392. *Heats of Combustion and Formation of Some Linear Polydimethylsiloxanes ; the* Si–C *and* Si–O *Bond-energy Terms.*

By Raymond Thompson.

The heats of combustion of the four lowest linear polydimethylsiloxanes (DC200 fluids) have been measured in a commercial bomb calorimeter of single-valve type. Combustion of these compounds is not complete under the conditions usually employed for an organic liquid, and an insulating skin of silica formed on the surface of the burning liquid prevents complete combustion of that beneath. A technique in which a glass ampoule containing the liquid bursts explosively at the time of firing is described. Under such conditions the liquids were found to burn quantitatively to silica, carbon dioxide, and water according to the equation :

$$CH_3{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3\ (l) + (4n + 8)O_2\ (g) = (n + 1)SiO_2\ (s) + (2n + 4)CO_2\ (g) + (3n + 6)H_2O\ (l)$$

The following heats of combustion (at 22°) were obtained [in kcal./mole (abs. k-joules/mole in parentheses)] : hexamethyldisiloxane, 1401 (5863) ; octamethyltrisiloxane, 1860 (7784) ; decamethyltetrasiloxane, 2289 (9578) ; dodecamethylpentasiloxane, 2756 (11,530). Energy increments are approximately equal for each $\cdot SiMe_2{\cdot}O\cdot$ unit added, and values for the heats of formation of the compounds are calculated to be 194 kcal./mole (812 abs. k-joules/mole), 337 (1410), 509 (2130), and 643 (2690) respectively. The heats of formation from monatomic gases have been calculated and, by application of simultaneous equations to the results obtained, the Si–C and Si–O bond-energy terms are deduced. The strength of the C–H linkage being assumed to be the same as in the paraffins, the Si–C energy term is found to be 64 kcal./mole (on the basis of 171·7 kcal./g.-atom for the heat of atomisation of carbon) ; a value of 117 kcal./mole has been obtained for the Si–O linkage. The observed heats of formation of other organo-silicon compounds are compared with values calculated by using bond-energy terms derived as above and with those obtained from the heats of formation of carborundum and silica.

Attention has recently been drawn (*J.*, 1952, 3292) to the difficulties encountered in obtaining from combustion data the heats of formation of organic compounds containing elements other than carbon, hydrogen, nitrogen, and oxygen. There is, in consequence, little published information concerning such heats of formation, and in particular about the thermochemically derived strength of the linkage between carbon and the " other " element. Major difficulties of combustion calorimetry often relate to the ascertainment of an equation for the bomb reaction, and it is somewhat surprising to find that little attention has been paid to the thermochemistry of organo-silicon compounds, in which the reaction is unusually straightforward provided that complete combustion is attained. Data concerning the heats of combustion of five organo-silicon compounds have recently been reported by Tanaka, Takahishi, Okawara, and Watase (*J. Chem. Phys.*, 1951, **19**, 1330), and the heat of formation of ethyl orthosilicate has been estimated from its heat of hydrolysis by Ogier (*Ann. Chim. Phys.*, 1880, **20**, 5). However, comparison of the observed ΔHf° values and those calculated from published values for the energy terms of the bonds concerned (*e.g.*, Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1945) reveals that revision of these energy terms is necessary (see Table 5). There has previously been no systematic investigation designed to provide fundamental quantitative data, and the present experiments were undertaken with the aim of beginning to fill this gap.

The polydimethylsiloxane homologous series is $CH_3{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$, with values of n from unity up to 2000 or more. The compounds burned in the course of this research were the first four members. In conformity with other work on these compounds the symbols employed by Wilcock (*J. Amer. Chem. Soc.*, 1946, **68**, 691) are used here: M denotes the end-group $SiMe_3{\cdot}O_{\frac{1}{2}}$ and D represents the incremental group $[SiMe_2{\cdot}O]$.

EXPERIMENTAL

Materials.—The polydimethylsiloxanes used were DC200 liquids supplied by Midland Silicones Ltd. This series is classified according to viscosity, the liquids of 0·65, 1·0, 1·5, and 2·0 centistokes corresponding fairly closely with M_2, M_2D, M_2D_2 and M_2D_3, respectively. That the materials were substantially pure before distillation was indicated by the narrow boiling range of each (<2°). The liquids were further twice distilled before use, the middle fraction of the first distillation being again distilled and the middle fraction of the second distillation taken for combustion. The b. p.s of the purified samples are listed, together with the temperatures quoted by Wilcock (*loc. cit.*) and Patnode and Wilcock (*J. Amer. Chem. Soc.*, 1946, **68**, 358) in Table 1.

TABLE 1.

Compound	Wilcock	Patnode and Wilcock	Present work
M_2	100°/757 mm.	100°/760 mm.	100°/759 mm.
M_2D	151·7°/747 mm.	153°/760 mm.	153°/774 mm.
M_2D_2	194°/760 mm.	194°/760 mm.	194°/760 mm.
M_2D_3	229°/760 mm.	229°/760 mm.	228·5°/766 mm.

The complete identity of the infra-red absorption spectrograms (wave-length 2—15μ) obtained from the present samples with those in the literature (Wright and Hunter, *ibid.*, 1947, **69**, 803) was further evidence of purity. A Perkin–Elmer Model 21 double-beam recording spectrophotometer was used in the present work.

Calorimetry.—The apparatus was the standard commercial Mahler–Cook bomb calorimeter, incorporating a 300-ml. stainless-steel bomb of the single-valve type and a Beckmann thermometer. The liquids, being volatile, were sealed into thin glass ampoules before weighing and combustion. It was found, however, that the normal techniques of combustion of a liquid could not be applied to organo-silicon compounds, for despite the observation by Tanaka *et al.* in connection with their compounds, the liquids were not found to " burn smoothly." If a single ampoule, designed to collapse during the process of charging the bomb with oxygen, was employed, combustion was incomplete; the silica produced during the early stages of combustion formed an insulating layer on the surface of the liquid so that access of oxygen was denied to that beneath and much carbon and incompletely burnt silicone were left on the base of the crucible. This also happened if the ampoule merely collapsed at the time of ignition. (It is rather surprising that Tanaka *et al.*, while giving full details of ampoule dimensions, did not indicate that other than the normal technique for the combusion of a liquid is necessary for organo-silicon compounds. Although the compounds employed in the present research did not include those which they burned, their materials contained similar percentages of silicon and it seems most likely that the silica produced would interfere with combustion. Since these authors claim an overall uncertainty in their values of not more than ±0·10%, weights of materials burned were presumably assessed by determination of the water and carbon dioxide produced.)

For the combustion of the liquids in quantities conducive to accuracy in weighing and measuring temperature rise, it was found that the ampoule should burst explosively at the moment of electrically firing the charge, and scatter the siloxane throughout the (dry) bomb. When this happened, combustion was complete. But the preparation of an ampoule strong enough not to collapse at 25 atm. and yet to be capable of being burst by the heat generated by the fuse (of, say, 25 cal.) was largely a matter of chance : a stronger ampoule will burst readily if a large fuse, or promoter such as benzoic acid, is used; use of a large amount of promoter is undesirable since it is then responsible for much of the observed temperature rise. However, as the (lower) polydimethylsiloxanes are themselves readily ignited, it was decided to employ the liquid as its own promoter. This was effected by dividing the sample approximately equally between two ampoules, one of which was designed to collapse at a pressure of several atmospheres to produce a pool of liquid in the crucible; the other was designed to burst a fraction of a second after firing owing to the heat produced by the combustion of the liquid from the first. The ampoules were spheres of soft glass approximately 1 cm. in diameter and having a 1-cm. tail of 1 mm. bore, sealed at the tip. The weaker ampoules weighed between 0·07 and 0·10 g., and the stronger 0·4—0·7 g. The latter were temporarily sealed at the tip and pre-tested to 25 atm. before being filled. All were filled from a hypodermic syringe having a gauge 14 needle, and the combined weight of sample of about 0·8—1·0 g. gave a temperature rise in the range 1·5—2°. Ignition was effected by applying 12 v to a 4 × 0·009 cm. platinum wire, with 0·005—0·007 g. of dried Whatman No. 1 filter-paper (3·99 kcal./g.) as a fuse. It should be emphasised that for complete combustion it is essential that the crucible as well as the ampoules be shattered. Since one crucible per combustion was thus required, a less expensive alternative to the usual silica was sought. (A shallow crucible of stainless steel 3 cm. in diameter had been tried, but although the maximum depth was only about 2 mm. the pool of liquid did not burn completely.) The most satisfactory substitute was found to be the bottom of a thin-walled 1″-diameter glass boiling-tube, cut to a depth of ¾″ and with lips pulled out as on the orthodox (Mahler–Cook) combustion bomb crucible.

Under the above conditions combustion was complete and results were reproducible almost to the maximum precision attainable with the apparatus. Five determinations were made with each liquid, the results of which are recorded in Table 2.

TABLE 2.

Compound	M.W.	Heat of combustion, kcal./mole	Mean
M_2	162·32	1396, 1412, 1406, 1397, 1394	1401
M_2D	236·45	1858, 1864, 1867, 1851, 1858	1860
M_2D_2	310·58	2297, 2285, 2291, 2280, 2290	2289
M_2D_3	384·71	2767, 2754, 2738, 2764, 2756	2756

The relative mean deviation of the water equivalent value of the apparatus was about 0·2%, a deviation high by comparison with modern precision techniques but of sufficient precision for bond-energy term purposes in view of the other uncertainties involved. Allowance has been made for nitric acid formation, and results are corrected to 15°-calories, but no other Washburn corrections were applied and weights were not corrected to vacuum. The determinations were made at a temperature of 22° ± 1°; for subsequent calculations the heats of formation at 25° are considered to be the same. No correction has been applied for heat of adsorption on to silica of the water and nitric acid formed during combustion.

Stoicheiometry and Analysis.—The inside surfaces of the bomb were, after combustion, covered with a loosely-adherent layer of finely divided silica, the fragments of broken glass lying at the bottom. The silica was found by *X*-ray powder photography to be completely amorphous. Pieces of glass which had been melted were often dark, but Jessup (*J. Res. Nat. Bur. Stand.*, 1937, **18**, 115, RP 966) has shown that such darkening is not of thermochemical significance. The contents of the bomb were washed quantitatively into a tared asbestos Gooch crucible and dried for 3 hr. at 140°. The use of a trimmed feather instead of a rubber " policeman " was found to be of considerable advantage in the operation of transferring the silica. Silicon contents of the various liquids were found to be as follows: M_2, calc. 34·50, found 34·2, 34·1; M_2D, calc. 35·5, found 35·0; M_2D_2, calc. 36·10, found 36·1; M_2D_3, calc. 36·50, found 36·3%.

The results are seen to be generally lower than the calculated values. This is considered not to be a reflection upon the purity of materials, of which b. p. and range and infra-red absorption spectra provide better indications, or upon the combustion. Complete transference of the dispersed silica from the complex inner surfaces of the bomb is difficult; there is also the possibility of slight loss by solution of the fine silica in the wash water.

RESULTS AND DISCUSSION

The equation given on p. 1908 being used, together with ΔHf° values of $-94{\cdot}05$ and $-68{\cdot}32$ kcal./mole (Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) for the heats of formation of carbon dioxide and water, respectively, and a ΔHf° value of $-208{\cdot}14$ kcal./mole for amorphous silica (calculated from the results of Humphrey and King, *J. Amer. Chem. Soc.*, 1952, **74**, 2041), heats of formation (ΔHf°) of the siloxanes are calculated to be: M_2, -194; M_2D, -337; M_2D_2, -509; M_2D_3, -643 kcal./mole. When these values are plotted against molecular weight the four points fall close to (alternately on either side of), but not exactly on, a straight line. If it is assumed that the energy increments between successive members of the series will be equal, the values obtained for ΔHf° by interpolation from this straight line are -189, -343, -496, and -649 kcal./mole. It is not possible, however, to distinguish between the deviation from linearity attributable to experimental error and that arising from other factors. It is to be noted that the oscillation of physical properties (including the wave-length shift of ultra-violet absorption peaks) is more pronounced than is usual in homologous series, and the heats of formation may in some way be affected also.

With a knowledge of the heats of formation of the polydimethylsiloxanes in their standard states, it is now possible to assign values for the heats of formation of the gaseous compounds from atoms of the elements. The latent heats of evaporation of the liquids are known from the work of Wilcock (*loc. cit.*) and are reproduced in Table 3; heats of atomisation of the constituent elements (other than carbon) are known with an accuracy probably commensurate with that of the heats of combustion. The heats of formation in the gaseous state from atoms, $-\Delta E$, have therefore been calculated from the heats of combustion of these compounds of formula $C_aH_bO_cSi_d$ by use of the expression:

$$-\Delta E = Q_{\text{comb.}} + L_{\text{vap.}} - 265{\cdot}7a - 86{\cdot}25b - 59{\cdot}16c - 296{\cdot}2d$$

The values for the heats of atomisation involved in the *a*, *b*, *c*, and *d* terms are taken from "Selected Values of Chemical Thermodynamic Properties" (Nat. Bur. Stand., Washington, 1950). Values of 52·098 and 59·159 kcal./g.-atom are now generally accepted for hydrogen and oxygen, respectively. The corresponding value for carbon may still be regarded as a matter of some controversy, later evidence tending strongly towards a value of the order of 170 rather than 125 kcal./g.-atom (Marshall and Norton, *J. Amer. Chem. Soc.*, 1950, **72**, 2166, and references cited therein) although evidence for a value of about 141 has recently been strengthened (Doehard, Goldfinger, and Waelbroeck, *J. Chem. Phys.*, 1952, **20**, 757); the actual figure of 171·7 kcal. incorporated in the *a* term above is taken from Brewer, Gilles, and Jenkins (*ibid.*, 1948, **16**, 797) and is that quoted in "Selected Values," etc. The heat of atomisation of silicon is reported to be 88·04 kcal./g.-atom (*op. cit.*; unpublished work of Brewer *et al.*). $-\Delta E$ values of the four polydimethylsiloxanes are listed in Table 3.

TABLE 3.

Compound	$L_{\text{vap.}}$ (kcal./mole)	$-\Delta E$ (kcal./mole)	Incremental change in $-\Delta E$
M_2	8·3	2389	
M_2D	9·45	3333	944
M_2D_2	11·5	4306	973
M_2D_3	12·7	5242	936

Si–C *and* Si–O *Bond-energy Terms*.—Three types of bond are involved in the breakdown of these compounds, namely, C–H, Si–C, and Si–O. Since the *ratio* of the Si–C to Si–O linkages varies as the series is traversed, it is possible, after certain assumptions, to evaluate the strength of a particular type of bond by application of simultaneous equations to $-\Delta E$ values of any two of the homologues. The only bonds involved are single, largely covalent linkages and no contribution is made by resonance or strain energy in the normally accepted sense of these terms. The equations employed are :

$$E_{\mathrm{M_2}} = 6E_{\mathrm{Si-C}} + 2E_{\mathrm{Si-O}} + 18E_{\mathrm{C-H}} \quad (1)$$

$$E_{\mathrm{M_2D}} = 8E_{\mathrm{Si-C}} + 4E_{\mathrm{Si-O}} + 24E_{\mathrm{C-H}} \quad (2)$$

$$E_{\mathrm{M_2D_2}} = 10E_{\mathrm{Si-C}} + 6E_{\mathrm{Si-O}} + 30E_{\mathrm{C-H}} \quad (3)$$

$$E_{\mathrm{M_2D_3}} = 12E_{\mathrm{Si-C}} + 8E_{\mathrm{Si-O}} + 36E_{\mathrm{C-H}} \quad (4)$$

These four equations can be solved in six different ways; solutions are listed in Table 4, from the mean values of which the Si–C and Si–O energy terms are found to be 64 and 117 kcal./mole, respectively.

In practical application to the siloxane type of compound the Si–C and Si–O energy terms are frequently taken together; it will be seen from cols. *C* and *D* that the summation reduces the range of deviation. The energy term for the Si–C linkage is based on the assumption that the strength of the C–H bonds of the methyl group when the carbon is directly attached to the silicon is the same as when it is attached to another carbon atom, since the equations can be solved only for (Si–C + 3C–H). A difference of 1 kcal./mole in the mean strength of the C–H bond (*e.g.*, by taking the mean C–H value of methane rather than of the C–H bonds of the CH_2 group, see below) would, of course, alter the Si–C value by 3 kcal./mole; however, in many polysiloxanes the two types of bond are not separated.

TABLE 4.

Pairs of equations	*A.* Si–C	*B.* Si–O	*C.* Si–C + Si–O	*D.* 3Si–C + Si–O
(1) and (2)	65	111	176	306
(1) and (3)	62	122	184	308
(1) and (4)	64	116	180	308
(2) and (3)	53	139	192	298
(2) and (4)	60	121	181	301
(3) and (4)	78	94	172	328
Mean	64	117	181	308
Calc. from ΔHf° SiC and SiO_2	72	104	176	320

The earlier bond-energy term values for the Si–C bond, derived from the heat of formation of carborundum, are given by Pauling (*op. cit.*) as 57·6, by Sidgwick (" The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, p. 556) as 69·1, and by Paul (" Principles of Chemical Thermodynamics," McGraw-Hill, 1951, p. 146) as 143·2 kcal./mole; it is likely that the value intended by Paul is half that given, namely 71·6 kcal./mole. Rochow (" An Introduction to the Chemistry of the Silicones," Chapman and Hall, 2nd edn., 1951, p. 19) considers that since the melting temperature of carborundum (*ca.* 2700°) is lower than the sublimation temperature of carbon (*ca.* 3500°) the Si–C must be considerably weaker than the C–C bond. Since the usually accepted value for the latter is about 83 on the basis of the 171·7 kcal./mole value for the heat of atomisation of carbon (Coates and Sutton, *J.*, 1948, 1187, give 83·0 kcal./mole), the present value of 64 kcal./mole is in conformity with such a view; so are the value derived from the heats given in the " Selected Values, etc." (71·8 kcal./mole) and Sidgwick's value of 69·1 compared with his 81·6 for the C–C bond-energy term, although it should be noted that the heat of formation (ΔHf°) of SiC is quoted by Sidgwick as $-57·6$ against the usual value of $-27·6$ kcal./mole (" Selected Values, etc."). Energy terms derived from silica for the Si–O bond are listed by both Pauling and Sidgwick as 89·3, by Syrkin and Dyatkina (" Structure of Molecules," Butterworth, 1950, p. 260) as 89 kcal./mole, and by Paul (*op. cit.*) as 104 kcal./mole. A value of 103·8 is calculated from the data of " Selected Values, etc." and ΔHf° for amorphous silica = $-208·14$. The reason for Pauling's choice of 89·3 is not apparent from his text; the figure, which may possibly involve an arithmetical error, is quoted extensively in the literature.

The energy terms obtained in the present work for the Si–C and Si–O bonds are thus lower and higher, respectively, than those calculated from the data in "Selected Values, etc." A degree of ionic character of 50% is assigned by Pauling to the Si–O linkage; Sauer and Mead (*J. Amer. Chem. Soc.*, 1946, **68**, 1794) assess the value at 37%. Both quote a 12% ionic character for the Si–C linkage. But it is well known (*e.g.*, Rochow, *op. cit.*) that the polarity of the Si–C bond is reduced by the addition of positive substituents to the carbon and negative to the oxygen atom; this will be the case with the polydimethylsiloxanes, hydrogen and oxygen being the respective substituents, and it is not unreasonable to suppose that the Si–O and Si–C bond-energy terms will be respectively stronger and weaker in the methylsiloxanes than in those compounds containing homogeneous bonds. It is not suggested that the present bond-energy terms are necessarily superior to those derived from the heats of combustion of silicon and carborundum, or that they should supersede the earlier ones for all purposes; but the new values should be more appropriately applicable to many organo-silicon compounds, and it is of interest to compare them with the few observed heats of formation of members of this class. Results so obtained are given in Table 5.

The values given in col. (i) have been recalculated from the combustion data of Tanaka *et al.* (*loc. cit.*) on the basis of the more recent heat of formation of silica (—208·14 instead of —203·34 kcal./mole). Bond-energy terms, in addition to those for Si–C and Si–O, employed in the calculation of the heats of formation of col. (iii) were as used by Coates and Sutton ("*B*" values, *loc. cit.*); C–H, 98·5 (derived from the CH_2 group of the higher paraffins); O–H, 110; C–O, 85·5; C–C, 83·0; C=C, 146·5; and 36 kcal./mole for the resonance energy of the benzene ring. The figures of col. (iv) differ from those of (iii) only in that the Si–C and Si–O energy terms employed were those derived from carborundum and silica. Latent heats of evaporation used for cols. (iii) and (iv) were calculated by Trouton's rule, values of 9 being taken for the first four compounds and 11 kcal./mole for the fifth; since the first three compounds are solid at 25°, latent heat of fusion is involved, and a value of 4 kcal./mole has arbitrarily been taken in each case.

TABLE 5.

	$\Delta Hf°$, in kcal./mole.			
Compound	(i) Obs. by Tanaka *et al.*	(ii) Calc. by Tanaka *et al.*	(iii) Calc. from Me siloxanes	(iv) Calc. from SiC & SiO_2
1. $(Me_2SiO)_3$	−369·1	−353·5	−463	−431
2. $(Ph_2SiO)_3$	−232·6	−139	−216	−184
3. $Et_2Si(OH)_2$	−222·8	−193·6	−228	−217
4. $Me_2Si(OEt)_2$	−199·8	−174	−214	−203
5. $Pr^n{}_2Si(OEt)_2$	−241·2	−203·6	−233	−222

From the $\Delta Hf°$ values of the last three compounds of Table 5 it will be seen that, as far as agreement between those observed and calculated is concerned, there is little to choose between cols. (iii) and (iv); the values in each case are closer to the observed than are those of col. (ii). The calculated and observed values for the heat of formation of hexamethyl*cyclo*trisiloxane (D_3) given in the original paper of Tanaka *et al.* agreed with each other to within 1%; such close agreement was purely accidental, for (*a*) the $\Delta Hf°$ values for SiO_2 then available have since been shown to be incorrect (Humphrey and King, *loc. cit.*) and (*b*) the Si–O bond-energy term listed by Pauling is erroneous. Employing the present data for the Si–O and Si–C bond-energy terms, derived from the polydimethylsiloxanes or otherwise, we see that the calculated values of $\Delta Hf°$ for D_3 differ from the observed by at least −60 kcal./mole. It is not altogether apparent why there should be this large discrepancy, unless it be that strain energy considerably affects the true heat of formation (Pauling and Simonetta, *J. Chem. Phys.*, 1952, **20**, 29, report that the strain energy connected with the distortion of each of the three C–C–C bond angles in *cyclo*propane to 60° is 22 kcal./mole). Frevel and Hunter (*J. Amer. Chem. Soc.*, 1945, **67**, 2275) have found the hexamethyl*cyclo*trisiloxane ring to possess an essentially planar configuration, yet the Si–O–Si bond angle of hexamethyldisiloxane (M_2) has been claimed from dipole-moment evidence (Sauer and Mead, *loc. cit.*) to be 160° ± 15°, and 140° from electron-diffraction measurements (Rochow, *op. cit.*, quoting a personal communication from Lucht and Harker). If this angle were maintained in D_3, an unusually acute O–Si–O angle of 80° ± 15°, or 100°, would result. The angles within the ring are, in fact, known to be: Si–O–Si, 125° ± 5°; O–Si–O, 115° ± 5° (Sutton and Allen, *Acta Cryst.*, 1950, **3**, 60, quoting a personal communication from Weller and Bauer). Increments in ΔHf° for the D unit are calculated from the polydimethylsiloxanes to be -153 kcal./mole, whereas $\frac{1}{3}[\Delta Hf^\circ(Me_2SiO)_3 -$ Latent heat$] = -122$ kcal./mole; such a discrepancy is well outside the limits of experimental error. It is of interest that the infra-red absorption peak assigned to the Si–O stretching vibration is at 1020 cm.$^{-1}$ in the case of D_3, whereas in D_4 and the higher cyclic members the peak is at about 1080 cm.$^{-1}$ (Richards and Thompson, *J.*, 1949, 124). The calculated heat of formation of hexaphenyl*cyclo*trisiloxane [col. (iii)], while considerably closer to the observed value than is that of Tanaka *et al.*, is still about 16 kcal./mole lower than the experimental value. In addition to the uncertainty of strain-energy contributions, unreliability of any calculated value for the heat of formation arises from the facts that the result is the difference between two large numbers, and that the resonance-energy contribution of the six benzene rings is not known accurately; but it is possible that the effect of aryl carbon atoms attached to silicon will be to alleviate much of the strain (Freiser, Charles, Speier, and Eagle, *J. Amer. Chem. Soc.*, 1951, **73**, 5229), although Roth (*ibid.*, 1947, **69**, 474) considers the O–Si–O angle to be " soft " even when two methyl groups are attached to the silicon.

The heat of formation of tetraethyl orthosilicate is listed in "Selected Values, etc." as $\Delta Hf^\circ = -318$ kcal./mole; this value had been calculated from Ogier's original measurements of the heat of hydrolysis of the ester (*loc. cit.*). Ogier had found the hydrolysis to be instantaneous and the maximum temperature rise to be attained in 5 min.; it is now known that the ethyl ester does not react immediately with pure water, but does so if the pH of the solution is sufficiently low or if another substance such as ethanol is present, *inter alia*, to increase the mutual solubility of the reactants. The boiling point of the ester is given by Ogier as 165° (cf. 168·55° ± 0·05°, Solana and Moles, *Anal. real. Soc. esp. Fis. Quim.*, 1932, **30**, 886) and it is possible that a trace of impurity served to expedite hydrolysis. His value of $\Delta H = -21{\cdot}6$ kcal./mole for the heat of hydrolysis compares favourably with a preliminary value of $\Delta H = -18{\cdot}0$ kcal./mole obtained by the author for immediate hydrolysis in 0·1N-hydrochloric acid. A value of 10 kcal./mole being used for the latent heat of evaporation of the ester (*idem, ibid.*), ΔHf° of tetraethyl orthosilicate is calculated on the 104 kcal./mole Si–O value to be -330, and on the 117 value to be -382 kcal./mole. It is of interest that the observed value lies much closer to that calculated on Si–O bond-energy terms derived from a purely inorganic compound than to that derived from organosilicon compounds containing carbon attached directly to silicon.

As is the case with many classes of compound, it seems that calculations of heats of formation of the silicones should employ bond-energy terms derived from compounds of a closely similar nature to those to which they are applied.

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