Kinetics and Thermochemistry of the Reaction $\text{Si}(\text{CH}_3)_3 + \text{HBr} \rightleftharpoons \text{Si}(\text{CH}_3)_3\text{H} + \text{Br}$: Determination of the $(\text{CH}_3)_3\text{Si}-\text{H}$ Bond Energy

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The reaction $\text{Si}(\text{CH}_3)_3 + \text{HBr} \rightarrow \text{Si}(\text{CH}_3)_3\text{H} + \text{Br}$ (1) has been investigated using flash photolysis/photoionization mass spectrometry detection of $\text{Si}(\text{CH}_3)_3$ and flash photolysis/resonance fluorescence spectroscopy detection of Br. The measured rate constants are $k_1 = (1.06 \pm 0.13) \times 10^{-11} \exp((6.14 \pm 0.31) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $T = 296\text{--}702 \text{ K}$ and $k_1 = (8.1 \pm 2.0) \times 10^{-12} \exp((5.12 \pm 0.72) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $T = 289\text{--}515 \text{ K}$, respectively. The 1σ uncertainties represent precision only. Combination with k_{-1} data and analysis by second and third law methods yields $\Delta H^\circ_{298} = -31.1 \text{ kJ mol}^{-1}$ for (1), with accuracy limits of about $\pm 2.0 \text{ kJ mol}^{-1}$. The results imply an Si–H bond dissociation enthalpy of $397.4 \pm 2 \text{ kJ mol}^{-1}$ and an enthalpy of formation for trimethylsilyl of $16.4 \pm 6.0 \text{ kJ mol}^{-1}$.

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 trimethylsilyl radical. Previous recommendations,^{1,2} based partly on iodination kinetics, suggested that the bond strength was similar to that measured for SiH_4 ,³ while spectroscopic studies suggested significant Si–H bond weakening by methyl groups.^{4,5} Two previous studies of the kinetics of the system

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 SiH_4 .

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 procedures^{9–11} 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 ($\approx 5 \text{ m s}^{-1}$ when the small reactor was used and $\approx 3 \text{ m s}^{-1}$ 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 $\text{Si}_2(\text{CH}_3)_6$ as the $\text{Si}(\text{CH}_3)_3$ radical precursor.^{12,13} Additional experiments were conducted using $\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3$ ¹³ 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 $\text{Si}(\text{CH}_3)_3$ radical formation:

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 $\text{Si}(\text{CH}_3)_3$ radical). Initial concentrations were chosen to essentially isolate the reaction of interest. The initial concentration of $\text{Si}(\text{CH}_3)_3$ was kept low ($(1.0\text{--}8.0) \times 10^{11} \text{ molecules cm}^{-3}$) to ensure that radical–radical recombination had a negligible rate compared to the elementary reaction of interest.

Under the typical conditions used, trimethylsilyl radicals, $\text{Si}(\text{CH}_3)_3$, were lost only by reaction 1 and by a kinetically first-order heterogeneous loss process:

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Figure 1. Plot of the pseudo-first-order rate constant of $\text{Si}(\text{CH}_3)_3$ radical decay vs HBr concentration measured by FP-PIMS at 419 K. Insert shows the actual $\text{Si}(\text{CH}_3)_3^+$ ion signal profile recorded during the measurement which is marked by the solid circle on the k' vs $[\text{HBr}]$ plot. For this experiment $[\text{HBr}] = 8.99 \times 10^{12} \text{ molecules cm}^{-3}$. The first-order decay constant is $807 \pm 17 \text{ s}^{-1}$.

Measurements of the radical exponential decay constant, k' , as a function of the concentration of the second reactant, $[\text{HBr}]$, yielded the rate constant of reaction 1. A sample measured decay profile of $\text{Si}(\text{CH}_3)_3$ and a plot of the decay constants vs $[\text{HBr}]$ from one set of experiments are shown in Figure 1.

The wall loss rate constant k_w of the trimethylsilyl radical in an uncoated 1.05-cm-i.d. Pyrex reactor is too high ($> 1000 \text{ s}^{-1}$) to permit kinetic measurements. The halogenated material, Halocarbon Wax,¹⁵ used as a coating in previous studies of other silicon-centered radicals¹² was found to increase the wall loss rate for this particular radical, rather than reduce it. To reduce the wall loss rate constant a boron oxide, B_2O_3 , coating was used.¹³

Most of the measurements in this study were performed with a 1.05-cm-i.d. Pyrex reactor coated with boron oxide. One series of experiments was conducted in a similarly coated 2.2-cm-i.d. Pyrex reactor to change the surface/volume ratio in order to verify that proper account was taken of the heterogeneous reactions. Use of either reactor yielded the same rate constants, indicating that heterogeneous bimolecular reactions involving HBr, if they occurred, were of negligible importance in these experiments. The majority of experiments were done using a total gas density of $6 \times 10^{16} \text{ molecules cm}^{-3}$. Although the latter parameter is not expected to affect the rate constant of reaction 1 over the range of densities of this study, additional measurements at ambient temperature were performed at a total gas density of $2 \times 10^{16} \text{ molecules cm}^{-3}$. These measurements resulted in the same rate constant within the accuracy of measurements.

$\text{Si}(\text{CH}_3)_3$ radicals were detected at $m/z = 73$ (parent peak) using a Hg resonance lamp with a quartz window as a photoionization source ($h\nu = 6.706 \text{ eV}$; ionization potential of $\text{Si}(\text{CH}_3)_3 \approx 6.5 \text{ eV}^{16}$). The photon energy of the mercury lamp is higher than the ionization potential of the $\text{Si}(\text{CH}_3)_3$ radical only by 0.2 eV. This made it possible to obtain a very clean signal of the trimethylsilyl ion that was virtually free from the baseline component which originates from dissociative photoionization and photoelectron impact dissociative ionization of the radical precursor.

The reagents were obtained from Aldrich: $\text{Si}_2(\text{CH}_3)_6$, 98%; $\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3$, 99%; HBr, >99%. Helium (HP) obtained from Matheson was used as supplied. The free-radical precursors

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, $(3.0 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the uncertainty includes possible systematic errors, is in excellent agreement with kinetic data published earlier,¹⁷ and the result for *tert*-butyl of $(4.1 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in reasonable agreement.

Flash Photolysis/Resonance Fluorescence Spectroscopy.

The details of the FP-RF apparatus have been given earlier,^{18,19} as has a preliminary report of room-temperature measurements of k_1 .⁷ Briefly, $\text{Si}(\text{CH}_3)_3$ was generated in the presence of excess HBr by photolysis of $\text{Si}_2(\text{CH}_3)_6$ with a small flash lamp through magnesium fluoride or Suprasil quartz optics. $\text{Si}(\text{CH}_3)_3$ 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,²⁰ excited from a microwave resonance lamp through which flowed a dilution of CH_2Br_2 in Ar, with photon counting and multichannel scaling. The lamp had calcium fluoride optics to block any Lyman α 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 $\approx 1 \text{ Hz}$). Around 10^{15} – $10^{16} \text{ molecules cm}^{-3}$ of H_2 were added to the mixtures to ensure any excited $\text{Br}(^2\text{P}_{1/2})$ was rapidly quenched to the $^2\text{P}_{3/2}$ state and thus the observed Br was in thermal equilibrium.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 $\text{Br}(^2\text{P}_{1/2})$.

In addition to reaction 1, processes that affect $[\text{Br}]$ are

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 $[\text{Br}]$, less than 10% of the $[\text{Br}]$ obtained when $\text{Si}(\text{CH}_3)_3$ reacted with HBr. Thus $[\text{Br}]$ is expected^{21–24} to vary as

$$[\text{Br}] = A \exp(-k_4 t) - B \exp(-k' t) \quad (5)$$

where $k' = k_1[\text{HBr}] + k_3$. The four parameters in eq 5 were obtained in two steps for each $[\text{HBr}]$ 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 $[\text{HBr}]$, whose slope is the desired k_1 .

Several experimental parameters were varied to see if they affected the measured k_1 . The initial $[\text{Si}(\text{CH}_3)_3]$ was changed by altering $[\text{Si}_2(\text{CH}_3)_6]$ and/or the flash energy F . The average gas residence time in the heated reactor before photolysis, τ_{res} ,

Figure 2. Plot of the pseudo-first-order rate constant of $\text{Si}(\text{CH}_3)_3$ radical decay vs HBr concentration measured by FP-RF at 396 K and $[\text{Ar}] = 5.9 \times 10^{17}$ molecules cm^{-3} . Insert shows the Br fluorescence signal plus background recorded during the measurement which is marked by the solid circle on the k' vs $[\text{HBr}]$ plot.

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 reaction zone in the latter system led to smaller k_4 values because diffusion of Br to the walls took longer. There is a possibility of loss of HBr by adsorption on surfaces in the gas-handling system or reactor, so that separate experiments were carried out 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 reactor sidearms were extended to provide a path length for absorption of around 70 cm. In the Pyrex reactor absorption cross sections ϵ (base e) with static HBr mixtures of 1.85 and 1.92×10^{-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 ϵ of 1.77,²⁵ 2.20,²⁶ 2.2,²⁷ and $2.42^{28} \times 10^{-18}$ cm^2 molecule $^{-1}$. Static mixtures in the steel reactor gave ϵ values smaller by a factor of 4 or more but slow flows, similar to those employed in the kinetic experiments, yielded $\epsilon = 1.84$ and 2.11×10^{-18} cm^2 molecule $^{-1}$. Thus there was no significant loss of HBr under slow flow conditions, and ϵ reached a steady value after about 20 min. It was noted that in the kinetic experiments any k_1 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 ϵ were based on Beer–Lambert plots over the approximate $[\text{HBr}]$ range 0 – 10^{16} cm^{-3} . Kinetic experiments were made over the lower range 0 – 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 $\text{C}_2\text{H}_5 + \text{HBr}$ was $(7.2 \pm 0.4) \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} , close to earlier values of $(8.1 \pm 1.6)^{21}$ and $(9.3 \pm 0.6) \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1} ,¹⁷ where the errors represent $\pm 2\sigma$. For *tert*- $\text{C}_4\text{H}_9 + \text{HBr}$ 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 $(2.7 \pm 0.3)^{21}$ $(3.2 \pm 0.4)^{17}$ and $(3.2 \pm 1.0) \times 10^{-11}$ cm^3 molecule $^{-1}$ s^{-1} .²⁴

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 $\text{Si}_2(\text{CH}_3)_6$,¹ but the rate constants for H and CH_3 with HBr are an order of magnitude smaller than k_1 .^{17,21–23} In the Pyrex reactor Br diffusion was so slow that a minor, slow contribution to $[\text{Br}]$ growth was visible with MgF_2 , but not Suprasil, photolysis. This

TABLE 1: FP-PIMS Reaction Conditions and Rate Constants for the $\text{Si}(\text{CH}_3)_3 + \text{HBr}$ Reaction

T^a (K)	$[\text{He}]$ (10^{16} molecules cm^{-3})	$[\text{HBr}]$ (10^{12} molecules cm^{-3})	k_w (s^{-1})	k^b (10^{-11} cm^3 molecule $^{-1}$ s^{-1})
296	6.00	1.23–4.61	339	11.8 ± 0.71
300 ^c	2.12	1.10–3.94	162	13.2 ± 0.65
300 ^{c,d}	5.97	1.34–4.02	235	13.2 ± 0.70
301	6.00	1.83–4.54	370	12.2 ± 0.59
301 ^c	5.94	1.32–4.75	169	11.9 ± 0.21
305	6.00	0.79–4.24	428	12.6 ± 0.46
322	6.00	1.30–4.64	347	9.30 ± 0.38
349	6.00	2.07–4.87	322	7.49 ± 0.36
419	6.00	2.64–8.99	254	6.16 ± 0.14
419 ^d	5.98	1.21–7.64	260	7.75 ± 0.36
436 ^c	6.00	1.30–4.77	130	6.84 ± 0.25
529	6.00	2.15–9.72	252	4.78 ± 0.11
605	6.00	1.65–11.1	255	3.48 ± 0.12
626 ^c	6.00	1.82–7.44	115	3.20 ± 0.11
626 ^{c,d}	6.02	3.43–7.79	150	3.32 ± 0.19
702	5.99	3.36–13.2	247	2.79 ± 0.11

^a Temperature uncertainty ± 3 K. ^b Errors are 1σ and refer to statistical uncertainties only. ^c 2.20-cm-i.d. B_2O_3 -coated Pyrex reactor, in all other experiments 1.05-cm-i.d. B_2O_3 -coated Pyrex reactor. ^d $\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3$ as a free-radical precursor (193 nm photolysis), in all other experiments $\text{Si}_2(\text{CH}_3)_6$ as a precursor (193 nm).

is possibly attributable to formation by photolysis of 10% or less of H and/or CH_3 relative to $\text{Si}(\text{CH}_3)_3$ 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_1 values. At higher temperatures MgF_2 photolysis was employed exclusively because it gave higher $[\text{Si}(\text{CH}_3)_3]$.

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. $\text{Si}_2(\text{CH}_3)_6$ (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_1 is shown in Figure 3, and the best fit is

$$k_1 = (1.06 \pm 0.13) \times 10^{-11} \times \exp((6.14 \pm 0.31) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for $T = 296$ – 702 K, where the quoted errors in the Arrhenius parameters are 1σ and are statistical only. The 1σ precision of the fitted k_1 itself is about 5%.

The FP-RF results are summarized in Table 2, and the Arrhenius plot of the k_1 data averaged at each temperature is

Figure 3. Arrhenius dependence of the rate constant of the reaction $\text{Si}(\text{CH}_3)_3 + \text{HBr}$ measured using FP-PIMS with different reactor diameters and free-radical precursors: (○) 1.05-cm-i.d. reactor and $\text{Si}_2(\text{CH}_3)_6$ as a precursor; (■) 1.05-cm-i.d. reactor and $\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3$; (□) 2.20-cm-i.d. reactor and $\text{Si}_2(\text{CH}_3)_6$; (△) 2.20-cm-i.d. reactor and $\text{C}_3\text{H}_5\text{Si}(\text{CH}_3)_3$. All at $[\text{He}] = 6 \times 10^{16} \text{ molecules cm}^{-3}$. (◆) $[\text{He}] = 2.12 \times 10^{16} \text{ molecules cm}^{-3}$, 2.20-cm-i.d. reactor and $\text{Si}_2(\text{CH}_3)_6$ as a precursor.

Figure 4. Arrhenius dependence of the rate constant of the reaction $\text{Si}(\text{CH}_3)_3 + \text{HBr}$ measured using FP-RF. The points represent averages of 4–10 measurements at each temperature.

shown in Figure 4. The best fit expression is

$$k_1 = (8.1 \pm 2.0) \times 10^{-12} \times \exp((5.12 \pm 0.72) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for $T = 289\text{--}515 \text{ K}$, where the statistical errors are 1σ . The statistical uncertainty in the fitted k_1 is about 10%.

Both experimental techniques yield the rate constant for the removal of trimethylsilyl radicals by HBr. In preliminary experiments $\text{Si}(\text{CH}_3)_3\text{I}$ photolysis through MgF_2 optics combined with resonance fluorescence detection of atomic H (without a CaF_2 window) gave no H-atom signal, suggesting that the methyl C–H bonds were not significantly photolyzed and that the ratio k_{1b}/k_1 , where k_{1b} describes the channel

is small and less than about 0.1. Thus the measured k_1 can be attributed entirely to reaction 1. $k_1 = (7.8 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained previously with the $\text{Si}(\text{CH}_3)_3\text{I}$ precursor at $T \approx 293 \text{ K}$,⁷ close to the values found in this work with different sources of $\text{Si}(\text{CH}_3)_3$.

The FP-PIMS and FP-RF techniques yielded values for k_1 that are in fair accord, and both confirm negative activation energies for reaction 1. The Arrhenius parameters agree, although the FP-PIMS fit is about a factor of 1.8 higher than

TABLE 2: FP-RF Reaction Conditions and Rate Constants for the $\text{Si}(\text{CH}_3)_3 + \text{HBr}$ Reaction

T , K	P , mbar	τ_{res} , s	F , J	$[\text{Si}_2(\text{CH}_3)_6]$, $10^{14} \text{ molecules cm}^{-3}$	$[\text{HBr}]_{\text{max}}$, $10^{13} \text{ molecules cm}^{-3}$	$k_1 \pm \sigma_{k_1}$, $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
287	42.7	0.7	4.05	1.45	9.31	6.92 ± 0.50^a
287	42.7	0.7	4.05	2.38	11.50	5.83 ± 0.30^a
289	31.5	0.5	5.00	1.36	10.60	6.19 ± 0.67^a
289	31.5	0.5	2.45	1.36	7.13	6.49 ± 0.12^a
289	31.6	0.5	4.05	2.45	11.90	6.59 ± 0.52^a
289	31.5	0.5	5.00	1.30	9.91	6.50 ± 0.47^a
289	31.5	0.5	2.45	1.30	9.91	6.22 ± 0.44^a
289	31.3	0.5	4.05	0.87	7.90	6.42 ± 0.17^a
290	32.0	0.5	4.05	0.90	9.95	4.47 ± 0.15^a
290	32.0	0.5	4.05	1.61	8.32	5.96 ± 0.40^a
289						5.94 ± 0.16^b
295 ^c	31.0	1.0	4.05	0.91	4.39	7.22 ± 0.48^a
295 ^c	30.2	1.0	4.05 ^d	0.83	4.26	7.33 ± 0.20^a
295 ^c	31.4	1.9	4.05 ^d	1.03	7.65	5.92 ± 0.37^a
295 ^c	31.4	1.9	4.05 ^d	2.05	7.60	7.43 ± 0.12^a
295 ^c	29.1	1.8	4.05 ^d	0.96	5.53	6.93 ± 0.48^a
295 ^c	29.7	0.9	4.05 ^d	0.97	4.89	6.64 ± 0.30^a
295 ^c	31.0	1.9	5.00 ^d	2.03	10.70	6.11 ± 0.53^a
295 ^c	31.0	1.9	2.45 ^d	2.03	10.70	6.16 ± 0.71^a
295						7.17 ± 0.20^b
323	31.3	0.5	4.05	1.05	7.93	5.52 ± 0.24^a
323	31.3	0.5	4.05	2.58	7.92	4.84 ± 0.29^a
327	40.0	0.6	4.05	2.44	10.20	5.63 ± 0.27^a
327	40.0	0.6	4.05	2.44	9.96	5.74 ± 0.69^a
325						5.38 ± 0.20^b
396	32.0	0.4	4.05	1.60	7.63	4.17 ± 0.13^a
396	32.0	0.4	4.05	0.60	7.61	5.39 ± 0.24^a
404	31.2	0.4	5.00	1.33	7.24	3.73 ± 0.28^a
404	31.2	0.4	2.45	1.33	7.24	4.13 ± 0.19^a
400						4.29 ± 0.14^b
444	40.0	0.4	4.05	1.56	10.00	2.87 ± 0.73^a
444	40.0	0.4	4.05	3.01	9.95	2.93 ± 0.12^a
444	40.0	0.4	5.00	1.33	10.20	2.75 ± 0.13^a
444	40.0	0.4	2.45	1.33	10.20	2.90 ± 0.20^a
449	32.0	0.4	4.05	1.42	5.68	3.36 ± 0.18^a
449	32.0	0.4	4.05	0.78	5.69	3.62 ± 0.23^a
446						3.00 ± 0.10^b
512	32.0	0.3	4.05	1.13	3.77	3.10 ± 0.44^a
515	33.1	0.3	4.05	3.33	5.76	2.28 ± 0.20^a
515	33.1	0.3	4.05	1.27	5.81	2.60 ± 0.19^a
517	32.0	0.3	4.05	1.62	7.08	2.93 ± 0.39^a
515						2.55 ± 0.14^b

^a 1σ statistical precision of the slope of a plot of k' vs $[\text{HBr}]$. ^b 1σ precision of weighted average combined with instrumental precisions. ^c Pyrex reactor employed. All other measurements made in a stainless steel reactor. ^d Photolysis through Suprasil quartz optics. MgF_2 used for all other experiments.

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 ($k_1/k_{-1} = K_c \equiv K_p$ 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

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

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

$$\ln(K_p) + \text{correction} = \Delta S^\circ_{298}/R - \Delta H^\circ_{298}/RT \quad (7)$$

TABLE 3: Calculated Thermodynamic Functions of $\text{Si}(\text{CH}_3)_3\text{H}$ (Standard State 1 bar $\equiv 10^5$ Pa)^a

T (K)	S°_T (J mol ⁻¹ K ⁻¹)	$H^\circ_T - H^\circ_0$ (kJ mol ⁻¹)	C_p° (J mol ⁻¹ K ⁻¹)
150	275.93	8.53	81.30
200	300.84	12.87	92.24
250	322.67	17.77	104.10
298.15	342.04	23.07	115.97
300	342.75	23.29	116.42
350	361.60	29.39	128.64
400	379.56	36.13	140.37
450	396.72	43.41	151.42
500	413.22	51.24	161.72
550	429.10	59.58	171.31
600	444.42	68.39	180.23
650	459.17	77.62	188.6
700	473.43	87.25	196.42
750	487.24	97.27	203.73
800	500.60	107.64	210.59
850	513.55	118.33	217.01
900	526.13	129.33	223.01
950	538.34	140.64	228.62
1000	550.20	152.21	233.85
1100	572.94	176.08	243.32
1200	594.48	200.84	251.54
1300	614.90	226.37	258.70
1400	634.31	252.56	264.91
1500	652.78	279.33	270.32
1600	670.37	306.59	275.06
1700	687.17	334.29	279.20
1800	703.23	362.38	282.83
1900	718.61	390.81	286.03
2000	733.36	419.55	288.86

^a $\text{Si}(\text{CH}_3)_3\text{H}$ molecular parameters: molecular mass 74.055 23 amu; vibrational frequencies (cm⁻¹) 190, 190, 228, 573, 603, 603, 662, 662, 672, 832, 832, 859, 897, 898, 1296, 1296, 1303, 1428, 1430, 1430, 1439, 1439, 1444, 2080, 2846, 2847, 2848, 2904, 2905, 2907, 2908, 2910, and 2910; main moments of inertia^b of 1.599×10^{-45} , 2.714×10^{-45} , and 1.599×10^{-45} kg m²; symmetry number for external rotation, $\sigma_{\text{ext}} = 3$; three hindered rotors with the reduced moments of inertia^b of 4.982×10^{-47} , 4.985×10^{-47} , and 4.988×10^{-47} kg m², and barriers for internal rotations^c of 3.91, 4.89 and 4.93 kJ mol⁻¹, respectively; symmetry numbers for all internal rotors $\sigma_{\text{introt}} = 3$; electronic degeneracy = 1. ^b Moments of inertia of external and internal rotation calculated using *ab initio* molecular geometry.³³ ^c See text.

correction =

$$-(\Delta S^\circ_T - \Delta S^\circ_{298})/R + (\Delta H^\circ_T - \Delta H^\circ_{298})/RT \quad (8)$$

where ΔS°_{298} is the standard entropy of reaction 1 at 298 K.

The correction was calculated using the thermodynamic functions of HBr, Br,³² $\text{Si}(\text{CH}_3)_3$,¹³ and $\text{Si}(\text{CH}_3)_3\text{H}$ (Tables 3 and 4). Thermodynamic properties of $\text{Si}(\text{CH}_3)_3\text{H}$ were determined by statistical mechanics from its calculated HF/6-31G* structural parameters and vibrational frequencies reported by Allendorf and Melius.³³ The parameters used and results of thermodynamic calculations for $\text{Si}(\text{CH}_3)_3\text{H}$ 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

Figure 5. Modified van't Hoff plot of the equilibrium constant of the reaction $\text{Si}(\text{CH}_3)_3 + \text{HBr} \rightleftharpoons \text{Si}(\text{CH}_3)_3\text{H} + \text{Br}$. 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).

hindered rotors were obtained by linear interpolation of tables.³⁴ Because similar hindered internal rotors are present in $\text{Si}(\text{CH}_3)_3$ 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, ΔH°_{298} . 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 $\ln(K_p) + \text{correction}$ vs $1/T$ (Figure 5). The fit yielded

$$\begin{aligned} \Delta H^\circ_{298} &= -34.6 \pm 1.6 \text{ kJ mol}^{-1} \\ &\quad (\text{second law procedure, FP-PIMS data}) \quad (9) \\ &= -33.5 \pm 2.0 \text{ kJ mol}^{-1} \\ &\quad (\text{second law procedure, FP-RF data}) \end{aligned}$$

The 1σ uncertainties indicated are 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 ΔH°_{298} . For the standard entropy of reaction 1, ΔS°_{298} , the intercept of the same fit yielded

$$\begin{aligned} \Delta S^\circ_{298} &= -35.8 \pm 3.8 \text{ J mol}^{-1} \text{ K}^{-1} \\ &\quad (\text{second law procedure, FP-PIMS data}) \quad (10) \\ &= -37.9 \pm 4.2 \text{ J mol}^{-1} \text{ K}^{-1} \\ &\quad (\text{second law procedure, FP-RF data}) \end{aligned}$$

The 1σ uncertainties reflect the combined errors of the preexponential A factors for k_1 and k_{-1} since, in the absence of the correction term, $\Delta S^\circ_{298} = R \ln(A_1/A_{-1})$.

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^a for HBr, $\text{Si}(\text{CH}_3)_3$, Br, and $\text{Si}(\text{CH}_3)_3\text{H}$

molecule	a_1	a_2	a_3	a_4	a_5
HBr ^b	3.4450	7.3294e-4 ^c	-3.2715e-6	5.8600e-9	-2.9366e-12
$\text{Si}(\text{CH}_3)_3$ ^d	7.2023	7.7492e-3	6.8011e-5	-1.0502e-7	4.9169e-11
Br ^b	2.4930	7.4172e-5	-2.5340e-7	2.8937e-10	-2.2604e-14
$\text{Si}(\text{CH}_3)_3\text{H}^e$	6.4373	1.4566e-2	6.1734e-5	-1.0177e-7	4.8438e-11

^a Polynomial representation of heat capacities: $C_p^\circ(T)/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$. ^b Fitting of the data from ref 32 over the temperature range 200–800 K. ^c $AeB \equiv A \times 10^B$. ^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, ΔH°_{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 ΔS . 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 ΔS and this value is shown as the intercept (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:

$$\begin{aligned} \Delta H^\circ_{298} &= -31.9 \pm 1.1 \text{ kJ mol}^{-1} \\ &(\text{third law procedure, FP-PIMS data}) \quad (12) \\ &= -30.2 \pm 1.2 \text{ kJ mol}^{-1} \\ &(\text{third law procedure, FP-RF data}) \end{aligned}$$

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_{-1} , as well as the temperature uncertainty (± 3 K) and an allowance for possible $\pm 1 \text{ J mol}^{-1} \text{ K}^{-1}$ systematic errors in the calculated ΔS°_{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 ΔH°_{298} and ΔS°_{298} are generally consistent at the 2σ significance level, except that the second law values for ΔH°_{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.³⁵ We combine the estimates of ΔH°_{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 ΔH°_{298} derived from the two different techniques, and suggested accuracy limits are about $\pm 2 \text{ kJ mol}^{-1}$.

ΔH°_{298} for reaction 1 is the difference between the bond dissociation enthalpies $D_{298}(\text{H}-\text{Br}) - D_{298}(\text{Si}(\text{CH}_3)_3-\text{H})$. $D_{298}(\text{H}-\text{Br})$ is well-characterized at $366.3 \text{ kJ mol}^{-1}$,³² so that $D_{298}(\text{Si}(\text{CH}_3)_3-\text{H}) = 397.4 \pm 2 \text{ kJ mol}^{-1}$. This value is higher than most previous measurements^{4-7,36-42} summarized in Table 5, which have been discussed previously.^{6,43} The two *ab initio* values^{6,33} in Table 5 are in excellent agreement with our result. Our $D_{298}(\text{Si}(\text{CH}_3)_3-\text{H})$ may be combined with the $\Delta H^\circ_{f,298}$ of $218.0 \text{ kJ mol}^{-1}$ for atomic H^{32} and $-163 \pm 4 \text{ kJ mol}^{-1}$ for $\text{Si}(\text{CH}_3)_3\text{H}^1$ to yield $\Delta H^\circ_{f,298}$ for the trimethylsilyl radical of $16.4 \pm 6 \text{ kJ mol}^{-1}$. The most recent independent measurement of $\Delta H^\circ_{f,298}(\text{Si}(\text{CH}_3)_3) = 14 \pm 7 \text{ kJ mol}^{-1}$, derived from an RRM fit to $\text{Si}_2(\text{CH}_3)_6$ pyrolysis by Bullock et al.,⁴⁴ is in excellent accord.

Comparison of the Si-H bond strength of trimethylsilane with that measured for SiH_4 , $384.1 \pm 2.0 \text{ kJ mol}^{-1}$,³ shows that methyl substitution *increases* the Si-H bond strength. This effect is opposite to hydrocarbons, where $D_{298}(\text{CH}_3-\text{H})^{10}$ is 441 kJ mol^{-1} and $D_{298}(\text{C}(\text{CH}_3)_3-\text{H})$ is 404 kJ mol^{-1} .¹⁷ A possible

TABLE 5: Measurements of the Si-H Bond Dissociation Enthalpy in Trimethylsilane

$D_{298}(\text{H}-\text{Si}(\text{CH}_3)_3)^a$ kJ mol ⁻¹	technique	ref
368 ± 42	electron impact	36
356	HT yield from reaction with hot T atoms	37
372 ± 17	electron impact	38
364	pulsed stirred-flow reactor	39
378 ± 6	iodination	40
382 ± 7 ^b	pulsed photolysis-resonance absorption	41
377 ± 5	very low pressure reactor	42
357	overtone spectroscopy	4
324	overtone spectroscopy	5
398 ± 6	FP-RF	6
397	ab initio theory	6
396	ab initio theory	33
398 ± 2	FP-RF	7
397 ± 2	FP-PIMS and FP-RF	this work

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

rationalization is based on the relative electronegativities of silicon and carbon. The electron-deficient central C atom in $\text{C}(\text{CH}_3)_3$ is stabilized by donation from the methyl groups, the inductive effect. C is more electronegative than Si, so that the $\text{Si}(\text{CH}_3)_3$ 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 $\text{Si}(\text{CH}_3)_3$ with HBr, yield ΔS and ΔH 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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