

# The gas-phase thermochemistry of TiH

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The homolytic bond dissociation energy of the titanium neutral hydride  $D^0(\text{Ti-H})$  is determined experimentally for the first time by using guided ion beam tandem mass spectrometry to measure the kinetic energy dependence of the endothermic hydride abstraction reactions of  $\text{Ti}^+$  with methylamine, dimethylamine, and trimethylamine. From the thresholds of these reactions, the value of  $D^0(\text{Ti-H}) = 2.12 \pm 0.09$  eV ( $48.9 \pm 2.1$  kcal/mol) at 298 K is derived. Other 298 K thermodynamic values obtained are  $D^0(\text{Ti}^+-\text{H}^-) = 8.19 \pm 0.09$  eV ( $188.8 \pm 2.1$  kcal/mol), I.E. ( $\text{TiH}$ ) =  $6.59 \pm 0.14$  eV, P.A. ( $\text{Ti}^-$ ) =  $15.64 \pm 0.09$  eV ( $360.6 \pm 2.1$  kcal/mol), and  $\Delta_f H(\text{TiH}) = 116.4 \pm 2.3$  kcal/mol. This thermochemistry is compared with theoretical values and its relationship to hydride bond energies for the other first row transition metals is discussed.

## INTRODUCTION

A recent review of the properties of gas phase transition metal hydrides<sup>1</sup> pointed out that there has been little experimental work on the titanium hydride diatom. While spectroscopic studies<sup>2</sup> of TiH and measurements of  $D^0(\text{Ti}^+-\text{H})$  have been performed,<sup>3</sup> no experimental determination of the bond energy of the neutral diatom  $D^0(\text{Ti-H})$  has been reported. Such a determination would be useful for comparison with the results of a number of theoretical calculations of this bond energy.<sup>4-8</sup> The most recent calculations of three groups are in good accord and give 0 K bond energies of 1.96,<sup>6(c)</sup> 1.91,<sup>7(c)</sup> and 1.85 eV.<sup>8,9</sup>

In this study, we report the first experimental determination of  $D^0(\text{Ti-H})$ , measured by using guided ion beam techniques to examine the endothermic hydride abstraction reactions (1),



The hydride donors chosen for this study are the mono-, di-, and trimethylamines  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ , and  $(\text{CH}_3)_3\text{N}$ . These compounds have been used previously to bracket neutral metal hydride bond energies by Tolbert and Beauchamp.<sup>10</sup> In addition, we have used these molecules in our laboratories to study the diatomic hydrides of scandium, vanadium, and chromium.<sup>11</sup>

## EXPERIMENTAL SECTION

### General

Complete descriptions of the apparatus and experimental procedures are given elsewhere.<sup>12</sup>  $\text{Ti}^+$  production is described below. The ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass-selected ions are slowed to a desired kinetic energy and focused into an octopole ion guide which radially traps the ions. The octopole passes through a static gas cell containing the neutral reactant. Neutral gas pressures in the cell are kept low (less than 0.2

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 where they are focused into a quadrupole mass filter for mass analysis and then detected. Ion intensities are converted to absolute cross sections as described previously.<sup>12</sup> Uncertainties in cross sections are estimated to be  $\pm 20\%$ .

The absolute zero and the full width at half-maximum (FWHM) of the ion kinetic energy distribution are determined by using the octopole beam guide as a retarding potential analyzer.<sup>12</sup> The uncertainty in the absolute energy scale is  $\pm 0.05$  eV (lab). The distribution of ion energies has an average FWHM of  $\sim 0.7$  eV (lab). Laboratory ion energies (lab) are converted to energies in the center-of-mass frame (c.m.) by using the formula  $E_{\text{c.m.}} = E_{\text{lab}} m / (m + M)$ , where  $M$  and  $m$  are the ion and neutral reactant masses, respectively. All energies quoted in this work correspond to the c.m. frame. Below  $\sim 0.3$  eV lab, energies are corrected for truncation of the ion beam energy distribution as described previously.<sup>12</sup> Two effects broaden the data: the ion energy spread and thermal motion of the neutral gases, which has a width of  $\sim 0.4E_{\text{c.m.}}^{1/2}$  eV for the reactions of  $\text{Ti}^+$  with the methylamines.<sup>13</sup>

### Ion source

$\text{Ti}^+$  is produced by surface ionization (SI). In the SI source, the metal is introduced to the gas phase as  $\text{TiCl}_4$  (Aldrich 99.9%). The metal containing vapor is directed toward a resistively heated rhenium filament where it decomposes and the resulting metal atoms are ionized. It is generally assumed that ions produced by SI equilibrate at the temperature of the filament (here either  $2100$  or  $2300 \pm 100$  K) and the state populations are governed by a Maxwell-Boltzmann distribution. The validity of this assumption has been discussed previously<sup>14</sup> and is also found to be consistent with the results of Weisshaar and co-workers.<sup>15</sup> Table I lists the energies and populations of states for  $\text{Ti}^+$  produced at the SI temperatures used in these experiments. Since all transitions between states in Table I are parity forbidden, the radiative lifetimes of the excited states (on the order of se-

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TABLE I. Electronic states of  $\text{Ti}^+$  and their populations produced by surface ionization.

State	Electron configuration	Energy <sup>a</sup> (eV)	Population <sup>b</sup>	
			2100 K	2300 K
$a^4F$	$3d^24s$	0.0279	0.632 93	0.617 53
$b^4F$	$3d^3$	0.1346	0.350 38	0.359 95
$a^2F$	$3d^24s$	0.5929	0.013 93	0.017 84
$a^2D$	$3d^24s$	1.0824	0.000 66	0.001 07
$a^2G$	$3d^3$	1.1239	0.000 95	0.001 57
$a^4P$	$3d^3$	1.1718	0.000 49	0.000 82
$a^2P$	$3d^3$	1.2317	0.000 17	0.000 30
$b^4P$	$3d^24s$	1.2359	0.000 34	0.000 59
Others		>1.5754	0.000 14	0.000 31

<sup>a</sup> Energies are a statistical average over the  $J$  levels. Values are from Ref. 30.

<sup>b</sup> Maxwell-Boltzmann distribution at the indicated temperature.

conds long)<sup>16</sup> are expected to be much greater than the flight time between the ionization and reaction regions ( $\sim 10$ – $100 \mu\text{s}$ ). Thus, very few excited ions relax radiatively before reaction.

### Thermochemical analyses

Theory<sup>17,18</sup> and experiment<sup>19–21</sup> indicate that the cross sections for endothermic reactions can be modeled with Eq. (2),

$$\sigma(E) = \sum_i g_i \sigma_{i0} (E - E_0 + E_i)^n / E, \quad (2)$$

which involves an explicit sum of the contributions of individual states, denoted by  $i$ , weighted by their populations  $g_i$ . Here,  $\sigma_{i0}$  is an energy-independent scaling factor,  $E$  is the relative kinetic energy,  $n$  is an adjustable parameter,  $E_0$  is the threshold for reaction of the lowest electronic level ( $a^4F$ ) of the  $\text{Ti}^+$  ion, and  $E_i$  is the electronic excitation energy of each particular  $J$  level (for convenience, these are the  $J$  averaged values for  $\text{Ti}^+$  given in Table I). The  $\sigma_{i0}$ ,  $n$ , and  $E_0$  parameters are optimized by using a nonlinear least-squares analysis to give the best fit to the data, after convoluting over the neutral and ion kinetic energy distributions as described previously.<sup>12</sup> Error limits for  $E_0$  are calculated from the range of threshold values for different data sets and the absolute energy scale error. We assume that the reactant neutral 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 neutral reactant and report all of our derived thermochemistry as 298 K values.

### RESULTS

The reactions of  $\text{Ti}^+$  with each of the three methylamines are complex. We observed nine ionic products with cross sections in excess of  $0.01 \text{ \AA}^2$  in the case of monomethylamine and 12 such ionic products for dimethylamine. For the trimethylamine system, 12 products with cross sections above  $0.1 \text{ \AA}^2$  were observed. A more detailed discussion of this chemistry is planned for publication in the future,<sup>22</sup> but

in this paper, we concentrate on reaction (3),

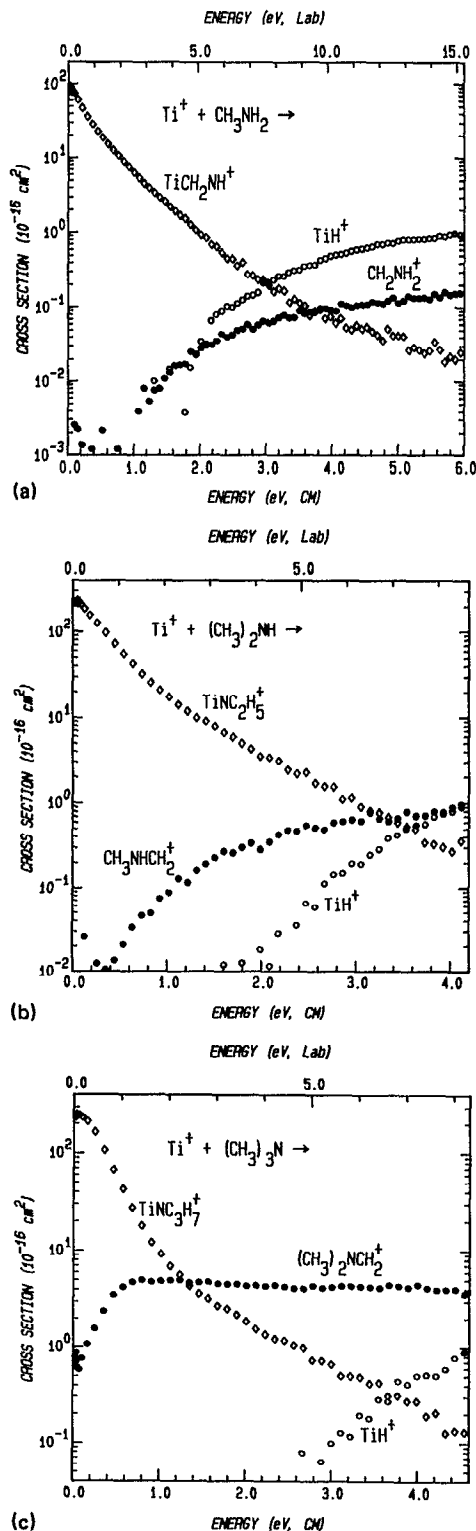
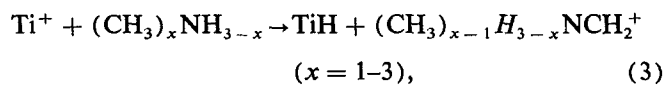
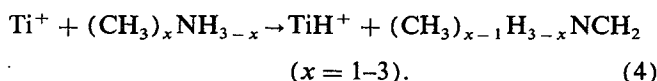


FIG. 1. Cross sections for reactions of  $\text{Ti}^+$  with (a) methylamine; (b) dimethylamine; and (c) trimethylamine as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). Other reactions are observed, but only results for reactions (3)–(5) are shown (see the text).

the equivalent of reaction (1) in the methylamine systems. The cross sections for these reactions for conditions where  $\text{Ti}^+$  is formed at an SI filament temperature of  $2100 \pm 100$  K are shown in Fig. 1. It can be seen that the magnitudes of the cross sections for reaction (3) increase by over a factor of 10 in going from the mono- to the trimethylamine. This is partially due to the increase in the number of equivalent hydrogens available for hydride donation, but also reflects the gross difference in endothermicities for the three methylamines. These cross sections were not observed to vary when the SI filament temperature was increased to 2300 K, nor did they change over a methylamine neutral pressure ranging from 0.02 to 0.15 mTorr.

Also shown in Fig. 1 are the cross sections for reactions (4),



These processes can potentially compete directly with reaction (3) since the products differ only in location of the charge. Indeed, it has been observed<sup>23</sup> that the competition between a hydrogen atom transfer reaction, like process (4), and a competing hydride transfer reaction, like process (3), can shift the threshold of the reaction with the higher endothermicity to higher energy. Figure 1 shows that the thresholds for reaction (4) are higher than those for reaction (3) in all three methylamine systems, such that the thresholds for reaction (3) are unlikely to be shifted by competition with reaction (4). In the monomethylamine case ( $x = 1$ ), however, we observe that reaction (4) has a larger cross section than reaction (3) at high energies. This may be because formation of  $\text{TiH}^+$  can occur via cleavage of either the C–H or the N–H bonds, while there is a strong preference for C–H bond cleavage in reaction (3) due to the lower I.E. of  $\text{CH}_2\text{NH}_2$  compared with  $\text{CH}_3\text{NH}$ .<sup>24</sup>

In all three systems, the exothermic reactions (5),



are the dominant processes at low kinetic energies (Fig. 1). Since this reaction also involves removal of H from the methylamines, it is possible that competition from this process (and other exothermic reactions) could also influence the thresholds for reaction (3). However, this effect should influence the three systems differently since the endothermicities for reaction (3) vary greatly for the three systems (see below). As shown below, we find that the thermochemical values derived in the three methylamine systems are consis-

tent with one another. This clearly suggests that the thresholds measured for reaction (3) represent the true thermodynamic limits and are not affected by competition with other reaction channels.

All data files collected at neutral reactant pressures below 0.15 mTorr were analyzed by using Eq. (2). The observation that the reaction cross sections do not depend on the SI filament temperature suggests that the reactivities of the high-lying excited states above 0.5 eV are not significantly larger than the  $a^4F$  and  $b^4F$  states (Table I). Since the populations of these excited states change significantly as the filament temperature increases from 2100 to 2300 K, we would have expected to observe this difference if these states contributed significantly to the observed cross sections. (Indeed this type of temperature dependence has been observed previously in other reaction systems.<sup>19,25</sup>) Until more specific information regarding the state-specific reactivity of the different electronic states becomes available, we make the reasonable assumption that the values of  $\sigma_{i0}$  in Eq. (2) are the same for all states. Between nine and 13 independent data sets were analyzed for each system and the average fitting parameters obtained are summarized in Table II. Figure 2 shows that the empirical models reproduce nicely the cross sections for reaction (3) in all three methylamine systems. The trimethylamine case [Fig. 2(c)] is interesting since features corresponding to the different electronic states ( $a^4F$ ,  $b^4F$ , and higher states) are apparent in the unconvoluted model. In this system, the higher electronic states have sufficient energy that reaction (3) ( $x = 3$ ) is exothermic for these states, explaining why this cross section does not go to zero at low energies. This is experimental verification that the excited states do participate in the reaction.

## DISCUSSION

If there is no reaction barrier in excess of the reaction endothermicity, as is often the case for endothermic ion-molecule reactions,<sup>26,27</sup> then the observed thresholds for reaction (3) from ground state ions  $E_0$  are equal to the difference between the heterolytic bond energies [Eq. (6)]

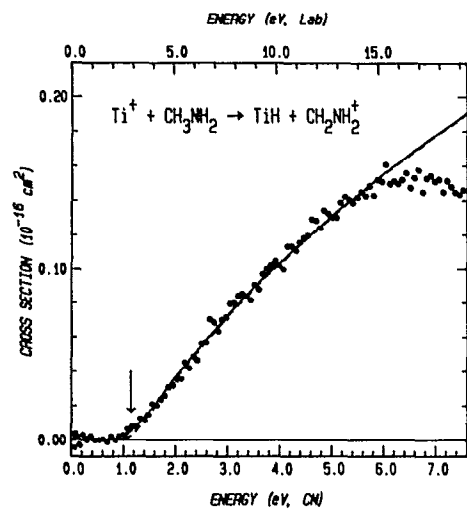
$$E_0 = D^0(\text{R}^+ - \text{H}^-) - D^0(\text{Ti}^+ - \text{H}^-). \quad (6)$$

The heterolytic bond energies of the methylamines can be calculated from appearance energy measurements of Lossing *et al.*<sup>28</sup> However, these authors used older literature values for the 298 K heats of formation of  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  (34.0 and 25.7 kcal/mol, respectively) to determine average heats of formation of 178 kcal/mol for  $\text{H}_2\text{NCH}_2^+$ , 166 kcal/mol for  $\text{CH}_3\text{NHCH}_2^+$ , and 158 kcal/mol for  $(\text{CH}_3)_2\text{NCH}_2^+$

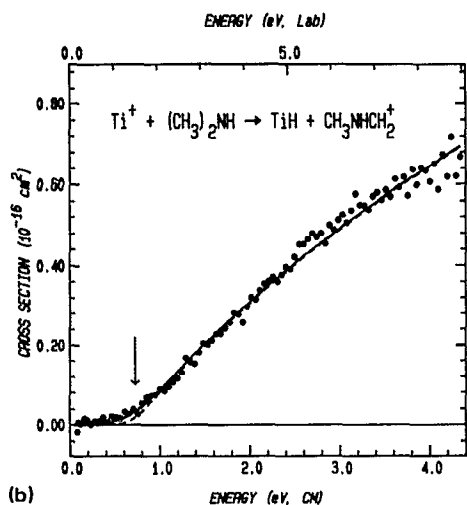
TABLE II. Fitting parameters of Eq. (2) for reactions (3) and derived bond energies in electron-volts.<sup>a</sup>

RH	$\sigma_0$	$n$	$E_0$ (eV)	$D^0(\text{Ti}^+ - \text{H}^-)$	$D^0(\text{Ti}-\text{H})$
$\text{CH}_3\text{NH}_2$	0.08(0.02)	1.6(0.1)	1.14(0.06)	8.26(0.11)	2.20(0.11)
$(\text{CH}_3)_2\text{NH}$	0.45(0.12)	1.6(0.1)	0.72(0.05)	8.15(0.10)	2.09(0.10)
$(\text{CH}_3)_3\text{N}$	5.5(0.3)	0.6(0.1)	0.43(0.03)	8.14(0.09)	2.08(0.09)

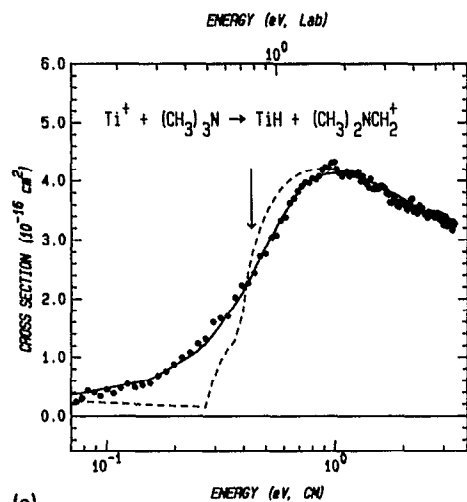
<sup>a</sup>Uncertainties, in parentheses, are one standard deviation.



(a)



(b)



(c)

FIG. 2. Cross sections for reactions (3) in the (a) methylamine; (b) dimethylamine; and (c) trimethylamine systems as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis). The solid lines indicate fits to the cross sections convoluted over the beam and neutral energy distributions. Dashed lines are the same fits without convolution. Arrows indicate the average  $E_0$  from different data files in each reaction system.

(stationary electron convention). If the alkyl heats of formation are replaced by the presently accepted values of 34.8<sup>24</sup> and 28.4<sup>29</sup> kcal/mol, respectively, the average heats of formation become 176.6 kcal/mol for H<sub>2</sub>NCH<sub>2</sub><sup>+</sup>, 165.5 kcal/mol for CH<sub>3</sub>NHCH<sub>2</sub><sup>+</sup>, and 157.3 kcal/mol for (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub><sup>+</sup>, with uncertainties estimated as  $\pm 2$  kcal/mol, as per Lossing *et al.* These values are used to calculate the bond energies  $D^0(\text{H}_2\text{NCH}_2^+ - \text{H}^-) = 9.40$  eV,  $D^0(\text{CH}_3\text{NHCH}_2^+ - \text{H}^-) = 8.87$  eV, and  $D^0[(\text{CH}_3)_2\text{NCH}_2^+ - \text{H}^-] = 8.57$  eV, all with uncertainties of  $\pm 0.09$  eV.

When the threshold measurements listed in Table II are combined with these heterolytic bond energies in Eq. (6), we obtain the values for  $D^0(\text{Ti}^+ - \text{H}^-)$  also listed in Table II. Although the endothermicities for reaction (3) in the three methylamine systems cover a relatively broad threshold range of about 0.9 eV, we still obtain consistent values for  $D^0(\text{Ti}^+ - \text{H}^-)$ . This consistency indicates that the measured thresholds represent the true thermodynamic thresholds for reaction and that no activation barriers in excess of the endothermicity or kinetic shifts are present for these systems.

We take the average of these three  $D^0(\text{Ti}^+ - \text{H}^-)$  values  $8.19 \pm 0.09$  eV ( $188.8 \pm 2.1$  kcal/mol) to be our best determination of the gas-phase Ti–H bond strength at 298 K. This heterolytic bond energy can be converted to the homolytic bond energy  $D^0(\text{Ti} - \text{H})$  according to Eq. (7)

$$D^0(\text{Ti} - \text{H}) = D^0(\text{Ti}^+ - \text{H}^-) - \text{I.E.}(\text{Ti}) + \text{E.A.}(\text{H}). \quad (7)$$

Here I.E. (Ti) is the ionization energy of the titanium atom  $6.820 \pm 0.006$  eV<sup>30</sup> and E.A. (H) is the electron affinity of H  $0.754$  eV.<sup>24</sup> This yields an average value for  $D_{298}^0(\text{Ti} - \text{H})$  of  $2.12 \pm 0.09$  eV ( $48.9 \pm 2.1$  kcal/mol). To compare this result to the theoretical values, we adjust our experimental value to 0 K<sup>31</sup> and obtain  $D_0^0(\text{Ti} - \text{H}) = 2.08 \pm 0.09$  eV ( $48.0 \pm 2.1$  kcal/mol). This value is slightly higher than the most recent theoretical calculations, but in a recent compilation of their work, Bauschlicher *et al.*<sup>32</sup> suggest that the calculated values are typically low due to basis set incompleteness. They correct for this by adding 1 kcal/mol to their calculated value, such that the bond energy that they list for comparison with experiment is  $D_0^0(\text{Ti} - \text{H}) = 46.3$  kcal/mol, within experimental error of the value obtained here.

Additional thermochemistry for the TiH molecule can be obtained with supplementary thermodynamic information. Using the values of  $\Delta_f H(\text{Ti}) = 113.2 \pm 1.0$  kcal/mol,<sup>33</sup>  $\Delta_f H(\text{H}) = 52.10 \pm 0.001$  kcal/mol,<sup>13</sup> and the  $D^0(\text{Ti} - \text{H})$  value obtained from this study, we derive  $\Delta_f H_{298}(\text{TiH}) = 116.4 \pm 2.3$  kcal/mol. Equations (8) and (9),

$$\text{P.A.}(\text{Ti}^-) = D^0(\text{Ti} - \text{H}) + \text{I.E.}(\text{H}) - \text{E.A.}(\text{Ti}), \quad (8)$$

$$\text{I.E.}(\text{TiH}) = D^0(\text{Ti} - \text{H}) + \text{I.E.}(\text{Ti}) - D^0(\text{Ti}^+ - \text{H}^-), \quad (9)$$

where  $\text{E.A.}(\text{Ti}) = 0.079 \pm 0.014$  eV,<sup>34</sup>  $\text{I.E.}(\text{H}) = 13.598$  eV,<sup>24</sup> and  $D_{298}^0(\text{Ti}^+ - \text{H}^-) = 2.35 \pm 0.11$  eV<sup>3</sup> can be used to determine the proton affinity P.A. for Ti<sup>−</sup> of  $15.64 \pm 0.09$  eV ( $360.6 \pm 2.1$  kcal/mol) and an ionization energy for TiH of  $6.59 \pm 0.14$  eV.

This value for I.E. (TiH) offers an opportunity to inde-

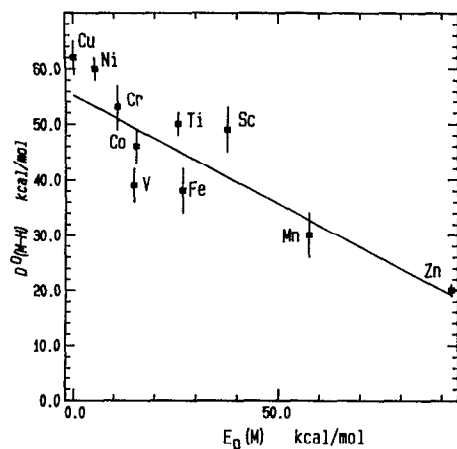


FIG. 3. First row transition metal neutral hydride bond energies vs metal atom production energy to a  $4s3d^{n+1}$  spin-decoupled state (see the text). The line is a linear regression fit to the data. All the data are taken from Ref. 1 excluding  $D^0(\text{Ti-H})$  which is from this study.

pendently check our determination of  $D^0(\text{Ti-H})$  by comparing the threshold difference between reactions (3) and (4). These relative thresholds depend only on the difference between the I.E.s of TiH and R, and we find that the thresholds for reactions (4) are higher than those of reactions (3) in all three cases, meaning that  $\text{I.E.}(\text{TiH}) > \text{I.E.}(\text{R})$ . Thus, a lower limit to  $\text{I.E.}(\text{TiH})$  is provided by the highest  $\text{I.E.}(\text{R})$  value  $\text{I.E.}(\text{CH}_2\text{NH}_2) = 6.0 \pm 0.1 \text{ eV}$ ,<sup>35</sup> consistent with the  $\text{I.E.}(\text{TiH})$  value derived above. A more direct measurement of  $\text{I.E.}(\text{TiH})$  can be obtained from the threshold difference between reactions (3) and (4). Thresholds for reactions (4) are measured by analysis with Eq. (2) to be  $1.94 \pm 0.11$ ,  $2.19 \pm 0.15$ , and  $2.38 \pm 0.08 \text{ eV}$  for the reaction systems of  $\text{Ti}^+$  with methylamine, dimethylamine, and trimethylamine, respectively. Combining these values with the thresholds for reactions (3) listed in Table II and  $\text{I.E.}(\text{R})$  leads to values for  $\text{I.E.}(\text{TiH})$  of 6.8, 7.4, and 7.6 eV, respectively, all  $\pm 0.2 \text{ eV}$ . Because the thresholds for reaction (4) can be shifted to higher energy due to competition with reaction (3), as discussed above, these I.E.s are best viewed as upper limits. This is again in agreement with the value derived above, and the value obtained in the monomethylamine case is within experimental error of this value.

One of the means used to understand the periodic trends in the bond energies for transition metal hydride diatoms is the promotion energy  $E_p(\text{M})$ .<sup>1,36-38</sup> This is defined as the energy necessary to take a metal atom in its ground state to an electron configuration where there is one electron in the  $4s$  orbital (which bonds with the H atom) that is spin decoupled from the nonbonding  $3d$  electrons. As shown in Fig. 3, the value for  $D^0(\text{Ti-H})$  determined in the present work correlates reasonably well with the promotion energy and to the bond energies of the other first row transition metal hydrides.

An alternate way of understanding the periodic trends in  $D^0(\text{M-H})$  is the correlation of the bond energies with electron affinity of the metals  $\text{E.A.}(\text{M})$ . This correlation predicts a constant gas-phase acidity for the metal hydrides

$D^0(\text{M}^--\text{H}^+) = \text{P.A.}(\text{M}^-)$ . The constant acidity value originally noted by Squires<sup>38</sup> was  $341 \pm 5 \text{ kcal/mol}$  and an updated correlation finds a value of  $346 \pm 7 \text{ kcal/mol}$ .<sup>1</sup> Our value for  $\text{P.A.}(\text{Ti}^-)$  of  $361 \pm 2 \text{ kcal/mol}$  is much higher than either of these predictions. Squires suggests that this deviation may be due to a strong ionic character in TiH, however, the good correlation with promotion energy suggests covalent bonding in TiH. Furthermore, Chong *et al.* find theoretically that the dipole moment of TiH has an intermediate value compared with those of the other first row transition metal hydride diatoms,<sup>6(b)</sup> also suggesting no anomalous ionic character.

## ACKNOWLEDGMENT

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