Gas-phase thermochemistry of VH and CrH

Yu-Min Chen, D. E. Clemmer, and P. B. Armentrout

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

(Received 18 November 92; accepted 10 December 1992)

The homolytic bond dissociation energies of the transition-metal neutral hydrides, $D'(M-H)$ ($M=V$, Cr), are experimentally determined by using guided ion beam tandem mass spectrometry to measure the kinetic energy dependence of the endothermic hydride abstraction reactions of $M^+$ with mono-, di-, and trimethylamine. From the thresholds of these reactions, we derive the 0 K values of $D'(V-H)=2.13 \pm 0.07$ eV and $D'(Cr-H)=1.93 \pm 0.07$ eV. This thermochemistry is compared with theoretical values and previous experimental results.

I. INTRODUCTION

An accurate knowledge of the bond energies for simple transition metal-hydrogen species is of obvious fundamental interest and also has implications in understanding a variety of catalytic reactions by transition metal ligand systems. Recently, we reported the first experimental measurement of the gas-phase bond dissociation energy for neutral titanium hydride, $D'(Ti-H)$. Here, we extend this work to two neighboring transition-metal neutral hydrides, VH and CrH. Values for these early transition-metal neutral hydrides are not well established. As shown in Table I, two previous experimental results for VH agree with each other and with an early theoretical result, but they differ appreciably from the most recent theoretical calculations, which agree nicely. The agreement between three previous experimental values for CrH (Refs. 5, 9, 10) is poor, and again disagree with the most recent theoretical values. The present study was undertaken to provide more accurate experimental values for these bond energies and to resolve some of the discrepancies in the literature.

As in our study of TiH, we measure the MH bond energies by using guided ion beam techniques to examine the endothermic hydride abstraction reaction

$$M^++RH\rightarrow MH+R^+, \quad (1)$$

where $M=V$ and Cr. The hydride donors chosen are monomethylamine, $CH_3NH_2$, dimethylamine, $(CH_3)_2NH$, and trimethylamine, $(CH_3)_3N$, systems that have $R^+-H^-$ bond energies that vary over a range of 0.8 eV. In the case of titanium, results from these three systems are in good agreement with one another, verifying that there are no systematic errors in the determination of the thermodynamic thresholds due to competition with other reactions.

II. EXPERIMENT

A. General

Complete descriptions of the apparatus and experimental procedures are given elsewhere. Metal ions are produced as described below. The ions are extracted from the source, accelerated, and focused into a magnetic sector mass analyzer. Cross sections are determined by using the octopole beam guide as a retarding potential analyzer. The uncertainty in the absolute energy scale is ±0.05 eV (lab). The distribution of ion energies has an average FWHM of ~0.7 eV (lab) for the surface ionization ion source and ~0.4 eV (lab) for the flow tube ion source. Laboratory ion energies (lab) are converted to energies in the center-of-mass frame (CM) by using the formula, $E_{CM}=E_{lab}/m/(m+M)$, where $M$ and $m$ are the ion and neutral reactant masses, respectively. Unless otherwise noted, all energies stated in this work correspond to the CM frame. Below ~0.3 eV (lab), energies are corrected for truncation of the ion beam energy distribution as described previously.

B. Ion source

In most of this work, atomic metal ions were produced by surface ionization (SI). In the SI source, the metals are introduced to the gas phase as VOCl$_3$ or CrO$_2$Cl$_2$ vapor. The metal containing vapor is directed toward a resistively heated rhenium filament where it decomposes and the resulting metal atoms are ionized. It is assumed that ions produced by SI equilibrate at the temperature of the filament and the state populations are governed by a Maxwell–Boltzmann distribution. The validity of this assumption has been discussed previously, and recent work by van Koppen et al. has verified this assumption in the case of Co$^+$. Table II shows the energies and populations of states for $M^+$ produced at the SI temperatures used in...
TABLE I. Metal hydride bond energies (in kcal/mol) at 0 K. *

<table>
<thead>
<tr>
<th>M-H</th>
<th>( D_e^0(M-H) )</th>
<th>Method*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-H</td>
<td>40(4)</td>
<td>GIBMS</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>37(3) [( &gt; 34 )]</td>
<td>ICR</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>40.9, 38.5</td>
<td>Theory</td>
<td>6(a), 6(b)</td>
</tr>
<tr>
<td></td>
<td>51.4 (52.4)</td>
<td>Theory</td>
<td>8(b) [8(c)]</td>
</tr>
<tr>
<td></td>
<td>51.4*</td>
<td>Theory</td>
<td>7(b)</td>
</tr>
<tr>
<td></td>
<td>49.0(1.6)</td>
<td>GIBMS</td>
<td>This work</td>
</tr>
<tr>
<td>Cr-H</td>
<td>&lt;45</td>
<td>HTMS</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>40(3) [( &gt; 37 )]</td>
<td>ICR</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>66(12)</td>
<td>Spec.</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>43.9</td>
<td>Theory</td>
<td>6(b)</td>
</tr>
<tr>
<td></td>
<td>46.8 (47.8)</td>
<td>Theory</td>
<td>8(b) [8(c)]</td>
</tr>
<tr>
<td></td>
<td>47.1</td>
<td>Theory</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>44.6(1.6)</td>
<td>GIBMS</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Uncertainties in parentheses. Values originally reported at 298 K have been corrected to 0 K by subtracting 0.9 kcal/mol = 3kT/2.

**GIBMS = guided ion beam mass spectrometry; HTMS = high temperature mass spectrometry; ICR = ion cyclotron resonance; Spec. = spectroscopy, Birge-Sponer analysis.

**Values in square brackets are obtained from a more conservative interpretation of the data. See text.

**Numbers in square brackets include an estimate of 1 kcal/mol for basis set incompleteness.

The \( D_e^0 \) values reported by these authors are converted to \( D_e^0 \) by using vibrational frequencies reported in Ref. 0(b).

these experiments. Because all transitions between states in Table II are parity forbidden, the radiative lifetimes of the excited states are expected to be on the order of seconds long, much greater than the flight time between the ionization and reaction regions (~10–100 \( \mu s \)). Thus, very few excited ions radiatively relax before reaction.

Vanadium ions are also produced in a recently constructed dc-discharge flow tube (DC/FT) source. Here, a dc-discharge is used to accelerate argon ions into a vanadium metal cathode to create \( V^+ \). The resulting ions are swept downstream in a flow of helium and argon at a total pressure of \( \sim 0.5 \) Torr encountering \( >10^5 \) collisions with these gases in the meter long flow tube. It is believed that most excited state vanadium ions are quenched to the ground state by these collisions. Quenching of high-lying electronic states of \( V^+ \) was facilitated by exothermic reactions with methane, introduced into the flow tube at pressures of 3–5 mTorr. The extent of quenching was verified by examining the reaction of \( V^+ \) with methane. Comparison of these data with previous state-specific results, the present results presented below, and other work in progress in our laboratory suggests that the excited state vanadium ions are efficiently quenched to their electronic ground state.

C. Thermochemical analyses

Theory and experiment indicate that the cross sections for endothermic reactions can be modeled with Eq. (2),

\[
\sigma(E) = \sum_i g_i \sigma_{ij} (E-E_i-E_0)^m / E^m
\]

which involves an explicit sum of the contributions of individual electronic, vibrational, and rotational states of the reactants, denoted by \( i \), weighted by their populations \( g_i \) and having energy \( E_i \). The other parameters in Eq. (2) include \( \sigma_{ij} \), an energy-independent scaling factor for each state, \( E_0 \), the threshold for reaction of the lowest state of the reactants; and \( n \) and \( m \), which are adjustable parameters. Except where noted, we utilize \( m=1 \) because this form of the equation has been derived as a model for translationally driven reactions and has been found to be quite useful in reproducing the shapes of endothermic reaction cross sections and in deriving accurate thermochemistry for a wide range of systems. After convoluting this model over the neutral and ion kinetic energy distributions as described previously, the \( \sigma_{ij} \) and \( E_0 \) parameters are optimized by using a nonlinear least squares analysis to give the best fit to the data. Uncertainties in \( E_0 \) are calculated from the range of threshold values for different data sets and the uncertainty in the absolute energy scale. Because all sources of energy are explicitly accounted for in this treatment, \( E_0 \) corresponds to the threshold for reaction at 0 K.

If there is no reaction barrier in excess of the reaction endothermicity, as is often the case for ion–molecule reactions, then the measured threshold for reaction (1) from ground state ions, \( E_0 \), is equal to the difference between the heterolytic bond energies, Eq. (3),

\[
E_0 = D_e^0(R^+\cdot-H^-) - D_e^0(M^+\cdot-H^-)
\]

We have evaluated the heterolytic bond energies for the methylamines previously\(^\text{a}1\) and chosen to use the values \( D_e^0(\text{CH}_3\text{NHCH}_2\text{+} \cdot -\text{H}^-) = 9.40 \) eV, \( D_e^0(\text{CH}_3\text{NHCH}_2\text{+} \cdot -\text{H}^-) = 8.87 \) eV, and \( D_e^0(\text{CH}_3\text{NHCH}_2\text{+} \cdot -\text{H}^-) = 8.57 \) eV, all with uncertainties of \( \pm 0.09 \) eV. To convert these values to 0 K, we assume ideal gas behavior and use \( D_e^0(R^+\cdot-H^-) = D_e^0(R^+\cdot-H^-) + U_T(RH) + U_f(RH) - U_f(R^+\cdot-H^-) - U_f(R^+\cdot-H^-) - \Delta n kT \), where the translational term, \( U_T(RH) - U_f(R^+\cdot-H^-) \), is just \(-3kT/2\) and \( \Delta n kT = kT \). To a reasonable approximation,

J. Chem. Phys., Vol. 98, No. 6, 15 March 1993

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the internal energy terms cancel, i.e., \( U_f(R^+ + H^-) \approx U_f(RH) \), such that the difference between the 0 and 298 K heterolytic bond energies should be close to \( 5kT/2 = 0.064 \text{ eV} \). Thus, the three methylamine bond energies at 0 K are taken as 9.34, 8.81, and 8.51 eV, respectively, all with uncertainties of \( \pm 0.09 \text{ eV} \).

### III. RESULTS

The reactions of \( M^+ \) with mono-, di-, and trimethylamine are complex and we observe up to nine, twelve, and nineteen product ions, respectively. Although a more detailed discussion of this chemistry may be published in the future, we concentrate here on reaction (4),

\[
M^+ + (\text{CH}_3)_x \text{NH}_3-x \\
\rightarrow \text{MH}^+ + (\text{CH}_3)_{x-1} \text{H}_{3-x} \text{NCH}_2^+ \quad (x=1-3)
\tag{4}
\]

the equivalent of reaction (1) in the methylamine systems. We have previously observed\(^{29}\) that such hydride transfer reactions can compete with hydrogen atom transfer reactions, process (5),

\[
M^+ + (\text{CH}_3)_x \text{NH}_1-x \\
\rightarrow \text{MH}^+ + (\text{CH}_3)_{x-1} \text{H}_{3-x} \text{NCH}_2 \quad (x=1-3)
\tag{5}
\]

because the products differ only in location of the charge. Such competition can shift the threshold of the reaction with the higher endothermicity to higher energy. It is also possible that other reactions may influence the threshold for reaction (4), especially if they involve C-H bond activation and are very efficient at energies in the threshold region. The particular reactions that are most likely to exert such an influence in the present study include reactions (6)–(8),

\[
M^+ + (\text{CH}_3)_x \text{NH}_3-x \rightarrow \text{MNC}_x \text{H}_{2x+1}^+ + \text{H}_2 \quad (x=1-3),
\tag{6}
\]

\[
M^+ + (\text{CH}_3)_x \text{NH}_3-x \rightarrow \text{MNC}_x \text{H}_{2x+1}^+ + \text{CH}_4 \quad (x=1-3),
\tag{7}
\]

\[
M^+ + (\text{CH}_3)_x \text{NH}_1-x \rightarrow \text{M}(\text{CH}_3)_x \text{NH}_1-x \quad (x=1-3). \tag{8}
\]

Reactions (6) and (7) have large cross sections in the \( V^+ \) systems, while reaction (8) is the key exothermic reaction in the \( Cr^+ \) systems. (The cross sections for these latter processes show a linear dependence on reactant pressure, indicating that they are formed by collisional stabilization of the adduct.) In all cases, the effects of competition between these various reactions can be tested by comparing the metal-hydride thermochemistry obtained from the different methylamines. Because the acidities of the three methylamines vary by 0.8 eV, inconsistent thermochemistry will be obtained if other reactions are unduly influencing the thresholds for reaction (4).

### A. Reactions of \( Cr^+ \)

We observed six, ten, and twelve ionic products in the reaction of \( Cr^+ \) with mono-, di-, and trimethylamine, respectively. Results for reactions (4), (5), and (8) are shown in Fig. 1 for conditions where \( Cr^+ \) is formed at a SI

![FIG. 1. Cross sections for reactions of \( Cr^+ \) produced by surface ionization with methylamine (a), dimethylamine (b), and trimethylamine (c) as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). Other reactions are observed, but only results for reactions (4), (5), and (8) are shown.](image-url)
TABLE III. Fitting parameters of Eq. (2) for reaction (4) and derived bond energies.*

<table>
<thead>
<tr>
<th>M⁺</th>
<th>RH</th>
<th>σ₀</th>
<th>n</th>
<th>E₀ (eV)</th>
<th>D⁰(M⁺—H⁻) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr⁺</td>
<td>CH₃NH₂</td>
<td>0.077(0.014)</td>
<td>1.6(0.1)</td>
<td>1.65(0.08)</td>
<td>7.69(0.12)</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂NH</td>
<td>1.13(0.14)</td>
<td>1.0(0.1)</td>
<td>0.90(0.06)</td>
<td>7.91(0.11)</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₃N</td>
<td>26.0(6.8)</td>
<td>0.7(0.1)</td>
<td>0.54(0.03)</td>
<td>7.97(0.09)</td>
</tr>
<tr>
<td>V⁺</td>
<td>CH₃NH₂</td>
<td>0.12(0.03)</td>
<td>1.6(0.2)</td>
<td>1.57(0.13)</td>
<td>7.77(0.16)</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂NH</td>
<td>0.89(0.11)</td>
<td>1.2(0.1)</td>
<td>1.27(0.04)</td>
<td>8.14(0.10)</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₃N</td>
<td>21.3(3.1)</td>
<td>0.4(0.3)</td>
<td>0.47(0.03)</td>
<td>8.09(0.09)</td>
</tr>
</tbody>
</table>

*Uncertainties, in parentheses, are one standard deviation.

The fitting parameters are the averages of those obtained where m in Eq. (2) was set to 1, 1.5, and 2, respectively.

 filament temperature of 1800 K. Adduct formation, reaction (8), is the largest exothermic process observed in these systems, with dehydrogenation, reaction (6), smaller by at least an order of magnitude. It can be seen that the magnitudes of the cross sections for reaction (4) increases by about a factor of 100 in going from the monomethylamine to the trimethylamine. This primarily reflects the gross difference in acidities of the three methyamines, although there is also an increase in the number of equivalent hydrogens available for hydride donation (a factor of 3). Figure 1 also shows that the ionic hydride channels, reaction (5), have higher thresholds than reaction (4) in all three systems, meaning that the thresholds for reaction (4) cannot be shifted by competition with reaction (5).

Six, eight, and six independent data sets for the monomethylamine, dimethylamine, and trimethylamine systems, respectively, were analyzed by using Eq. (2). Only the ground electronic state of Cr⁺ is included in this analysis because the filament temperature of 1800 K, the population of excited states is very small (Table II) and no features attributable to excited states are obvious in the results obtained here. The vibrational and rotational energies of the reactant methyamines are included in Eq. (2) as outlined previously. The vibrational and rotational frequencies of the methyamines used in the analyses are taken from the literature. The average fitting parameters obtained are summarized in Table III and, as shown in Fig. 2, the models reproduce the data very nicely. When these thresholds are combined with the heterolytic bond energies of the methyamines in Eq. (3), we obtain the values for D⁰(Cr⁺—H⁻) also listed in Table III. The D⁰(Cr⁺—H⁻) values obtained from the di- and trimethylamine systems are consistent each other, suggesting that these thresholds are free from shifts due to competition with other channels. In contrast, the value obtained from the monomethylamine system is over 0.2 eV smaller. Although reaction (4) is a major product channel in the di- and trimethylamine systems, it is only a minor process in the monomethylamine system due to the higher R⁺—H⁻ bond energy. This may mean that competition with other more favorable reactions suppresses the cross section for reaction (4) in the monomethylamine system at its true threshold, thereby shifting its apparent threshold to higher energy. Therefore, our best determination of D⁰(Cr⁺—H⁻) is taken as the weighted average of the values obtained from the di- and trimethylamine systems.

FIG. 2. Cross sections for reaction (4) with Cr⁺ produced by surface ionization and methyamine (a), dimethylamine (b), and trimethylamine (c) as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). The solid lines show the fits to the cross sections convoluted over the kinetic, vibrational, and rotational energy distributions of the reactants. Dashed lines are the same fits without convolution. Arrows indicate the average 0 K threshold energies.
FIG. 3. Cross sections for reactions of $V^+$ produced by surface ionization with methylamine (a), dimethylamine (b), and trimethylamine (c) as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). Other reactions are observed, but only results for reactions (4)-(7) are shown. In (a), the cross section for 66 m/s corresponds to formation of $VNH^++CH_3$; reaction (7), at low energies, and $VCH^2++NH_2$, at higher energies.

FIG. 4. Cross sections for reaction (4) with $V^+$ and methylamine (a), dimethylamine (b), and trimethylamine (c) as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). Triangles and circles show data for $V^+$ produced by surface ionization and in the flow tube source, respectively. The solid lines show the fits to the cross sections convoluted over the kinetic, vibrational, and rotational energy distributions of the reactants. Dashed lines are the same fits without convolution. Arrows indicate the average 0 K threshold energies.
ues derived from the di- and trimethylamine systems, 7.95 ±0.07 eV.

B. Reactions of V⁺

Nine, twelve, and nineteen ionic products were observed in the reactions of V⁺ with mono-, di-, and trimethylamine, respectively. The cross sections corresponding to reactions (4)–(7) are shown in Fig. 3 for V⁺ formed at a SI filament temperature of 2000±100 K for the monomethylamine system and 2100±100 K for the di- and trimethylamine systems. The magnitudes of the cross sections for reaction (4) increase by over a factor of 100 in going from mono- to trimethylamine, again reflecting the decreasing acidity. Reaction (5) has a higher threshold than reaction (4) in all three systems, so there is no competition between these processes at the thresholds for reaction (4). The dominant reactions at low kinetic energies in the vanadium systems are reactions (6) and (7).

In all three systems, the cross sections for reaction (4) were observed to vary when the SI filament temperature was increased to 2400±100 K. This suggests that the reactivities of the excited states are significantly larger than ground state and thermochemical values cannot be derived from these SI data without information regarding the state-specific reactivity of the different electronic states. To avoid this problem, the reactions were also studied with vanadium ions produced in the DC/FT ion source. As discussed in Sec. II, the ions formed in this source are believed to be primarily in their electronic ground state. This is consistent with a comparison of the results for V⁺ produced in the SI and DC/FT sources (Fig. 4). In all three systems, the thresholds of the DC/FT data are higher than those of the SI data.

Four, two, and two independent DC/FT data sets were analyzed for the mono-, di-, and trimethylamine systems, respectively. We assume that only the ground electronic state of V⁺ is present and include the internal energies of the methylamines in the analysis as in the Cr⁺ case. The average fitting parameters obtained are summarized in Table III. Figure 4 shows that these models nicely reproduce the cross section for reaction (4) in all three methylamine systems. When these thresholds are converted to ΔE₂(V⁺–H⁻) obtained in the di- and trimethylamine systems, 8.11±0.07 eV, is taken as our best determination.

IV. DISCUSSION

As discussed above, our best determination of the gas-phase heterolytic bond strengths for VH and CrH at 0 K are taken as averages of two values from the di- and trimethylamine systems. The results are ΔE(V⁺–H⁻) values of 8.11±0.07, and 7.95±0.07 eV for VH and CrH, respectively. The heterolytic MH bond energies can be converted to homolytic bond energies, ΔE₂(M–H), according to Eq. (9),

\[ \Delta E_2(M–H) = \Delta E_2(M⁺–H⁻) – \text{IE}(M) + \text{EA}(H). \]  

Here, EA(H) is the electron affinity of H, 0.754 eV, and IE(M) is the ionization energy of the metal atom listed in Table IV. This yields ΔE₂(V–H) =1.93±0.07 eV (44.6 ±1.6 kcal/mol), and ΔE₂(Cr–H) =1.93±0.07 eV (44.6 ±1.6 kcal/mol).

Table I shows that the VH and CrH bond energies measured here are similar to the most recent theoretical values, although systematically lower by 2–3 kcal/mol. Our value for the CrH bond energy agrees with the upper limit, <45 kcal/mol, from high temperature mass spectrometry which was based on the failure to observe CrH. Our value is somewhat higher than that determined by Sallans et al. in ion cyclotron resonance (ICR) experiments that bracketed the metal hydride bond energy by studying the reactions of M⁻ with a series of proton donors. As discussed in detail elsewhere, such experiments actually provide only a rigorous lower limit to the homolytic bond energies, as indicated in Table I. This is because the upper limit is provided by the failure to observe reaction, a result that could be due to constraints on the reaction other than thermodynamic ones. The "spectroscopic" value for ΔE(Cr–H) (Ref. 10) derived from a linear Birge-Sponer extrapolation is clearly in error.

The ΔE(V–H) value derived here is much higher than the value obtained by Sallans et al. but is consistent with this work when the latter is viewed conservatively as a lower limit. A previous guided ion beam measurement, ΔE(V–H) =40±4 kcal/mol, from our laboratory was based on the threshold for reaction (10),

\[ V⁺ + HC(CH₃)₃ → VH + C(CH₃)₃⁺, \]  

Table IV. Transition metal hydride thermochemistry (eV).

<table>
<thead>
<tr>
<th>M</th>
<th>IE(M)</th>
<th>EA(M)</th>
<th>ΔE₂(M⁺–H⁻)</th>
<th>ΔE₂(M–H)</th>
<th>PA(M⁻)</th>
<th>ΔE₂(M⁺–H⁻)</th>
<th>IE(MH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>6.740f</td>
<td>0.525(0.012)</td>
<td>8.11(0.07)</td>
<td>2.13(0.07)</td>
<td>15.20(0.07)</td>
<td>2.05±0.06d</td>
<td>6.82(0.09)</td>
</tr>
<tr>
<td>Cr</td>
<td>6.767f</td>
<td>0.666(0.012)</td>
<td>7.95(0.07)</td>
<td>1.93(0.07)</td>
<td>14.86(0.07)</td>
<td>1.37(0.09)e</td>
<td>7.33(0.11)</td>
</tr>
</tbody>
</table>


This study.


J. Chem. Phys., Vol. 98, No. 6, 15 March 1993

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\[ V^+ + \text{HC(CH}_3\text{)}_3 \rightarrow \text{VH} + \text{C}_2\text{H}_2^+ + \text{CH}_4. \]  

(11)

This study also found evidence that \( D^0(\text{V-H}) \) could be \( 56\pm5 \text{ kcal/mol} \) based on the threshold measured for reaction (11), although the lower value was believed to be more reliable. In this study, neither the electronic states effects evident in Fig. 4 nor the internal energy of the isobutane reactant were considered, such that neither of these values will be very accurate. It is likely that the threshold for reaction (10) is shifted to higher energies due to competition with the \( \text{VH}^+ + \text{C}(\text{CH}_3)_3 \) product channel, more efficient by an order of magnitude than reaction (10), and with a very efficient dehydrogenation reaction. Interestingly, if the bond energy from reaction (11) is approximately corrected for the internal energy of the \( \text{HC(CH}_3\text{)}_3 \) reactant, we obtain \( D^0(\text{V-H}) \approx 53\pm5 \text{ kcal/mol} \), within experimental error of the thermochemistry derived here.

One means of qualitatively checking our determination of \( D^0(\text{M-H}) \) is to calculate ionization energies (IE) for MH by using Eq. (12),

\[ \text{IE} (\text{MH}) = D^0(\text{M-H}) + \text{IE} (\text{M}) - D^0(\text{M}^+ - \text{H}) \]  

(12)

and compare these to results obtained from the difference in thresholds between reactions (4) and (5), which depend on the difference between the IEs of MH and R. Given the cationic bond energies listed in Table IV, we calculate IE(MH) values of 6.82\pm0.09 and 7.13\pm0.11 eV for VH and CrH, respectively. As noted above, the threshold for reaction (5) is higher than reaction (4) in all cases. These results indicate that lower limits of IE(VH) and IE(CrH) are provided by the highest IE(R) value, IE(\text{CH}_3\text{NH}_2) = 6.0\pm0.1 eV,33 consistent with the IE(MH) values derived above. A more direct measurement of IE(MH) can be obtained from the threshold difference between reactions (4) and (5), but the values derived in this way are only upper limits because the thresholds for reaction (5) can be shifted to higher energy due to competition with reaction (4), as discussed above. Such a procedure34 yields upper limits for IE(MH) of 7.3\pm0.2 and 7.5\pm0.2 eV for VH and CrH, respectively, in agreement with the IE values derived above by using Eq. (12).

Another way of examining this thermochemistry is to compare the neutral bond energy with the electron affinity of the metal, EA(M), as discussed by Squires.35 He found that there was a reasonable correlation between these two quantities for many transition metals, a result that implies a common proton affinity for the metal anion, PA(M^-) = \( \Delta H_{\text{acid}} \) (MH). The relationship between these quantities is given by Eq. (13),

\[ \text{PA} (\text{M}^-) = D^0(\text{M-H}) + \text{IE} (\text{H}) - \text{EA} (\text{M}), \]  

(13)

where \( \text{IE} (\text{H}) = 13.598 \text{ eV} \). The present results yield PA(M^-) values of 15.20\pm0.07 and 14.86\pm0.07 eV for V and Cr, respectively. Only PA(Cr^-) is close to the average transition metal anion proton affinity of 14.79\pm0.22 eV given by Squires.35 The failure of these proton affinities to agree is evidence that the bonding in these two metal hydrides is different.

Indeed, theory finds that CrH has a ground state that is well characterized by a 3d^4\sigma^2 molecular configuration where the \( \sigma \) orbital is largely a 4s\&1s bond.6 This is directly analogous with the 3d^4\sigma^2 electron configuration of ground state Cr-. Similarly, V- has 3d^4\sigma^2 ground state configurations, but the metal hydrides do not have analogous electron configurations. VH has a ground state that mixes the 3d^4\sigma^2 molecular configuration with one characterized as 4sp^3d^2\sigma^2, where the 4sp nonbonding orbital is a 4s\&4p hybrid and the \( \sigma \) orbital is largely 4p\&1s.8 Thus, the VH bond energy should not be expected to correlate well with EA(V^-), as we observe.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant No. CHE-8917980 and CHE-9221241.

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Vibrational frequencies of the mono-, di-, and trimethylamines are


See Ref. 2 and the references therein.

Thresholds for reaction (5) are measured by analysis with Eq. (2) to be
2.83±0.18, 2.89±0.09, and 2.97±0.03 eV for reaction of V⁺ with mono-, di-, and trimethylamine, respectively; and 3.10±0.07, 3.76 ±0.33, and 3.84±0.15 eV for reactions of Cr⁺ with mono-, di-, and trimethylamine, respectively.