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Does Alkyl Substitution Affect the Si-H Bond Strength in Silane? Kinetic Studies of the Reactions of Atomic Chlorine and Bromine with Trimethylsilane and an ab Initio Investigation

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Abstract: The kinetics of the elementary reactions of Cl and Br with $HSi(CH_3)_3$ (**1** and **2**) have been measured by flash-photolysis/time-resolved atomic resonance spectroscopy over the approximate temperature range 300–460 K. The results are $k_1 = (1.24 \pm 0.35) \times 10^{-10} \exp(1.3 \pm 0.8 \text{ kJ mol}^{-1}/RT)$ cm^3 s^{-1} and $k_2 = (7.6 \pm 3.3) \times 10^{-10} \exp(-28.4 \pm 1.3 \text{ kJ mol}^{-1}/RT)$ cm^3 s^{-1}, with confidence limits of about ±20%. The activation energy of **2**, combined with an estimated activation energy for the reverse reaction, yields a bond dissociation enthalpy of $D_{298}(H{-}Si(CH_3)_3) = 398 \pm 6$ kJ mol^{-1}, which is about 14 kJ mol^{-1} larger than $D_{298}(H{-}SiH_3)$. This difference is supported by ab initio calculations. Implications for $\Delta H_f(Si(CH_3)_3)$ and the Si–Si bond strength in disilanes are discussed in the text.

1. Introduction

Fast-flow experiments on the reactions of O atoms with SiH_4 and methyl-substituted silanes have shown that the room-temperature rate constant increased with the degree of methylation.[1] We have recently confirmed this using the flash-photolysis resonance fluorescence (FPRF) method and measured activation energies (E_a) for the reactions of atomic O with SiH_4 and $HSi(CH_3)_3$; the results were 14.4 ± 0.2 and 9.0 ± 0.2 kJ mol^{-1}, respectively.[2] The difference in E_a is unexpected in the context of the equal Si–H bond dissociation enthalpies in these molecules recommended by Walsh[3] and provides the impetus for the present study. The aim of this work is to extend the comparisons of the reactivity of SiH_4 and $HSi(CH_3)_3$ to include the reactions with atomic Cl and Br.[4] Our kinetic measurements are used to derive a new value for the $H{-}Si(CH_3)_3$ bond enthalpy, which is confirmed by the results of ab initio calculations. This bond enthalpy is used to derive the enthalpy of formation of the $Si(CH_3)_3$ radical and to resolve a disagreement concerning the thermochemistry of hexamethyldisilane.[5] Such thermochemical data are central to a quantitative understanding of silanes and the possible mechanisms important in their chemistry.

2. Methodology

1. Experimental Technique. $HSi(CH_3)_3$ was synthesized by reduction of a solution of $ClSi(CH_3)_3$ in dibutyl ether with excess $LiAlH_4$ and separated by room temperature distillations followed by "freeze–pump–thaw" cycles to remove dissolved air. Gas-phase IR spectroscopy confirmed the presence of the Si–H stretching frequency, at approximately 2110 cm^{-1} and in accord with the literature value.[6] A GC analysis indicated that the $HSi(CH_3)_3$ was at least 98% pure and contained below 0.5% of unreacted starting material.

The FPRF measurements are made as described in our previous study of Cl and Br reactions with SiH_4, where full details may be found.[4] Halogen atoms are generated by flash lamp photolysis of a precursor, CCl_4 or CH_2Br_2, and are monitored by time-resolved atomic resonance fluorescence as they react with an excess of $HSi(CH_3)_3$ on a time scale of the order of 1–100 ms. Under these pseudo-first-order conditions the second-order rate constants k_1 and k_2 for the reactions

$$Cl + HSi(CH_3)_3 \rightarrow \text{products} \tag{1}$$

$$Br + HSi(CH_3)_3 \rightarrow HBr + Si(CH_3)_3 \tag{2}$$

are derived from the slopes of plots of the pseudo-first-order decay coefficients k_{ps1} vs. $[HSi(CH_3)_3]$ (see Figure 1). The uncertainty in these slopes is the dominant contribution to σ_{k_1} and σ_{k_2}.

2. Computational Method. Ab initio analysis of the homodesmic reaction

$$SiH_3 + HSi(CH_3)_3 \rightarrow SiH_4 + Si(CH_3)_3 \tag{3}$$

was carried out using theoretical methods[7] implemented in the Gaussian90 program.[8] Structures of the species in reaction 3 were optimized at the HF/6-31G* level. Harmonic vibrational frequencies were derived at these minimum energy geometries and scaled by a standard factor of 0.89 for use in determining zero-point energies (ZPE) and the temperature dependence of enthalpies. Finally, electronic energies were obtained at the HF/6-31G* geometries while making corrections for electron correlation at the MP2 and MP3 levels of theory with the 6-31G* basis set.

3. Results

1. Kinetic Analysis. Preliminary experiments showed that photolysis of $HSi(CH_3)_3$ alone yielded no detected H atoms, which therefore did not interfere with the fluorescence detection of halogen atoms. Nine measurements of k_1 from 295 to 468 K are summarized in Table I. The profiles of relative [Cl] vs. time showed good fits to exponential decays, which is consistent with attainment of pseudo-first-order conditions. It may be seen that the k_1 results are independent of the flash lamp energy, F. This demonstrates that the initial [Cl] does not affect the measurements of reaction 1, which has therefore been isolated from any secondary chemistry. Similarly, the k_1 determinations do not depend on the average residence time of the gas inside the heated reactor before photolysis, τ_{res}, which shows that thermal decomposition of the reactants is negligible. The Arrhenius plot of the k_1 values is shown in Figure 2 and may be summarized in the form $A \exp(-E_a/RT)$ as

$$k_1 = (1.24 \pm 0.35) \times 10^{-10} \exp(1.3 \pm 0.8 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \tag{4}$$

where the errors in the Arrhenius parameters are ±1σ. The

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Table I. Summary of Rate Constant Measurements for Cl + $(CH_3)_3SiH$

T, K	P, kPa	$[M] \approx [Ar]$, 10^{18} cm^{-3}	τ_{res}, s	F, J	$[CCl_4]$, 10^{14} cm^{-3}	$[(CH_3)_3SiH]_{max}$, 10^{11} cm^{-3}	$k_1 \pm \sigma_{k_1}$, 10^{-10} cm^3 s^{-1}
295	6.63	1.63	1.0	4.05	9.36	7.78	1.73 ± 0.09
295	6.63	1.63	1.0	5.00	9.36	7.77	2.24 ± 0.05
295	6.63	1.63	1.0	2.45	9.36	7.77	2.27 ± 0.11
317	6.73	1.54	2.0	4.05	9.86	7.85	1.37 ± 0.08
348	13.0	2.71	2.0	4.05	7.89	15.2	2.02 ± 0.07
378	13.3	2.54	1.0	4.05	9.36	5.80	2.25 ± 0.12
421	9.89	1.70	1.0	4.05	7.89	5.83	1.84 ± 0.05
468	6.71	1.04	1.0	4.05	7.99	5.90	1.61 ± 0.08
468	6.56	1.02	2.0	4.05	7.96	11.4	1.59 ± 0.12

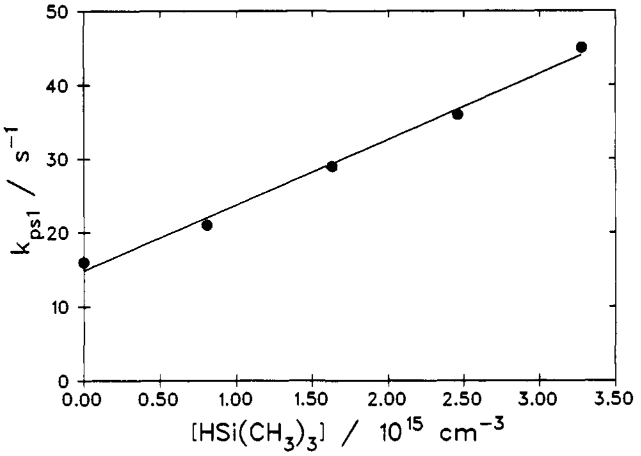

Figure 1. Plot of the pseudo-first-order rate constants for the removal of Br vs. $[HSi(CH_3)_3]$ at T = 296 K and P = 6.67 kPa.

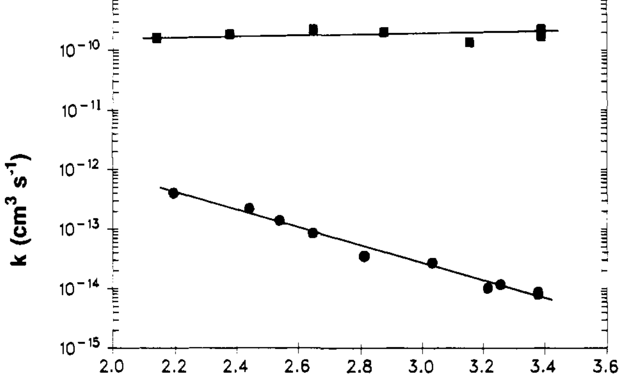

Figure 2. Arrhenius plot of the rate constant measurements for the reactions of trimethylsilane with atomic chlorine (■) and bromine (●).

covariance[9] of A and E_a and an allowance of ±5% for possible systematic errors led to 95% confidence limits of about ±20% of k_1. The slightly negative E_a is not significantly different from zero at the 95% level, and an alternative summary of the k_1 data is the mean $k_1 = (1.88 \pm 0.11) \times 10^{-10}$ cm^3 s^{-1}, again quoting a 1σ uncertainty.

k_2 was determined over the range 296-456 K, and the results are summarized in Table II. The measurements were sufficiently reproducible to reveal a small but consistent variation of k_2 with F, which presumably reflects secondary chemistry arising from the reaction of Br with photolytic or reaction products such as $Si(CH_3)_3$. k_2 was observed to vary approximately linearly with F, so plots of k_2 vs F were extrapolated to zero flash energy to determine k_2 at each temperature. The largest variation of k_2 with F was by a factor of 1.5 (see Table II), while at two temperatures the slope was negligible and instead the k_2 values were averaged. The 1σ uncertainty of each individual k_2 reflects the uncertainty of a plot such as Figure 1; the uncertainty in the extrapolated k_2 values reflects the uncertainty of the intercept of plots of k_2 vs F. Secondary chemistry of Br with radicals R can become significant when $k_R[R] \sim k_2[HSi(CH_3)_3]$, where k_R is the rate constant for reaction of Br with the radicals. On the assumption that k_R is gas-kinetic, interference is possible when [R] is of the order 10^{10}–10^{11} cm^{-3}. Under similar conditions kinetic interference in the Cl atom experiments is undetectable because k_1 is three orders of magnitude larger than k_2. The k_2 results are plotted in Figure 2 and are summarized as

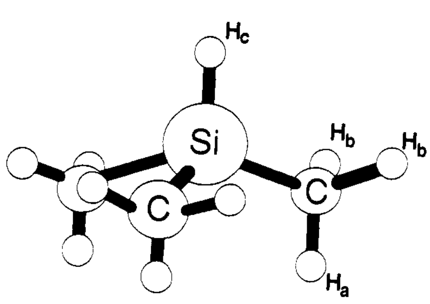

Figure 3. The conformation of trimethylsilane analyzed by *ab initio* methods.

$$k_2 = (7.6 \pm 3.3) \times 10^{-10} \exp(-28.4 \pm 1.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (5)$$

with a 95% confidence interval, including a 5% allowance for possible systematic errors, of ±23% of k_2.

2. Thermochemical Analysis. Our measured E_a for reaction 2 may be combined with an *estimated* E_a' for the reverse reaction to obtain the bond dissociation enthalpy $D_{298}(H-Si(CH_3)_3)$. We averaged the recently measured E_a for the reactions of SiH_3 and $C(CH_3)_3$ with HBr, −0.7 ± 1.2 and −5.8 ± 0.9 kJ mol^{-1},[10,11] respectively, to obtain an assumed E_a' of −3 ± 5 kJ mol^{-1}. ΔH for reaction 2 at the approximate midpoint of the range of $1/T$ studied, 350 K, is derived from

$$\Delta H_{350} = E_a - E_a' \quad (6)$$

as 31.4 kJ mol^{-1}. This value is extrapolated to 298 K, using experimental C_p values[12] for Br and HBr together with C_p values for $HSi(CH_3)_3$ and $Si(CH_3)_3$ derived[13] from ab initio frequencies (see section 3.3) at 298 and 350 K. The average value of ΔC_p over this range is estimated as 2 J K^{-1} mol^{-1}, which leads to a value of ΔH_{298} for reaction 2 of 31.3 kJ mol^{-1}. The Si-H bond strength is derived from the relation

$$\Delta H_{298} = D_{298}(H-Si(CH_3)_3) - D_{298}(H-Br) \quad (7)$$

coupled with the known D_{298}(H-Br) of 366.3 kJ mol^{-1},[12] to yield $D_{298}(H-Si(CH_3)_3)$ = 397.6 kJ mol^{-1}. The main source of un-

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Table II. Summary of Rate Constant Measurements for Br + $(CH_3)_3SiH$

T, K	P, kPa	[M] ≈ [Ar], 10^{18} cm^{-3}	τ_{res}, s	F, J	$[CH_2Br_2]$, 10^{14} cm^{-3}	$[(CH_3)_3SiH]_{max}$, 10^{15} cm^{-3}	$k_1 \pm \sigma_{k_1}$, 10^{-14} cm^3 s^{-1}
296	6.67	1.63	1.0	4.05	7.25	2.93	0.80 ± 0.04
296	6.67	1.63	2.0	5.00	7.50	3.28	0.88 ± 0.06
297	6.67	1.63	2.0	4.05	7.46	3.27	0.89 ± 0.07
296	6.67	1.63	2.0	2.45	7.50	3.28	0.88 ± 0.04
							0.88 ± 0.01
307	13.3	3.14	2.0	5.00	7.36	3.11	1.29 ± 0.09
307	13.3	3.14	2.0	3.20	7.36	3.11	1.27 ± 0.13
307	13.3	3.14	2.0	1.80	7.36	3.11	1.21 ± 0.06
							1.17 ± 0.02[a]
311	6.67	1.55	1.0	5.00	6.76	2.09	1.33 ± 0.13
311	6.67	1.55	1.0	3.20	6.76	2.10	1.22 ± 0.04
311	6.67	1.55	1.0	1.80	6.76	2.10	1.13 ± 0.04
							1.02 ± 0.01[a]
330	6.67	1.46	1.7	5.00	6.25	2.05	2.80 ± 0.19
331	6.80	1.49	1.7	4.05	6.37	2.04	2.66 ± 0.14
330	6.67	1.46	1.7	2.45	6.25	2.06	2.73 ± 0.36
							2.73 ± 0.07
356	13.3	2.71	2.0	5.00	6.34	1.12	4.94 ± 0.35
356	13.3	2.71	2.0	3.20	6.34	1.12	4.47 ± 0.37
356	13.3	2.71	2.0	1.80	6.34	1.12	4.03 ± 0.30
							3.53 ± 0.05[a]
378	6.80	1.30	2.0	5.00	3.36	0.80	13.4 ± 1.0
378	6.80	1.30	2.0	3.20	3.36	0.80	12.4 ± 1.2
378	6.80	1.30	2.0	1.25	3.36	0.80	9.37 ± 1.41
							8.53 ± 1.15[a]
394	6.80	1.25	1.0	5.00	5.68	0.32	16.8 ± 0.8
394	6.80	1.25	1.0	3.20	5.68	0.32	16.1 ± 1.6
394	6.80	1.25	1.0	1.80	5.68	0.32	14.8 ± 1.9
							14.1 ± 0.5[a]
410	13.4	2.37	2.0	5.00	4.97	0.36	27.4 ± 1.3
410	13.4	2.37	2.0	3.20	4.97	0.36	25.4 ± 1.4
410	13.4	2.37	2.0	1.80	4.97	0.36	24.3 ± 1.9
							22.4 ± 0.4[a]
456	6.67	1.06	1.0	5.00	4.70	0.20	57.1 ± 3.6
456	6.67	1.06	1.0	3.20	4.70	0.20	51.9 ± 4.8
456	6.67	1.06	1.0	1.80	4.70	0.20	45.9 ± 4.8
							40.2 ± 1.5[a]

[a] Obtained by extrapolation to $F = 0$.

Table III. Geometries and Frequencies at the HF/6-31G* Level[a]

species	r_{Si-C}	r_{Si-H_c}	r_{C-H_a}	r_{C-H_b}	∠$CSiH_c$	∠H_aCSi	∠H_bCSi	∠HCH[b]
$HSi(CH_3)_3$	1.891	1.484	1.087	1.087	108.6	111.4	111.4	107.5
ν = 132, 147 (2), 190 (2), 228, 571, 602 (2), 660 (2), 671, 830 (2), 857, 895 (2), 1291 (2), 1299, 1424, 1426 (2), 1434 (2), 1440, 2070, 2836 (2), 2838, 2895 (2), 2897, 2898, 2899 (2)								
$Si(CH_3)_3$	1.898		1.089	1.086	108.4	111.2	111.3	107.6
ν = 129, 139 (2), 186 (2), 216, 559, 650 (2), 676, 700 (2), 842 (2), 856, 1283 (2), 1293, 1422, 1426 (2), 1431 (2), 1439, 2830 (2), 2832, 2889 (2), 2891, 2905, 2907 (2)								

[a] Bond lengths in 10^{-10} m, angles in deg, and frequencies in cm^{-1}, scaled by 0.89. The atoms are labeled as shown in Figure 2. [b] The three HCH angles in each CH_3 group are essentially identical.

certainty is the estimated E_a'; error propagation leads to approximate error limits of about ±6 kJ mol^{-1}.

An approximate check of this bond enthalpy is provided by comparison of E_a for H abstraction by Br from SiH_4 and $HSi(CH_3)_3$. We have previously measured E_a for the SiH_4 analogue of reaction 2 to be about 17 kJ mol^{-1},[4] which is 11 kJ mol^{-1} smaller than that for reaction 2. Thus an approximate estimate of $D_{298}(H{-}Si(CH_3)_3)$ is 11 kJ mol^{-1} more than $D_{298}(H{-}SiH_3)$,[10] i.e., about 395 kJ mol^{-1}.

3. Theoretical Analysis. The lowest energy conformer of $Si(CH_3)_3$ located by Cartledge and Piccione[14] at the HF/6-21G level was reoptimized here at the HF/6-31G* level of theory. The corresponding $HSi(CH_3)_3$ structure (see Figure 3) was also optimized at this level. The resulting C_{3v} geometries and frequencies of these two molecules are listed in Table III. The three lowest frequency normal modes in the two molecules are assumed to correspond to internal rotations of the methyl groups, with similar barriers of approximately 5 kJ mol^{-1} in both $HSi(CH_3)_3$ and $Si(CH_3)_3$. The calculated ZPE of these molecules are 296.2 and 273.9 kJ mol^{-1}, respectively. SiH_4 and SiH_3 were also analyzed in the same way using HF/6-31G* theory; the results are in accord with previous calculations.[7,15,16] Next, energies of these four

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Table IV. Ab Initio Energies Calculated with the 6-31G* Atomic Basis Set[a]

species	$\langle S^2 \rangle$	HF	MP2=fc	MP3=fc
SiH_3	0.754	−290.606 12	−290.674 45	−290.690 52
SiH_4	0	−291.225 13	−291.307 03	−291.325 41
$Si(CH_3)_3$	0.753	−407.743 28	−408.206 41	−408.251 99
$HSi(CH_3)_3$	0	−408.366 67	−408.842 88	−408.891 07

[a] At the HF/6-31G* optimized geometries. Electronic energies are quoted in atomic units: 1 hartree ≈ 2625 kJ mol^{-1}.

species were obtained by means of single-point MP2 and MP3 calculations with frozen core electrons, and the results are given in Table IV. These energies were combined with the ZPE information to derive ΔH_0, the enthalpy change for reaction 3 at 0 K. At the HF, MP2, and MP3 levels ΔH_0 = 13.9, 12.6, and 13.5 kJ mol^{-1}, respectively. The consistency between these values is suggestive that electron correlation effects cancel to a high degree in this homodesmic reaction, and therefore that the ab initio ΔH_0 is reliable. The MP3 value was extrapolated to 298 K by means of the relation

$$\Delta H_{298} = \Delta H_0 + \sum \nu_i [H_{298} - H_0(S_i)] \qquad (8)$$

where ν_i is the stoichiometric number of the species S_i involved in reaction 3. $H_{298} - H_0$ for SiH_4 is 10.54 kJ mol^{-1},[12] and for SiH_3 it has been calculated by Hudgens to be 10.43 kJ mol^{-1},[17] while the difference between $H_{298} - H_0$ for $HSi(CH_3)_3$ and $Si(CH_3)_3$ was derived[13] from our ab initio vibrational frequencies to be 0.3 kJ mol^{-1}. Enthalpy contributions from hindered internal rotors cancel and therefore introduce negligible error into this result. Thus ΔH_{298} for reaction 3 is estimated as 13.3 kJ mol^{-1} at the MP3/6-31G* level. This enthalpy change may also be viewed as $D_{298}(H-Si(CH_3)_3) - D_{298}(H-SiH_3)$: we employed the experimental value[10] $D_{298}(H-SiH_3)$ = 384.1 ± 2.0 kJ mol^{-1} to calculate $D(H-Si(CH_3)_3)_{298}$ = 397.4 kJ mol^{-1}.

This analysis provides an independent check on the experimental result derived in section 3.2. The extremely close agreement between the two estimates is probably fortuitous but nevertheless encouraging.

4. Discussion

1. Comparison of Kinetic Results with Earlier Measurements. Our previous experiments on Cl and Br reactions with SiH_4 in the present apparatus gave good accord with results obtained from other techniques.[4] Here, there are no earlier data for comparison with k_1, although the zero or slightly negative activation energy is consistent with the reaction proceeding via a bound intermediate complex,[18] similar to those proposed in the reactions of SiH_4 with halogen atoms,[4,10] or with an interpretation based on transition-state theory.[4] Abstraction of H by Cl from either the CH_3 or the SiH group in trimethylsilane is exothermic,[3] which makes product assignment for reaction 1 ambiguous.

There is an earlier determination of k_2 by Choo and Choe at four temperatures in the 299–328 K range by the very low pressure reactor (VLPR) technique.[19] Choo and Choe assumed a preexponential A factor of 6.6 × 10^{-11} cm^3 s^{-1} and fitted their four k_2 values to obtain E_a = 18.4 ± 1.7 kJ mol^{-1}. Alternatively, we find that a direct Arrhenius fit to their data yields A = 6.1 × 10^{-9} cm^3 s^{-1} and E_a = 28.7 kJ mol^{-1}. Thus Choo and Choe may have underestimated the uncertainty in their E_a.[19] The VLPR rate constants are significantly larger than ours, e.g. by a factor of 7 at 298 K. In the VLPR experiments atomic Br was generated by passage of Br_2 through a microwave discharge. This could yield products that contain a significant fraction of excited metastable Br*, which will be quenched only slowly under VLPR conditions (pressures of 10^{-4}–10^{-2} Torr) and will be more reactive than an equilibrium mixture of Br and Br*. We have previously argued that under conditions similar to those employed in the present FPRF work (pressures around 100 Torr) an equilibrium distribution of Br and Br* is maintained, so that our k_2 measurements correspond to true thermal rate constants.[4]

Table V. Measurements of the Si–H Bond Dissociation Enthalpy in Trimethylsilane

$D_{298}(H-Si(CH_3)_3)$,[a] kJ mol^{-1}	technique	ref
368 ± 42	electron impact	22
356	HT yield from reaction with hot T-atoms	23
372 ± 17	electron impact	24
364	pulsed stirred-flow reactor	25
378 ± 6	iodination	26
392 ± 7[b]	pulsed photolysis-resonance absorption	21
377 ± 5	very low pressure reactor	19
398 ± 6	flash photolysis-resonance fluorescence	this work

[a] Not all authors quote uncertainties. [b] Obtained here from the measured $D(D-Si(CH_3)_3)$ by addition of the ZPE difference of 4 kJ mol^{-1} between the D–Si and H–Si stretching modes.

Walsh[20] has suggested that the preexponential A factor measured here for k_2 (7.6 ± 3.3 × 10^{-10} cm^3 s^{-1}) may be too high, because it is larger than measured A factors for Br + SiH_4 of 0.9 ± 0.15 and 1.6 ± 0.6 × 10^{-10} cm^3 s^{-1}.[4,11] If the Arrhenius plot for k_2 is forced to fit A = 2 × 10^{-10} cm^3 s^{-1}, then E_a is reduced by about 4 kJ mol^{-1}, implying $D_{298}(H-Si(CH_3)_3)$ ≈ 394 kJ mol^{-1}. Such a change in D_{298} is within the error limits quoted in section 3.2. Measurements on Br + H_3SiCH_3 and $H_2Si(CH_3)_2$ may decrease the uncertainty by providing further checks on the magnitude of the A factors.

2. Comparison of Thermochemical Results with Earlier Measurements. Previous estimates of $D_{298}(H-Si(CH_3)_3)$ are listed in Table V. Our value is the highest to date but is in accord, within experimental error, with the value obtained via modeling of a system where $Si(CH_3)_3$ is generated by pulsed mercury-sensitized photolysis in the presence of D_2 (in Table V we have corrected the quoted D–Si bond strength for ZPE effects to find the H–Si bond strength, which diminishes the apparent accord with earlier measurements).[21] Our value disagrees with three of the four earliest results listed in Table V, which probably reflects unavoidable uncertainties in those pioneering studies.[22-25]

More significantly, the iodination[26] and VLPR determinations,[19] which have previously been regarded as reliable,[3] instead support $D_{298}(H-Si(CH_3)_3)$ ≈ 378 kJ mol^{-1}. In section 4.1 we indicated a possible source of error in the kinetics of the VLPR experiments, and this idea is reinforced by comparison of the equilibrium constant at 298 K measured for the reaction of Br with $HC(CH_3)_3$ by Choo and Choe,[19] of 160, with the value determined by Russell et al.,[11] 1.7 × 10^{-4}.

The main source of the difference between our $D_{298}(H-Si(CH_3)_3)$ and that measured by the iodination method is the assumed activation energy for the reaction of $Si(CH_3)_3$ with hydrogen halides. Doncaster and Walsh[26] employed a value of 9.5 ± 1.7 kJ mol^{-1} for $Si(CH_3)_3$ + HI. By contrast, subsequent direct measurements by Gutman and co-workers of related reactions involving C–H bonds yielded *negative* activation energies, such as −6.3 ± 0.8 kJ mol^{-1} for $C(CH_3)_3$ + HI.[27] This controversial topic has been reviewed recently,[28] while Walsh and co-workers

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have later recognized[5] that bond energies determined by iodination[3] may need to be reassessed. However, the difference between the earlier[26] and present experiments is not completely resolved: Walsh has noted[20] that application of the present approach to the iodination data yields $D_{298}(H-Si(CH_3)_3) \approx 390$ kJ mol^{-1}.

3. Implications of the Derived $D_{298}(H-Si(CH_3)_3)$. Our estimate of $D_{298}(H-Si(CH_3)_3) = 398 \pm 6$ kJ mol^{-1} may be combined with $\Delta H_{f,298}(H)^{12} = 218.0$ kJ mol^{-1} and $\Delta H_f(HSi(CH_3)_3)^{29} = -163 \pm 4$ kJ mol^{-1} to yield a new value of $\Delta H_{f,298}(Si(CH_3)_3) = 17 \pm 7$ kJ mol^{-1}. In turn, this ΔH_f may be combined with the recently redetermined $\Delta H_{f,298}(Si_2(CH_3)_6, g)^5 = -304 \pm 6$ kJ mol^{-1} to derive a new value of $D_{298}((CH_3)_3Si-Si(CH_3)_3) = 338 \pm 12$ kJ mol^{-1}. Interestingly, this is almost the same as the value of 344 ± 10 kJ mol^{-1} discussed by Pilcher et al.,[5] even though that value is based instead on $\Delta H_{f,298}(Si(CH_3)_3) = -3 \pm 7$ kJ mol^{-1}. This observation provides a resolution of the discrepancy noted by Pilcher et al. between their $\Delta H_{f,298}(Si_2(CH_3)_6, g) = -304 \pm 6$ kJ mol^{-1} determined via reaction-solution calorimetry and the value of -349 ± 15 kJ mol^{-1} derived from kinetics: the kinetic analysis was based on an essentially correct Si-Si bond energy coupled with an erroneous $\Delta H_{f,298}(Si(CH_3)_3)$.

We can also compare the Si-Si bond energy in $Si_2(CH_3)_6$ with that in Si_2H_6. The $\Delta H_{f,298}(Si_2H_6)^{30}$ of 80.3 ± 1.5 kJ mol^{-1} and the recently determined $\Delta H_{f,298}(SiH_3)^{10}$ of 200.8 ± 3.4 kJ mol^{-1} imply $D_{298}(H_3Si-SiH_3) = 321 \pm 5$ kJ mol^{-1}. Methyl substitution therefore appears to increase both the Si-H and Si-Si bond strengths. Further experiments to test this idea, by examination of the thermochemistry of $H_2Si(CH_3)_2$ and H_3SiCH_3, are desirable. It is also important to make direct observations of the reverse of reaction 2, i.e. $Si(CH_3)_3 + HBr$, which is critical in the estimation of $\Delta H_f(Si(CH_3)_3)$. Clearly, the greater reactivity of $HSi(CH_3)_3$ toward O atoms, by comparison with SiH_4, does *not* reflect a lower Si-H bond energy in the former molecule: work on this topic is continuing.

5. Conclusions

The kinetics of the reactions of Cl and Br with trimethylsilane have been measured. The results are used to derive a new Si-H bond dissociation enthalpy of 398 ± 6 kJ mol^{-1}, which suggests that methyl substitution in SiH_4 increases the Si-H bond strength. This observation is confirmed by the ab initio investigation of a homodesmic reaction that links the bond strength of SiH_4 and $HSi(CH_3)_3$. The bond strength is used to derive a new value for $\Delta H_f(Si(CH_3)_3)$, which rationalizes a previous discrepancy concerning $\Delta H_f(Si_2(CH_3)_6)$. The results also suggest that methyl substitution in Si_2H_6 increases the Si-Si bond dissociation enthalpy.

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Registry No. SiH_3, 13765-44-1; SiH_4, 7803-62-5; atomic chlorine, 22537-15-1; atomic bromine, 10097-32-2; trimethylsilane, 993-07-7; trimethylsilyl, 16571-41-8.

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Study of Quadrupole-Perturbed Quartets in the Solid-State Magic-Angle Spinning ^{31}P NMR Spectra of Phosphine-Cu(I) Complexes. ^{63}Cu Electric Field Gradients and Anisotropy in the $^{31}P,^{63}Cu$ Scalar Coupling

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Abstract: High-resolution solid-state ^{31}P NMR spectra of phosphine-containing Cu(I) complexes show field-dependent, distorted quartets in which the line separations are not constant. This phenomenon is due to the combination of scalar $J(^{31}P,^{63}Cu)$ coupling with incompletely averaged dipolar and anisotropic J interactions. A simple analysis is presented on literature data involving a series of compounds of the P_nCuX_m type (P = triphenylphosphine and derivatives, X = halide) having different Cu coordination numbers and core geometries. It is concluded that the quartet distortion is related to structural data (P-Cu bond distances and ligand-Cu-ligand angles) and interesting molecular data (^{63}Cu quadrupole coupling constants and anisotropy (ΔJ) in the $^{31}P,^{63}Cu$ scalar coupling constant). In cases in which most of these data are available, ΔJ can be obtained and shows a fairly constant value of ca. +0.6 kHz. Extension to other cases leads to the calculation of $\chi(^{63}Cu)$, both magnitude and sign. This information is discussed in light of a simple EFG analysis for the copper atom based on s-p hybridization schemes involving vacant Cu^+ 4p orbitals.

Introduction

Great attention has been focused on copper(I) complexes as they show a remarkably wide variety of structures and Cu coordination numbers.[1-5] Halides of Cu(I) are known to form both mono- and multinuclear complexes with phosphine ligands with coordination numbers ranging from 2 to 4.[6] Likewise, halogenocuprate anions react with phosphines to give several mono- and multinuclear structures.[6,7] In an elegant series of papers, Healy,

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