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## The Si–C Bond Energy in Alkylsilanes

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There is considerable discrepancy in the reported values for the Si–C bond energy. Pauling[1] gives a value of 57.6 kcal./mole for crystalline carborundum, whereas Gilman and Dunn[2] calculate a value of 75.0 kcal./mole using newer heats of atomization for carbon and silicon. Thompson[3] found an average value of 64 kcal./mole for the Si–C bond in polydimethylsiloxanes. In order to add to the information available, it was considered worthwhile to calculate the Si–C bond energy in some alkylsilanes from heats of combustion recently obtained at this Laboratory.[4]

Table I lists the heats of formation for the alkylsilanes and the energies calculated for the Si–C bond[5] using the elemental heats of atomization and other required bond energies given by Gilman and Dunn[2] and by Thompson.[3] Except for vinylsilane, the values in the last two columns of Table I agree very well. The heats of formation differ slightly from those originally reported by Tannenbaum, *et al.*[4] Corrections were made for the newer value of the heat of formation of amorphous $SiO_2$ (−208.14 kcal./mole) formed in the combustion process as calculated by Thompson from the data of Humphrey and King.[6] The heats of vaporization of triethylsilane and dimethyldi-*n*-propylsilane, not previously measured, were estimated from Trouton's rule.

There appears to be a definite dependence of Si–C bond energy on the nature of the alkyl group joined to the silicon. The maximum estimated uncertainty in the measurement of the heat of combustion was −1.5 to +0.5%. This could result in a maximum error in the heats of formation of from 12 to 30 kcal./mole depending on the heat of combustion of the alkylsilane.[4] However, either the data are considerably more accurate than the uncertainty indicates, or the same relative error was involved in each determination, for there is little scatter within the methyl and ethyl series. It therefore appears that the trend observed in Table I is too large to be dismissed as within the experimental error.

Although no simple propylsilanes were investigated, a value of 57 kcal./mole for the Si–propyl bond was obtained from a plot of the average Si–C bond energy *vs.* type of alkyl group. Using this value along with the value of 74 kcal./mole for Si–methyl, the average Si–C bond energy in dimethyldi-*n*-propylsilane would be 65 kcal./mole compared to a value of 61 kcal./mole actually found.

TABLE I

HEATS OF FORMATION AND SI–C BOND ENERGY OF ALKYL SILANES

| Compound | $\Delta H_{form}$, kcal./mole | | Si–C bond energy, kcal./mole | |
|---|---|---|---|---|
| | Liquid | Gas | Calcd. from values Gilman and Dunn[a] | Calcd. from values of Thompson[b] |
| $(CH_3)_2SiH_2$ | −47 | −42 | 76 | 72 |
| $(CH_3)_3SiH$ | −66 | −60 | 76 | 74 |
| $(CH_3)_4Si$ | −75 | −69 | 74 | 72 |
| | | | Av. 75 | Av. 73 |
| $C_2H_5SiH_3$ | −26 | −21 | 64 | 61 |
| $(C_2H_5)_2SiH_2$ | −43 | −36 | 66 | 65 |
| $(C_2H_5)_3SiH$ | −47 | −39 | 62 | 63 |
| $(C_2H_5)_4Si$ | −47 | −37 | 59 | 60 |
| | | | Av. 62 | Av. 62 |
| *i*-$C_4H_9SiH_3$ | −31 | −24 | 52 | 56 |
| *n*-$C_4H_9SiH_3$ | −32 | −14 | 52 | 56 |
| $CH_2{=}CHSiH_3$ | + 1 | + 6 | 71 | 63 |
| $(CH_3)_2Si(n\text{-}C_3H_7)_2$ | −50 | −41 | 60 | 61 |

[a] The C=C value was calculated from $\Delta H_{form}$ $C_2H_4$ (g) = $-12.5^7$ kcal./mole, C–H energy = 98.1 kcal./mole, and heat of atomization of C = 170 kcal./mole. [b] The Si–H value was calculated from $\Delta H_{form}$ $SiH_4$ (g) = $-14.8^7$ kcal./mole and heat of atomization of Si = 88.0 kcal./mole.

These results are similar to those obtained in studies of the bond dissociation energies of tetraalkylsilanes. The activation energy for the thermal decomposition of tetramethylsilane was found to be 79 kcal./mole,[8] whereas the values for tetraethylsilane and tetrapropylsilane were 50.5 and 46.0 kcal./mole, respectively.[9]

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[1] L. Pauling, "The Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1949, p. 53.

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

[3] R. Thompson, *J. Chem. Soc.*, 1908 (1953).

[4] S. Tannenbaum, S. Kaye and G. F. Lewenz, THIS JOURNAL, **75**, 3753 (1953).

[5] A recent article by M. L. Huggins, *ibid.*, **75**, 4125 (1953), lists values for bond energies based on a heat of atomization of C = 137 kcal./mole. Calculations of the Si–C bond energy using these data result in values about 10 kcal./mole less than those in Table I; however, the same type of dependence on alkyl group is found.

[6] G. L. Humphrey and E. G. King, *ibid.*, **74**, 2041 (1952).

[7] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, Natl. Bur. Standards, Feb. 1, 1952.

[8] D. F. Helm and E. Mack, THIS JOURNAL, **59**, 60 (1937).

[9] C. E. Waring, *Trans. Faraday Soc.*, **36**, 1142 (1940).

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## The Solubility of Phosphine in Aqueous Solutions[1]

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In the course of recent work[2] it became necessary to determine the solubility of phosphine in water and aqueous solutions. Because of the low solubility, the solubility coefficient was determined by measuring directly the concentration of gas in a saturated solution, rather than by the usual procedure of measuring the pressure decrease upon

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] R. E. Weston, Jr., and J. Bigeleisen, THIS JOURNAL, to be published.