Activation of Carbon–Hydrogen and Carbon–Carbon Bonds by Transition-Metal Ions in the Gas Phase. Exhibition of Unique Reactivity by Scandium Ions

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Abstract: The activation of carbon–carbon and carbon–hydrogen bonds by scandium ions in the gas phase has been studied by using an ion-beam apparatus. Analysis of thresholds for the endothermic reactions of Sc^+ with H_2 and C_2H_6 yields $D°(Sc^+-H)$ = 54 ± 4 kcal/mol and $D°(Sc^+-CH_3)$ = 65 ± 5 kcal/mol, respectively. Results also indicate that Sc^+ forms a *second* strong σ-bond to CH_3 and H, rendering oxidative addition of C–C and C–H bonds an exothermic process. The reactions of Sc^+ with butane and larger alkanes result in the formation of products of the general form $Sc(C_nH_{n+2})^+$, which are not seen in similar reactions with other first-row transition metals. We postulate these products to be dialkylscandium ions. The mechanism proposed for the formation of these products, supported by studies of deuterium-labeled hydrocarbons, invokes β-alkyl transfers and reversible olefin insertions. For the reaction of Sc^+ with *n*-butane the proposed mechanism involves the formation of an activated scandium dimethylethylene intermediate. Although the reductive elimination of ethane from this intermediate is thermodynamically preferred, the favored decomposition route is observed to be loss of ethylene. This indicates a barrier for reductive elimination of ethane in excess of the endothermicity. In comparison to the first-row group 8 metal ions, another unique process involves selective 1,3-dehydrogenation of alkanes by Sc^+. It is proposed that Sc^+ initially inserts into a C–H bond, followed by addition of a γ-C–H bond across the Sc–H bond, with H_2 being eliminated from this four-center transition state. Two factors are responsible for the unique reactivity of Sc^+ among the first-row transition metal ions. Only two valence electrons are available for the formation of strong σ-bonds, and the formation of more than two such bonds is unlikely. In addition, the absence of additional d electrons on the metal center reduces the binding energy of π-acceptors in scandium(III) intermediates and modifies activation parameters for competitive processes.

Transition-metal ions in the gas phase readily activate the carbon–hydrogen and carbon–carbon bonds of completely saturated hydrocarbons. Extensive studies have probed the mechanism and energetics of these reactions, in which alkanes are dehydrogenated or cleaved to yield smaller alkanes and alkenes.[1–3] Although the available data reveal periodic trends in reactivity, it is recognized that certain processes can be highly metal specific. For example, Ni^+ distinguishes itself in comparison to the remaining first-row group 8 metal ions by dehydrogenating alkanes in a highly selective 1,4-process.[4]

The ability to understand and even predict metal ion reactivity is firmly based on a knowledge of the strengths of particular metal–ligand bonds and the activation parameters for individual reaction steps. These parameters relate to the motion of the system across barriers which interconnect stable configurations assumed by the reaction intermediates. Oxidative addition of C–H and C–C bonds must be an exothermic process in order for hydrocarbons to react readily at transition-metal centers. This requires the formation of relatively strong metal–hydrogen and metal–carbon bonds. On the basis of this consideration alone, what can be predicted for scandium? Scandium is one of the remaining first-row transition metals for which bonding energetics and reactions have not yet been reported.

The low-lying states of Sc^+ are summarized in Table I.[5] First-row transition metal ions with ground states derived from $3d^n4s^1$ configurations are found to have strong metal–hydrogen and metal–methyl bonds.[6] The σ-bond strengths of metal ions

Table I. Low-Lying States of Sc^{+a}

state	configuration	energy,[b] eV	population[c]
a^3D	$3d4s$	0	85.4%
a^1D	$3d4s$	0.315	7.0%
a^3F	$3d^2$	0.596	7.5%
b^1D	$3d^2$	1.36	0.1%
a^1S	$4s^2$	1.46	
a^3P	$3d^2$	1.50	
a^1G	$3d^2$	1.77	

a Data from ref 5. *b* Listed numbers are the lowest energy *J* level of that term. *c* Boltzmann population at 2500 K.

not meeting this requirement decrease with increasing promotion energy from their ground state to the lowest state derived from the $3d^n4s^1$ configuration. Hence we expect scandium ions, with a ^3D ground state derived from the $3d^14s^1$ configuration, to form a strong σ-bond to both H and CH_3. Moreover, there is no electron exchange energy lost in forming a *second* bond to the single d electron. It might therefore be expected that Sc^+ will react readily with hydrocarbons. While our observations generally support this conjecture, there are some surprising features in the reactions of Sc^+. The absence of additional d electrons on the metal center reduces the binding energy of π-acceptors in scandium(III) intermediates and modifies activation parameters for competitive processes. This endows scandium with unique reactivity in comparison to other first-row ions and provides further clues to the enigma of hydrocarbon activation at transition-metal centers.

Experimental Section

The ion-beam apparatus used in the present study has been described previously.[7] Briefly, singly charged scandium ions are produced by vaporization of anhydrous $ScCl_3$ onto a hot rhenium filament and subsequent surface ionization of the Sc at 2500 K. The estimated beam composition at this temperature is included in Table I. The metal ions are collimated, mass and energy selected, and focused into a collision chamber containing the neutral reactant at ambient temperature. The pressure in the collision chamber is held constant at 1.5 mtorr as measured with a capacitance manometer. Product ions scattered in the

(1) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981,** *103,* 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982,** *1,* 963. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983,** *2,* 1818.

(2) (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979,** *101,* 1332. (b) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980,** *102,* 7129.

(3) (a) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982,** *104,* 3565. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983,** *105,* 5197.

(4) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982,** *104,* 6293.

(5) Moore, C. E. "Atomic Energy Levels"; National Bureau of Standards: Washington, DC, 1949.

(6) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981,** *103,* 6501.

(7) (a) Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980,** *50,* 21. (b) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981,** *74,* 2819.
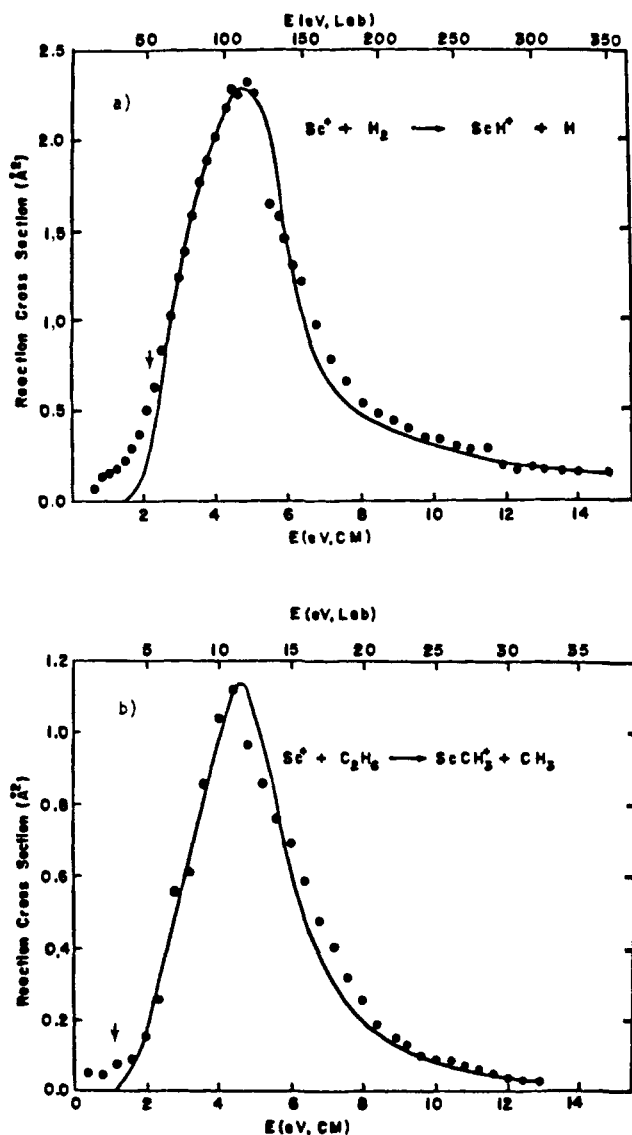
Figure 1. Variation in the experimental cross section with relative kinetic energy for the reaction of Sc^+ with (a) H_2 to form ScH^+ and (b) ethane to form $ScCH_3^+$. The solid lines are fits to the data as described in the text. Arrows indicate the threshold energies at 2.15 eV (for ScH^+) and 1.08 eV (for $ScCH_3^+$).

forward direction are analyzed by using a quadrupole mass spectrometer. Labeled propane (2,2-d_2, 98% D), n-butane (1,1,1,4,4,4-d_6, 98% D), and 2-methylpropane (2-d_1, 98% D) were obtained from Merck, Sharp and Dohme.

Results

Determination of Sc^+–H and Sc^+–CH_3 Bond Dissociation Energies. The endothermic reaction 1 of Sc^+ with H_2 leads to the formation of ScH^+. The cross section for reaction 1 as a function

$$Sc^+ + H_2 \rightarrow ScH^+ + H \qquad (1)$$
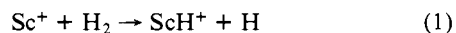
of relative kinetic energy is shown in Figure 1a. The data were fit by using the method described previously to find the reaction threshold, $E_o = 2.15$ eV.[8] From the threshold value and the H_2 bond energy,[9] a value for $D^\circ(Sc^+$–H) of 54 ± 4 kcal/mol is determined. The presence of excited-state scandium ions in the beam may be responsible for the low-energy tail in Figure 1a. The quality of the data and the lack of information relating to the
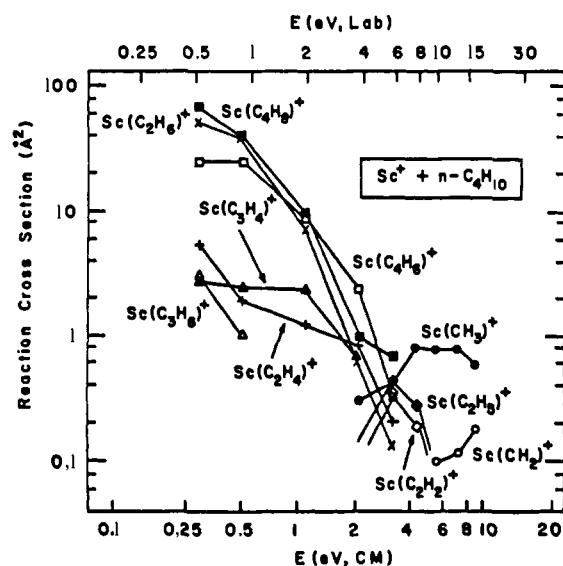
excited-state distribution precluded a fit including multiple states. The constants were chosen to fit the major rising part of the curve. The bond energy obtained from this fitting procedure is consistent with the observed reactivity of Sc^+.

The endothermic reactions 2 and 3 of scandium ions with ethane result in the formation of $ScCH_3^+$ and ScH^+, respectively. The

$$Sc^+ + C_2H_6 \rightarrow ScCH_3^+ + CH_3 \qquad (2)$$
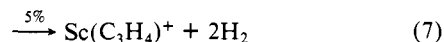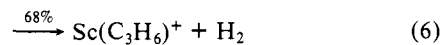
$$\rightarrow ScH^+ + C_2H_5 \qquad (3)$$
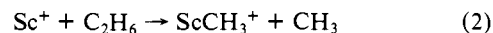
cross section for the formation of $ScCH_3^+$ as a function of relative kinetic energy is shown in Figure 1b. The data are fit as described previously to obtain a threshold for reaction 2 of $E_o = 1.08$ eV.[10] Combining this value with the C–C bond dissociation energy for ethane, 90.0 kcal/mol, gives $D^\circ(Sc^+$–CH_3) = 65 ± 5 kcal/mol. Scandium ions dehydrogenate ethane in accordance with reaction 4. The cross section for reaction 4 is 0.74 Å^2 at a relative kinetic

$$Sc^+ + C_2H_6 \rightarrow Sc(C_2H_4)^+ + H_2 \qquad (4)$$
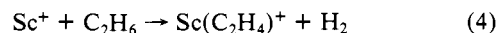
energy of 0.5 eV and decreases with increasing kinetic energy. This behavior suggests that reaction 4 is exothermic and indicates $D^\circ(Sc^+$–$C_2H_4) \geq 33$ kcal/mol.[11] Very small amounts of $Sc(H_2)^+$ are formed in an endothermic process which has a maximum cross section of less than 0.1 Å^2 at a relative kinetic energy of 2 eV.

Reactions of Sc^+ with Alkanes. The exothermic reactions 5–7

$$Sc^+ + C_3H_8 \xrightarrow{27\%} Sc(C_2H_4)^+ + CH_4 \qquad (5)$$

$$\xrightarrow{68\%} Sc(C_3H_6)^+ + H_2 \qquad (6)$$

$$\xrightarrow{5\%} Sc(C_3H_4)^+ + 2H_2 \qquad (7)$$

account for the main products observed when Sc^+ interacts with propane at a relative kinetic energy of 0.5 eV with a total reaction cross section of ~ 7 Å^2 at this energy. At higher energies, ScH^+, $ScCH_3^+$, and $Sc(CH_4)^+$ are formed in endothermic reactions.[12]

Figure 2. Variation in the experimental cross section for the reactions of Sc^+ with n-butane as a function of the relative kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale).

(8) (a) Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *48*, 315. (b) Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 37. The fitting parameters used in the threshold region as defined in the above references are $E_o = 2.15$ eV and $\sigma_o = 4.3$ Å^2.
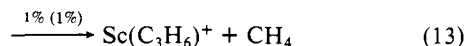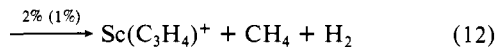
(9) Darwent, B. de B. *Natl. Stand. Ref. Data Ser.* (*U.S, Natl. Bur. Stand.*), **1970**, *NSRDS-NBS 31*.

(10) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819. The fitting parameters, defined in the above reference, are $n = 4$, $E_o = 1.08$, $\sigma_o = 3.5$ Å^2, and $a = 0.73$. When the parameters $n = 3$ and $n = 5$ were used, the best fit obtained resulted in values for E_o of 1.3 eV and 0.79 eV, respectively. The curves obtained using $n = 3$ and $n = 5$ clearly did not fit the data. The energies obtained from these fits were used to determine the error estimate for the Sc^+–CH_3 bond energy.

(11) Auxiliary heats of formation are taken from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

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Table II. Product Distributions in the Reactions of Sc^+ with Deuterium-Labeled Alkanes at a Relative Kinetic Energy of 0.5 eV

neutral lost	alkane		
	propane-2,2-d_2	2-methyl-propane-2-d_1	butane-1,1,1,4,4,4-d_6
H_2	0.21	0.41	
HD	0.33	0.27	0.38
D_2			0.04^a
$2H_2$	0.02^a	0.10	
H_2 + HD	0.03	0.06	
2HD (H_2 + D_2)	0.02		0.13
$2D_2$			
CH_4	0.17		
CH_3D	0.12		
C_2H_4		0.05	0.28
C_2H_3D	0.03	0.11	0.03
$C_2H_2D_2$	0.07		0.03
C_2HD_3			0.08
C_2D_4($C_2H_4D_2$)			0.03

^{a} This product could correspond to loss of D_2 or to loss of $2H_2$. The masses of the products in either case are identical, and thus the exact formula could not be determined.

The reaction of Sc^+ with *n*-butane at low energy yields a number of different products, as indicated in reactions 8–13. The product

$$Sc^+ + C_4H_{10} \xrightarrow{37\% \, (69\%)} Sc(C_4H_8)^+ + H_2 \qquad (8)$$

$$\xrightarrow{36\% \, (13\%)} Sc(C_2H_6)^+ + C_2H_4 \qquad (9)$$

$$\xrightarrow{22\% \, (16\%)} Sc(C_4H_6)^+ + 2H_2 \qquad (10)$$

$$\xrightarrow{2\%} Sc(C_2H_4)^+ + C_2H_6 \qquad (11)$$

$$\xrightarrow{2\% \, (1\%)} Sc(C_3H_4)^+ + CH_4 + H_2 \qquad (12)$$

$$\xrightarrow{1\% \, (1\%)} Sc(C_3H_6)^+ + CH_4 \qquad (13)$$
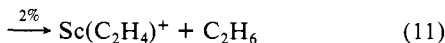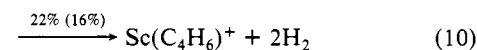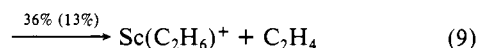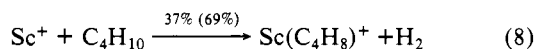
distributions shown were measured at a relative kinetic energy of 0.5 eV. Variation of the cross sections for these reactions with relative kinetic energy is shown in Figure 2. The observed decrease in the cross sections for reactions 8–13 with increasing kinetic energy indicates that all of these processes are exothermic. At higher energies, endothermic reaction pathways primarily result in the formation of $ScCH_3^+$ and $Sc(C_2H_5)^+$.[13] Products analogous to those observed with *n*-butane are also observed with isobutane, with a somewhat different product distribution indicated parenthetically in reactions 8–13, and a total reaction cross section of ~43 Å² at a relative kinetic energy of 0.5 eV.

Reaction of Sc^+ with alkanes larger than butane results in a large number of products. In contrast to the first-row group 8 metal ions, Sc^+ dehydrogenates neopentane exothermically, a process which accounts for 67% of the total observed product at a relative kinetic energy of 0.5 eV. Processes analogous to reaction 9 result in the formation of $Sc(C_3H_8)^+$ and $Sc(C_2H_6)^+$ from *n*-pentane, and $Sc(C_4H_{10})^+$ and $Sc(C_3H_8)^+$ from *n*-hexane. Total reaction cross sections for these larger alkanes are comparable to those observed for *n*-butane in Figure 2.

Further information about the reaction mechanisms and the structure of reaction products has been obtained by a study using deuterium-labeled compounds. A summary of the reactions of Sc^+ with several labeled alkanes at low energy is given in Table II.

Reaction of Sc^+ with Carbonyl Compounds. First-row group 8 metal ions react with acetone as indicated in equation 14.[14] This

$$M^+ + (CH_3)_2CO \rightarrow M(CH_3)_2^+ + CO \qquad (14)$$
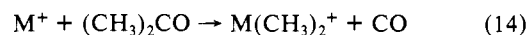
process yields a lower limit for the second metal–methyl bond dissociation energy in the product, a quantity useful in assessing the energetics of alkane reactions with transition-metal ions. This process is *not* observed with Sc^+. Instead, reaction 15 is observed,

$$Sc^+ + (CH_3)_2CO \rightarrow ScO^+ + C_3H_6 \qquad (15)$$

$$Sc^+ + CH_3CHO \rightarrow ScO^+ + C_2H_4 \qquad (16)$$
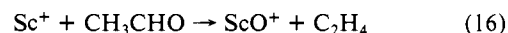
and the analogous process 16 occurs with acetaldehyde.[15] Cross sections for both reactions exhibit the characteristic behavior of exothermic processes, with maximum cross sections at low energy. When the known bond energy of ScO^+, 6.9 ± 0.3 eV,[16] is used, reactions 15 and 16 are exothermic by 43 and 48 kcal/mol, respectively.[17] Formaldehyde reacts with Sc^+ in an exothermic process to yield the scandium dihydride ion, reaction 17, with a

$$Sc^+ + CH_2O \rightarrow ScH_2^+ + CO \qquad (17)$$
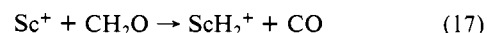
cross section of 1.4 Å² at a relative kinetic energy of 0.5 eV. When the first Sc^+–H bond dissociation energy determined above (54 kcal/mol) is used, reaction 17 indicates that $D°(ScH^+-H) \geq 50$ kcal/mol.

Discussion

Thermochemistry. The measured bond dissociation energies, $D°(Sc^+-H) = 54 \pm 4$ kcal/mol and $D°(Sc^+-CH_3) = 65 \pm 5$ kcal/mol, conform to the expectation that the first metal–ligand σ-bond to Sc^+ will be strong. The results are in complete accord with similar data for other first-row transition metal ions, including the observation that metal–methyl bonds are stronger than metal–hydrogen bonds.[6,18] Ab initio calculations (generalized valence bond, dissociation consistent, configuration interaction) on the ground $^2\Delta$ state of ScH^+ yield a value for the bond dissociation enthalpy of $D°(Sc^+-H) = 56$ kcal/mol,[19] in excellent agreement with our measured value. The hybridization of the scandium orbital used for bonding is ~41% 3d and ~59% 4s and 4p. The nonbonding electron on scandium occupies what is predominantly a d orbital. Formation of a second strong bond is thus possible, with a bond angle which may vary reasonably over a wide range (45–135°), depending on which of the d orbitals is used. Since the ground state of ScH^+ is $^2\Delta$, one would expect the bond angle in ScH_2^+ to be close to 90°. The angle may open up slightly in order to decrease the interaction between the two Sc^+–H bonds.

When the measured value of $D°(Sc^+-H)$ is used, the proton affinity of Sc is found to be 217 ± 4 kcal/mol. This is higher than any other first-row transition-metal atom,[20] a factor which can be attributed to the low ionization potential of scandium (6.56 eV).[5]

Since reaction 14 was not observed with Sc^+, we were not able to derive a lower limit for the second bond dissociation energy in $Sc(CH_3)_2^+$. In the case of the dihydride, however, reaction 17 indicates that the strength of the second scandium hydrogen bond is comparable to the first. Interestingly, with the sum of the two bond energies being greater than 104 kcal/mol, ScH_2^+ is predicted

(12) The identity of these products was confirmed by using propane-d_8. Although the same products appeared in both cases, the product distributions were somewhat different. For example, the double dehydrogenation product formed in reaction 7 using propane-d_8 constituted 41% of the total observed products.

(13) At high energies, not all of the reaction products were monitored. The products pertinent to the discussion in the text are shown in Figure 2.

(14) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L., submitted for publication in *Organometallics*.

(15) The identity of the product formed in reaction 16 was checked by using CD_3CDO.

(16) Murad, E. *J. Geophys. Res.* **1978**, *83*, 5525.

(17) Similar processes have been observed for neutral scandium atoms reacting with acetone and acetaldehyde: Liu, K.; Parson, J. M. *J. Phys. Chem.* **1979**, *83*, 970. From the internal state distributions they concluded that the neutrals lost were carbenes. When $\Delta H_f[(CH_3)_2C] = 62.5$ kcal/mol and $\Delta H_f[CH_3CH] = 77.5$ kcal/mol, calculated from this reference, were used, formation of dimethylcarbene and methylcarbene in reactions 15 and 16 would be endothermic by 15 and 18 kcal/mol, respectively.

(18) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

(19) Schilling, J. B.; Goddard, W. A., III, unpublished results.

(20) The proton affinity of metal atoms can be calculated by using the method described in ref 1a, with supplemental data from ref 6. See, also: Stevens, A. E.; Beauchamp, J. L. *Chem. Phys. Lett.* **1981**, *78*, 291.

Table III. Product Distributions of Exothermic Reactions of First-Row Transition Metal Ions with *n*-Butane at a Relative Kinetic Energy of 0.5 eV

| neutral product lost	metal ion[a]				
	Sc^+	Ti^{+b}	Fe^{+c}	Co^{+c}	Ni^{+c}
H_2	0.37		0.20	0.29	0.48
$2H_2$	0.22	1.0			
CH_4	0.01		0.41	0.12	0.06
$CH_4 + H_2$	0.02				
C_2H_4	0.36				
C_2H_6	0.02		0.39	0.59	0.45

[a] Cr^+ and Mn^+ do not react at all with alkanes.[6] [b] Ion cyclotron resonance data from ref 3a. [c] Data from ref 1c.
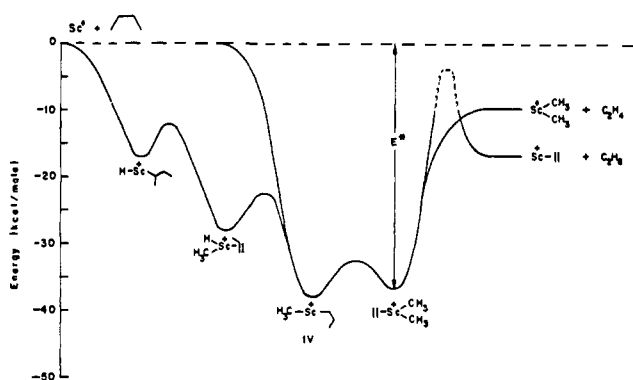
Figure 3. Simplified potential energy diagram for the reaction of Sc^+ with *n*-butane to form the products $Sc(CH_3)_2^+$ and $Sc(C_2H_4)^+$.

to be stable with respect to the reductive elimination of H_2. Since the second metal–hydrogen bond is strong, we surmise that the same will hold for the second metal–methyl bond. Hence, we have confirmed the expectation that both the first and second metal–ligand σ-bonds to Sc^+ are strong. The species formed correspond formally to Sc(III) compounds, which leaves the metal in its favored oxidation state.
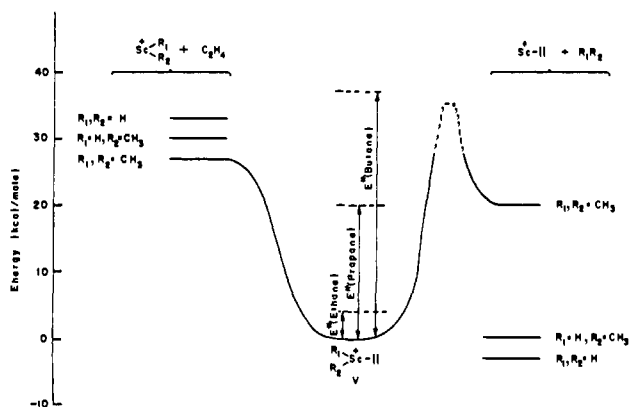
Reactions of Sc^+ with Hydrocarbons. Reactions of Sc^+ with alkanes smaller than butane yield results similar to those obtained for the first-row group 8 metal ions.[1b] The first major departure in behavior is observed in the reaction of Sc^+ with *n*-butane, where a major product with the empirical formula $Sc(C_2H_6)^+$ is observed, This is illustrated by the data in Table III, which summarizes the product distribution for the reactions of first-row transition-metal ions with *n*-butane. Related products are observed in the reaction of Sc^+ with *n*-pentane [$Sc(C_3H_8)^+$ and $Sc(C_2H_6)^+$] and *n*-hexane [$Sc(C_4H_{10})^+$ and $Sc(C_3H_8)^+$]. Again, these products are *not* observed when these alkanes react with other first-row transition-metal ions.

Possible structures of the $Sc(C_2H_6)^+$ product observed in the exothermic reaction of Sc^+ with *n*-butane are indicated by I–III.
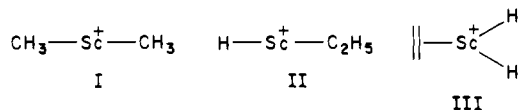
On the basis of thermochemical estimates in the Appendix, the heats of formation of I, II, and III are 189, 205, and 218 kcal/mol, respectively. When these values are used, the reactions of Sc^+ with *n*-butane to form II and III are predicted to be endothermic by 6 and 19 kcal/mol, respectively. Structure I, however, is formed in a reaction which is estimated to be exothermic by 10 kcal/mol and is therefore the only structure which seems energetically feasible.[21]

Figure 4. Simplified potential energy diagram for the decomposition of $R_1R_2Sc(C_2H_4)^+$ to form $Sc(R_1R_2)^+$ or $Sc(C_2H_4)^+$. The curve is drawn for the decomposition of $(CH_2)_2Sc(C_2H_4)^+$ formed in the reaction of Sc^+ with *n*-butane.

The energetics of a proposed mechanism for the formation of $Sc(CH_3)_2^+$ from reaction of Sc^+ with *n*-butane are indicated in Figure 3. The energies of the reaction intermediates were obtained from estimates given in the Appendix. Sc^+ may initially insert into either a C–C or a C–H bond (on energetic grounds). With *n*-butane, the most straightforward route to $Sc(CH_3)_2^+$ involves insertion into a terminal C–C bond, followed by β-methyl transfer and subsequent loss of ethylene. Alternatively, insertion into a secondary C–H bond may be followed by β-methyl transfer and subsequent olefin insertion into the scandium hydrogen bond to give intermediate IV. This sequence also accommodates the formation of $Sc(CH_3)_2^+$ from isobutane. We have previously suggested β-alkyl transfer reactions to explain product distributions for the reactions of Fe^+ with labeled hydrocarbons.[1c] The processes suggested in the above mechanism are well documented in condensed phase studies of organometallic reactions.[22] In particular, facile olefin insertions into $Cp_2^*Sc–H$ have been observed recently.[23]

The mechanism in Figure 3 predicts that $Sc(CD_3)_2^+$ would be the only dimethyl product formed in the reaction of Sc^+ with butane-*1,1,1,4,4,4-d_6*. As seen in Table II, $Sc(CD_3)_2^+$ is indeed the main dimethyl product, but some deuterium scrambling is also observed. This can be explained by assuming that both olefin insertion and β-hydrogen transfer are reversible in the mechanism of Figure 3.

An observation deserving attention is the absence of major products analogous to I, namely ScH_2^+ and $HScCH_3^+$, which might be formed in the reaction of Sc^+ with ethane and propane, respectively. A general intermediate (V) for the formation of these three products is $R_1R_2Sc(C_2H_4)^+$, shown in Figure 4. The decomposition products that result from loss of ethylene are shown on the left, and those that result from reductive elimination of R_1R_2 are shown on the right. The energies of these products relative to V are obtained by using the bond energies and heats of formation estimated in the Appendix. The total amount of internal energy available to V for decomposition is indicated by ϵ^* (alkane) for the three cases. With propane and ethane, V does not have sufficient internal energy to lose ethylene in an exothermic process. Therefore, the only exothermic reaction products are those corresponding to reductive elimination of R_1R_2. In the reaction with butane, however, intermediate V has sufficient energy to render the formation of *both* decomposition products exothermic. Although the energy of $Sc(C_2H_4)^+$ is estimated to be lower than the energy of $Sc(CH_3)_2^+$ by 7 kcal/mol, the latter is the favored product by a factor of 20 at low relative kinetic energy. This

(21) The formation of a similar product has recently been observed with yttrium, which is a congener of scandium. In a study of the collision-induced dissociation of $Y(C_2H_6)^+$, the major reaction seen is loss of methane (Freiser, B. S., private communication). This is a commonly seen product in the dssociation of dimethyl species.

(22) (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (c) Theoretical study of olefin insertion reactions: Thorn, D. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079 and references cited therein.

(23) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. The symbol Cp* indicates the pentamethyl cyclopentadienyl ligand.

Activation of Carbon-Hydrogen and Carbon-Carbon Bonds

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suggests that there must be an activation barrier of at least 7 kcal/mol for the reverse process (oxidative addition of the C–C bond of ethane by $ScC_2H_4^+$).[24]

It is interesting to note that small amounts of $ScHCH_3^+$ and ScH_2^+ are formed in endothermic reactions of Sc^+ with propane and ethane, respectively. Ther reaction cross sections are too small to determine accurate thresholds for these processes. The formation of $ScHCH_3^+$ from propane appears to be endothermic by approximately 0.5 ± 0.5 eV and the formation of ScH_2^+ from ethane endothermic by 1–2 eV. These results are in qualitative agreement with the potential energy diagram shown in Figure 4.

It is also interesting to note the relative ordering of the activation barriers for reductive elimination of R_1R_2. If the dehydrogenation of ethane proceeds via intermediate V, then the activation energy for reductive elimination of H_2 must be less than 4 kcal/mol.[25] The activation barrier for reductive elimination of CH_4 from V can be bracketed betwen 0 and 20 kcal/mol, whereas that for elimination of C_2H_6 is greater than 27 kcal/mol. This in in qualitative agreement with condensed phase studies of reductive elimination at transition-metal centers, where it has been noted that dialkyl complexes are much more stable than dihydro- and hydridoalkyl complexes.[26,27]

As stated previously, the formation of a dimethyl species is not observed in the reactions of the group 8 transition-metal ions with *n*-butane. This indicates that the potential energy diagrams for decomposition of intermediates analogous to V must be substantially different than that shown in Figure 4 for Sc^+. There are a number of possible explanations for this behavior. The strength of the second σ-bond in group 8 metals might be less than in Sc^+ due to the electron exchange energy lost in forming a second bond. Reactions with group 8 metal ions which lead to the formation of dialkyl products would therefore be less energetically favorable and perhaps even endothermic. An unusually low olefin bond strength to Sc^+ might also be responsible for the unique behavior observed. The absence of additional d electrons available for back-donation in Sc(III) complexes is probably responsible for a weak scandium–ethylene bond in reaction intermediates such as V. In the reductive-elimination reaction of V, the ethylene bond may remain quite weak until the reaction is near completion. This could be the reason for an activation barrier in the exit channel for reductive elimination of ethane from V as shown in Figure 4. The ethylene bond to Sc(I) may also be weaker than those to other transition metals, rendering reductive elimination of ethane less energetically favorable for V than for the analogous group 8 intermediates.

The reactions of Sc^+ with larger alkanes result in the abundant formation of products of the general composition $Sc(C_nH_{2n+2})^+$. These products are postulated to be dialkyl species which are formed by mechanisms similar to those proposed for the formation of $Sc(CH_3)_2^+$ from *n*-butane. In intermediates analogous to V the favored decomposition pathway is loss of ethylene to form the dialkyl species, presumably for the same reasons as discussed above for *n*-butane.

Dehydrogenation of Alkanes by Sc^+. The first-row group 8 transition-metal ions have been found to dehydrogenate alkanes in a highly specific manner.[1c] Dehydrogenation of small alkanes (propane, isobutane) proceeds exclusively by a 1,2-elimination process at Fe^+, Co^+, and Ni^+ centers. The suggested mechanism involves insertion of M^+ into a C–H bond, followed by β-hydrogen transfer and reductive elimination of H_2. The final product is thus an olefin bound to the metal center. The dehydrogenation of larger
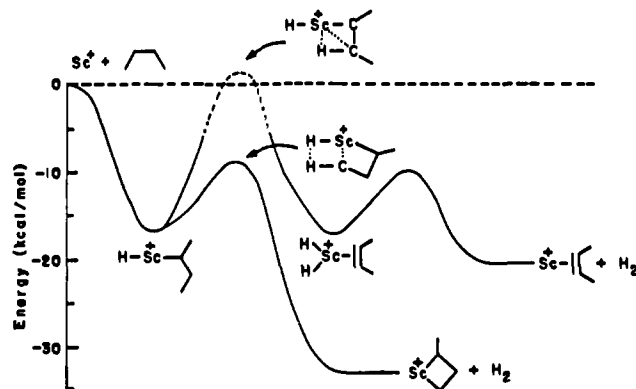

Figure 5. Simplified potential energy diagram for 1,2- and 1,3-dehydrogenation of *n*-butane by Sc^+.

linear alkanes by Ni^+ was found to proceed exclusively via a 1,4-elimination,[4] yielding a bis(olefin) complex. Iron and cobalt ions were observed to dehydrogenate larger alkanes by both a 1,2- and 1,4-elimination process.

In marked contrast to the group 8 metal ions, Sc^+ appears to dehydrogenate alkanes via predominantly 1,3-elimination (see Table II). A straightforward explanation for the observed product distributions might simply be that insertion into C–H bonds is relatively nondiscriminatory and a 1,3-elimination process occurs whenever possible. For example, in the reaction of Sc^+ with butane-*1,1,1,4,4,4-d6*, insertion into any of the C–H (or C–D) bonds can lead to 1,3-elimination due to the availability of γ-hydrogens. In fact, the overwhelming dehydrogenation reaction is loss of HD, supporting this conjecture. However, in the reactions of Sc^+ with propane-*2,2-d2* and 2-methyl-propane-*2-d1*, only initial insertion into a terminal C–H bond can lead to 1,3-elimination. Thus, for these cases, both 1,2- and 1,3-elimination processes are observed.[28] Further evidence for a unique 1,3-elimination mechanism is the fact that Sc^+ cleanly dehydrogenates neopentane,[29] a reaction that is not observed for the first-row group 8 metal ions.[1b] Following insertion into a C–H bond in neopentane only α- and γ-hydrogens are available. On the basis of the above results for labeled alkanes, a 1,3-elimination mechanism is likely.

A comparison of the energetics for 1,2- and 1,3-dehydrogenation of *n*-butane is given in Figure 5. A 1,3-mechanism is suggested in which initial insertion into a C–H bond is followed by a four-center process leading to metallacyclobutane[30] formation (Figure 5). A concerted mechanism may be required in order that scandium remains in a favorable oxidation state during the course of the reaction. The thermochemical estimates predict that although both dehydrogenation pathways are exothermic overall, the metallacycle is preferred by ∼13 kcal/mol. The failure of 1,2-elimination to compete with the 1,3-process indicates that formation of the metallacycle may also be kinetically preferred. The potential energy curve shown in Figure 5 for 1,2-elimination illustrates a two-step mechanism, where β-hydrogen transfer is followed by reductive elimination of H_2. The activation barrier for reductive elimination of H_2 from intermediate V was previously shown to be quite small. Hence, we suggest that the β-hydrogen transfer process is energetically unfavorable. An alternative mechanism is a one-step β-hydrogen elimination process proceeding via a strained four-center transition state. In either case,

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(24) This does not necessarily imply an activation barrier of 7 kcal/mol for oxidative addition of the C–C bond in ethane by free Sc^+. Addition of ligands such as CO to Fe^+ and Co^+ has been shown to reduce the reactivity of these metal ions with hydrocarbons: Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(25) It is likely that dehydrogenation of ethane does not proceed through intermediate V, but instead occurs directly from the more stable intermediate $HScC_2H_5^+$, via a four-center transition state. If this is the case, then the activation energy for β-hydrogen elimination must be less than 21 kcal/mol.
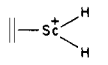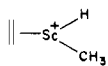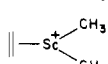
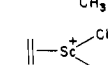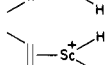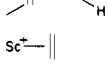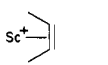(26) Norton, J. *Acc. Chem. Res.* **1979**, *12*, 139.

(27) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *21*, 2162.

(28) More 1,2-elimination is observed than would be predicted by nonselective insertion into any C–H bond. The secondary hydrogens in these compounds are more labile than the terminal hydrogens, leading to the observed nonstatistical behavior.

(29) Titanium ions have also been shown to dehydrogenate neopentane; see ref 3a. Of the second-row transition-metal ions examined thus far, Pd^+, and to a lesser extent Rh^+, also dehydrogenate neopentane (to be submitted for publication).

(30) (a) A similar mechanism has been proposed for the formation of thoracyclobutanes via γ-C–H abstraction: Bruno, J. W.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (b) Recent calculations indicate that a similar molecule, dichlorotitanacyclobutane, is a stable, planar molecule: Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 297.

Table IV. Thermochemical Estimates for Sc^+ Reaction Intermediates and Products

intermediate or product	sum of bond energies[a]	ΔH_f[b]
H—Sc^+—H	108 ± 7	238 ± 7
H—Sc^+—CH_3	115 ± 6	214 ± 6
H—Sc^+—C_2H_5	115 ± 6	205 ± 6
CH_3—Sc^+—CH_3	122 ± 7	189 ± 7
H—Sc^+—$CH(CH_3)(C_2H_5)$	115 ± 6	195 ± 6
CH_3—Sc^+—C_3H_7	122 ± 7	174 ± 7
$\parallel$—Sc^+(H)(H)	141 ± 8	218 ± 8
$\parallel$—Sc^+(H)(CH_3)	145 ± 8	197 ± 8
$\parallel$—Sc^+(CH_3)(CH_3)	149 ± 9	175 ± 9
propene—Sc^+(CH_3)(H)	150 ± 8[c]	184 ± 8
butene—Sc^+(H)(H)	148 ± 9[c]	195 ± 9
Sc^+—$\parallel$	40 ± 5	215 ± 5
Sc^+—(propene)	48 ± 5[d]	191 ± 5
Sc^+(metallacycle)	122 ± 7	179 ± 7[e]

[a] All values in kcal/mol. [b] $\Delta H_f(Sc^+) = 242$ kcal/mol from ref 33. $\Delta H_f(CH_3) = 35.1$ kcal/mol and $\Delta H_f(C_2H_5) = 25.9$ kcal/mol from ref 34. Auxiliary heats of formation are taken from ref 11. [c] The strengths of the bonds to propylene and butene in Sc(III) complexes were estimated to be 35 and 40 kcal/mol, respectively, on the basis of trends seen for Li^+ in ref 32. [d] The strength of the Sc^+ bond to butene was estimated to be 48 kcal/mol on the basis of trends seen in ref 31 and 32. [e] The following assumptions were used in estimating the heat of formation of this compound. (1) There is no strain energy involved in forming the metallacycle as suggested in ref 30b. (2) The primary and secondary C–H bond strengths in *n*-butane are 98 and 95 kcal/mol, respectively.

a prohibitive activation barrier must exist in order to explain the absence of 1,2-elimination products from reaction with *n*-butane.

Appendix

Thermochemical Estimates for Reaction Intermediates and Products. Although we have measured several Sc^+–ligand bond dissociation energies, there are others which have not been measured. We have estimated these energies by comparison with other systems. The errors that this introduces in the thermochemical estimates probably do not affect the general trends discussed in the text. The thermochemical values used for con-

structing Figures 3–5 are listed in Table IV. The assumptions that were used in assigning these values are discussed below.

The hydrogen and methyl bond strengths used for the first σ-bond to Sc^+ are $D°(Sc^+-H) = 54 \pm 4$ kcal/mol and $D°(Sc^+-CH_3) = 65 \pm 5$ kcal/mol. As discussed previously, the second Sc^+ bond to hydrogen was found to be greater than 50 kcal/mol, and thus we have assigned $D°(ScH^+-H) = 54 \pm 4$ kcal/mol. The second methyl bond in $Sc(CH_3)_2^+$ is known to be greater than 50 kcal/mol because it is formed in an exothermic reaction with isobutane. It is expected that the polarizable first methyl group in $Sc(CH_3)_2^+$ causes a slight delocalization of the charge on Sc^+, rendering the strength of the second methyl bond less than that of the first. This affect will be less pronounced if the first methyl group is replaced by a hydrogen as in $ScH(CH_3)^+$. Thus, the second σ-methyl bond strengths are estimated to be $D°(ScCH_3^+-CH_3) = 57 \pm 5$ kcal/mol and $D°(ScH^+-CH_3) = 61 \pm 5$ kcal/mol.

The strength of the olefin bond to Sc^+ has not be measured. We have estimated this bond strength by comparison to other metal–olefin bonds. For example, the metal–ethylene bonds in two Ni^+ compounds are estimated to be $D°(CpNi^+-C_2H_4) = 38 \pm 5$ kcal/mol[31] and $D°(Ni^+-C_2H_4) = 50$ kcal/mol,[4] although the latter is probably on the high side. For lithium ions, where no electrons are available for back-donation, the bond to ethylene is much weaker, $D°(Li^+-C_2H_4) = 18 \pm 5$ kcal/mol.[32] The bond to ethylene in Sc(I) was shown above to be greater than 33 kcal/mol from the exothermic reaction of Sc^+ with ethane. Therefore, we have assigned this bond strength a value of $D°(Sc^+-C_2H_4) = 40 \pm 5$ kcal/mol. In Sc(III) complexes where no electrons are available for back-donation, we have assigned $D°(ScR_1R_2^+-C_2H_4) = 30 \pm 5$ kcal/mol for $R_1 = H$, $R_2 = CH_3$. If R_1 and R_2 are both methyl groups, the ethylene bond will be somewhat weaker (as in the case of $CpNi^+$ compared to Ni^+) and, if R_1 and R_2 are hydrogens, the ethylene bond somewhat stronger. We have assigned the olefin bonds to be 3 kcal/mol weaker or stronger for the two cases, respectively.

(31) This value was obtained by extrapolation of Cp–Ni^+–olefin bond strengths from: Corderman, R. R. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1977.

(32) This value was obtained by extrapolation of Li^+–olefin bond strengths from: Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920.

(33) Franklin, J. L.; Dillard, J. G; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions"; (U.S., Natl. Bur. Stand.), *NSRDS-NBS 26*, 1969.

(34) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.