Thermochimica Acta, 176 (1991) 259–265
Elsevier Science Publishers B.V., Amsterdam

THEORETICAL THERMOCHEMISTRY: ENTROPIES AND HEAT CAPACITIES FOR SERIES OF ORGANOSILICON COMPOUNDS. Part II

JU GUAN-ZHI and BIAN WEN-SHENG

Institute for Theoretical Chemistry, Shandong University, Jinan (People's Republic of China)

(Received 25 May 1990)

ABSTRACT

Ab initio molecular orbital theory was used to compute entropies and heat capacities for $HSiCH_3$, $HSiSiH_3$, CH_3SiCH_3, $FSiSiH_3$, $CH_3HSi{=}CH_2$ and $FHSi{=}SiH_2$ in the temperature range 300–1500 K. For this series of organosilicon compounds, the members of which are often considered to be reactive intermediates and are all unstable, there is currently almost no information available about entropies or heat capacities. On the basis of the calculated heat capacities for the compounds involved, we have fitted the temperature-dependent functions for heat capacities to functions of the form $(a + bT + cT^2)$ and $(a' + b'T + c'T^{-2})$ over the range 300–1500 K. It was found that the first form is superior to the latter for all species considered. Finally, 1 e.u. is suggested to be the upper limit of the deviation for calculations of entropies and heat capacities over the temperature range concerned, and 2 $J K^{-1} mol^{-1}$ the deviation limit for our fittings of heat capacities.

INTRODUCTION

Having shown in Part I [1] the reliability and practicality of our purely theoretical approach to the calculation of entropy and heat capacity values, we now go on to predict the thermodynamic properties of some other important organosilicon compounds for which there is so far almost no available data, experimental or theoretical, concerning entropy and heat capacity values.

The organosilicon compounds we have selected in this work are derivatives of $H_2Si{=}SiH_2$, $H_2Si{=}CH_2$ and SiH_2, which we discussed in our first work [1]. Research into the structures, reactivities and other properties of these compounds has been the subject of a large number of theoretical and experimental papers [2–8]. However, all the compounds are unstable and often used as reactive intermediates [9], and the direct experimental measurement of their thermodynamic properties is therefore difficult. Hence we think it desirable to calculate the values of certain important thermodynamic quantities using our purely theoretical method.

0040-6031/91/$03.50

In contrast to the thermochemistry of the unstable organosilicon compounds discussed in this work, the study of that of stable organosilicon compounds has provided much useful information. Recently, Luo and Benson [10] studied the heats of formation of a number of alkylsilanes and their derivatives by utilizing a new electronegativity scale derived from various known experimental data, and Gordon et al. [11] have calculated the heats of formation for several alkylsilanes theoretically, the results being in excellent agreement with the available experimental and additivity values [11]. Furthermore, the additivity scheme for these compounds has been established [12,13]. When we come to the unstable organosilicon compounds considered in this paper, however, the situation is rather different. The thermodynamic data which can be found in the literature is limited to the experimental standard heats of formation for part of the series [15–18]. We hope to compensate for this lack of experimental data by theoretical means.

COMPUTATIONAL METHODS

Quantum chemical calculations were carried out by way of well-known ab initio self-consistent field (SCF) methods, and the calculation of entropy and heat capacity values was performed according to a general statistical thermodynamic method [19].

The absolute entropy of an ideal gas at 1 atm can be written as

$$S^\circ = S_t^\circ + S_r^\circ + S_v^\circ \tag{1}$$

where S_t°, S_r°, and S_v° are the translational, rotational and vibrational entropies respectively. According to statistical thermodynamics, these quantities follow the equations

$$S_t = R \cdot \ln(f_t \; 2.718/N) + 1.5(R) \tag{2}$$

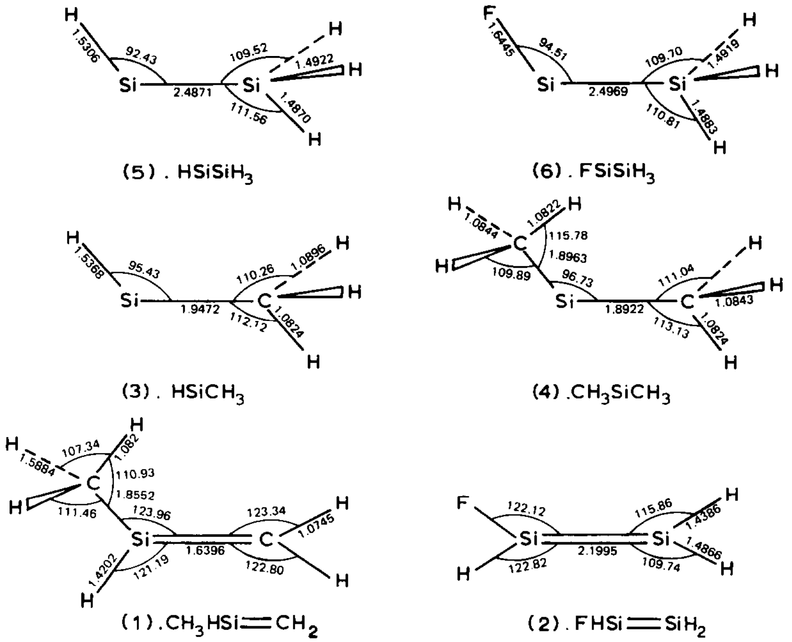
where f_t is the translational molecular partition function which is dependent upon the mass of molecule and the temperature, N is Avogadro's number and R the gas constant;

$$S_r = R \cdot \ln(f_r) + 1.5(R)(\text{for the non-linear molecules}) \quad \text{or } R(\text{for the linear molecules}) \tag{3}$$

where f_r is the rotational molecular partition function, which is dependent upon the molecular masses and the molecular geometric configurations, which we have optimized;

$$S_v = R \cdot \ln(f_v) + U_v/T \tag{4}$$

where f_v is the sum of various harmonic vibrational partition functions and U_v is the sum of various harmonic vibrational energies, both of which are dependent upon the harmonic vibrational frequencies, which we have calculated with the IMSPAK program. The optimized molecular configurations



(5) . $HSiSiH_3$ (6) . $FSiSiH_3$

(3) . $HSiCH_3$ (4) . CH_3SiCH_3

(1) . $CH_3HSi{=}CH_2$ (2) . $FHSi{=}SiH_2$

Fig. 1. Configurations for every species involved. Bond lengths in Å and angles in degree.

involved are given in Fig. 1 and the various vibrational frequencies in Table 1.

The heat capacity at 1 atm can be written as

$$C_p^\circ = C_t^\circ + C_v^\circ + C_r^\circ + R$$

TABLE 1

The harmonic vibrational frequencies (cm^{-1})

$CH_3HSi{=}CH_2$ (C1):	3817.0	3763.0	3727.4	3660.7	3560.8	2887.6	1852.5
	1842.6	1768.1	1675.2	1288.4	1106.8	1061.5	1056.1
	974.6	844.6	839.8	810.1	378.1	269.9	164.3
$FHSI{=}SiH_2$ (C1):	2352.2	2306.0	2289.8	986.5	965.4	909.2	612.8
	565.3	486.7	364.2	308.7	193.4		
$HSiCH_3$ (Cs):	3302.0	3225.0	3159.0	2027.0	1633.0	1618.0	1456.0
	1051.0	791.4	728.4	676.7	404.1		
CH_3SiCH_3 (C_{2v}):	3742.3	3740.2	3706.8	3695.9	3534.5	3531.4	1867.5
	1864.6	1862.6	1851.4	1676.7	1665.6	1093.6	971.2
	889.7	837.6	832.0	801.2	340.1	146.0	104.2
$HSiSiH_3$ (Cs):	2304.0	2252.0	2236.0	2055.0	1062.0	996.5	939.7
	728.4	695.8	464.1	289.7	213.2		
$FSiSiH_3$ (Cs):	2291.4	2249.8	2244.4	1000.8	982.9	924.3	892.5
	529.7	390.4	338.3	141.3	105.8		

where C_t° is the translational contribution, C_r° is the rotational contribution, and C_v° is the vibrational contribution, which is mainly dependent upon various harmonic frequencies. Calculation of numerical values was achieved using the GAUSSIAN-80 program suite and optimization of the equilibrium geometric configuration was performed under the 3-21G basis set. IMSPAK programs were used to calculate the harmonic vibrational frequencies of the various compounds. All the above work was carried out on the FACOM-M340S computer at Shangdong University.

The calculation of the entropy and heat capacity and the fitting of the temperature-dependent function for heat capacity was accomplished using self-compiled programs on the Hewlett-Packard HP9816 micro-computer of our institute.

RESULTS

The calculated entropies and heat capacities in the temperature range 300–1500 K are listed in Tables 2 and 3. The maximum deviation is suggested to be 1 e.u.

Two forms of function, $a + bT + cT^2$ and $a + bT + cT^{-2}$, were used to fit heat capacities. The fitting results for heat capacities over the temperature range 300–1500 K are listed in Table 4. As to the first kind of fitting form of heat capacity, the square deviations are less than two, which is acceptable [1]. The fittings to the second functional form are less satisfactory, but are reasonable.

According to our fitting results (first form) and applying the formulae $(\partial S/\partial T)p = C_p/T$ and $(\partial H/\partial T)p = C_p$, we have derived S° and $H_T - H_{298}$

TABLE 2

The S° values of series of organosilicon compounds (J K^{-1} mol^{-1})

T (K)	$CH_3HSi{=}CH_2$	$FHSi{=}SiH_2$	$HSiCH_3$	CH_3SiCH_3	$HSiSiH_3$	$FSiSiH_3$
300	282.78	294.70	247.75	293.49	277.36	307.85
400	304.75	317.57	262.23	315.31	297.6	330.74
500	325.0	337.3	275.27	335.04	315.34	350.4
600	343.82	354.66	287.29	353.25	331.22	367.7
700	361.39	370.17	298.49	370.21	345.63	383.17
800	377.83	384.2	308.97	386.11	358.84	397.2
900	393.29	397.02	318.84	401.09	371.03	410.02
1000	407.88	408.83	328.17	415.26	382.36	421.83
1100	421.68	419.76	337.01	428.71	392.91	432.78
1200	434.77	429.94	345.41	441.51	402.79	442.97
1300	447.23	439.46	353.4	453.71	412.07	452.49
1400	459.11	448.38	361.02	465.37	420.8	461.43
1500	470.45	456.79	368.3	476.52	429.04	469.85

TABLE 3

The C_p° of series of organosilicon compounds (J K^{-1} mol^{-1})

T (K)	$CH_3HSi{=}CH_2$	$FHSi{=}SiH_2$	$HSiCH_3$	CH_3SiCH_3	$HSiSiH_3$	$FSiSiH_3$
300	69.171	74.277	46.395	69.724	65.356	74.852
400	84.116	84.62	54.635	82.553	75.439	84.362
500	97.529	92.193	62.44	94.521	83.633	91.82
600	109.03	98.143	69.486	105.27	90.527	97.868
700	118.88	103.04	75.755	114.83	96.411	102.89
800	127.45	107.14	81.329	123.37	101.42	107.1
900	135.02	110.58	86.3	131.05	105.66	110.62
1000	141.77	113.48	90.742	137.98	109.23	113.57
1100	147.81	115.92	94.711	144.24	112.24	116.04
1200	153.22	117.97	98.255	149.89	114.76	118.11
1300	158.07	119.71	101.42	154.97	116.9	119.86
1400	162.41	121.19	104.24	159.54	118.71	121.34
1500	166.3	122.45	106.75	163.64	120.25	122.6

TABLE 4

The fitting parameters of the heat capacity [a]

Parameter	$CH_3HSi{=}CH_2$	$FHSi{=}SIH_2$	$HSiCH_3$	CH_3SiCH_3	$HSiSiH_3$	$FSiSiH_3$
a	25.9509	50.4581	19.8015	29.5332	37.9161	50.7809
b (−3)	164.8438	97.3044	98.3413	148.9608	107.3489	96.2305
c (−6)	−48.199	−33.4983	−27.1705	−40.0968	−35.4944	−32.7949
S [b]	1.6860	1.7762	0.1747	0.4758	0.9371	1.2217
a	84.7065	92.2832	52.2320	77.6016	81.2696	91.2814
b (−3)	57.7343	22.1021	38.4935	60.4797	28.4067	22.9505
c (+6)	−3.2048	−2.3473	−1.7229	−2.5679	−2.3704	−2.2439
S	7.7657	2.2780	3.4178	6.9641	4.0179	2.7928

[a] a' and a have units of J K^{-1} mol^{-1}, b' and b have J K^{-2} mol^{-1}, c has the unit of J K^{-3} mol^{-1} and c' has J K mol^{-1}. The temperature range is 300–1500 K.

[b] S is the fitting square deviation.

TABLE 5

The derived S° values (J K^{-1} mol^{-1}) [a]

T (K)	$CH_3HSi{=}CH_2$	$FHSi{=}SiH_2$	$HSiCH_3$	CH_3SiCH_3	$HSiSiH_3$	$FSiSiH_3$
400	305.04	317.78	262.33	315.47	297.76	330.94
500	325.15	337.26	275.36	335.16	315.36	350.42
600	343.71	354.35	287.31	353.23	331.06	367.49
700	361.06	369.68	298.43	370.07	345.33	382.81
800	377.40	383.63	308.87	385.91	358.47	396.76
900	392.84	396.46	318.73	400.87	370.65	409.57
1000	407.48	408.33	328.07	415.07	382.01	421.43
1100	421.38	419.35	336.93	428.57	392.63	432.45
1200	434.58	429.62	345.37	441.43	402.58	442.72
1300	447.12	4392	353.39	453.68	411.91	452.31
1400	459.02	448.15	361.02	465.35	420.67	461.27
1500	470.30	456.5	368.28	476.47	428.87	469.64

[a] S is calculated according to $(\partial S/\partial T)p = C_p/T$, C_p takes the first form of our fitting results, and S_{300}° takes the calculated value.

TABLE 6

The derived values of $H_T - H_{298}$ (kJ mol^{-1}) [a]

T (K)	$CH_3HSi{=}CH_2$	$FHSi{=}SiH_2$	$HSiCH_3$	CH_3SiCH_3	$HSiSiH_3$	$FSiSiH_3$
300	0.13	0.14	0.09	0.13	0.12	0.14
400	7.90	8.18	5.17	7.80	7.23	8.18
500	16.93	16.92	11.03	16.64	15.14	16.93
600	27.13	26.30	17.59	26.57	23.75	26.3
700	38.40	36.26	24.81	37.51	33.02	36.25
800	50.65	46.71	32.64	49.38	42.86	46.69
900	63.77	57.61	41.01	62.09	53.21	57.58
1000	77.67	68.87	49.88	75.58	64.00	68.84
1100	92.25	80.44	59.19	89.75	75.14	80.4
1200	107.43	92.24	68.88	104.52	86.58	92.21
1300	123.09	104.21	78.91	119.83	98.24	104.19
1400	139.15	116.29	89.21	135.58	110.06	116.28
1500	155.51	128.4	99.73	151.7	121.95	128.41

[a] $H_T - H_{298}$ is calculated according to $(\partial H/\partial T)p = C_p$, and C_p takes the first form of our fitting results.

for all temperatures concerned. These are shown in Table 5 and 6. From Tables 2 and 5, it can be seen that the differences between the calculated entropies and derived entropies are less than 0.5 J K^{-1} mol^{-1}. The derived values of $H_T - H_{298}$ in Table 6 are also thought to be quite reliable, with the maximum error less than 0.5 kJ mol^{-1} [1].

DISCUSSION

So far, theoretical estimate of heats of formation are subject to some uncertainties [1] and inconsistencies exist between different results [8,14]. However, it is reasonable to think that errors will be greatly reduced when entropies and heat capacities are considered at the same level of calculation [1]. Thus, despite the lack of other data with which to compare our results, we believe that the maximum deviation of the present caculations for the entropies and heat capacities is about 1 e.u. [1] for all compounds discussed, in the temperature range 300–1500 K, which is a similar result to that of Benson [20,21].

The only listed data for entropies and heat capacities of particular compounds known to us is that provided in ref. 15, which predicts that for Me_2Si, $S°$ is 286 J K^{-1} mol^{-1} at 298.15 K, and $C_p°$ is 74, 101 and 132 J K^{-1} mol^{-1} at 300, 500 and 800 K respectively. These data are in approximate agreement with our results, the differences being about 7.0 J K^{-1} mol^{-1} for S at 298.15 K and 4.28 J K^{-1} mol^{-1} for $C_p°$ at 300 K. Considering that Walsh [15] obtained the above data by assuming that values for the known Me_2S may be used [20] according to structural analogue principles, we think that our results are likely to be more accurate and that the above approximate estimates of ref. 15 should be revised slightly.

CONCLUSIONS

The temperature dependence function obtained by fitting the heat capacities is very useful in understanding the thermochemistry of particular compounds. We have also derived some thermodynamic data from the fitting results.

Apart from predictions for entropies and heat capacities of this series of organosilicon compounds which we hope will receive experimental support in the future, we also hope that the calculated results in the present work can form part of a thermochemical data base from which the thermodynamic data of more complicated unstable or unsaturated organosilicon compounds may be estimated. Of course, when this kind of data base is large enough, it should prove possible to derive the additivity scheme, which is similar to that of saturated organosilicon compounds [12,13].

REFERENCES

1 G.-Z. Ju and W.-S. Bian, Thermochim. Acta, 167 (1990) 37.
2 G. Raabe and J. Michl, Chem. Rev., 85 (1985) 419.
3 M.S. Gordon, in J.F. Liebman and A. Greenberg (Eds.), Molecular Structure and Energetics, VCH, Deerfield Beach, FL, 1986.
4 R.T. Conlin and Y.W. Kwak, J. Am. Chem. Soc., 108 (1986) 834.
5 M.S. Gordon, T.N. Truong and E.H. Bonderson, J. Am. Chem. Soc., 108 (1986) 1421.
6 I.M.T. Davidson and K.J. Hughes, Organometallics, 6 (1987) 639.
7 G.-Z. Ju and W.-Y. Ma, Int. J. Quant. Chem. Symp., 22 (1988) 343.
8 R.S. Grev, G.E. Scuseria, H.F. Schaefer and M.S. Gordon, J. Am. Chem. Soc., 110 (1988) 7337.
9 P.P. Gaspar, in M. Jones, Jr. (Ed.) Reactive intermediates, Vol. 3, Wiley, New York, 1985.
10 Y.-R. Luo and S.W. Benson, J. Phys. Chem., 93 (1989) 1674, 3306, 3791, 4643.
11 M.S. Gordon, J.A. Boatz and R. Walsh, J. Phys. Chem., 93 (1989) 1584.
12 H.E. O'Neal and M.B. Runy, J. Organomet. Chem., 213 (1981) 419.
13 A.M. Doncaster and R. Walsh, J. Chem. Soc., Faraday Trans. 2, 82 (1986) 707.
14 K.K. Baldridge, J.A. Boatz, S. Koseki and M.S. Gordon, Ann. Rev. Phys. Chem., 38 (1987) 211.
15 R. Walsh, J. Phys. Chem., 90 (1986) 389.
16 J.E. Baggott, M.A. Blitz and R. Walsh, Chem. Phys. Lett., 135 (1987) 39.
17 R. Walsh, Organometallics, 7 (1988) 75.
18 S.K. Shin, K.K. Irikura, J.L. Beauchamp and W.A. Goddard III, J. Am. Chem. Soc., 110 (1988) 24.
19 T.L. Hill, Statistical Thermodynamics, Addison-Wesley, Reading, MA, 1960.
20 S.W. Benson, Thermochemical Kinetics, 2nd. edn., Wiley, New York, 1976.
21 S.W. Benson, Pure Appl. Chem., 52 (1980) 1767.