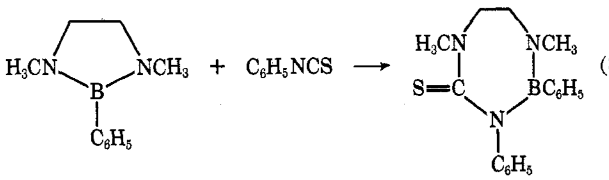
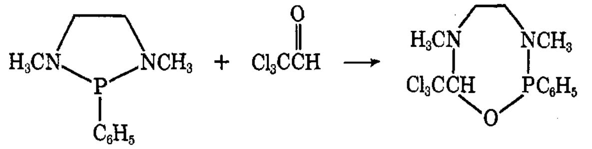
the 1:1 adduct in an exothermic reaction

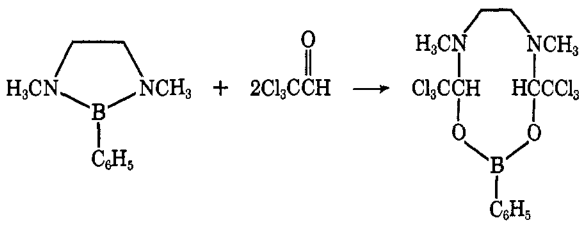

(3)

Presumably the insertion of 1 mol of the isothiocyanate deactivates the heterocycle for further insertion.

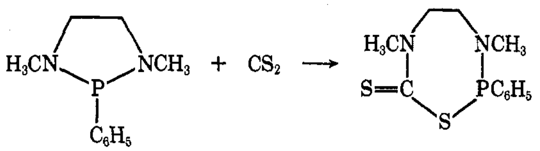
Chloral behaves similarly toward the phosphorus imidazolidine in benzene to give a 1:1 adduct in an exothermic reaction


(4)

With the boron heterocycle, on the other hand, 2 mol of chloral was taken up in an exothermic reaction


(5)

The addition of carbon disulfide to the phosphorus imidazolidine is highly exothermic and produces the 1:1 adduct as a blood red solid


(6)

A similar coloration was observed when bis(dimethylamino)phenylphosphine was treated with carbon disulfide.[5]

Our investigation shows that the reactivity of the boron and phosphorus imidazolidines toward insertion is in general similar but depends in the particular case on the inserting moiety.

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Raman Intensity of the A_1 Line and Bond Order of the Perbromate Ion

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The recent synthesis of the perbromate ion, BrO_4^-, by Appelman[3] and Brown, *et al.*,[4] has ended the need for attempts to explain the apparent nonexistence of this species. Included in past speculation about possible causes of the apparent instability of BrO_4^- are a number of theoretical considerations which have been summarized by Cox and Moore.[5] One kind of experimental measurement involved in attempting to account for the history of failures to prepare the BrO_4^- ion is the Raman intensity of the A_1 line[6] and later bond orders obtained from these Raman intensities.[7] In view of general interest in the BrO_4^- ion and the role played by Raman intensities in an attempt to account for the apparent nonexistence of the BrO_4^- ion based on a possible low bond order for the Br–O bond,[7] it now seemed appropriate to measure the Raman intensity of the A_1 line of the BrO_4^- ion and compare this intensity and resulting bond order to results for the ClO_4^- and IO_4^- ions.

Experimental Section

Chemicals.—Potassium perbromate was a gift from Dr. E. H. Appelman of Argonne National Laboratory. Reagent grade potassium perchlorate (Baker & Adamson) and potassium periodate (Fisher) were used as received.

Spectrometer.—Raman spectra were recorded on a system consisting of a Spex Model 1401 double monochromator equipped with a Coherent Radiation Laboratory Model 52 Ar ion laser source (~1.3 W at 5145 Å) and photon counting detection *via* an ITT FW-130 photomultiplier maintained at *ca.* −20° by a thermoelectric cooler (Products for Research, Inc.). The incident radiation from the laser was plane polarized and depolarization ratios were measured using the analyzer method recommended by Scherer and Bailey.[8] A polarization scrambler was located between the analyzer and the entrance slit of the monochromator.

Intensity Measurements.—Raman intensities were measured using the ν_1 (A_1) line of the perchlorate ion as the internal standard following the procedure of Chantry and Plane.[6,9] Observed depolarization ratios were indistinguishable from the expected value of zero for all three XO_4^- ions. Once this fact was established, the analyzer was removed from the optics to enhance the signal and attempt to improve the accuracy and reproducibility of band area measurements on the very dilute solutions employed. A total of fourteen measurements at two concentrations for perbromate and five measurements at one concentration for periodate were made, concentrations being *ca.* $(1\text{–}5) \times 10^{-3}\ M$. Band areas were measured by planimeter.

Calculations.—For a tetrahedral molecule, the observed intensity for a totally symmetric (A_1) Raman line is given by[10]

$$I = \frac{KM(\nu_0 - \nu_1)^4[45(\partial\bar{\alpha}/\partial Q_1)^2]}{\nu_1[1 - \exp(-h\nu_1/kT)]} \tag{1}$$

where K is a constant, M is the molar concentration of the scattering species, ν_0 is the frequency of the exciting line, ν_1 is the frequency of normal coordinate Q_1, $\bar{\alpha}$ is the mean molecular polarizability, and h, k, and T have their usual meanings. Since we wish to relate the measured intensity to bond properties, the

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[5] M. M. Cox and J. W. Moore, *J. Phys. Chem.*, **74**, 627 (1970), and references therein.

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[9] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[10] Combination of the equations for scattered intensity at 90° and depolarization ratio for plane-polarized incident radiation

$$I = \frac{KM(\nu_0 - \nu_1)^4[45(\bar{\alpha}'_Q)^2 + 7(\gamma'_Q)^2]}{\nu_1[1 - \exp(-h\nu_1/kT)]}$$

$$\rho = \frac{3(\gamma'_Q)^2}{45(\bar{\alpha}'_Q)^2 + 4(\gamma'_Q)^2}$$

yields

$$I = \frac{KM(\nu_0 - \nu_1)^4[45(\bar{\alpha}'_Q)^2]}{\nu_1[1 - \exp(-h\nu_1/kT)]}\left[\frac{3(1 + \rho)}{(3 - 4\rho)}\right]$$

Equation 1 is the special case of $\rho = 0$. All symbols are defined in the text except γ'_Q the normal-coordinate derivative of the polarizability tensor anisotropy.

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

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

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

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

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.*

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

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.

Acknowledgments.—We thank Dr. E. H. Appelman of Argonne National Laboratory for kindly providing us with a sample of potassium perbromate. Thanks are also due to Dr. Charles E. Hathaway of the Department of Physics, Kansas State University, for allowing us large amounts of time on his Raman spectrometer. J. D. W. wishes to express gratitude for an NDEA fellowship.

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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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