solid tetrahedral chromium(II) compounds. Gruen and McBeth[11] presented spectral evidence for such a tetrahedral species from the spectrum of $CrCl_2$ in a KCl–LiCl eutectic. They assigned a band at 9800 cm^{-1} ($\epsilon \sim 45$) to the $^5E \leftarrow {}^5T_2$ absorption in T_d symmetry. Other bivalent first-row transition metal ions give typical tetrahedral spectra in this melt. In a CdS(s) crystal, the spectrum[12] and paramagnetic resonance[13] have suggested that the chromium(II) occupies a slightly distorted tetrahedral site. A spectral band near 5500 cm^{-1} is reported.[12] Thus a 4300 cm^{-1} separation exists between what presumably is the $^5E \leftarrow {}^5T_2(T_d)$ absorption of chromium(II) in the two media studied. This apparent discrepancy could be due to the presence of a *distorted* tetrahedral arrangement (compare with the data on $CuCl_4^{2-}$ in ref 1) about the chromium(II) in the eutectic.

The spectrum[14] of $CrCl_2$ in anhydrous $AlCl_3$(l), where octahedral holes exist, shows a band slightly different in position from the band in the eutectic. Unfortunately, intensities could not be measured.[14] Anhydrous $CrCl_2$, which contains six-coordinate[15] chromium(II), also shows a band[9] at nearly the same frequency. The reflectance spectrum suggests the intensity ($\epsilon \sim 1$–10) of this band is not significantly different from that[9] of other six-coordinate chromium(II) complexes, however.

Unlike copper(II) chloride,[16] there is no evidence for MCl_4^{2-} formation in acetonitrile or ethanol on addition of excess chloride.

With $CrBr_2 \cdot 2CH_3CN$, however, spectral changes consistent with solvolysis[17] occur in acetonitrile (Figure 1). Addition of bromide causes a shift of the principal visible absorption to lower energy and a fourfold increase in the extinction coefficient. Qualitatively similar changes occur when tetrahedral MX_4^{2-} complexes of the other bivalent transition metals are formed[18] in this solvent.[3]

While the extinction coefficient rules out the formation of a centrosymmetric six-coordinate $CrBr_6^{4-}$ ion, the absorption appears at rather higher energies than predicted for a regular tetrahedral species and, in fact, appears near the energy of the $CrCl_4^{2-}$ band in the KCl–LiCl eutectic.[11] Thus one reasonably concludes that a distorted tetrahedral anion predominates in the solution.

As indicated previously, all attempts to isolate a tetrahedral CrX_4^{2-} complex failed. Unfavorable radius ratios[19] may be responsible in part for this since chromium(II) is the largest bivalent, first-row transition metal ion which gives any evidence at all for tetrahedral anion formation. We are currently attempting to correct these unfavorable size effects by preparing complexes of the type L_2CrX_2, where L is sterically large.

Acknowledgments.—The support of the National Science Foundation, GP-4253, and the donors of the Petroleum Research Fund is gratefully appreciated.

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(14) H. A. Øye and D. M. Gruen, *Inorg. Chem.*, **3**, 836 (1964).

(15) J. W. Tracy, N. W. Gregory, E. C. Lingafelter, J. D. Dunitz, H. C. Mez, R. E. Rundle, C. Scheringer, H. L. Yakel, Jr., and M. K. Wilkinson, *Acta Cryst.*, **14**, 927 (1961).

(16) A further difference between copper(II) and chromium(II) is obvious from the acetonitrile complexes themselves. The chromium(II) halides form complexes with two CH_3CN molecules while copper(II) chloride and bromide form mono(acetonitrile) complexes. Attempts to prepare[7] $CuCl_2 \cdot 2CH_3CN$ were not successful.

(17) Solvolysis of some transition metal halides in nonaqueous solvents has been discussed previously. For example, the articles by S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961), and D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962), consider the various complexes formed with cobalt(II) halides in a number of solvents, *i.e.*, $[MX_4]^{2-}$, $[MX_3S]^-$, $[MX_2S_2]$, etc., where X = Cl, Br, I and S = solvent. Equilibria, leading to the formation of similar complexes, are thought to exist in the $CrBr_2$–CH_3CN solution.

(18) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959). These authors also stated that a later paper would consider tetrahedral Cr(II), but such a paper has not appeared.

(19) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., Chapter X.

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Polarographic Investigation of the Allyl Alcohol Complex of Copper(I) in Aqueous Solution

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Received September 8, 1965

An investigation of the solubility of cuprous chloride in aqueous solutions of allyl alcohol has shown that copper(I) ion forms a 1:1 complex with allyl alcohol.[1] A stability constant of $10^{4.7}$ was determined for the species $Cu(alc)^+$. The investigation was complicated, however, by the formation of the chloride complexes $CuCl_2^-$ and Cu(alc)Cl.

Using polarography we have determined the formation constant of the allyl alcohol complex of copper(I) in aqueous media 0.1 M in $NaClO_4$. The concentration of allyl alcohol ranged from 1.00×10^{-2} to 1.00 M. Half-wave potential values were obtained for both the Cu(I),Cu(Hg) couple and the Cu(II),Cu(I) couple at both the dropping mercury electrode and the dropping copper amalgam electrode. In the former case copper(II) was added to the solution as the perchlorate and in the latter case copper was not present in solution. The values of $E_{3/4} - E_{1/4}$ for all the polarographic waves fell within the range of 0.056–0.060 v, indicating reversibility of the electrode reactions.[2] The half-wave potentials measured at the mercury electrode were in close agreement with the half-wave potentials obtained at the amalgam electrode.

The polarographic reduction of Cu^{2+} to Cu(Hg) at the dropping mercury electrode (or oxidation of Cu(Hg) to Cu^{2+} at the dropping copper amalgam electrode) in aqueous noncomplexing media proceeds *via* a one-step, two-electron process. The addition of

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(1) R. M. Keefer, L. J. Andrews, and R. E. Kepner, *J. Am. Chem. Soc.*, **71**, 3906 (1949).

(2) J. Tomes, *Collection Czech. Chem. Commun.*, **9**, 12, 81, 150 (1937).

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, $Cu^{2+} + e + p\text{alc} = Cu(\text{alc})_p^+$ and $Cu(\text{alc})_p^+ + e + Hg = Cu(Hg) + p\text{alc}$.

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, β_p is the over-all formation constant of the complex species $Cu(\text{alc})_p^+$, 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 $-0.0591p$ and an intercept of $-0.0591 \log \beta_p$, whereas for the Cu(II),Cu(I) couple the plot should have a slope of $+0.0591p$ 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 1.00×10^{-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 ± 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, $Cu(\text{Alc})^+$.

The value of $\log \beta_1$ ($\beta_1 = [Cu(\text{alc})^+]/[Cu^+][\text{alc}]$) calculated from the Cu(I),Cu(Hg) data is 4.8, and the value calculated from the Cu(II),Cu(I) data is 4.5. The average value of $\log \beta_1$ is 4.7 ± 0.2, identical with the value[1] determined from solubility measurements.

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 β_1[b]	$(E_{1/2})_{Cu(I),Cu(Hg)}$	log β_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 β_1 calculated from copper(II),copper(I) couple. [c] Log β_1 calculated from copper(II),copper(Hg) couple.

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 1×10^{-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 5×10^{-4} F and was approximately the same in the amalgam. The solutions were deoxygenated with Air Products nitrogen.

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[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.

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

A Study of Boron Halide–Phosphorus Halide Complexes

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Received September 13, 1965

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-

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