Kinetics and Thermochemistry of the Reaction Si(CH₃)₃ + HBr ⇌ Si(CH₃)₂H + Br: Determination of the (CH₃)₃Si–H Bond Energy

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The reaction Si(CH₃)₃ + HBr → Si(CH₃)₂H + Br (1) has been investigated using flash photolysis/photoionization mass spectrometry detection of Si(CH₃)₃ and flash photolysis/resonance fluorescence spectroscopy detection of Br. The measured rate constants are $k_1 = (1.06 ± 0.13) \times 10^{-11} \text{exp}(6.14 ± 0.31) \text{kJ mol}^{-1}/\text{RT} \text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$ for $T = 296-702 \text{K}$ and $k_1 = (8.1 ± 2.0) \times 10^{-12} \text{exp}(5.12 ± 0.72) \text{kJ mol}^{-1}/\text{RT} \text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$ for $T = 289-515 \text{K}$, respectively. The 1σ uncertainties represent precision only. Combination with $k_1$ data and analysis by second and third law methods yields $\Delta H^0_{298} = -31.1 \text{kJ mol}^{-1}$ for (1), with accuracy limits of about ±2.0 kJ mol⁻¹. The results imply an Si–H bond dissociation enthalpy of 397.4 ± 2 kJ mol⁻¹ and an enthalpy of formation for trimethylsilyl of 16.4 ± 6.0 kJ mol⁻¹.

Introduction

The aim of this work is to remove uncertainty in the Si–H bond strength of trimethylsilane and the enthalpy of formation of the trimethylysilyl radical. Previous recommendations,¹² based partly on iodination kinetics, suggested that the bond strength was similar to that measured for SiH₄, while spectroscopic studies suggested significant Si–H bond weakening by methyl groups.⁴５ Two previous studies of the kinetics of the system

$$\text{Si(CH}_3\text{)}_3 + \text{HBr} \rightleftharpoons \text{Si(CH}_3\text{)}_2\text{H} + \text{Br} \quad (1, -1)$$

and the equilibrium constant $K = k_1/k_{-1}$, relying either⁶ on measurements of the reverse rate constant $k_{-1}$ and assumptions about $k_1$ or on $k_1/k_{-1}$ at room temperature only,⁷ suggested that methylation instead strengthens the Si–H bonds relative to SiH₄.

Here we present studies of the temperature dependence of $k_1$, carried out using two different techniques, the flash photolysis/photoionization mass spectrometry (FP-PIMS) method at the Catholic University of America and the flash photolysis/resonance fluorescence (FP-RF) method at the University of North Texas. The results are combined with $k_1$ data to obtain thermochemical information by second law and third law methods.

Experimental Section

Flash Photolysis/Photoionization Mass Spectrometry. The FP-PIMS apparatus⁸ and experimental procedures⁹¹¹¹ used have been described previously. Briefly, gas flowing through the 1.05-cm (or 2.20-cm) i.d. heatable Pyrex tubular reactor contained the radical precursor (see below), HBr in varying amounts and an inert carrier gas in large excess (He, >99%). Reaction was initiated by pulsed unfocused radiation from a Lambda Physik 201 MCS laser (193 nm) directed along the axis of the tubular reactor. The flow velocity (≈5 m s⁻¹ when the small reactor was used and ≈3 m s⁻¹ when the larger reactor was utilized) was adequate to replenish gas in the reactor completely between consecutive laser pulses.

Gas emerging from a small sampling orifice in the wall of the reactor is formed into a molecular beam by a conical skimmer and analyzed continuously using a photoionization quadrupole mass spectrometer. Vacuum UV radiation from atomic resonance lamps was used for photoionization.

The majority of experiments were done using Si₂(CH₃)₆ as the Si(CH₃)₃ radical precursor.¹²¹³ Additional experiments were conducted using C₃H₅Si(CH₃)₃ as the precursor to verify independence of the rate constants measured on the precursor used. There are indications¹⁴ that the most important channels of photodissociation of these precursors at 193 nm are those leading to Si(CH₃)₃ radical formation:

$$\text{Si}_2\text{(CH}_3\text{)}_6 + \text{hv} (193 \text{ nm}) \rightarrow 2\text{Si(CH}_3\text{)}_3$$

$$\text{C}_3\text{H}_5\text{Si(CH}_3\text{)}_3 + \text{hv} (193 \text{ nm}) \rightarrow \text{C}_3\text{H}_5 + \text{Si(CH}_3\text{)}_3$$

Decay of the radical concentration was monitored in time-resolved experiments in the absence and presence of HBr (using varied concentrations) to obtain the second-order rate constant $k_1$ of reaction 1. Experiments were conducted under pseudo-first-order conditions (HBr in large excess over Si(CH₃)₃ radical). Initial concentrations were chosen to essentially isolate the reaction of interest. The initial concentration of Si(CH₃)₃ was kept low (1.0–8.0) × 10¹¹ molecules cm⁻³ to ensure that radical—radical recombination had a negligible rate compared to the elementary reaction of interest.

Under the typical conditions used, trimethylsilyl radicals, Si(CH₃)₃, were lost only by reaction 1 and by a kinetically first-order heterogeneous loss process:

$$\text{Si(CH}_3\text{)}_3 \rightarrow \text{heterogeneous loss} \quad (2)$$

¹ Deceased November 1993.
* To whom correspondence should be addressed.
the latter parameter is not expected to affect the rate constant in these experiments. The majority of experiments were done using a total gas density of $6 \times 10^{12}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$, where the uncertainty includes possible systematic errors, is in excellent agreement with kinetic data published earlier.\textsuperscript{17} and the result for tert-butyl of (4.1 $\pm$ 0.6) $\times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is in reasonable agreement.

**Flash Photolysis/Resonance Fluorescence Spectroscopy.** The details of the FP-RF apparatus have been given earlier.\textsuperscript{18,19} as has a preliminary report of room-temperature measurements of $k_1$.\textsuperscript{7} Briefly, Si(CH$_3$)$_3$ was generated in the presence of excess HBr by photolysis of Si$_2$(CH$_3$)$_6$ with a small flash lamp through magnesium fluoride or Suprasil quartz optics. Si(CH$_3$)$_3$ reacted under pseudo-first-order conditions and the kinetics were monitored by vacuum UV resonance fluorescence of the atomic Br product at 134–140 nm,\textsuperscript{20} excited from a microwave resonance lamp through which flowed a dilution of CH$_3$Br$_2$ in Ar, with photon counting and multichannel scaling. The lamp had calcium fluoride optics to block any Lyman $\alpha$ radiation. A slow flow of reagents, diluted in a large excess of Ar buffer gas, passed through the reactor to ensure a fresh mixture was photolyzed by each flash (repetition rate $\approx$ 1 Hz). Around $10^{15}$–$10^{16}$ molecules cm$^{-3}$ of HBr were added to the mixtures to ensure any excited Br($^3P_x$) was rapidly quenched to the $^3P_y$ state and thus the observed Br was in thermal equilibrium.\textsuperscript{21} For some experiments the H$_2$ was left out with no observed effect, and in fact (see below) reaction 1 is insufficiently exothermic to produce Br($^3P_x$).

In addition to reaction 1, processes that affect [Br] are

$$\text{Si(CH}_3\text{)}_3 \rightarrow \text{loss without generation of Br} \quad (3)$$

$$\text{Br} \rightarrow \text{loss} \quad (4)$$

and these are described by the pseudo-first-order coefficients $k_3$ and $k_4$. $k_3$ reflects diffusion of trimethylsilyl radicals to the reactor walls and any reactions other than 1 that might consume the radicals. $k_4$ similarly takes account of Br loss through diffusion or reaction and was found to be slow (around 100 s$^{-1}$ or less). Preliminary experiments carried out without precursor showed that photolysis of HBr alone yielded very small [Br], less than 10% of the [Br] obtained when Si(CH$_3$)$_3$ reacted with HBr. Thus [Br] is expected\textsuperscript{21–24} to vary as

$$[\text{Br}] = A \exp(-k_4t) - B \exp(-k_3t) \quad (5)$$

where $k' = k_1[HBr] + k_3$. The four parameters in eq 5 were obtained in two steps for each [HBr] investigated. First, $k_4$ and the background signal from scattered light were obtained from an experiment with a long time base by fitting to the slow exponential decay portion of the Br fluorescence signal. Then this fixed $k_4$ was used in a nonlinear least-squares fit of the fast growth profile, obtained with a short timebase, to the form of eq 5. An example is shown as the insert on Figure 2. Also shown there is a plot of $k'$ vs [HBr], whose slope is the desired $k_3$.

Several experimental parameters were varied to see if they affected the measured $k_1$. The initial [Si(CH$_3$)$_3$] was changed by altering [Si$_2$(CH$_3$)$_6$] and/or the flash energy $F$. The average gas residence time in the heated reactor before photolysis, $\tau_{\text{res}}$, were degassed using freeze–pump–thaw cycles and used without further purification. HBr was passed through six ethanol traps (156 K) to remove Br$_2$ and was distilled daily to remove residual Br$_2$ and H$_2$ as well as other possible impurities. The Br$_2$ impurity in HBr was measured daily and found to be $\leq 0.1\%$. In addition, the purity of HBr was controlled in an indirect way by means of periodical measurements of the rate constants of the reactions of alkyl radicals with HBr at room temperature. The result for methyl plus HBr, (3.0 $\pm$ 0.5) $\times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, where the uncertainty includes possible systematic errors, is in excellent agreement with kinetic data published earlier.\textsuperscript{17} and the result for tert-butyl of (4.1 $\pm$ 0.6) $\times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is in reasonable agreement.

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The Reaction \( \text{Si(CH}_3\text{)}_3 + \text{HBr} \leftrightarrow \text{Si(CH}_3\text{)}_3\text{H} + \text{Br} \)

was varied to verify that no thermal decomposition of the reagents occurred. At room temperature two different reactors were employed, one constructed from stainless steel with i.d. 2.2 cm and one from Pyrex tubing with i.d. 2.7 cm. The larger reactor gave to verify \([\text{HBr}]\) in the reactor by the extent of absorption of the vacuum UV Hg spectral line at 185 nm. The steel or Pyrex were employed, one constructed from stainless steel with i.d. 5.9 cm and one from Pyrex tubing with i.d. 2.7 cm. The larger reactor sidearms were extended to provide a path length for yield was saturated after 20 min. All reported data were taken after 20 min of the start of experiments were lower than the rest. Apparently, steel but not Pyrex adsorbed HBr, and the surface was no significant loss of HBr under slow flow conditions, and was occasionally lost in the gas-handling system or by the extent of absorption of the vacuum UV Hg spectral line at 185 nm. The steel or Pyrex reactor sidearms were extended to provide a path length for absorption of about 70 cm. In the Pyrex reactor absorption cross sections \(\epsilon\) (base e) with static HBr mixtures of 1.85 and 1.92 \(\times 10^{-18}\) cm\(^2\) molecule\(^{-1}\) were obtained, and \(\epsilon = 1.95 \times 10^{-18}\) cm\(^2\) molecule\(^{-1}\) with a slow flow of diluted HBr. These values agree with literature data for \(\epsilon = 1.77,25 2.20,26 2.27,27\) and \(2.428 \times 10^{-18}\) cm\(^2\) molecule\(^{-1}\). Static mixtures in the steel reactor gave \(\epsilon\) values smaller by a factor of 4 or more but slow flows, similar to those employed in the kinetic experiments, yielded \(\epsilon = 1.84 \times 10^{-18}\) cm\(^2\) molecule\(^{-1}\). Thus there was no significant loss of HBr under slow flow conditions, and \(\epsilon\) reached a steady value after about 20 min. It was noted that in the kinetic experiments any \(k_t\) measurements taken within 20 min of the start of experiments were lower than the rest. Apparently, steel but not Pyrex adsorbed HBr, and the surface was saturated after 20 min. All reported data were taken after this had occurred. These checks of \(\epsilon\) were based on Beer-Lambert plots over the approximate \([\text{HBr}]\) range 0 to \(10^{-16}\) cm\(^{-3}\). Kinetic experiments were made over the lower range 0 to \(10^{-15}\) cm\(^{-3}\), so \([\text{HBr}]\) was also tested by measuring \(k\) for ethyl and tert-butyl radicals plus HBr under various conditions (Pyrex and steel reactors. MgF\(_2\) and Suprasil photolysis windows) at 295 K. The result for C\(_2\)H\(_5\) + HBr was \((7.2 \pm 0.4) \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), close to earlier values of \((8.1 \pm 1.6) \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \(\pm 2\sigma\). For tert-C\(_3\)H\(_5\) + HBr we obtained \(k = (2.8 \pm 0.7) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \((\pm 2\sigma)\), in good accord with previous room-temperature values of \((2.7 \pm 0.3) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \(\pm 2\sigma\), and \((3.2 \pm 1.0) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

The wavelength cutoff of the actinic radiation was varied at room temperature by using MgF\(_2\) (\(\lambda > 120\) nm) or Suprasil quartz (\(\lambda > 165\) nm) optics. The photolysis photons are sufficiently energetic to break C-H or Si-C bonds in Si\(_2\)(CH\(_3\))\(_3\), but the rate constants for H and CH\(_3\) with HBr are an order of magnitude smaller than \(k_t\). In the Pyrex reactor Br diffusion was so slow that a minor, slow contribution to [Br] growth was visible with MgF\(_2\), but not Suprasil, photolysis. This is possibly attributable to formation by photolysis of 10% or less of H and/or CH\(_3\) relative to Si(CH\(_3\))\(_3\) at the shorter wavelengths (probably CH\(_3\); see below), which then reacted slowly with HBr to release Br. This slow pathway did not affect the derived \(k_t\) values. At higher temperatures MgF\(_2\) photolysis was employed exclusively because it gave higher [Si(CH\(_3\))]$_3$. Ar (Big Three, 99.998%) was used directly from the cylinder. Commercial HBr (Matheson, 99.8%) was separated from large fractions, around 40%, of more volatile impurities such as H\(_2\) by repeated freeze–pump–thaw cycles at 77 K. Then less volatile impurities such as Br\(_2\) were removed by distilling the HBr three times from 156 to 77 K. The pure HBr and all dilutions in Ar were stored in darkened Pyrex bulbs, and the gas-handling line was also darkened. Periodic condensations and distillations at 77 K verified that no H\(_2\) formed during storage of the HBr, which was redistilled periodically during the course of the experiments, and checks based on vacuum UV photometry and the rate constants with alkyl radicals have been outlined above. Si\(_2\)(CH\(_3\))\(_6\) (Aldrich, 98%) was degassed by multiple freeze–pump–thaw cycles at 77 K.

Results

The conditions used in the FP-PIMS experiments and a summary of the results obtained (rate constants of reaction 1) are presented in Table 1. The Arrhenius plot of \(k_t\) is shown in Figure 3, and the best fit is

\[
k_t = (1.06 \pm 0.13) \times 10^{-11} \times e^{-(6.14 \pm 0.31) \times 10^{-1}} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}
\]

for \(T = 296-702\) K, where the quoted errors in the Arrhenius parameters are \(1\sigma\) and are statistical only. The \(1\sigma\) precision of the fitted \(k_t\) itself is about 5%.

The FP-RF results are summarized in Table 2, and the Arrhenius plot of the \(k_t\) data averaged at each temperature is
removal of trimethylsilyl radicals by HBr. In preliminary
measurements performed with resonance fluorescence detection of atomic H (without a CaF2 window) gave no H-atom signal, suggesting that the reaction precursor at T = 289–515 K, where the statistical errors are 1σ. The statistical uncertainty in the fitted kl is about 10%.

Both experimental techniques yield the rate constant for the removal of trimethylsilyl radicals by HBr. In preliminary experiments Si(CH3)3 photolysis through MgF2 optics combined with resonance fluorescence detection of atomic H (without a CaF2 window) gave no H-atom signal, suggesting that the methyl C–H bonds were not significantly photolyzed and that the ratio kl/klb, where klb describes the channel

\[
\text{Si(CH}_3\text{)}_3 + \text{HBr} \rightarrow \text{Si(CH}_3\text{)}_2\text{Br} + \text{H}
\]  

(1b)
is small and less than about 0.1. Thus the measured kl can be attributed entirely to reaction 1. kl = (7.8 ± 0.8) × 10^{-11} cm^3 molecule^{-1} s^{-1} was obtained previously with the Si(CH3)3I precursor at T ≈ 293 K,7 close to the values found in this work with different sources of Si(CH3)3.

The FP-PIMS and FP-RF techniques yielded values for kl that are in fair accord, and both confirm negative activation energies for reaction 1. The Arrhenius parameters agree, although the FP-PMS fit is about a factor of 1.8 higher than the FP-RF fit. There are no obvious sources of error and, especially given the good accord for the analogous alkyl radical + HBr reactions, the difference is unexplained but has a minor impact on the thermochemical analysis.

**Thermochemical Calculations**

To calculate the equilibrium constant of reaction 1 (k_f/k_i = K_c ≡ Kp, here) the rate constants measured as a function of temperature in this study were combined with the rate constants for the reverse reaction measured by Ding and Marshall:6

\[
k_{-1} = (7.6 ± 3.3) \times 10^{-10} \times \exp(-28.4 \pm 1.3 \text{ kJ mol}^{-1}/RT) \tag{6}
\]

The standard enthalpy of reaction 1 was determined from the slope of the modified van’t Hoff plot:29–31

\[
\ln(K_p) + \text{correction} = \Delta S^0_{p,298} - \Delta H^0_{p,298}/RT \tag{7}
\]
TABLE 3: Calculated Thermodynamic Functions of Si(CH₃)₃H (Standard State 1 bar = 10⁻¹⁰ Pa)*

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<th>T (K)</th>
<th>S°₁ (J mol⁻¹ K⁻¹)</th>
<th>H°F₂₉₈ - H°F₁₉₈ (kJ mol⁻¹)</th>
<th>C°E₂₉₈ (J mol⁻¹ K⁻¹)</th>
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</table>

* Si(CH₃)₃H molecular parameters: molecular mass 74.055 23 amu; vibrational frequencies (cm⁻¹) 190, 192, 273, 503, 603, 662, 677, 832, 832, 859, 897, 998, 1296, 1303, 1428, 1430, 1439, 1439, 1444, 2080, 2846, 2847, 2848, 2904, 2905, 2907, 2908, 2910, and 2910; main moments of inertia of 1.599 × 10⁻⁴⁵ kg m², 1.599 × 10⁻⁴⁵ kg m², and 1.599 × 10⁻⁴⁵ kg m²; symmetry number for external rotation, αₑₓ = 3; three hindered rotors with the reduced moments of inertia of 4.982 × 10⁻⁴⁵ kg m², 4.985 × 10⁻⁴⁵ kg m², and 4.988 × 10⁻⁴⁵ kg m², and barriers for internal rotations of 3.91, 4.89, and 4.93 kJ mol⁻¹, respectively; symmetry numbers for all internal rotors αₖⁱᵐ⁻¹ = 3; electronic degeneracy = 1. b Moments of inertia of internal and external rotation calculated using ab initio molecular geometry.}

The reaction Si(CH₃)₃ + HBr ⇌ Si(CH₃)₃H + Br. Shown are the second law (dashed lines) and third law (solid lines) fits of the FP-PIMS (○) and FP-RF (●) data. The point at 1/T = 0 (●) used in the third law procedure was calculated from the standard entropies of the reagent and product molecules (see text). The correction was calculated using the thermodynamic functions of HBr, Br, 32 Si(CH₃)₃, 32 Si(CH₃)₃H, Si(CH₃)₃H (Tables 3 and 4). Thermodynamic properties of Si(CH₃)₃H were determined by statistical mechanics from its calculated HF/6-31G* level of theory. Allendorf and Melius. The parameters used and results of thermodynamic calculations for Si(CH₃)₃H are presented in Tables 3 and 4. Barriers to internal rotation of the methyl groups were calculated from the ab initio torsional frequencies and assumed three-cycle sinusoidal potentials for the internal rotations. Contributions to thermodynamic functions by these hindered rotors were obtained by linear interpolation of tables. Because similar hindered internal rotors are present in Si(CH₃)₃, also, their contributions to ΔH and ΔS for reaction 1 largely cancel and the thermodynamic calculations are insensitive to uncertainties in the rotational potentials.

Both second law and third law methods were used to obtain the standard enthalpy of reaction, ΔH₂₉₈. In the second law procedure, the standard entropy and enthalpy of reaction 1 in eq 7 were determined as the parameters of the best linear fits to a plot of ln(Kₚ) + correction vs 1/T (Figure 5). The fit yielded

ΔH₂₉₈ = -34.6 ± 1.6 kJ mol⁻¹ (second law procedure, FP-PIMS data) (9)

ΔS₂₉₈ = -35.8 ± 3.8 J mol⁻¹ K⁻¹ (second law procedure, FP-RF data) (10)

The 1σ uncertainties indicate the combined errors of the activation energies for the reverse and forward reactions, since in the absence of the correction term in eq 7 the outlined procedure is equivalent to assigning the difference of the activation energies of forward and reverse reaction to ΔH₂₉₈. For the standard entropy of reaction 1, ΔS₂₉₈, the intercept of the same fit yielded

ΔS₂₉₈ = -37.9 ± 4.2 J mol⁻¹ K⁻¹ (second law procedure, FP-RF data) (10)

The 1σ uncertainties reflect the combined errors of the preexponential A factors for k₁ and k⁻¹ since, in the absence of the correction term, ΔS₂₉₈ = R ln(A₁/A⁻¹). The third law procedure uses the calculated value of the standard entropy of reaction, and, therefore, has only one fitting

TABLE 4: Coefficients of NASA Polynomials for HBr, Si(CH₃)₃, Br, and Si(CH₃)₃H

<table>
<thead>
<tr>
<th>molecule</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
<th>a₄</th>
<th>a₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td>3.4450</td>
<td>7.3294e⁻⁴</td>
<td>-3.2715e⁻⁶</td>
<td>5.8600e⁻⁹</td>
<td>-2.9366e⁻¹²</td>
</tr>
<tr>
<td>Si(CH₃)₃</td>
<td>7.2023</td>
<td>7.7492e⁻⁴</td>
<td>6.8011e⁻⁵</td>
<td>-1.0592e⁻⁷</td>
<td>4.916e⁻¹¹</td>
</tr>
<tr>
<td>Br</td>
<td>2.4930</td>
<td>7.4172e⁻⁴</td>
<td>-2.5340e⁻⁷</td>
<td>2.8937e⁻¹⁰</td>
<td>2.2604e⁻¹⁴</td>
</tr>
<tr>
<td>Si(CH₃)₃H</td>
<td>6.4573</td>
<td>1.4566e⁻²</td>
<td>6.1734e⁻⁵</td>
<td>-1.0177e⁻⁷</td>
<td>4.8453e⁻¹¹</td>
</tr>
</tbody>
</table>

* Polynomial representation of heat capacities: C_p(T)/R = a₁ + a₂T + a₃T² + a₄T³ + a₅T⁴. b Fitting of the data from ref 32 over the temperature range 200–800 K. c AeB = A × 10^B. d Fitting of the data from ref 13 over the temperature range 200–800 K. e Temperature range of the fit 200–800 K.
parameter, $\Delta H^\circ_{298}$. The statistical mechanical value of the standard entropy of reaction 1 is

$$\Delta S^\circ_{298} = -28.3 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{(calculated)} \quad (11)$$

This value is somewhat more positive than the values in eq 10. The absolute theoretical entropies depend strongly on loose torsional motions, which are the degrees of freedom least reliably characterized ab initio. However, as noted above, this uncertainty mainly cancels in $\Delta S$. On the other hand the extrapolated intercept of a van't Hoff plot may be affected by small systematic errors at the ends of the temperature range. We prefer the calculated $\Delta S$ and this value is shown as the intercept ($\Delta S^\circ_{298}/R$) of the straight lines drawn through the corrected equilibrium constants in the third law procedure (Figure 5). The slopes of these lines yielded the standard enthalpy of reaction 1:

$$\Delta H^\circ_{298} = -31.9 \pm 1.1 \text{ kJ mol}^{-1}$$

(third law procedure, FP-PIMS data) \quad (12)

$$= -30.2 \pm 1.2 \text{ kJ mol}^{-1}$$

(third law procedure, FP-RF data)

The 1σ statistical uncertainties indicated were estimated as follows. The accuracy of the equilibrium constant was estimated in the middle part of the reciprocal temperature range studied. This includes uncertainties in the fit preexponential factors and activation energies in the expressions for $k_1$ and $k_2$, as well as the temperature uncertainty (±5 K) and an allowance for possible ±1 J mol$^{-1} \text{ K}^{-1}$ systematic errors in the calculated $\Delta S^\circ_{298}$. The effect of these uncertainties on the slope of the lines in the third law procedure (Figure 5) was then evaluated and resulted in the σ values indicated above.

The second and third law values for $\Delta H^\circ_{298}$ and $\Delta S^\circ_{298}$ are generally consistent at the 2σ significance level, except that the second law values for $\Delta H^\circ_{298}$ are more negative than those from the third law calculations. The third law values are inherently more precise because errors in the Arrhenius parameters tend to cancel in the fitted rate constant, i.e., positive errors in A correlate with a positive error in the activation energy through the covariance.\textsuperscript{35} We combine the estimates of $\Delta H^\circ_{298}$ above to recommend a value of $-31.1 \text{ kJ mol}^{-1}$, based on the more precise third law analyses. Possible systematic errors may be assessed from the values of $\Delta H^\circ_{298}$ derived from the two different techniques, and suggested accuracy limits are about ±2 kJ mol$^{-1}$.

$\Delta H^\circ_{298}$ for reaction 1 is the difference between the bond dissociation enthalpies $D_{298}(\text{H-Si})$ and $D_{298}(\text{H-B})$. $D_{298}(\text{H-Si})$ is well-characterized at 366.3 kJ mol$^{-1}$,\textsuperscript{32} so that $D_{298}(\text{H-B}) - D_{298}(\text{H-Si}) = 397.4 \pm 2 \text{ kJ mol}^{-1}$. This value is higher than the most previous measurements$^{37-39,42}$ but can be compared with the results of this work.

The two $a b$ initio values$^{6,33}$ in Table 5 are in excellent agreement with our result. Our $D_{298}(\text{Si(\text{CH}_3)})$ may be combined with the $D_{298}(\text{Si(\text{CH}_3)})$ of 218.0 kJ mol$^{-1}$ for atomic H$^2$ and $-163 \pm 4 \text{ kJ mol}^{-1}$ for Si(\text{CH}_3)$^2$ to yield $\Delta H^\circ_{298}$ for the trimethylsilyl radical of 16.4 ± 6 kJ mol$^{-1}$. The most recent independent measurement of $\Delta H^\circ_{298}(\text{Si(\text{CH}_3)}) = 14 \pm 7 \text{ kJ mol}^{-1}$, derived from an RRKM fit to Si(\text{CH}_3)$_3$ pyrolysis by Bullock et al.,\textsuperscript{44} is in excellent accord.

Comparison of the Si–H bond strength of trimethylsilane with that measured for SiH$_4$, 384.1 ± 20 kJ mol$^{-1}$,\textsuperscript{3} shows that methyl substitution increases the Si–H bond strength. This effect is opposite to hydrocarbons, where $D_{298}$(CH$_3$–H)$^{10}$ is 441 kJ mol$^{-1}$ and $D_{298}$(C(\text{CH}_3)$_3$–H) is 404 kJ mol$^{-1}$,\textsuperscript{17} A possible

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**TABLE 5: Measurements of the Si–H Bond Dissociation Energy in Trimethylsilane**

<table>
<thead>
<tr>
<th>$D_{298}(\text{Si(\text{CH}_3}))^\circ$</th>
<th>technique</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>368 ± 42</td>
<td>electron impact</td>
<td>36</td>
</tr>
<tr>
<td>356</td>
<td>HT yield from reaction with hot T atoms</td>
<td>37</td>
</tr>
<tr>
<td>372 ± 17</td>
<td>electron impact</td>
<td>38</td>
</tr>
<tr>
<td>364</td>
<td>pulsed stirred-flow reactor</td>
<td>39</td>
</tr>
<tr>
<td>378 ± 6</td>
<td>ionization</td>
<td>40</td>
</tr>
<tr>
<td>382 ± 7</td>
<td>pulsed photolysis-resonance absorption</td>
<td>41</td>
</tr>
<tr>
<td>377 ± 5</td>
<td>very low pressure reactor</td>
<td>42</td>
</tr>
<tr>
<td>357</td>
<td>overture spectroscopy</td>
<td>4</td>
</tr>
<tr>
<td>324</td>
<td>overture spectroscopy</td>
<td>5</td>
</tr>
<tr>
<td>398 ± 6</td>
<td>FP-RF</td>
<td>6</td>
</tr>
<tr>
<td>397</td>
<td>ab initio theory</td>
<td>6</td>
</tr>
<tr>
<td>396</td>
<td>ab initio theory</td>
<td>33</td>
</tr>
<tr>
<td>398 ± 2</td>
<td>FP-RF</td>
<td>7</td>
</tr>
<tr>
<td>397 ± 2</td>
<td>FP-PIMS and FP-RF</td>
<td>this work</td>
</tr>
</tbody>
</table>

* Rounded to the nearest 1 kJ mol$^{-1}$. Not all authors quote uncertainties. \textsuperscript{b} Obtained from the measured $D(\text{D-Si(\text{CH}_3}))$ by subtrac down the zero-point vibrational energy difference of 6 kJ mol$^{-1}$ from $D(\text{Si(\text{CH}_3}))$.

Rationalization is based on the relative electronegativities of silicon and carbon. The electron-deficient central C atom in C(CH$_3)_3$ is stabilized by donation from the methyl groups, the inductive effect. C is more electronegative than Si, so that the Si(CH$_3)_3$ radical is destabilized by electron withdrawal by the methyl groups.

**Conclusions**

Data obtained via two independent techniques, which follow the kinetics of the reactants and products of the reaction of Si(CH$_3)_3$ with HBr, yield $\Delta S$ and $\Delta H$ values via second and third law methods in good accord. The results imply an Si–H bond strength and enthalpy of formation for trimethylsilyl in accord with the most recent of other experimental and theoretical determinations and confirm that methyl substitution increases the Si–H bond energy by about 13 kJ mol$^{-1}$ relative to SiH$_4$.

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**References and Notes**


The Reaction $\text{Si(CH}_3\text{)}_3 + \text{HBr} \rightleftharpoons \text{Si(CH}_3\text{)}_3\text{H} + \text{Br}$

(15) Halocarbon Wax is a product of Halocarbon Wax Corp., Hackensack, NJ.