[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

The Reaction of 2-Vinylpyridine with Copper(II) Chloride

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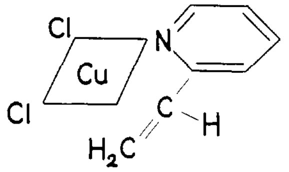
Continuous variations experiments in absolute alcohol showed that 2-vinylpyridine and copper(II) chloride react to form dichloro-(2-vinylpyridine)-copper(II). This compound was also isolated. Its reactions lead to the conclusion that both the nitrogen atom and the double bond are attached to the copper atom. No 2-vinylpyridine complex was formed in aqueous solution.

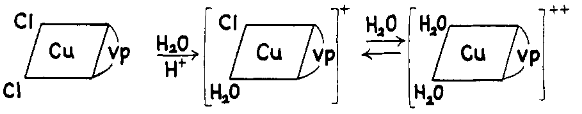
The compound 2-vinylpyridine should be able to form coördination compounds through the nitrogen atom (in the manner of pyridine), through the double bond (in the manner of styrene[2]), or through both at the same time. Therefore, an investigation was made of the ability of 2-vinylpyridine to form complexes with copper(II) chloride.

Using the method of continuous variations developed by Vosburgh, *et al.*,[3,4] we have found that in absolute alcohol copper(II) chloride and 2-vinylpyridine unite in a 1:1 ratio to give dichloro-(2-vinylpyridine)-copper(II), $Cu(C_7H_7N)Cl_2$. This compound was obtained as a brown powder by the interaction of anhydrous copper(II) chloride and 2-vinylpyridine in 95% alcohol. It is only slightly soluble in water but the addition of a few drops of acid increases the solubility and makes possible the preparation of moderately concentrated solutions. These aqueous solutions vary from a light yellow to a golden yellow as the concentration increases.

A study of its reactions leads us to propose the following structure for dichloro-(2-vinylpyridine)-copper (II)



Being an inner complex its water solubility would be expected to be slight. Solubility in acid is probably brought about by hydrolysis which can be represented as

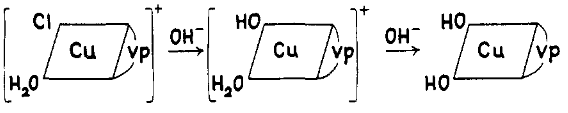


I II III

Evidence for the equilibrium between structures II and III was obtained from the analytical determination of the chloride ion with silver nitrate. It was noted that during each titration, coagulation of the silver chloride precipitate took place at a point roughly corresponding to the titration of one chloride ion but that further addition of the reagent was needed to reach an endpoint. This, however, fell short of the theoretical value.

A very striking property of dichloro-(2-vinylpyridine)-copper (II) is its behavior in basic solutions. When a few drops of ammonium hydroxide was added to slightly acid solutions of the complex, a deep wine-red color was instantly formed which could easily be seen in concentrations as low as 10^{-5} to 10^{-6} molar. Other weak bases, such as sodium carbonate, cause the same coloration. No such color is observed when base is added to 2-vinylpyridine in the absence of copper. The red color is destroyed by the addition of acid to give the original yellow color. The behavior of the system was like that of an acid-base indicator. Dilute sodium or potassium hydroxide gave a more intense coloration and soon produced a brownish-black precipitate.

The changes are explainable on the basis of the following hypothetical reactions



II IV V

in which IV is the soluble wine-red compound and V is the brownish-black dihydroxy-(2-vinylpyridine)-copper (II).

Doering and Weil[5] have shown that concentrated aqueous sodium bisulfite reacts rapidly and completely with 2-vinylpyridine to give β-(2-pyridyl)-ethylsulfonic acid which is quite resistant to hydrolysis by both acids and bases. If this reagent is added to solutions of dichloro-(2-vinylpyridine)-copper (II), the color changes from golden yellow to greenish yellow. Addition of ammonium hydroxide now produces no red color; sodium hydroxide causes the precipitation of a bulky orange product. We believe that the wine-red color formed by bases is dependent on the presence of a copper-olefin linkage and that the addition of sodium bisulfite destroys this unsaturation, thereby preventing the formation of compound IV. Using this color as a qualitative test for the copper-olefin linkage, it was found that heating with strong nitric acid or sulfuric acid did not disrupt this linkage in compound I.

It is of interest to note that no such complex resulted when 2-vinylpyridine was added to aqueous solutions of copper(II) chloride. Instead, a new hydroxychloride of copper, $5CuO \cdot 2CuCl_2 \cdot 7H_2O$, was formed.

Experimental

Continuous Variations Experiment.—Extinction values were determined by a Bausch and Lomb Universal Spectro-

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[1] Taken from part of a dissertation submitted by John F. Pudvin to the Graduate School of the University of Buffalo in partial fulfillment of the requirements for the Ph.D. degree.

[2] J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

[3] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[4] R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

[5] W. E. Doering and R. A. N. Weil, THIS JOURNAL, **69**, 2461 (1947).

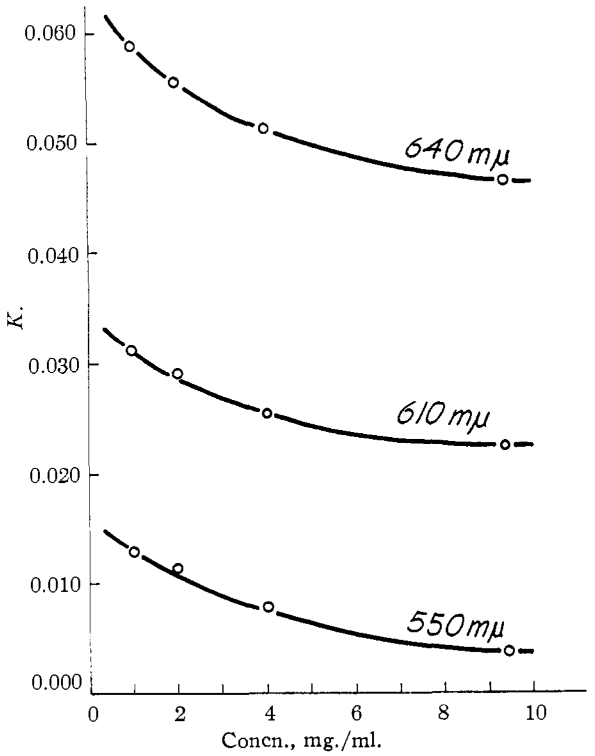

Fig. 1.—Specific extinction coefficient for copper(II) chloride in absolute alcohol.

photometer containing a polarization photometer. Since anhydrous copper(II) chloride[6] dissolved in absolute alcohol does not obey Beer's law, the specific extinction coefficient, *k*, was determined as a function of concentration at three wave lengths (640, 610 and 550 μ). These data are shown in Fig. 1. Following the procedure of Vosburgh and Cooper,[3] a series of solutions was prepared containing different mole fractions, *X*, of 2-vinylpyridine[7] and extinction coefficients measured. The difference, *Y*, between the observed extinction and that calculated on the basis of no complex formation was plotted as a function of X. Figure 2 shows a series of such curves prepared from a stock solution of 4.04 g./l. of copper (II) chloride in absolute alcohol for the wave lengths 640, 610 and 550 mμ. The maximum at 640 mμ is seen to be very close to 0.50 indicating a 1:1 complex. The maxima at the lower wave lengths are shifted somewhat to higher mole fractions. This indicates that other complexes, such as CuCl$_2$·2C$_7$H$_7$N, are probably present in the solution.

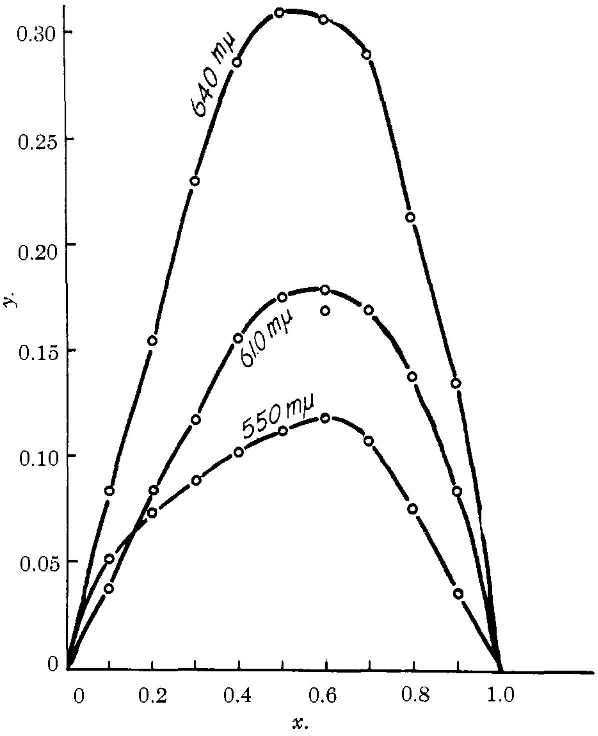

Fig. 2.—Continuous variations experiments for copper(II) chloride and 2-vinylpyridine in absolute alcohol.

Dichloro-(2-vinylpyridine)-Copper(II).—Ten ml. (0.0955 mole) of 2-vinylpyridine was added to a solution of 6.4 g. (0.0474 mole) of anhydrous copper(II) chloride in 100 ml. of 95% alcohol. The color of the solution changed immediately from a dark green to black. A black viscous tar formed within 2 minutes and was transferred to another beaker where it was boiled gently with fresh alcohol to give a brown powdery precipitate. Alternate centrifugation and boiling with alcohol was continued until the supernatant liquid was pale green. The product was dried at room temperature under vacuum. The yield was 10 g. (85%).

Anal. Calcd. for CuC$_7$H$_7$NCl$_2$: Cu, 26.52; Cl, 29.60. Found: Cu, 26.25; Cl, 27.05.

Reaction of 2-Vinylpyridine and Copper(II) Chloride in Aqueous Solution.—Ten ml. (0.0955 mole) of 2-vinylpyridine was added slowly with rapid stirring to a solution of 12.5 g. (0.0735 mole) of copper(II) chloride dihydrate in 100 ml. of water. A light-green, finely divided precipitate formed immediately. Centrifugation and washing with water was repeated until the supernatant liquid was colorless. The product was dried in a desiccator over calcium chloride. The yield was 3-4 g.

Anal. Calcd. for 5CuO·2CuCl$_2$·7H$_2$O: Cu, 56.11; Cl, 17.89. Found: Cu, 56.30; Cl, 17.62.

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(6) Obtained from Eimer and Amend. It was heated in a drying oven at 135° for several days prior to use.

(7) Obtained from Reilly Tar and Chemical Corporation and purified as needed by vacuum distillation.