Heats of Combustion and Formation of Some Methoxy-polysilanes and -polysiloxanes: Si-O *Bond Energy*[*]

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In the preceding paper[1], data on the heats of combustion and formation of some organosilicon compounds, containing alkyl or phenyl group, were presented. The compounds measured therein have such a large number of C-C and C-H bonds, etc., that the bond energies between silicon and other elements calculated from the results turn out to be small differences between large quantities, and may be unreliable. In order to derive the bond energies between silicon and other elements, it is desirable to measure the heat of combustion of organosilicon compounds having the least possible number of C-C and C-H bonds, etc., in the molecule. In the present work the heats of combustion of some methoxy-polysilanes and -polysiloxanes have been measured, and the heats of formations of them and Si-O bond energy have been calculated therefrom.

Experimental

Materials. — Hexamethoxy disilane $(CH_3O)_3Si \cdot Si(OCH_3)_3$ was synthesized by methanolysis of hexachlorodisilane.[2] Tetramethoxysilane $Si(OCH_3)_4$, hexamethoxydisiloxane $(CH_3O)_3Si \cdot O \cdot Si(OCH_3)_3$ and octamethoxytrisiloxane $(CH_3O)_3Si \cdot O \cdot Si(OCH_3)_2 \cdot O \cdot Si(OCH_3)_3$ were prepared by methanolysis of the corresponding polychloro-silane and -siloxanes, respectively. These hexachlorodisiloxane and octachlorotrisiloxane were obtained from the distillation residue of industrial tetrachlorosilane with careful fractionation through a helices packed-column of about 20 plates. (Si_2OCl_6 b.p. 137°C, Cl % calcd. 74.7, found 74.6; $Si_3O_2Cl_8$ b.p. 73°C/13 mm, Cl % calcd. 70.9, found 70.8.). These compounds prepared by methanolysis could not be freed from a trace of chlorine by the fractional distillation, so careful dehydrochlorination using dry ammonia[2] or sodium carbonate[3] was carried out. After that these products were carefully distilled through a Stedman column of about 30 theoretical plates. Physical constants and analytical data on these samples are shown in Table I.

TABLE I

DATA ON THE SAMPLES USED FOR COMBUSTION MEASUREMENTS

Formula	b. p. °C/mm Hg	d_4^{20}	n_D^{20}	Si Found	% Calcd.
$Si(OCH_3)_4$	122/760	1.034	1.3688	18.48	18.45
$Si_2O(OCH_3)_6$	118.5/30	1.122	1.3818	21.77	21.74
$Si_3O_2(OCH_3)_8$	95–6/2	—	—	23.17	23.12
$Si_2(OCH_3)_6$	98/20	1.095	1.4070	22.99	23.18

Calorimetry.—The apparatus was the Nenken-type adiabatic bomb calorimeter, incorporating a 300 ml. stainless steel-made bomb and Beckmann thermometers. The temperatures in the calorimeter vessel and water jacket were observed with an accuracy of 0.001°C as described previously[1].

For the complete burning of liquid organosilicon compounds containing alkyl or phenyl group, we previously described the technique using a glass ampoule and promotor.[1] However, the poly-silanes and -siloxanes containing only methoxy group are readily burnt completely by themselves without ampoule, by the ignition of the liquid pool in the crucible.

The procedure used in the combustion experiments was the same as previously described.[1] The calibration experiments of the calorimeter were carried out at a temperature of 20°C. (based on the heat of combustion of benzoic acid at 20°C=6319.0 cal./g.[4], and its water equivalent value was determined to be 2494 cal./degree (relative mean deviation ±0.1%).

By the complete burning of the organosilicon compounds, gaseous carbon dioxide, liquid water and silicon dioxide were involved as the end products. The completeness of combustion was ascertained by visual inspection of the bomb contents for traces of black or yellow materials, and sometimes by the chemical analysis. Four to six combustion measurements were made with each liquid sample, the results of which are recorded in Table II.

TABLE II

Formula	Heat of combustion at constant volume, cal./g.						Mean
$Si(OCH_3)_4$	4548	4560	4556	4548	4553	4554	4553
$Si_2O(OCH_3)_6$	4086	4084	4086	4085	—	—	4085
$Si_3O_2(OCH_3)_8$	3836	3832	3840	3838	3833	—	3836
$Si_2(OCH_3)_6$	4731	4743	4738	4735	4740	—	4737

Each deviation from the mean is somewhat high compared with modern precision techniques, but

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[*] A part of this paper was published in Letter section of *J. Chem. Phys.*, 22, 1268 (1954).

[1] T. Tanaka U. Takahashi, R. Ōkawara and T. Watase, This Bulletin, 28, 15 (1954).

[2] R. Ōkawara and T. Tanaka, This Bulletin, 27, 119 (1954).

[3] R. Ōkawara, T. Tanaka and I. Ishimaru, This Bulletin, 27, 45 (1954).

[4] Calculated from the results of Prosen and Rossini, *J. Research NBS.*, 33, 439 (1944).

of sufficient precision for bond energy term purpose in view of the other uncertainties involved.

Results and Discussion

Table III contains the summary of the data for the heats of combustion of four organosilicon compounds with some important thermal data calculated therefrom.

The value of the bomb process was calculated per mole and corrected to the standard constant-volume process where the reactants were at 1 atm. pressure by means of Washburn's equation.[5] The energies evolved in this hypothetical standard process were denoted in Table III by the symbol $-\Delta U_R$. From this quantity the heat evolved in the isobaric process at 1 atm. pressure, $-\Delta H_c$, was obtained by addition of the proper work term. The heats of formation, $-\Delta H_f$, of these compounds from the standard elements (gaseous H_2 and O_2, graphitic C and metallic Si) were calculated from $-\Delta H_c$ by using data -68.32,[6] -94.05[6] and -208.14[7] kcal./mol. for the heats of formation of water, carbon dioxide and amorphous silica, respectively.

Values of 52.1 and 59.2 kcal./g. atom are now generally accepted for the heats of atomization of hydrogen and oxygen, respectively.[8] The corresponding value for carbon may still be regarded as a matter of some controversy. Direct and various indirect measurements give varying values which fall into three main groups centering around 124,[9] 140[10] and 170[11,12] kcal./g. atom, later evidence tending strongly toward the latter two values rather than the former. Here the actual value 171.7 kcal./g. atom[8,12] was adopted. The heat of atomization of silicon is more dubious. In the present work the value 89.9 kcal./g. atom presented by Baughan[13] was adopted. The heats of formation in the gaseous state from monoatomic gases, ΔE, were obtained from ΔH_f of these compounds of formula $Si_aC_bH_cO_d$ by use of the formula:

$$\Delta E = \Delta H_f - 89.9a - 171.7b - 52.1c - 59.2d - H_v$$

The heats of vaporization of these compounds, H_v, were estimated from Trouton's rule. The values ΔE of the four compounds are listed in Table III.

Si-O bond energy.—The value ΔE may be shown by the following formula:

$$\Delta E = pE_{Si-O} + qE_{Si-Si} + rE_{C-O} + sE_{C-H}$$

In this equation E represents the energy value of bond corresponding to each suffix and the factors p, q, r and s the number of bonds in the molecules coming into question. As the energy terms of C-O and C-H bonds are well known, Si-O bond energy can be evaluated. In the case of hexamethoxydisilane, Si-Si bond energy was considered as equal to the negative value of half of atomization heat for silicon. The Si-O bond energy computed in this manner is shown in Table III, using 98.9[14] and 84.1[15] kcal./mol. for C-H and C-O bond energies, respectively.

TABLE III

HEAT OF COMBUSTION AND FORMATION AND Si-O BOND ENERGY (kcal./mol.)

Formula	Mole. wt.	$-\Delta U_R$	$-\Delta H_c$	$-\Delta H_f$	$-\Delta E$	$-E_{Si-O}$
$Si(OCH_3)_4$	152.23	693	694	300	1929	102
$Si_2O(OCH_3)_6$	258.38	1054	1056	539	3090	101
$Si_3O_2(OCH_3)_8$	364.54	1397	1399	798	4271	102
$Si_2(OCH_3)_6$	242.38	1148	1150	445	2937	101

The earlier energy term value for the Si-O bond, derived from the heat of formation of silica, was given by Pauling as 89.3[16], by Syrkin and Dyatkina as 89[17], by Paul as 104[18] and by Gilman and Dunn as 104[19] kcal./mol. From the consideration of repulsive interactions of the bonding orbital of one with the inner shell of the other, Pitzer[20] estimated for Si-O bond energy to be 106 kcal./mol., using the value 90 kcal./g.

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[5] E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

[6] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research NBS.*, **34**, 143 (1945).

[7] R. Thompson, *J. Chem. Soc.*, **1953**, 1908.

[8] "Selected Values of Chemical Thermodynamics Properties", Nat. Bur. Stand., Washington, (1950).

[9] G. Herzberg, *J. Chem. Phys.*, **10**, 306 (1942); L.H. Long and R.G.W. Norrish, *Proc. Roy. Soc.* (*London*), **A187**, 337 (1951).

[10] F.H. Field, *J. Chem. Phys.*, **19**, 793 (1951); Th. Doehard, P. Goldfinger and F. Waelbroeck, ibid., **20**, 757 (1952).

[11] G. Glockler, ibid., **19**, 124 (1951).

[12] Brewer, Gilles and Jenkins, ibid., **16**, 797 (1948).

[13] E.C. Baughan, *Quart. Rev.*, **7**, 103 (1953).

[14] Calculated by the method of least squares from the heats of formation of lower members (from thanee to hexane) in paraffin series, other than methane; E. J. Prosen, W. E. Johnson and F. D. Rossini, *J. Research NBS.*, **37**, 51 (1946), and their preceding papers.

[15] Calculated from the heat of formation of dimethyl ether (H.A. Skinner, *Trans. Farad. Soc.*, **41**, 645 (1945).) using above C-H bond energy.

[16] L. Pauling, "The Nature of the Chemical Bonds", Cornell Univ. Press, Ithaca, New York, (1940).

[17] J. K. Syrkin and M. E. Dyatkina, "Structure of Molecules", Butterworth, (1950).

[18] Paul, "Principle of Chemical Thermodynamics", McGraw-Hill, (1951).

[19] H. Gilman and G.E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

[20] K.S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

atom for the heat of atomization of silicon and Pauling's electronegativity formula. The value 104 kcal./mol. was also calculated by Thompson[7] from ΔH_f for amorphous silica. The only Si-O bond energy derived from the heats of formation of organosilicon compounds was proposed by Thompson[7] as 117 kcal./mol. However, his combustion experiments contain considerable deviations, so we are not satisfied with that energy value. Also, from the molecular orbital calculation of ionic resonance energy the energy value of 118 kcal./mol. was obtained by Pearson.[21]

The Si-O bond energy term derived here from four organosilicon compounds is in good agreement and slightly lower than the value of 104 kcal./mol. for that bond energy in amorphous silica, calculated from the following data: $\Delta H_{\text{atom.}}$ for Si=89.9, $\Delta H_{\text{atom.}}$ for O=59.2 and ΔH_f for amorphous silica= −208.14 kcal./mol. There is also such an example between the C—C bond energies for diamond structure and paraffin series compounds.[16]

Summary

1. The heats of combustion of the following four compounds have been measured at 20°C and at constant volume: Tetramethoxysilane, hexamethoxydisiloxane, octamethoxytrisiloxane and hexamethoxydisilane.

2. From these combustion results the corresponding heats of combustion and formation at constant pressure and Si-O bond energy have been calculated, and it has been found that the Si-O bond energy in methoxy-polysilanes and -polysiloxanes was slightly lower than that in amorphous silica.

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[21] P.G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).