products at the lowest energies. This indicates that the bottleneck to reaction is *not* at transition state B in Figure 2.

At higher energies (>1 eV), considerably more of reaction 4a and 4c begin to occur until at the highest energies, these processes dominate that of reaction 4b. These processes can also be observed as the shoulders in the cross sections for reactions 3, 4, and 5 at around 2 eV in Figure 3. This process is clearly separate from the low-energy reaction and cannot be explained by random scrambling. The fact that it involves preferential 1,1-dihydrogen elimination indicates that this process is probably formation of scandium ethylidene, $ScCHCH_3^+$. Previous studies of gas-phase metal-ion chemistry have not observed competitive, 1,1- and 1,2-dihydrogen elimination from ethane (or any hydrocarbon). In many cases, this may be due to not examining reactions with the selectively deuteriated ethane. However, no 1,1-elimination was observed in reaction of V^+ with CH_3CD_3.[7] This is further evidence of the uniquely high reactivity of Sc^+.

The production of $ScCHCH_3^+$ is presumed to occur via a four-center α-hydrogen elimination, III in Figure 2. The viability of such a process is verified by the observation of reaction 6 in

$$Sc^+ + CH_4 \rightarrow ScCH_2^+ + H_2 \qquad (6)$$
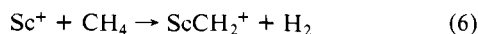
related studies.[19] The threshold for this reaction is about 0.4 eV.

While it is impossible to measure the threshold for the Sc–ethylidene ion formation because of the overlap with the low-energy Sc^+–ethene ion formation, a threshold near 0.4 eV is consistent with the energy dependence of $ScC_2HD_3^+$ formation, Figure 4. An alternative pathway via intermediate IV is considered
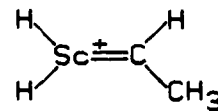

IV

unlikely because the metal does not have enough electrons to support four covalent bonds. While delocalized bonding in such a species is possible, thermochemical estimates still suggest that this molecule is too high in energy to account for the process observed.[28]

Statistically, one would expect reactions 4a and 4c to have the same cross sections at all energies. While this is true at low energies, at 2 eV the reaction of Sc^+ with CH_3CD_3 produces $ScC_2H_3D^+$ and $ScC_2HD_3^+$ in a 1:3 ratio, Figure 4. The predominance of reaction 4c is consistent with the preference for initial C–H bond insertion over C–D bond insertion discussed above. At this point, transfer of a β-hydrogen results in a symmetric product distribution for the Sc–ethene ion, while elimination of an α-hydrogen to form Sc–ethylidene ion does not.
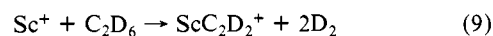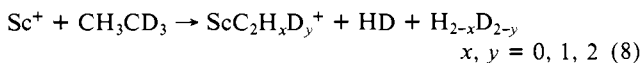
A preference for C–H bond activation (bottleneck at transition state A) provides a consistent explanation for the relative efficiencies of reactions 3, 4, and 5 and for the intramolecular isotope effect observed in the Sc–ethylidene ion formation. The second possibility discussed above (slower β-D transfer than β-H transfer, bottleneck at B) can also explain both effects. In the latter isotope effect, a slow β-D transfer would allow α-H elimination to compete more effectively. As noted above, however, if the bottleneck to reaction were at B, it is difficult to explain the scrambling observed. The third possibility (bottleneck at C) cannot explain the isotope effect observed in the $ScCHCH_3^+$ formation. While it is certainly possible that isotope effects at all three transition states in Figure 2 contribute to the observed experimental behavior, a bottleneck at A provides the easiest explanation of all observations.

$ScC_2H_2^+$. Intermolecular Isotope Effects. The $ScC_2H_4^+$ product can react further by eliminating a second hydrogen molecule to form $ScC_2H_2^+$, Figure 1. The ratio of $\sigma(ScC_2H_4^+)$ to $\sigma(ScC_2H_2^+)$ is about 10:1 and is nearly constant below about 0.4 eV. Above ≈ 0.5 eV the cross section rises, indicating the onset of a new process for $ScC_2H_2^+$ formation. As noted above, this rise correlates precisely with the depletion of $ScC_2H_4^+$ at higher energies. This cross section must correspond to reaction 7 since no other neutral

$$Sc^+ + C_2H_6 \rightarrow ScC_2H_2^+ + 2 H_2 \qquad (7)$$
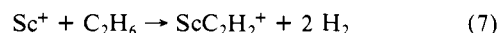
products can possibly lead to reaction at these low energies. The cross section for $ScC_2H_2^+$ decreases slowly until 3 eV where it begins to drop sharply. This probably corresponds to decomposition to $Sc^+ + C_2H_2$, which has a thermodynamic threshold of 3.2 eV, Table II.

The intermolecular isotope effects in the double dehydrogenation processes, reactions 7, 8, and 9, are shown in Figure 5. Clearly, reactions 7 and 8 both have exothermic components while reaction 9 does not. All three of these reactions show the high-energy-

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2H_xD_y^+ + HD + H_{2-x}D_{2-y}$$
$$x, y = 0, 1, 2 \quad (8)$$

$$Sc^+ + C_2D_6 \rightarrow ScC_2D_2^+ + 2D_2 \qquad (9)$$

channel with an apparent threshold of around 0.5 eV. The reason that reaction 9 does not exhibit an exothermic channel is likely to be due to changes in the zero-point energies of reactions 7, 8, and 9. As shown in Table III, the energy required to eliminate

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(28) For IV to be formed with a threshold of 0.4 eV, the data in Table II and the thermochemistry section indicate that $D°((H_2Sc^+-CHCH_3)$ would have to be 88 kcal/mol. This is unreasonably strong for a single dative bond.
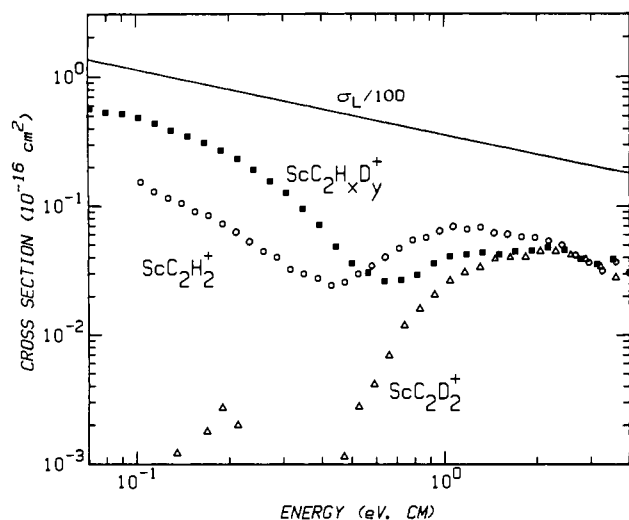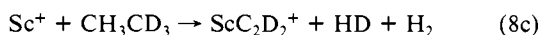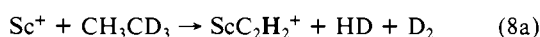
Figure 5. Variation of cross section for reactions 7 (O), 9 (△), and the sum of 8a, 8b, and 8c (■), with translational energy in the center-of-mass frame (lower axis). The solid line is the LGS collision cross section, eq 2, divided by 100.

ground-state hydrogen from isotopically labeled ethane changes appreciably due to variations in vibrational frequencies. In reaction with Sc$^+$, the endothermicities shown in Table III are overcome by the binding energy between the scandium ion and the ethene or ethyne molecule. It seems a reasonable assumption that $D°(Sc^+-C_2H_4)$ and $D°(Sc^+-C_2H_2)$ do not change appreciably upon isotopic substitution. Therefore, it is feasible for reaction 7 and 8 to be exothermic while reaction 9 is endothermic.
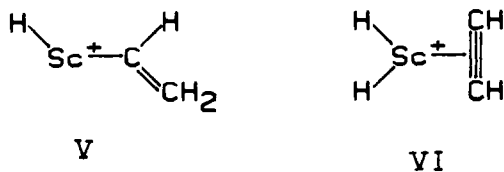
The observation that reaction 8 is more efficient (by a factor of ≈3) at low energies than reaction 7, Figure 5, is an odd isotope effect which we do not understand completely.[29] It is not an experimental artifact as this result was reproduced several times. This interesting observation may be related to the loss of symmetry when HD is eliminated rather than H$_2$.

ScC$_2$H$_2$$^+$. Intramolecular Isotope Effects. Insight into the nature of this reaction can be obtained by examining the intramolecular isotope effects in the reaction of Sc$^+$ with CH$_3$CD$_3$. The cross section for reaction 8b is 4–5 times those for 8a and 8c (which are approximately equivalent) throughout the energy

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2H_2^+ + HD + D_2 \qquad (8a)$$

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2HD^+ + HD + HD \qquad (8b)$$

$$Sc^+ + CH_3CD_3 \rightarrow ScC_2D_2^+ + HD + H_2 \qquad (8c)$$

range of the low-energy feature. Statistical dehydrogenation of the ScC$_2$H$_2$D$_2$$^+$ product would lead to a 1:4:1 ratio for reaction 8a:8b:8c. Since the observed ratio is nearly this, scrambling of hydrogen isotopes appears to be nearly complete at low energies. Scrambling must occur after loss of the first hydrogen molecule since scrambling before this loss is observed to stop by ≈0.2 eV, Figure 3. The near-statistical isotope effect means that no direct structural information for the ScC$_2$H$_2$$^+$ product at low energy is obtained.

The scrambling observed for reactions 8a, 8b, and 8c is most easily explained by an equilibrium between V and VI. Indeed,

V   VI

(29) A similar isotopic enhancement has been observed in the reaction of Kr$^+$ with dihydrogen. Here, the cross section to form KrH$^+$ or KrD$^+$ with HD is twice that with H$_2$ or D$_2$. The mechanism for this enhancement is also not clear in this system but is discussed in Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.*, in press.

the alternative, scrambling via Sc$^+$–ethylidene, is not energetically possible until higher energies. Since the ScC$_2$H$_4$$^+$ intermediate has access to structure VI, elimination of H$_2$ from ScC$_2$H$_4$$^+$ can easily form the Sc–ethyne ion. However, it is also possible that elimination of H$_2$ from V to yield Sc$^+$=C=CH$_2$ occurs.

Although the isotope ratio could not be measured precisely for the high-energy feature due to its small size, reaction 8b is favored by a factor of ≈10 compared to processes 8a and 8c (which are again approximately equal). This preference for 1,2-dehydrogenation of ScC$_2$H$_2$D$_2$$^+$ may suggest that the product at high energies is the Sc$^+$–ethyne complex. The isotope ratio measurement is unfortunately not definitive in this regard.

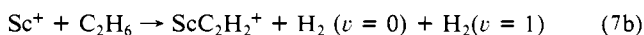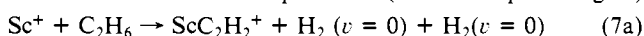**ScC$_2$H$_2$$^+$. High-Energy Feature.** The bimodal energy dependence of the ScC$_2$H$_2$$^+$ product is quite unusual. This type of behavior has not been observed in any other study of transition-metal ion chemistry (although we have now observed such an effect for the reactions of Ti$^+$, Y$^+$, and La$^+$ with ethane[19]). Several possible explanations exist: excited state reactants, product isomers, excited state products, and internal energy effects.

The first and most obvious explanation for the two features seen in $\sigma(ScC_2H_2^+)$ is the involvement of electronic states of Sc$^+$. As described above, this is checked via an examination of the dependence of the cross sections on the surface ionization filament temperature. Indeed these detailed studies were performed primarily to test whether excited states were responsible for either of the ScC$_2$H$_2$$^+$ features. Within experimental error, no temperature dependence is seen in the cross section for ScC$_2$H$_2$$^+$ formation at low or high energies. Both features are primarily due to ground state Sc$^+$.
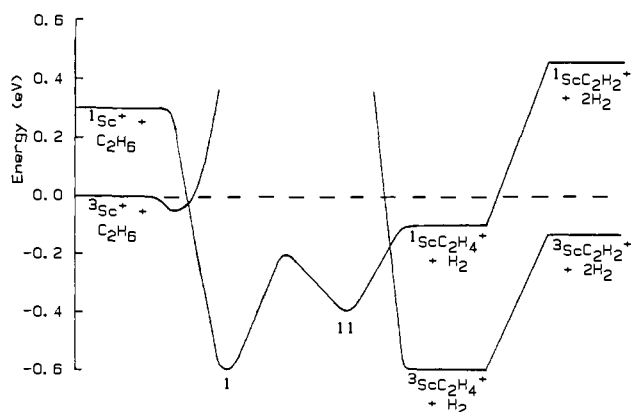
A second explanation is that the two features correspond to the formation of different isomers of ScC$_2$H$_2$$^+$. As discussed in the thermochemistry section, both a Sc$^+$–ethyne complex and Sc$^+$–vinylidene are thermodynamically feasible structures. However, if a homogeneous population of ScC$_2$H$_4$$^+$ were to decompose to two structures (one in an overall exothermic process and one in an endothermic process), decomposition of ScC$_2$H$_4$$^+$ into the exothermic ScC$_2$H$_2$$^+$ channel should gradually increase as the available energy increases. This is inconsistent with the fact that the ratio of $\sigma(ScC_2H_2^+)$ to $\sigma(ScC_2H_4^+)$ is constant below 0.4 eV. This observation suggests that there are two distinct populations of ScC$_2$H$_4$$^+$ which do *not* interconvert: one which reacts completely to form ScC$_2$H$_2$$^+$ at low energy and one which reacts only at higher energy. The following two explanations are consistent with this observation.

An electronically excited product state could also be responsible for the second feature. For example, there are presumably both low-lying singlet and triplet states of ScC$_2$H$_4$$^+$ (corresponding to the singlet and triplet states of Sc$^+$ bound to ethene). Likewise, there probably are low-lying singlet and triplet states of ScC$_2$H$_2$$^+$. Dehydrogenation of II would presumably form ScC$_2$H$_4$$^+$ on a singlet potential energy surface but could also yield a triplet ScC$_2$H$_4$$^+$ via a curve crossing similar to that in the entrance channel. This is shown in Figure 6. This would yield two separate populations of ScC$_2$H$_4$$^+$ which can react further by loss of hydrogen, one to form ground-state ScC$_2$H$_2$$^+$ in an exothermic reaction, the other to form an excited state of ScC$_2$H$_2$$^+$ in an endothermic reaction. This proposal suggests that the reason why little ScC$_2$H$_2$$^+$ is formed at the lowest energies is that a singlet–triplet curve crossing is necessary for this reaction. The difference in energy between the experimentally observed features (≈0.5 eV) is a reasonable figure for a singlet–triplet splitting. Theoretical calculations on this system would be very useful in determining the validity of this mechanism.

Another intriguing explanation for the ScC$_2$H$_2$$^+$ features involves energy disposal in the first dehydrogenation. Specifically, we speculate that the exothermic channels in Figure 5 correspond to reaction 7a (and its isotopic analogues) while the endothermic channels are associated with process 7b (and its isotopic analogues)

$$Sc^+ + C_2H_6 \rightarrow ScC_2H_2^+ + H_2 \ (v = 0) + H_2(v = 0) \qquad (7a)$$

$$Sc^+ + C_2H_6 \rightarrow ScC_2H_2^+ + H_2 \ (v = 0) + H_2(v = 1) \qquad (7b)$$

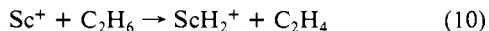where one of the two molecules of H$_2$ is left in its first vibrationally

Figure 6. Proposed potential energy surface for the first and second dehydrogenation of C_2H_6 by Sc^+. Superscript 3 and 1 denote triplet and singlet states, respectively. Crossings between the two surfaces are assumed to be inefficient but not forbidden.

Figure 7. Proposed potential energy surface for the first and second dehydrogenation of C_2H_6 by Sc^+. The continuous line is for reaction of Sc^+ with C_2H_6, while the short segments show the relative energy levels for products from reaction of Sc^+ with CH_3CD_3 and C_2D_6. In all cases, the latter is farthest from the C_2H_6 line. The top curve is for production of the first H_2 molecule with one quanta of vibrational excitation, while the bottom curve is for production of the first H_2 molecule in the ground vibrational state.

excited state. A tendency to eliminate excited H_2 is consistent with a mechanism involving a tight transition state for reductive elimination of H_2 from II. Such a proposal is not without precedent[30] but is an unusual nonstatistical effect. This contrasts with the observations of Hanratty et al.[31] that the kinetic energy release in the 1,2-dehydrogenation of alkanes by Co^+ can be described by using statistical phase space theory. However, these systems do not exhibit the bimodal behavior seen here, and so the comparison is inexact. Measurements of the kinetic energy release in the Sc^+ + ethane system would be of obvious interest.
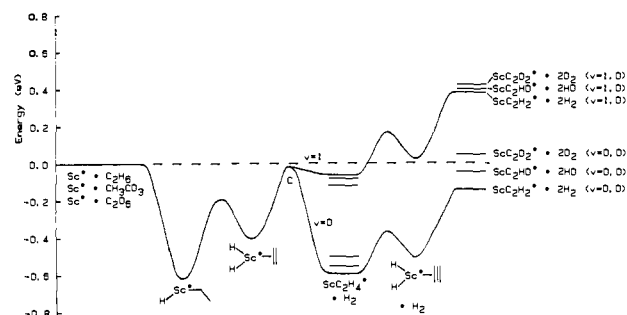
If this proposal is true, differences in zero-point energies of the isotopic variants must be consistent with the isotope effects observed. As discussed above, the energy required to dehydrogenate isotopically labeled ethane changes appreciably when both hydrogen molecules are eliminated with $v = 0$, Table III. However, when one of the hydrogen product molecules is excited vibrationally, the energetics are comparable for all three isotopic variants. On the basis of Table III, the thresholds for reactions 7b with all three isotopic variants of ethane should be about 0.4 eV, consistent with observation. It seems probable that the branching point for reactions 7a and 7b occurs for the elimination of the first H_2, transition-state C. This is shown in Figure 7. A similar competition cannot occur for elimination of the second H_2 since in this case the transition state for reaction 7a cannot exceed the energy of the reactants (since it is exothermic) while the transition state for reaction 7b must exceed this energy.

ScH_2^+. One of the most unusual and interesting species observed in the reaction of Sc^+ with ethane is the scandium dihydride ion, Figure 1. Energetically, this must correspond to reaction 10.

$$Sc^+ + C_2H_6 \rightarrow ScH_2^+ + C_2H_4 \qquad (10)$$

Again, no SI filament temperature dependence is seen for this reaction indicating it is primarily due to reaction of ground-state Sc^+. In reaction with CH_3CD_3, $ScHD^+$ is formed almost exclusively, consistent with the preponderance of 1,2-elimination seen in reaction 4. The cross sections for $ScHD^+$ formation and for ScD_2^+ formation in reaction with C_2D_6 are comparable to that observed for reaction 10.

The most straightforward mechanism for production of ScH_2^+ is decomposition of intermediate II by loss of C_2H_4, Scheme I. This means that process 10 competes directly with reactions 3 and 7, which are much more energetically favorable. Nevertheless, this endothermic process has an appreciable cross section. This result may be due to the relative phase space of these processes and to angular momentum considerations. Since reaction 10 is a bond fission reaction, it should have a loose transition state and

thus a high density of states. In contrast, reactions 3 and 7 are reductive eliminations which should involve fairly tight transition states and, therefore, lower state densities.

A second factor favoring reaction 10 over processes 3 and 7 involves angular momentum conservation arguments which require a somewhat more involved explanation. Consider a bimolecular reaction which produces only two products. We assume the rotational angular momentum of the reactants, J, is negligible compared with the orbital angular momentum, $L = \mu v b$, where μ is the reduced mass of the reactants, v is their relative velocity $[= (2E/\mu)^{1/2}]$, and b is the impact parameter. Similar quantities can be defined for the products and are indicated by primes. As a first approximation, we presume J', the product's rotational angular momentum, is also small. Thus, $L = L'$, which after substituting and rearranging gives eq 11 which is directly related

$$b^2 = b'^2(\mu' E'/\mu E) \qquad (11)$$

$$b^2 < (\mu'/\mu)b'^2 \qquad (12)$$

to the cross section since $\sigma(E) = \pi b^2$. For endothermic reactions, $E > E'$ which yields eq 12. Since b' is restricted to molecular dimensions, cross sections for endothermic products with small reduced masses, $\mu' < \mu$, must be small because of the limited range of impact parameters which can lead to their production. For nonzero J', two possibilities need to be considered. If L' and J' are parallel, this limits b' even further. If they are antiparallel, L' and thus b' can be larger. However as J' increases, the relative translational energy of the products, E', is reduced further which again limits b'.
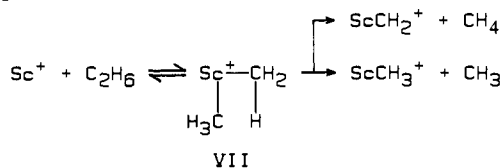
For exothermic reactions the situation is less clear since now the reaction exothermicity can be released as relative translational energy of the products such that $E' > E$. However, such an energy release is usually small[31] so that $E' \approx E$. This approximation replaces the inequality in eq 12 with an equality. Again if $\mu' < \mu$, the range of impact parameters which can lead to product is limited. In the present case, reaction 3 is exothermic with $\mu = 18.01$ u and $\mu' = 1.96$ u such that a large reduction in reduced mass takes place. In contrast, μ' for reaction 10 is 17.56 u, virtually no change from μ. This effect will tend to favor reaction 10 when it is energetically accessible.

Formation of MH_2^+ from the reaction of metal ions with alkanes has not been reported for any metal besides scandium. However, experiments in our lab have shown that Y^+ and La^+, isovalent with Sc^+, also form MH_2^+ in the reaction with C_2H_6.[19] All three of these metals have only two valence electrons. Since one electron is needed for each M^+-H bond, no valence electrons are available to bond to the C_2H_4 in intermediate II. This bond is thus only a dative bond, with the electrons in the ethane π bond

(30) Beauchamp et al. [Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967–978.] observed that $CpNi^+$ and c-C_5H_{10} react such that one H_2 molecule is lost 49% of the time and two H_2 molecules are lost 51% of the time. They suggest that the reason for this branching ratio is that the second dehydrogenation can no longer occur if the first H_2 comes off with one vibrational quantum.

(31) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 1788–1789.

Scheme II

$$Sc^+ + C_2H_6 \rightleftharpoons Sc^{+}_{-}CH_2 \longrightarrow \begin{cases} ScCH_2^+ + CH_4 \\ ScCH_3^+ + CH_3 \end{cases}$$
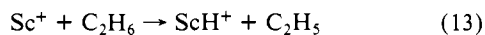
$$H_3C \quad H$$

VII

being donated into an accepting orbital on the metal. This bond should be much weaker than a bond to metals with more electrons since these can back bond from a 3d orbital on the metal into the π^* orbital of the ethene. This increase in $H_2M^+-C_2H_4$ bond strength presumably makes MH_2^+ formation energetically unfavorable in comparison to $MC_2H_4^+$ formation.[32]

At energies above about 2 eV, the cross section for ScH_2^+ is observed to fall. Two processes could account for this behavior. First, ScH_2^+ can decompose to $Sc^+ + H_2$ beginning at 1.42 eV, Table II. The fact that the cross section decline is delayed from this thermodynamic onset suggests that excess energy is tied up in translation or in internal modes of the C_2H_4 product. Alternatively, a precursor to ScH_2^+ could decompose more readily to other products, and thus production of ScH_2^+ would decrease. As discussed in the next section, intermediate I can decompose to form ScH^+ beginning at about 2 eV. Since this latter process is a bond fission while reaction 10 requires a rearrangement, formation of ScH^+ could rapidly deplete the population of intermediate I.

ScH⁺. At high energies, the intermediates shown in Scheme I can begin decomposing via new pathways. Chief among these is the dissociation of intermediate I via direct bond cleavage to produce ScH^+ in reaction 13. The competing process to form

$$Sc^+ + C_2H_6 \rightarrow ScH^+ + C_2H_5 \tag{13}$$

$ScC_2H_5^+ + H$ is not observed. While these two processes should have similar energetics, the latter product is disfavored due to the angular momentum constraints discussed in detail above. A similar observation was made for the reaction of V^+ with ethane.[7]
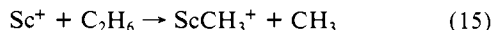
In reaction with CH_3CD_3, the cross sections for formation of ScH^+ and ScD^+ are equal immediately above threshold but at higher energies; ScD^+ is favored by a factor of about 1.5 over that of ScH^+. This cannot be an angular momentum effect. Instead, it is possible that this results from the higher density of states for ScD^+ compared with ScH^+. This favors production of ScD^+ by a factor of ≈ 2.8. This effect may then be mediated by the preference for C–H insertion postulated above. At threshold, the latter is the dominant effect, but at higher energies, the insertion may become less selective allowing the density of states to govern the isotope ratio.

The cross section for ScH^+ rises rapidly above threshold, consistent with a bond fission process. At still higher energies, the ScH^+ may be formed with enough internal energy to dissociate. The fact that $\sigma(ScH^+)$ does not decrease above the threshold for reaction 14, 4.36 eV (Table II), indicates that most of the excess

$$Sc^+ + C_2H_6 \rightarrow Sc^+ + H + C_2H_5 \tag{14}$$

energy is contained in translation and in internal modes of the C_2H_5 fragment rather than in internal modes of ScH^+. This is not surprising given that the ratio of internal degrees of freedom for C_2H_5 and ScH^+ is 6:1 and that the ethyl radical has two heavy atoms and, therefore, lower frequency vibrational modes.

ScCH₃⁺. The other major product observed at high energies, Figure 1, is $ScCH_3^+$, reaction 15. This species could be formed by C–C bond cleavage in intermediate I (to yield $HScCH_2^+$) or
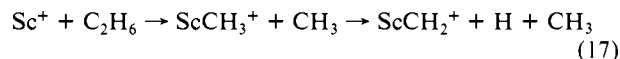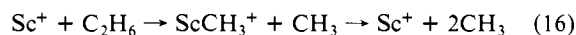
$$Sc^+ + C_2H_6 \rightarrow ScCH_3^+ + CH_3 \tag{15}$$

via C–C bond insertion to form intermediate VII, followed by direct bond cleavage of a methyl group (to yield Sc–methyl ion),

Scheme II. The latter is generally presumed to be the mechanism. In this case, the $HSc=CH_2^+$ structure is unlikely since a scandium ion cannot support the three covalent bonds necessary for such a structure. Even if a species like $HSc^{\cdot}-CH_2^+$ (with the p electron on carbon donated into an empty $d\pi$ orbital on Sc) is considered, the available thermochemistry (see below) supports the scandium methyl ion as the most stable $ScCH_3^+$ isomer.[33]
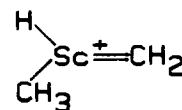
The cross section for $ScCH_3^+$ production rises rapidly from threshold until about 4 eV, where the cross section begins to drop. This could be due to decomposition of $ScCH_3^+$ by either reaction 16 or 17. (A third possibility, loss of H_2 to yield $ScCH^+$, is not

$$Sc^+ + C_2H_6 \rightarrow ScCH_3^+ + CH_3 \rightarrow Sc^+ + 2CH_3 \tag{16}$$

$$Sc^+ + C_2H_6 \rightarrow ScCH_3^+ + CH_3 \rightarrow ScCH_2^+ + H + CH_3 \tag{17}$$
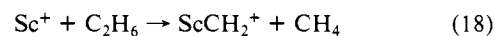
observed.) The thermodynamic threshold for reaction 16 is given by the C–C bond energy in C_2H_6 of 3.92 eV, Table II. As the kinetic energy of the reactants rises above this value, the internal energy of the $ScCH_3^+$ increases and with it the probability of dissociation. In this case, there are 12 internal degrees of freedom and two heavy atoms in $ScCH_3^+$ and nine and one in CH_3, so more energy might be expected to reside in the ionic fragment after the initial cleavage. Indeed, the cross section for $ScCH_3^+$ falls off much more rapidly than the cross section for ScH^+. Reaction 16 cannot be detected directly because the ionic product is indistinguishable from the reactant beam. Reaction 17 is observed as the rise in the cross section for $ScCH_2^+$ formation at high energies. This increase in $ScCH_2^+$ accounts for less than $\approx 10\%$ of the decrease in the $ScCH_3^+$ cross sections over the energy range examined. Consequently, the dominant decomposition channel for $ScCH_3^+$ must be reaction 16. This is a further indication that the most stable structure of $ScCH_3^+$ is the scandium–methyl ion rather than a hydrido–metal–methylidene ion, $HScCH_2^+$. A similar conclusion was drawn concerning VCH_3^+ in our study[7] of $V^+ + C_2H_6$ and in other studies of MCH_3^+ species.[10,11]

The reaction of Sc^+ with CH_3CD_3 at 4.0 eV produces $ScCH_3^+$ and $ScCD_3^+$ in a 5:4 ratio, with negligible production of $ScCH_2D^+$ and $ScCHD_2^+$. This clearly indicates that in this reaction the methyl groups are kept intact. The fact that $ScCH_3^+$ is favored slightly over the perdeuterio species is in qualitative accordance with the earlier argument based on conservation of angular momentum. This predicts a ratio of 8:7 for these reactions.

ScCH₂⁺. A four-center elimination from intermediate I or VII can result in $ScCH_2^+$, reaction 18. Formation of this ion by an alternate pathway, methane elimination from intermediate VIII

$$\begin{array}{c} H \\ \diagdown \\ Sc^{+}_{-}CH_2 \\ \diagup \\ CH_3 \end{array}$$

VIII

$$Sc^+ + C_2H_6 \rightarrow ScCH_2^+ + CH_4 \tag{18}$$
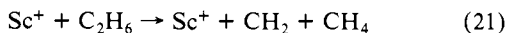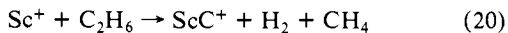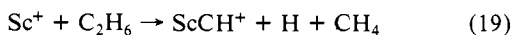
(which can be formed by an α-hydrogen migration from VII), is considered unlikely because of the inability of Sc^+ to form the four covalent bonds necessary for intermediate VIII to be thermodynamically feasible.[34] The low threshold for formation of $ScCH_2^+$, Figure 1, indicates unequivocally that the neutral product is CH_4. This is supported by the observation of reaction 17 at higher energy.

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(32) This argument assumes that the activation energy for loss of H_2 is fairly independent of the metal. This means that at the transition state for loss of H_2, complete backbonding has not occurred in $H_2ScC_2H_4^+$, an entirely reasonable assumption.

(33) For $HScCH_2^+$ to be the species formed at the threshold, data from Table II and the thermochemistry section indicate that $D^\circ(HSc^{+\cdot}-CH_2)$ would have to be 114 kcal/mol, stronger than a full double bond.

(34) Given that $D^\circ(HSc^+-H) \approx D^\circ(CH_3Sc^+-H)$ (a result which we have verified experimentally), data from Table II and the thermochemistry section indicate that $D^\circ[H(CH_3)Sc^+-CH_2]$ would have to be 67 kcal/mol for VIII to be a thermodynamically reasonable intermediate in this process. It seems unlikely that this dative bond is stronger than a single covalent bond of ≈ 59 kcal/mol.

At around 2.5 eV the cross section for $ScCH_2^+$ begins to drop rapidly. This cannot correspond to decomposition of $ScCH_2^+$ since $ScCH^+$ and ScC^+, the ionic products of reactions 19 and 20, are not detected, and reaction 21 is endothermic by 4.1 eV, Table II.

$$Sc^+ + C_2H_6 \rightarrow ScCH^+ + H + CH_4 \qquad (19)$$

$$Sc^+ + C_2H_6 \rightarrow ScC^+ + H_2 + CH_4 \qquad (20)$$
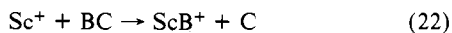
$$Sc^+ + C_2H_6 \rightarrow Sc^+ + CH_2 + CH_4 \qquad (21)$$

The cause must be a depletion of the intermediate leading to $ScCH_2^+$ formation by some other, more efficient reaction. Indeed, the cross sections for reactions 13 and 15 both rise rapidly at about 2 eV. These bond fission processes should be much more efficient than reaction 18, a reductive elimination requiring a tight transition state. In the case of V^+ reacting with C_2H_6,[7] formation of VCH_2^+ + CH_4 could definitely be assigned as originating from the C–C insertion intermediate VII. Since the qualitative behavior of the cross sections for formation of the VCH_2^+ and VCH_3^+ products is comparable to that observed here for scandium, it is probable that the majority of the $ScCH_2^+$ seen arises from decomposition of VII.

C–H vs. C–C Activation. It is of interest to compare the sum of the cross sections for products in which the C–C bond is left intact and those for products where the C–C bond is broken. The total cross section for formation of ScH^+, ScH_2^+, $ScC_2H_2^+$, and $ScC_2H_4^+$ (C–H activation) drops rapidly from ≈ 2.0 Å^2 at low energies to ≈ 0.2 Å^2 near 1.0 eV, after which it rises back to 0.8 Å^2 at the highest energies examined. Compared with the LGS estimate of the collision rate, eq 2, it is clear that the overall reaction efficiency is higher at the higher energies. This is consistent with only a few of the spin–orbit components of $Sc^+(^3D)$ being able to access the C–H insertion species, intermediate I. Presumably, the other components can react in more direct interactions at higher energies. Indeed, this is exactly what Upton and Rappe's calculations for H_2 activation by Sc^+ suggest.[5]

The cross section for formation of $ScCH_2^+$ and $ScCH_3^+$ (C–C activation) is zero until ≈ 1 eV and then rises to almost 1 Å^2 until decomposition of $ScCH_3^+$ sets in at 4 eV. It is unclear from the data whether the products due to C–H and those due to C–C activation are coupled, i.e., whether or not intermediates I and VII are in equilibrium or instead whether insertion into a C–C or C–H bond is irreversible. The fact that the cross sections for C–C cleavage products and those for C–H cleavage products are comparable at higher energies suggests that activation of either type of bond is equally facile. At first glance, the fact that only products from C–H activation are observed at low energies seems to imply that this process is favored over C–C activation. However, if intermediate VII is formed, it has no low-energy reactions except decomposition back to reactants. In fact, the inefficiency of the dehydrogenation reactions at low energies could be due partially to a preference for C–C insertion which does not lead to products.

Thermochemical Analyses. The kinetic energy dependence of bimolecular exchange reactions, such as process 22, is not well understood, particularly in reactions involving more than three atoms. However, theory[35–38] and experiment[7,10,11,17,20,23,39] indicate

$$Sc^+ + BC \rightarrow ScB^+ + C \qquad (22)$$

that for endothermic reactions, cross sections in the threshold region can be parameterized by a function of the form

$$\sigma(E) = \sigma_0(E - E_T)^n/E^m \qquad (23)$$

where σ_0 is a scaling factor having units of Å^2 eV$^{(m-n)}$, E is the relative translational energy of the reactants, and E_T is the reaction endothermicity. If n and m were known for a given system, finding E_T would be straightforward. Unfortunately, various theoretical predictions are not in accord, and no one theory works well for all data. Values for m of 0,[35] 1,[36] 1.5,[37] 3,[38] and $n^{7,39}$ have

Table IV. Fitting Parameters for Reactions in This Paper

reactn prod.	m	n	σ_0	E_T	no. of files
ScH^+	0	1.0	0.18	2.07	3
	1	1.5	0.50	1.99	
	3	2.6	3.03	1.83	
ScH_2^+	0	0.8	0.05	0.80	7
	1	1.1	0.08	0.79	
	3	2.1	0.22	0.74	
$ScCH_2^+$	0	1.5	0.02	0.77	3
	1	2.2	0.03	0.69	
	3	3.8	0.06	0.59	
$ScCH_3^+$	0	1.8	0.19	1.45	4
	1	2.4	0.36	1.35	
	3	3.9	1.10	1.18	

been predicted for various classes of reacttions. In this study, we have explicitly examined eq 23 with all half-integer values of m between 0 and 3 and also $m = n$. The other parameters, σ_0, E_T, and n, are optimized by using a nonlinear least-squares analysis to give the best fit to the data. In general, the best parameter values are determined by comparison to a data set which is an average of several data sets taken at different times and under different experimental conditions. Except for the case when $n = m$, acceptable fits to the data after convolution could be obtained for all values of m examined. We have chosen to report (Table IV) results for $m = 0$, which gives a reasonable upper limit to E_T; $m = 3$, which gives a reasonable lower limit to E_T, and $m = 1$, which gives an intermediate value of E_T. The latter form is expected to be the most appropriate for translationally driven direct reactions[36] and has been found to work exceptionally well in our studies of the reactions of atomic transition metals with H_2 and D_2.[17,23,40–42] The "best" threshold is taken to be the average of the maximum and minimum thresholds for the best fits for $m = 0$ to 3. Error limits for E_T are calculated from the range in these threshold values, the error in the absolute energy scale (0.04 eV), and deviations of the threshold values for individual data sets.

One potential difficulty with this analysis involves excited electronic states of Sc^+ which can lower the apparent reaction threshold. While the measurement of SI temperature dependent cross sections clearly indicates that all reactions observed are due predominantly to ground-state Sc^+, this procedure does not imply that excited states do not contribute at all. Indeed we anticipate that the ^1D state in particular should be fairly reactive. In contrast, we assume that the ^3F state is *not* reactive, because is does not adiabatically correlate to the ground-state products.[5] We have evaluated the possible effect of excited states in the following manner. The assumption is made that the forms of the excitation functions for the ^3D and ^1D states are the same except for the values of E_T, which are taken to differ by the electronic energy of the states, Table I. An implicit assumption is that these two states have equivalent reactivities. This may not be quantitatively correct but is nevertheless the only reasonable assumption in the absence of more detailed information. The sum of the two contributions is convoluted and compared to the data, and, as above, the values of σ_0, n, and E_T are adjusted to give an optimum fit. Thermodynamic data obtained by using this method differ by less than 0.05 eV from that reported in Table IV for all endothermic channels. This indicates that the measured thresholds are relatively insensitive to the presence of the small amounts of excited states present in the SI-produced beam. Further studies in our laboratories hope to address the extent to which the ^1D and ^3F states participate in these reactions more directly.

The threshold energies derived are converted to thermochemical values of interest by using eq 24 where E_{el} is the electronic energy

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(36) Chesnavich, M. J.; Bowers, M. T. *J. Phys. Chem.* **1979**, *83*, 900–905.
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(39) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819–2826.
(40) Elkind, J. L.; Armentrout, P. B. *Inorg. Chem.* **1986**, *25*, 1078–1080.
(41) Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 4862–4871.
(42) (a) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.*, in press. (b) Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.*, submitted for publication.

Reaction of Scandium Ions with Ethane

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of the Sc^+ reactant. This expression assumes that the neutral

$$D°_{298}(Sc^+ - B) = D°_{298}(B - C) - E_T - E_{el} \quad (24)$$

reactants and the products formed at the threshold of an endothermic reaction are characterized by a temperature of 298 K in all degrees of freedom. Thus, we make no correction for the energy available in internal modes of the reactants. When the excited states are not explicitly considered, we take E_{el} (0.033 eV) to be the average excitation energy of the ^3D and ^1D states at the filament temperature, 2250 K. As noted above, the ^3F state is assumed to be unreactive.

We have previously discussed the limitations on converting threshold energies, E_T, to metal ion–ligand bond energies, $D°(M^+-B)$.[7] Ideally, such bond energies are measured in several systems to avoid systematic errors and the effects of activation barriers and kinetic shifts. Since this is not possible in the single system studied here, we have included preliminary results for auxiliary studies which bear on the values in question.

$ScC_2H_4^+$. TB note from the exothermicity of reaction 3 that $D°(Sc^+-C_2H_4) \geq 1.42$ eV. As discussed above, we expect that $D°(Sc^+-C_2H_4)$ should be invariant with respect to replacing some or all of the H atoms with D atoms. The fact that loss of D_2 in the perdeuteriated analogues of reaction 3, process 5, is also exothermic thus allows us to refine the bond energy slightly to $D°(Sc^+-C_2H_4) \geq 1.52 \pm 0.05$ eV (35 ± 1 kcal/mol). On the basis of comparisons of Li^+, $D°(Li^+-C_2H_4) = 0.8 \pm 0.2$ eV,[1] and Ni^+, $D°(Ni^+-C_2H_4) = 2.2 \pm 0.2$ eV,[43] TB estimates $D°(Sc^+-C_2H_4) = 1.7 \pm 0.2$ eV.
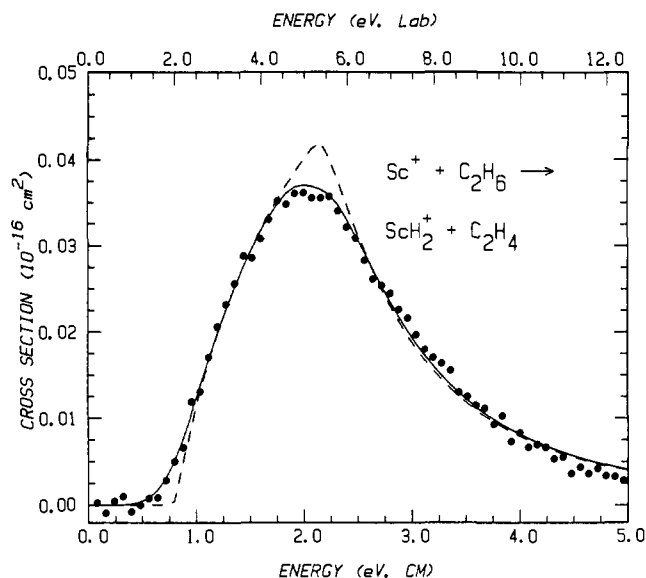
If we further presume that reaction 3 is exothermic for elimination of H_2 in its first excited vibrational level, the binding energy of Sc^+ and C_2H_4 must be larger, Table III. This gives $D°(ScC_2H_4^+) \geq 1.94$ eV (45 kcal/mol). This value is not unreasonable compared to that measured for Ni^+ and estimated for V^+,[7] 2.2 eV.

$ScC_2H_2^+$. This ion and its isotopic variants are formed exothermically in reaction with C_2H_6 and CH_3CD_3, reactions 7 and 8, but endothermically in reaction with C_2D_6, reaction 9. Again we do not expect this bond strength to be sensitive to isotopic substitution of the H atoms. Therefore, the values from Table III can be used to give $D°(Sc^+-C_2H_2) = 3.38 \pm 0.10$ eV (78 kcal/mol).

This thermochemical result is by definition for dissociation to Sc^+ and ethyne and does not imply a structure for $ScC_2H_2^+$, for which there are several possibilities. The dicarbyne $Sc(\equiv CH)_2^+$ is unreasonable because of the lack of electrons on the Sc^+. The ethynyl structure HSc^+-CCH is also not energetically feasible. For this to be an exothermic product, $D°(HSc^+-CCH)$ would have to be ≥ 6.5 eV, an unreasonably high value. The vinylidene structure, $Sc^+=C=CH_2$, is a possibility which could be formed via a four-center elimination from IV. For this to be an exothermic product, $D°(Sc^+=CCH_2)$ would have to be ≥ 4.95 eV. This is somewhat higher than the value determined below for $D°(Sc^+=CH_2)$, ≥ 4.05 eV. However, if this isomer were responsible for the second $ScC_2H_2^+$ feature, $D°(Sc^+=CCH_2)$ would be about 4.5 eV, a high but reasonable value. Lastly, the Sc^+–ethyne structure (or metallocyclopropene) is a thermodynamically reasonable possibility. The second π bond in C_2H_2 has a strength of 2.4 eV (by comparison with the double bond in ethene), Table II. Breaking this bond and forming two Sc^+-C bonds (≈ 2.56 eV each, see below) should be exothermic by ≈ 2.7 eV. Strain energy would weaken this bond, but delocalization of the second pair of C–C π electrons into an empty $Sc(3d\pi)$ orbital would strengthen it. It seems plausible that this latter effect could account for the ≈ 0.7 eV necessary to give the measured 3.38-eV bond energy. These thermochemical arguments cannot conclusively differentiate between the Sc^+–ethyne structure and the Sc^+–vinylidene as the most stable species. Indeed, these two structures and HSc^+-CCH may be able to readily interchange with minimal barriers.[44]

(43) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293–6297.
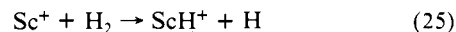
(44) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461–1506.

Figure 8. Cross section for reaction 10 as a function of center-of-mass energy (lower scale) and laboratory energy (upper scale). The solid line is the best $m = 1$ fit to the data convoluted with the energy broadening as discussed in the text. The dashed line is the same fit, unconvoluted.
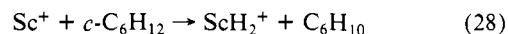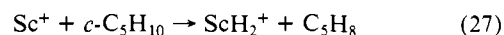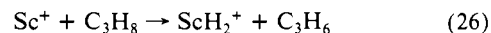
$D°(V^+-C_2H_2)$ has been measured to be 2.20 ± 0.21 eV,[7] significantly weaker than the $Sc^+-C_2H_2$ bond. This change may be due to the fact that in order for V^+ to bond to C_2H_2, electrons must be taken out of an energetically favorable high spin $3d^4$ configuration. Since Sc^+ has only two electrons, the energy required to decouple these bonding electrons is reduced. A rough measure of the magnitude of this effect is the difference in energies between the ground state and the lowest lying low-spin configuration. In Sc^+, this is only 0.3 eV while in V^+ it is 1.1 eV. No other $M^+-C_2H_2$ bond energies have been reported.

ScH^+. The threshold for reaction 13 is 1.95 ± 0.15 eV, which gives $D°(Sc^+-H) = 2.38 \pm 0.15$ eV. By using reaction 25, TB measure a bond energy of 2.34 ± 0.17 eV[1] while Elkind and Armentrout get 2.44 ± 0.10 eV (56.2 ± 2 kcal/mol)[40] from the same process. Theoretical calculations of the bond energy are

$$Sc^+ + H_2 \rightarrow ScH^+ + H \quad (25)$$

2.43,[3] 2.32,[4] and 2.24 eV.[5] The value from this experiment is thus consistent with the relatively extensive literature data for ScH^+. $D°(Sc^+-H)$ is one of the largest first-row metal hydride ion bond energies, Table V. The periodic variations in these values have been discussed in several recent papers.[3,40]

ScH_2^+. The cross section for production of ScH_2^+ is shown in Figure 1 and again in Figure 8, which also shows the best fit for $m = 1$. The threshold for formation of ScH_2^+ is measured to be 0.77 ± 0.10 eV, Table IV. This gives 5.13 ± 0.10 eV for the sum of the first and second hydride bond energies. To help provide a reasonably accurate value for the second scandium hydride bond energy, preliminary studies on three other systems, reactions 26–28, have been carried out. In all three cases the formation
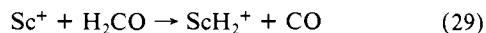
$$Sc^+ + C_3H_8 \rightarrow ScH_2^+ + C_3H_6 \quad (26)$$

$$Sc^+ + c\text{-}C_5H_{10} \rightarrow ScH_2^+ + C_5H_8 \quad (27)$$

$$Sc^+ + c\text{-}C_6H_{12} \rightarrow ScH_2^+ + C_6H_{10} \quad (28)$$

of ScH_2^+ is endothermic. It is reasonable to assume that the neutral products of these reactions are propene, cyclopentene, and cyclohexene, respectively. Other efficient exothermic channels, e.g., dehydrogenation to form the Sc^+–alkene, are in direct competition with reactions 26–28. This may tend to raise the apparent reaction threshold for these processes. This effect may be particularly important in the latter two systems because of their large size. The effect of excited states of Sc^+ was not investigated, but it is likely that ground-state ions dominate the observed cross section. The results for the sums of the first and second scan-

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dium–hydride bond energies are 5.09 ± 0.08, ≥4.99 ± 0.09, and ≥4.83 ± 0.11 eV, respectively. These values are in reasonable agreement with the measurement of 5.13 ± 0.10 eV obtained above. These four systems give an average for the sum of the first and second bond energies of 5.01 ± 0.13 eV (115.5 ± 3.0 kcal/mol). By using $D°(Sc^+-H)$ = 2.44 ± 0.10 eV, this leads to $D°(HSc^+-H)$ = 2.57 ± 0.16 eV (59.3 ± 3.7 kcal/mol). We take this value to be our best determination of the second scandium hydride bond energy.

The HSc^+-H bond energy is somewhat higher than the Sc^+-H bond energy. The difference can be explained by the fact that no electron exchange energy is lost by making the second bond.[3,40] For atomic scandium ions, the exchange energy lost is half the singlet–triplet splitting of the two lower states, (0.315–0.013)/2 = 0.15 eV, Table I. This is in good agreement with the difference measured here, $D°(HSc^+-H) - D°(Sc^+-H)$ = 2.57 − 2.44 = 0.13 eV. This analysis is consistent with explanations for periodic trends in diatomic metal ion–hydride bond energies. In fact in a recent communication,[40] Elkind and Armentrout predict a hydride bond energy of ≈60 kcal/mol for a first-row metal with a sterically unhindered orbital containing a single electron which is electronically decoupled from other electrons. ScH^+ is such a species.

TB obtain a lower limit for the second bond energy of 2.2 eV by noting that reaction 29 is exothermic. They go on to estimate its value as the same as the first bond energy, 2.34 ± 0.17 eV.
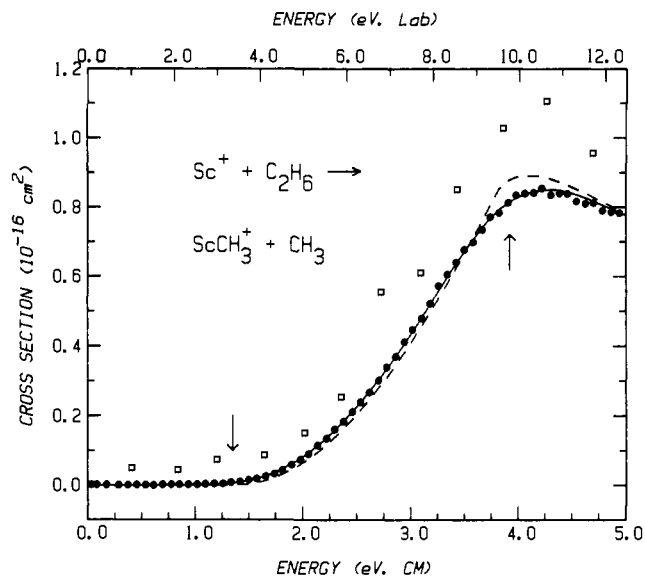
$$Sc^+ + H_2CO \rightarrow ScH_2^+ + CO \qquad (29)$$

Two theoretical calculations for the second bond energy give values that are lower than experiment: Alvarado–Swaisgood and Harrison[4] calculate $D°(Sc^+-H) + D°(HSc^+-H)$ = 4.44 eV and Rappe and Upton[5] calculate 4.48 eV. This discrepancy is surprising in view of the excellent agreement obtained for the Sc^+-H bond energy. However, if our number is inaccurate it is likely to be low since the values from the cyclopentane and cyclohexane systems may be lower than the ethane and propane data due either to a small barrier for reaction with cyclic alkanes or to a shift in the apparent threshold caused by the high efficiency of competing reactions. Note that while the theoretical values suggest that reductive elimination of H_2 from ScH_2^+ is near thermoneutral, $D°(H_2)$ = 4.52 eV, the experimental results imply that ScH_2^+ is stable by 0.49 ± 0.13 eV. This is consistent with the observation of such a species in these experiments. The theoretical calculations may be prone to a consistent underestimation of bond strengths.[3]

Also shown in Figure 8 is a fit to the high-energy behavior of reaction 10 by using a model recently outlined.[45,46] As discussed above, the decline in this cross section could be due to either depletion of intermediate I by reaction 13 or by decomposition of ScH_2^+ by loss of H_2. The model indicates that the apparent onset of dissociation is 2.1 eV.[46] This is consistent with the threshold for reaction 13, formation of ScH^+, at 1.95 eV. Alternatively, if the high-energy falloff is due to H_2 loss (which has a thermodynamic threshold of 1.42 eV), the model[46] suggests that about half of the total excess energy is carried away by the C_2H_4 product or is in translational modes.

$ScCH_3^+$. Figure 9 compares our cross section for reaction 15 in the threshold region with that measured by TB. While the data are in rough agreement, cross sections are somewhat higher for the TB data than for our data. In addition, the TB data near the threshold is offset above zero by about 0.04 Å². The falloff of cross section above around 4.0 eV is faster in the TB data than in ours, presumably due to incomplete product collection of products with high kinetic energy. The nonzero data near the threshold is the only effect which will influence the derived thermochemistry.

Figure 9 shows the best fit for m = 1 and a fit to the high-energy behavior.[45,47] The best fits for m = 0 and 3 are indistinguishable

(45) Weber, M. E.; Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 1521–1529.

(46) The high-energy fit parameters used for ScH_2^+ are D = 0.63 eV, f = 0.47, and p = 2. The thermodynamic onset of dissociation is given by $D + E_T$ = 1.42 eV while the apparent onset is given by $D/f + E_T$ = 2.13 eV. See ref 45 for a discussion of these parameters.


Figure 9. Cross section for reaction 15 in the threshold region as a function of center-of-mass energy (lower scale) and laboratory energy (upper scale). Closed circles show the present data, while open squares show the data from ref 1. The solid line is the best m = 1 fit to the data convoluted with the energy broadening as discussed in the text. The dashed line is the same fit, unconvoluted. The arrows indicate the derived threshold and the C–C bond energy of ethane, 3.92 eV.

Table V. First-Row Transition-Metal Hydride, Methylene, and Methyl Ion Bond Energies (kcal/mol)[a]

M	$D°(M^+-H)$	$D°(M^+-CH_3)$	$D°(M^+-CH_2)$
Sc	56.2 (2)[b]	59.0 (3.0),[f] 65 (5)[g]	≥93.4 (2.5)[f]
Ti	56.0 (2)[b]	56 (5),[h] 65[i]	85 (5)[h]
V	48.2 (1.4)[b]	50 (2)[j]	76 (2)[j]
Cr	32.3 (2.5)[c]	30 (5),[h] 37 (7)[k]	52 (3),[h] 65 (7)[k]
Mn	48.4 (3.4)[b]	51 (5),[h] 71 (7)[k]	94 (7)[k]
Fe	49.8 (1.4)[d]	59 (3),[h] 68 (4)[k]	82 (5),[l] 96 (5)[k]
Co	46.6 (1.4)[e]	61 (4)[k]	84 (5),[l] 85 (7)[k]
Ni	39.5 (1.8)[e]	49 (5),[h] 48 (5)[k]	86 (6)[k]
Cu	22.1 (3.0)[e]		

[a] All values at 298 K. Uncertainties in parentheses. [b] Reference 40. [c] Reference 42b. [d] Reference 23. [e] Reference 42a. [f] This work. [g] Reference 1. [h] Aristov, N.; Georgiadis, R.; Sunderlin, L. S.; Schultz, R. H.; Armentrout, P. B., work in progress. [i] Reference 20. [j] Reference 7. [k] Reference 9. [l] Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537–2540.

from this fit below 3.5 eV. These analyses give values for E_T in the range of 1.32 ± 0.15 eV, Table IV, leading to $D°(Sc^+-CH_3)$ = 2.57 ± 0.15 eV. Analysis of reaction 30, the analogue of process

$$Sc^+ + C_3H_8 \rightarrow ScCH_3^+ + C_2H_5 \qquad (30)$$
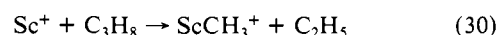
15 in reaction with propane, gives $D°(Sc^+-CH_3)$ = 2.56 ± 0.13 eV. The average of these two determinations gives a best value of 2.56 ± 0.13 eV (59.0 ± 3.0 kcal/mol). In their analysis of process 15, TB measure 2.82 ± 0.22 eV for the Sc^+-CH_3 bond energy. If the TB fitting parameters (n = m = 4 in eq 23) are used to analyze our data, then a bond energy of 2.66 eV is obtained. Thus, most of the difference in bond energy is due to differences in the data. The other factor which lowers our measurement of the bond energy relative to the TB vale is the use of lower values of n and m to fit the threshold.

A theoretical study[4] has calculated the value of $D°(Sc^+-CH_3)$ to be 1.99 eV. The geometry of the methyl group was not optimized, which may have caused this calculation to be too low. The Sc^+-CH_3 bond energy is similar to those of other first-row transition-metal ions, Table V. The periodic variations in this

(47) The high-energy fit parameters for $ScCH_3^+$ are D = 2.45 eV, f = 1, and p = 2. This indicates that dissociation of $ScCH_3^+$ to $Sc^+ + CH_3$ begins promptly at the thermodynamic limit. See ref 45 for a complete discussion of these parameters.

series of bond energies follow those for M^+-H bond energies.

$ScCH_2^+$. The threshold for reaction 18 is 0.68 ± 0.09 eV, Table IV. This leads to a bond energy of 3.44 ± 0.10 eV (79.3 ± 2.3 kcal/mol). As noted above we have also studied the formation of this species in the reaction with methane, reaction 6. Analysis of the threshold behavior for this system is incomplete, but preliminary results indicate $D°(Sc^+-CH_2)$ is 4.33 ± 0.11 eV, a value well above that derived in the ethane system. It is possible that this higher value corresponds to reaction of $Sc^+(^1D)$, which would lower the true bond energy to 4.05 eV. SI filament temperature dependence measurements for this small cross section are inconclusive in this regard. Nevertheless, the discrepancy between these values suggests that an activation barrier of 0.6 or 0.9 eV is observed for reaction 18.

A theoretical study by Steigerwald and Goddard[48] found activation barriers ranging from 0 to ~1 eV for four-center reactions at transition-metal centers. Low barriers require that the bonding orbital on the metal have significant d character and that the bonds be covalent. Both of these conditions are probably met by intermediate VII. The calculated barriers vary with the charge on the metal (ionic species had lower barriers due to more d character in the bonding) and with the number of nonbonding electrons (since these must be in orbitals which are orthogonal to orbitals involved in the bonding). The apparent activation barrier observed here for elimination of CH_4 from $ScC_2H_6^+$ is quite reasonable in light of these calculations. However, note that *no* activation barrier is apparent in reaction 6, H_2 elimination from $ScCH_4^+$. This is consistent with calculations which find that elimination of CH_4 from $HPdCH_3$ has a barrier of 0.45 eV while H_2 elimination from $HPdH$ has a barrier of only 0.07 eV.[49] The reason given for the increased barrier in the case of methyl groups is that the sp^3 orbital on the CH_3 radical is directional while the Is orbital on the H atom is not. Therefore, at the transition state, a CH_3 group cannot bond to both the metal and the H atom as well as a hydrogen atom can.

The value for $D°(Sc^+-CH_2)$ of 4.33 ± 0.11 eV (100 ± 2.5 kcal/mol) is higher than other gas-phase metal-ion-methylidene bond energies, Table V. The value of 4.05 eV (93 kcal/mol) seems more in keeping with periodic trends. Both values are quite a bit higher than results from theoretical calculations:[4] $D_e \approx 3$ eV for a $^1A_1$ state of $ScCH_2^+$, $D_e \approx 1.8$ eV for a $^3A_1$ state. Again these values may be low since the geometry of the CH_2 moiety was not optimized. However, this comparison surely indicates that the $ScCH_2^+$ species observed here is a singlet state implying a metal–carbon double bond. Indeed, the increase in metal–carbon bond strength observed for $ScCH_3^+$ and $ScCH_2^+$ is consistent with going from a single to a double bond.[50] In the vanadium system, we found that the V^+-CH_2 bond energy is 1.5 times stronger than the V^+-CH_3 bond energy.[7,50] Here, the increase is higher, a factor of 1.69 or 1.58. However, this is still less than 1.93, the ratio of single to double bond strengths for carbon–carbon bonds (using C_2H_6 and C_2H_6 as standards). Work is underway to determine more accurately the electronic state dependence of reactions 6 and 18. In the meantime, we report $D°(Sc^+-CH_2)$ to be $\geq 4.05 \pm 0.11$ eV (93.4 ± 2.5 kcal/mol).

Summary

In this detailed study of the reaction of Sc^+ with ethane, we have confirmed that this ion exhibits "unique reactivity"[1] among the first transition series. Only Sc^+ and Ti^+ are observed to dehydrogenate and doubly dehydrogenate ethane in exothermic reactions. We find, however, that while these reactions with Sc^+ have no thermodynamic barriers they occur very inefficiently, ≈ 1 in every 60 and 600 collisions, respectively. In addition, these reactions show strong inter- and intramolecular isotope effects. These effects demonstrate that single dehydrogenation primarily

yields 1,2-dihydrogen loss to form a Sc^+-ethene complex at low energies but that scrambling does occur. At high energies, 1,1-dihydrogen loss to form Sc^+-ethylidene is favored. Further interpretation of the results suggests that the inefficiency of the overall reaction is primarily due to the need for a triplet–singlet surface crossing in the formation of the C–H bond activated intermediate, $H-Sc^+-C_2H_5$.

Double dehydrogenation, formation of $ScC_2H_2^+$, is observed to have two features in its excitation function: an exothermic channel and an apparent endothermic channel commencing at about 0.5 eV. The intermolecular isotope effect for the exothermic channel is most unusual. The cross section increases in going from C_2H_6 to CH_3CD_3 and disappears altogether for C_2D_6. Part of this behavior is believed to be due to changes in the zero-point energies with the degree of deuteration. Possible reasons for the apparent endothermic channel include the formation of different isomers of $ScC_2H_2^+$, formation of electronically excited products, and the elimination of vibrationally excited H_2.

As with many atomic metal ions, scandium ions activate both carbon–hydrogen and carbon–carbon bonds to form species like ScH^+ and $ScCH_3^+$ at high energies. On the basis of comparisons with other experimental systems and theoretical values, these endothermic reactions are observed to begin at the thermodynamic limit. Analyses of the threshold behavior of these reactions (and supplementary ones) provide the bond energies, $D°(Sc^+-H) = 56.2 \pm 2$ kcal/mol and $D°(Sc^+-CH_3) = 59.0 \pm 3$ kcal/mol. Sc^+ also reacts with ethane to form $ScCH_2^+$ via elimination of methane in an endothermic process. By comparison with thermochemistry derived in other systems, $D°(Sc^+-CH_2) \geq 93.4 \pm 2.5$ kcal/mol, this reaction is found to have a barrier of 0.6 or 0.9 eV. The increase in bond strength in going from ScH^+ and $ScCH_3^+$ (which presumably have single metal–ligand bonds) to $ScCH_2^+$ (which then would have a double bond) is consistent with the trend previously noted in such species for V^+.[50] It its interesting to note too that while a very strongly bound VCH^+ species (with a triple metal–ligand bond)[50] is formed in the reaction of V^+ with ethane,[7] no such $ScCH^+$ species is observed here. This is consistent with the fact that since Sc^+ has only two electrons it cannot form a covalent triple bond.

Formation of ScH_2^+ is the *most* unique aspect of the "unique reactivity" of scandium ions with ethane. Unseen with all other first-row metal ions, this process can compete with reductive elimination of H_2 to form $ScC_2H_4^+$ because the scandium ion has only two electrons. These can tightly bind either the two H atoms or an ethene molecule but not both. Analysis shows that the sum of the first and second hydride–scandium ion bond energies is 115.5 ± 3.0 kcal/mol. Thus, the ScH_2^+ intermediate is bound relative to reductive elimination of dihydrogen by 11.3 kcal/mol. Both the first and second scandium ion–hydride bond energies, 56.2 and 59.3 kcal/mol, are strong compared with other first-row metal–hydride bond energies.[40] This is in keeping with predictions of the periodic trends in these bond strengths.[3,40]

Gas-phase ion beam studies have long been able to provide thermochemical data for specific metal–ligand bonds. This study, however, is one of the first to measure a *second* metal–ligand bond energy where the bond is covalent, i.e., the ligand is a radical. Such information is very important in understanding reductive elimination–oxidative addition processes prevalent in organometallic chemistry. Work in progress in our laboratory shows that other similar species, $HScCH_3^+$ and $Sc(CH_3)_2^+$, are also strongly bound. Unfortunately, the experimental approach used to obtain these results is probably not general because of the unique reactivity of Sc^+. Work is underway to overcome this obstacle for other metals.

(48) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308–311.

(49) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 8321–8322.

(50) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065–4066.