polarizability derivative with respect to Q_1, $\bar{\alpha}'_Q \equiv \partial\bar{\alpha}/\partial Q_1$, must be transformed to a derivative with respect to an A–B bond stretch

$$\bar{\alpha}'_{r_{\mathrm{AB}}} = \frac{\sqrt{M_{\mathrm{B}}}}{2}\bar{\alpha}'_Q \tag{2}$$

where M_{B} is the mass of atom B in an AB_4 tetrahedral molecule.

Long and Plane have proposed[7] the following equation for the calculation of bond orders from experimentally determined polarizability derivatives

$$\bar{\alpha}'_{r_{\mathrm{AB}}} = \frac{2}{3}(g\sigma/Za_0)\left(\frac{n}{2}\right)r_{\mathrm{AB}}^3 \tag{3}$$

where $n/2$ is the bond order, σ is the Pauling covalent bond character, a_0 is the Bohr radius, Z is the effective nuclear charge, g is the δ-function strength, and r is the internuclear distance. For a heteronuclear bond A–B, Z is taken to be the geometric mean of Z_{A} and Z_{B}, $(Z_{\mathrm{A}}Z_{\mathrm{B}})^{1/2}$, where Z is the atomic number minus the number of inner-shell electrons. The δ-function strength, g, is taken to be $(X_{\mathrm{A}}{}^{1/2}X_{\mathrm{B}}{}^{1/2})^{1/2}$ where X_{A} is the Pauling electronegativity of atom A. The Pauling covalent bond character, σ, is $\exp[(-1/4)(X_{\mathrm{A}} - X_{\mathrm{B}})^2]$.

Results and Discussion

The results of intensity measurements on BrO_4^- and IO_4^- using 5145-Å excitation are presented in Table I along with the X–O stretching force constants for XO_4^- ions of group VII. Molecular polarizability derivatives were calculated using eq 1 and 2. These were placed on an absolute scale[9] using $\bar{\alpha}'_r$ of 2.04 Å^2 for CCl_4 (see footnote *f* of ref 7) which changes the ClO_4^- value from 1.73 Å^2 used by Chantry and Plane[6,9] to that shown in Table I. Bond orders were calculated from eq 3.

Table I

	ν_1, cm^{-1}	R[a]	$\bar{\alpha}'_Q$, Å^2 (amu)$^{-1/2}$	$\bar{\alpha}'$, Å^2	$n/2$[c]	$f_{\mathrm{X-O}}$[d]
ClO_4^-	935	0.675	0.88	1.76	1.79	8.24
BrO_4^-	800	1.56 ± 0.06	1.22 ± 0.02	2.44 ± 0.04	1.93	6.05
IO_4^-	792	2.25 ± 0.17	1.455 ± 0.05	2.91 ± 0.11 (2.79)[b]	1.95 (1.84)[b]	5.90

[a] R is molar intensity, relative to $R[\nu_1(CCl_4)] = 1.00$, *i.e.*

$$R_{\mathrm{i}} = \left[\frac{I_{\mathrm{i}}M_{\mathrm{ClO_4^-}}}{M_{\mathrm{i}}I_{\mathrm{ClO_4^-}}}\right]\left[\frac{I_{\mathrm{ClO_4^-}}}{M_{\mathrm{ClO_4^-}}}\,\frac{M_{\mathrm{CCl_4}}}{I_{\mathrm{CCl_4}}}\right]$$

where the term in the second set of brackets has been taken to be 0.675 as determined by Chantry and Plane.[6,9] The correction for instrumental sensitivity was estimated to be 0.75%.[e] The uncertainties shown for R and for the polarizability derivatives are probable errors at the 90% confidence level based on the reproducibility of the measured band areas. [b] Values in parentheses are original values from ref 7 recomputed using new values for $\bar{\alpha}'_r$ of ClO_4^-. [c] Bond orders were calculated using the following parameters: $X_{\mathrm{Cl}} = 3.00$, $X_{\mathrm{Br}} = 2.80$, $X_{\mathrm{I}} = 2.50$, $X_{\mathrm{O}} = 3.50$, $Z_{\mathrm{Cl}} = Z_{\mathrm{Br}} = Z_{\mathrm{I}} = 7$, $Z_{\mathrm{O}} = 6$. Bond lengths were taken to be 1.44, 1.61, and 1.79 Å, respectively, for Cl–O[7], Br–O,[f] and I–O[7] bonds. [d] Force constants in millidynes per ångström taken from ref 4. [e] The instrumental response curve with 5145-Å excitation has not been determined for the instrument used in this study. However, since the frequency of the internal standard is very close to those of the molecules of interest, the correction is expected to be very small. The estimate of 0.75% was based on numbers presented in a paper by H. J. Sloane, *et al.*, at the 1970 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. (The paper is available from Cary Instruments under the title "Analytical Raman Spectroscopy II: Intensity Considerations.") Since our value for periodate is a little larger than that of Chantry and Plane,[6] we may have underestimated the correction factor somewhat. Even so, the conclusions reached in the paper will not be affected by any small changes in the instrument sensitivity correction. [f] S. Siegel, B. Tani, and E. Appelman, *Inorg. Chem.*, **8**, 1190 (1969).

Since the concentrations used in this study were considerably lower than those in previous work on XO_4^- ions, we have also remeasured the intensity of the A_1 line of periodate. The agreement between our value and that of Chantry and Plane[6] is within 4%.

Examination of bond orders in Table I leads to a not unexpected conclusion: the perbromate ion exhibits a considerable degree of multiple bonding which is similar in magnitude to periodate. This similarity in bonding has also been suggested by Brown, *et al.*,[4] using the X–O stretching force constants in Table I and thermal stabilities of perhalates. Thus, the measurement of experimental Raman intensities provides further evidence for the normal stability of the perbromate ion.

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1-Silyl Derivatives of Pentaborane(9)

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A previous paper[1] described the preparation of a number of bridge-substituted group IV derivatives of pentaborane(9) and the isomerization of several of these to the corresponding 2-substituted derivatives in the presence of ethers (for the purpose of this paper group IV refers to all group IV elements except carbon). Subsequently we have found that gas-phase thermolysis of μ-$(CH_3)_3SiB_5H_8$ at about 80° also results in irreversible formation of 2-$(CH_3)_3SiB_5H_8$ at a moderate rate. At higher temperatures further isomerization occurs to produce 1-$(CH_3)_3SiB_5H_8$. This isomerization, however, is reversible and 1-$(CH_3)_3SiB_5H_8$ predominates by a factor of about 3.3 at 120°. Gas-phase thermolysis of 2-$H_3SiB_5H_8$ at 150° results in a similar conversion to 1-$H_3SiB_5H_8$. This isomerization also appears to be reversible. (Traces of 1-$H_3GeB_5H_8$ are observed when 2-$H_3GeB_5H_8$ is passed through a Pyrex-glass spiral heated above 300°. Other reactions predominate, however, and no conclusion about the relative thermodynamic stability of 2-$H_3GeB_5H_8$ and 1-$H_3GeB_5H_8$ can be made at this time.)

Formation of 1-$(CH_3)_3SiB_5H_8$ can also be achieved at room temperature by using selected moderately strong Lewis bases such as 2,6-dimethylpyridine or, better, hexamethylenetetramine. The starting material may be either μ- or 2-$(CH_3)_3SiB_5H_8$, as both give rise to an equilibrium mixture of 1- and 2-$(CH_3)_3SiB_5H_8$ in which the 1 isomer predominates by a factor of about 4. Isomerization experiments were carried out in nmr tubes so that ^{11}B nmr spectra could be obtained periodically without disturbing the system. These experiments

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(1) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **90**, 6617 (1968).

showed that μ-$(CH_3)_3SiB_5H_8$ is rapidly and irreversibly converted to 2-$(CH_3)_3SiB_5H_8$ (less than 1 hr using hexamethylenetetramine; about 18 hr using 2,6-dimethylpyridine). The reversible isomerization of 2-$(CH_3)_3SiB_5H_8$ to 1-$(CH_3)_3SiB_5H_8$ is much slower, requiring several days to reach equilibrium. Starting with 1-$(CH_3)_3SiB_5H_8$ and hexamethylenetetramine catalyst, the same equilibrium mixture of the 1 and 2 isomers is obtained in about 5 days at room temperature.

Two seemingly unrelated observations about 1-silyl derivatives of pentaborane(9) are of interest. First, when a silyl group is attached to B(1) in place of hydrogen, the ^{11}B nmr resonance of that boron is shifted to higher field, and, second, this 1 isomer is more thermodynamically stable than the corresponding 2 isomer. These observations also obtain in the case of 1-IB_5H_8.[2] In all other known 1-substituted derivatives of pentaborane(9)[2-6] the substituent causes the B(1) resonance to shift to lower field and the 2-substituted isomer appears to be more thermodynamically stable (an apparent exception is 1-$(CF_3)_2PB_5H_8$[7]).

In summary, our studies have shown that each of the three unique hydrogen positions in pentaborane(9) can be replaced by a silyl group and that the thermodynamic stability of the isomers increases in the order μ- < 2- < 1-$R_3SiB_5H_8$.

Experimental Section

Standard high-vacuum techniques were used for manipulation and purification of the boron-containing compounds.[8] Hexamethylenetetramine was recrystallized from ethanol and dried under vacuum; 2,6-dimethylpyridine was distilled from barium oxide. The μ-$(CH_3)_3SiB_5H_8$, 2-$(CH_3)_3SiB_5H_8$, and 2-$H_3SiB_5H_8$ were prepared as previously.[1] The μ-$(CH_3)_3SiB_5H_8$ preparation has been scaled up to 100 mmol with no difficulties and no reduction in yield.

1-Trimethylsilylpentaborane, 1-$(CH_3)_3SiB_5H_8$. A. Pyrolysis.—In a typical preparation 0.329 g (2.43 mmol) of μ-$(CH_3)_3SiB_5H_8$ was heated in the gas phase in a 1 l. flask for 4 hr at 145°. The recovered volatile products that distilled through a −45° trap and condensed in a −78° trap consisted of a mixture of about 20% 2-$(CH_3)_3SiB_5H_8$ and 80% 1-$(CH_3)_3SiB_5H_8$. The yield of recovered 1- and 2-$(CH_3)_3SiB_5H_8$ was 0.299 g (2.21 mmol) or 91%. In other experiments in which 2-$(CH_3)_3SiB_5H_8$ was used as the starting material similar results were obtained.

Preliminary gas-phase kinetic studies at 129° indicate that the equilibrium constant is about 3.3 ± 0.2 for the process 2-$(CH_3)_3SiB_5H_8 \rightleftharpoons$ 1-$(CH_3)_3SiB_5H_8$. Starting with pure 2-$(CH_3)_3SiB_5H_8$, this equilibrium is reached in about 3 days. Further studies of the kinetics of this isomerization are presently being developed.

B. Base Catalysis.—In a typical preparation 0.666 g (4.92 mmol) of μ-$(CH_3)_3SiB_5H_8$ was left in contact with about 0.5 g of hexamethylenetetramine overnight. The volatile products recovered that distilled through a −30° trap and condensed in a −78° trap consisted of a mixture of about 20% 2-$(CH_3)_3SiB_5H_8$ and 80% 1-$(CH_3)_3SiB_5H_8$. The yield of 1- and 2-$(CH_3)_3SiB_5H_8$ was 0.617 g (4.56 mmol) or 93%. No starting material was recovered.

In order to follow the course of the isomerization, nmr tubes were made up containing about 2 mmol of μ-, 2-, or 1-$(CH_3)_3SiB_5H_8$ and 20–30 mg of hexamethylenetetramine or 10 μl of 2,6-dimethylpyridine. The tubes were warmed to room temperature and the ^{11}B nmr spectrum of each sample was recorded periodically over several weeks, well beyond the time when no further changes could be detected. When the catalyst was 2,6-dimethylpyridine, the samples developed a yellow color soon after warming to room temperature, but the ^{11}B nmr spectra did not seem to be affected by this change. When equilibrium was reached, the equilibrium constants of all the samples had the same value of 4.0 ± 0.3 (within the rather large experimental error) at 24 ± 1° as determined by integration of the ^{11}B nmr spectra. When the nmr tubes were opened, between 90 and 95% of each sample was recovered as a mixture of the 1 and 2 isomers.

C. Purification.—The volatilities of 1- and 2-$(CH_3)_3SiB_5H_8$ are so similar that a pure sample of the former could not be obtained using standard vacuum line techniques. Samples of high purity were obtained, however, by distillation on a high-vacuum low-temperature spinning-band column. The column is essentially the same as the Dobson column[9] except that it contains a magnetically driven, three-turn stainless steel gauze spinning band, and a magnetically operated valve has been placed between the head of the column and the sample collection trap. Pure samples of 1-$(CH_3)_3SiB_5H_8$ were collected when the column temperature was raised above its melting point (about −55°); vapor pressure 1.5 mm at 0° and 7 mm at 25°.

1-$H_3SiB_5H_8$.—In a typical experiment 0.332 g (3.57 mmol) of 2-$H_3SiB_5H_8$ was heated in the gas phase in a 1-l. flask at 150° for 13 hr. The products were subsequently separated by trap-to-trap distillation in the vacuum line. The major product was slowly distilled through a trap at −50° and was shown to be 0.300 g (3.22 mmol) of 1-$H_3SiB_5H_8$, mp −27 to −28° (Stock ring method); vapor pressure 6.5 mm at 0° and 26 mm at 25°.

Nmr Spectra.—These were obtained using Varian HA-100 and A-60A spectrometers equipped with standard Varian accessories and modifications.

The ^{11}B nmr spectra of 1-H_3Si and 1-$(CH_3)_3SiB_5H_8$ consist of a low-field doublet from B(2–5) of area 4 and a high-field singlet from B(1) of area 1. The chemical shifts referenced to $BF_3 \cdot O(C_2H_5)_2$ (and coupling constants) are shown below.

	B(2–5)	B(1)
1-$H_3SiB_5H_8$	11.8 (167)	60.0
1-$(CH_3)_3SiB_5H_8$	12.9 (168)	58.0

The ^1H nmr spectra of 1-H_3Si- and 1-$(CH_3)_3SiB_5H_8$ consist of a 1:1:1:1 quartet from terminal hydrogens bound to ^{11}B, a broad singlet from bridge hydrogens, and a moderately sharp singlet from the substituent. Chemical shifts (τ) referenced to TMS (and coupling constants) are shown below.

	H(terminal)	H(bridge)	Substituent
1-$H_3SiB_5H_8$	7.48 (168)	12.13	6.75
1-$(CH_3)_3SiB_5H_8$	7.74 (177)	12.8	10.25

In the spectrum of 1-$H_3SiB_5H_8$, the H_3Si– resonance also shows ^1H–^{29}Si satellites with a coupling of 184 Hz.

Infrared Spectra.—Gas-phase spectra were obtained at about 5 Torr in 10-cm cells using a Perkin-Elmer Model 700 spectrometer. Quoted frequencies in cm^{-1} (±10) are as follows: **1-$H_3SiB_5H_8$:** 2610 (vs), 2170 (sh), 2140 (vs), 2110 (sh), 2090 (sh), 1850 (s), 1790 (w), 1475 (m), 1410 (s), 1045 (w), 970 (w, sh), 955 (w, sh), 905 (vs), 860 (s, sh), 670 (s), 600 (w), 565 (w). **1-$(CH_3)_3SiB_5H_8$:** 2970 (s), 2920 (w), 2600 (s), 1940 (w), 1835 (m), 1780 (w), 1480 (sh), 1445 (sh), 1390 (m), 1330 (w), 1250 (s), 1170 (w), 1050 (m), 900 (sh), 850 (s), 830 (s), 745 (m), 690 (m), 665 (m).

Mass Spectra.—These were recorded using a Consolidated Electrodynamics Corp. 21-103C spectrometer. The spectra were nearly indistinguishable from those obtained for the μ and 2 isomers.[1] The only differences were small changes in some of the relative intensities.

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