Heats of Formation of Lower Members of Dimethyl- and Methylisopropoxy-cyclopolysiloxanes

By Toshio TANAKA

(Received July 30, 1959)

From the investigation on the redistribution equilibrium between dimethylcyclopolysiloxanes and linear polysiloxanes catalyzed by sulfuric acid, it was concluded by Scott that the ring in the trimer of cyclosiloxanes had a slight strain, while the ring structures of tetramer and the polymer of larger size were probably free from strain. He attributed this strain to the deformation of normally large Si-O-Si angle in forming the small-membered ring1). Before and after that, it was indicated from X-ray2,3) and electron4) diffraction studies that the six-membered ring in the trimer was planer or nearly planar. While, the siloxane rings of the tetramer5) and the octamer6) were reported to have *zigzag* form from X-ray diffraction study, and the former ring was supposed to have *cradle* (rather than *crown*) form from electron diffraction study7). As the results of these studies, the difference between the molecular structures of the cyclic trimer and the cyclic tetramer exist in the Si-O-Si angle, which is 125° for the former and 140° for the latter, and it has been supposed that a value of about 140° would be probable for a strain free Si-O-Si valency angle7).

In this paper, the heats of combustion of the members represented by C_n and D_n (see below) have been measured at 20°C and a constant volume, and the corresponding heats of combustion and formation in isobaric process have been calculated. From the results, it will be indicated

---

1) D. W. Scott, *J. Am. Chem. Soc.*, **69**, 803 (1947).

2) G. Peyronel, *Atti accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.*, **15**, 402 (1953); **16**, 78, 231 (1954); *Chem. Abstr.*, **48**, 7971*b*, 10401*h* (1954).

3) W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).

4) E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 420 (1950).

5) H. Steinfink, B. Post and I. Fankuchen, *Acta Cryst.*, **5**, 802 (1954).

6) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).

7) M. Yokoi, This Bulletin, **30**, 100 (1957).

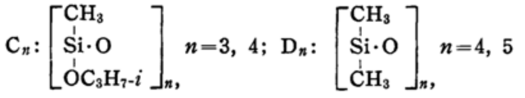
TABLE I. PHYSICAL CONSTANTS AND ANALYTICAL DATA OF C_n

Compound	b.p. °C/mmHg	d_4^{20}	n_D^{20}	Mol. wt. Found[a] (Calcd.)	MR_D Found (Calcd.)[b]	Si % Found (Calcd.)
C_3	67/1	0.9912	1.3973	348 (355)	86.23 (85.98)	23.80 (23.76)
C_4	97/1	1.0009	1.4023	— (473)	115.09 (114.64)	23.77 (23.76)

a) Cryoscopic measurement in benzene.

b) Calculated from bond refractivities by E. W. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

that the cyclotetrasiloxane and the cyclopentasiloxane are free from strain, while the cyclotrisiloxane will have a slight strain.



$$C_n:\left[\begin{array}{c}CH_3\\ |\\ Si\cdot O\\ |\\ OC_3H_7\text{-}i\end{array}\right]_n,\quad n=3,\ 4;\quad D_n:\left[\begin{array}{c}CH_3\\ |\\ Si\cdot O\\ |\\ CH_3\end{array}\right]_n,\quad n=4,\ 5$$

Experimental

Materials.—The members of C_n were prepared by hydrolyzing methylisopropoxydichlorosilane with considerable dropping rate using pyridine as an acid acceptor and were characterized*. The physical constants and the analytical data are shown in Table I.

The members of D_n, supplied from Shin-etsu Chem. Ind. Co., have been rigorously fractionated through a semi-micro Stedman column of about 20 theoretical plates and the physical constants have been compared with them reported in the literature of the subject. The results are shown in Table II.

TABLE II. PHYSICAL CONSTANTS OF D_n[a]

Compound	b.p. °C/mmHg	d_4^{20}	n_D^{20}	Mol. wt. Found[b] (Calcd.)
D_4	70/18 [175/760]	0.9558 [0.9558]	1.3968 [1.3968]	291 (297)
D_5	80/8 [210/760]	0.9596 [0.9593]	1.3984 [1.3982]	362 (371)

a) The values in brackets are those reported in the publication; E. G. Rochow, "An Introduction to the Chemistry of the Silicones", 2nd Ed., John Wiley & Sons, Inc., New York (1951), p. 185.

b) Cryoscopic measurements in benzene.

Calorimetry.—The apparatus used in this experiment was described elsewhere[8]. Each liquid sample has been weighed in a gelatine capsule and it has been burned by electrical ignition, as described in the case of methylethoxypolysiloxane in the previous paper[9]. After the burning of the samples, a bulky product, consisting of silica and incomplete combustion products of a part, are yielded in the combustion vessel. The incomplete combustion products in the experiments of C_3, C_4 and D_4 have been found to contain amorphous carbon and, sometimes, a trace of carborundum**. In addition to these products, a polymer-like substance containing a silicon atom has been yielded in the combustion experiment of D_5, as in the case of 1,3,5,7,9-pentamethylcyclopentasiloxane[10]. The incomplete combustion products included in the silica have been determined in quantities and the thermal corrections for them have been calculated according to the method in the previous paper[9,10].

Results and Discussion

Five to six combustion experiments have been carried out with each liquid sample of the same material, and the results are shown in Table III, excepting that of D_5.

The result of the combustion experiment of D_5 is shown in Table IV.

In Table IV, the energy evolved per gram at 20°C and a constant volume is represented by $-\Delta U_B^{low}$, in which the thermal corrections for carbon and, sometimes, for carborundum have been made, but the correction for the polymer-like substance only is not taken into account;

TABLE III. EXPERIMENTAL RESULTS OF C_3, C_4 AND D_4

Compound	cal./g.							Relative mean deviation
	Heat of combustion						Mean	%
C_3	6140	6133	6121	6126	6113	6138	6129	±0.14
C_4	6099	6077	6096	6088	6090	—	6090	±0.06
D_4	6357	6336	6355	6346	6332	—	6345	±0.09

---

* Details of the preparation of these compounds will soon be published by Dr. Ōkawara.

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

[9] T. Tanaka, ibid., **32**, 1258 (1959).

** In the combustion experiment of D_4, polymer-like substance, though only a trace in quantity, has sometimes been found in the combustion product, as in the case of D_5 described below, but such an experimental result of D_4 has been rejected here.

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

TABLE IV. EXPERIMENTAL RESULTS OF D_5

Wt. of sample	$-\Delta U_B^{low}$	Amount of SiO_2 produced from the polymer-like substance		$-\Delta U_B^{high}$
g.	cal./g.	mg.	α(%)	cal./g.
0.45543	6326	1.90	0.52	6359
0.45763	6277	2.75	0.74	6323
0.44446	6317	2.03	0.56	6352
0.45899	6292	1.79	0.48	6322
0.45121	6311	1.48	0.41	6337
0.45404	6321	1.52	0.41	6347
Mean	6307			6340
Average value		6324		

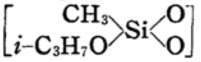
$-\Delta U_B^{low}$, will be therefore considered as underestimated value for the heat of combustion of D_5. The third column in this table is the number of grams of silica produced from the polymer-like substance by the further ignition in the course of analysis of incomplete combustion product, and the fourth column indicated by α is its percentage for the amount of silica equivalent to the weight of the sample in each run. As the thermal correction for the formation of the polymer-like substance could not be evaluated exactly in this experiment, it has been calculated under the assumption that the amount of sample equivalent to the amount of silica produced from the polymer-like substance remained, not burned at all, and $-\Delta U_B^{high}$ in th last column of the Table IV has been obtained by the following expression:

$$-\Delta U_B^{high} = -\Delta U_B^{low}(1+\alpha\cdot 10^{-2}).$$

This will be evidently overestimated value for its heat of combustion. Accordingly, the average value of these $-\Delta U_B^{low}$ and $-\Delta U_B^{high}$ values has here been adopted as the reasonable one for the heat of combustion of D_5.

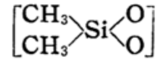
Table V is a summary of thermal data of C_n and D_n calculated from the combustion results.

Notations in this table are as follows: $-\Delta U_R$, the heat of combustion at standard constant volume process, where the reactants are one atmospheric pressure; $-\Delta H_f$, the heats of formation of the members of C_n and D_n in the liquid state from standard elements; $-\Sigma E$, the heats of formation of those in the gaseous state from mono-atomic gases. These energy values have been calculated by the method described in the previous paper[8]. In the calculation of $-\Sigma E$, values of 52.1, 59.2, 171.7 and 89.9 kcal./g.-atom have been adopted for the heats of atomization of hydrogen, oxygen, carbon and silicon, respectively, which are the same values used in the previous paper[8]. And then, values of 10.9[11] and 11.2[12] kcal./mol. have been used for the heats of vaporization of D_4 and D_5, respectively, and the corresponding energy values of C_3 and C_4 have been estimated to be 10.1 and 11.0 kcal./mol. from the Trouton's rule, respectively. The $-\Sigma E/n$ in the last column of the Table V, derived in this manner, will be considered as the sums of bond energies in structural units*** of



$\left[\begin{smallmatrix}CH_3\\ i\text{-}C_3H_7O\end{smallmatrix}>Si<\begin{smallmatrix}O\\ O\end{smallmatrix}\right]$

for C_n and of



$\left[\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}>Si<\begin{smallmatrix}O\\ O\end{smallmatrix}\right]$

for D_n.

No Strain in the Cyclic-tetramer and -pentamer. —If the $-\Sigma E/n$ of D_5 in Table V, though involving a considerable uncertainty, will be accepted as the reasonable value for the sum of bond energies in its structural unit, this is somewhat higher than the corresponding value of D_4. Such an energy difference between these compounds will perhaps be attributed to the difference between their polymer sizes, as in the case of methylmethoxypolysiloxanes, $CH_3O\cdot[(CH_3)(CH_3O)SiO]_nCH_3$[9], and methoxy end-blocked dimethylpolysiloxanes, $CH_3O\cdot[(CH_3)_2SiO]_nCH_3$[13], in which the values of

TABLE V. HEATS OF COMBUSTION AND FORMATION OF C_n AND D_n

Compound	Mol. wt.	kcal./mol.				
		$-\Delta U_R$	$-\Delta H_c$	$-\Delta H_f$	$-\Sigma E$	$-\Sigma E/n$
C_3	354.63	2173	2177	601	4839	1613
C_4	472.84	2879	2885	819	6473	1618
D_4	296.63	1882	1887	518	3728	932
D_5	370.79	2344	2350	656	4670	934

---

[11] R. C. Osthoff, W. T. Grubb and C. A. Burkhard, *J. Am. Chem. Soc.*, **75**, 2227 (1953).

[12] D. F. Wilcock, ibid., **68**, 691 (1946).

*** For example, in D_n, the term of "structural unit" will be used for $[(CH_3)_2SiO_2]$, but not $[(CH_3)_2SiO]$, on the number of each chemical bond in the compounds.

[13] T. Tanaka, to be published in *J. Inorg. & Nuclear Chem.*

$-E\left[\begin{matrix}C\\O\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]^{****}$ and $-E\left[\begin{matrix}C\\C\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]^{****}$ were found to be increasing with their polymer sizes, respectively.

If the value of 98.8 kcal./mol.[9,10] is here adopted for C–H bond energy in D_n, the values of $-E\left[\begin{matrix}C\\C\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ for D_4 and D_5 result in 339 and 341 kcal./mol., respectively. While, the corresponding values in methoxy end-blocked dimethylpolysiloxanes, which are linear compounds, were obtained to be 329, 335 and 336 kcal./mol. for the monomer, the dimer and the trimer, respectively[13]. The value of $-E\left[\begin{matrix}C\\C\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ in the cyclic tetramer is somewhat larger than that in the linear trimer, and the energy difference between them will be attributed to the difference between their polymer sizes and, if possible, partly to the difference between the cyclic and the linear structures. As the linear polysiloxanes under consideration will probably have no strain in their molecular structures, the ring structures of the cyclic-tetramer and -pentamer may also be free from strain, when one compares the $-E\left[\begin{matrix}C\\C\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ with those in the linear compounds.

Strain in the Cyclic Trimer.—The value of $-\Sigma E/n$ in C_3 is 5 kcal. lower than that in C_4, as shown in Table V. The energy difference will not by itself correspond to the strain per the structural unit of $\left[\begin{matrix}CH_3\\i\text{-}C_3H_7O\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ in C_3, because it must be taken into consideration that the value of $-\Sigma E/n$ in C_n will also increase with increasing of the polymer size, as in the case of D_n. Now, if it is assumed that the $-\Sigma E/n$ for C_3 should be 2 kcal. lower than that for C_4, by applying the energy difference in $-\Sigma E/n$ between D_4 and D_5, the extra lowering energy in C_3 comparing from C_4, 3 kcal. per the structural unit, will be due to the strain in the cyclic trimer; the ring of cyclic trimer, then, will be anticipated to have a strain corresponding to 9 kcal./mol. as a whole. However, the incremental change in $-\Sigma E/n$ between the cyclic-trimer (C_3) and -tetramer (C_4), attributed to the difference of their polymer sizes, will perhaps be larger than that between the cyclic-tetramer (D_4) and -pentamer (D_5), because the incremental change in energy between the neighboring members will be decreasing as their polymer sizes increase, as observed in the previous works on the linear polysiloxanes[9,13]. It has also been found in the previous paper[9] that the value of $-E\left[\begin{matrix}C\\O\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ in the first member of methylmethoxypolysiloxanes were 4 kcal. lower than that in the second member. As the cyclic trimer is the smallest-membered ring in the cyclopolysiloxanes, the larger part of the incremental change (5 kcal.) in $-\Sigma E/n$ between C_3 and C_4 may be attributed to the difference of their polymer sizes. Thus, the ring of the cyclic trimer will be considered to have a strain corresponding to a few or several kcal./mol. at most, being fairly smaller than 9 kcal./mol.

Though the Si–O–Si angle in the cyclic trimer has been considered to be subjected to a considerable distortion in comparing with its normal angle, the magnitude of energy due to strain obtained here seems to be too small. Such a slight strain in the six-membered ring will however be explained as due to the siloxane linkage having the nature represented by the term of "*ball and joined socket*", as explained previously by Roth and Harker[3].

The energy due to strain derived here comes out from the small difference between large quantities, so that it may not be a conclusive value. Notwithstanding, it may be said that the above results are parallel with the conclusions obtained from the investigation on redistribution equilibrium[1] and on molecular structures of cyclopolysiloxanes[2-7].

Summary

Heats of combustion of lower members of dimethyl- and methylisopropoxy-cyclopolysiloxanes have been measured at 20°C and a constant volume, and the corresponding heats of combustion and formation in isobaric process have been calculated. From the results, the heats of formation of structural units, $\left[\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$ and $\left[\begin{matrix}CH_3\\i\text{-}C_3H_7O\end{matrix}\!>\!\mathrm{Si}\!<\!\begin{matrix}O\\O\end{matrix}\right]$, of these compounds from mono-atomic gases have been derived, and it has been found that the ring structures

---

**** Sums of bond energies in the structural units of $CSiO_3$ and C_2SiO_2, in which C-H and C-O bonds are excepted, in methylmethoxypolysiloxanes and methoxy end-blocked dimethylpolysiloxanes, respectively. These sums were obtained under the assumption that the C-H and the C-O bond energies were not varied from molecule to molecule in the previous papers[9,13].

of the cyclic-tetramer and pentamer would be free from strain. Further, the effect of distortion of Si-O-Si valency angle in the cyclic trimer on the heat of formation has been discussed.

The author wishes to express his sincere thanks to Professor T. Watase, Dr. R. Ōkawara and Dr. M. Kakudo for their helpful discussions, and to Mr. H. Mimura for his aid in a part of this work.

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