Journal of Organometallic Chemistry, 359 (1989) 169–177
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Thermochemistry of organosilicon compounds

II *. 1-Organylsilatranes

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(Received May 25th, 1988)

Abstract

The enthalpies of combustion and sublimation of 1-organylsilatranes with the general formula $X\overline{Si(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N}$ ($n = 0$–3) have been determined. The enthalpies of formation in the solid and liquid state and the enthalpy of atomization have been evaluated. The enthalpies of atomization have been calculated by an additive scheme ignoring the total stress energy of the silatrane skeleton and the transannular interaction between the silicon and nitrogen atoms ($E_{cycl.} - E_{Si \leftarrow N}$). The enthalpies of formation of the silatrane group $\overline{Si(OCH_2CH_2)_3N}$ ($\Delta H^\circ_{f,298.15\,\overline{Si(OCH_2CH_2)_3N}}$) have been estimated as -782 ± 10 kJ mole^{-1}. The proportion of this value due to contributions by the heterocyclic system stress and the transannular Si ← N interaction, the latter ranging from 30 to 50 kJ mole^{-1} depending on the nature of the substituent X at the silicon atom, was also estimated. Sequential introduction of methyl groups to the 3-, 7- and 10-positions of the silatrane skeleton increases the $E_{cycl.} - E_{Si \leftarrow N}$ value up to 62.8 and 90.0 kJ mole^{-1}, respectively, because of a concomitant increase in the Prelog strain. The enthalpy of formation of finely dispersed hydrated amorphous silicon dioxide produced in a calorimetric bomb on detonation has been measured.

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* For part I see ref. 14.

0022-328X/89/$03.50

Table 1

Thermochemical constants of the silatranes $X\overline{Si(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N}$ (kJ mole^{-1})

X	n	$-\Delta H^\circ_{C,298.15}$ solid	$-\Delta H^\circ_{f,298.15}$ solid	ΔH°_S	$-\Delta H^\circ_{f,298.15}$ gas	$+\Delta H^\circ_{f,298.15}$		$E_{cycl.} - E_{Si\leftarrow N}$
						found	calc.	
CH_3	3	4915 ± 7	923 ± 7	82 ± 0.8	841 ± 8	10798	10830	32
CH_3	2	5586 ± 9	931 ± 10	92 ± 0.8	839 ± 11	11949	12011	62
CH_3	1	6247 ± 12	949 ± 13	101 ± 0.8	848 ± 14	13110	13191	81
CH_3	0	6895 ± 13	981 ± 14	115 ± 0.9	866 ± 15	14281	14371	90
C_2H_5	3	5584 ± 7	933 ± 7	81 ± 0.9	852 ± 8	11962	12000	38
C_3H_7	3	6239 ± 9	957 ± 10	84 ± 0.8	873 ± 11	13135	13174	39
$(CH_3)_2CH$	3	6222 ± 10	974 ± 11	92 ± 0.9	882 ± 12	13144	13177	33
$CH_2{=}CH$	3	5344 ± 10	887 ± 11	85 ± 0.8	802 ± 12	11475	11511	36
C_6H_5(α-form)	3	7267 ± 11	824 ± 12	126 ± 1.4	698 ± 13	14674	14711	37
$C_6H_5CH_2CH_2$	3	8616 ± 11	834 ± 12	108 ± 0.9	726 ± 13	17006	17051	45
$C_6H_5OCH_2$	3	7817 ± 11	953 ± 12	108 ± 0.8	845 ± 13	16223	16264	41
$C_6H_5COOCH_2$	3	7998 ± 11	1166 ± 12	109 ± 0.9	1057 ± 13	17401	17439	38
4-$CH_3C_6H_4COOCH_2$	3	8639 ± 12	1204 ± 13	123 ± 0.9	1081 ± 14	18581	18622	41
4-$CH_3OC_6H_4COOCH_2$	3	8496 ± 12	1347 ± 13	143 ± 1.1	1204 ± 14	18950	18999	49
CH_3CH_2O	3	5322 ± 10	1195 ± 11	81 ± 0.8	1114 ± 12	12473	12504	31

Introduction

Silatranes, the derivatives of pentacoordinate silicon with the general formula $X\overline{Si(OCH_2CH_2)_3N}$, as well as their C-derivatives have attracted attention for some time because of their unique (i) molecular and electronic structure, (ii) chemical properties, and (iii) biological activity. Silatranes have been studied by use of nearly all the available physicochemical techniques, but up to now their thermochemical properties have not been investigated. This is primarily due to the lack of both a simple and reliable technique for the combustion of organosilicon compounds and an exact enthalpy of formation of silicon dioxide formed in the bomb calorimeter. A number of problems concerning the stereoelectronic structure and reactivity of silatranes have prevented elucidation of the thermochemical features.

Results and discussion

The experimentally determined enthalpies of formation and atomization of silatranes are listed in Table 1.

The calculation was based on the following key values of $\Delta H^{\circ}_{f,298.15}$ (kJ mole^{-1}):

$(H_2O_{liq}) = -285.83 \pm 0.04$ [1,2]

$(CO_{2_{gas}}) = -393.514 \pm 0.056$ [1,2]

$(SiO_{2_{sol}}) = -939.39 \pm 0.52$ [3]

$(C_{gas}) = -716.67 \pm 0.44$ [4]

$(H_{gas}) = 217.997 \pm 0.66$ [4]

$(Si_{gas}) = 450.0 \pm 0.8$ [4]

$(O_{gas}) = 249.170 \pm 0.1$ [4]

$(N_{gas}) = 472.680 \pm 0.12$ [4]

The data of Table 1 indicate that the standard enthalpies of formation of 1-alkylsilatranes decrease non-linearly with increase in length and an increased degree of branching in the alkyl group attached to the silicon, which can be attributed to the steric effect of the alkyl substituent. The standard enthalpy of formation of 1-vinylsilatrane is higher than that of 1-ethylsilatrane (in the gaseous state) by 50 kJ mole^{-1}. Similarly, the standard enthalpy of formation of vinyltriethoxysilane is higher than that of ethyltriethoxysilane by 49.2 kJ mole^{-1} [5]. Thus, the replacement of the ethyl group bonded to the silicon atom by a vinyl group usually increases the enthalpy of formation by about 50 kJ mole^{-1}. The standard enthalpies of formation of 1-phenylsilatrane and 1-(2-phenylethyl)silatrane were approximately the same (824 and -834 kJ mole^{-1}). This means that the insertion of two methylene groups between the phenyl and the silatrane skeleton has little effect on the enthalpy of formation.

The sequential introduction of more methyl groups into the 3-, 7-, and 10-positions of the silatrane skeleton decreases the standard enthalpy of formation, $\Delta H^{\circ}_{f,298.15}$ for 1-methyl-, 1,3-dimethyl-, 1,3,7-trimethyl-, and 1,3,7,10-tetramethyl-

Table 2

Enthalpies of atomization and formation of silatrane fragments (kJ mole^{-1})

Fragment	$\Delta H^{\circ}_{a,298.15}$	$\Delta H^{\circ}_{f,298.15}$	Fragment	$\Delta H^{\circ}_{a,298.15}$	$\Delta H^{\circ}_{f,298.15}$
C(1)–C(2) [a]	2003.57	−56.57	O–C(2)	756.10	−55.18
C(2)–C(2)	1173.40	−20.74	O–C(3)	483.57	−47.43
C(1)–C(3)	1727.41	−45.15	Si–H	325.1	5.4
C(1)–C(4)	1590.80	−40.97	$C_{ar'}$–Si	320.6	−28.93
C(2)–C(3)	898.78	−10.98	C_{ar}–C_{ar}	920.86	13.86
C(1)–Si	1540.00	−56.84	C_{ar}–$C_{ar'}$	708.51	27.58
C(2)–Si	706.43	−17.6	O–$C_{ar'}$	410.50	−106.75
C(3)–Si	432.00	−5.94	$C_{ar'}$–C(2)	780.50	−25.0
C_{α}–Si	550.1	−126.04	$C_{ar'}$–C(1)	1607.28	−57.45
C_{β}–C_{α}	1670.58	105.19	$C_{ar'}$–CO	797.22	−135.13
O–Si	454.38	−217.3	CO–O	788.68	−181.17
O–C(1)	1573.70	−78.5	C(2)–N	712.9	21.17

[a] C(1), C(2), C(3), C_{α}, C_{β} stand for $-CH_3$, $-CH_2$, $-CH$, $=CH$, and $=CH_2$, respectively; C_{ar} is a CH-group in the benzene ring; $C_{ar'}$ is the substituted carbon in the benzene ring.

silatrane (in the solid state) being −923, −931, −949, and −981 kJ mole^{-1}, respectively. Thus, one, two or three methyl groups in the 1-methylsilatrane molecule causes a non-linear decrease in the enthalpy of formation by 8, 18, or 32 kJ mole^{-1}, respectively. This is because the energy required to stabilize the silatrane skeleton strain increases non-linearly since the intramolecular repulsion of two methyls is stronger than that of a methyl and a hydrogen, or that of two hydrogens.

The enthalpies of atomization of silatranes were calculated on the basis of the additive scheme of Tatevskii [6] ignoring the total energy of cycle strain ($E_{\text{cycl.}}$) and transannular interaction between the nitrogen and silicon atoms ($E_{\text{Si}\leftarrow\text{N}}$) viz. $E_{\text{cycl.}}-E_{\text{Si}\leftarrow\text{N}}$:

$$\Delta H^{\circ}_{a,298.15} = \sum n_{ij}\, \Delta H_{ij} \qquad ij = 1 \quad i \leqslant j \tag{1}$$

where $\Delta H^{\circ}_{a,298.15}$ is the enthalpy of atomization of silatrane ignoring $E_{\text{cycl.}}-E_{\text{Si}\leftarrow\text{N}}$; ΔH_{ij} is the enthalpy (kJ mole^{-1}) of fragments allowing for the interaction of atoms separated by not more than two atoms in the chain; n_{ij} is the number of fragments.

The various fragments that make up the silatranes under study are listed in Table 2. Their enthalpies of atomization and formation ($\Delta H^{\circ}_{f,298.15}$ and $\Delta H^{\circ}_{a,298.15}$) were calculated from reliable values of the thermochemical constants, obtained earlier in this laboratory [5], for the simplest organosilicon compounds with a tetrahedral silicon atom. These values were used to calculate the enthalpies of atomization, ignoring the silatrane cycle strain energy and the transannular interaction (Si ← N) strain energy in terms of 1 (Table 1).

The energy $E_{\text{cycl.}}-E_{\text{Si}\leftarrow\text{N}}$ was calculated in terms of the relation:

$$E_{\text{cycl.}}-E_{\text{Si}\leftarrow\text{N}} = \Delta H^{\circ}_{a,298.15\ \text{gas calc.}} - \Delta H^{\circ}_{a,298.15\ \text{gas exp}} \tag{2}$$

It should be noted that $E_{\text{cycl.}}$ and $E_{\text{Si}\leftarrow\text{N}}$ are antagonistic in terms of their contributions to the heterocycle enthalpy.

From Table 1 it can be seen that the energy $E_{\text{cycl.}}-E_{\text{Si}\leftarrow\text{N}}$ in 1-alkylsilatranes grows significantly on going from $X = CH_3$ to larger alkyl groups. This growth appears to result from the increased silatrane cycle strain due to the greater volume of the alkyl group. As the length and branching of the alkyl group increases, the energy of interaction $E_{\mathrm{Si} \leftarrow \mathrm{N}}$ falls. In this way the $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ value for $X = (CH_3)_2CH$ is smaller than that for $X = C_3H_7$ (33 and 39 kJ mole^{-1}, respectively).

The $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ values for 1-phenyl- and 1-vinylsilatrane are practically identical. This is quite natural since the electronegativities and the modes of interaction of the vinyl and phenyl groups with the silicon atom are similar.

In going from 1-phenylsilatrane to 1-(2-phenylethyl)silatrane, i.e. on insertion of two methylene groups between the silicon atom and phenyl radical, $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ increases by 8 kJ mole^{-1}. This is apparently due to a large amount of strain in the silatrane skeleton since the Si ← N interaction is much weaker when $X = C_6H_5CH_2CH_2$. Introduction of electronegative substituents such as C_6H_5O, C_6H_5COO, $4\text{-}CH_3C_6H_4COO$, and $4\text{-}CH_3OC_6H_4COO$ into the methyl group of 1-methylsilatrane causes $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ to increase by 9, 6, 9, and 17 kJ mole^{-1}, respectively. Here again the key role is played by steric effects due to the substituent X rather than the changes in the energy of transannular interaction. The value of $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ for 1-ethoxysilatrane is 31 kJ mole^{-1}, which apparently is due to a low silatrane skeleton stress.

The sequential introduction of methyl groups into the 3-, 7-, and 10-positions of 1-methylsilatrane increases the $E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}$ by 30, 49, and 58 kJ mole^{-1}, respectively, probably also due to growing silatrane skeleton strain due to the increasing mutual Prelog repulsion of the methyl groups and hydrogen atoms.

Variation of substituent X at Si causes changes in the strain and in the Si ← N interaction energies, which was manifested in changes in the enthalpy of formation of the silatrane skeleton. This was confirmed by comparison of the formation of the corresponding silatranes $\mathrm{X}\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$ with that of the Si-substituted trialkyl- and triethoxysilanes $X\text{–}SiR_3$ (the gaseous state) (here, the X–Si bond energy in both cases was assumed to be approximately the same).

The enthalpies of formation were compared in terms of the schemes:

$$\begin{aligned}\Delta\ \Delta H^{\circ}_{\mathrm{f},298.15} &= \Delta H^{\circ}_{\mathrm{f},298.15(\mathrm{X}-\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}})} - \Delta H^{\circ}_{\mathrm{f},298.15(\mathrm{X'}-\mathrm{SiR_3})} \\ &= \Delta H^{\circ}_{\mathrm{f},298.15[-\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}]'} - \Delta H^{\circ}_{\mathrm{f},298.15(-\mathrm{SiR_3})}. \end{aligned} \tag{3}$$

$$\begin{aligned}\Delta'\ \Delta H^{\circ}_{\mathrm{f},298.15} &= \Delta H^{\circ}_{\mathrm{f},298.15[\mathrm{X'}\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}]'} - \Delta H^{\circ}_{\mathrm{f},298.15(\mathrm{X'SiR_3})} \\ &= \Delta H^{\circ}_{\mathrm{f},298.15[-\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}]'} - \Delta H^{\circ}_{\mathrm{f},298.15(-\mathrm{SiR_3})}. \end{aligned} \tag{4}$$

Then the difference of the right hand sides of equations 3 and 4 should give the difference in the enthalpies of formation of the silatrane skeleton for a given substituent:

$$\begin{aligned}\Delta\ \Delta H^{\circ}_{\mathrm{f},298.15} - \Delta'\ \Delta H^{\circ}_{\mathrm{f},298.15} &= \Delta H^{\circ}_{\mathrm{f},298.15[-\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}]^-} \\ &\quad - \Delta H^{\circ}_{\mathrm{f},298.15[-\overleftarrow{\mathrm{Si(OCH_2CH_2)_3N'}}]'}. \end{aligned} \tag{5}$$

The value of $\Delta\ \Delta H^{\circ}_{\mathrm{f},298.15} - \Delta'\ \Delta H^{\circ}_{\mathrm{f},298.15}$ has the same significance as the difference $[E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}] - [E_{\mathrm{cycl.}}-E_{\mathrm{Si} \leftarrow \mathrm{N}}]'$, for compounds with the same substituents. Thus, with $X = CH_3$, $X = C_2H_5$, and $R = C_2H_5$, the difference between the enthalpies of formation of the silatrane skeleton in 1-methyl- and that of 1-ethylsilatrane is 5 kJ

Table 3

Comparison of the standard enthalpies of formation of $\mathrm{X\overline{Si(OCH_2CH_2)_3N}}$ and $\mathrm{XSiR_3}$ and the difference in their enthalpies of formation determined from eqs. 3 and 4 ($\mathrm{kJ\ mole^{-1}}$)

X	X′	$-\Delta H^{\circ}_{f,298.15(g)}$		R[a]	$-\Delta H^{\circ}_{f,298.15(g)}$		$-\Delta\,\Delta H^{\circ}_{f,298.15}$	$-\Delta'\,\Delta H^{\circ}_{f,298.15}$	$\Delta'\,\Delta H^{\circ}_{f,298.15} - \Delta\,\Delta H^{\circ}_{f,298.15}$	$(E_{cycl.} - E_{Si \leftarrow N}) - (E_{cycl.} - E_{Si \leftarrow N})$
		$\mathrm{XSi(OCH_2CH_2)_3N}$	$\mathrm{X'Si(OCH_2CH_2)_3N}$		$\mathrm{XSiR_3}$	$\mathrm{X'SiR_3}$				
Me	Et	841	852	Et	281	297	−11	−16	5	5
Me	Vin	841	802	Me	229	191	39	38	1	4
Me	EtO	841	1114	Me	229	499	−273	−270	−3	−1
Me	Vin	841	802	OEt	1045	1005	39	40	−1	4
Me	EtO	841	1114	OEt	1045	1315	−273	−270	−3	−1
Me	$\mathrm{PhCOOCH_2}$	841	1057	OEt	1045	1265	−216	−220	4	6

[a] Data from Table 1.

Table 4

Standard enthalpy of formation of the silatrane group $\overline{Si(OCH_2CH_2)_3N}$ in $X\overline{Si(OCH_2CH_2)_3N}$ calculated according to equation 7 (kJ mole^{-1})

X	R	$-\Delta H^{\circ}_{f,298.15\,gas}$ $X\overline{Si(OCH_2CH_2)_3N}$	$-\Delta H^{\circ}_{f,298.15\,gas}$ $XSiR_3$	$-\Delta H^{\circ}_{f,298.15\,gas}$ SiR_3 calc.	$-\Delta H^{\circ}_{f,298.15\,gas}$ $-\overline{Si(OCH_2CH_2)_3N}$
CH_3	CH_3	841 ± 8.0	229 ± 3.0	171	783
CH_3	C_2H_5	841 ± 8.0	281 ± 5.0	223	783
CH_3	C_3H_7	841 ± 8.0	343 ± 5.0	285	783
C_2H_5	C_2H_5	852 ± 8.0	297 ± 5.0	223	778
C_3H_7	C_3H_7	873 ± 11	378 ± 5.0	285	780
$CH_2{=}CH$	CH_3	802 ± 12	191 ± 5.0	171	782
$CH_2{=}CH$	OC_2H_5	802 ± 12	1005 ± 6.0	987	784
CH_3CH_2O	CH_3	1114 ± 12	499 ± 5.0	171	786
CH_3CH_2O	OC_2H_5	1114 ± 12	1315 ± 6.0	987	786
C_6H_5	OC_2H_5	698 ± 13	904 ± 6.0	987	781
$C_6H_5COOCH_2$	OC_2H_5	1057 ± 13	1265 ± 6.0	987	779

mole^{-1}. At the same time, the difference, $[E_{cycl.}-E_{Si\leftarrow N}]' - [E_{cycl.}-E_{Si\leftarrow N}]$, for the same silatranes (Table 3) is also 5 kJ mole^{-1}. The difference in the enthalpies of formation of the silatrane skeleton for other silatrane pairs was calculated in the same manner, the results of which are listed in Table 3.

In all cases, the difference between $\Delta' \Delta H^{\circ}_{f,298.15} - \Delta\, \Delta H^{\circ}_{f,298.15}$ and $[E_{cycl.}-E_{Si\leftarrow N}]' - [E_{cycl.}-E_{Si\leftarrow N}]$ is within experimental error. The results confirm the relevance of the obtained enthalpies of formation of 1-(organyl)silatranes.

The standard enthalpies of formation of the silatrane group $-\overline{Si(OCH_2CH_2)_3N}$ in the gaseous state were calculated for a number of silatranes on the basis of experimental and calculated data (Table 4) according to equations 6 and 7:

$$\Delta H^{\circ}_{f,298.15\,X-\overline{Si(OCH_2CH_2)_3N}} - \Delta H^{\circ}_{f,298.15(XSiR_3)}$$

$$= \Delta H^{\circ}_{f,298.15[-\overline{Si(OCH_2CH_2)N}]} - \Delta H^{\circ}_{f,298.15(SiR_3)}. \tag{6}$$

$$\Delta H^{\circ}_{f,298.15[-\overline{Si(OCH_2CH_2)_3N}]} - \Delta H^{\circ}_{f,298.15(SiR_3)} + \Delta H^{\circ}_{f,298.15(-SiR_3)calc.} \tag{7}$$

$\Delta H^{\circ}_{f,298.15(SiR_3)calc.}$

was determined by the scheme of Tatevskii.

The data of Table 4 indicate that the enthalpy of formation of the silatrane group $-\overline{Si(OCH_2CH_2)_3N}$ varies only slightly, and the value of 782 ± 10 kJ mole^{-1} may be taken for all the silatranes studies.

Experimental

1. Evaluation of enthalpies of combustion and sublimation

The silatranes $X\overline{Si(OCH_2CH_2)_n[OCH(CH_3)CH_2]_{3-n}N}$ studied were prepared by a procedure described previously [7–9] and purified by recrystallization and repeated vacuum distillations. The purity assessed from the melting point curve was better than 99.3% in all cases [10].

The enthalpy of combustion was determined in a precision-made calorimeter equipped with an isothermal jacket. The calorimeter was rotated around two perpendicular axes [3]. The 340 cm^3 bomb of the calorimeter was made of stainless steel. Samples were burned in an iridium crucible (m 4.7 g, d 20 mm, h 7.5 mm) under 30.39×10^5 Pa of oxygen in the presence of 2 cm^3 of water. The energy equivalent of the calorimetric system determined with K-1 grade standard benzoic acid purchased from the All-Union Mendeleev Research Institute (Leningrad) was 151.16 ± 0.02 J ohm^{-1} (mean of 20 measurements).

The enthalpy of combustion of benzoic acid allowing for the Jessup factor was -26433.26 J g^{-1}.

For complete combustion of the silatranes the temperature must be above 2073 K. At this temperature, the formation of a layer of silicon carbide, silicon hydroxycarbide, or silicon dioxide, which impairs penetration of oxygen to the burning matter, was prevented. For this reason ultradispersed carbon with particle size of 0.001–0.1 μ was used for burning. Its combustion was accompanied by a slight explosion, the flame temperature of which was above 2273 K. The enthalpy of combustion of ultradispersed carbon is 33388.0 ± 7.0 kJ kg^{-1} (mean of 8 measurements).

The substances were burned as a mixture with ultradispersed carbon in a mass ratio of 2/1. The components were kept in vacuo for 48 h over P_2O_5 prior to mixing. A portion of the mixture (0.32–0.35 g) was placed to a terylene container (0.02 g) in the dry combustion chamber. The degree of combustion was determined from the mass of CO_2 produced, and was found to be 99.7–99.9% [11]. As judged from IR spectroscopy data, no silicon carbide, silicon hydroxycarbides, and silicon nitride were present in the condensed products. An X-ray phase analysis showed that the silicon dioxide formed in the bomb was entirely amorphous. In calculating the enthalpy of combustion, it was assumed that the unburned substance did not undergo pyrolysis, the mass of burned matter being directly proportional to the amount of CO_2 produced. This was confirmed by burning one sample of 1-methylsilatrane several tens of times. The unburnt matter was extracted from the silicon dioxide with chloroform. IR spectroscopy of the evaporated chloroform extract revealed that the 1-methylsilatrane content in the SiO_2 formed was about 0.2%.

2. *Enthalpy of formation of silicon dioxide in the calorimeter*

To calculate the enthalpies of formation of the organosilicon compounds from the enthalpies of their combustion in oxygen, a reliable value of the standard enthalpy of formation of the hydrated amorphous silicon dioxide is needed. The values used up to now have ranged from -850.77 to -939.39 kJ $mole^{-1}$ [3,12,13]. We have used a $\Delta H^{\circ}_{f,298.15(SiO_2)}$ value of -939.39 ± 0.5 kJ $mole^{-1}$ [3] which corresponds most closely to the conditions we chose for the combustion experiments. Nevertheless, this value was refined as follows:

$$SiO_{2(anhydr.)} + nH_2O = SiO_2 \cdot nH_2O; \ \Delta H^{I} \quad (8)$$

$$SiO_{2(anhydr.)} + xHF \cdot yH_2O = H_2SiF_6(x-6)HF(y+2)H_2O; \ \Delta H^{II} \quad (9)$$

$$SiO_{2(\alpha\text{-quartz})} + xHF \cdot yH_2O = H_2SiF_6(x-6)HF(y+2)H_2O; \ \Delta H^{III} \quad (10)$$

$$Si + O_2 \rightarrow SiO_2(\alpha\text{-quartz}) \ \Delta H^{\circ}_{f,298.15SiO_2(\alpha\text{-quartz})} \quad (11)$$

Summation of these equations gives common equation 12

$$\mathrm{Si} + \mathrm{O_2} + n\mathrm{H_2O} = \mathrm{SiO_2} \cdot n\mathrm{H_2O};\ \Delta H^{\mathrm{IV}}_{\mathrm{react.}} = \Delta H^{\circ}_{\mathrm{f,298.15(SiO_2 \cdot \mathit{n}H_2O)}} \tag{12}$$

$$\Delta H^{\mathrm{IV}}_{\mathrm{react.}} = \Delta H^{\mathrm{I}}_{\mathrm{react.}} - \Delta H^{\mathrm{II}}_{\mathrm{react.}} + \Delta H^{\mathrm{III}}_{\mathrm{react.}} + \Delta H^{\circ}_{\mathrm{f,298.15(SiO_2,\ \alpha\text{-quartz})}} \tag{13}$$

$$\Delta H^{\circ}_{\mathrm{f,298.15(SiO_2 \cdot \mathit{n}H_2O)}} = \Delta H^{\mathrm{I}}_{\mathrm{react.}} - \Delta H^{\mathrm{II}}_{\mathrm{react.}} + \Delta H^{\mathrm{III}}_{\mathrm{react.}} + \Delta H^{\circ}_{\mathrm{f,298.15(SiO_2,\ \alpha\text{-quartz})}} \tag{14}$$

The silicon dioxide formed in the bomb calorimeter was dehydrated for 16 h at 423 K to constant weight. One portion of $\mathrm{SiO_2}$ was then dissolved in hydrofluoric acid and another was moistened with 0.2 N nitric acid. The enthalpies of these processes as well as the enthalpy of dissolution of the α-quartz in hydrofluoric acid at 298.15 K were measured in a DAK-1-1A differential automatic calorimeter equipped with a teflon vessel. The values obtained were:

$$\Delta H^{\circ}_{\mathrm{f,298.15(SiO_2,\ \alpha\text{-quartz})}} = -910 \pm 2\ \mathrm{kJ\ mole^{-1}} \tag{15}$$

$$\Delta H^{1} = -26.8 \pm 0.4\ \mathrm{kJ\ mole^{-1}}$$

$$\Delta H^{\mathrm{II}} = -108.3 \pm 1.5\ \mathrm{kJ\ mole^{-1}}$$

As a result, $\Delta H^{\circ}_{\mathrm{f,298.15SiO_2}}$ was found to be -934.4 ± 3.1 kJ $\mathrm{mole^{-1}}$. The obtained enthalpy of formation of hydrated fine-dispersed amorphous silicon dioxide thus obtained is close to the value of -939.39 kJ $\mathrm{mole^{-1}}$ determined previously by direct combustion of silicon [3].

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