Heats of Combustion and Formation of Some Organosilicon Compounds

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Recently the heats of combustion of organosilicon compounds have been reported by a few investigators[1,2,3,4] using the bomb calorimeter. We measured the heats of combustion of organosilicon compounds in order to derive the bond energies between silicon and other elements. In this paper we shall summerize the conditions of complete burning of organosilicon compounds and the data obtained in our measurements for the heats of combustion of the five following substances; i.e. dimethyl diethoxysilane $(CH_3)_2Si(OC_2H_5)_2$, di-*n*-propyl diethoxysilane $(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$, diethyl silanediol $(C_2H_5)_2Si(OH)_2$, hexamethyl cyclotrisiloxane $[(CH_3)_2SiO]_3$ and hexaphenyl cyclotrisiloxane $[(C_6H_5)_2SiO]_3$.

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Method and Apparatus

The apparatus was the commercial Berthelot Mahler-type bomb calorimeter, incorporating a 300-ml. stainless-steel-made bomb and a Beckmann thermometer. The calorimeter was set in the thermostat (20±0.2°C), and it was held for an hour in the thermostat before measurement. The temperature rise in the calorimeter was measured through the magnifying-glass attached in front of the thermometer, using a telescope. In order to prevent "sticking" of the mercury of the thermometer, the capillary was continuously kept in a slight vibratory motion5), that is, the thermometer was ticked by an electromagnetic instrument, placed over the top of it, 150 times per minute, and read with an accuracy of 0.001°C.

Iron wire was employed as the ignition medium, and the value 1490 cal./g. was adopted for the heat of its combustion6). For the complete burning of solid organosilicon compounds it was not a desirable method to burn the tablet. The silica produced during the early stage of combustion floated over the surface of the tablet so that there was no access of oxygen beneath it and incompletely burnt residues were left on the base of the crucible. Each solid sample was stuffed into a bag of Ganpi-paper, which was burned with it. The heat of combustion of Ganpi-paper was found to be 3971 cal./g.

After some preliminary work on the method of burning under various pressures, it was successfully found to burn completely under 30 atm. pressure. Before each combustion 1 ml. of water was in the bomb, which was then filled with pure oxygen up to the pressure of 30 atm. at 20°C. In our experiments the air initially present in the bomb was not driven out by filling the bomb with oxygen, bacause of the considerable volatility used for measurements. Accordingly there was always present a small amount of nitrogen within the bomb and the nitric acid produced in the combustion process was titrated with N/14.55-sodium carbonate solution. The magnitude of the thermal correction for this nitric acid, calculated on the basis of an evolution of 14.55 kcal./mole of aqueous nitric acid formed5), was about 10 calories. The corrected temperature rise was calculated by the method described by Dickinson7).

To determine the water equivalent of the calorimeter at 20°C, we used the value 6319.0 cal./g.8) for the heat of combustion of standard benzoic acid (Kahlbaum, *zur Analyse*). Eight calibration experiments of calorimeter were performed with these materials, and its water equivalent value was determined to be 2348 cal./degree (the relative mean deviation ±1.0 cal./degree).

Complete Burning of Liquid Compounds.—Reuther1) measured the heats of combustion of six organosilicon compounds. However, it is difficult to understand why he did not refer to the technique for the combustion of liquid. For the purpose of complete combustion of polydimethyl siloxane, which could be itself employed as the promoter, Thompson3) divided the sample into two glass ampoules of nearly the same volume, the more breakable one of which was collapsed at an oxygen pressure of several atm. to produce a pool of liquid in the crucible, and the other stronger ampoule was burnt after firing, owing to the heat produced by the combustion of the liquid pool. But in our experimemt, when the weaker ampoule collapsed, a portion of liquid was scattered, and the liquid attached to the inside surface of the bomb ended in incomplete combustion.

In our experiments the liquid samples were sealed into a thin walled glass ampoule of soft glass. We filled up the ampoule with the liquid so that there might be no air left within it and so that the ampoule might remain filled up at the temperature in the calorimeter. We performed its preliminary ignition by using a cotton string tied to an iron wire, the string being soaked with promoter which was kept in touch with the ampoule. In the combustion measurements of volatile carbon compounds Moore and his coworkers9) employed specially formed glass capsules, 0.5 to 0.8 ml. in volume and 0.065 to 0.085 g., in empty weight while in our experiments the ampoules were of a single spherical form and the relation of weight to volume was similar to Moore's. The ampoules must be made so as to withstand the oxygen pressure (30 atm.) within the bomb, and also when one weighed more than 0.100 g. it tended to explode on ignition, and then the liquid therein was splashed out of the crucible resulting in incomplete burning. In our combustion measurements about 0.02 g. of liquid paraffin was used as a promoter, and its heat of combustion was found to be 10,868 cal./g. as the average of six measurements. Even under these conditions about half the experiments ended in incomplete combustion, so it was found to be necessary to carry out 10 or more experiments before several consistent values were obtained.

Materials.—Dimethyl diethoxysilane was prepared as follows; the Grignard solution was added drop by drop to diethoxy dichlorosilane diluted with ether for three hours10,11). For the preparation of di-*n*-propyl diethoxysilane, the procedure of addition was reversed, that is, diethoxy dichlorosilane dissolved in dry ether was dropped into the Grignard solution for an hour while keeping the reacting mixture below 10°C under cooling and vigorous stirring10). Hexamethyl cyclotrisiloxane12) and hexaphenyl cyclotrisiloxane13) were prepared by the hydrolysis of dimethyl dichloro-

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6) H. M. Huffmann and E. L. Ellis, *J. Am. Chem. Soc.*, **57**, 41 (1935).

7) H. C. Dickinson, *Bull. Bureau* of *Standards*, **11**, 189 (1914).

8) Calculated from the result of Prosen and Rossini, *J. Research NBS.*, **33**, 439 (1944).

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silane and diphenyl dichlorosilane, respectively. Another was prepared according to the method of Digiorgio et. al.[14] The physical constants of these samples used for the measurements are shown in Table I.

TABLE I

PHYSICAL CONSTANTS OF THE SAMPLES USED FOR COMBUSTION MEASUREMENTS

Sample	b.p. °C/mm Hg	m.p. °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calcd.
$(CH_3)_2Si(OC_2H_5)_2$	113/760	—	0.8410	1.3815	41.10	41.00
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$ a)	85/20	—	0.8558	1.4100	59.10	59.26
$(C_2H_5)_2Si(OH)_2$ b)	—	96	1.134	—	—	—
$[(CH_3)_2SiO]_3$	134/760	64	—	—	—	—
$[(C_6H_5)_2SiO]_3$ c)	290-300/1	190	—	—	—	—

Anal. a) Si % found 13.5, calcd. 13.7 b) C % found 39.86, calcd. 39.97; H % found 10.12, calcd. 10.07. c) Si % found 14.20, calcd 14.16.

Results and Discussion

By complete burning, gaseous carbon dioxide, liquid water and silicon dioxide evolved as the end products. The completeness of combustion was ascertained by visual inspection of the bomb contents for traces of black or yellow materials[15], and sometimes by chemical analysis. The experimental data for the combustion of dimethyl diethoxysilane are presented in Table II.

TABLE II

THE EXPERIMENTAL DATA FOR DIMETHYL DIETHOXYSILANE AT 20°C

Wt. of sample g.	Total heat evolved cal.	Σ cal.	Σ' cal.	$-\Delta U_B$ cal./g.	Δ cal./g.
0.2530	2177.1	26.5	245.9	7528	− 8
.2650	2406.9	18.0	389.0	7547	+11
.2848	2461.4	20.3	297.7	7526	−10
.2945	2652.2	18.3	412.9	7542	+ 6
.3271	2726.5	19.1	240.3	7542	+ 6
.3316	2904.7	20.6	386.8	7531	− 5
			mean......	7536 (±0.1%)	

The energy evolved per gram at 20°C is represented by $-\Delta U_B$ and the deviations of the individual runs from the mean by Δ. Σ is the sum of the calorific values from nitric acid, iron wire used as the ignition medium, and Joule's energy due to the electric current. Σ' is the sum of the heats of combustion of the promoter and the cotton string. The detailed experimental data for the remaining four samples have been omitted here, involving an overall uncertainty of not more than ±0.1% in relative mean deviation.

Table III contains the summary of the experimental data for the heats of combustion of five substances together with some important thermal data calculated therefrom. The number of satisfied combustion measurements in each case are given in the third column. The values of the bomb process were then recalculated per mole and corrected to the standard constant-volume process where the reactants are at 1 atm. pressure by means of Washburn's equation[16]. The energy evolved in this hypothetical standard process was denoted in Table III by the symbol $-\Delta U_R$. From this quantity the heat evolved in the isobaric process at 1 atm., $-\Delta H_c$, was obtained by the addition of the proper work term. Finally, the heats of formation, $-\Delta H_f^\circ$ (obs.), of these five substances from the standard

TABLE III

HEATS OF COMBUSTION AND DERIVED DATA FOR FIVE COMPOUNDS

Compounds	Mol. wt.	No. of satisfied combustion	$-\Delta U_B$ cal./g.	$-\Delta U_R$ kcal./mol.	$-\Delta H_C$ kcal./mol.	$-\Delta H_f^\circ$ kcal./mol. obs.	$-\Delta H_f^\circ$ kcal./mol. calcd. from Pauling's data	$-\Delta H_f^\circ$ kcal./mol. calcd. by Gilman and Dunn	$-\Delta H_f^\circ$ kcal./mol. calcd. by Thompson
$(CH_3)_2Si(OC_2H_5)_2$	148.25	6	7536	1117	1119	200	180	198.3	214
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	204.35	6	8552	1747	1751	217	205	226.7	233
$(C_2H_5)_2Si(OH)_2$	120.20	3	6495	781	782	212	193	228.2	228
$[(CH_3)_2SiO]_3$	222.38	5	6314	1404	1407	396	357	421.9	463
$[(C_6H_5)_2SiO]_3$	594.78	4	8086	4805	4810	225	151	—	216

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[14] P. A. Digiorgio, L. H. Sommer and F. C. Whitemore, ibid., **68**, 344 (1946).

[15] L. H. Long and R. G. W. Norrish, *Proc. Farad. Soc.*, **A241**, 587 (1949).

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

elements (gaseous H_2 and O_2, graphitic C, and metallic Si) were calculated from $-\Delta H_c$ by using -68.32[17], -94.05[17] and -208.14[3] kcal./mole for the heats of formation of water, carbon dioxide and amorphous silica, respectively.

Then, we calculated $-\Delta H_f^\circ$ (calcd.) in Table III by using the following data in accordance with the pressumption mentioned below: Data—Heats of atomization of elements; 85.0, 59.1, 51.7, and 124.3 kcal./g.-atom[18] for Si, O, H and C. Bond energies; 87.3, 57.6, 89.3, 58.6, 100 and 110.2 kcal./mole[18] for C-H, Si-C, Si-O, C-C, C=C and O-H, respectively. Resonance energy for benzene nucleus; 39 kcal./mole[18]. The heat of sublimation for hexamethyl-cyclotrisiloxane was found to be 13.2 kcal./mole by Osthoff, et. al.[19] The heats of vaporization for other compounds were presume from Trouton's Rule, and the heats of fusions were assumed to be one-tenth of those of vaporization.

As is shown in Table III the differences between the observed and calculated values of the heats of formation are not small. Uncertainty in the Si-O and Si-C bond energies proposed by Pauling may be the most probable reason for such disagreement.

The values of 52.0 and 59.2 kcal./g.-atom are now generally accepted for the heats of atomization of hydrogen and oxygen, respectively[20]. The corresponding value for carbon is controversial. Direct and various indirect measurements give varying values which fall into three main groups centering around 124,[21] 140[22] and 170[23] kcal./g.-atom. The value of silicon is in even greater doubt. Gilman and Dunn[24] calculated the Si-C and Si-O bond energies using the values 170 and 102 kcal./g.-atom for the heats of atomization of carbon and silicon, respectively, from the heats of formation of carborundum and silica. The resulting values are as follows: Si-C, 75.0; Si-O, 106 kcal./mole. Thompson[3] measured the heats of combustion of some polydimethyl siloxane, and calculated as 64 and 117 kcal./mole for the Si-C and Si-O bond energies from his results. (These values correspond to the following heats of atomization: C, 171.7; Si, 88.04 kcal./g.-atom). They also calculated the heats of formation of dimethyl diethoxysilane etc. These results are shown in Table III and comparatively near to the observed values except those of cyclic compounds.

However, the bond energies obtained by Gilman and Dunn were those derived from the heats of formation of silica and carboundum. It is also very desirable to derive these corresponding bond energies from the organosilicon compounds. The combustion measurements carried out by Thompson[3] contain considerable deviations, so we are not satisfied with bond energies derived from his measurements.

The compounds used here in our measurements, except hexamethyl cyclotrisiloxane, have such a large number of C-C and C-H bond etc. that Si-O and Si-C bond energies calculated from them turn out to be small differences between large quantities, so that they may be unreliable.

Recently we have measured the heats of combustion of some methoxy-polysilane and -polysiloxane, and calculated their heats of formation. The details will soon be published.

Summary

1. A bomb calorimeter has been used for the measurements of the heats of combustion of the following five compounds at 20°C and at constant volume: dimethyl diethoxysilane, di-*n*-propyl diethoxy silane, diethyl silanediol, hexamethyl cyclotrisiloxane and hexaphenyl cyclotrisiloxane.

2. From these experimental results the corresponding heats of combustion and formation at constant pressure have been calculated, and the latter values were compared with the calculated values of the heats of formation derived from the data of the bond energies.

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