Infrared Spectra of Metaborate Monomer and Trimer Ions[1]

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The alkali halide pressed disk method has been used to observe the infrared spectra of the unstable metaborate monomer and its cyclic trimer anions. These anions were prepared directly in the host halide matrices by the oxidation of KBH_4 or by the dehydration of $KB(OH)_4$. A tentative assignment of the fundamental vibrational frequencies of the cyclic trimer is presented.

Although the use of alkali halide pressed disks[2] to obtain the infrared spectra of solid compounds is a standard procedure in spectroscopic laboratories, only a few attempts have been reported in which this technique was employed to study spectroscopically the reaction kinetics[3a] in the solid state or to observe the infrared spectra of unstable chemical species.[3b] These obvious extensions of the disk method have not received much attention of spectroscopists, perhaps because of recognition by them of solid state anomalies[4] associated with this technique and of the difficulty in interpreting the nature of the environmental effects[5] on the vibrational modes of the solute species. While solutions to these problems are necessary ultimately for a complete interpretation of experimental results obtained by the disk method, we wish to show here that even without these solutions the pressed disk method can be used as a convenient means of trapping unstable ionic species and of carrying out controlled chemical reactions in the solid state.

Simple boron oxide anions were chosen for this study since good infrared spectra of such anions[6] are difficult to obtain and since some spectroscopic work[7,8] on hydrated forms of some of these ions have been reported. Also, while our work was in progress, Morgan and Staats[9] reported the infrared spectrum of the metaborate anion present as an impurity in some commercial alkali halide crystals. In our work, the boron oxide anions were prepared directly in the alkali halide matrices by the oxidation of BH_4^- ion or by the dehydration of the $B(OH)_4^-$ ion.

Experimental

Chemicals.—KCl, KBr (powdered), KI, NaCl, and CsBr were Harshaw optical grade crystals. Reagent NaBr crystals from Fisher were used without purification, but reagent NaI crystals

from the same source were recrystallized from water before use. $NaBH_4$ and KBH_4 were reagent chemicals from Matheson Coleman and Bell and were used directly. Boric acids enriched in B^{10} isotope (96.5%) and in B^{11} isotope (98.9%) were obtained from the Oak Ridge National Laboratory and were used without purification.

Infrared Instruments.—A Perkin-Elmer Model 21 double-beam instrument with NaCl and CsBr prisms was used for most of our work. However, measurements in the shorter wave length region and frequency checks were made on a single-beam, double-pass, Perkin-Elmer Model 112 instrument with CaF_2, NaCl, KBr, and CsBr prisms.

Disk Preparation.—We used no special precautions other than those normally required to produce good disks. The solute and powdered matrix salt were ground in an agate vial with an agate ball on a mechanical vibrator for 1 min. The quantity of solute and matrix material was chosen to give a finished disk weighing about 4–500 mg. and with a solvent-to-solute mole ratio of about 100:1 to about 2300:1. The powder was transferred to a Perkin-Elmer 13-mm. die assembly, evacuated for 5–10 min., and then pressed on a 30-ton hydraulic press (Research and Industrial Instruments Co., England). Normally a pressure of 163,000 p.s.i. (dial pressure 15 tons) for 5 min. was used, but with NaCl or NaBr matrices a pressure of 218,000 p.s.i. (dial pressure 20 tons) for 15–30 min. was employed. Disks of about 1-mm. thicknesses were obtained in the above manner.

To prepare disks containing $B(OH)_4^-$ ions the freeze–dry method was used. Boric acid and the matrix salt KBr were dissolved in a minimum volume of water, and the solution was made alkaline by adding an excess of aqueous KOH.[10] The solution was transferred to a vacuum line, frozen with liquid nitrogen, and then evacuated for about 12 hr. A high capacity pump was used so that the evacuation of the solid could be carried out without cooling the sample. Disks obtained in this manner were generally cloudy, although their infrared spectra could still be recorded. KBH_4 disks made by the freeze–dry method, on the other hand, gave good quality pellets. This method of disk preparation was used also in acidic, basic, or neutral hydrolysis experiments on matrices containing boron oxide anions.

Heating of the Disks.—After the spectrum of a disk was taken, the pellet was placed in a covered ceramic crucible and heated in a small laboratory furnace at a fixed temperature between 500 and 600°. The disk was removed from the oven after a given heating period and cooled to room temperature. Since the most pronounced change in the appearance of the disk occurred during the initial heating period, this period was normally kept at 5 or 10 min. Successive heating periods were extended to hours, days, or weeks.

After the initial heating, the disk generally expanded in size, turned opaque, and often showed blistered surfaces. Heating at temperatures near 600° produced etching of the disk surfaces. Such an opaque disk was broken into several large pieces and repressed without grinding. Transparency of the disk was then

(1) Abstracted in part from the M.S. thesis submitted by N. H. S. to the Graduate School, Pennsylvania State University, June, 1963.

(2) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952); U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1952).

(3) (a) H. A. Bent and B. Crawford, Jr., *J. Am. Chem. Soc.*, **79**, 1793 (1957); (b) H. T. J. Chilton and G. Porter, *Spectrochim. Acta*, **16**, 390 (1960).

(4) A. W. Baker, *J. Phys. Chem.*, **61**, 450 (1957).

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(6) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(7) D. White, *et al.*, *J. Chem. Phys.*, **32**, 488 (1960).

(8) J. Goubeau and D. Hummel, *Z. Physik. Chem.* (Frankfurt), **20**, 15 (1959).

(9) H. W. Morgan and P. A. Staats, *J. Appl. Phys.*, **33**, 364 (1962).

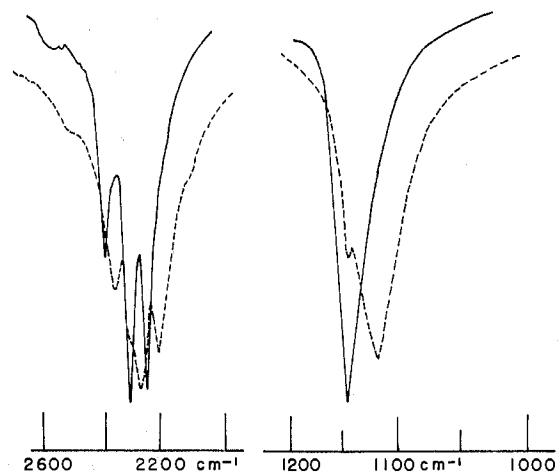(10) J. O. Edwards, *et al.*, *J. Am. Chem. Soc.*, **77**, 266 (1955).

Fig. 1.—The spectrum of BH_4^- in KCl matrix at 25°. Dotted curve is the initial spectrum, and the solid curve after heating for 5 min. at 540°. Boron isotopes in natural abundance.

restored and a good spectrum was obtained. However, the color of the heated disk ranged from light tan to black. Disks without any solute showed no changes in color and retained their transparency even when heated for many days.

Results

BH_4^- Spectrum.—In the initial spectrum of this ion in various salt matrices, the absorption bands in the B–H stretch region at about 2300 cm.$^{-1}$ and in the B–H bond bend region at about 1100 cm.$^{-1}$ were broad and asymmetric. Disks prepared by the freeze–dry method gave sharper bands. On heating the disks these bands sharpened markedly and the peak frequencies shifted to higher values. A typical example of these changes is shown in Fig. 1. Successive heating caused further small frequency shifts, but eventually constant frequency values were obtained. In sodium or potassium halide matrices, the final frequencies were the same whether we used $NaBH_4$ or KBH_4. These final values from different matrices are listed in Table I.

The relative intensities of the bands also were influenced by the matrix. In the potassium halide matrices, which gave the sharpest bands, $2\nu_4$ became progressively weaker compared to ν_3 in going from KCl to KBr to KI. A similar trend was noted in the sodium halide matrices, although the absorption bands were somewhat broader. These bands were even broader in CsBr matrix, and in the B–H stretch region a single peak with only partially resolved maxima was observed.

TABLE I
SPECTRUM OF $B^{11}H_4^-$ AT 25°

Matrix	$\nu_2 + \nu_4$	ν_3	$2\nu_4$	ν_4
NaCl	2486	2373	2307 (2322)	1166 (~1174)
NaBr	2427	2328	2254 (~2268)	1136
NaI	...	2278	2202 (~2214)	1111
KCl	2422	2324 (2334)	2257 (2269)	1144 (~1152)
KBr	2387	2293 (2304)	2226 (2238)	1128 (~1136)
KI	~2341	2258 (~2270)	2191 (~2202)	1108 (~1115)

Frequencies, cm.$^{-1a}$

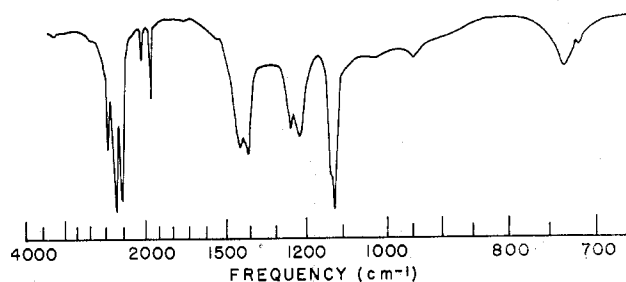[a] Frequencies in parentheses are from $B^{10}H_4^-$ in natural abundance.

Fig. 2.—The spectrum of partially oxidized BH_4^- in KBr matrix at 25°. Boron isotopes in natural abundance.

BO_2^- Spectrum.—Disks prepared by the procedure of grinding, evacuating, and then pressing have an appreciable amount of air trapped in them, so that when they are heated at high temperatures the solute BH_4^- is partially oxidized. A typical spectrum obtained from such partial oxidation of the solute ion in KBr matrix is shown in Fig. 2. Here, the triplet band at 2300 cm.$^{-1}$ and another band at 1100 cm.$^{-1}$ belong to the parent ion. Two pairs of very sharp bands, one near 2000 cm.$^{-1}$ and another somewhat weaker one near 600 cm.$^{-1}$ (not shown in Fig. 2), are due to the linear symmetric metaborate monomer ion. Other bands in this spectrum arise from the cyclic metaborate trimer ion which will be discussed in the next section.

The yield of the metaborate ion was found to be the best in KBr or KI matrices. In sodium salts, absorption bands due to this ion were very weak or not present at all. The BO_2^- ion was also formed when disks containing $B(OH)_4^-$ were dehydrated by heating. However, dehydration of boric acid in the disks never produced the metaborate absorption bands. The yield of the metaborate in KBr could also be increased substantially by allowing the oxidation of BH_4^- to go to completion. This was accomplished by initially incorporating in the matrix either $KClO_3$ or $KClO_4$. Since these oxidizing reagents decomposed completely to form KCl at the temperatures used here, even when the disk had contained an excess of these ions the final spectrum was that of the boron oxide anions only. An example of a spectrum resulting from complete oxidation of BH_4^- in KBr matrix is shown in Fig. 4(A). With KI matrix, the oxidizing reagent reacted not only with the solute ion but also with the matrix itself. Interestingly, oxidation with chlorate or perchlorate produced disks which were colorless.

Under higher resolution, the doublet band at 2000 cm.$^{-1}$ resolved into two pairs of very sharp doublets as shown in Fig. 3. The low-frequency component in each pair is a hot band for it disappeared when the spectrum was recorded with the sample cooled to liquid nitrogen temperature. The observed frequencies of the metaborate ion in various matrices are listed in Table II.

The metaborate monomer trapped in the matrices is not stable. When matrices containing this species were ground in air and then the powder repressed, the absorption bands due to this ion disappeared or weakened considerably as shown in Fig. 4(B). Also, if the

Fig. 3.—The ν_3 band of BO_2^- in KBr matrix at 25°. Boron isotopes in natural abundance.

TABLE II
SPECTRUM OF $B^{11}O_2^-$ AT 25°

		Frequency, cm.$^{-1a}$	
Matrix	ν_3	$\nu_2 + \nu_3 - \nu_2$	ν_2
NaCl	1995 (2066)	...	...
NaBr	1971 (2041)	...	...
NaI	1948 (2018)	...	...
KCl	1972 (2043)	1964 (2033)	589 (610)
KBr	1959 (2029)	1950 (2019)	588 (608)
KI	1943 (2013)	1934 (2003)	586 (607)
CsBr	1948 (2017)	1938 (2007)	...

^{a} Frequencies in parentheses are from $B^{10}O_2^-$ in natural abundance.

disk containing the monomer was allowed to stand over a long period, the monomer absorption bands gradually diminished in intensity. Figure 5 shows the spectrum of a disk which had stood in a desiccator for 4 months. The initial spectrum of this sample was similar to the one shown in Fig. 4(A). When a reground or an aged disk was reheated, the metaborate absorption bands appeared again. Hydrolysis of the disks in neutral, basic, or acidic aqueous media also destroyed the monomer bands. Reheating of the hydrolyzed samples produced the monomer again except in acid hydrolysis cases. In the latter cases, a spectrum of boric acid was obtained first, and the spectrum changed to that of dehydrated boric acid on heating.

$(BO_2^-)_3$ **Spectrum.**—The oxidation of BH_4^- or the dehydration of $B(OH)_4^-$ in alkali halide matrices forms not only the metaborate monomer ion but also the cyclic trimer of this ion as shown in Fig. 2 and 4(A). The trimer spectra resulting from these different preparative methods were the same. Generally the absorption bands of the trimer were much stronger than those of the monomer. Like the monomer, the trimer is unstable, and on regrinding, prolonged heating, or aging of the disks containing this species, the trimer absorption bands degraded into a spectrum characteristic of polymers such as those shown in Fig. 4(B) and
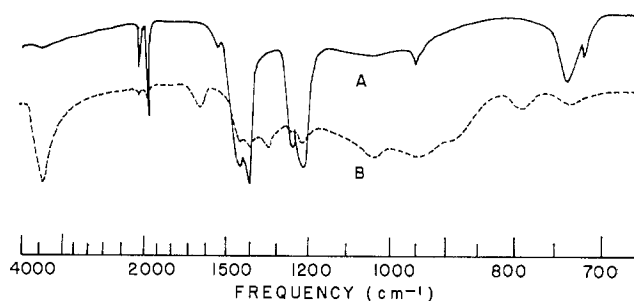

Fig. 4.—Grinding effect on the spectrum of metaborate ions in KBr matrix at 25°. Solid curve is the initial spectrum, and the dotted curve after grinding. Boron isotopes in natural abundance.

5. Reheating of the ground or aged disks produced only a small amount of the trimer. The highest concentration of the trimer was obtained with chlorate or perchlorate oxidation, but this oxidation also formed polymers when the initial BH_4^- concentration was high. These polymers showed broad absorption bands in the 800 to 1500 cm.$^{-1}$ region which often obscured the trimer bands. Absorptions due to the polymers are evident in Fig. 2, 4, 5, and 6.

Prominent features in the spectrum of the trimer were a pair of very intense doublets near 1450 and 1250 cm.$^{-1}$, a medium intensity singlet at about 950 cm.$^{-1}$, a strong doublet near 730 cm.$^{-1}$, and another strong singlet around 390 cm.$^{-1}$. The relative intensities and peak frequencies of the components of the doublet bands were found to be influenced by the matrix material. For a given cation, the anion species of the matrix gave different relative intensities of the component bands but had essentially no effect on their peak frequencies as shown in Table III. The cation, on the other hand, produced marked differences in both intensity and frequency. An example of these effects is shown in Fig. 6.

TABLE III
MATRIX EFFECTS ON SOME $(BO_2^-)_3$ FUNDAMENTALS AT 25°^{a}

Band	NaCl	NaBr	NaI	KCl	KBr	KI
ν_6	1466	1465	1462	1440	1440	1439
	1436	1439	1434	1405	1405	1405
ν_7	1264	1264	1260	1250	1249	1250
	1241	1240	1239	1225	1225	1228
ν_{11}	724	721	722	735	734	734
	708	706	708	717	717	717

^{a} Boron isotopes in natural abundance. Frequencies in cm.$^{-1}$.

Metaborate trimer ions containing essentially pure B^{10} or B^{11} isotopes were also prepared in KBr matrices by freeze-drying the respective isotopic boric acid from alkaline media. The spectra of these samples showed the 1450 cm.$^{-1}$ bands as triplets, the 1250 cm.$^{-1}$ bands as doublets, and the 730 cm.$^{-1}$ bands as singlets. The latter bands of the B^{10} and B^{11} isotopic trimer ions are shown in Fig. 7. This figure also shows the same band system of trimer ions containing boron isotopes in natural abundance and enriched in approximately 50% B^{10}. The observed infrared bands of the trimer ions

TABLE IV
SPECTRUM OF $(BO_2^-)_3$ IN KBr MATRIX AT 25°[a]

B^{nat}	B^{syn}	B^{11}	B^{10}	Assignment	B^{nat}	B^{syn}	B^{11}	B^{10}	Assignment
387 m	387 m	387 m	388 m	ν_{12}		1137 w	1138 w		ν_1
400 vw		400 vw		$2\nu_{10}$		1152 w	1153 vw		$\nu_8 + \nu_{10}$
408 vw	410 vw	410 vw	410 vw	$2\nu_{10}$	1166 w		1167 vw	~1176 vw	$\nu_4 + \nu_9$
419 vw	423 vw	419 vw	420 vw	$2\nu_{10}$	~1200 w	1200 w		1210 w	ν_1
456 vw	~455 vw			ν_5	1225 vs	1233 s	1222 vs	1238 s	ν_7
	460 vw		~460 vw	ν_5	1249 s	1257 vs	1247 s	1265 vs	ν_7
473 w	476 w	473 vw	478 w	ν_9		~1340 w	~1340 vw		$\nu_3 + \nu_{11}$
497 vw	~493 vw	491 vw	520 vw	ν_9	~1350 vw	~1350 vw		1350 w	$\nu_3 + \nu_{11}$
537 vw	537 vw		~553 vw	$2\nu_{14}$	1405 vs	1406 vs	1400 vs		ν_6
565 vw				$2\nu_{14}$				1410 w	$\nu_5 + \nu_8$
~613 vw		616 vw	633 vw	ν_3			1414 s		$\nu_7 + \nu_{10}$
	~635 w	635 vw	645 vw	$\nu_5 + \nu_{10}$		~1430 vs	1434 s	1429 s	$\nu_7 + \nu_{10}$
668 vw	668 vw	668 vw	668 vw	$\nu_{12} + \nu_{14}$	1440 s	1448 vs			$\nu_7 + \nu_{10}$
~680 vw	680 w	~679 vw	~679 vw	$\nu_9 + \nu_{10}$		~1462 vs		1460 vs	ν_6
	690 w	~690 w		ν_4	~1480 w	~1480 w	1478 w	1477 s	$\nu_7 + \nu_{10}$
~700 w	~707 m		708 w	ν_4				~1508 w	$\nu_7 + \nu_{14}$
717 m	717 m			ν_{13}	1510 w	~1510 w		~1514 w	$\nu_7 + \nu_{14}$
734 s	736 s	728 s		ν_{11}	1533 vw		~1530 vw	~1527 w	$\nu_7 + \nu_{14}$
	746 s		754 s	ν_{11}	1544 w	~1546 w		1550 w	$\nu_3 + \nu_8$
758 vw		755 vw		$\nu_9 + \nu_{14}$	1557 vw	1578 vw			$\nu_3 + \nu_8$
765 w		763 vw		$\nu_9 + \nu_{14}$	1654 vw				$\nu_8 + \nu_{13}$
773 w	772 w			$2\nu_{12}$	~1700 vw		~1700 vw		$\nu_5 + \nu_7$
~775 vw	778 w		782 vw	$2\nu_{12}$	1718 w	1719 w	1718 w	1723 w	$\nu_7 + \nu_9$
~798 vw	793 w	~790 vw	797 w	$\nu_3 + \nu_{10}$		1746 w			$\nu_7 + \nu_9$
823 vw	~825 vw	~823 vw		ν_2	1798 w	~1837 vw	1793 w	1837 w	$\nu_7 + \nu_{10} + \nu_{12}$
~840 vw	838 w	~834 vw	837 vw	ν_2	1906 w	1913 vw	1906 vw	1917 vw	$\nu_4 + \nu_7$
~870 vw	855 w	~860 vw		$\nu_4 + \nu_{10}$				1988 w	$\nu_4 + \nu_7$
~947 w	~930 w	~942 w	~950 w	$2\nu_9$	2015 w	~2023 w	2011 w	2041 w	$\nu_3 + \nu_6$
950 m	952 m	950 m	957 m	ν_8	2250 w		2246 w		$\nu_2 + \nu_6$
~1005 vw		~1000 vw	~1000 vw	$\nu_{13} + \nu_{14}$	~2340 vw	~2330 w	2330 w	~2340 vw	$\nu_3 + \nu_7 + \nu_9$
	~1020 vw			$\nu_2 + \nu_{10}$	2394 vw				$\nu_4 + \nu_7 + \nu_9$
~1031 vw	~1040 vw	~1037 vw	~1037 vw	$\nu_2 + \nu_{10}$	2458 vw	2448 w	2457 vw	2471 w	$2\nu_7$
1072 vw	1072 vw		~1078 vw	$\nu_3 + \nu_{10} + \nu_{14}$	~2640 vw	2654 w	2650 w	2651 w	$\nu_6 + \nu_7$
1082 vw	1082 vw	1081 vw	~1087 vw	$\nu_3 + \nu_9$	2842 vw	2847 vw	2847 vw	~2842 vw	$2\nu_6$
	~1100 vw		1117 vw	$\nu_{12} + \nu_{13}$	~2899 vw	2880 vw	2894 vw	2918 vw	$2\nu_7 + 2\nu_{10}$
						2964 vw		2962 vw	$2\nu_7 + 2\nu_{10}$

[a] Frequency units in cm.$^{-1}$. Column headings give boron isotopic compositions: B^{nat} = natural abundance, B^{syn} = 50% B^{11}, B^{11} = 98.9%, and B^{10} = 96.5%.

containing different isotopic compositions of boron are listed in Table IV. In this isotopic work, only the KBr matrix was used.

Boron Oxide Polymer Spectra.—The infrared spectra of boron oxide polymers were quite complex, and we made no attempt to study them at this time.[11] However, certain interesting features of these spectra, which are pertinent to the present work, will be described. The spectra resulting from the polymerization of metaborate monomer and trimer were entirely different from those obtained from the dehydration of boric acid carried out in the matrices. While the former polymers regenerated the monomer on heating, in no case did we observe the monomer spectrum by heating the dehydrated boric acid polymers. However, acid hydrolysis of the metaborate polymers gave boric acid which was readily identified from the infrared spectrum. In the dehydration of boric acid, the spectrum differed according to the extent of dehydration and to the manner in which the reaction was carried out. Spectra resulting from heating of the disks were relatively simple, but those from heating of powdered samples showed rich fine structures in the 700 to 1500 cm.$^{-1}$ region.

Discussion

Ketelaar and Schutte[12] have reported the infrared spectrum of BH_4^- in solid solution of several alkali halide matrices common to those used here, and our frequencies listed in Table I are in good agreement with their results. Evidently, heating of the disks containing this solute at 500–600° produces solid solutions with no change in the ion symmetry for we did not observe any fine structures in the bands other than those due to isotopic boron atoms nor any Raman active bands such as the symmetric B–H stretch mode ν_1. The fact that sodium and potassium salts of BH_4^- gave the same final frequencies in a given matrix is also good evidence of solid solution formation. The spectra of these disks had much sharper bands than those from either freeze-dried samples or disks prepared

(11) Experimental data and spectra of the boron oxide polymers may be found in the M.S. thesis of N. H. S. A copy of this thesis is deposited at the Pattee Library, Pennsylvania State University, University Park, Pa. Interested individuals may borrow this thesis from the library or may write to I. C. Hisatsune for the data.

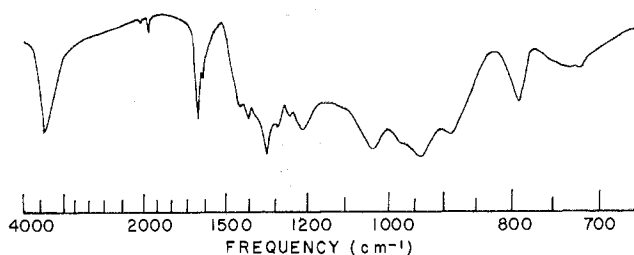(12) J. A. A. Ketelaar and C. J. H. Schutte, *Spectrochim. Acta*, **17**, 1240 (1961).

Fig. 5.—Aging effect (4 months) on the spectrum of metaborate ions in KBr matrix at 25°. Initial spectrum similar to solid curve of Fig. 4. Boron isotopes in natural abundance.

without heating. However, Fig. 1 shows that some solid solution is formed even without heating.

As mentioned earlier disks prepared in a routine manner will contain oxygen even though the powder had been under vacuum before pressing, and heating such disks will cause oxidation of the solute. With BH_4^- ion this reaction was presumably one in which hydrogen gas and BO_2^- were formed. Although we did not attempt to detect the hydrogen gas, blistering of the disks on initial heating may perhaps be due to this gas evolution. In disks prepared essentially free of oxygen, the BH_4^- ion appeared stable even at temperatures near 600°. Heating also removed H_2O from the disks, and boric acid disks subjected to dehydration often showed blistered surfaces. Thus, small gaseous species such as H_2O or H_2 readily diffuse out of the matrix during heating. Larger molecules such as CO_2 and N_2O have been trapped in heated disks in other studies in our laboratory. Bent and Crawford[3a] also trapped CO_2 in KBr matrices.

The exceedingly sharp absorption bands (see Fig. 3) of the metaborate monomer ion formed in our matrices indicate that this ion must also be in solid solution with the matrix salt. Furthermore, since we were not able to detect any absorption band which could be assigned to the symmetric stretch mode ν_1, we may conclude that the ion retains the linear symmetric structure. Among the frequencies listed in Table II those from KCl and KBr matrices are in good agreement with values reported by Morgan and Staats.[9] These investigators observed the monomer ion as an impurity in reagent grade KBr and KCl crystals. Indeed, some of the alkali halide crystals used in our work also contained this impurity. It was readily detected in heated disks made without the solute. Another impurity, the cyanate ion, was found to be present in some of our heated disks. The most prominent band of this ion appears around 2170 cm.$^{-1}$. Frequencies of this and other bands observed in our potassium salts are in good agreement with those reported by Maki and Decius.[13] The ν_3 band in NaBr at 2188 cm.$^{-1}$ and in NaI at 2166 cm.$^{-1}$ was not reported by these workers.

Interpretation of the $(BO_2^-)_3$ Spectrum.—The crystal structure of the potassium salt of the metaborate trimer ion has been reported by Zachariasen.[14] The ion has

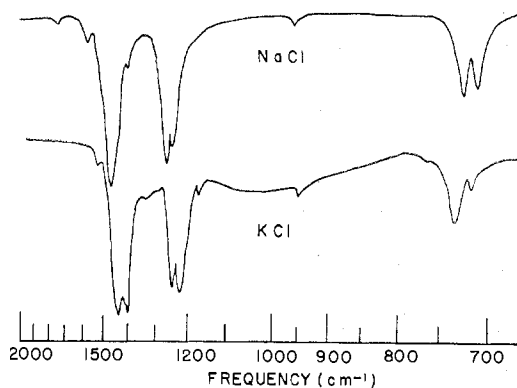Fig. 6.—Spectra of (BO_2^-) in NaCl and KCl matrices at 25°. Boron isotopes in natural abundance.

a D_{3h} symmetry with a ring B–O distance of 1.38 Å., a B–O$^-$ distance of 1.33 Å., and a ring O–B–O angle of 113.5°. The sodium salt, on the other hand, is reported to have a ring B–O distance of 1.433 Å. and a B–O$^-$ distance of 1.280 Å.[15] Some infrared absorption bands of the sodium salt have been reported by Goubeau and Hummel.[8] These authors also interpreted the spectrum of the trimer ion using the spectra of its hydrates (HOBO)$_3$ and (DOBO)$_3$. More recently, Parsons has re-examined the spectra of these hydrates and has presented a new assignment of the trimer ion spectrum.[16]

On the basis of a D_{3h} symmetry, the 21 vibrational modes of the trimer ion may be classified according to species and spectral activities listed in the first column of Table V. We expect only 7 modes to be active in the infrared with 5 of them being doubly degenerate. The observed spectra of the trimer ion in various alkali halide matrices are relatively simple, and we may assume reasonably that the ion still retains a D_{3h} symmetry. However, a closer examination of these spectra, particularly in the 1450, 1250, and 730 cm.$^{-1}$ regions, suggests that the trapped ion may be distorted slightly to a symmetry lower than D_{3h}. Evidences for this conclusion are the observed changes in frequencies (Table III) and relative intensities (Fig. 6) of components of multiplets in these regions with different matrix salts and the persistence of multiplicities of some bands in the spectra of isotopically pure ions (Table IV).

The spectrum of the trimer ion containing boron isotopes in natural abundance shows that there is a breakdown in the D_{3h} selection rule due to an isotope effect as well. When one of the boron atoms in the trimer ring is replaced by an isotope of a different mass, the symmetry of the ion reduces to C_{2v}. Consequently, all vibrational modes which were inactive in the infrared by D_{3h} symmetry now become infrared active. This isotope effect is illustrated in Fig. 7 for the 730 cm.$^{-1}$ band system. Isotopically pure B^{10} or B^{11} trimer ion gave only a single band in this region at 754 or 728 cm.$^{-1}$, respectively, as shown on the left.

(13) A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959).
(14) W. H. Zachariasen, *ibid.*, **5**, 919 (1937).

(15) M. Marezio, *et al.*, *Acta Cryst.*, **16**, 594 (1963).
(16) J. L. Parsons, *J. Chem. Phys.*, **33**, 1860 (1960).

TABLE V

D_{8h} FUNDAMENTAL BANDS OF $(BO_2^-)_3$ IN KBr MATRIX AT 25°

Species and activity	Approximate mode		Frequency, cm.$^{-1}$ B^{11}	B^{10}
A_1'	Ring stretch	ν_1	1138	1210
Raman	B–O$^-$ stretch	ν_2	823	837
	Ring bend	ν_3	616	633
A_2'	Ring bend	ν_4	690	708
inactive	B–O$^-$ bend	ν_5	455	460
E'	Ring stretch	ν_6	1400	1460
infrared and	Ring stretch	ν_7	1222	1265
Raman	B–O$^-$ stretch	ν_8	950	957
	Ring bend	ν_9	473	478
	B–O$^-$ bend	ν_{10}	$(200)^a$	$(205)^a$
A_2''	Ring out-of-plane bend	ν_{11}	728	754
infrared	B–O$^-$ out-of-plane bend	ν_{12}	387	388
E''	B–O$^-$ out-of-plane bend	ν_{13}	717	717
Raman	Ring out-of-plane bend	ν_{14}	$(280)^a$	$(280)^a$

^{a} Estimated.

Trimer ions containing mixed boron isotopes, on the other hand, showed multiplets like those on the right. The upper spectrum is that of a sample containing boron isotopes in natural abundance and the lower one from a sample enriched in approximately 50% B^1_0. The lowest frequency component of the bands in these spectra occurs at 717 cm.$^{-1}$, which is lower by 11 cm.$^{-1}$ than the frequency of the pure B^{11} ion. This band must therefore be assigned to a mode which is infrared inactive by D_{3h} but active under C_{2v}. The remaining peak of the 19% B^{10} spectrum may be assigned to unresolved fundamentals of 11-11-11 and 11-11-10 isotopic ions. Similarly, in the 50% B^{10} spectrum the central peak is assigned to the same isotopic species and the strongest peak to 10-10-10 and 10-10-11 species.

An assignment of the fundamentals of the cyclic metaborate trimer ion on the basis of D_{3h} symmetry is presented in Table V. In the second column of this table approximate descriptions of the normal modes are given, but these descriptions may change completely according to the outcome of a normal coordinate analysis. The choice of the infrared bands for ν_6, ν_7, ν_8, and ν_{11} is straightforward, and the pattern here is similar to that reported by Fisher and co-workers[17] for $(FBO)_3$. The remaining strong band observed at 387 cm.$^{-1}$ has been assigned to ν_{12} because the first overtone of this band was observed only in the spectra (Table IV) of ions containing mixed boron isotopes. This overtone is allowed for C_{2v} symmetry but not for D_{3h}. For $(HOBO)_3$ Goubeau and Hummel[8] reported a band at 415 cm.$^{-1}$ and not at 387 cm.$^{-1}$, but this fact is not inconsistent with the present choice of ν_{12} since we expect hydrogen bonding to shift this band to a higher frequency. A weak band at 473 cm.$^{-1}$ was taken for ν_9, and this may correspond to the medium intensity infrared band at 462 cm.$^{-1}$ reported by

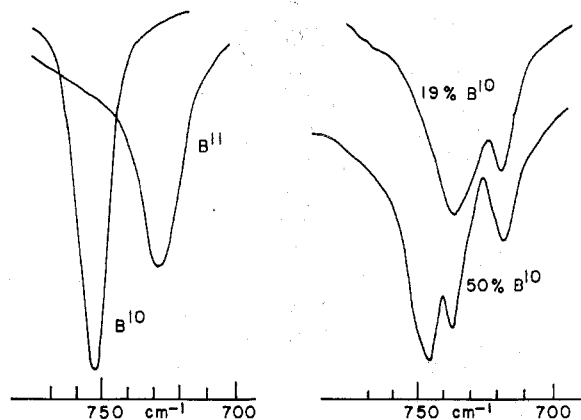(17) H. D. Fisher, W. J. Lehmann, and I. Shapiro, *J. Phys. Chem.*, **65**, 1166 (1961).

Fig. 7.—The 730 cm.$^{-1}$ band system of $(BO_2^-)_3$ with various boron isotopic compositions. KBr matrices at 25°.

Parsons[16] in $(HOBO)_3$ and to the strong Raman line at 451 cm.$^{-1}$ observed in $(CH_3BO)_3$ by Goubeau and Hummel.[8] The latter workers also reported two medium intensity Raman lines at 170 and 232 cm.$^{-1}$ for the methyl compound, and one of these may be associated with ν_{10}. We estimate ν_{10} as 200 cm.$^{-1}$ in $(BO_2^-)_3$ ion.

In the Raman active A_1' species, our assignment may be compared to Raman lines[8,16] reported at 1155, 807, and 539 cm.$^{-1}$ in $(CH_3BO)_3$ and at 819 and 598 cm.$^{-1}$ in $(HOBO)_3$. Although we took 1138 cm.$^{-1}$ as ν_1, the infrared band at 1166 cm.$^{-1}$ is equally satisfactory for this mode. The remaining Raman active modes are in the E'' species, and here we took for ν_{13} the 717 cm.$^{-1}$ band which was described previously in reference to Fig. 7 as a D_{3h} forbidden but C_{2v} allowed infrared band. Our preference of assigning 717 cm.$^{-1}$ to ν_{13} rather than to ν_4 is based upon intensity considerations. Under C_{2v} symmetry both ν_{13} and ν_{11} will belong to the same symmetry, and hence the intensity of ν_{13} can be enhanced through Fermi resonance with the strong ν_{11} band. Such interaction would not be possible if the 717 cm.$^{-1}$ was ν_4, and consequently we would expect its intensity to be much weaker. For ν_{14} we took the medium intensity band at 280 cm.$^{-1}$ reported by Goubeau and Hummel[8] in $(HOBO)_3$. We attempted to look for this band using the Perkin-Elmer Model 21 instrument with CsBr prism, but we were not able to confirm its existence. In this spectral region the absorption of the radiation by the prism becomes appreciable, and the presence of strong water absorption makes it difficult to detect weak absorption bands even if the instrument was flushed with dried air. However, $(CH_3BO)_3$ has two fairly intense Raman lines[8] near 200 cm.$^{-1}$ which must be fundamentals. One of these has been associated with ν_{10} earlier, and the remaining one must therefore be an E'' line. Hence it is not unreasonable to take at this time a value of 280 cm.$^{-1}$ for ν_{14}. We can offer no arguments at the present time for our choice of ν_4 and ν_5 in the inactive A_2' species either except that our values appear reasonable when they are compared to frequencies of similar modes in other symmetry blocks. Tests of such assignments of inactive modes and other low-frequency modes must be made by a normal coordinate analysis.

Conclusions

The alkali halide pressed disks of infrared spectroscopy are convenient systems in which unstable chemical species can be trapped for spectroscopic studies. These unstable species can be formed directly in the matrices by carrying out chemical reactions in them. In the present work, chemical reactions were initiated thermally, but other methods of initiation such as irradiation appear possible. Events occurring in the disks may be followed spectroscopically and by chemical means since the disks can be dissolved in liquids, ground under liquids and gases, or subjected to chemical analysis. Quantitative studies of solid-state reactions in these disks also are possible. Examples of such studies will be presented in subsequent reports.

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Mass Spectrometric Study of Phosphine and Diphosphine[1]

BY YASUO WADA AND ROBERT W. KISER

The appearance potentials of the principal positive ions in the mass spectra of phosphine, diphosphine, and phosphine and diphosphine containing various numbers of deuterium atoms are reported. Assignments of the probable processes of ionization and dissociation are made, consistent with the observed energetics. The molecular ionization potentials of phosphine and diphosphine are found to be 10.2 and 8.7 e.v., respectively. Based on the appearance potential of the $P_2H_3{}^+$ ion, it is suggested that the vapor phase decomposition of diphosphine, to give PH_3 and a solid of approximate composition P_2H, proceeds through the intermediate P_2H_3.

Introduction

Only a relatively few phosphorus compounds have been studied mass spectrometrically. In an attempt to learn more of the properties of the gaseous ions containing phosphorus and their origin in electron impact experiments, we have studied the two hydrides, PH_3 and P_2H_4. It has been found that because of the ease of decomposition of diphosphine, the $P_2H_3{}^+$ and $PH_x{}^+$ ions are not formed by simple dissociative ionization of diphosphine. Further, some evidence is presented which leads us to believe that the thermal decomposition of diphosphine may proceed through the intermediate P_2H_3.

Experimental

The samples of phosphine and diphosphine were prepared by hydrolyzing calcium phosphide in a vacuum system.[2] The impure phosphine gas generated by the hydrolysis was dried by passing it through a soda-lime column. The diphosphine present was separated from the phosphine by condensing it in a CO_2–acetone trap. White, crystalline phosphine was trapped out at liquid nitrogen temperature and was purified by repeated sublimations. The diphosphine trapped in the CO_2–acetone bath was then repeatedly distilled at low temperatures until a reasonably pure sample was obtained. Low voltage mass spectrometry was used to judge the approximate purities of the samples prepared and used. The samples of deuteriophosphine and deuteriodiphosphine were prepared in similar manner, but deuterium oxide was used in the hydrolysis.

Only fresh samples were used in our studies. Particular care was taken to do so in the case of diphosphine, since decomposition is known to occur.[2] After several hours, yellow deposits were easily observable on the walls of the sample flasks, so that the individual studies with diphosphine samples were necessarily hurried.

The ionization and appearance potentials were determined using a time-of-flight mass spectrometer, described previously.[3] The experimental ionization efficiency curves for the phosphine study were interpreted using the extrapolated voltage differences method[4] and the method of Lossing, Tickner, and Bryce.[5] The results were checked using the energy compensation technique.[6] The voltage scale was calibrated using krypton (ionization potential = 14.00 e.v.) mixed intimately with the sample. For the diphosphine study, we used only the energy compensation technique, since we wished to obtain the results quickly, before serious decomposition of the samples occurred. To partially compensate for lack of precision in the determinations, repeated measurements were made, using a fresh sample each time.

Results

The mass spectral cracking patterns and appearance potentials for ions from the phosphines and diphosphines are given in Tables I to IV. The relative abundances are reported for 70-e.v. electrons. The probable processes shown in Tables I and II were arrived at from considerations of the energetics, as is indicated in the Discussion. The heats of formation of

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(1) This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-751 with Kansas State University. It is a portion of a dissertation to be presented by Y. Wada to the Graduate School of Kansas State University in partial fulfillment of the requirements for the Ph.D. degree.

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