Figure 1. Symmetrized,[11] absolute value contour plots of the *J*-correlated 2-D spectra of (a) 2,3-(C$_2$H$_5$)$_2$C$_2$B$_4$H$_6$ and (b) 6-[C$_5$(CH$_3$)$_5$]CoB$_9$H$_{13}$. In each spectrum, peaks on the diagonal correspond to the conventional proton-decoupled ^{11}B NMR spectrum shown below; numerals by the diagonal peaks correspond to framework boron positions as shown. Boron–boron couplings (hence connectivities) are indicated by horizontal and vertical lines linking the diagonal and cross peaks. Peaks R and I are, respectively, impurities and artifacts at the transmitter frequency.

We are examining a series of boranes, carboranes, and metalla derivatives via the 2-D method and will present a detailed report at a later date.

Ge–H Bond Strengths in Germanes

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Received April 26, 1982

In a recent review[1] we have summarized our measurements of Si–H bond-dissociation energies. This work has helped to provide a fundamental basis for discussion of kinetics and mechanism in the area of silane, and in particular organosilane, chemistry. We now report results pertinent to germane chemistry that indicate that, while absolute values of bond strengths are different from those of silanes, there are several aspects of striking similarity.

Some years ago,[2] we measured D(Me$_3$Ge–H) and obtained a value of 340 kJ mol^{-1} (81 kcal mol^{-1}). At that time the benchmark reference bond strength, D(H$_3$Ge–H) was, and has remained until now, rather uncertain, with values spanning the range 326–386 kJ mol^{-1} (78–92 kcal mol^{-1}).[3-5] Thus, it has not been possible from absolute measurements to say whether methyl substitution strengthens or weakens Ge–H bonds. The parallel of Si–H bonds would suggest little effect,[1] but on the other hand methyl groups are well-known to weaken C–H bonds in organic compounds. This point has been given added pertinence by the recent work of McKean et al.[6] who claim that methyl substitution *does* significantly weaken both Si–H and Ge–H bonds. We report here a new measurement of D(H$_3$Ge–H) that throws light on this and other questions.

This study employs the thoroughly tested and reliable technique pioneered by Golden and Benson[7] and applied by us already to silanes[1] and Me$_3$GeH,[2] viz., the investigation of the kinetics of the gas-phase iodination process. The reaction between I$_2$ and GeH$_4$ takes place conveniently at 445 K and may be monitored spectrophotometrically. The principal products formed are HI and two or more iodinated germanes. At low ratios of GeH$_4$ to I$_2$ there is a sequential development of three UV peaks at 240, 270, and 350 nm. From comparison with known UV spectra and from independent corroboration by IR spectra, the initial product is GeH$_3$I, followed by GeH$_2$I$_2$, while the third product is as yet unidentified. This evidence is consistent with the occurrence of reaction 1 in the early stages.

$$I_2 + GeH_4 \rightarrow GeH_3I + HI \qquad (1)$$
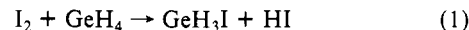
At high [GeH$_4$]$_0$/[I$_2$]$_0$ ratios this reaction predominates throughout, since [GeH$_4$] is always much greater than [GeH$_3$I]. At lower ratios the secondary UV absorptions develop quickly, and this is consistent with GeH$_3$I reacting with I$_2$ to form GeH$_2$I$_2$

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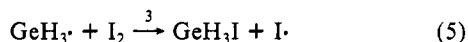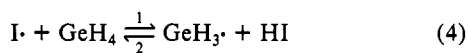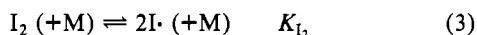Table I. Measured, Derived, and Related Bond Dissociation Energies

bond	$D/$ (kJ mol^{-1})	ref	bond	$D/$ (kJ mol^{-1})	ref
H$_3$Ge–H	346	this work	H$_3$Si–H	378	1
Me$_3$Ge–H	340	2	Me$_3$Si–H	378	1
H$_3$Ge–GeH$_3$	276	this work	H$_3$Si–SiH$_3$	308	1
Me$_3$Ge–GeMe$_3$	305	13	Me$_3$Si–SiMe$_3$	337	14

and other products. Similar behavior has been observed previously in the reaction of SiH$_4$ with I$_2$.[8]

Initial rates were found to fit rate eq 2 for a range of I$_2$ pressures

$$-d[I_2]/dt = k[I_2]^{1/2}[GeH_4] \qquad (2)$$

from 0.2 to 3.3 torr and GeH$_4$ pressures from 2.8 to 58 torr. The data from 20 runs give a value of $k = (4.92 \pm 0.35) \times 10^{-5}$ torr$^{-1/2}$ s^{-1}. Excluding the five runs for which $[GeH_4]_0/[I_2]_0 < 4$ gives a value of $k = (4.78 \pm 0.23) \times 10^{-5}$ torr$^{-1/2}$ s^{-1}. Integrated plots of 2 up to 75% conversion fit the data with the same rate constant, providing $[GeH_4]_0/[I_2]_0 > 100$. Inhibition of the reaction by HI is very slight, and only becomes important at high conversion. These observations are consistent with the mechanism shown in equations 3–5.

$$I_2 \; (+M) \rightleftharpoons 2I\cdot \; (+M) \qquad K_{I_2} \qquad (3)$$

$$I\cdot + GeH_4 \underset{2}{\overset{1}{\rightleftharpoons}} GeH_3\cdot + HI \qquad (4)$$

$$GeH_3\cdot + I_2 \overset{3}{\longrightarrow} GeH_3I + I\cdot \qquad (5)$$

The steady-state expression for this mechanism is eq 6, which

$$-\frac{d[I_2]}{dt} = \frac{k_1 K_{I_2}^{1/2}[I_2]^{1/2}[GeH_4]}{1 + (k_2/k_3)[HI]/[I_2]} \qquad (6)$$

reduces to eq 2 in the initial stages of reaction, at which point $k = k_1 K_{I_2}^{1/2}$. From the known value[9] of $K_{I_2}^{1/2}$, $k_1 = (8.21 \pm 0.40) \times 10^4$ dm^3 mol^{-1} s^{-1}. Further measurements of k_1 in the temperature range 402–445 K give the Arrhenius equation (7). The

$$\log (k_1/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) =$$
$$(11.03 \pm 0.13) - (52.3 \pm 1.0 \text{ kJ mol}^{-1})/(RT \ln 10) \quad (7)$$

high A factor for k_1 is in accord with expectations for H atom abstractions by I·.[1,7] This lends further support to the mechanism. The inhibition constant (k_2/k_3) was measured by addition of an excess of HI to the reaction mixture. The value obtained at 445 K is 0.060 ± 0.010, and there is only a very slight temperature dependence. Because of the large scatter and weak temperature dependence, it is difficult to measure the Arrhenius parameters for the ratio k_2/k_3 with reliability, but the data are consistent with $E_2 - E_3 = 4 \pm 4$ kJ mol^{-1}. E_2 cannot be obtained separately, but by analogy with hydrocarbon[7] and silane[1] chemistry E_3 should be zero, and hence $E_2 = 4 \pm 4$ kJ mol^{-1}. Thus $\Delta H_{12}° = E_1 - E_2 = 48 \pm 5$ kJ mol^{-1}. With assumption of a negligible effect of temperature, $D(H_3Ge-H) = D(H-I) + (48 \pm 5) = 346 \pm 5$ kJ mol^{-1} (83 ± 1 kcal mol^{-1}). The uncertainty quoted here is based only on an analysis of random error. In the light of the assumptions made to derive E_2, a more realistic estimate of uncertainty might be ±10 kJ mol^{-1}.

The value for $D(H_3Ge-H)$ is within the range previously reported[3-5] but is a good deal lower than the upper limit.[5] It is in disagreement with the electron impact based value[4] but in reasonably good agreement with the results from an IR chemiluminescence study (upper limit originally of 326 kJ mol^{-1},[3] recently revised upward to 338 kJ mol^{-1} [10]). As Table I shows, the value

for $D(H_3Ge-H)$ is the same within experimental error as the value previously reported for D(Me$_3$Ge–H). Thus contrary to the work of McKean et al.[6] there is little or no effect of methyl substitution on the Ge–H bond dissociation energy.[11] This parallels the situation in the analogous silanes.

Finally $D(H_3Ge-H)$ can be used to calculate two other quantities of thermochemical interest. Based on the known values[12] for $\Delta H_f°$ of GeH$_4$ and Ge$_2$H$_6$ we derived $\Delta H_f°(GeH_3\cdot) = 219$ kJ mol^{-1} and $D(H_3Ge-GeH_3) = 276$ kJ mol^{-1}. The latter is compared with the Ge–Ge dissociation energy of Ge$_2$Me$_6$ in the table. Once again there is a striking parallel with the silanes. Methyl groups appear to be acting as *bond strengtheners*, although the effect is only ca. 5 kJ mol^{-1}/methyl group. Since both Ge and Si are relatively electropositive compared with carbon, it is perhaps not too surprising that methyl groups cannot function as inductive electron donors when attached to Ge or Si.

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Microbial Degradation of the Phytosterol Side Chain. 1. Enzymatic Conversion of 3-Oxo-24-ethylcholest-4-en-26-oic Acid into 3-Oxochol-4-en-24-oic Acid and Androst-4-ene-3,17-dione

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Cholesterol, sitosterol, and campesterol are abundant naturally occurring sterols, and they have long been recognized as valuable intermediates for steroid hormone production to supplement or supplant the commercial processes from diosgenin.[1] In recent years, several economical microbiological processes[2] have been developed for the conversion of these sterols into useful steroid hormones via the selective cleavage of the hydrocarbon side chain without degrading the steroid nucleus.

In 1968,[3,4] we defined the intermediates and reaction sequence for the microbial transformation of cholesterol into 17-keto steroids. This pathway proceeds via 3-oxochol-4-en-24-oic acid (1) and 3-oxobisnorchol-4-en-22-oic acid with the concomitant formation of 2 mol of propionic acid and 1 mol of acetic acid. However, until now the mechanism of degradation of the branched hydrocarbon side chain of sitosterol was not understood. As a first step toward deducing the degradative pathway, we have developed cell-free systems capable of catalyzing the conversion

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