Hydrides, Inc., Beverly, Mass.), have given maximum yields of 97% diammoniate.

Approximately equimolar amounts of diammoniate of diborane and ammonia-borane have been synthesized in the apparatus in Fig. 1. Diborane was dispersed in tetrahydrofuran at −78° to form $THF \cdot BH_3$. About 10 ml. of liquid NH_3 was distilled onto the THF solution and the system was stirred for approximately 1 hr. at −78°. Ammonia and THF were distilled away and H_3NBH_3 was extracted with ether from the remaining solid mixture of ammonia–borane and diammoniate of diborane.

TABLE I
POWDER DIFFRACTION DATA[a]
FOR THE DIAMMONIATE OF DIBORANE

Relative intensity	*d*, Å.	Relative intensity	*d*, Å.
w	7.60	m	2.68
vw	6.69	m	2.59
w	5.99	w	2.51
w	5.37	w	2.40
w	5.13	m	2.31
vs	4.63	w	2.14
vs	4.25	m	2.089
w	4.05	vw	1.986
w	3.88	w	1.788
vw	3.62	w	1.753
vs	3.50	w	1.732
vw	3.10	w	1.696
m	2.93	m	1.667
m	2.83		

[a] Cu Kα radiation.

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A New Compound, Boron Triiodide–Phosphorus Triiodide

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Lewis acid–base complexes of BBr_3 with PCl_3 and PBr_3 have been reported by Holmes.[1] Garrett and Urry[2] report a complex between B_2Cl_4 and PCl_3. This subject has also been reviewed recently by Stone.[3] In work relating to the preparation of boron phosphide, the authors have recently synthesized a new compound, boron triiodide–phosphorus triiodide, $I_3B{:}PI_3$. The only earlier reported results on iodides of boron and phosphorus are those of Moissan,[4] who reported the reaction $2BI_3 + 3P \rightarrow 2BPI_2 + PI_2$. Heating the BPI_2 in hydrogen produces BPI and finally BP.

Experimental

Synthesis.—Phosphorus triiodide is prepared from the elements in carbon disulfide solution, a modification of the method of Germann and Traxler.[5] Boron triiodide is also prepared directly from the elements using the method of McCarty and Carpenter.[6] For the synthesis of $I_3P{:}PI_3$, BI_3 (about 0.1 mole) in 100 ml. of CS_2 is added to 200 ml. of CS_2 containing PI_3 (about 0.1 mole). The purple color of the latter solution indicates the presence of excess iodine. A yellow precipitate forms immediately, which is collected by filtering and washed with CS_2 until the filtrate is colorless. All operations are performed under a helium atmosphere. The material is then vacuum dried and stored in an inert atmosphere.

The boron content was determined by the quinalizarin method,[7] the phosphorus by the magnesium pyrophosphate method,[8] and the iodine by precipitation as AgI.[9] *Anal.* Calcd. for $I_3B{:}PI_3$: B, 1.34; P, 3.86; I, 94.8. Found: B, 1.33; P, 3.85; I, 97.4. This would correspond more closely to $BPI_{6.2}$; the excess iodine probably is the result of iodine occlusion in the precipitate.

Results

Properties.—The compound formed does not melt below 225° but some decomposition is observed even below this temperature. The vapor pressure at 20°

TABLE I
X-RAY STRUCTURE OF IODIDE COMPOUNDS[a]

BPI_6		BI_3		PI_3	
I/I_0	*d*, Å.	I/I_0	*d*, Å	I/I_0	*d*, Å.
m	3.57	m	3.71	vw	4.70
w	3.39	w	3.49	m	3.67
m	3.30	s	3.18	w	3.52
m	3.23	vw	2.79	vw	3.28
w	3.19	m	2.55	s	3.19
s	3.09	w	2.30	vw	2.83
w	2.84	s	2.035	m	2.55
w	2.74	w	1.955	vw	2.32
vw	2.55	w	1.87	m	2.05
vw	2.47	m	1.785	m	2.02
vw	2.42	m	1.71	vw	1.96
w	2.16	w	1.685	vw	1.84
m	2.10	w	1.65	m	1.79
w	1.99	w	1.59	m	1.725
w	1.90	vw	1.54	w	1.66
w	1.87	vw	1.452	w	1.64
m	1.795	w	1.435	vw	1.60
m	1.775	m	1.375	vw	1.545
vw	1.74			w	1.44
vw	1.72			vw	1.38
vw	1.705			vw	1.37
vw	1.695				
+15 very weak lines down to 1.1 Å.					

[a] I/I_0 = relative intensity; I_0 is the intensity of the strongest line. s, strong; m, medium; w, weak; vw, very weak.

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[6] L. V. McCarty and D. A. Carpenter, *J. Electrochem. Soc.*, **107**, 38 (1960).

[7] D. Boltz, Ed., "Colorimetric Determination of Non-metals," Interscience Publishers, New York, N. Y., 1958, p. 343.

[8] J. H. Hildebrand, *et al.*, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 702.

[9] Reference 8, p. 734.

determined by the gas saturation method,[10] is 0.09 mm. The chemical analysis of sublimed material is approximately the same as before sublimation. The solubility in CS_2 is about 0.05 g./100 ml., and in benzene about 0.2 g./100 ml. The material tends to decompose slowly in both solvents. X-Ray diffraction patterns of $I_3B:PI_3$, PI_3, and BI_3 were obtained with a Debye–Scherrer powder camera (Table I). The results shown in this table indicate the pattern of the compound does not correspond to the patterns of the reagents used.

Hydrogen iodide is evolved when the material hydrolyzes at room temperature in water or with moisture in air. In dry air it reacts slowly with the evolution of iodine. Nitric acid reacts rapidly with the material with the evolution of iodine. Vapor phase decomposition of the material at 900° in an inert atmosphere produces a gray coating on the reactor wall. X-Ray patterns of this material correspond to the published pattern for cubic boron phosphide.[11]

(10) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Company, New York, N. Y., 1954, p. 448.

(11) J. Perri, ASTM Card Index No. 11-119.

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The Kinetics of Aquation of Bromopentaaquochromium(III) Ion in Acidic Solution[1]

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The aquation of inner-sphere complexes of chromium(III) ion in acidic solution generally proceeds *via* several pathways with which are associated transition states containing different numbers of protons. The relative importance of the several pathways is of interest, as are the associated activation parameters. The present study deals with aquation of bromopentaaquochromium(III) ion

$$Cr(OH_2)_5Br^{2+} + H_2O = Cr(OH_2)_6^{3+} + Br^-$$

in acidic solution ($[H^+] = 0.06$–$1.0\ M$) of constant ionic strength ($I = 1.0\ M$). In solutions with this range of acidity, the rate law established by this study is

$$-\frac{d \ln [CrBr^{2+}]}{dt} = k_0 + k_{-1}[H^+]^{-1}$$

A term first order in hydrogen ion, observed for aquation of analogous species with relatively basic ligands (*e.g.*, azide ion[3a] and fluoride ion[3b]), is not observed for this species with a less basic ligand. Measurements were made at 30, 45, and 60°.

Experimental Details and Results

Acidic solutions containing bromopentaaquochromium(III) ion, hereafter called bromochromium(III) ion, as the only species containing either bromide ion or chromium(III) ion were prepared in the following way. Chromium(III) perchlorate solution was prepared by reduction of potassium dichromate with hydrogen peroxide in perchloric acid solution. After excess hydrogen peroxide was decomposed by heating the solution, oxygen was removed by aeration with carbon dioxide; then chromium(III) ion was reduced to chromium(II) ion with lightly amalgamated zinc. Bromochromium(III) ion was prepared by reaction of chromium(II) ion with bromine,[4] the excess of which was removed by extraction with carbon tetrachloride. After absorption of bromochromium(III) ion onto Dowex 50-W, X-8 resin (100–200 mesh), bromide ion was rinsed from the column with chilled 0.1 *M* perchloric acid, followed by elution of cationic bromochromium(III) ion with 0.8–1.0 *M* perchloric acid. Solutions prepared in this way contained zinc ion. These stock solutions were stored at ~0° for use in kinetic experiments.

The bromide and chromium contents of solutions prepared in this manner were determined by applying standard procedures to portions of completely aquated complex (bromide by the Volhard method and chromium by spectrophotometry after conversion to chromate by alkaline peroxide). The ratio of concentrations of these elements was found to be 1.000 ± 0.003.

Lithium perchlorate solutions containing perchloric acid were prepared by reaction of reagent grade lithium carbonate with a slight excess of perchloric acid.

Reaction solutions were prepared by mixing stock solutions of perchloric acid, lithium perchlorate, and bromochromium(III) ion in perchloric acid. Aliquots, withdrawn at 7–9 different times during each kinetic experiment, were quenched with an approximately equal amount of ice. The resulting solution was analyzed for free bromide ion and, in some experiments, for unreacted bromochromium(III) ion also by an ion-exchange procedure coupled with the Volhard analysis for bromide ion. Uncomplexed bromide ion present in a quenched aliquot was washed from the column of cation-exchange resin with a limited volume of chilled 0.1 *M* perchloric acid. Then unreacted bromochromium(III) ion was eluted with chilled 0.8 *M* perchloric acid. This eluent was analyzed for bromide ion after allowing it to aquate completely, or for chromium by the spectrophotometric method already mentioned. Extents of reaction determined in the two ways, analysis for bromide ion produced or for unreacted bromochromium ion, agreed reasonably well. (The average difference of the concentrations of bromochromium(III) ion in twenty aliquots determined both ways was 4%.)

In each experiment, aquation conformed to a first-order rate equation

$$\frac{\Delta \ln [CrBr^{2+}]}{\Delta t} = k$$

to >95% reaction. The absence of retardation due to the reverse reaction is consistent with the known equilibrium quotient for the aquation reaction, which is ~270 at 45° and $I = 2.00\ M$.[5] For the initial concentration of bromochromium(III) ion employed (~0.01 *M*), the equilibrium extent of aquation of bromochromium(III) ion is ~99.5%. Values of the first-order rate coefficient k are presented in Table I. Treatment of these empirical rate coefficients to obtain rate parameters for each of the two pathways yielded the enthalpies and entropies of activation given in Table II[6]; values of k_0 and k_{-1} for 45°

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(2) N.S.F. Summer Research Participant from Rose Polytechnic Institute, Terre Haute, Ind.

(3) (a) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964); (b) T. W. Swaddle and E. L. King, forthcoming publication.

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(6) These values were obtained by T. W. Newton of the Los Alamos Scientific Laboratory using a least-square program written by R. H. Moore to obtain values of ΔH^* and ΔS^* for each term of a multi-term rate law using the original data at all temperatures.