Both the position and the intensity of the second (shorter wave length) observed electronic bands of the furan, 2-methylfuran, pyrrole and N-methylpyrrole–iodine complexes indicate that these bands are also charge transfer bands (for the anisole–iodine complex[15] two charge transfer bands have also been detected). The extinction coefficients are much too large for these bands to be perturbed bands of the donors. LCAO MO calculations[16] on thiophene, pyrrole and furan give values of 0.252β, 0.423β and 0.876β for the energy difference between the two highest filled π-molecular orbitals of these molecules. There is a qualitative agreement if one considers the longer wave length band as due to a transition involving the highest filled orbital and the shorter wave length band as involving the next highest filled orbital. Since thiophene has the two closest orbitals, one would expect the thiophene–iodine complex to have two charge transfer bands lying very close together. The fact that only one band was observed for thiophene may be due to the unresolvable superposition of two adjacent, overlapping bands; this might also explain the very high value of the half width for this band.

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[16] S. Nagakura and T. Hosoya, *Bull. Chem. Soc. Japan*, **25**, 179 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

The Determination of Silicon–Carbon and Silicon–Hydrogen Bond Dissociation Energies by Electron Impact[1]

BY W. C. STEELE,[2] L. D. NICHOLS[3] AND F. G. A. STONE[4]

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Appearance potentials of selected ions in the mass spectra of silane, tri- and tetrachlorosilane and the methyl-, ethyl-, isopropyl- and *tert*-butylsilanes and trichlorosilanes have been measured. The silicon–carbon bond dissociation energies in the organosilanes have been calculated, the results being in general higher than the carbon–carbon bond dissociation energies in the corresponding alkanes. A definite dependence on the nature of the alkyl group is observed. The silicon–hydrogen bond dissociation energies in silane and trichlorosilane are found to be 94 ± 2 and 93 ± 4 kcal. mole^{-1}, respectively. The silicon–chlorine bond dissociation energy in tetrachlorosilane is calculated to be 106 ± 4 kcal. mole^{-1}.

In common with several other areas of inorganic chemistry, silicon chemistry lacks a body of reliable and systematic thermochemical data. Indeed, only recently have consistent results been obtained for the heat of formation of silane itself.[5,6] This situation has resulted in a corresponding lack of knowledge of the strengths of bonds formed between silicon and other elements, such as carbon and hydrogen. Furthermore, only silane,[7] tetrachlorosilane,[8] tetrafluorosilane[9] and tri- and tetramethylsilane[10] have been studied by electron impact. The present investigation, involving silane, tri- and tetrachlorosilane and the series $RSiH_3$ and $RSiCl_3$, where R is methyl, ethyl, isopropyl and *tert*-butyl, represents an attempt to correct this deficiency partially. The appearance potentials reported in this paper, taken with known heats of formation and free radical ionization potentials, permit calculation of silicon–carbon and silicon–hydrogen bond dissociation energies and the heats of formation of the several silicon compounds. The ionization potentials and heats of formation of the silyl and trichlorosilyl radicals are also calculated, and an indirect evaluation of the silicon–silicon bond dissociation energy in disilane is reported.

Experimental

A sample of ethyltrichlorosilane was kindly provided by Professor E. G. Rochow, while trichloro-, tetrachloro-, and methyltrichlorosilane were commercial samples. Isopropyltrichlorosilane was prepared by treating isopropylmagnesium bromide with tetrachlorosilane in diethyl ether. These silicon compounds were purified by high vacuum distillation. *tert*-Butyltrichlorosilane was prepared by treating tetrachlorosilane with *tert*-butyllithium in *n*-pentane.[11] The volatile solid product was exhaustively purified, but a small amount of a higher molecular weight impurity remained evident in the mass spectrum.

The alkyltrichlorosilanes were cleanly reduced[12] by lithium aluminum hydride in diglyme to give the corresponding alkylsilanes in high yield. These hydrides were purified by distillation in a high vacuum system, and by gas chromatography.

The appearance potentials were measured using a Consolidated Electrodynamics Model 21-103C mass spectrometer, modified to allow magnetic scanning. Where possible the data were evaluated[13] by the separation between the linear portion of the semi-log ionization efficiency curve (normalized for 70 volt electrons) and the parallel curve from a standard material. In cases where the semi-log plots were not parallel to the standard, appearance potentials were obtained from extrapolation of voltage differences to

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] Postdoctoral Fellow, Harvard University.

[3] Standard Oil of California Fellow, Harvard University, 1961–1962.

[4] Correspondence concerning this paper should be addressed to this author at the Department of Chemistry, Queen Mary College, University of London, London, E1, England.

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[7] H. Neuert and H. Clasen, *Z. Naturforschg.*, **7a**, 410 (1952).

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[9] V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **40**, 25 (1948).

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[13] See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

TABLE I

APPEARANCE POTENTIALS OF SELECTED IONS OF THE SILANES AND CHLOROSILANES

Compound	Ion	A_p(e.v.)[a]	Compound	Ion	A_p(e.v.)[a]
SiH_4	SiH_3^+	12.40 ± 0.02	$SiCl_4$	$SiCl_3^+$	12.48 ± 0.02
	SiH_2^+	11.91 ± .02	$HSiCl_3$	$SiCl_3^+$	11.91 ± .03
CH_3SiH_3	SiH_3^+	12.80 ± .1	CH_3SiCl_3	$CH_3SiCl_3^+$	11.36 ± .03
	SiH_2^+	11.62 ± .1		$SiCl_3^+$	11.90 ± .08
	CH_3^+	15.1 ± .3		CH_3^+	15.0 ± .2
$C_2H_5SiH_3$	$C_2H_5SiH_3^+$	10.18 ± .05	$C_2H_5SiCl_3$	$C_2H_5SiCl_3^+$	10.74 ± .04
	SiH_3^+	12.8 ± .2		$SiCl_3^+$	12.10 ± .03
	SiH_2^+	12.0 ± .1		$C_2H_5^+$	12.77 ± .05
	$C_2H_5^+$	12.6 ± .2		$C_2H_4^+$	12.48 ± .05
i-$C_3H_7SiH_3$	$C_3H_7SiH_3^+$	9.85 ± .1	i-$C_3H_7SiCl_3$	$C_3H_7SiCl_3^+$	10.28 ± .1
	$C_3H_7^+$	11.33 ± .03		$SiCl_3^+$	13.1 ± .2
	$C_3H_6^+$	10.81 ± .04		$C_3H_7^+$	11.36 ± .1
	SiH_3^+	13.1 ± .2		$C_3H_6^+$	10.92 ± .1
t-$C_4H_9SiH_3$	$C_4H_9SiH_3^+$	9.5 ± .2	t-$C_4H_9SiCl_3$	$C_4H_9SiCl_3^+$	...
	$C_4H_9^+$	10.25 ± .02		$SiCl_3^+$	13.0 ± .1
	$C_4H_8^+$	9.89 ± .05		$C_4H_9^+$	10.72 ± .1
	SiH_3^+	13.7 ± .2		$C_4H_8^+$	10.26 ± .2

[a] ± figures represent reproducibility of several replicate measurements.

zero intensity on linear paper, and checked by extrapolation of the individual curves to zero intensity. Argon (I = 15.76 e.v.), krypton (I = 14.00 e.v.) and the mass 69 peak from CF_3H (A_p = 14.53 e.v.) were used as standards, the gas used as the standard being introduced simultaneously with the sample.

For the higher alkylsilanes the mass spectral peaks of the alkyl and olefin ions include small contributions from ions containing silicon; *e.g.*, $CSiH_3^+$ at m/e = 43 in the spectrum of isopropylsilane. Such ions are formed by rupture of several bonds and are expected to have appearance potentials well above that of the alkyl or olefin ion.

Results and Discussion

The appearance potentials of selected ions in the mass spectra of the various silanes are listed in Table I. Unlike the results of Neuert and Clasen,[7] no parent ion was observed in the mass spectrum of silane. However, the two spectra can be made to coincide by shifting their spectrum to lower mass by one unit. A discrepancy of a similar nature in the Neuert and Clasen mass spectrum of germane has also been reported.[14] Appearance potential measurements for comparison with our results are only available for silane and tetrachlorosilane. Neuert and Clasen[7] report values of 12.2 ± 0.2 e.v. for both SiH_3^+ and SiH_2^+ from silane (assuming the one mass unit shift), while Vought[8] reports 12.9 ± 0.2 e.v. for $SiCl_3^+$ from tetrachlorosilane. The present results depart from these values by about 0.3 e.v., but both authors employed the linear extrapolation technique to evaluate their data, a method now believed to yield unreliable results when applied to fragment ions.[13]

Silane, methylsilane, trichlorosilane, and *tert*-butyltrichlorosilane all yield parent peaks of small or vanishing intensity. The remaining alkylsilanes and trichlorosilanes yield parent ions in sufficient abundance to permit measurement of their ionization potentials (Table I). In general, substitution of a silyl group for a methyl group in an alkane lowers the ionization potential by 0.7 to 0.9 e.v., while substitution by the trichlorosilyl group results in a reduction of about 0.3 e.v. This relationship, together with the small size, in other spectra, of peaks associated with loss of a silicon bonding electron, suggests that ionization of the silicon compound proceeds by removal of an electron localized on the alkyl group. The reduction in ionization potential caused by the electropositive (with respect to methyl) silyl group, and the lesser reduction due to trichlorosilyl, is in contrast to the elevation in ionization potential brought about by the electronegative boron difluoride group.[15] The methyl derivatives may represent an exception, however. Removal of an electron from both silane and methylsilane results in unstable species, and the ionization potential of methyltrichlorosilane is sufficiently close to those of chlorine[13] and tetrachlorosilane[8] to indicate that ionization occurs by removal of a non-bonding chlorine electron.

Interpretation of the appearance potentials of fragment ions is complicated by the possible presence of excess energy in the formation of the ion, manifest either as kinetic energy of the fragments or by their formation in excited states. It has been observed[16] that in dissociation of λ an R_1R_2 molecule under electron impact to give either R_1^+ or R_2^+ and the corresponding neutral fragment, excess energy is more likely to be associated with formation of the ion whose radical has the higher ionization potential. This result is consistent with predictions based on the quasi-equilibrium rate theory of the origin of mass spectra.[17,18] In the activated complex $(R_1R_2)^+$ for decomposition into the fragments R_1 and R_2, the bond joining R_1 and R_2 will be a one-electron bond having two electronic states, a lower attractive one and a higher repulsive one. If $I(R_1) < I(R_2)$, dissociation into $R_1^+ + R_2$ is correlated with the lower state and occurs without kinetic energy, while dissociation into $R_2^+ + R_1$ correlates with the repulsive state and is accompanied by kinetic

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[14] G. P. Van der Kelen and D. F. Van de Vondel, *Bull. soc. chim. Belg.*, **69**, 504 (1960).

[15] W. C. Steele, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 1154 (1962).

[16] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

[17] M. Krauss, A. L. Wahrhaftig and H. Eyring, *Ann. Rev. Nuclear Sci.*, **5**, 241 (1955).

[18] D. P. Stevenson and D. O. Schissler, "The Chemical and Biological Action of Radiations," M. Haissinsky, Ed., Vol. V, Academic Press, New York, N. Y., 1961, p. 167.

TABLE II

BOND DISSOCIATION ENERGIES AND HEATS OF FORMATION

Compound ($R-SiX_3$)	Reaction	I(radical) (e.v.)	ΔH_f (kcal. mole^{-1}) Ion	Neutral fragment	Compound	$D(R-SiX_3)$ (kcal. mole^{-1})
$H-SiH_3$	$SiH_3^+ + H$	8.32^a	241^a	52.1^b	$+7.5^c$	94 ± 3
CH_3-SiH_3	$SiH_2^+ + CH_4$	...	282^a	-17.9^b	−4 ± 4	86 ± 4
$C_2H_5-SiH_3$	$SiH_2^+ + C_2H_6$	...	282^a	-20.2^b	−15 ± 4	89 ± 3
	$C_2H_5^+ + SiH_3$	8.72^d	225^e	49.5^a	−16 ± 4	89 ± 3
$i-C_3H_7-SiH_3$	$C_3H_7^+ + SiH_3$	7.90^d	197.5^e	49.5^a	−14 ± 4	79 ± 3
$t-C_4H_9-SiH_3$	$C_4H_9^+ + SiH_3$	7.42^d	176^e	49.5^a	−11 ± 4	65 ± 3
$H-SiCl_3$	$SiCl_3^+ + H$	7.88^a	113^a	52.1^b	−110 ± 5	93 ± 4
CH_3-SiCl_3	$SiCl_3^+ + CH_3$	7.88^a	113^a	32^e	−129 ± 5	93 ± 4
$C_2H_5-SiCl_3$	$SiCl_3^+ + C_2H_5$	7.88^a	113^a	24^e	−140 ± 5	95 ± 4
$i-C_3H_7-SiCl_3$	$C_3H_7^+ + SiCl_4$	7.90^d	197.5^e	-69^a	−133 ± 6	80 ± 3
$t-C_4H_9-SiCl_3$	$C_4H_9^+ + SiCl_3$	7.42^d	176^e	-69^a	−140 ± 6	76 ± 3
$Cl-SiCl_3$	$SiCl_3^+ + Cl$	7.88^a	113^a	19^f	-145.7^f	106 ± 4

[a] See Table III. [b] See ref. 22. [c] Assumed, see ref. 5 and 6. [d] See ref. 20. [e] See ref. 21. [f] See ref. 24.

energy. In fact, R_2^+ may often be formed as a secondary dissociation product rather than by direct dissociation of the parent ion.

It has also been noted[19] that excess energy is often associated with ions whose appearance potential curves show greater tailing than the simple ionization efficiency curves of the rare gases. In this work, the isopropyl and *tert*-butyl ions gave simple curves for both the silyl and trichlorosilyl compounds. In contrast, the ethyl ion from ethyltrichlorosilane behaved simply while that from ethylsilane did not, and the methyl ion curves showed tailing for both methylsilane and methyltrichlorosilane. Simple curves were obtained for the silyl ion from only silane and methylsilane, while the trichlorosilyl ion yielded simple curves in all cases except isopropyl and *tert*-butyltrichlorosilane.

The silicon–carbon bond dissociation energies in the isopropyl and *tert*-butyl derivatives of both silane and tetrachlorosilane can be calculated directly (Table II) as the difference between the appearance potential of the alkyl ion and the ionization potential[20] of the alkyl radical. It should be emphasized that possession of the lower free radical ionization potential, together with a simple appearance potential curve, does not insure the absence of excess energy. The calculated bond dissociation energies should be regarded as upper limits.

Unfortunately, ionization potentials have not been measured for the silyl and trichlorosilyl radicals. However, it is possible to evaluate them indirectly as follows. Inspection of Table I reveals that in each case measured, the appearance potential of the olefin ion is below that of the corresponding alkyl ion. The olefin ion, therefore, does not originate from decomposition of the alkyl ion, which would require a higher energy, but must result from elimination of a molecule from the parent ion. Thus, for example

$$t\text{-}C_4H_9SiH_3 + e^- \longrightarrow C_4H_9^+ + SiH_3 + 2e^-$$

$$t\text{-}C_4H_9SiH_3 + e^- \longrightarrow C_4H_8^+ + SiH_4 + 2e^-$$

Then

$$\Delta H_f(SiH_3) - \Delta H_f(SiH_4) = A_p(C_4H_9^+) - A_p(C_4H_8^+) - \Delta H_f(C_4H_9^+) + \Delta H_f(C_4H_8^+)$$

Since, by definition

$$D(H_3Si-H) = \Delta H_f(H) + \Delta H_f(SiH_3) - \Delta H_f(SiH_4)$$

the silicon-hydrogen bond dissociation energy for silane can be calculated directly from the measured appearance potentials and the known heats of formation of the alkyl[21] and olefin[22] ions. Calculations from isopropyl and *tert*-butylsilane yield 95 and 93 kcal. mole^{-1}, respectively, for an average value $D(H_3Si-H) = 94 \pm 2$ kcal. mole^{-1}. Similar calculations on the ethyl, isopropyl and *tert*-butyltrichlorosilanes yield 89, 93, and 96 kcal. mole^{-1}, respectively, or an average value for $D(Cl_3Si-H) = 93 \pm 4$ kcal. mole^{-1}. The above calculations are based on the assumption that the $C_nH_{2n}^+$ ions formed in the dissociative process are identical to those formed by ionization of the olefins. That this is the case is not obvious for the ethyl and isopropyl compounds, but the *tert*-butyl derivatives represent cases where SiH_4 or $HSiCl_3$ must be formed by elimination of a β-hydrogen. α-Elimination from the ethyl or isopropyl derivatives would be expected to yield an ion having a higher heat of formation, resulting in a low value for the calculated silicon-hydrogen bond dissociation energy. This may account for the relatively low value calculated from ethyltrichlorosilane, but the values obtained from the isopropyl and *tert*-butyl derivatives agree, within the limits of our knowledge of the heats of formation of the alkyl ions.

TABLE III

CALCULATED VALUES OF INTEREST

	ΔH_f (ion) (kcal. mole^{-1})	ΔH_f (radical) (kcal. mole^{-1})	I(radical) (e.v.)
SiH_3	241	49.5 ± 2	8.32 ± 0.15
$SiCl_3$	113	−69 ± 4	7.88 ± 0.2
SiH_2	282	....	....

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(19) J. A. Morrison, *Revs. Pure and Applied Chem.*, **5**, 22 (1955).

(20) F. P. Lossing, P. Kebarle and J. B. DeSousa, "Advances in Mass Spectrometry," ed., J. D. Waldron, Pergamon Press, London, 1959.

(21) M. L. Wallenstein and M. Krauss, *J. Chem. Phys.*, **34**, 929 (1961).

(22) Calculated from the ionization potentials (R. Bralsford, P. V. Harris and W. C. Price, *Proc. Roy. Soc.* (*London*), **258**, 459 (1960)) and heats of formation (F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953) of the olefins.

The ionization potentials (Table III) of the silyl and trichlorosilyl radicals are obtained immediately from the difference between the appearance potential of SiH_3^+ from silane, and of $SiCl_3^+$ from trichlorosilane, and the corresponding silicon–hydrogen bond dissociation energy. Calculation of the silicon–chlorine bond dissociation energy in silicon tetrachloride and the silicon–carbon bond dissociation energy in methyltrichlorosilane may then be made from the respective appearance potentials of the $SiCl_3^+$ ion. Both the ethyl and trichlorosilyl ions from ethyltrichlorosilane yielded simple appearance potential curves, and the silicon–carbon bond dissociation energy in this compound may be calculated from either ion, yielding values of 93 and 97 kcal. mole^{-1}, respectively. The higher value obtained from the trichlorosilyl ion may indicate the presence of a small amount of excess energy, or that the calculated value of $I(SiCl_3)$ is slightly low.

Both the alkyl and silyl ions from methyl and ethylsilane show tailing at the foot of their appearance potential curves, suggesting the presence of excess energy. For both of these organosilanes the SiH_2^+ ion has a simple appearance potential curve and it is possible to calculate silicon–carbon bond dissociation energies in these compounds by comparison of the SiH_2^+ appearance potentials with that of the SiH_2^+ ion from silane. The fact that $A_p(SiH_2^+) < A_p(SiH_3^+)$ in each case indicates that SiH_2^+ is formed by elimination of a molecule from the parent ion. Thus

$$SiH_4 + e^- \longrightarrow SiH_2^+ + H_2 + 2e^-$$

$$RSiH_3 + e^- \longrightarrow SiH_2^+ + RH + 2e^-$$

The difference in SiH_2^+ appearance potentials together with the heat of formation of silane and of the hydrocarbon RH leads directly to the heat of formation of $RSiH_3$ (Table II). This value, when combined with the known heats of formation of the alkyl[21] and silyl (Table III) radicals, allows the calculation of $D(R\text{-}SiH_3)$ (Table II). These results are lower than those calculated directly from $A_p(SiH_3^+)$ or $A_p(CH_3^+)$ for methylsilane and from $A_p(SiH_3^+)$ for ethylsilane. Interestingly, in spite of the tailing observed for the ethyl ion, the bond dissociation energy derived from its appearance potential is the same as that obtained above.

The behavior of the ethyl and silyl ions from ethylsilane is in contrast with that expected from simple consideration of the radical ionization potentials. Thus, although $I(SiH_3) < I(C_2H_5)$, $A_p(SiH_3^+) > A_p(C_2H_5^+)$. Other exceptions have been noted to the appearance potential rule for complementary ions.[17,18] In each case, as in the present instance, the molecule has an insufficient number of electron pairs of nearly equivalent energy for the quasi-equilibrium theory to be applied with assurance.

The heats of formation of the various other silanes (Table II) also can be calculated from the appearance potentials used in the bond energy calculations, providing that heats of formation of the silyl and trichlorosilyl radicals are known. $\Delta H_f(SiH_3^+)$ and $\Delta H_f(SiCl_3^+)$ can be obtained (Table III) from their appearance potentials from silane and tetrachlorosilane and the known heats of formation of these compounds. The radical heats of formation (Table III) can be calculated directly from their ionization potentials and their positive ion heats of formation. Tannenbaum[23] has derived the heats of formation of some alkylsilanes from their heats of combustion. The only compound available for comparison is ethylsilane, where the present -15 kcal. mole^{-1} value agrees with Tannenbaum's -21 kcal. mole^{-1} value within the rather wide limits of error set for both results. Among the trichloro compounds, the present values of $\Delta H_f(CH_3SiCl_3) = -129$ kcal. mole^{-1} and $\Delta H_f(HSiCl_3) = -110$ kcal. mole^{-1} agree well with the recently tabulated[24] values of -126.4 kcal. mole^{-1} and -112 ± 15 kcal. mole^{-1}.

It is known[25,26] that, in general, bonds formed between silicon and other elements are stronger than analogous bonds involving carbon. The exceptions to this rule have been the silicon–hydrogen and silicon–carbon bonds. The recent determination[5] of the thermochemical bond energy $E = 76.5$ kcal. mole^{-1} [27] in silane is much lower than the corresponding $E = 99.3$ kcal. mole^{-1} [26] for the carbon–hydrogen bond in methane. The results reported in this paper show a much smaller difference in the bond dissociation energies: 94 kcal. mole^{-1} *versus* 102 kcal. mole^{-1}.[26] In trichlorosilane the silicon–hydrogen bond dissociation energy is found to be 3 kcal. mole^{-1} higher than the carbon–hydrogen bond energy[28] in chloroform.

Tannenbaum[23] has calculated silicon–carbon thermochemical bond energies from the heats of formation of several alkylsilanes. However, the calculations were based on values for the heat of formation of silane and the heat of atomization of silicon now thought to be in error. Recalculation, using the newer values[27] gives results for $E(Si\text{–}C)$ of from 81 to 76 kcal. mole^{-1} in di-, tri- and tetramethylsilane, from 80 to 63 kcal. mole^{-1} in mono- to tetraethylsilane, and 74 kcal. mole^{-1} for *n*- and isobutylsilane. Similar calculations can be performed with the heats of formation determined in this work. The results are 68, 74, 69 and 61 kcal. mole^{-1} for methyl-, ethyl-, isopropyl-, and *tert*-butylsilane, respectively. These results are all somewhat lower than the accepted $E(C\text{–}C)$ of 82.6 kcal. mole^{-1}.[26]

This study shows that the silicon–carbon bond dissociation energies D lie slightly above the corresponding carbon–carbon bond dissociation energies. For example, $D(H_3C\text{–}SiH_3) = 86$ kcal. mole^{-1} compares with $D(H_3C\text{–}CH_3) = 83$ kcal. mole^{-1} [26] and $D(H_3Si\text{–}CH_2CH_3) = 89$ kcal. mole^{-1} compares with $D(H_3C\text{–}CH_2CH_3) = 85$ kcal. mole^{-1}.[26] The greater strength of the silicon–

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[23] S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).

[24] "JANAF Interim Thermochemical Tables," The Dow Chemical Company, Thermal Laboratory, Midland, Michigan, December 31, 1960; and references cited therein.

[25] C. Eaborn, "Organosilicon Chemistry," Butterworths, London, 1960.

[26] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.

[27] $\Delta H_f(Si(g)) = 110$ kcal. mole^{-1} (ref. 24) and $\Delta H_f(SiH_4) = 7.5$ kcal. mole^{-1} (ref. 5 and 6) lead to $E(Si\text{-}H) = 77.7$ kcal. mole^{-1}. Other values used are $E(C\text{–}C) = 82.6$ kcal. mole^{-1} and $E(C\text{-}H) = 98.7$ kcal. mole^{-1} (ref. 26).

[28] J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

carbon bond is in agreement with the observation that the Si–C distances in all the methylsilanes are significantly less than that expected from the addition of covalent radii.[29]

It should also be mentioned that the heat of formation of the silyl radical, taken with the heat of formation of disilane,[5] leads to a bond dissociation energy $D(H_3Si–SiH_3)$ = 82 kcal. mole^{-1}. This result is much higher than the recent E(Si–Si) = 46.4 kcal. mole^{-1} [5,30] and the earlier estimates[26] of D from the activation energy for the pyrolysis of disilane. However, it is in better accord with the observation[31] that silicon–silicon bonds are in some cases more stable thermally than the corresponding carbon–carbon bond.[32] The large difference between E and D implies a large energy difference between the free silyl radical and the silyl group in its bonding state.

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[29] See F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.

[30] This becomes 49 kcal. mole^{-1} using the values given in footnote 27.

[31] A. G. MacDiarmid in "Advances in Inorganic Chemistry and Radiochemistry," Vol. III, eds., H. J. Emeleus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1961, p. 207.

[32] NOTE ADDED IN PROOF.—We have recently measured $A_p(SiH_3^+)$ from disilane which leads to a value of 81.3 kcal. mole^{-1} for $D(H_3Si–SiH_3)$. See W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962). This result is in excellent agreement with that predicted from the results presented here.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

A Raman Study of Gallium Bromide Solutions[1]

BY JAMES NIXON[2] AND ROBERT A. PLANE

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Raman spectral intensity measurements were made for gallium bromide solutions which contained various ratios of these two ions. The only spectrum evident was that of the tetrahedral $GaBr_4^-$ ion. The frequencies, depolarization ratios and intensities, relative to ν_1 of this species, were found to be: ν_1, 210 cm.$^{-1}$, ρ = 0.10, (1); ν_2, 71 cm.$^{-1}$, ρ = 0.76, 0.55; ν_3, 280 cm.$^{-1}$, ρ = 0.83, 0.22; ν_4, 102 cm.$^{-1}$, ρ = 0.84, 0.74. From Raman intensities, the concentration of $GaBr_4^-$ in a variety of solutions at temperatures up to 95° was found and used to evaluate the thermodynamic parameters for its formation in solution. The enthalpy and entropy values were found to be independent of temperature but varied somewhat with solution composition. At an ionic strength of 10 M, the enthalpy of formation was found to be +9.5 kcal./mole and the entropy 12.5 cal./mole-degree. Because of partial cancellation of the ionic strength changes of entropy and enthalpy, the association equilibrium quotient was reasonably constant. At 25° the average value for the log of the association quotient was determined to be −4.3. Finally, the entropy of hydration of $GaBr_4^-$ was evaluated as −63 cal./mole-degree.

A recent study involving $ZnBr_2$ and $CdBr_2$ solutions showed that Raman spectroscopy can be applied to study quantitatively complex ion equilibria in aqueous solution.[3] In that study it was concluded that Raman spectra can show the extent to which complex ion formation occurs in a stepwise manner. Thus, for the Zn^{++}–Br^- system it was found that in addition to $ZnBr_4^=$, two complexes containing less Br were present in measurable concentrations. For the Cd^{++}–Br^- system, relative to $CdBr_4^=$, lower species were of much less importance than for the Zn case. The present study was undertaken partly to determine the extent of lower species for a similar system of different charge type, Ga^{+3}–Br^-. In addition, the study was extended to higher temperatures in order to determine enthalpy and entropy changes accompanying complex ion formation. It should be noted that Raman measurements require relatively concentrated solutions so that the results cannot be extrapolated to infinite dilution. Thus the enthalpy and entropy values obtained apply to these solutions and necessarily include enthalpy and entropies of dilution. Change of temperature is relatively easily accomplished experimentally for Raman studies. The interpretation of such measurements is made simple through use of an internal standard which compensates for the small changes in refractive index of solutions and changes in their density with temperature. Furthermore, the temperature dependence of the inherent Raman intensity is known.[4]

Woodward and Nord obtained the Raman spectrum of 1.5 M gallium solution prepared by dissolution of the metal in 10.5 M HBr.[5] The four-line spectrum obtained was that of a tetrahedral $GaBr_4^-$ species. The study was not designed to investigate either the quantitative aspects of the equilibrium nor the possible existence of lower species. These questions have not previously been investigated for gallium bromide; although for gallium chloride there is both Raman[6] and anion exchange[7] evidence that only $GaCl_4^-$ forms in solution.

Experimental

Measurements were made with a Cary model 81 Raman spectrophotometer using the same techniques described previously.[3] In some experiments, a Kodak 2-A Wratten gelatin filter was used to improve the background by removal of the 4047Å. line of the mercury arc which may excite fluorescences in trace impurities. In every case, the ν_1 line of ClO_4^- in the solution measured served as internal standard. All intensities were corrected for the temperature change of inherent intensity through multiplication by the factor $[1 - \exp(-h\nu/kT)]$.

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