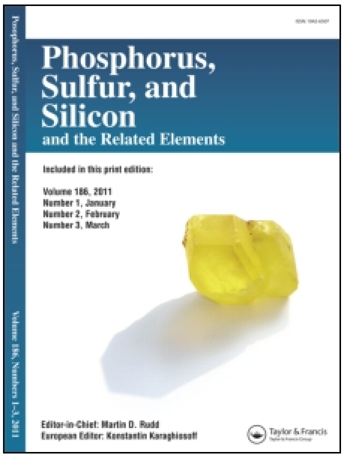

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AB INITIO AND SEMI-EMPIRICAL, CALCULATIONS ON THE OXYHALIDES OF SILICON

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AB INITIO AND SEMI-EMPIRICAL CALCULATIONS ON THE OXYHALIDES OF SILICON

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In 1982 the heats of formation of the silicon oxyhalides were determined by experiment to be −267.9 Kcal/mole ($SiOF_2$), −167.8 ($SiOCl_2$), −137.4 ($SiOBr_2$), and −99.4 ($SiOI_2$). MNDO-PM3 semiempirical calculations indicate that the heats of formation are nearer to −229.4, −121.2, −94.1, and −50.2 Kcal/mole, respectively. *Ab-initio* calculations using a 6-31G(d) basis set confirm the semiempirical results for the fluoride and chloride systems.

Key words: PM3; thermochemical data; silicon oxyhalides; SiOF2; SiOCl2; SiOBr2; SiOI2.

INTRODUCTION

While surveying the applicability of a new semi-empirical model,[1] MNDO-PM3, to silicon systems, various anomalies in thermodynamic data became evident. In their investigations on halogen-filled incandescent lamps, Dittmer and Niemann had been frustrated by the lack of reliable thermochemical data, and had determined the experimental heats of formation for a large number of main-group compounds including the silicon oxyhalides.[2] Their recommended heats of formation for several silicon compounds, based on their thermochemical measurements and critically revised literature data, are given in Table I, along with the results of PM3 calculations. In order to allow comparison with other work, we include their cited literature data. References put in parentheses relate to data which differs from their recommended values by more than 2.4 Kcal/mole.

From these experimental results, the predicted heats for the metathetic reactions of the type

$$SiO_2 + SiX_4 \Rightarrow 2SiOX_2$$

are −78.3 (F), −91.8 (Cl), −94.1 (Br), and −95.5 (I) Kcal/mole. From PM3 calculations, the corresponding heats of reaction are +24.0 (F), +3.3 (Cl), +8.6 (Br), and +2.7 (I) Kcal/mole. The differences between calculated and experimental heats of reaction were surprising and indicate that either the

TABLE I

Reported recommended experimental heats of formation

Compound	$H_f(298)$ Kcal/mole	Ref.[*]	Calc(PM3) Kcal/mole
SiO_2	−72.9	a, b	−88.9
SiF_4	−384.6	c, d, e	−390.6
$SiCl_4$	−170.9	(a, f, g, h, i)	−156.4
$SiBr_4$	−107.8	(j, d, h, k, l)	−107.9
SiI_4	−30.4	c, g, h, m, j	−14.2
$SiOF_2$	−267.9	a	−229.4
$SiOCl_2$	−167.8		−121.2
$SiOBr_2$	−137.4		−94.1
$SiOI_2$	−99.4		−50.2

[*] Taken from Reference 1.

[a] JANAF Thermochemical Tables, 2nd ed., Dow Chemicals Midland, Michigan, (1971); [b] K. F. Zmbov, L. L. Ames and J. L. Margrave, *High Temp. Sci.* **5,** 235 (1973); [c] JANAF Thermochemical Tables, 1978 Supplement, *J. Phys. Chem. Ref. Data* **7,** 793 (1978); [d] J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, *Adv. in Chem. Ser.* **72,** 261 (1968); [2] A. F. Vorob'ev V. P. Kolesov and S. M. Skuratov, *Zh. Neorgan, Khim.* **5,** 1902 (1960); [f] I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin 1973; [g] H. Schafer, H. Bruderreck and B. Morcher, *Z. Anorg. Allg. Chem.*, **352,** 122, (1967); [h] H. Schafer and H. Heine, *Z. Anorg. Allg. Chem.*, **332**, 25 (1964); [i] E. Wolf, *Z. Anorg. Allg. Chem.*, **313,** 228 (1961); [j] I. Barin, O. Knacke and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances," Supplement, Springer-Verlag, Berlin 1977; [k] E. Wolf and C. Herbst, *Z. Anorg. Allg. Chem.*, **347,** 113 (1966); [l] E. Wolf, W. Stahn and M. Schonherr, *Z. Anorg. Allg. Chem.*, **319,** 168 (1962); [m] G. A. Kokovin and T. Thieme, *Z. Phys. Chemie (Leipzig)* **259,** 1129 (1978).

experimental or computational results are severely in error. Dittmer and Niemann commented on the fact that their enthalpies of formation were more negative than those assumed by JANAF, but noted that their values were supported by tungsten transport measurements in an SiF_4/O_2 mixture. There was nothing in the computational method to suggest that errors of this magnitude were likely. The average error in heats of formation for 763 compounds was 8.6 Kcal/mole and the standard deviation 12.4 Kcal/mole.[1] For 24 normal-valent silicon–halogen compounds, the average error (Reference 1) at the PM3 level was 6.5 Kcal/mol, while for three normal-valent compounds involving an Si–O bond the average error was 7.6 Kcal/mol. Interestingly, of the three Si-O systems studied, SiO_2 had the largest error in the heat of formation, being too stable by 16 Kcal/mol. From this we conclude that there is nothing to indicate that errors in the calculated results on the order of 80–100 Kcal/mol are likely.

Nonetheless, since the theoretical results were based on parametric fitting of semi-empirical functions, we decided to carry out considerably more reliable 6-31G(d)//6-31G(d) calculations using the Gaussian-86(3) program on the fluoride and chloride systems. The geometries for these systems optimized at the 6-31G(d) and PM3 level are shown in Table II. With the exception of $SiBr_4$, in which the calculated Si–Br bond is far too short, the agreement between the PM3

TABLE II

Calculated and experimental geometries* for silicon species

Molecule (Point Gp)	Geometric quantity	PM3	6-31G(d)	Exp[a]
SiX_4(Td)	Si—F	1.580	1.557	1.552
	Si—Cl	2.039	2.029	2.017
	Si—Br	1.795		2.150
	Si—I	2.435		2.430
$SiO_2(D_{\infty h})$	Si—O	1.495	1.482	
$SiOX_2$ (C_{2v})	Si—F	1.570	1.556	
	Si—O	1.508	1.482	
	F—Si—O	126.1	127.6	
	Si—Cl	2.008	2.008	
	Si—O	1.497	1.487	
	Cl—Si—O	125.7	125.5	
	Si—Br	1.853		
	Si—O	1.492		
	Br—Si—O	130.3		
	Si—I	2.445		
	Si—O	1.482		
	I—Si—O	126.6		

* Distances in Angstroms, angles in degrees.

[a] M. W. Chase, C. A. Davies, J. R. Downey, D. R. Frurip, R. A. McDonald, and A. N. Syverud, JANAF Thermochemical Tables, Third Edition, *J. Phys. Chem. Ref. Data,* **14,** Suppl. 1 (1985).

and the experimental or 6-31G(d) geometries is quite satisfactory. The heat of reaction for the chloride system was 3.3 Kcal/mole at the SCF level; 5.1 Kcal/mole at the MP2 level, and after adding in the zero point vibrational energy, 5.6 Kcal/mole. The corresponding values for the fluoride system are +19.9, +22.8, and +23.2 kcal/mole, respectively. All these calculations refer to the system at 0 K; however, the results for the system at 298 K would be similar. The very close agreement between the semi-empirical and *ab-initio* calculations is remarkable, and lends credence to the semi-empirical results for the higher halides.

DISCUSSION

Although Dittmer and Nieman assume an uncertainty in their reported results of 7.2 Kcal/mole, the actual error is likely to be considerably higher. Their SiO_2, SiF_4 and SiI_4 results are in agreement with other published values, while the $SiCl_4$ value recommended is only 12.5 kcal more negative than the JANAF value,[4] and the $SiBr_4$ value is 8.5 more negative than the NBS value.[5] On the other hand, there appear to be no previously reported values for the heats of formation of the oxyhalides other than the JANAF value of −231.0 for $SiOF_2$. As a result, we conclude that it is likely that the reported values for the oxyhalides are substantially too negative. Assuming the JANAF values for SiO_2 (−73 Kcal/mole) and $SiCl_4$, and the *ab initio* value for the heat of reaction, then the heat of formation of $SiOCl_2$ is predicted to be −110.1 Kcal/mole. As the heats of most metathetic reactions are in the order of a few Kcal/mole, and high-level *ab initio* calculations indicate that this is the case for one of the reactions in question, we conclude that the experimental values for the oxyhalides of silicon reported by Dittmer and Nieman are in error by approximately 50 Kcal/mole.

Experimental measurements of very unstable species are fraught with difficulty. At present there does not exist any simple method for checking the accuracy of these methods. On the other hand, semiempirical methods are now becoming very easy to use, and are of known, although at present not very high, accuracy. For computational methods, an unstable or exotic species is no more difficult to calculate than a stable or well-behaved species. For this reason, in the future, experimentalists are likely to use the available rapid computational methods to survey the systems they plan to investigate. Additional caution would then be suggested if there was a large difference between the calculated and experimental results. If the accuracy of the calculated result was questioned, then more rigorous techniques, such as high level *ab initio* methods, as used here, could be used to confirm or refute the semiempirical results.

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