allyl alcohol, however, stabilizes copper(I) and a two-step polarogram is observed. For the reduction of cupric ion at the dropping mercury electrode in the presence of allyl alcohol, the electrode reactions are, therefore, $Cu^{2+} + e + p$alc $= Cu(alc)_p^+$ and $Cu(alc)_p^+ + e + Hg = Cu(Hg) + p$alc.

The value of the ligand number, $p$, may be obtained from the shift of the polarographic half-wave potential with ligand concentration. Assuming that copper(II) is not complexed appreciably by allyl alcohol, the following approximate equation holds[3]

$$(E_{1/2})_c - (E_{1/2})_s = \pm 0.0591 \log \beta_p \pm 0.0591 p \log [\text{alc}]$$

In the equation above $(E_{1/2})_c$ is the half-wave potential observed in the presence of allyl alcohol, $(E_{1/2})_s$ is the half-wave potential observed in the absence of ligand, $\beta_p$ is the over-all formation constant of the complex species $Cu(alc)_p^+$, and [alc] is the alcohol concentration. The terms on the right-hand side of the equation are positive for the Cu(II),Cu(I) couple and negative for the Cu(I),Cu(Hg) couple. The above equation provides a method of evaluating from a single plot both the ligand number and the over-all formation constant of a complex species. For the Cu(I),Cu(Hg) couple a plot of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log [alc] should have a slope of $-0.0591 p$ and an intercept of $-0.0591 \log \beta_p$, whereas for the Cu(II),Cu(I) couple the plot should have a slope of $+0.0591 p$ and an intercept of $+0.0591 \log \beta_p$.

It is impossible to evaluate $(E_{1/2})_s$ directly for either the $Cu^+$,Cu(Hg) couple or the $Cu^{2+}$,$Cu^+$ couple. The standard potentials, *i.e.*, $+0.146$ v *vs.* sce for the $Cu^+$,Cu(Hg) couple and $-0.089$ v *vs.* sce for the $Cu^{2+}$, $Cu^+$ couple[4], have been used to approximate the values of the hypothetical half-wave potentials. The validity of such an approximation has been demonstrated for the case of copper in ammonia media.[5]

The half-wave potentials determined at allyl alcohol concentrations ranging from $1.00 \times 10^{-2}$ to $1.00$ $M$ are given in Table I. The potentials are averages of the values obtained at both the dropping mercury electrode and dropping copper amalgam electrode. The polarograms were obtained at $25 \pm 1°$.

## Results and Discussion

A plot of $(E_{1/2})_c - E°$ *vs.* log [alc] for the Cu(I), Cu(Hg) couple is linear throughout the alcohol concentration range examined. The slope of the plot is $-0.057$, corresponding to a ligand number, $p$, of 1.0. For the Cu(II),Cu(I) couple the plot is likewise linear with a slope of $+0.059$, corresponding to a $p$ value of 1.0. This latter result proves, as had been assumed, that there is no coordination between copper(II) and allyl alcohol. The formula of the complex is, therefore, $Cu(Alc)^+$.

The value of $\log \beta_1$ ($\beta_1 = [Cu(alc)^+]/[Cu^+][alc]$) calculated from the Cu(I),Cu(Hg) data is 4.8, and the

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, 2nd ed, Interscience Publishers, New York, N. Y., 1952, p 214.
(4) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, **22**, 279 (1961), and references given therein.
(5) I. M. Kolthoff and J. J. Lingane, ref 3, p 224.

### TABLE I
HALF-WAVE POTENTIALS[a] FOR THE Cu(II),Cu(I) AND Cu(I), Cu(Hg) COUPLES IN AQUEOUS MEDIA CONTAINING ALLYL ALCOHOL

| log [alc] | $(E_{1/2})_{Cu(II),Cu(I)}$ | log $\beta_1$[b] | $(E_{1/2})_{Cu(I),Cu(Hg)}$ | log $\beta_1$[c] |
|---|---|---|---|---|
| $-2.00$ | 0.065 | 4.6 | $-0.029$ | 5.0 |
| $-1.82$ | 0.074 | 4.5 | $-0.037$ | 4.9 |
| $-1.70$ | 0.073 | 4.4 | $-0.042$ | 4.9 |
| $-1.52$ | 0.092 | 4.6 | $-0.051$ | 4.9 |
| $-1.40$ | 0.094 | 4.5 | $-0.061$ | 4.9 |
| $-1.30$ | 0.105 | 4.6 | $-0.066$ | 5.0 |
| $-1.15$ | 0.107 | 4.5 | $-0.072$ | 4.8 |
| $-1.00$ | 0.126 | 4.6 | $-0.080$ | 4.8 |
| $-0.82$ | 0.129 | 4.5 | $-0.089$ | 4.8 |
| $-0.70$ | 0.136 | 4.4 | $-0.096$ | 4.8 |
| $-0.52$ | 0.148 | 4.5 | $-0.106$ | 4.8 |
| $-0.40$ | 0.155 | 4.5 | $-0.115$ | 4.8 |
| $-0.30$ | 0.161 | 4.5 | $-0.120$ | 4.8 |
| $-0.15$ | 0.171 | 4.6 | $-0.126$ | 4.8 |
| 0.00 | 0.185 | 4.7 | $-0.133$ | 4.7 |

[a] Volts *vs.* sce, average of values taken at both the dropping mercury electrode and dropping copper amalgam electrode. [b] Log $\beta_1$ calculated from copper(II),copper(I) couple. [c] Log $\beta_1$ calculated from copper(II),copper(Hg) couple.

value calculated from the Cu(II),Cu(I) data is 4.5. The average value of log $\beta_1$ is $4.7 \pm 0.2$, identical with the value[1] determined from solubility measurements.

The allyl alcohol complex of copper(I) can be readily prepared in aqueous solution by refluxing a mixture of cupric perchlorate, 5 $M$ allyl alcohol, and $1 \times 10^{-2}$ $M$ $HClO_4$ in contact with copper metal. If the alcohol is distilled off, the blue color of the cupric ion reappears and copper metal is precipitated.

### Experimental Section

Polarograms were obtained with a Sargent Model XV polarograph. The dropping mercury electrode was of the conventional design; the dropping copper amalgam electrode was especially designed to protect the amalgam from air oxidation.

Fisher sodium perchlorate, purified, was used as supporting electrolyte. Allyl alcohol, Fisher Certified Reagent, was used without further purification. The source of copper(II) was G. F. Smith cupric perchlorate. The concentration of copper(II) in solution was $5 \times 10^{-4}$ $F$ and was approximately the same in the amalgam. The solutions were deoxygenated with Air Products nitrogen.

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CONTRIBUTION FROM THE AIR FORCE CAMBRIDGE
RESEARCH LABORATORIES, OFFICE OF
AEROSPACE RESEARCH, BEDFORD, MASSACHUSETTS

## A Study of Boron Halide–Phosphorus Halide Complexes

BY A. F. ARMINGTON, J. R. WEINER, AND G. H. MOATES

Boron triiodide–phosphorus triiodide is used as an intermediate in the preparation of boron phosphide films.[1] In an effort to find a more volatile intermedi-

(1) R. F. Mitchell, J. A. Bruce, and A. F. Armington, *Inorg. Chem.*, **3**, 915 (1964).

ate, a study was made of other boron halide–phosphorus halide (iodine, bromine, chlorine) complexes. The results of this study are discussed in this paper. Comparison is also made to the results of other workers for compounds of this series which have been previously reported in the literature.

### Experimental Methods and Results

The complexes were formed by adding approximately 0.1 mole of the phosphorus halide to approximately 0.1 mole of the boron halide dissolved in 100 ml of carbon disulfide cooled to −40°. Carbon disulfide is used since the complexes are relatively insoluble in this solvent while the boron and phosphorus halides are soluble in carbon disulfide. Thus excess reagents can be removed by simple washing in carbon disulfide. The carbon disulfide was cooled to determine if some of the complexes might be stable at lower temperatures but unstable at room temperatures. Since the complexes are sensitive to moisture, and oxygen (to some extent), all operations were performed in a dry helium or argon stream.

Standard reagent grade starting materials were used except for boron triiodide which was prepared and purified by the authors.[2]

The boron content was determined by the quinalizarin method[3] and the phosphorus was determined as magnesium ammonium phosphate.[4]

For halide analysis, the complexes were weighed and transferred to a separatory funnel containing trichloroethylene and ether. A very dilute $HNO_3$ solution was added to hydrolyze the sample. The reduced halides were extracted and determined as the silver salt. Where two halides were involved, it was assumed that both halides were present in equimolar amounts.

*Anal.* Calcd for $I_3B$=$PI_3$: B, 1.34; P, 3.86; I, 97.4. Found: B, 1.33; P, 3.83; I, 97.4.

*Anal.* Calcd for $I_3B$=$PBr_3$: B, 1.5; P, 4.7; I, 57.6; Br, 36.3. Found: B, 1.6; P, 7.2; I, 47.7; Br, 30.1.

*Anal.* Calcd for $I_3B$=$PCl_3$: B, 1.9; P, 5.9; I, 72.1; Cl, 20.1. Found: B, 1.2; P, 4.8; I, 67.1; Cl, 21.0.

*Anal.* Calcd for $Br_3B$=$PI_3$: B, 1.5; P, 4.5; I, 57.6; Br, 36.3. Found: B, 1.8; P, 5.8; I, 50.2; Br, 24.9.

*Anal.* Calcd for $Br_3B$=$PBr_3$: B, 2.1; P, 5.9; Br, 92.0. Found: B, 2.0; P, 5.4; Br, 89.9.

In this study six complexes were formed. These complexes are all the boron triiodide and boron tribromide adducts with the three phosphorus halides. No boron trichloride complexes were detected even at −40°.

$I_3B$=$PI_3$ is an orange solid, stable under vacuum, and sublimes slowly at 100°. This complex forms easily at room temperature.

$I_3B$=$PBr_3$, also orange colored, is stable under vacuum to about 80°. It sublimes slowly at about 65°. It also can be formed at room temperature. $I_3B$=$PCl_3$ is a yellow-white solid which undergoes halogen exchange at 35°. $Br_3B$=$PI_3$ is also a yellow solid which decomposes near 50°; it can be formed at room temperature. $Br_3B$=$PCl_3$ is a white solid which decomposes on standing at 0°.

### Discussion

Cross halogenation (exchange of halogens between boron and phosphorus) occurs in the phosphorus trichloride compounds with both boron bromide and boron triiodide, resulting in the formation of boron trichloride. The boron bromide–phosphorus chloride converted overnight at 0°, while the boron triiodide–phosphorus trichloride was stable at room temperature

(2) A. F. Armington, R. F. Mitchell, and G. F. Dillon, *Trans. AIME,* **230,** 350 (1964).

(3) D. F. Boltz, "Calorimetric Determinations of Non-Metals," Interscience Publishers, New York, N. Y., 1958, p 343.

(4) N. H. Furman, Ed, "Scott's Standard Methods of Chemical Analysis," 5th ed, D. Van Nostrand, New York, N. Y., 1939, p 696.

for several weeks, but cross halogenated rapidly when heated to 35°. However, $I_3B$=$PBr_3$ and $Br_3B$=$PI_3$ did not appear to be cross-halogenated even after heating at 100° (15 min). In an infrared study Cowley and Cohen[5] were also unable to detect cross halogenation in $Br_3B$=$PI_3$.

The order of stability of the complexes is $BI_3$ > $BBr_3$ > $BCl_3$, in agreement with Cook,[6] who investigated boron halide complexes with xanthone. For the phosphorus halides, the order of stability is $PI_3$ > $PBr_3$ > $PCl_3$. Cook also reports the relative stability of $BBr_3$ and $BI_3$ complexes is very close, which is probably the reason no exchange is found between $Br_3B$=$PI_3$ and $I_3B$=$PBr_3$.

The results for the boron trichloride–phosphorus trichloride complex are in agreement with Holmes,[7] who found no compound formed, but disagree with Steiber,[8] who did report a compound between these reagents which was not stable above 0°. Neither of these workers employed a solvent in their reactions, but used direct mixing of the reagents. The authors also made several attempts to produce this complex using no solvent and were unsuccessful in all attempts. No previous work on other boron chloride compounds with phosphorus tribromide or triiodide could be found. $PI_3$=$BBr_3$ was recently reported by Cowley and Cohen[5] using a technique similar to that employed in this work. Holmes[7] also reported synthesizing $Br_3B$=$PBr_3$ with a melting point of 61°, similar to the value reported in this study.

(5) A. H. Cowley and S. T. Cohen, *Inorg. Chem.,* **4,** 1200 (1965).

(6) D. Cook, *Can. J. Chem.,* **41,** 522 (1963).

(7) R. R. Holmes, *J. Inorg. Nucl. Chem.,* **12,** 266 (1960).

(8) A. Steiber, *Compt. Rend.,* **195,** 610 (1932)

Contribution from Aerospace Corporation, El Segundo, California

## Data for $LaTaO_4$ and $PrTaO_4$, a New Structure Type, and a Series of New Rare Earth Compounds, $K_{0.5}Ln_{0.5}Ta_2O_6$, with the $PbNb_2O_6$ Structure

By G. M. Wolten and A. B. Chase

Several authors, by comparing unpublished powder patterns, have concluded[1-4] that $LaTaO_4$, $CeTaO_4$, and $PrTaO_4$ do not have the fergusonite structure ($YNbO_4$) assumed by the remaining rare earth orthotantalates and all the rare earth orthoniobates.

It proved easy to prepare single crystals of $LaTaO_4$

(1) H. P. Rooksby and E. A. D. White, *Acta Cryst.,* **16,** 888 (1963).

(2) A. J. Dyer and E. A. D. White, *Trans. Brit. Ceram. Soc.,* **63,** 301 (1964).

(3) V. S. Stubican, *J. Am. Ceram. Soc.,* **47,** 55 (1964).

(4) C. Keller, *Z. Anorg. Allgem. Chem.,* **318,** 89 (1962).