sublimed aluminum chloride and sealed off *in vacuo*. One of these weighed ampules was placed in a side arm of the reaction tube and broken with a glass-enclosed magnetically operated hammer. The aluminum chloride was sublimed into place, the side arm sealed off and the fragments of the glass ampule collected and weighed. The technique was thoroughly tested both as to the quantitativeness of the transfer and the purity of the aluminum chloride samples.[10]

Action of Water on Aluminum Chloride.—A number of observations were made of the action of water on anhydrous aluminum chloride. Although the objective of the experiments, catalysis of the combination of hydrogen chloride and aluminum chloride, was not attained, the results are of considerable interest in their own right.

To a sample of 0.79 g. of aluminum chloride (5.98 mmoles) in the reaction tube, cooled to −80°, 0.132 mmole of gas-free water was added as vapor. The temperature was raised to 24°; the pressure in the tube rose to 9 mm. In the course of 70 min. the pressure rose slowly to 12 mm. The tube was heated at 100° for 5 hours. The final pressure observed was 25 mm. at 24°. The gas was pure hydrogen chloride, 1.40 moles per mole of water added. As mentioned previously the product did not absorb hydrogen chloride at low temperatures.

Additional water, 0.76 mmole, was added to the product of the previous experiment and the treatment repeated. An additional quantity of hydrogen chloride, 0.94 mmole, was recovered. This represents 1.23 moles per mole of water added.

Pines and Wackher[6d] had previously noted similar phenomena in the action of water on aluminum bromide: treatment with an equimolar quantity of water yielded 1.25 moles of hydrogen bromide per mole of water. Treatment with 2 moles and 3 moles of water, respectively, yielded only 1.06 and 0.85 moles of hydrogen bromide per mole of water. A satisfactory explanation of these observations would be desirable.

Aluminum Chloride, Hydrogen Chloride and Neohexane.—The neohexane (Phillips Petroleum Company, Research Grade) was introduced into the vacuum apparatus and placed over sublimed aluminum chloride for 15 minutes at 25°. The neohexane was distilled over sublimed aluminum chloride for 15 minutes at 25°. The neohexane was distilled away and placed on fresh aluminum chloride. After 15 minutes at room temperature there was observed only a very faint color formation.

Neohexane was measured as a liquid in a calibrated vessel of the high vacuum apparatus. A magnetically operated agitator was introduced to facilitate attainment of equilibrium with the hydrogen chloride. In spite of extended contact with aluminum chloride and hydrogen chloride at temperatures between 22 and −87°, no chemical interaction was noted. The individual components were quantitatively recovered in pure state; no color formation was observed.

LAFAYETTE, IND.

RECEIVED OCTOBER 16, 1950

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[10] Both aluminum and chlorine were determined by the method of Snyder, *Anal. Chem.*, **17**, 37 (1945).

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. I. Copper(II) Complex with *o,o'*-Dihydroxyazobenzene[1]

BY HANS B. JONASSEN, MAE M. COOK AND JOHN S. WILSON

The complex compound formed between the dye *o,o'*-dihydroxyazobenzene and copper(II) ion has been investigated by spectrophotometric and conductometric methods. A previously postulated one to one copper(II) dye complex was verified. Experimental evidence is presented for the formation of a copper(II) dye-monohydroxy complex in the presence of potassium hydroxide. Further addition of the base seems to break up the complex forming the potassium salt of the dye and the copper hydroxy complex $Cu(OH)_5^{-3}$. The coördinatively unsaturated copper(II) dye complex seems to make possible the formation of a copper hydroxy complex anion without the precipitation of copper hydroxide.

Ortho-substituted azo dyes form stable lakes with most of the transition metals. Melting points indicated that in the lakes of ortho-hydroxy azo compounds, the metal ion displaced a hydrogen of the hydroxyl groups and that it coördinated to one of the nitrogen atoms of the azo group.[2]

Drew and Landquist[3] reported a one to one coördinatively unsaturated complex between *o,o'*-dihydroxyazobenzene and copper(II) ion based on analytical methods verified by the formation of monopyridine and monoquinoline compounds with the Cu(II)–dye complex.

An investigation was undertaken to verify the structure of the Cu(II)–dye complex and to study the behavior of this complex in the presence of excess potassium hydroxide.

A. Absorption Studies

Experimental.—Absorptions were determined between the wave lengths of 360 and 800 mμ with a Beckman spectrophotometer, model DU, using 1-cm. matched corex cells and standard solutions of 0.0002 *M* in 95% alcohol. *o,o'*-Dihydroxyazobenzene, prepared according to the literature, was recrystallized from methanol, m.p. 172–173°. C.P. Baker Analyzed $CuCl_2 \cdot 2H_2O$ was dried for 24 hours over partially dehydrated $CuSO_4 \cdot 5H_2O$.

Figure 1 shows the absorptions of the solutions of the dye and of the mixture of dye and copper salt. The absorption of the latter (0.0002 *M*), alone, was below 0.02 at all wave lengths measured.

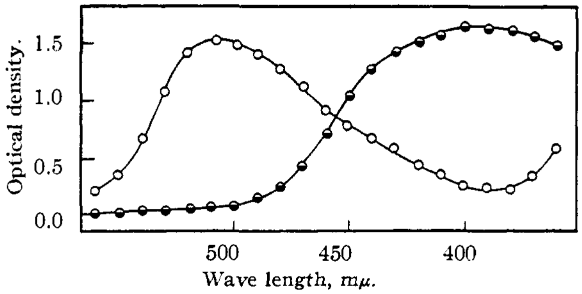

Fig. 1.—Absorption spectra of 0.0002 *M* *o,o'*-dihydroxyazobenzene, ●; and 0.0001 *M* Cu(II)-*o,o'*-dihydroxyazobenzene, ○.

Using the continuous variation method as modified by Vosburgh and Cooper[4] the Cu(II)–dye complex solutions of 0.0002 *M* $CuCl_2 \cdot 2H_2O$ and 0.0002 *M* dye in 95% alcohol were mixed in varying proportions such that the total solute

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[1] Presented in part before the Physical and Inorganic Section of Southwide Chemical Conference, Atlanta, Georgia, October 16–18, 1950.

[2] M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

[3] H. D. K. Drew and J. K. Landquist, *ibid.*, 292 (1938).

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

concentration was the same in each solution. The optical density of the resulting solution was measured at 510 and 380 mμ, where the difference in absorption of the dye and Cu(II)-dye complex was greatest. The difference between the calculated optical density and observed optical density was plotted against the mole ratio of dye in Fig. 2.

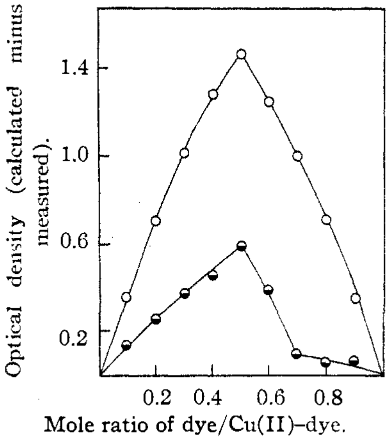

Fig. 2.—Continuous variation study of *o,o'*-dihydroxyazobenzene and Cu(II): ○, 510 mμ; ◒, 380 mμ.

Since a difference between the observed and calculated values occurred, with a minimum at a mole ratio of one dye molecule to one copper(II) ion, a one to one compound must be formed. This is in agreement with the analytical results.

B. Conductometric Titration of Copper(II) Ions and *o,o'*-Dihydroxyazobenzene

The conductance of the solution was measured by Kohlrausch's method, using a cell with vertical platinized electrodes.

An aqueous solution of 0.142 millimole of $CuCl_2 \cdot 2H_2O$ was diluted to 230 ml. and titrated at 23° with a 0.01 *M* alcoholic solution of the dye. Figure 3 shows the resulting conductance curve. The complex precipitated immediately in the aqueous solution as a brown flocculent solid.

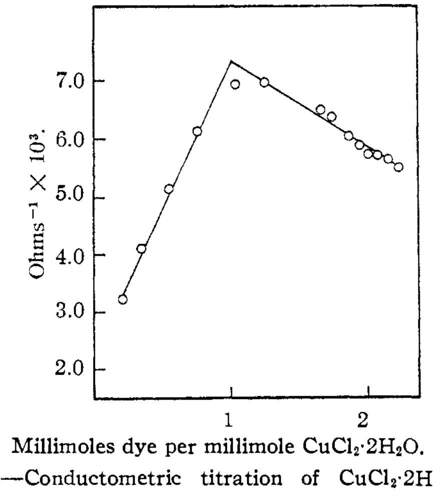

Fig. 3.—Conductometric titration of $CuCl_2 \cdot 2H_2O$ with *o,o'*-dihydroxyazobenzene.

The break in the conductance curve occurred at 14.4 ml. of 0.01 *M* dye solution. This indicates a one to one compound between the dye and the copper(II) ion. The increase in conductance up to the equivalence point is due to the displacement of the hydrogens of the hydroxyl groups in the dye by the copper(II) ions.

C. Spectrophotometric Titrations

An 0.00025 *M* solution of the dye in 95% alcohol was freed from oxygen by bubbling with nitrogen for two hours, mixed with varying amounts of potassium hydroxide, and the optical density was measured at 525 mμ under nitrogen.[5] The plot of optical density against millimoles of potassium hydroxide per millimole of dye is shown in Fig. 4.

Addition of potassium hydroxide increased the optical density of the dye solution changing the color from reddish-orange to deep red. The breaks at one and two equivalent amounts of potassium hydroxide indicate that it reacts with the dye in a stepwise fashion giving the dipotassium salt. Further addition of potassium hydroxide has no effect upon the optical density of the solution.

Using the same precautions, 0.000125 *M* solutions of the Cu(II)-dye complex were prepared in 95% alcohol by mixing equal amounts of the dye and $CuCl_2 \cdot 2H_2O$ and measured at 525 mμ in the presence of varying amounts of potassium hydroxide. The results are shown in Fig. 4.

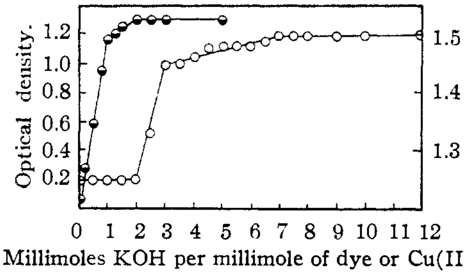

Fig. 4.—Spectrophotometric titrations of *o,o'*-dihydroxyazobenzene, ◒; and Cu(II)-*o,o'*-dihydroxyazobenzene, ○; with KOH. Optical density measured at 525 mμ. Scale on right refers to copper compound.

No increase in optical density occurred until two equivalents of potassium hydroxide were added. The third equivalent, however, produced a marked increase. From the fourth to the seventh equivalent a slow increase in optical density was observed. Further addition of the base produced no change in absorption characteristics.

Since two hydrogen ions were released by the reaction of the copper(II) ion and the dye, the first two hydroxide ions react with these. The third apparently goes in the coördination sphere of the copper(II) ions to form the new Cu(II)-dye-hydroxy complex with rapid increase in optical density. Further addition of potassium hydroxide seems to break up the complex giving the potassium salt of the dye.

Since no copper precipitates and four more hydroxyl ions are necessary to reach the maximum optical density, a Cu(II)-hydroxy complex seems to be formed. With one hydroxyl ion already in the coördination sphere of the copper(II) ion and four more added, the complex formed seems to be $[Cu(OH)_5]^{-3}$. This does not obviate a coördination number of six for copper(II) ions in which the sixth position is occupied by a solvent molecule.

The postulation of a coördination number larger than four for the copper(II) ion is in accord with the work of Bjerrum[6] and of Jonassen, LeBlanc and Rogan[7] in Cu(II) amine complexes.

New Orleans 15, La. Received March 16, 1951

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(5) The system autoxidizes in the presence of air.

(6) J. Bjerrum and J. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

(7) H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, This Journal **72**, 4968 (1950).