J. Phys. Chem. A **2001,** *105,* 4114−4117

Thermochemistry of Gaseous OSiI, $OSiI_2$, SiI, and SiI_2

D. L. Hildenbrand* and K. H. Lau
SRI International, Menlo Park, California 94025

J. W. Baglio and C. W. Struck
Osram Sylvania, Inc., Beverly, Massachusetts 01915

Received: October 31, 2000; In Final Form: January 12, 2001

Gaseous reaction equilibria in the Si−O−I system were investigated by mass spectrometry, leading to identification and thermochemical characterization of the species OSiI, $OSiI_2$, SiI, and SiI_2. Species were generated by the addition of gaseous I_2 to an effusion cell reactor containing a Si/SiO_2 mixture of composition “SiO”. Equilibria involving the Si−O−I species were measured in the range 1350 to 1540 K. From third law analysis, the enthalpies of formation of OSiI, $OSiI_2$, SiI, and SiI_2 were derived as $\geq -21.7 \pm 5$, $\geq -74.5 \pm 5$, 61.0 ± 2, and 21.6 ± 3.3 kcal mol^{-1}, respectively. Although the values for SiI and SiI_2 are in good agreement with selected values in a recent compilation, the results for OSiI and $OSiI_2$ are 25−30 kcal mol^{-1} less stable than semiempirical estimates developed for modeling of metal halide lamp chemistry. In some instances, other estimated thermochemical database values differ substantially from both theoretical and experimental results; reasons for these discrepancies are discussed.

Introduction

Thermochemical modeling has been a useful tool in the analysis and design of many high-temperature chemical processes. A particularly active area has been the analysis of tungsten halogen lamp systems, where considerable attention has been given to the development of thermochemical databases pertinent to lamp applications. With reference to lamp chemistry, Dittmer and Niemann[1−3] have reported thermodynamic data (enthalpy of formation, entropy, heat capacity) for the gaseous halides, oxides, and oxyhalides of B, Si, P, As, S, Se, Te, Mo, and W; data for some of the pertinent condensed phases are also included. In the many instances where experimental data are missing, these quantities were estimated using methods developed by the authors. The standard enthalpies of formation, $\Delta_f H°_{298}$, are the most critical items here, because entropy and heat capacity data generally can be estimated with acceptable accuracy. In estimating missing or uncertain $\Delta_f H°_{298}$ values, Dittmer and Niemann[1−3] used a semiempirical concept based on electronegativity relationships among the elements in the molecule. Comparisons with experimental values were generally made, but when discrepancies arose, reliance was placed primarily on their estimated values,[1−3] which were assigned accuracies of ± 7 kcal mol^{-1}. This was a useful first step, but because of well-known difficulties in estimating $\Delta_f H°_{298}$ values with this accuracy by semiempirical methods, it is prudent to consider such estimates to be provisional, until confirmed or revised by more accurate experimental or theoretical procedures.

In considering the possible transport of silica lamp components in the presence of metal iodide additives and consequent effects on component lifetimes, we were concerned by the high partial pressure of $OSiF_2$ predicted by the model calculations of Dittmer and Niemann[2] for the $SiO_2 + SiF_4$ reaction at 1000−2500 K and 0.01 atm. In fact, the data reported[2] showed that $OSiF_2$ was the only significant species present under these conditions, raising questions about the role of gaseous silicon oxyhalides as transport species under lamp-operating conditions. Our own equilibrium model calculations made with the Philips data[2] for the Si−O−I system showed OSiI and $OSiI_2$ to be major product species in the $SiO_2 + SiI_4$ reaction at 1000−1500 K at 0.01 atm. We therefore undertook an experimental study of the high-temperature chemistry of the Si−O−I system, using mass spectrometric monitoring of the species generated by the interaction of I_2(g) with a solid mixture of “SiO” composition in an effusion cell reactor equipped with a gas inlet tube. The results of these studies are presented here.

Experimental Section

The basic design of the gas inlet cell is identical with the double-chamber cell described earlier,[4] except that an open-ended extension tube is connected to the gas inlet line; the cell assembly was fabricated from molybdenum. I_2(g) was generated by room-temperature sublimation of I_2(s) from a storage bulb and was admitted through the inlet tube to the base of the cell. Si/SiO_2 chips of overall composition “SiO” were packed into the base of the cell to provide baffling, to ensure effective gas−solid collisions and to promote equilibration. The I_2 flow was controlled with a precision leak valve, and the experimental procedure was the same as that used in other gas inlet work.[5,6] Gaseous species exited the cell through a 0.15-cm-diameter orifice in the lid, aligned with the ion source entrance slit. Cell temperature was measured by optical pyrometry, focusing on a blackbody cavity in the lid. Species in the effusing beam were ionized and detected with the magnetic-deflection mass spectrometer system described in earlier publications.[7,8] Threshold appearance potentials (AP) of the species were evaluated by the vanishing current method. All measured ion signals were checked for their effusion cell origin by response to translation of the neutral beam defining slit. All other aspects of the measurements, analysis, and interpretation were as described earlier.[7,8] Both “SiO” and I_2 samples were of reagent grade

10.1021/jp004026o CCC: $20.00

TABLE 1: Equilibrium Constants and Third Law Enthalpies for the Gaseous Reactions 1 and 2

T (K)	K_1 (atm^{-1})	$\Delta H^\circ_{298}(1)$ (kcal mol^{-1})	K_2 (atm^{-2})	$\Delta H^\circ_{298}(2)$ (kcal mol^{-1})
1356	0.13	−23.9		
1426			5400	−101.5
1429	0.074	−23.6	4800	−101.4
1429	0.079	−23.8	4900	−101.4
1441	0.040	−22.1	3200	−101.1
1441	0.040	−22.0	3300	−101.2
1453	0.12	−25.3		
1472	0.080	−24.7		
1472	0.092	−24.9		
1475	0.044	−22.8	1500	−101.2
1475			1600	−101.4
1509	0.042	−23.1	3600	−106.2
1535	0.034	−22.8	470	−101.8
1535	0.043	−23.6	500	−102.0
1540	0.044	−23.7		
	Av.	−23.6	Av.	−101.9

quality; the “SiO” sample, prepared with Si/O in exact 1/1 stoichiometry, was obtained from Alfa Aesar.

Results

Initial studies were made by admitting I_2 to the cell containing a sample of silica, plus a small amount of excess Si. With this arrangement, only parent ion signals from the neutral species Si, SiO, SiI, SiI_2, and I were observed at temperatures above 1400 K, with APs of 8.3, 11.8, 7.5, 8.3, and 10.5 eV, respectively, all ±0.3 eV. Near 1500 K, very weak signals appeared at the mass numbers corresponding to $OSiI^+$ and $OSiI_2^+$ at 30 eV ionizing energy, the latter signal barely above the detection limit (5×10^{-11} atm). To substantially increase the SiO partial pressure and thereby enhance the oxyiodide signal levels, a new series of measurements was made with the commercial sample of stoichiometric “SiO”(s), in which the oxygen potential is adjusted for maximum partial pressure of gaseous SiO. This new sample did yield steady SiO^+ parent signals that were higher by a factor of 10 or more, and correspondingly larger signals at the mass positions of $OSiI^+$ and $OSiI_2^+$ when I_2 was admitted to the cell. Even so, the resulting oxyiodide signals were still too weak for meaningful ionization threshold energy measurements, but they were sufficient for equilibrium measurements that could be used to set a limit on the stabilities of the Si−O−I species. Because we prefer to evaluate reaction equilibria with ion intensities measured within a few electronvolts of threshold to minimize fragmentation effects, the 30-eV oxyiodide ion signals could be converted to AP + 3 eV with an approximate correction factor derived from the larger $OSiI^+$ signal.

A series of SiO^+ and I^+ parent ion intensities were then measured at AP + 3 eV, together with $OSiI^+$ and $OSiI_2^+$ signals at 30 eV, over the range 1350 to 1540 K. Equilibrium constants, K, for the gaseous reactions

$$\mathrm{SiO + I = OSiI} \tag{1}$$

and

$$\mathrm{SiO + 2I = OSiI_2} \tag{2}$$

were evaluated using the oxyiodide signals corrected to AP + 3 eV, and combined with pressure calibration factors measured previously. At 1535 K, the corrected signals at AP + 3 eV were in the ratio 1170/180/0.001/0.00025 for $SiO^+/I^+/OSiI^+/OSiI_2^+$, respectively. The derived K values for reactions 1 and 2 are summarized in Table 1. Both the intensities of the oxyiodide ions and the derived equilibrium constants of the two reactions are considered to be upper-limit values.

For use in third law calculations, thermal functions of the two oxyiodide species were calculated from spectroscopic and molecular constants estimated by comparison with the very complete set of values derived from molecular theory for the species OSiX and $OSiX_2$, where X = F, Cl, and Br.[9,10] For a bent OSiI molecule with an I−Si−O angle of 125°, r(Si−O) = 153 pm and r(Si−I) = 240 pm, the moment of inertia products $I_xI_yI_z = 3.76 \times 10^{-114}$ g^3 cm^6, the vibrational frequencies 1160, 100, and 260 cm^{-1}, and a statistical weight of two for the electronic ground state were evaluated. For $OSiI_2$ with C_{2v} symmetry and an I−Si−O angle of 125° with r(Si−O) = 152 pm and r(Si−I) = 240 pm, $I_xI_yI_z = 8.38 \times 10^{-112}$ g^3 cm^6, frequencies of 1230, 240, 100, 220, 400, and 200 cm^{-1}, and a ground-state statistical weight of one were derived. Established thermal functions and other thermochemical data for SiO and I were taken from the IVTANTHERMO Database.[11] At 1500 K, the change in Gibbs energy function, $-\Delta(G^\circ - H^\circ_{298}/T)$ was −21.6 and −54.1 cal K^{-1} mol^{-1} for reactions 1 and 2, respectively.

The resulting third law enthalpies of reactions 1 and 2 are also shown in Table 1, leading to the average values $\Delta H^\circ_{298}(1) \geq -23.6$ kcal mol−^{1} and $\Delta H^\circ_{298}(2) \geq -101.9$ kcal mol^{-1} (i.e., the true enthalpies are equal to or more positive than the stated values). Despite the weak signals, the second law enthalpies $\Delta H^\circ_{298}(1) = -24.2 \pm 16$ kcal mol^{-1} and $\Delta H^\circ_{298}(2) = -79 \pm 30$ kcal mol^{-1} are at least reasonable. The selected third law enthalpies lead to the standard enthalpies of formation, $\Delta_f H^\circ_{298}$, of ≥ -21.7 and ≥ -74.5 kcal mol^{-1} for OSiI and $OSiI_2$, respectively. Uncertainties of ± 5 kcal mol^{-1} are estimated for these values, based largely on potential errors of a factor of 5 in oxyiodide ion intensities and the conversion to partial pressures. Because the estimated molecular constants of the Si−O−I species are based on reliable molecular theory values for the corresponding F, Cl, and Br species, potential uncertainties in the calculated thermal functions contribute only about 1 kcal mol^{-1} to the overall uncertainties in third law enthalpies. Again, these selected values are upper limits to the stabilities, so that the true values of $\Delta_f H^\circ_{298}$ will be equal to or more positive than the stated values. These oxyiodide enthalpies of formation are 25−30 kcal mol^{-1} less stable than the estimated values of Dittmer and Niemann.[2] Our results yield the bond strengths D°_{298}(OSi−I) ≤ 24 kcal mol^{-1} and D°_{298}(OISi−I) ≤ 80 kcal mol^{-1}. Clearly, the first Si−I bond formed by addition of an I atom to SiO is much weaker than the second.

Because the species SiI and SiI_2 were also observed in the course of the measurements, as noted above, a few equilibrium measurements were made to check their thermochemical properties. The observed APs of SiI^+ and SiI_2^+ were 7.5 and 8.3 eV, respectively, close to the expected ionization potentials of the corresponding neutrals. From intensity measurements at AP + 3 eV, K values for the gaseous reactions

$$\mathrm{SiI = Si + I} \tag{3}$$

and

$$\mathrm{SiI_2 + Si = 2\,SiI} \tag{4}$$

were evaluated at several temperatures in the range 1498 to 1682 K. The SiI_2 signal became too small above 1600 K for accurate measurement. At 1591 K, intensities of Si^+, SiI^+, SiI_2^+, and I^+ at AP + 3 eV were in the ratio 0.155/0.336/0.01/180, respectively. K was independent of I(g) partial pressure at 1591 K,

TABLE 2: Equilibrium Constants and Third Law Enthalpies for the Gaseous Reactions 3 and 4

T (K)	K_3 (atm^{-1})	$\Delta H^\circ_{298}(3)$ (kcal mol^{-1})	K_4	$\Delta H^\circ_{298}(4)$ (kcal mol^{-1})
1499	3.60×10^{-6}	72.0	81.7	-7.2
1499	3.80×10^{-6}	71.8	83.8	-7.3
1548	6.60×10^{-6}	72.5	75.2	-7.2
1548	6.80×10^{-6}	72.4	78.1	-7.3
1591	1.30×10^{-5}	72.4	72.1	-7.2
1591	1.40×10^{-5}	72.1	74.1	-7.3
1591	1.40×10^{-5}	72.1	Av.	-7.2
1653	3.30×10^{-5}	72.2		
1653	3.80×10^{-5}	71.7		
1682	4.80×10^{-5}	72.2		
1682	4.80×10^{-5}	72.2		
	Av.	72.1		

TABLE 3: Comparison of Published Enthalpies of Formation

	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})[a]	
gas species	estimate[b]	theory[c]
BF_2	-140[2]	-118.9[12]
BCl_2	-28	-5.9,[12] -6.8[13]
SiF_3	-260	-238.7[14]
OSiF	-136	-86.5[9]
$OSiF_2$	-268	-206.2[9]
$SiCl_3$	-104	-75.4[15]
OSiCl	-87	-40.0,[10] -36.3[9]
$OSiCl_2$	-168	-105.2,[10] -104.4[9]
OSiBr	-71	-27.0[9]
$OSiBr_2$	-137	-83.8[9]

[a] References to the data listed are given in superscript italic numbers. [b] Estimated accuracy: ±7 kcal mol^{-1}. [c] Demonstrated accuracy: 2−4 kcal mol^{-1}.

TABLE 4: Trends in Bond Dissociation Energies

	D°_{298} (kcal mol^{-1})			
	X = F		X = Cl	
bond	theory[a]	estimate[b]	theory[a]	estimate[b]
Si−X	141	131	100	91
XSi−X	156	156	106	115
X_2Si−X	107	138	65	92
X_3Si−X	166	144	112	96
OSi−X	82	131	42	92
OXSi−X	139	151	97	110
BX	179	175	120	126
XB−X	113	136	80	93
X_2BX	172	150	120	102

[a] Refs 9, 10, 12−15. [b] Ref 2.

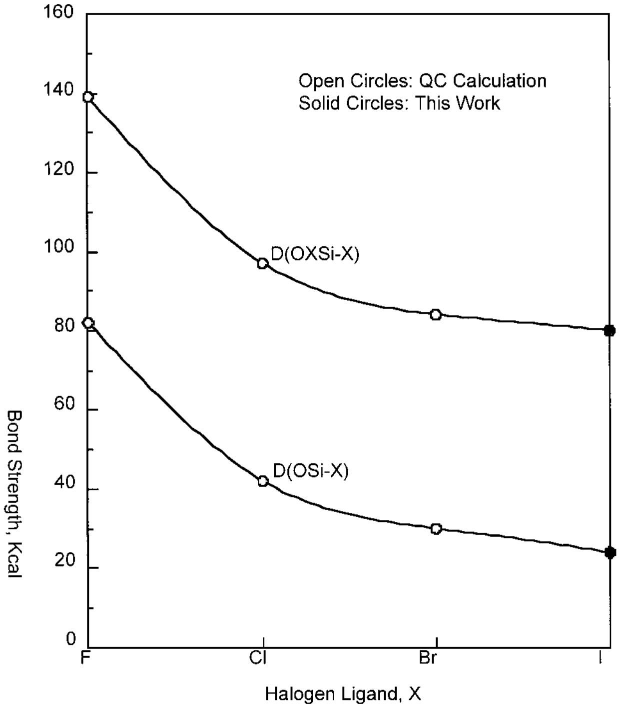

Figure 1. Correlation of OSi−X and OXSi−X bond strengths from theoretical calculations with those from equilibrium measurements.

indicative of equilibration. Third law enthalpies were derived using thermal functions from the IVTANTHERMO Database,[11] plus a pressure calibration where necessary, and the results are given in Table 2. The average third law enthalpies are 72.1 ± 2 and −7.2 ± 3 kcal mol^{-1} for reactions 3 and 4, respectively. Second law values are in good agreement. For these same reactions, the IVTANTHERMO Database[11] gives values of 70.2 ± 2.2 and −4.1 ± 4.8 kcal mol^{-1}, so we can properly assume that the thermochemical properties of SiI and SiI_2 are established within these limits. Our measurements reported here yield the standard enthalpies of formation $\Delta_f H^\circ_{298}(\text{SiI,g}) = 61.0 \pm 2$ kcal mol^{-1} and $\Delta_f H^\circ_{298}(\text{SiI}_2\text{,g}) = 21.6 \pm 3.3$ kcal mol^{-1}.

Discussion

Although the semiempirical estimation technique of Dittmer and Niemann[2] yields reasonable enthalpies of formation for some molecular species, the discrepancies of 25−30 kcal mol^{-1} between their values[2] and our experimental results on the Si oxyiodides indicate a major problem. A review of recent thermochemical results shows that the estimated database values[2] grossly overestimate the stability of other oxyhalide and related species, as shown in Table 3. References to the data listed are given in italics. These recent results[9,10,12−15] were obtained from quantum chemical calculations, which are now becoming increasingly available with an accuracy of about 2 kcal mol^{-1} for first and second row elements. Assessments of the accuracy levels of the theoretical calculations are given by Curtiss et al.[16] and Redfern et al.[17] Table 3 shows disparities ranging from 20 to 60 kcal mol^{-1}, with the semiempirical estimates[2] uniformly more negative (thermodynamically stable). The theoretical value for BF_2[12] is in close agreement with an earlier experimental value obtained from mass spectrometric equilibrium studies,[18] but rejected by Dittmer and Niemann.[2] In any event, the serious discrepancies between the semiempirical estimates and the theoretical values in Table 3 are a matter of some concern and need explanation.

A more fundamental way of looking at this problem is to examine the chemical bond strengths, or bond dissociation energies (BDE), associated with the two approaches. In considering the bond strengths D(OSi−F) and D(FB−F), for example, an F atom is being added to the fully closed-shell species SiO and BF, isoelectronic with the highly stable species N_2 and CO. Before formation of the OSi−F or FB−F bond, SiO and BF must be excited to a higher valence state with unoccupied orbitals, and this excitation energy is supplied at the expense of the subsequent bond formed. Similar considerations apply to the bonds F_2Si−F, OSi−Cl, Cl_2Si−Cl, and ClB−Cl, where the species SiX_2 are pseudo-closed shell. As seen in Table 4, the BDEs for F_2Si−F, Cl_2Si−Cl, OSi−F, OSi−Cl, FB−F, and ClB−Cl derived from quantum chemical calculations[9,10,12−15] are 13−50 kcal mol^{-1} lower than the estimated values,[2] with an average of 32 kcal mol^{-1} lower. In accord with the BDE data, Junker and Schnockel,[10] in their article on the Si−O−Cl system, comment specifically that the OSi−Cl bond is significantly weaker than that of OClSi−Cl, as indicated by the calculated Si−Cl bond length and stretching force constant in OSiCl. They state, "This discussion clearly shows that the radical character of ClSiO with the single electron on the HOMO weakens the Si−Cl as well as the Si−O bond in comparison with bonds of the normal valent species SiO, SiO_2, and Cl_2-SiO."[10] The BDEs derived from theory clearly reflect this point, but one cannot expect the same from semiempirical estimates, which do not consider subtle differences in electronic structure.

We conclude that our new experimental values for OSiI and $OSiI_2$ are fully in accord with the quantum chemical calculations.[9,10,12−15] In Figure 1, where the OSi-X and OXSi-X bond strengths are plotted as a function of the halogen ligand, it can be seen that our equilibrium data for the iodides are consistent with an extrapolation of the theoretical values for the fluorides, chlorides, and bromides. Users should be very cautious in selecting thermochemical data from published databases, depending on how the database values were derived and how they compare with the most recent and reliable results. It is unwise to assume that successive BDEs in polyvalent halides and oxyhalides are relatively constant, and full account must be taken of valence electronic structure and promotional energy considerations. We believe that the present best values of $\Delta_f H^\circ_{298}$ for the species OSiI and $OSiI_2$ are $\geq -21.7 \pm 5$ and $\geq -74.5 \pm 5$ kcal mol^{-1}, respectively.

Regarding the species SiI and SiI_2, our new $\Delta_f H^\circ_{298}$ values of 61.0 ± 2 kcal mol^{-1} and 21.6 ± 3.3 kcal mol^{-1}, respectively, are in close accord with the corresponding IVTANTHERMO Database[11] values of 62.8 ± 2 and 22.2 ± 4 kcal mol^{-1} derived from electronic spectra and equilibrium measurements. Both sets of results differ somewhat from the estimated values of Dittmer and Niemann[2], 76 and 29 kcal mol^{-1}, respectively.

Acknowledgment. We are grateful for support of this work by Osram Sylvania, Inc.

References and Notes

(1) Dittmer, G.; Niemann, U. *Philips J. Res.* **1981**, *36*, 89.
(2) Dittmer, G.; Niemann, U. *Philips J. Res.* **1982**, *37*, 1.
(3) Dittmer, G.; Niemann, U. *Mater. Res. Bull.* **1983**, *18*, 3555.
(4) Hildenbrand, D. L. *J. Chem. Phys.* **1970**, *52*, 5751.
(5) Hildenbrand, D. L. *J. Phys. Chem.* **1973**, *77*, 897.
(6) Hildenbrand, D. L. *J. Chem. Phys.* **1975**, *62*, 3074.
(7) Hildenbrand, D. L. *J. Chem. Phys.* **1968**, *48*, 3657.
(8) Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1987**, *86*, 2949.
(9) Alikhani, M. E.; Silvi, B. *J. Comput. Chem.* **1998**, *19*, 1205.
(10) Junker, M.; Schnockel, H. *J. Chem. Phys.* **1999**, *110*, 3769.
(11) IVTANTHERMO *Database on Thermodynamic Properties of Individual Substances*; CRC Press: Boca Raton, FL, 1993.
(12) Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem. A* **1999**, *103*, 4313.
(13) Schlegel, H. B.; Harris, S. *J. Phys. Chem.* **1994**, *98*, 11178.
(14) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem. A* **1998**, *102*, 876.
(15) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1997**, *276*, 47.
(16) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
(17) Redfern, P. C.; Blaudeau, J.-P.; Curtiss, L. A. *J. Phys. Chem. A* **1997**, *101*, 8701.
(18) Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1980**, *72*, 4928.