An Electron Impact Study of Ionization and Dissociation of Trimethylsilanes

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Appearance potentials of ions from a series of trimethylsilanes were measured, yielding molecular and ionic heats of formation, as well as dissociation energies for the bonds $(CH_3)_3Si-Y$ having a variety of groups Y. In agreement with recent data on alkylsilanes, $R-SiH_3$, the dissociation energies of bonds to silicon are found to be greater than had been assumed.

Introduction

During the last 2 decades electron impact studies have provided chemists with a considerable body of knowledge concerning energetic properties of gaseous molecules, ions, and free radicals.[1,2] A very large fraction of this thermochemical information pertains to compounds of carbon and has proved to be of great value in many studies of reactions involving hydrocarbons and derivatives containing elements of the first long period.

However, in the analogous organosilicon compounds very little such energetic information is available[3,4] even though in recent years interest in organosilicon chemistry has been continually increasing. Moreover, even among the meager data available in the open literature there are numerous significant discrepancies.[5,6] (The most serious of these is between the values of Gunn and Green and those of Feher, Jansen, and Rohmer for the heats of formation of SiH_4 and Si_2H_6.[5a] The former workers report $+7.3$ and $+17.1$ kcal./mole, respectively; whereas the latter group gives -11.3 and -36.2 kcal./mole, respectively.) These discrepancies are undoubtedly due in no small measure to the difficulties involved in the use of conventional combustion bomb calorimetry with silicon-containing systems.[7]

Steele, Nichols, and Stone[6b] have used electron impact techniques to determine Si–C bond dissociation energies in a series of alkyl-substituted silanes, $R-SiH_3$, and in a series of alkyl-substituted trichlorosilanes, $R-SiCl_3$. Steele and Stone[8] have used the same technique to determine Si–H and Si–Si bond-dissociation energies in silane and disilane, respectively. The general indications found by these workers,[6b,8] namely, that the dissociation energies were considerably greater than suggested by thermochemical bond energy considerations, were found also to apply to the bond dissociation energies in some substituted trimethylsilanes.[9]

We report here further electron impact studies of trimethylsilyl systems as well as some of the details necessarily omitted in our earlier communication.[9]

Experimental Section

All measurements were carried out in a Bendix Model 14-101 time-of-flight mass spectrometer[10] which had been modified by the incorporation of differential pumping on the source region and by the installation of a four-grid electron gun system to allow use of the retarding potential difference technique[11] for the measurement of ionization and appearance potentials. The electron energy was controlled by a pair of ten-turn 50K potentiometers with $\pm 0.1\%$ linearity and was measured using a Hewlett-Packard automatic d.c. digital voltmeter (Model 405 BR). Electron energies were stable to better than ± 0.01 e.v.

The potential configuration of the electron gun grids which afforded optimum performance was determined empirically. The arrangement used was as follows. (a) The first and third grids (grid adjacent to filament taken as grid No. 1) contained large slits, 0.9 × 5.08 mm., and carried the 1.4-μsec. pulse admitting the electron beam into the ionization region. The d.c. level upon which this pulse was superimposed was kept at least 10 v. negative with respect to electron energy (filament potential) to prevent completely electrons from entering the ionization region when the pulse was off. The top of the pulse was about 7 v. positive with respect to the filament potential. (b) A retarding potential of -0.2 to -0.3 v., relative to electron energy, was applied to the second grid, which had a small slit, 0.4 × 2.07 mm. (When this grid contained a large slit, the appearance potentials obtained were in error by 0.1 to 0.5 e.v.) (c) The fourth grid, at the entrance to the ionization region, contained a large slit and was maintained at ground, as was the source itself. (d) The trap anode was kept at -150 v.

In determining appearance potentials changes in ion intensity (ΔI), resulting from 0.1-v. changes in retarding potential, were obtained at 0.1-v. intervals in electron energy. A least-squares line was passed through the points extending about 1 v. above the threshold unless

(1) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

(2) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth & Co. (Publishers) Ltd., London, 1958.

(3) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960.

(4) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, London, 1963.

(5) For sizeable discrepancies in molecular heats of formation, see (a) S. R. Gunn and L. G. Green, *J. Phys. Chem.* **65**, 779 (1961); F. Feher, G. Jansen, and H. Rohmer, *Angew. Chem.*, **75**, 859 (1963); (b) R. Thompson, *J. Chem. Soc.*, 1908 (1953); K. B. Goldblum and L. S. Moody, *Ind. Eng. Chem.*, **47**, 847 (1955); (c) W. F. Lautsch, *Chem. Tech.* (Berlin), **10**, 419 (1958); S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).

(6) For variations in bond energies, see (a) H. Gilman and G. E. Dunn, *Chem. Rev.*, **52**, 77 (1953); (b) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 4441 (1962).

(7) W. D. Good, J. L. Lacina, B. L. DePrater, and J. P. McCullough, *J. Phys. Chem.*, **68**, 579 (1964).

(8) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).

(9) G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **86**, 3174 (1964).

(10) W. C. Wiley and I. H. McLaren, *Rev. Sci. Instr.*, **26**, 1150 (1955).

(11) R. E. Fox, W. M. Hickam, D. J. Grove, and T. Kjeldass, Jr., *ibid.*, **26**, 1101 (1955).

a break in the ionization efficiency curve was obvious in this region. The ionization potential of a rare gas, admitted with the compound to be studied, was measured for each measurement of an unknown ionization or appearance potential to ensure the greatest accuracy possible.

Compounds Studied. Trimethylchlorosilane, obtained from the Dow Corning Corp., was purified by fractional distillation before use (typical b.p. 56.5° at 731 mm.).

Dimethylsilane and a purified sample of *tetramethylsilane* were generously provided by D. K. Snediker of the radiochemistry group at this university.

Trimethylsilane was prepared by the procedure of Finholt, *et al.*,[12] using di-*n*-butyl ether as solvent to permit easy separation of the trimethylsilane.

Ethyltrimethylsilane, b.p. 61–62° (734 mm.), $n^{25}D$ 1.3820, was prepared by treating the Grignard of methyl bromide with ethylmethyldichlorosilane (obtained from the Dow Corning Corp.) in ether.

Isopropyltrimethylsilane was prepared by Kerr[13] and was purified by fractional distillation, b.p. 85–86° (745 mm.), $n^{19}D$ 1.3976.

t-Butyltrimethylsilane, b.p. 100–105° (735 mm.), m.p. 72–73°, was prepared by the method of Tyler.[14] The *t*-butyllithium used was obtained from the Lithium Corp. of America as a 1.66 *M* solution in pentane.

Hexamethyldisilane, b.p. 111° (742 mm.), $n^{22}D$ 1.4224, was prepared by the method of Bygdén,[15] using Anderson Chemical Co. "pure grade" hexachlorodisilane.

Hexamethyldisiloxane, obtained from the Dow Corning Corp. was purified by fractional distillation, b.p. 98.0° (434 mm.).

Trimethylmethoxysilane, b.p. 56.0–56.5° (737 mm.), $n^{25}D$ 1.3684, was obtained according to the procedure of Sauer.[16]

Trimethylfluorosilane was prepared using the reagents employed earlier by Emeléus and Wilkins.[17] A 3-ft. length of 6-mm. glass tubing was packed with anhydrous zinc difluoride. Several milliliters of trimethylchlorosilane were poured into the top of the column, and the bottom was connected *via* a rubber stopper to a partially evacuated glass bulb in a liquid nitrogen bath. After about 6 hr., one-half the column had been wet by the trimethylchlorosilane, and the trimethylfluorosilane collected in the bulb was transferred to a storage bulb on the vacuum line.

Trimethylbromosilane, b.p. 73–75° (730 mm.), was prepared by bromination of trimethylsilane at −78°, using excess bromine in toluene. The product was obtained by distillation through a spinning-band column (equipped with a platinum band) purged with nitrogen. While the trimethylbromosilane seemed to be amenable to storage in an evacuated bulb for several weeks before appreciable reaction took place with the stopcock

(12) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 69, 2692 (1947).
(13) G. T. Kerr, II, M. S. Thesis, Pennsylvania State College, 1946, Part I, pp. 39–42.
(14) L. J. Tyler, Ph.D. Thesis, Pennsylvania State College, 1948, p. 59 ff.
(15) A. Bygdén, *Ber.*, 45, 707 (1912).
(16) R. O. Sauer, *J. Am. Chem. Soc.*, 66, 1707 (1944).
(17) H. J. Emeléus and C. J. Wilkins, *J. Chem. Soc.*, 454 (1944).

grease, it was extremely reactive towards the water vapor adsorbed on the interior of the mass spectrometer and any leaking into the source. No spectrum could be obtained which did not indicate the presence of appreciable hexamethyldisiloxane resulting from the hydrolysis of the trimethylbromosilane by water vapor. For example, when the 50-v. spectrum of trimethylbromosilane was determined, the amount of hexamethyldisiloxane in the spectrum was such that its 100% peak, m/e 147, was equivalent to a 15.4% peak in the trimethylbromosilane spectrum (corrected for the contribution from the disiloxane). The presence of hexamethyldisiloxane in the trimethylbromosilane must have a negligible effect on the appearance potential of m/e 73, $(CH_3)_3Si^+$, from $(CH_3)_3SiBr$ since this is nearly 5 e.v. lower than that of m/e 73 from the $(CH_3)_6Si_2O$.

Obtaining the appearance potentials of the ions from the trimethylbromosilane, however, was made difficult by the fact that the $(CH_3)_3SiBr$ concentration in the source changed with time owing to its reaction with water vapor in the mass spectrometer. The source differential pumping was utilized to minimize the problem at hand. Pumping very rapidly on the source allowed large quantities of trimethylbromosilane to stream through it at reasonably low pressures ($\sim$2 $\times$ 10^{-5} mm.). The constant influx of fresh trimethylbromosilane maximized its partial pressure in the source.

The operating procedure used was to open the stopcock connecting the reservoir to the source, and then to obtain immediately one ionization efficiency curve for an ion in the trimethylbromosilane spectrum. Next, a xenon ionization efficiency curve was determined. Following this, the mass spectrometer was pumped out, and fresh sample was admitted from the reservoir for the next pair of determinations.

Operating in this manner, the heights of the peaks in the $(CH_3)_3SiBr$ spectrum decreased by about one-third in 10 min. Since changes in pressure do not exert a very dramatic effect on appearance potentials determined by the retarding potential difference (r.p.d.) method, it is felt that the values obtained under these conditions are quite reliable.

Xenon and *krypton* were obtained from the Matheson Co. and were used as received.

The purity of the compounds studied was ascertained by mass spectrometry and gas chromatography. The mass spectrum was a sensitive indicator of the presence of any chlorosilanes, hexamethyldisiloxane, and compounds of higher molecular weight than the sample. Gas chromatography easily detected impurities such as low molecular weight alkylsilanes. The chromatograph used was a Perkin-Elmer Model 123, containing two 20-ft. columns in series. The first was packed with dipropylene glycol dibenzoate and the latter with transformer oil, both at a concentration of 20% by weight on firebrick. This chromatograph was calibrated for a considerable number of alkylsilanes, including dimethylsilane, trimethylsilane, tetramethylsilane, hexamethyldisiloxane, and hexamethyldisilane. The last compound mentioned had a retention time of approximately 2.5 hr. with good peak shape, indicative of the performance of the column.

A trace (<0.1%) of hexamethyldisiloxane was present in a number of the compounds studied. Trimethyl-

Table I. Ionization and Appearance Potentials Obtained by the R.p.d. Method[a]

Compd.	I_z, e.v.	$A[(CH_3)_3Si^+]$, e.v.	$A[(CH_3)_2SiY^+]$,[b] e.v.
$(CH_3)_2SiH_2$			11.94 ± 0.04 (4)
$(CH_3)_3SiH$		10.78 ± 0.07 (8)	11.70 ± 0.06 (4)
$(CH_3)_3SiCH_3$	9.98 ± 0.03 (3)	10.63 ± 0.13 (13)	10.63 ± 0.13 (13)
$(CH_3)_3SiC_2H_5$	9.70 ± 0.01 (3)	10.53 ± 0.09	11.41 ± 0.06^c (4)
$(CH_3)_3SiCH(CH_3)_2$	9.50 ± 0.03 (3)	10.56 ± 0.16	...
$(CH_3)_3SiC(CH_3)_3$	9.34 ± 0.06 (3)	10.53 ± 0.09 (6)	...
$(CH_3)_3SiSi(CH_3)_3$	8.79 ± 0.08 (6)	10.69 ± 0.04 (6)	10.74 ± 0.08 (6)
$(CH_3)_3SiOSi(CH_3)_3$	9.59 ± 0.04 (3)	15.36 ± 0.13^d(5)	10.20 ± 0.07 (6)
$(CH_3)_3SiOCH_3$	9.79 ± 0.04 (3)	12.43 ± 0.18 (5)	10.25 ± 0.05 (4)
$(CH_3)_3SiF$	10.55 ± 0.06 (3)	11.7 ± 0.5^d (8)	11.11 ± 0.05 (3)
$(CH_3)_3SiCl$	10.58 ± 0.04 (3)	12.40 ± 0.06 (6)	11.00 ± 0.16 (7)
$(CH_3)_3SiBr$	10.24 ± 0.02 (3)	10.69 ± 0.06 (5)	10.97 ± 0.02 (4)
$(CH_3)_3SiN(C_2H_5)_2$	8.06 ± 0.02 (3)	12.61 ± 0.03 (4)	...

[a] Number of determinations indicated in parentheses. [b] Appearance potential for loss of H from dimethylsilane; for loss of CH_3 from all others. [c] Ion could be $(CH_3)_3SiCH_2^+$ or $(CH_3)_2SiC_2H_5^+$. [d] See text for discussion of this value.

fluorosilane, although free of trimethylchlorosilane, was contaminated with sufficient hexamethyldisiloxane that it contributed 1.6% to the measured m/e 73 peak height in the trimethylfluorosilane spectrum (not enough to affect the appearance potential measurements, in view of the very high appearance potential of m/e 73 from the hexamethyldisiloxane).

The dimethylsilane contained a trace of trimethylchlorosilane and some dimethyldichlorosilane, but trimethylsilane and tetramethylsilane were definitely shown to be absent by the lack of a peak at m/e 73. Since it appeared that the impurities observed would not make a significant contribution to the ion, $(CH_3)_2$-SiH^+, to be studied, no effort was made to further purify the material.

Tetramethylsilane was shown *via* gas chromatography to be free of trimethylsilane.

Results

Typical data obtained in these studies are shown in Figure 1. Table I gives all the ionization and appearance potentials obtained, together with the average deviations of replicate measurements and the number of determinations for each ion in parentheses. The values for all the ions except $(CH_3)_5Si_2^+$ were determined using Xe ($I_z = 12.13$ e.v.) as the standard; the pentamethyldisilyl cation was evaluated using Kr ($I_z = 14.00$ e.v.) as the standard owing to mass interference of the xenon isotopes with the pentamethyldisilyl cation.

The accuracy of the appearance potential measurements was checked by determining the differences between the known ionization potentials of some rare gases. In separate sets of measurements, the Kr–Xe difference was found to be 1.90 ± 0.02 and 1.85 ± 0.04 e.v., compared with the spectroscopic difference of 1.87 e.v. The Ar–Xe difference was found to be 3.68 ± 0.03 e.v. (four determinations), only slightly higher than the spectroscopic difference of 3.63 e.v.

The reproducibility of the values was very good. The appearance potentials of the ions m/e 73 and 93 from trimethylchlorosilane were determined in two sets of measurements made 9 months apart. The values obtained in the early runs were $A = 12.42 \pm 0.03$ (m/e 73) and 10.97 ± 0.12 (m/e 93) e.v. The results of the later runs were $A = 12.38 \pm 0.05$ (m/e 73) and 11.04 ± 0.10 (m/e 93) e.v. The poorest

agreement obtained between two sets of measurements in which the precision of each set was good was that obtained for the ionization potential of hexamethyldisilane, where the two sets gave average values differing by 0.17 e.v. It was difficult to obtain good precision for some ions (*e.g.*, m/e 73 from tetramethylsilane) even within a given set of determinations, but after replicate runs, nearly all the ions yielded appearance potentials with an average deviation of 0.15 e.v. or less.
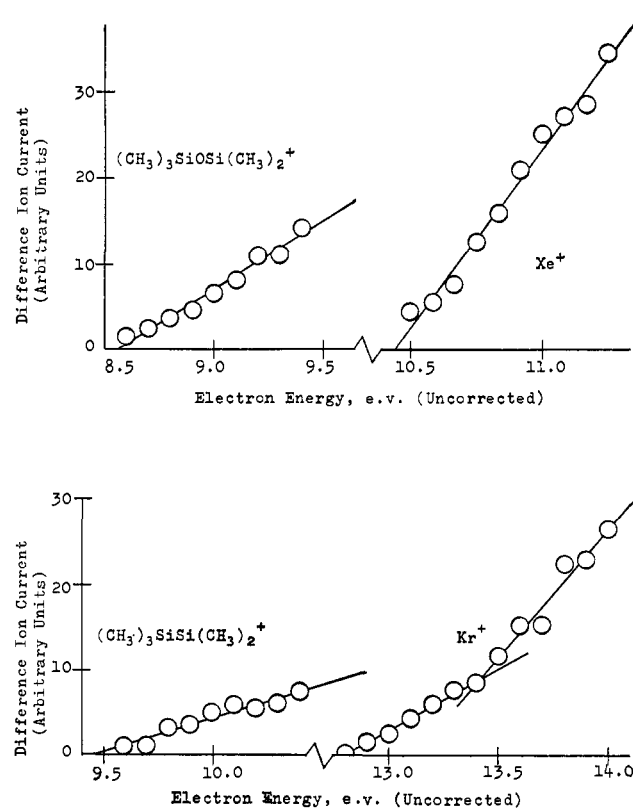

Figure 1. Typical r.p.d. appearance potential data.

In view of the precision commonly realized for the appearance potentials and the agreement obtained with known ionization potential differences of rare gases, it is felt that the appearance potentials reported in this research are accurate to within ± 0.15 e.v.

Reproducible results were never obtained for the appearance potential of m/e 73 (an ion of 1.6% intensity) from trimethylfluorosilane. m/e 73 could be attributed to $C_2H_2SiF^+$, but that seems unlikely in view of the low appearance potential obtained. The appearance potential of 11.7 e.v. implies as will be seen later, $D[(CH_3)_3Si-F] = 110$ kcal./mole, if one assumes the process given in eq. 1. Since this value is lower than

$$(CH_3)_3SiF + e \longrightarrow (CH_3)_3Si^+ + F + 2e \quad (1)$$
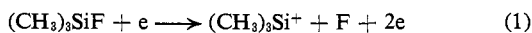
that obtained for $D[(CH_3)_3Si-Cl]$ and $D[(CH_3)_3Si-OCH_3]$, it is not very satisfying. If, on the other hand, one assumes that ion-pair production (eq. 2) is the

$$(CH_3)_4SiF + e \longrightarrow (CH_3)_3Si^+ + F^- + e \quad (2)$$
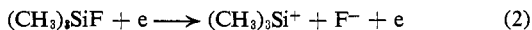
process occurring, then he calculates $D[(CH_3)_3Si-F]$ = 193 kcal./mole, using 83.5 kcal./mole[18] as the electron affinity of the fluorine atom.

It is not unreasonable to expect ion-pair production to be important. Dibeler and Mohler concluded from appearance potential data in the study of SiF_4 that the process occurring upon electron impact was that given in eq. 3.[19] If ion-pair production (eq. 2) were the

$$SiF_4 + e \longrightarrow SiF_3^+ + F^- + e \quad (3)$$
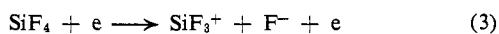
reaction occurring at the appearance potential of m/e 73 from the trimethylfluorosilane, one might expect to observe a break in the ionization efficiency curve at 3.6 e.v. above the threshold which would correspond to the onset of the process 1. Several attempts made to find such a break gave indications that a break was present, but nothing approaching a reproducible value for it could be obtained. Therefore, while the evidence remains inconclusive, it seems likely that the appearance potential measured for m/e 73 from $(CH_3)_3SiF$ must be associated with the ion-pair process (eq. 2), but that excess energy in this reaction leads to too high a value for $D[(CH_3)_3Si-F]$.

Of the remaining appearance potentials the value for m/e 73 from trimethylmethoxysilane is the least certain. That ion has an abundance of only 2.7% in the mass spectrum, and its ionization efficiency curve approaches the energy axis with a rather small slope.

Radical heats of formation used to calculate thermodynamic quantities from the mass spectroscopic data are given in Table II. Unless otherwise specified, all calculations assume simple dissociation processes (involving no excess energy) such as that in eq. 4. It

$$(CH_3)_3SiH + e \longrightarrow (CH_3)_2SiH^+ + CH_3 + 2e \quad (4)$$
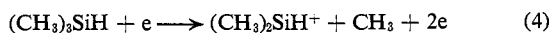
must be recognized, therefore, that since the appearance potentials may be higher than the true heat of reaction, owing to excess energy, the thermodynamic quantities calculated will be upper or lower limits depending on their relationship to the mass spectroscopic data.

The use of Tannenbaum's heat of formation data for trimethylsilane and tetramethylsilane[20] in combination with the appropriate radical heats of formation permits the calculation of $\Delta H_f°[(CH_3)_3Si^+]$ from two independent sets of measurements. The results obtained for $\Delta H_f°[(CH_3)_3Si^+]$ are 137 (from trimethyl-

(18) H. O. Pritchard, Chem. Rev., 52, 529 (1953).
(19) V. H. Dibeler and F. L. Mohler, J. Res. Natl. Bur. Std., 40, 25 (1948).
(20) S. Tannenbaum, J. Am. Chem. Soc., 76, 1027 (1954).

Table II. Radical Heats of Formation Used in Thermodynamic Calculations

Radical	$\Delta H_f°$, kcal./mole	Reference
H	52.1	a
CH_3	33	b
C_2H_5	25.5	b
$CH(CH_3)_2$	12.2	c
$C(CH_3)_3$	4.5	c
OCH_3	2.6	Calculated from appearance potential data on a series of methoxy compounds obtained in this laboratory[d]
F	18.7	e
Cl	28.9	f
Br	26.7	a
$N(C_2H_5)_2$	38	Calculated from $\Delta H_f°$-$[HN(C_2H_5)_2(g)]^g$ assuming $D[H-N(C_2H_5)_2]$ to be the same as $D[H-N(CH_3)_2]^h$

[a] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Theromdynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952. [b] J. V. Davies, A. E. Pope, and H. A. Skinner, Trans. Faraday Soc., 59, 2233 (1963). [c] J. L. Franklin and F. W. Lampe, ibid., 57, 1449 (1961). [d] R. H. Martin, personal communication, Sept. 1964. [e] Reference 18. [f] Reference 2. [g] P. A. Fowell and C. T. Mortimer, J. Chem. Soc., 2913 (1959). [h] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962.

silane) and 143 kcal./mole (from tetramethylsilane), values which agree well within the uncertainties in Tannenbaum's data and the present data.

Molecular Heats of Formation. Combining the average heat of formation of the trimethylsilyl cation with the appearance potentials of that ion from the various compounds studied and with the appropriate radical heats of formation, one can calculate the previously unreported heats of formation of the following trimethylsilanes: ethyl, isopropyl, t-butyl, methoxy, chloro, and bromo.

Neither the heat of formation of hexamethyldisilane nor that of the trimethylsilyl radical has been reported. Therefore the heat of formation of hexamethyldisilane has been estimated, using Franklin's group parameter method.[21] It is not known whether this method is applicable to organosilicon systems, but it does afford some reasonable estimate from the limited data available. The value -32 kcal./mole was calculated for the group parameter[21] for tetravalent silicon from the heats of formation of tetramethylsilane and ethyltrimethylsilane. A correction for adjacent quaternary silicon atoms (-2.7 kcal./mole) was estimated assuming the interactions in hexamethyldisilane to be intermediate between those of hexamethylethane and hexamethyldistannane. (The interaction in hexamethyldistannane was determined from thermodynamic data of Davies, Pope, and Skinner.[22]) The result is $\Delta H_f°[(CH_3)_6Si_2]$ = -126 kcal./mole.

The molecular heats of formation of the compounds so determined are given in Table III.

Bond Dissociation Energies. Using the estimated heat of formation of hexamethyldisilane, the appearance potential of the trimethylsilyl cation from hexamethyldisilane, and the assumption of no excess energy in the

(21) J. L. Franklin, Ind. Eng. Chem., 41, 1070 (1949).
(22) See footnote b, Table II.

Table III. Gas Phase Molecular Heats of Formation and Bond Dissociation Energies[a]

Compound	$\Delta H_f°$, kcal./mole	$D[(CH_3)_3Si-Y]$, kcal./mole
(CH)₂SiH–H	-42[b]	...
(CH₃)₃Si–H	-60[b]	88
(CH₃)₃Si–CH₃	-69[b]	85
(CH₃)₃Si–C₂H₅	-77	83
(CH₃)₃Si–CH(CH₃)₂	-91	84
(CH₃)₃Si–C(CH₃)₃	-98	83
(CH₃)₃Si–Si(CH₃)₃	-126[c]	86
(CH₃)₃S–OSi(CH₃)₃	-186[d]	194[e]
(CH₃)₃Si–OCH₃	-143	127
(CH₃)₃Si–F	...	193[e]
(CH₃)₃Si–Cl	-117	126
(CH₃)₃Si–Br	-80	86
(CH₃)₃Si–N(C₂H₅)₂	-113	131

[a] Where discrepancies appear between this paper and a previous note (*J. Am. Chem. Soc.*, **86**, 3174 (1964)), the present results supersede the earlier ones. [b] Reference 20. [c] Estimated; see text for procedure. [d] Reference 7. [e] Probably too high; see text for discussion.

dissociation, one calculates $\Delta H_f°[(CH_3)_3Si] = -20$ kcal./mole. The uncertainty in this value is probably about ±10 kcal./mole, arising primarily in the estimation of the heat of formation of hexamethyldisilane. Subtracting the heat of formation of the trimethylsilyl radical from that of the corresponding cation gives an ionization potential of 160 kcal./mole, or 6.94 e.v., for the $(CH_3)_3Si$ radical.

The value obtained for the ionization potential of $(CH_3)_3Si$ receives some indirect support from the following consideration. The appearance potential of m/e 57 (an ion of 2.2% intensity in the 50-v. spectrum) from t-butyltrimethylsilane is 11.9 e.v., too high to reflect a simple dissociation to give $C(CH_3)_3^+$ and $(CH_3)_3Si$. If Stevenson's rule[23] is applicable to organosilicon systems, its use here would lead to the conclusion that $I_z[(CH_3)_3Si] < I_z[(CH_3)_3C] = 7.42$ e.v.,[24] since the t-butyl apparently is not formed without excess kinetic energy by simple bond rupture. Thus I_z-$[(CH_3)_3Si]$ could be, at most, 0.48 e.v. too low. This is equivalent to saying that the bond dissociation energies calculated using this value are high by no more than 0.48 e.v., or 11 kcal./mole. On the other hand, if $I_z[(CH_3)_3Si]$ were lower than 6.94 e.v., this would result in higher values for the bond dissociation energies calculated therefrom. It will be seen that any higher values than those calculated would be very surprising, so that this lends support to the feeling that the trimethylsilyl ionization potential of 6.94 e.v. is nearly correct. Subtracting this value from the appearance potentials of m/e 73 ions from the compounds studied gives the bond dissociation energies recorded in Table III.

Although these bond dissociation energies may be uncertain by about ±10 kcal./mole, the *relative* bond dissociation energies should be accurate within the limit of the experimental uncertainties in the appearance potential measurements. The values of $D[(CH_3)_3Si-OSi(CH_3)_3]$ and $D[(CH_3)_3Si-F]$ are probably too high, reflecting the difficulty encountered in the appearance

(23) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).
(24) F. P. Lossing in "Mass Spectrometry," C. A. McDowell, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, Chapter 11.

potential measurements, and it should be remembered that the latter value is based on assumed ion-pair production upon electron impact.

Ionic Heats of Formation. Combining molecular and radical heats of formation with the appropriate appearance potentials, one calculates the heats of formation of a number of substituted dimethylsilyl cations in Table IV. Like the value given for $\Delta H_f°[(CH_3)_3Si^+]$, that for $\Delta H_f°[(CH_3)_2SiH^+]$ is the average of two values obtained in independent measurements. The appearance potentials of the dimethylsilyl cation from trimethylsilane and dimethylsilane were combined with Tannenbaum's heats of formation for these compounds[20] and the appropriate radical heats of formation; for $\Delta H_f°[(CH_3)_2SiH^+]$, the values 181 (from dimethylsilane) and 177 kcal./mole (from trimethylsilane) were obtained. This agreement again points to the internal consistency of Tannenbaum's thermochemical data.

Table IV. Heats of Formation of Various Dimethylsilyl Cations

Ion	$\Delta H_f°$, kcal./mole
(CH₃)₂SiH⁺	179
(CH₃)₂SiCH₃⁺	140
(CH₃)₂SiC₂H₅⁺, [(CH₃)₃SiCH₂⁺]?	153
(CH₃)₂SiSi(CH₃)₃⁺	89
(CH₃)₂SiOSi(CH₃)₃⁺	16
(CH₃)₂SiOCH₃⁺	60
(CH₃)₂SiCl⁺	104
(CH₃)₂SiBr⁺	140

Mass Spectra. In the course of this work, 50-v. mass spectra of the compounds studied were obtained. Space prohibits their publication herewith but they may be obtained from F. W. L. upon request.

Discussion

The appearance potentials for the trimethylsilyl cation from tetramethylsilane and trimethylsilane, the appearance potential for the dimethylsilyl cation from trimethylsilane, and the ionization potential of tetramethylsilane were measured by Hobrock and Kiser.[25] Within the experimental uncertainties, their values agree with those obtained in this research, except for $A(m/e$ 73) from tetramethylsilane. They reported 11.3 ± 0.15 e.v. for that appearance potential, a value 0.7 e.v. higher than that found in this study. The present value (10.63 ± 0.13 e.v.) is to be preferred, we think, because when it is combined with Tannenbaum's data[20] it leads to a heat of formation of the trimethylsilyl cation consistent with that obtained from the trimethylsilane.

The data of Steele, Nichols, and Stone[6b] are the only ones available for comparison with the bond dissociation energies obtained in this study. Probably the most important result of a comparison between the two studies is the fact that they both give quite large energies of dissociation of bonds to silicon. The dissociation energies of the bonds Si–Y in the compounds H_3Si-Y, studied by Steele, *et al.*, and (CH₃)₃-

(25) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **65**, 2186 (1961); **66**, 155 (1962).

Si–Y, examined in this research, fall, with but one exception, in the range from 79 to 94 kcal./mole (Y = Si, H, alkyl C). This is important because such high values stand in contradistinction to the best estimates of these quantities previously available; *viz.*, $D[(H_3Si-SiH_3]\cong 51$[26] and $D[(alkyl)_3Si-(alkyl)]\sim 50$ kcal./mole.[27]

One problem arises in comparing the results of the two studies which deserves comment. The dissociation energy of Si–C bonds in the trimethylsilyl series is obviously independent of what alkyl group is involved. On the other hand, the Si–C dissociation energies in the silyl series[6b] seem to decrease when the attached alkyl group is made progressively bulkier— with the exception of methyl, which seems to be out of order.

A priori one might suspect that the dissociation energies of bonds would decrease as the groups bonded together were made increasingly bulky and the steric respulsions became more severe. If one takes the standard heats of formation of the hydrocarbon radicals in Table II and the standard molecular heats of formation,[28] and defines the bond dissociation energy as the heat of the dissociation reaction, then it is seen that such a trend does exist for saturated hydrocarbons. For example, $D[H_3C-Y]$ decreases from 86 to 77 kcal./mole as Y goes from methyl to *t*-butyl. As the Si–C bond is considerably longer than the C–C bond (1.89 as compared with 1.54 Å.),[4] one would expect this trend to be less pronounced in alkylsilanes than in saturated hydrocarbons. The whole of the data of Steele, Nichols, and Stone[6b] on H_3Si-Y compounds indicate an even larger such trend, whereas our results for $(CH_3)_3Si-Y$ compounds indicate no such trend. While we have no complete explanation for these opposing conclusions, a few remarks can be made.

Steele, Nichols, and Stone[6b] used their appearance potentials of appropriate ions from methylsilane, ethylsilane, isopropylsilane, and *t*-butylsilane to calculate the standard heats of formation of these compounds as -4, -15, -14, and -11 kcal./mole, respectively. All available thermochemical data on saturated hydrocarbons, alkylgermanes,[29] alkylstannanes,[22] and alkylplumbanes[30] indicate that the compounds become thermodynamically more stable relative to the elements as the alkyl groups are made more complex. That the data of Steele, *et al.*, for isopropylsilane and *t*-butylsilane do not follow this general trend throughout group IV elements makes one suspect that their appearance potentials for these ions (and consequently their values for $D[H_3Si-Y]$ in the parent compounds) are somewhat low. Similar calculations from our data always followed this general trend of increasing stability with alkyl complexity, and for this reason we feel that our conclusions of *no* trend in $D[X_3Si-Y]$ with nature of Y is correct.

From a calorimetric study of the heat of reaction between trimethylchlorosilane and diethylamine in cyclohexane solution, Claydon and Mortimer[31] obtained the

difference between the liquid phase heats of formation of trimethylchlorosilane and N,N-diethylaminotrimethylsilane. Using the heats of vaporization for these compounds suggested in their paper, one calculates $\Delta H_f°[(CH_3)_3SiCl(g)] - \Delta H_f°[(CH_3)_3SiN(C_2H_5)_2(g)] = 2.3 \pm 1.4$ kcal./mole. The difference obtained in this study, -4 ± 5 kcal./mole, is in reasonable agreement with the value of Claydon and Mortimer.

The most glaring disparity between a result obtained in this study and that found by another worker appears in the case of N,N-diethylaminotrimethylsilane. Mortimer lists $\Delta H_f°[(CH_3)_3SiN(C_2H_5)_2(g)] = -60.0$ kcal./mole,[32] whereas the value obtained in this research is -113 kcal./mole. It is not possible to estimate directly the validity of Mortimer's heat of formation for this compound, since it is derived from unpublished work by Claydon and Mortimer. However, in view of the agreement obtained between this study and that of Claydon and Mortimer[31] on the difference between the gas phase heats of formation of trimethylchlorosilane and N,N-diethylaminotrimethylsilane, if Mortimer's heat of formation for the latter were correct, it would indicate that the heats of formation obtained in this study for both compounds must be in error by about 50 kcal./mole, a circumstance that seems rather unlikely.

The use of thermochemical, or average, bond energies to calculate heats of formation of saturated hydrocarbons has usually given values that nearly agree with experimentally determined values. It does not appear that such a system can be safely used with alkylsilanes. Tannenbaum's heats of formation for the methylsilanes,[20] which have been indicated to be internally consistent by the results of our appearance potential measurements, can be used to illustrate the problem. From the heat of formation of silane[33] and tetramethylsilane[20] one calculates the thermochemical bond energies for both the Si–H and Si–CH₃ bonds. Using these values, heats of formation of trimethylsilane and dimethylsilane are calculated which differ by 10 to 12 kcal./mole from Tannenbaum's measured values. The situation is no better if one considers halogen- or oxygen-containing silanes. The thermochemical Si–O bond energy in silica,[2] when combined with $E(Si-CH_3)$ from tetramethylsilane, leads to a heat of formation of hexamethyldisiloxane which differs by 21 kcal./mole from the measured value.[7]

A number of comparisons may be made to assess the stabilities of silicon cations relative to carbon cations. We feel that one of the most informative procedures is to determine the enthalpy changes for a series of reactions involving analogous carbon and silicon compounds. The following reactions are typical of the results one finds ($\Delta H°$ values ($C^+ \rightarrow Si^+$) in kcal./mole are given in parentheses).

$$(CH_3)_2SiH_2 + (CH_3)_2CH^+ = (CH_3)_2SiH^+ + (CH_3)_2CH_2 \qquad (2)$$

$$(CH_3)_3SiH + (CH_3)_3C^+ = (CH_3)_3Si^+ + (CH_3)_3CH \qquad (-8)$$

$$(CH_3)_3SiCH_3 + (CH_3)_3C^+ = (CH_3)_3Si^+ + (CH_3)_3CCH_3 \qquad (-7)$$

$$(CH_3)_3SiCl + (CH_3)_3C^+ = (CH_3)_3Si^+ + (CH_3)_3CCl \qquad (48)$$

$$(CH_3)_3SiCl + (CH_3)_2CCl^+ = (CH_3)_2SiCl^+ + (CH_3)_3CCl \qquad (6)$$

(26) H. J. Emeléus and C. Reid, *J. Chem. Soc.*, 1021 (1939).
(27) C. E. Waring, *Trans. Faraday Soc.*, **36**, 1142 (1940).
(28) See footnote *c*, Table II.
(29) A. E. Pope and H. A. Skinner, *Trans. Faraday Soc.*, **60**, 1404 (1964).
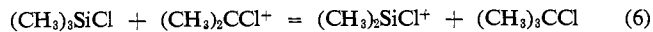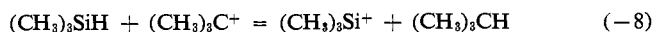(30) D. W. Scott, W. D. Good, and G. Waddington, *J. Phys. Chem.*, **60**, 1090 (1956); W. D. Good, D. W. Scott, J. L. Lacina, and J. P. McCullough, *ibid.*, **63**, 1139 (1959).

(31) A. P. Claydon and C. T. Mortimer, *J. Chem. Soc.*, 3212 (1962).
(32) See footnote *h*, Table II.
(33) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

The general conclusion is that, in equilibria between analogous silicon and carbon cations and their molecular precursors, there is an approximately equal tendency for the silicon or carbon cation to be formed, except when unusually strong bonds to silicon must be broken to form the cation. In the latter case the carbonium ion will be thermodynamically favored.

The Carbon-13 Nuclear Magnetic Resonance Spectra of Furan, Pyrrole, Thiophene, and Some of Their Methyl Derivatives[1a]

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The 15.085 Mc.p.s. C^{13} nuclear magnetic resonance spectra of furan, pyrrole, thiophene, and their 2-methyl and 2,5-dimethyl derivatives have been obtained and completely assigned. The assignment of the chemical shift data was based on C^{13}–H coupling constants in the parent compound and on the proton-induced multiplet structure in the dimethyl compounds. The initial assignment of chemical shift values for the 2-methyl series was based on additive substituent relationships and C^{13}–H coupling constants. These assignments were confirmed unequivocally with the proton-decoupling technique. Aromatic character in these compounds is inferred from the similarity of the corresponding chemical shift values with those of the ordinary benzenoid aromatics. Failure of the chemical shift data to correlate in every detail with estimates of the π-electron charge densities argues for the importance of σ-bond effects.

Introduction

The proton magnetic resonance spectra of furan, pyrrole, and thiophene as well as many of their derivatives have been studied extensively, and many of their n.m.r. spectral parameters have been correlated with such substituent properties as electronegativity and magnetic anisotropy.[2-6] In particular methyl substitution effects have received attention.[7] A close correlation between C^{13} chemical shifts and π-electron densities for both benzenoid and nonbenzenoid aromatic molecules has been noted experimentally[8-12] and theoretical justification for this correlation has been presented.[13,14]

It is widely accepted that furan, pyrrole, and thiophene all possess aromaticity in varying degrees, and this study has been undertaken to explore possible correlations between the carbon-13 chemical shift values and calculated π-electron charge distributions. To aid in the spectral interpretation of the parent compounds and to study the effects of methyl substitution, the C^{13} spectra of the 2-methyl and 2,5-dimethyl derivatives were also examined. Previous work by Spiesecke and Schneider[15] and Grant and Paul[16] has shown that the introduction of a methyl group into an alkane will shift the resonance of a directly bonded carbon-13 nucleus down field by approximately 9 p.p.m. provided that the carbon atom is not at a center of high branching. Shifts of similar magnitudes were found in this study, whereas no previous values have been published which will rationalize the remote methyl substituent effects recorded in this paper.

Experimental Section

A. Rapid-Passage Spectra. These spectra were obtained at 15.085 Mc.p.s. on a Varian HR-60 spectrometer operating in the dispersion mode. Both adiabatic "rapid" and "intermediate" passage conditions

(1) (a) This paper is considered to be the first in a series from the Battelle Memorial Institute and no. IV in the series from the laboratory at the University of Utah. Previous paper in this later series: R. J. Pugmire, D. M. Grant, R. K. Robins, and G. W. Rhodes, *J. Am. Chem. Soc.*, 87, 2225 (1965); (b) National Science Foundation Cooperative Fellow 1964–1966.
(2) (a) S. Gronowitz, G. Sorbin, B. Gestblom, and R. A. Hoffman, *Arkiv Kemi*, 19, 438 (1962); (b) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, 39, 905 (1961).
(3) R. J. Abraham and H. J. Bernstein, *ibid.*, 37, 1056 (1959).
(4) S. Gronowtiz and R. A. Hoffman, *Arkiv Kemi*, 19, 539 (1960), and preceding papers in this series.
(5) G. S. Reddy and J. H. Goldstein, *J. Phys. Chem.*, 65, 1539 (1961).
(6) S. Gronowitz, A. Hornfeldt, B. Gestblom, and R. Hoffman, *Arkiv Kemi*, 18, 133 (1961).

(7) G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, 83, 5020 (1961).
(8) P. C. Lauterbur, *ibid.*, 83, 1838 (1961).
(9) P. C. Lauterbur, *J. Chem. Phys.*, 38, 1432 (1963).
(10) P. C. Lauterbur, *ibid.*, 43, 360 (1965).
(11) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).
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(13) M. Karplus and J. A. Pople, *ibid.*, 38, 2803 (1963).
(14) J. A. Pople, *Mol. Phys.*, 7, 301 (1964).
(15) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 35, 722 (1961).
(16) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, 86, 2984 (1964).