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THE ABSOLUTE ENTROPIES OF SiH_2 AND SiH_3

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SUMMARY

The absolute entropies and free energy functions between 200°K and 900°K for the singlet state of silene ($^1SiH_2$) have been calculated using recently established molecular parameters.

Similar calculations have been performed for silyl (SiH_3) using recently measured parameters and a reasonable estimate of the Si–H bond length. These data allow estimation of the equilibrium constants of the reactions

$$SiH_4 \rightleftarrows SiH_3 + H \qquad (1)$$

$$SiH_4 \rightleftarrows SiH_2 + H_2 \qquad (2)$$

The implications of the above data with respect to the mechanism of monosilane pyrolysis are outlined.

INTRODUCTION

Recent work[1-4] on silane pyrolysis has established that, at least for disilane and higher homologues, the primary formation and subsequent reactions of silene (SiH_2) are the important processes. In the case of monosilane only, is opinion divided, a silene-based pyrolysis mechanism being favoured on the one hand[1] and a silyl-based scheme on the other[5]. The arguments advanced for either view depend heavily on the validity of available thermochemical information. Alkylsilane pyrolyses and photolyses also are known[6,7], in some instances, to proceed through the primary formation and subsequent reactions of silene-like species but, especially with highly alkylated molecules, silyl-based mechanisms have also been proposed. An attempt[8] at rationalisation of the mechanistics of alkylsilane pyrolyses in general, *i.e.* the change over from a silene-based to a silyl-based reaction, has recently been made but, here again, thermochemical arguments predominate. While reasonably reliable thermochemical data are available for monosilane and disilane, information is sparse for higher silanes and their alkyl derivatives; correspondingly, no reliable data are known for radicals of the silyl series and only the heat of formation is known[4] with any certainty for silene. It seems clear that establishment of reliable thermochemical information for the silicon containing species quoted is an immediate need, if only to clarify the kinetic situation.

The recent identification of the singlet state of silene as the predominant, if not the only reactive species formed in the flash photolysis of monosilane[9,10] has allowed the unambiguous measurements of molecular parameters and vibrational frequencies from the corresponding spectra. Compatible, and more comprehensive vibrational assignments have also since been given by Jacox and Milligan[11]. Thus computation of the absolute entropy of the singlet state of silene for any temperature is now possible. Some, though not all, of the necessary information for the silyl radical is also available [11,12]. Thus, a start may be made on the compilation of the required information, and fortunately this can be done for the two most important entities in this field of study.

RESULTS AND DISCUSSION

A computer programme was devised to calculate statistical thermodynamic data for both linear and non-linear polyatomic molecules and radicals. A rigid rotator–harmonic oscillator approximation was assumed. The calculational procedure underlying the computations followed that described by Purnell and Quinn[13]. Input data comprised the cartesian co-ordinates of the atoms, the number and masses of the atoms, the symmetry number and degeneracy of the molecule or radical and the fundamental vibration frequencies.

The programme was first checked by computation of the entropy of methyl for temperatures at 100° intervals between 200°K and 900°K; the data derived agreed precisely with those calculated by Purnell and Quinn[13]. As a second check, the entropy of monosilane, again at 100° intervals over the range 200°K to 900°K, was computed; the derived data agreed reasonably with those of Altschuller[14], the discrepancies arose from our use of some recently revised data.

The kinetic evidence[3,4], as well as the spectroscopic evidence[9,10], points unambiguously both to a ground singlet state of silene and to the absence of the triplet species in the kinetic systems studied to date. Thus, published information relates to this state only. It may be noted that silene insertion reactions[3,4] are thus likely to be kinetically cleaner than are methylene insertion reactions and may, therefore, attain comparable or greater interest.

The data employed in the calculations for singlet silene are as follows: Si–H bond length[10], 1.516 Å; H–Si–H bond angle[10], 92.5°; ν_1 2032 cm^{-1}, ν_2 1008 cm^{-1}, ν_3 2022 cm^{-1} (Jacox and Milligan[11]); symmetry number 2. The position with regard to silyl is not so clear cut. Jackel and Gordy[12] have isolated the silyl radical in a rare gas matrix and have determined that the H–Si–H bond angle (α) is 113° 30′ and that the pyramidal angle (β) is 74° 0′. These values are to be compared with those for an undistorted sp^3 hybridised pyramidal structure, α 109°28′ and β 70°32′. Since some distortion of structure may be expected to occur in a solid matrix, it is likely that, in the gas phase, the latter values of α and β are more relevant. Hence, these values, along with the vibrational assignments of Jacox and Milligan[11]; 1999 cm^{-1}, 1955 cm^{-1} (2), 996 cm^{-1}, 925 cm^{-1} (2) have been used in the calculation. Finally, although the Si–H bond length has not been measured it is thought[11] to be slightly larger than that in SiH_4 (1.48 Å). It is unlikely to be greater than that in SiH_2 (1.516 Å) and so, with small error, we can set it at 1.48 Å. The vibrational assignments are not unambiguous but the arguments advanced are reasonably firm and make it more than likely that they are correct.

TABLE 1

STATISTICAL THERMODYNAMIC FUNCTIONS OF SINGLET SiH_2 FROM 200°K TO 900°K
Standard state, ideal gas at 1 atm.

Temp. (°K)	S^0	$-\left(\frac{G^0-H^0_0}{T}\right)$	$\left(\frac{H^0-H^0_0}{T}\right)$
		$(\text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1})$	
200	46.28	38.32	7.96
300	49.58	41.55	8.03
400	52.05	43.88	8.17
500	54.09	45.73	8.36
600	55.85	47.27	8.58
700	57.43	48.61	8.82
800	58.86	49.80	9.06
900	60.18	50.88	9.30

TABLE 2

STATISTICAL THERMODYNAMIC FUNCTIONS OF SiH_3 FROM 200°K TO 900°K
Standard state, ideal gas at 1 atm.

Temp. (°K)	S^0	$-\left(\frac{G^0-H^0_0}{T}\right)$	$\left(\frac{H^0-H^0_0}{T}\right)$
		$(\text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1})$	
200	47.85	39.86	7.99
300	51.39	43.14	8.25
400	54.25	45.57	8.68
500	56.77	47.56	9.21
600	59.05	49.29	9.76
700	61.14	50.84	10.30
800	63.08	52.25	10.83
900	64.89	53.55	11.34

The computed entropies and statistical thermodynamic functions of the two species are listed in Tables 1 and 2.

Entropies of SiH_3 have also been calculated using the data of Jackel and Gordy[11] for α and β and were found to be 0.10 $\text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$ less than those quoted in Table 1, at all temperatures. Thus, no substantial error is introduced here.

The data used in the computation of silene entropies are well documented and an assessment of likely error carried out in the light of previous calculations for alkyl radicals[13] indicates that the tabulated data are good to better than ± 0.5 $\text{cal}\cdot\text{mole}^{-1}\cdot\text{deg}^{-1}$. The silyl data, on the other hand, are less securely based but, a similar assessment leads to the view that they are good to ± 1.0 $\text{cal}\cdot\text{mole}^{-1}\cdot\text{deg}^{-1}$. The only published estimate of S° for SiH_2 is that made by Bowrey and Purnell[4] who, following a suggestion made by Walsh, equated this to the known value for SH_2 at 300°K *i.e.* 49.5 $\text{cal}\cdot\text{mole}^{-1}\cdot\text{deg}^{-1}$. This approach is now seen to give a remarkably accurate estimate and so, the calculations regarding pre-exponential factors of silene insertion reactions based on this value[4] require no correction on this account.

The data also allow the question of the mechanism of monosilane pyrolysis to be looked at afresh on more certain thermochemical grounds. The heat of formation of SiH_2 has been measured kinetically[4] during the study of disilane pyrolysis. The value derived, 59.3 kcal · mole^{-1}, is not subject to argument since there is agreement on the mechanism and rate data. The results of this study also established that the heat of formation of $SiH_3 \geqslant 36.6$ kcal · mole^{-1}. Ring, Puentes and O'Neal[5] have argued recently that monosilane pyrolysis is initiated via the reaction (1) rather than reaction (2) favoured by Purnell and Walsh[1].

$$\mathrm{SiH_4} \rightarrow \mathrm{SiH_3}+\mathrm{H} \tag{1}$$

$$\mathrm{SiH_4} \rightarrow \mathrm{SiH_2}+\mathrm{H_2} \tag{2}$$

The theoretical argument advanced by Ring *et al.*[5] is dependent on the assumed thermochemistry of a number of reactions and, among other data, they used a value for the heat of formation of SiH_3 of 49.7 kcal · mole^{-1}. Using this value, that quoted above for SiH_2, and the tabulated entropy data, the equilibrium constant for the reaction (3)

$$\mathrm{SiH_3}+\mathrm{H} \rightleftarrows \mathrm{SiH_2}+\mathrm{H_2} \tag{3}$$

is $K_3 = 10^{15.9}$ at 600°K. There can be little doubt, therefore, that SiH_3 is thermodynamically totally unstable with respect to SiH_2 at typical silane pyrolysis temperatures. In extension, we may consider the further equilibrium (4) which relates to disilane

$$\mathrm{SiH_3}+\mathrm{SiH_3} \rightleftarrows \mathrm{SiH_2}+\mathrm{SiH_4} \tag{4}$$

pyrolysis as (3) relates to monosilane pyrolysis. The heat of formation[15] of monosilane is 7.3 kcal · mole^{-1} (accepted also in ref. 5), while the entropy at 600°K is 57.72 cal · mole^{-1} · deg^{-1}. These data yield $K_4 = 10^{11.3}$. Since disilane is undoubtedly agreed to dissociate to silene and monosilane[2–4], it would seem inconsistent, in the light of the above values of K_3 and K_4, to favour reaction (1) over (2) in the case of monosilane pyrolysis.

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