Experimental Thermochemistry of the SiCl and SiBr Radicals; Enthalpies of Formation of Species in the Si−Cl and Si−Br Systems

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Gaseous reaction equilibria involving the radical species SiCl and SiBr were studied by mass spectrometric monitoring of the molecular beam issuing from a heated effusion cell source, and the results were used to derive the enthalpies of formation $\Delta_f H^\circ_{298}$(SiCl,g) = 36.8 kcal mol^{-1} and $\Delta_f H^\circ_{298}$(SiBr,g) = 48.7 kcal mol^{-1}, along with the dissociation energies D°_0(SiCl) = 98.9 kcal mol^{-1} and D°_0(SiBr) = 84.7 kcal mol^{-1}, all ±2 kcal mol^{-1}. Thermochemical data were also obtained for the species $SiCl_2$ and $SiBr_2$, confirming earlier data in the literature. Nonobservance of the species $SiCl_3$ and $SiBr_3$ was used to set lower limits of −84 and −40 kcal mol^{-1} to the enthalpies of formation of the gaseous trichloride and tribromide, respectively. The results are compared with experimental and theoretical values in the literature, clarifying previous discrepancies regarding the species $SiCl_3$ and $SiBr_3$. From a full evaluation of the literature and this work, a recommended set of enthalpies of formation of the gaseous silicon mono-, di-, tri-, and tetrahalide species is given.

Introduction

Despite the need for reliable thermochemical information on the Si−Cl and Si−Br systems in the chemical modeling and optimization of chemical vapor deposition (CVD) processes for Si-based microelectronics, there has been considerable confusion about this topic in the thermochemical literature over the last several decades. In particular, there has been only one direct experimental determination of the enthalpy of formation for both SiCl and SiBr, and these from the same laboratory.[1,2] In a review of the thermochemistry of silicon-containing compounds, Walsh[3] rejected the experimental information[1,2] on SiCl and SiBr, as well as that on $SiCl_3$ and $SiBr_3$,[1,2] and chose instead to make estimates based on various indirect results. These estimates[3] on SiCl and SiBr were assigned relatively large uncertainties of ±10 kcal mol^{-1}, making them of limited value in accurate model calculations. More reliable experimental values for SiCl and SiBr would therefore be of value, along with any further thermochemical information on the silicon dihalides and trihalides that would lead to a more consistent set of thermochemical properties for gaseous species in these systems. In recent years, ab initio electronic structure calculations have been yielding relatively accurate enthalpies of formation for metal halides containing first- and second-row elements, including the Si−Cl species.[4−6] We report here new experimental data for the Si−Cl and Si−Br mono-, di-, and trihalides, obtained from equilibrium studies of gaseous reactions monitored by mass spectrometry.

Experimental Section

All mass spectrometric measurements were made with the magnetic deflection instrument and effusion cell source arrangement described in previous publications.[7−9] All of the Si−Cl and a portion of the Si−Br measurements were made with a molybdenum effusion cell and gas inlet assembly containing high-purity silicon spheres, while additional work on the Si−Br species was done with an identical graphite cell and gas inlet assembly containing silicon powder in the sample chamber. Cl_2(g) or Br_2(g) was added to the sample chamber from an external reservoir, with the flow rate controlled by a precision leak valve. Si−Cl and Si−Br reaction product species in the molecular effusion beam were monitored by means of their corresponding parent ion signals generated in the electron impact ion source. Effusion cell temperature was measured by optical pyrometry, sighting on a blackbody cavity in the cell lid. Ionization threshold energies, or appearance energies (AE), were evaluated by the vanishing current method, using background H_2O^+ to calibrate the energy scale. Neutral species in the effusion cell beam were identified from the masses, AEs, and isotopic spectra of the observed ions, and all signals were checked for their effusion cell origin by means of the characteristic response to translation of the neutral beam defining slit. All other aspects of the measurements, analysis, and interpretation were as described earlier.[7−9] The silicon sphere and powder samples and the Cl_2 and Br_2 gaseous reactants were of reagent-grade quality or better.

Results

Following the identification of neutral species in the cell beams, reaction equilibrium constants (K) were evaluated at a series of temperatures from the parent ion signals measured at ionizing energies of AE + 3 eV so as to eliminate ion fragmentation contributions. The ion intensity analogues of K were corrected for isotopic distribution and, where necessary, a pressure calibration constant determined from measurements on a laboratory standard was applied, along with estimated ionization cross sections. The values of K so derived are estimated to be accurate within a factor of 2. In the ensuing analysis of the equilibrium data, thermal functions for all species and auxiliary thermodynamic information for atomic Si, Cl, and Br were taken from the compilations of Gurvich et al.[10,11]

The Si−Cl System. At a cell temperature of about 1500 K with Cl_2 admitted to the sample chamber, the ion species Si^+, $SiCl^+$, $SiCl_2{}^+$, and Cl^+ with AEs of 7.6, 7.5, 10.5, and 13.0

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TABLE 1: Equilibrium Data and Third-Law Enthalpy Changes for Gaseous Reactions SiCl = Si + Cl (1) and Si + $SiCl_2$ = 2SiCl (2)

T (K)	K_1 (atm)	$\Delta H^\circ_{98}(1)$ (kcal mol^{-1})	K_2	$\Delta H^\circ_{298}(2)$ (kcal mol^{-1})
		Molybdenum Cell		
1629	7.54×10^{-9}	100.0	9.49	1.9
1629	7.11×10^{-9}	100.2	9.06	2.0
1669	1.51×10^{-8}	100.2	8.21	2.4
1669	2.03×10^{-8}	99.2	8.62	2.2
1669	1.79×10^{-8}	99.6	8.41	2.3
		Avg		
		99.8		2.2

eV, all ±0.5 eV, were found to result from electron impact ionization of neutrals in the effusion cell beam. The values for the atomic ions are in accord with the well-established ionization energies (IE) of the corresponding neutrals, while the value for $SiCl^+$ agrees with photoionization efficiency (7.33 eV)[12] and theoretical (7.30 eV)[6] IEs reported for the SiCl radical. For $SiCl_2^+$, our AE is consistent with what appears to be a vertical IE of 10.35 eV for the parent neutral from photoelectron spectroscopy[13] and an adiabatic IE of 9.62 eV from theory.[6] These IE values are at odds with the AEs of 10.5 and 13.0 eV reported by Farber and Srivastava[1] for $SiCl^+$ and $SiCl_2^+$, suggesting that these species were incorrectly identified.

With the presence of the neutral species Si, SiCl, $SiCl_2$, and Cl in the effusion beam thus established, several sets of intensity measurements were made with ionizing energies a few electronvolts above threshold and were used to evaluate K values for the gaseous equilibria:

$$\mathrm{SiCl} = \mathrm{Si} + \mathrm{Cl} \tag{1}$$

$$\mathrm{Si} + \mathrm{SiCl_2} = 2\mathrm{SiCl} \tag{2}$$

at temperatures of 1629 and 1669 K. The equilibrium data and derived third-law reaction enthalpies are summarized in Table 1, leading to $\Delta H^\circ_{298}(1) = 99.8 \pm 2$ kcal mol^{-1} and $\Delta H^\circ_{298}(2) = 2.2 \pm 2$ kcal mol^{-1} plus the standard enthalpies of formation $\Delta_f H^\circ_{298}(\mathrm{SiCl,g}) = 36.8 \pm 2$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(\mathrm{SiCl_2,g}) = -36.2 \pm 2$ kcal mol^{-1}. This derived $\Delta_f H^\circ_{298}$ value for SiCl is equivalent to the dissociation energy $D^\circ_0(\mathrm{SiCl}) = 98.9 \pm 2$ kcal mol^{-1} or 4.29 ± 0.09 eV.

Although no measurable signal was observed at the trichloride ion mass position, by setting an upper limit to the intensity of $SiCl_3^+$ as the smallest detectable signal at 3 eV above the calculated IE of 8.0 eV,[6] it was possible to derive for the gaseous reaction

$$\mathrm{SiCl} + \mathrm{SiCl_3} = 2\mathrm{SiCl_2} \tag{3}$$

$K_3 \geq 1.2 \times 10^4$ and the lower limit $\Delta H^\circ_{298}(3) \leq -29$ kcal mol^{-1} (more negative) and $\Delta_f H^\circ_{298}(\mathrm{SiCl_3,g}) \geq -84$ kcal mol^{-1} (more positive).

The Si−Br System. At 1600 K and above, with Br_2(g) addition, the ion signals Si^+, $SiBr^+$, $SiBr_2^+$, and Br^+ were observed to originate in the effusion cell beam, with AEs of 7.6, 7.1, 9.1, and 11.8 eV, respectively, all ±0.5 eV. With Si powder in the graphite cell, a small Al impurity gave rise to the additional signals Al^+ and $AlBr^+$ with AEs of 5.6 and 8.8 eV, respectively. Again, the AEs of the atomic ions are compatible with the established IEs of the neutral precursors. For SiBr, Rydberg analysis[14] yielded an IE of 6.67 eV, consistent with our measured AE of $SiBr^+$, while a thermochemical analysis[15] of the photoionization fragmentation energies of $SiBr_4$ suggests an IE of 8.5 ± 1.5 eV for $SiBr_2$, also in accord with our observed AE for the dibromide ion. And the AE of $AlBr^+$ agrees with earlier determinations of IE(AlBr).[16] As with the Si−Cl system, the reported AEs of 9.0 and 12.0 for $SiBr^+$ and $SiBr_2^+$, respectively, of Farber and Srivastava[2] are significantly higher and raise further questions about proper identification of these species. Creasey et al.[15] have concluded that there is a "systematic error" in the Si−Br ion AEs reported by Farber and Srivastava,[2] and that the correct values lie several electronvolts lower. For example, an IE of 7.6 eV was deduced for $SiBr_3$ from the photoionization work,[15] compared to the value 12.5 ± 1 eV reported for the AE of $SiBr_3^+$ by Farber and Srivastava.[2]

TABLE 2: Equilibrium Data and Third-Law Enthalpy Changes for Gaseous Reaction SiBr = Si + Br (4)

T (K)	K_4 (atm)	$\Delta H^\circ_{298}(4)$ (kcal mol^{-1})
	Graphite Cell	
1685	1.56×10^{-6}	84.6
1685	1.43×10^{-6}	84.9
1685	1.53×10^{-6}	84.6
1793	3.13×10^{-6}	87.6
1793	3.46×10^{-6}	87.3
1756	4.59×10^{-6}	84.4
1843	1.16×10^{-5}	85.3
1843	1.03×10^{-5}	85.7
1843	1.06×10^{-5}	85.6
1843	8.93×10^{-6}	86.2
	Avg	85.6

TABLE 3: Equilibrium Data and Third-Law Enthalpy Changes for Gaseous Reaction Si + $SiBr_2$ = 2SiBr (5)

T (K)	K_5	$\Delta H^\circ_{298}(5)$ (kcal mol^{-1})	T (K)	K_5	$\Delta H^\circ_{298}(5)$ (kcal mol^{-1})
	Molybdenum Cell			Graphite Cell	
1549	8.36	1.5	1561	11.1	0.7
1549	9.66	1.1	1561	11.3	0.6
1549	9.97	1.0	1561	12.4	0.3
1558	10.8	0.8	1561	12.5	0.3
1558	10.4	0.9	1629	10.3	0.9
1582	10.8	0.8	1629	10.5	0.9
1582	11.1	0.7	1629	12.0	0.4
1582	9.81	1.1	1629	12.2	0.4
1615	10.6	0.8			
1615	10.7	0.8			
1615	11.9	0.5			
1615	8.65	1.49			
1618	9.09	1.33			
1618	10.5	0.9			
1618	9.80	1.1			
	Avg	1.0		Avg	0.6

In any event, the AE data confirm the presence of the neutral equilibrium products Si, SiBr, $SiBr_2$, Br, Al, and AlBr in the beams from the heated effusion cell source. From a series of parent ion intensity measurements made at ionizing energies a few electronvolts above the respective AEs, values of K for the gaseous reactions

$$\mathrm{SiBr} = \mathrm{Si} + \mathrm{Br} \tag{4}$$

$$\mathrm{Si} + \mathrm{SiBr_2} = 2\mathrm{SiBr} \tag{5}$$

$$\mathrm{Si} + \mathrm{AlBr} = \mathrm{SiBr} + \mathrm{Al} \tag{6}$$

were evaluated at temperatures in the range 1549−1843 K. The equilibrium data and derived third-law reaction enthalpies for reactions 4 and 5 are summarized in Tables 2 and 3. With the larger temperature ranges covered, the second-law enthalpies are in reasonable accord with the preferred third-law values. The analysis yields $\Delta H^\circ_{298}(4) = 85.6$ kcal mol^{-1} and

TABLE 4: Comparison of Enthalpies of Formation at 298 K of Si−Cl Gaseous Species

species	method	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})
SiCl	exp, MS equil[a]	47.1 ± 0.6
	eval[b]	47.4 ± 1.6
	eval[c]	37 ± 10
	eval[d]	34.0 ± 10
	theory[e]	37.8
	theory[f]	36.5 ± 1.5
	theory[g]	37.1
	this work	36.8 ± 2
$SiCl_2$	exp, transport[h]	−40.2
	exp, transport[i]	−38.2
	exp, MS equil[a]	−40.6 ± 0.6
	eval[b]	−40.3 ± 0.8
	eval[c]	−40.3 ± 0.8
	eval[d]	−39.0 ± 1
	theory[e]	−37.6
	theory[f]	−38.6 ± 1.5
	theory[g]	−39.6
	this work	−36.2 ± 2
$SiCl_3$	exp, MS equil[a]	−93.3 ± 0.5
	eval[b]	−93.3 ± 4
	eval[c]	−80 ± 2
	eval[d]	−80.4 ± 2.4
	theory[e]	−76.5
	theory[f]	−75.8 ± 1.5
	theory[g]	−75.4
	this work	≥−84 (more pos)

[a] Reference 1. [b] Reference 19. [c] Reference 3. [d] Reference 11. [e] Reference 4. [f] Reference5. [g] Reference 6. [h] Reference 23. [i] Reference 24.

$\Delta H^\circ_{298}(5) = 0.8$ kcal mol^{-1}, both ±2 kcal mol^{-1}. And two determinations at 1793 K gave $K_6 = 0.0171$ and 0.0163 and $\Delta H^\circ_{298}(6) = 17.0 \pm 2$ kcal mol^{-1} before the Al and AlBr signal levels dropped to insignificant levels because of depletion of the small Al impurity. When combined with auxiliary thermochemical data, $\Delta H^\circ_{298}(4)$ and $\Delta H^\circ_{298}(6)$ both led fortuitously to $\Delta_f H^\circ_{298}(\mathrm{SiBr,g}) = 48.7 \pm 2$ kcal mol^{-1}. From $\Delta H^\circ_{298}(5)$, one derives $\Delta_f H^\circ_{298}(\mathrm{SiBr_2,g}) = -11.0 \pm 2$ kcal mol^{-1}. For SiBr, this derived enthalpy of formation leads to the corresponding dissociation energy $D^\circ_0(\mathrm{SiBr}) = 84.7 \pm 2$ kcal mol^{-1} or 3.67 ± 0.09 eV.

Just as with $SiCl_3$, the absence of an observable $SiBr_3^+$ signal at an ionizing energy a few electronvolts above the expected AE of 8 eV leads for the gaseous reaction

$$\mathrm{SiBr} + \mathrm{SiBr_3} = 2\mathrm{SiBr_2} \qquad (7)$$

to a lower limit value of $K_7 \geq 4.7 \times 10^3$ at 1843 K and $\Delta H^\circ_{298}(7) \leq -31$ kcal mol^{-1}, translating to $\Delta_f H^\circ_{298}(\mathrm{SiBr_3,g}) \geq -40$ kcal mol^{-1}.

Discussion

In Tables 4 and 5, our new experimental values of $\Delta_f H^\circ_{298}$ for gaseous SiCl, $SiCl_2$, $SiCl_3$, SiBr, $SiBr_2$, and $SiBr_3$ are compared with literature values for these species. The reported results include experimental (exp) determinations by mass spectrometric and transport methods; theoretical determinations (theory) from quantum chemical calculations; and values from critical evaluations (eval) of the literature. Note that the reported values for $SiCl_2$ and $SiBr_2$ are in close accord, with a maximum spread of only a few kilocalories per mole among all the results; clearly, we can assume that these values for the dihalides are well established, at $\Delta_f H^\circ_{298}(\mathrm{SiCl_2,g}) = -38.0 \pm 1.5$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(\mathrm{SiBr_2,g}) = -11.0 \pm 1$ kcal mol^{-1} and need no further comment.

TABLE 5: Comparison of Enthalpies of Formation at 298 K of Si−Br Gaseous Species

species	method	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})
SiBr	exp, MS equil[a]	46.5 ± 2.4
	eval[b]	56.2 ± 11
	eval[c]	47 ± 10
	eval[d]	41.9 ± 6
	this work	48.7 ± 2
$SiBr_2$	exp, transport[e]	−10.0
	exp, transport[f]	−12.2
	exp, MS equil[a]	−10.5 ± 2
	eval[b]	−12.5 ± 4
	eval[c]	−11 ± 2
	eval[d]	−12.2 ± 1.2
	this work	−11.0 ± 2
$SiBr_3$	exp, MS equil[a]	−48.0 ± 0.5
	eval[b]	−48.2 ± 15
	eval[c]	−38 ± 6
	eval[d]	−37.5 ± 6
	this work	≥−40 (more pos)

[a] Reference 2. [b] Reference 19. [c] Reference 3. [d] Reference 11. [e] Reference 25. [f] Reference 24.

For SiCl and $SiCl_3$, which show spreads of 10−18 kcal mol^{-1} among the reported results, the theoretical values[4−6] of $\Delta_f H^\circ_{298}$ are in exceptionally close agreement and in accord with the recommendations of Walsh,[3] as well as the experimental values reported here. Only the experimental values of Farber and Srivastava[1] are significantly out of line for both species, and we join Walsh[3] in rejecting those results. Bauschlicher and Partridge[6] have also commented on these earlier experimental results[1] in indicating that the computed thermochemical values[4−6] “support the conclusion that the experimental heats of formation for SiCl and $SiCl_3$ are in error.” As noted above, the reported AE values of Farber and Srivastava[1] for $SiCl^+$ and $SiCl_3^+$ are significantly higher than the values reported in this paper and by others,[6,12] suggesting that the neutral species were incorrectly identified. Actually, the $SiCl_3^+$ AE of 13 eV reported by Farber and Srivastava[1] is close to the AEs of 12.48 and 12.6 eV reported[17,18] for the trichloride fragment ion in the mass spectrum of gaseous $SiCl_4$, indicating that signals attributed to $SiCl_3$ probably originated with $SiCl_4$, thereby overestimating the stability of the trichloride. Discarding the results of Farber and Srivastava[1] for these reasons, along with the JANAF evaluation[19] based on them, we select, primarily from the theoretical calculations, $\Delta_f H^\circ_{298}(\mathrm{SiCl,g}) = 37.0 \pm 1$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(\mathrm{SiCl_3,g}) = -76.0 \pm 1$ kcal mol^{-1} as the present best values.

For SiBr and $SiBr_3$, showing spreads of 10−14 kcal mol^{-1} in the reported $\Delta_f H^\circ_{298}$ values, we remain doubtful of the earlier experimental results,[2] as noted by Walsh.[3] On the basis primarily of the results reported here and the recommendations of Walsh,[3] we select the values $\Delta_f H^\circ_{298}(\mathrm{SiBr,g}) = 48.7 \pm 2$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(\mathrm{SiBr_3,g}) = -38 \pm 2$ kcal mol^{-1} as present best values. The recommended values of $\Delta_f H^\circ_{298}$ based on the new analysis described here are summarized in Table 6. The well-established values for the gaseous tetrahalides $SiCl_4$ and $SiBr_4$ are included and were taken from the compilation of Gurvich et al.[11]

It is worth noting that the recommended $\Delta_f H^\circ_{298}$ estimates of Walsh[3] for gaseous SiCl and SiBr, although based largely on indirect results and intuition and presented with “caution but no great confidence” and with large estimated uncertainties, are uncannily close to our final selected values in Table 6. The latter were obtained from the new experimental and theoretical work described here, now with much tighter uncertainty limits. Walsh’s recommended values[3] for $SiCl_3$ and $SiBr_3$, based on values in selected halosilanes, are likewise close to the selected

TABLE 6: Recommended Enthalpies of Formation of Gaseous Si−Cl and Si−Br Species and Bond Dissociation Energies

species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	species	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})
SiCl	37.0 ± 1	SiBr	48.7 ± 2
$SiCl_2$	−38.0 ± 1.5	$SiBr_2$	−11.0 ± 1
$SiCl_3$	−76.0 ± 1	$SiBr_3$	−38 ± 2
$SiCl_4$	−158.3 ± 0.2	$SiBr_4$	−99.4 ± 1.2
bond	**D°_{298} (kcal mol^{-1})**	**bond**	**D°_{298} (kcal mol^{-1})**
Si−Cl	99.6	Si−Br	85.6
ClSi−Cl	104.0	BrSi−Br	88.7
Cl_2Si−Cl	67.0	Br_2Si−Br	53.7
Cl_3Si−Cl	111.3	Br_3Si−Br	88.1

values in Table 6. It is also worth mentioning that Walsh's recommended $\Delta_f H^\circ_{298}$ values for gaseous SiI and SiI_2 at 62 ± 10 and 22 ± 2 kcal mol^{-1}, respectively, are in full accord with the corresponding values of 61.0 ± 2 and 21.6 ± 3.3 kcal mol^{-1} determined recently in this laboratory.[20]

As noted above, the computed thermochemical values[4−6] for SiCl, $SiCl_2$, and $SiCl_3$ are in remarkably good accord with each other, despite the use of somewhat different computational procedures, and with the new thermochemical results presented here. It has been shown[21,22] that the G-2 and related computational methods can be extended with similar accuracy to the thermochemistry of third-row elements from Ga to Kr, thereby bringing the Si−Br species within range; however, we are not aware of any published computational results on the silicon bromides. The selected Si−Br thermochemical values presented here provide a good test case for the accuracy of the theoretical methods.

Also included in Table 6 are the individual bond dissociation energies (BDE) of the Si−Cl and Si−Br species, evaluated from the selected $\Delta_f H^\circ_{298}$ values. In both systems, the X_3Si−X BDE, where X is a halogen, is 35−38 kcal mol^{-1} smaller than the average of the other three BDEs, which are grouped narrowly around the means 105 ± 6 and 88 ± 2 kcal mol^{-1}. Walsh[3] discussed this weakening of the X_3Si−X BDE in terms of a stabilization of the lone pair of bonding electrons in the silicon dihalide species. It has also been described in terms of valence promotion effects in the B−X, Si−X, and OSi−X systems effected by the stability of the BX and SiO closed shell species, and the stable singlet-state lone pair species SiX_2.[20]

In conclusion, previous uncertainties about the thermochemistry of the Si−Cl and Si−Br gaseous species have now been clarified, and users can have a high degree of confidence in equilibrium model calculations made with the enthalpies of formation listed in Table 6. As an illustration of this point, equilibrium modeling of silicon CVD processing from a 10% $SiHCl_3$ in Ar feed at 1500 K and 0.1 atm, using the thermochemical data of Farber and Srivastava,[1] predicts that nearly 20% of the Si deposition would be contributed by the transport species $SiCl_3$, with the balance by $SiCl_2$. At lower temperatures in the deposition zone, both $SiCl_2$ and $SiCl_3$ disproportionate to yield Si(c) and $SiCl_4$(g). But predictions with the new selected values in Table 6 show that Si transport as $SiCl_3$ is entirely negligible and that the earlier data[1,19] overestimate the Si deposition rate.

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