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Abstract

Full Text

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THERMOCHEMISTRY OF TETRAETHYLSILANE AND HEXAETHYLDISILANE

In connection with the study of a number of processes involving alkyl compounds of elements (El) of the fourth group of the periodic system, it is important to determine the thermochemical characteristics of these substances, first of all their heats of combustion and formation. It is also of interest to compare the mean bond energies El—C and El—El in the indicated compounds. Earlier, the authors ([1,2]) studied the heats of combustion and formation of certain alkyl compounds of tin and germanium and calculated the mean bond energies Sn—C, Sn—Sn, Ge—C, and Ge—Ge. In the present work the heats of combustion and formation of tetraethylsilane and hexaethyldisilane have been determined, and the mean bond energies Si—C and Si—Si in these substances have been calculated.

Fig. 1. Infrared spectra: **a** $-\mathrm{Si(C_2H_5)_4}$, **b** $-\mathrm{Si_2(C_2H_5)_6}$

The synthesis of $\mathrm{(C_2H_5)_4Si}$ is described in ([3]). During distillation of the product, the fraction boiling in the range 152.5-153° (760 mm Hg) was collected. It had n_D^{20} 1.4269; ρ^{20} 0.7657 g/cm^3. $\mathrm{(C_2H_5)_6Si_2}$ was obtained by the reaction of $\mathrm{(C_2H_5)_3SiBr}$ with metallic sodium in an atmosphere of dry pure nitrogen ([4]). During distillation of the purified product, a fraction was collected that had a normal boiling point of 251°; n_D^{20} 1.4791; ρ^{20} 0.8352 g/cm^3. The indicated values of boiling point, refractive index, and density of the synthesized samples of silicon alkyl compounds are in good agreement with the data of ([4,5]). The infrared spectra of the same products, recorded in the regions 400-1500 and 2600-3200 cm^{-1} (Fig. 1)*, coincide with the spectra of ([6]). The heat of combustion was determined by the method described in ([7]). The heat equivalent of the calorimeter was established using standard benzoic acid obtained from VNIIM ($-\Delta H^{\mathrm{cr}} = 6324$ cal/g), and was 2210 ± 1 cal/deg.

The oxygen pressure in the bomb was 30 atm. Before the experiment, 10 ml of water was poured into the bomb. In the calorimeter jacket the temperature was maintained at $25.00 \pm 0.05^\circ$. The organosilicon compounds were burned in polyethylene ampoules, since, in comparison with glass ampoules, they ensured greater completeness of combustion, which agrees with the data of ([8]). According to the results of gas analysis, the amount of CO_2 in the combustion products was usually 99.8% of the corresponding theoretical value. X-ray analysis of the solid combustion product showed that amorphous silicon dioxide is formed in the bomb.

The weighed portions of substances for combustion were 0.2–0.3 g. Ignition of the thread was carried out with a platinum wire. The temperature rise in the experiment was about 2.5° and was measured with an accuracy of 0.001°. In calculating the heats of combustion (ΔH^{cr}), corrections were taken into account for heat exchange (by the Regnault-Pfaundler formula), the heat of combustion of the ampoule and thread, the formation of nitric acid, reduction to standard pressure, and the emergent mercury column of the thermometer.

* Spectra recorded by N. N. Vyshinskii.

10–15 experiments were carried out for each substance. Table 1 gives the mean values of ΔH_{comb} and their root-mean-square errors.

From the heats of combustion of the liquids studied and literature data ([9]) on the heats of formation of the products of their combustion, the standard heats of formation (ΔH^{form}) of tetraethylsilane and hexaethyldisilane in the condensed phase were calculated. From $\Delta H_\ell^{\text{form}}$ and the values of the heats of vaporization of these substances,

Table 1

Standard heats of combustion, formation, and atomization (kcal/mol)*

Substance	$-\Delta H_\ell^{\text{comb}}$	$-\Delta H_\ell^{\text{form}}$	$-\Delta H_{\text{g}}^{\text{form}}$	ΔH^{atom}
$(C_2H_5)_4Si$	1595 ± 2	49 ± 2	38 ± 3	2559 ± 8
$(C_2H_5)_6Si_2$	2485 ± 3	85 ± 3	70 ± 4	3908 ± 14

* The indices "ℓ" and "g" denote the liquid and gaseous phases.

Table 2

Thermochemical energies (kcal) of the El—C and El—El bonds in alkyl compounds of silicon, germanium, and tin (according to the authors' data)

Substance	$\bar{E}$(El—C)	$\bar{E}$(El—El)	Source
$(C_2H_5)_4Si$	63 ± 2		This work

Substance	$\bar{E}$(El—C)	$\bar{E}$(El—El)	Source
$(C_2H_5)_3Si—Si(C_2H_5)_3$		70 ± 10	This work
$(C_2H_5)_4Ge$	58.9 ± 1.5		(2)
$(C_2H_5)_3Ge—Ge(C_2H_5)_3$		62 ± 5	(2)
$(C_2H_5)_4Sn$	47.6 ± 0.8		(1)
$(C_2H_5)_3Sn—Sn(C_2H_5)_3$		50 ± 10	(1)

calculated by Klyates' s empirical formula (10), the heats of formation in the gas phase ($\Delta H_{\mathrm{g}}^{\mathrm{form}}$) were also calculated. From the values of $\Delta H_{\mathrm{g}}^{\mathrm{form}}$ for the compounds and atoms, the heats of atomization (ΔH^{atom}) were calculated. The standard heats of formation used in the calculations are: for amorphous silicon dioxide, 208.1 kcal/mol (11); for atomic hydrogen, carbon, and silicon, respectively: 52.1; 170.9; 112 ± 5 kcal/g-atom (12,13).

From the data obtained on the heats of atomization and the mean bond energies C–C (82.6 kcal) and C–H (98.7 kcal) (13,14) in aliphatic compounds, the mean energies of the Si–C bond in $(C_2H_5)_4Si$ and of the Si–Si bond in $(C_2H_5)_6Si_2$ were calculated, with the assumption that $\bar{E}$(Si—C) in both compounds is the same within the limits of the calculation error. The following results were obtained:

$$\bar{E}(\mathrm{Si—C}) = 63 \pm 2 \text{ kcal}, \qquad \bar{E}(\mathrm{Si—Si}) = 70 \pm 10 \text{ kcal}.$$

Tannenbaum (15,16), by the same method as the authors, found that the mean energy of the Si–C bond in $(C_2H_5)_4Si$, $(CH_3)_2Si(C_3H_7)_2$, and $(CH_3)_4Si$ is respectively 60, 61, and 72 kcal. However, he assumed that the heat of atomization of silicon is 88 kcal/g-atom. If one takes into account that, according to new data, it is 112 kcal/g-atom, then for $\bar{E}$(Si—C) in tetraethyl-, dimethyldipropyl-, and tetramethylsilane one obtains respectively 66, 67, and 78 kcal. From the data (15) it follows that the accuracy of these results is 3-8 kcal. In view of this, it is clear that, if one does not count the value obtained in (15) for $(CH_3)_4Si$, then the values $\bar{E}$(Si—C) found by the authors, on the one hand, and by Tannenbaum, on the other, agree with one another within the limits of the measurement errors. As for the value (15) for tetramethylsilane, the authors believe that it is overestimated by 10-13 kcal, which may have been caused by the difficulties of accurate

determining the heats of combustion of organosilicon compounds in general, and of tetramethylsilane, which boils at 26.5°, in particular.

Thompson (11) determined the heats of combustion and formation of a series of linear polymethylsiloxanes and, for $\bar{E}$(Si—C) in these substances, found a value of 64 ± 14 kcal. Recalculation taking into account $\Delta H_{298}^{\mathrm{form}}(\mathrm{Si,\ gas}) = 112$ kcal-g-atom gives $\bar{E}$(Si—C) $= 70 \pm 14$ kcal. The difference between this value and the authors' value of $\bar{E}$(Si—C) for tetraethylsilane amounts to half the error of the results (11).

The bond energy of Si—Si in alkyl compounds had not previously been studied. Literature data on this bond in disilane differ greatly. In work ([17]), from the heats of decomposition of this substance and silane, a value of $\bar{E}$(Si—Si) was found which, if the new value of the heat of atomization of silicon is taken into account, is 48 kcal. For the dissociation energy (D) of the same bond in disilane, the pyrolysis method gave a value of 51 kcal ([18]), with the assumption that the first and rate-determining stage of pyrolysis is the decomposition of the molecule into SiH_3 radicals, of which there is no complete certainty.

By mass spectrometry, however, from the appearance potential of SiH_3^+ ions in work ([19]), $D(H_3Si—SiH_3) = 81 \pm 4$ kcal was found. In the same work, from the appearance potential of $SiCl_3^+$ ions, $D(Cl_3Si—SiCl_3) < 85 \pm 6$ kcal was obtained.

The authors' value of $\bar{E}$(Si—Si) found for hexaethyldisilane is close to these mass-spectrometric values of D(Si—Si), which agree with one another within the limits of the errors of determination.

From the data of Table 2 it is seen that the results of determining $\bar{E}$(Si—C) and E(Si—Si) in the present work correspond to the authors' data on the magnitudes of $\bar{E}$(Ge—C), $\bar{E}$(Ge—Ge) ([2]) and $\bar{E}$(Sn—C), $\bar{E}$(Sn—Sn) ([1]). In the series of elements Si, Ge, Sn, the mean (thermochemical) bond energies El—C and El—El in alkyl compounds decrease with increasing atomic weight of the element; moreover, $\bar{E}$(El—C) and $\bar{E}$(El—El) for one and the same element have close values.

It is of interest that the values of $\bar{E}$ for the Si—Si, Ge—Ge, and Sn—Sn bonds in the compounds $(C_2H_5)_6El_2$ (Table 2) are close to the corresponding mass-spectrometric values of the dissociation energy of molecules in vapors of silicon (75 ± 5 kcal ([20,21,12])), germanium (65 ± 5 kcal ([22])), and tin (46 ± 5 kcal ([23,24])); $\bar{D}$(Si—Ge) = 72 kcal ([22]).

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