Heats of Combustion and Formation of Lower Members of Methyl- and Ethyl-methoxypolysiloxanes

By Toshio TANAKA

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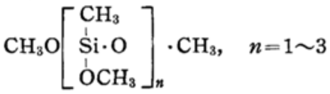
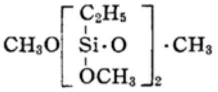
The heats of combustion of lower members of polydimethylsiloxanes were measured by Thompson[1], and with the aid of the results, average values of bond energy terms for Si–O and Si–C bonds were found to be 117 and 64 kcal./mol., respectively. Of these energy values, the former seems to be too great and the latter somewhat too small, in comparison with those calculated from heats of formation of silica and carborundum. In fact, the Si–O bond energy term has been calculated to be 102 kcal./mol. as the reasonable value, from the heats of formation of methoxy-polysilanes and -polysiloxanes in the preceding paper[2].

In the present work, the heats of combustion of lower members of methyl- and ethyl-methoxypolysiloxanes represented by L_n and $\mathrm{L'}_2$ have been measured, and thermal data derived therefrom have been discussed.



$$\mathrm{L}_n:\quad \mathrm{CH_3O}\left[\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{Si\cdot O}\\ |\\ \mathrm{OCH_3}\end{array}\right]_n\cdot\mathrm{CH_3},\quad n=1\sim3$$



$$\mathrm{L'}_2:\quad \mathrm{CH_3O}\left[\begin{array}{c}\mathrm{C_2H_5}\\ |\\ \mathrm{Si\cdot O}\\ |\\ \mathrm{OCH_3}\end{array}\right]_2\cdot\mathrm{CH_3}$$

Experimental

Materials. — The preparation and the physical constants of the members of L_n[3] and $\mathrm{L'}_2$[4] used in the present work were already reported.

Calorimetry. — The apparatus and procedure used in the combustion experiment have been similar to that described elsewhere[2,5]. The calibration experiment of the calorimeter was carried out at 20°C using benzoic acid (39f) supplied from National Bureau of Standards, Washington, and its energy equivalent value was determined to be 2459 cal./deg. (relative mean deviation ±0.1%).

A thin walled glass ampoule[5] has been used for the purpose of making possible complete combustion of each member of L_n. The completeness of combustion has been ascertained by the method as described in the previous paper[5]. A few other techniques which cause organosilicon compounds to burn completely was reported[1,6]. It seems, however, that satisfactory combustion is not always attained even when these techniques are employed. In the experiment of $\mathrm{L'}_2$, the techniques which are troublesome about the procedure have not been applied; a sample of about 0.4 g. has been weighed in a gelatine capsule, with a known heat of combustion, and the capsule has been vertically supported on a platinum combustion vessel by a platinum ignition wire, a piece of cotton being tied to it, which passes through two small holes at the top of capsule. The evaporation of $\mathrm{L'}_2$ through the very small holes on the capsule has been neglected in quantity, because of its high boiling point (97°C/20 mmHg). This neglect has no influence on the experimental results of $\mathrm{L'}_2$. After burning the sample by electrical ignition, carbon monoxide has not been identified by Winkler's reagent[7] in gaseous phase of bomb contents, and a bulky product, consisting of silica and an incomplete combustion product in a part, has been yielded on the combustion vessel. The incomplete combustion product contains amorphous carbon and, sometimes, a trace of carborundum, and these have been determined in quantity by the procedure described elsewhere[8]. Thermal corrections for carbon and carborundum have been calculated using the values of 7.84 cal./mg. (=32.8 joules/mg.)[9] and 6.86 cal./mg. for their heats of combustion, respectively. The latter value has been calculated from the figures of −26.7 kcal./mol. for the heat of formation of carborundum[10], and is that at standard constant volume process. The completeness of combustion in $\mathrm{L'}_2$ has been found to be 98.5∼99.7% by the analysis of incomplete combustion product.

Results and Discussion

Four to six combustion experiments have been made with each liquid sample, and the results are shown in Table I.

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

[2] T. Tanaka and T. Watase, This Bulletin, **28**, 258 (1955).

[3] T. Tanaka, A. Tasaka, R. Ōkawara and T. Watase, *Technol. Repts. Osaka Univ.*, **7**, 193 (1957).

[4] R. Ōkawara, This Bulletin, **28**, 360 (1955).

[5] T. Tanaka, U. Takahashi, R. Ōkawara and T. Watase, ibid., **28**, 15 (1955).

[6] S. Tannenbaum, S. Kaye and G. F. Lewenz, *J. Am. Chem. Soc.*, **75**, 3753 (1953).

[7] L. W. Winkler, *Z. anal. Chem.*, **102**, 99 (1935).

[8] T. Tanaka, *Technol. Repts. Osaka Univ.*, **8**, 437 (1958).

[9] F. D. Rossini, "Experimental Thermochemistry", Interscience Publishers, Inc., New York (1956), p. 46.

[10] F. D. Rossini et al., "Selected Values of Chemical Thermodynamic Properties", Natl. Bur. Standards, Washington (1952).

TABLE I. HEAT OF COMBUSTION AT CONSTANT VOLUME, cal./g.

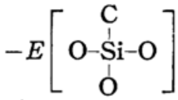
Compound							Mean
L_1	5632	5629	5617	5609	—	—	5622
L_2	5213	5228	5221	5212	5219	—	5219
L_3	5083	5055	5074	5072	—	—	5071
L'_2	5875	5865	5903	5856	5891	5868	5876

The relative mean deviation in each run is somewhat high compared with modern precision measurements, but of sufficient precision for bond energy term purpose in view of the other uncertainties involved.

Table II is the summary of important thermal data of four organosilicon compounds, calculated from the results of combustion experiments. Notations in Table II are as follows: $-\Delta U_R$, the heats of combustion at standard constant volume process where the reactants are one atmospheric pressure; $-\Delta H_c$, the heats of combustion in isobaric process at one atmospheric pressure; $-\Delta H_f$, the heats of formation of liquid compounds under consideration from standard elements (gaseous H_2 and O_2, graphitic carbon and metallic silicon); $-\Sigma E$, the heats of formation of the gaseous compounds from monoatomic gases. These energy values, except that in the last column of Table II, have been calculated by the same method as that used in the preceding paper²⁾, and in the calculation of $-\Sigma E$, heats of vaporization have been estimated to be 7.9, 9.1, 10.3 and 9.5 kcal./mol. for L_1, L_2, L_3 and L'_2, respectively, from Trouton's rule.

Bond Energy Term. — According to the additive law of bond energy, the value ΣE obtained experimentally in such a way may also be expressed by the formula

$$\Sigma E = pE_{\text{Si-O}} + qE_{\text{Si-C}} + rE_{\text{C-O}} + sE_{\text{C-H}} + tE_{\text{C-C}} \tag{1}$$

where E represents the energy value of bond corresponding to each suffix, and the factors p, q, r, s and t the number of bonds in the molecule under consideration. The energy terms of C–O, C–H and C–C bonds are well known, and if it is assumed that each value is not varied with the change of molecule, the bond energy values of bonds concerning the silicon atom may be estimated by formula 1. The value of  $-E\left[\text{O}-\overset{\overset{\text{C}}{|}}{\underset{\underset{\text{O}}{|}}{\text{Si}}}-\text{O}\right]$ presented in the last column of Table II has been estimated in this manner, using 98.8, 83.2 and 83.2 kcal./mol. for C–H, C–C and C–O bond energy terms, respectively. The former two values have been calculated by the method of least squares from heats of formation of lower members (from ethane to hexane) in normal paraffin¹¹⁾, other than methane, and the latter from the heat of formation of dimethylether¹⁰⁾ using the C–H bond energy obtained there. Two kinds of Si–O bond are contained in the molecules of L_n and L'_2; that of Si–O–CH_3 linkage and of Si–O–Si linkage. However, no energy difference between the two kinds of Si–O bond were observed in the preceding work on methoxy-polysiloxanes²⁾, and so these bonds will not be distinguished in the following discussion.

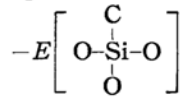
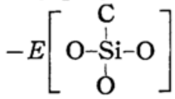
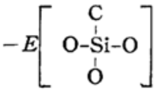
The  $-E\left[\text{O}-\overset{\overset{\text{C}}{|}}{\underset{\underset{\text{O}}{|}}{\text{Si}}}-\text{O}\right]$ in L_2 and L'_2 is in good agreement. However, this value increases with the polymer size of L_n, and further its energy difference between L_2 and L_3 is not so large as that between L_1 and L_2. This tendency has also been found in our recent investigation on heats of formation of methoxy end-blocked dimethylpolysiloxanes¹²⁾, and suggests that the  $-E\left[\text{O}-\overset{\overset{\text{C}}{|}}{\underset{\underset{\text{O}}{|}}{\text{Si}}}-\text{O}\right]$ may be close to a constant value as the polymer size increases*.

TABLE II. HEATS OF COMBUSTION AND FORMATION, AND BOND ENERGY, kcal./mol.

Compound	Mol. wt.	$-\Delta U_R$	$-\Delta H_c$	$-\Delta H_f$	$-\Sigma E$	 $-E\left[\text{O}-\overset{\overset{\text{C}}{\vert}}{\underset{\underset{\text{O}}{\vert}}{\text{Si}}}-\text{O}\right]$
L_1	136.23	766	767	227	1799	364
L_2	226.38	1181	1183	412	2847	368
L_3	316.54	1605	1608	589	3887	370
L'_2	254.43	1495	1498	422	3408	368

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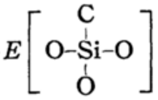
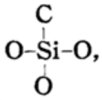
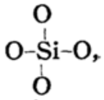
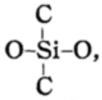
11) F. D. Rossini et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Institute of Technology, Pittsburgh, Pennsylvania (1953).

12) T. Tanaka, to be published in *J. Inorg. Nuclear Chem.*

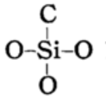
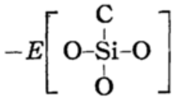
* Such a tendency for bond energy will always be found in lower members of a homologous series; for example, in calculation of C-C bond energy from heats of formation of normal paraffin, assuming that C-H bond energy is constant in the members.

The heats of combustion of various alkylsilanes were already measured by Tannenbaum[6], and Si–C bond energy estimated therefrom[13]. There was found an interesting tendency; namely, that the Si–C bond energy decreased as the size of the alkyl group joined to the silicon atom increased. It will here be assumed for the convenience of discussion that Si–O bond energy in $Si(OCH_3)_4$ (103 kcal./mol.**), which is 1 kcal. lower than that in amorphous silica, is the normal value for its bond energy. Similarly, if Si–C bond energy calculated from the heat of formation of $Si(CH_3)_4$[6] is assumed to be its normal value, it may be estimated to be 71 kcal./mol. using the heats of atomization and the C–H bond energy adopted in the present work. This value for Si–C bond energy is 1 kcal. lower than that*** in carborundum, and seems to be reasonable for its normal bond energy. If such assumptions are accepted for the normal bond energies of Si–O and Si–C bonds, the calculated value for  $-E\left[\text{O-}\overset{\text{C}}{\underset{\text{O}}{\text{Si}}}\text{-O}\right]$ results in 380 kcal./mol. under the additive law of bond energy, and is considerably higher than the observed value in L_3, not to speak of L_1, L_2 and L'_2. Such a deviation from the additive law of bond energy may be attributed to all of the bonds in the molecule under consideration. However, silicon atom has small electronegativity (1.8)[14] and its covalent radius is considerably larger than that of the carbon atom. Also it is well known that the silicon atom is, frequently, able to form a partially double bonding character with other atoms having lone-pair electron or electron donating power, by accepting the electron in its vacant *d*-orbital[15]. Considering these characteristics, the bonding orbital of the silicon atom seems to be liable to undergo any sort of distortion by the effect of neighboring groups.

The observed atomic distance of Si–O bond[16] is abnormally shorter than that (1.91 Å) expected from covalent radii, and this shortening has been considered to be due to the contribution of d_π-p_π bond character[17]. The π-bond character of each Si–O bond in structural unit,  $\text{O-}\overset{\text{C}}{\underset{\text{O}}{\text{Si}}}\text{-O}$, of the molecules considered in this paper will be undoubtedly less than that in  $\text{O-}\overset{\text{O}}{\underset{\text{O}}{\text{Si}}}\text{-O}$, being the structural unit of methoxypolysiloxanes, considering the numbers of resonance structures between Si–O bonds in both the structural units. As the result, the energy value of Si–O bond in L_n and L'_2 will be supposed to be lower than that in methoxy-polysiloxanes. In this manner, the considerable lowering of bond energy should be expected in the case of methoxy end-blocked dimethylpolysiloxanes, $CH_3O[Si(CH_3)_2\cdot O]_n\cdot CH_3$, the structural unit being  $\text{O-}\overset{\text{C}}{\underset{\text{C}}{\text{Si}}}\text{-O}$, and this expectation has been ascertained in the recent investigation on their lower members. This supposition on Si–O bond energy will correspond to the shortening of the silicon-halogen bond distance with the decrease of the number of halogen atoms attached to silicon[18].

Summary

1. The heats of combustion of lower members of methyl- and ethyl-methoxypolysiloxanes have been measured at 20°C and constant volume, and the corresponding heats of combustion and formation in isobaric process have been calculated.

2. The bond energy term in structural unit of  $\text{O-}\overset{\text{C}}{\underset{\text{O}}{\text{Si}}}\text{-O}$ has been calculated from the heat of formation, and it has been found that its value increases with the polymer sizes of the members. Finally, the  $-E\left[\text{O-}\overset{\text{C}}{\underset{\text{O}}{\text{Si}}}\text{-O}\right]$ has been compared with

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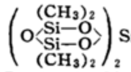
13) S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).

** The Si-O bond energy has been calculated to be 103, 102 and 103 kcal./mol. from heats of formation of $Si(OCH_3)_4$, $Si_2O(OCH_3)_6$ and $Si_3O_2(OCH_3)_8$, respectively, using 98.8 and 83.2 kcal./mol., instead of 98.9 and 84.1 kcal./mol. adopted in the preceding paper[2], for C-H and C-O bond energies.

*** Calculated to be 72 kcal./mol. from heat of formation of carborundum[10].

14) O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

15) For example, E. L. Reilly, C. Curran and P. A. McCusker, *J. Am. Chem. Soc.*, **76**, 3311 (1954).

16) 1.64±0.03 Å in  $\left(O\langle^{Si-O}_{Si-O}\rangle Si\right)$ with $(CH_3)_2$ above and below, W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948); 1.66±0.04 Å in $[(CH_3)_2SiO]_3$, E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950); 1.64±0.03 Å in $Si(OCH_3)_4$, 1.63±0.05 Å in $((CH_3)_3Si)_2O$, see Ref. 18.

17) L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

18) M. Yokoi, This Bulletin, **30**, 106 (1957).

that expected from the additive law of bond energy, and the lowering of bond energy in these molecules has been discussed in view of the resonance effect.

The author wishes to express his sincere thanks to Professor T. Watase for his gracious encouragement, Dr. R. Ōkawara for providing him with a part of the sample used in the present work, and Messrs. A. Tasaka and T. Ōtsuka for their aid during this experiment.

Department of Applied Chemistry
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka