Journal of Organometallic Chemistry, 169 (1979) 155—164

1,1-DIMETHYL-1-SILAETHYLENE

HEAT OF FORMATION, IONIZATION POTENTIAL AND THE ENERGY OF THE SILICON—CARBON π-BOND

L.E. GUSEL'NIKOV * and N.S. NAMETKIN

Topchiev Institute of Petrochemical Synthesis, Academy of Sciences, Moscow (U.S.S.R.)

(Received October 2nd, 1978)

Summary

The thermodynamic cycle consisting of thermal decomposition and dissociative ionization processes for 1,1-dimethyl-1-silacyclobutane is calculated. The heat of formation and the ionization potential (*IP*) for 1,1-dimethyl-1-silaethylene (DMSE) have been obtained: ΔH_f^0(DMSE) = 15.5 ± 5 kcal/mol; *IP*(DMSE) = 7.5 ± 0.3 eV. The silicon—carbon π-bond energy in DMSE is estimated: D_π(Si=C) = 28 ± 8 kcal/mol.

Introduction

In the last few years considerable interest has been shown in the chemistry of the unstable compounds $R_2Si{=}X$ (X = CR_2, NR, O, S, SiR_2) [1,2], the structure and the reactivity of which are explained in terms of a $(p{-}p)\pi$ bonding concept. Calculations on the $H_2Si{=}CH_2$ molecule by ab initio methods using extended basis and electron correlation [3] have shown that the energy of its singlet state is less by 28 kcal/mol than that of its low energy triplet. This result as well as the data of other quantum chemical calculations [4,5] shows that silaalkenes in their ground state can be represented by structures with a polarized silicon—carbon double bond ($Si^+{=}C^-$). Attempts have been made to study by low temperature infrared spectroscopy the intermediates $Me_2Si{=}CHMe$ [6,7] and $Me_2Si{=}CH_2$ [8] isolated in an argon matrix. However in order to classify the absorption bands observed, additional data will apparently be needed. The value of the silicon—carbon π-bond energy calculated by quantum chemical [3—5,9,10] and thermochemical [11—14] methods shows that in all cases such bonds are weaker than the π-bond in olefins. Unfortunately, the

---

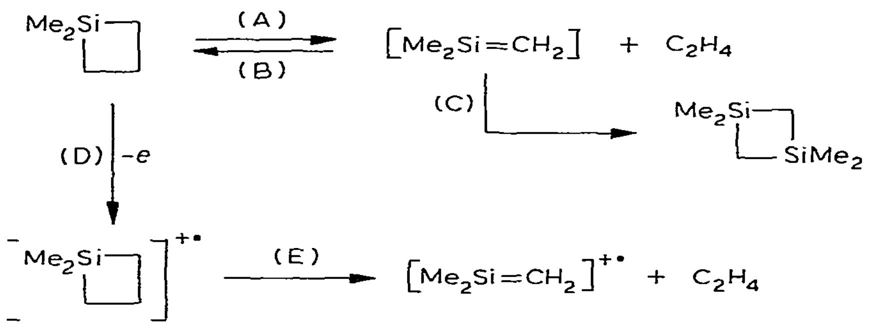
* Author to whom correspondence should be addressed.

values obtained by the various authors differ so much that it is difficult to accept any one of them as being the most reliable.

Results and discussion

The main aim of the present paper is to find the heat of formation, the ionization potential and the silicon—carbon π-bond energy for a molecule of 1,1-dimethyl-1-silaethylene (DMSE) from a kinetic study [15,16] of pyrolysis (Scheme 1, A, B and C) of 1,1-dimethyl-1-silacyclobutane (DMSCB), from a thermochemical determination of the heat of formation of silacyclobutanes [17], and from the study of processes D and E in Scheme 1 by photoionization mass-spectroscopy [18].

SCHEME 1



Calculations were made using eq. 1—3:

$$\Delta H^0_{\mathrm{A,B}} = \underline{\Delta H^0_{\mathrm{f}}(\mathrm{DMSE})} + \Delta H^0_{\mathrm{f}}(\mathrm{C_2H_4}) - \Delta H^0_{\mathrm{f}}(\mathrm{DMSCB}) \qquad (1)$$

$$\Delta H^0_{\mathrm{A,B}} = AP(\mathrm{DMSE})^{+\cdot}_{\mathrm{DMSCB}} - \underline{IP(\mathrm{DMSE})} \qquad (2)$$

$$\Delta H^0_{\mathrm{A,B}} = D(\mathrm{C{-}C}) + D(\mathrm{Si{-}C}) - \underline{D_\pi(\mathrm{Si{=}C})} - D_\pi(\mathrm{C{=}C}) - E_{\mathrm{S}} \qquad (3)$$

where $\Delta H^\circ_{\mathrm{A,B}}$ is the enthalpy of decomposition of DMSCB at 298 K; $\Delta H^\circ_{\mathrm{f}}$(DMSE), $\Delta H^\circ_{\mathrm{f}}(\mathrm{C_2H_4})$ and $\Delta H^\circ_{\mathrm{f}}$(DMSCB) are the standard values of heat of formation of DMSE, C_2H_4 and DMSCB respectively in gaseous phase; $AP(\mathrm{DMSE})^{+\cdot}_{\mathrm{DMSCB}}$ is the potential at which the ion $[\mathrm{Me_2Si{=}CH_2}]^{+\cdot}$ appears during the dissociative ionization of DMSCB; D(C—C), D(Si—C), D_π(Si=C) and D_π(C=C) are the bond dissociation energies and E_{S} is the strain energy of the monosilacyclobutane ring.

Equations of types 1 and 2 are generally used in kinetic and mass spectral methods for determining the heat of formation of free radicals [19], and eq. 3, which was used for the first time by Walsh [12], results from applying a structure-additive principle of thermochemical calculations to processes A and B. As is seen from these equations all unknown thermochemical values (underlined) are expressed in terms of enthalpy of the decomposition process of DMSCB, which when allowances are made for different assumptions [20], is equal to the difference in the activation energies of reactions A and B:

$$\Delta H^0_{A,B} = E_A - E_B \tag{4}$$

The activation energy of direct reaction E_A (62.3 ± 0.8 kcal/mol [15]) has been determined with sufficient accuracy from the rate constants for the decomposition of DMSCB at nine different temperatures in one series of experiments (from pressure change measurements) and for five temperatures in another series of experiments (analysis of reaction mixture by GLC) over the temperature range 394—451°C. The study of the kinetics of pyrolysis of DMSCB under similar conditions in the presence of ethylene [15] also gave eq. 5 linking E_B and E_C:

$$E_B - \tfrac{1}{2}E_C = 14.5 \pm 4.0 \text{ kcal/mol} \tag{5}$$

Using eq. 5 and by assuming that [DMSE] $\leqslant$0.1 [DMSCB] Walsh [12] estimated lower and upper limits of $\Delta H^\circ_{A,B}$ as follows:

$$35 < \Delta H^\circ_{A,B} < 52 \text{ kcal/mol}$$

Recently it was established [16] that reaction C is a non-activated process * ($E_C = 0$) and, therefore, $E_B = 14.5 \pm 4.0$ kcal/mol. Substituting the values of E_A and E_B in eq. 4, we find:

$$\Delta H^\circ_{A,B} = (62.3 \pm 0.8) - (14.5 \pm 4) = 47.8 \pm 4.8 \text{ kcal/mol.}$$

Heat of formation of $Me_2Si{=}CH_2$

The heat of formation of DMSE was found from eq. 1, which is an application of Hess' law to reactions A and B, in which the value calculated above, $\Delta H^\circ_{A,B}$, the heat of formation of ethylene (12.5 kcal/mol [21]) and the heat of formation of DMSCB all appear. Hajiev and coworkers [22] by studying the combustion of this compound in a rotating bomb calorimeter found ΔH°_f(DMSCB) = 43.6 kcal/mol. According to Dewar et al. [11], who calculated this value by the quantum chemical method MINDO/3, ΔH°_f(DMSCB) = —40.1 kcal/mol; while Genchel et al. [17], using data on combustion of DMSCB in the presence of benzotrifluoride, calculated ΔH°_f(DMSCB) = —19.8 ± 1.4 kcal/mol. The last value of ΔH°_f(DMSCB) was used in our calculation of ΔH°_f(DMSE), since it is apparently free from errors arising from incomplete combustion of the organosilicon compound:

$$(47.8 \pm 4.8) = \Delta H^\circ_f(\text{DMSE}) + 12.5 - (-19.8 \pm 1.4)$$
$$\Delta H^\circ_f(\text{DMSE}) = 15.5 \pm 6.2 \text{ kcal/mol.}$$

The heat of formation of DMSE obtained by us proved to be much higher than the same parameter calculated by the MINDO/3 method (—19.9 kcal/mol [11]). We compared both the values of ΔH°_f(DMSE) by calculating from them, using eq. 1 and the values given above for ΔH°_f (DMSCB), the enthalpy of thermal decomposition of DMSCB (Table 1). In doing so the plausibility of the

---

* It might be as well to point out that theoretical consideration of the cyclodimerization reaction $H_2Si{=}CH_2$ by quantum chemical, ab initio [3,10] and MINDO/3 [10] methods gives, respectively, much higher (14 kcal/mol) and even exaggerated value of activation energy (64 kcal/mol).

TABLE 1

ENTHALPY OF THERMAL DECOMPOSITION OF DMSCB ($\Delta H^0_{A,B}$, kcal/mol) DETERMINED FROM EQ. 1 FOR DIFFERENT VALUES OF ΔH^0_f(DMSCB) AND ΔH^0_f(DMSE)

ΔH^0_f(DMSCB) (kcal/mol)	ΔH^0_f(DMSE) (kcal/mol)	
	15.5 [a]	−19.9 [b]
43.6 [c]	−15.6	−51.0
−19.8 [d]	47.8	12.4
−40.1 [b]	68.0	32.6

[a] Value obtained in the present work. [b] Calculated by MINDO/3 [11] method. [c] Combustion in oxygen [22]. [d] Combustion in the presence of $PhCF_3$ [17].

value of $\Delta H^\circ_{A,B}$ obtained was considered as a criterion of the authenticity of values of thermochemical parameters used in the calculation.

As may be seen from Table 1 calculation of the heat of formation of DMSCB, determined by Hajiev and coworkers [22], and ΔH°_f (DMSE), obtained either in the present work or by MINDO/3 methods, gives negative values for $\Delta H^\circ_{A,B}$ (−15.6 kcal/mol, −51.0 kcal/mol). These values do not agree with the observed instability of the intermediate $Me_2Si{=}CH_2$ (the energy of activation of reaction B is 77.9 or 113.3 kcal/mol, respectively) and, apparently, stem mainly from the error in determining ΔH°_f(DMSCB). Similar calculation of $\Delta H^\circ_{A,B}$ from the data obtained by MINDO/3 method (32.6 kcal/mol) gives a value that lies at the level of lower limit of this parameter (after Walsh [12]). Values of $\Delta H^\circ_{A,B}$ deviate beyond probable limits, if mixed thermochemical data (12.4 kcal/mol or 68 kcal/mol), the incompatibility of which is evident, are used.

Thus, in the set of values for the heat of formation given in Table 1 ΔH°_f(DMSCB) = −19.8 kcal/mol and ΔH°_f(DMSE) = 15.5 kcal/mol show a satisfactory fit with the expected value of $\Delta H^\circ_{A,B}$.

Ionization potential of $Me_2Si{=}CH_2$

Although direct observation of $Me_2Si{=}CH_2$ by mass spectrometry has been made recently [16], experimental determination of the ionization potential of this unstable molecule *IP*(DMSE) is yet to be made. This value may however be found by quantum chemical methods and thermochemical calculations. Dewar and coworkers [11] through the use of MINDO/3 programme, estimated the ionization potential of DMSE, and found it to be 9.0 eV. The present authors calculated *IP*(DMSE) using eq. 2, which is generally employed for the deter-

SCHEME 2

$$\begin{tikzcd}
\Delta H_f^\circ(\mathrm{DMSCB}) \arrow[r] \arrow[d, "IP(\mathrm{DMSCB})"'] \arrow[dr, "AP(\mathrm{DMSE})^{+\bullet}_{\mathrm{DMSCB}}"] & \Delta H_f^\circ(\mathrm{DMSE}) + \Delta H_f^\circ(C_2H_4) \arrow[d, "IP(\mathrm{DMSE})"] \\
\Delta H_f^\circ(\mathrm{DMSCB})^{+\bullet} \arrow[r] & \Delta H_f^\circ(\mathrm{DMSE})^{+\bullet} + \Delta H_f^\circ(C_2H_4)
\end{tikzcd}$$

TABLE 2

ENTHALPHY OF THERMAL DECOMPOSITION OF DMSCB ($\Delta H^0_{A,B}$ kcal/mol) FOUND FROM EQ. 2 FOR DIFFERENT VALUES OF IP(DMSE)

IP(DMSE) (eV)	$AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}}$ (eV)
	9.61 [a]
7.5 [b]	47.8
9.0 [c]	14.1

[a] Value determined by photoionization mass spectrometry [18]. [b] Values obtained in the present work. [c] Calculated by the MINDO/3 method [11].

mination of heats of formation and bond dissociation energies according to the thermodynamic cycle suggested by Born-Haber [24]. This can be presented as in Scheme 2 for reactions A, B, D and E. In these calculations the value given above for $\Delta H^\circ_{A,B}$ and the appearance potential of the $[Me_2Si{=}CH_2]^{+\bullet}$ ion in the dissociative ionization of DMSCB (9.61 ± 0.05 eV) found by photoionization mass spectroscopy [18] were also used.

$$(47.8 \pm 4.8)/23.06 = (9.61 \pm 0.05) - IP(\text{DMSE})$$
$$IP(\text{DMSE}) = 7.5 \pm 0.3 \,{*}\ \text{eV}$$

As is seen, the ionization potential obtained for DMSE is lower by 1.5 eV than the value calculated by the MINDO/3 method [11]. As for ΔH°_f(DMSE), we estimated the accuracy of values of IP(DMSE) obtained by us and by Dewar and coworkers [11] after calculating from this value and the known value of $AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}}$ the enthalpy of thermal decomposition of DMSCB (Table 2).

As may be seen, the calculation based on IP(DMSE) = 9.0 eV gives a very low value for $\Delta H^\circ_{A,B}$, which corresponds to $E_B = 48.2$ kcal/mol.

Thereafter, we verified the whole set of thermochemical values: ΔH°_f(DMSCB), ΔH°_f(DMSE) and IP(DMSE) obtained by MINDO/3 [11] methods. Equation 6 was used for this purpose. It was obtained by comparing the right hand terms of eqs. 1 and 2:

$$\Delta H^\circ_f(\text{DMSE}) + \Delta H^\circ_f(C_2H_4) - \Delta H^\circ_f(\text{DMSCB}) = AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}} - IP(\text{DMSE})$$
$$(-19.9) + 12.5 - (-40.1) : 23.06 = AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}} - 9.0 \qquad (6)$$

whence

$$AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}} = 10.4\ \text{eV}$$

Thus, the appearance potential of DMSE ion calculated from MINDO/3 data is 0.8 eV higher than the experimentally found value of $AP(\text{DMSE})^{+\bullet}_{\text{DMSCB}}$ [18]. Apparently, this disagreement is associated with the errors in determining thermochemical data, which appear to be due to limitations of the MINDO/3 method regarding the above listed molecules [10].

---

* Since $IP(\text{DMSE}) < IP(C_2H_4)$ it is assumed that ion $[Me_2Si{=}CH_2]^{+\bullet}$ and uncharged C_2H_4 are formed in process E without additional energy [23].

TABLE 3

Si—C AND Si—H BOND DISSOCIATION ENERGIES IN ORGANOSILICON COMPOUNDS

$D(\equiv Si-CH_3)$	Compound	Ref.	$D(\equiv Si-H)$	Compound	Ref.
70.7	Me_4Si	14	76	Me_4Si [a]	29
71.8	$Me_3SiSiMe_3$ [b]	25, 26	77.3	SiH_4 [c, d]	11,34
73.0	Me_4Si [e]	27	77.7	SiH_4 [e]	32
74.4	Me_4Si [a]	28	80.3	Me_3SiH [f]	30
74.8	Me_2SiHCl, $MeSiHCl_2$, $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl [b]	46, 47	81		39
76	Me_2SiH_2, Me_3SiH [b]	38, 39	81 ± 2	Me_3SiH [a]	29
76 ± 2	Me_4Si [a]	29	81 ± 5	Me_3SiH [g]	35
76.5	Me_3SiH [f]	30	81.8	Me_2SiHCl, $MeSiHCl_2$,,$MeSiCl_3$, Me_2SiCl_2, Me_3SiCl [b]	46, 47
85 ± 4.5	[a]	31	86 ± 5	Cl_3SiH [g]	35
86 ± 4	$MeSiCl_3$ [a]	32	88.0	Me_3SiH [a,f]	36, 40
90.1	$MeSiCl_3$ [e]	33	89.9	Me_3SiH [h]	37
91.8	Me_4Si [e]	33	91.3	Cl_3SiH [h]	33
93 ± 4	$MeSiCl_3$ [a]	32	93 ± 4	$HSiCl_3$ [a]	32
			89 ± 4	[a]	31
			94 ± 3	SiH_4 [a]	32

[a] Mass spectrometry. [b] Calculation from calorimetric data. [c] Quantum chemical data. [d] Semi-empirical calculation. [e] Thermochemical calculation. [f] Pyrolysis kinetics. [g] Kinetics of H abstraction by methyl radical. [h] Kinetics of iodination.

TABLE 4

SILICON—CARBON π-BOND ENERGIES, D_π(Si=C) (kcal/mol), CALCULATED FROM EQ. 3 ($\Delta H^0_{A,B}$ = 47.8 kcal/mol; D(C—C) = 82 kcal/mol [12]; D(Si—C) = 76.0 kcal/mol [30, 41]). THE VALUES OBTAINED USING D(Si—C) = 85.0 kcal/mol ARE GIVEN IN PARENTHESIS

E_S (kcal/mol)	D_π(C=C) (kcal/mol)	
	59 [a]	63.1 [b]
18.9 [c]	32.3 (41.3)	28.2 (37.2)
20.0 [d]	31.2 (40.2)	27.1 (36.1)
25.9 [c]	25.3 (34.3)	21.2 (30.2)

[a] Thermochemical calculation [21]. [b] See ref. [5]. [c] Strain energy of triethane ring [42]. [d] Heat of polymerisation of DMSCB [48]. [e] Thermochemical data [15].

Energy of the silicon—carbon π-bond

The energy of the silicon—carbon π-bond was estimated by the methods proposed by Walsh and Dewar. According to Walsh [12] the enthalpy of thermal decomposition of DMSCB is written as the difference of the energies of rupturing σ-bonds and forming π-bonds minus the strain energy of the monosilacyclobutane ring (eq. 3). In this calculation we used the following values of carbon—carbon σ- and π-bond dissociation energies: D(C—C) = 82.0 kcal/mol [13], D_π(C=C) = 59 kcal/mol [12,21] and 63.1 kcal/mol [5]. More difficult was the selection of a proper value for the Si—C bond energy (Table 3). For a long time D(Si—C) = 76 kcal/mol was an established value, which complied with the results obtained by kinetic [30], thermochemical [38,39,47] and mass spectral methods [29]. However, much higher values of this parameter have been reported in the last few years (85—92 kcal/mol) [31,33]. Using kinetic methods, for example, such an increase is due to account not being taken of the contribution of the chain mechanism of thermal decomposition mentioned in earlier papers [30,41]. For this reason we used two values of Si—C cleavage energy in the calculation according to Walsh (76 kcal/mol and 85 kcal/mol) [31].

Another uncertainty appears when estimating the strain energy of the monosilacyclobutane ring (E_S). On the assumption that heterocycles of a given size which contain heteroatoms belonging to the same period have almost the same strain energies, Walsh used in his calculation a value for the strain energy of the thiethane ring of 18.9 kcal/mol [42]. The strain energy of the monosilacyclobutane ring estimated from thermochemical data [15] is 25.9 kcal/mol, and from polymerization enthalpy 20 kcal/mol. Using these three values of E_S we calculated D_π(Si=C). The results are given in Table 4.

According to Dewar [11] the energy of the silicon—carbon π-bond is expressed in terms of hydrogenation enthalpy of DMSE (eq. 7), which in turn may be determined as the difference of the heats of formation of trimethylsilane and DMSE (eq. 8):

$$\mathrm{Me_2Si{=}CH_2 + H_2 \rightarrow Me_3SiH}$$

$$\Delta H^0_{\text{hydro}} = D_\pi(\text{Si=C}) + D(\text{H—H}) - D(\text{Si—H}) - D(\text{C—H}) \tag{7}$$

$$\Delta H^0_{\text{hydro}} = \Delta H^0_f(\text{Me}_3\text{SiH}) - \Delta H^0_f(\text{DMSE}) \tag{8}$$

TABLE 5

SILICON—CARBON π-BOND ENERGY, D_π(Si=C) (kcal/mol) CALCULATED FROM EQ. 9: D(H—H) = 104.2 kcal/mol [21,27], D(≡SiCH$_2$—H) = 97.0 kcal/mol [43], D(Si—H) = 80.3 kcal/mol [29,35] THE VALUES OBTAINED FOR D(Si—H) = 89.9 kcal/mol [37] ARE IN PARENTHESIS

ΔH_f^0(Me$_3$SiH)$_{gas}$ (kcal/mol)	ΔH_f^0(DMSE)$_{gas}$ (kcal/mol)	
	15.5 [a]	—19.9 [b]
—37.3 [c]	20.3 (29.9)	55.7 (65.3)
—44.5 [b]	13.1 (22.7)	48.5 (58.1)
—55.0 [d]	2.6 (12.2)	38.0 (47.6)
—60.0 [e]	—2.4 (7.2)	33.0 (42.6)

[a] Values obtained in this work. [b] Data of MINDO/3 [11]. [c] Thermochemical calculation [44]. [d] Calculation from mass spectral data [29]. [e] Calculation from calorimetric data [38].

which gives:

$$D_\pi(\text{Si=C}) + D(\text{H—H}) - D(\text{Si—H}) - D(C\text{—}H) = \Delta H_f^0(\text{Me}_3\text{SiH}) - \Delta H_f^0(\text{DMSE}) \quad (9)$$

Using eq. 9 the silicon—carbon π-bond energy was found from the known values of heat of formation and binding energies. The values of H—H and ≡SiCH$_2$—H bond energies are 104.2 kcal/mol [21,27] and 97.0 kcal/mol [43], respectively. From the values of D(Si—H) listed in Table 3 we selected two values, 80.3 and 89.9 kcal/mol. The former was taken from kinetic data for the pyrolysis of trimethylsilane [30,41] (contribution from the chain process is ignored) and is in agreement with the values obtained by mass spectrometry [29], and also with the data from kinetic studies of the abstraction of an H atom from Si in Me$_3$SiH by a methyl radical [35]. The latter was found when studying Me$_3$SiH iodination kinetics [37] and agrees with D(Si—H) = 88.0 kcal/mol [36], a value derived from the kinetic data on pyrolysis of this compound in the presence of *m*-xylene. In this calculation known values for the heat of formation of trimethylsilane, ΔH_f°(Me$_3$SiH): —37.5 kcal/mol [44], —44.5 kcal/mol [11], —55 kcal/mol [29], —60 kcal/mol [38] were also verified. The results are presented in Table 5.

It is seen from Tables 4 and 5 that the π-bond energy in DMSE found by different methods depends upon the data selected for calculation. The following values of bond energies, strain energy of the monosilacyclobutane ring and heats of formation (kcal/mol) were used in the calculation: D(H—H) = 104.2; D(≡SiCH$_2$—H) = 97.0; D(C—C) = 82.0; D(C=C) = 59—61.3; D(Si—C) = 76—85.0; D(Si—H) = 80.3—89.9; E_S = 18.9—25.9; ΔH_f°(Me$_3$SiH) = —(37.3—44.5); ΔH_f°(DMSCB) = —19.8; ΔH_f°(DMSE) = 15.5. Consideration of the values of D_π(Si=C) in Tables 4 and 5, which are in accord with this set of thermochemical data, leads to the following value for the π-bond energy in DMSE:

D_π(Si=C) = 28.8 ± 8 * kcal/mol

It is of interest to compare the value of D_π(Si=C) obtained in the present work with other estimates of this value (Table 6).

---

* Standard deviation.

TABLE 6

SILICON—CARBON π-BOND ENERGY, D_π(Si=C) (kcal/mol)

Value obtained in this work	Calculation by quantum mechanical methods	Thermochemical calculations
28 ± 8 [a]	2.63 [b]	17 [c]
	9.0 [d]	26—46 [e]
	9.54 [f]	28 [g]
	19.8 [h]	37.8 [i]
	22.3 [j]	42.3 [k]
	46.0 [l]	

[a] $Me_2Si=CH_2$, calculation based on kinetic [15,16] and thermochemical [17] data. [b] $H_2Si=CH_2$, EHMO using spd basis [4]. [c] $Me_2Si=CH_2$, from kinetic data [14]. [d] $H_2Si=CH_2$, EHMO using *sp* basis [4]. [e] $Me_2Si=CH_2$, calculation [12] from kinetic data [15]. [f] $H_2Si=CH_2$, CNDO [4]. [g] Calculation [13] based on the dissociation energy of C—Si. [h] $\overline{CH=CHCH=CHC}=SiMe_2$, CNDO/2 [9]. [i] $MeHSi=CH_2$, calculation [12] from kinetic data [30]. [j] $H_2Si=CH_2$, FSGO [5]. [k] Calculation from the heats of formation obtained by MINDO/3 [11] method. [l] $H_2Si=CH_2$, ab initio method using extended basis and electron correlation [3,10].

As is seen, our value of D_π(Si=C) is in good agreement with the data of quantum chemical calculations [5,9], in which the barrier of rotation about the Si=C bond was determined. This also agrees with thermochemical calculations [12,14], kinetic data [14,15,30], and with the calculation based on the dissociation energy of Si—C [13]. But in other cases the quantum chemical methods either underestimate [4] or overestimate [3,10] D_π(Si=C). An overestimated value for Si=C π-bond energy was also obtained from the heats of formation found by a semi-empirical calculation method, MINDO/3 [11].

References

1 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Accounts Chem. Res., 8 (1975) 18.
2 H. Sakurai, J. Japan. Chem. (Kagaki no ryoiki), 20 (1975) 742.
3 R. Ahlrichs and R. Heinzmann, J. Amer. Chem. Soc., 99 (1977) 7452.
4 M.D. Curtis, J. Organometal. Chem., 60 (1973) 63.
5 P.H. Blustin, J. Organometal. Chem., 105 (1976) 161.
6 O.L. Chapman, C.C. Chang, J. Kole, M.J. Jung, J.A. Lowe, T.J. Barton and M.L. Tumey, J. Amer. Chem. Soc., 98 (1976) 7844.
7 M.R. Chidekel, M. Skoglund, R.L. Kreeger and H. Chechter, J. Amer. Chem. Soc., 98 (1976) 7846.
8 A.K. Maltsev, V.N. Khabashesky and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 223 (1977) 421.
9 Yu.A. Ustynuk, P.I. Zakharov, A.A. Azizov, G.A. Shehembelov and I.P. Glorizov, J. Organometal. Chem., 96 (1975) 195.
10 S. Bantle and R. Ahlrichs, Chem. Phys. Lett., 53 (1978) 148.
11 M.J.S. Dewar, D.H. Lo and C.A. Ramsden, J. Amer. Chem. Soc., 97 (1975) 1311.
12 R. Walsh, J. Organometal. Chem., 38 (1972) 245.
13 R.A. Jackson, Chem. Soc. Spec. Publ. No. 24, (1970) 299.
14 R.P. Clifford, B.G. Gowenlock, C.A.F. Johnson and J. Stevenson, J. Organometal. Chem., 34 (1972) 53.
15 M.C. Flowers and L.E. Gusel'nikov, J. Chem. Soc. B, (1968) 419, 1396.
16 L.E. Gusel'nikov, K.S. Konobeevsky, V.M. Vdovin, N.S. Nametkin, Dokl. Akad. Nauk SSSR, 235 (1977) 1086.
17 V.G. Genchel, N.V. Demidova, N.S. Nametkin, L.E. Gusel'nikov, E.A. Volnina, E.N. Burdasov and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2337.
18 L.E. Gusel'nikov, V.K. Potapov, E.A. Volnina, V.Yu. Orlov, V.M. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 229 (1976) 1364.
19 H.E. O'Neal and S.W. Benson in J.K. Kochi (Ed.) Free Radicals, Vol. 2, Wiley, N.Y., 1973, p. 275.
20 J.A. Kerr, Chem. Rev., 66 (1966) 465.
21 S.W. Benson, J. Chem. Educ., 42 (1965) 502.

22 S.N. Hajiev, G.G. Nurullaev and M.J. Agarunov, Proc. 3rd Intern. Conf. Chemical Thermodynamics, Vienna, September 1975, Vol. 2, paper 5.
23 D.B. Chambers, F. Glockling and J.R.C. Light, Quart. Rev. Chem. Soc., 22 (1968) 317.
24 R.I. Reed, Quart. Rev. Chem. Soc., 20 (1966) 527.
25 V.I. Tel'noi, Trudy po khimii i khimicheskoi tekhnologii, Vol. 1, Gorky, 1974, p. 28.
26 B.S. Iseard, J.B. Pedley and J.A. Treverton, J. Chem. Soc. A, (1971) 3095.
27 D.A. Johnson, Some Thermodinamic Aspects of Inorganic Chemistry, Cambridge University Press, 1968.
28 M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding, J. Organometal. Chem., 29 (1971) 195.
29 S.J. Band, I.M.T. Davidson and C.A. Lambert, J. Chem. Soc. A, (1968) 2068.
30 I.M.T. Davidson and C.A. Lambert, J. Chem. Soc. A, (1971) 882.
31 P. Potzinger, A. Ritter, K. Krause, IVth Intern. Symp. Organosilicon Chemistry, Moscow, July 1975, Abstracts Vol. 1, part 1, p. 31.
32 W.C. Steele, L.D. Nichols and F.G.A. Stone, J. Amer. Chem. Soc., 84 (1962) 4441.
33 R. Walsh and J.M. Wells, J. Chem. Soc. Faraday Trans. I, 72 (1976) 1212.
34 P.C. Jordan, J. Chem. Phys., 44 (1966) 3400.
35 J.A. Kerr, D.H. Slater and J.C. Young, J. Chem. Soc. A, (1967) 134.
36 I.M.T. Davidson and B. Howard, J. Chem. Soc. Chem. Commun., (1973) 323.
37 R. Walsh and J.M. Wells, J. Chem. Soc. Faraday Trans. I, 72 (1976) 100.
38 S. Tannenbaum, J. Amer. Chem. Soc., 76 (1954) 1027.
39 A.M. Mosin and Yu.Kh. Shaulov, Zh. Phys. Khim., 46 (1972) 1832.
40 G.G. Hess, F.W. Lampe and L.H. Sommer, J. Amer. Chem. Soc., 87 (1965) 5327.
41 I.M.T. Davidson, Quart. Rev. Chem. Soc., 25 (1971) 111.
42 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haungen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
43 J.A. Kerr, A. Stephens and J.C. Young, Int. J. Chem. Kinet., 1 (1969) 339.
44 A.M. Mosin and Yu.Kh. Shaulov, Zh. Phys. Khim., 46 (1972) 1838.
45 I.M.T. Davidson, Specialist Periodical Report: Reaction Kinetics, Vol. 1, The Chemical Society, London, 1975.
46 S.N. Hajiev and M.J. Agarunov, J. Organometal. Chem., 22 (1970) 305.
47 S.N. Hajiev and M.J. Agarunov, J. Organometal. Chem., 11 (1968) 415.
48 B.N. Lebedev. I.B. Rabinovich, N.K. Lebedev and N.V. Ushakov, Dokl. Akad. Nauk SSSR, 239 (1978) 1140.