

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA**Reactions of Triethylamine with Copper(I) and Copper(II) Halides¹**

By JOHN T. YOKE III, JOSEPH F. WEISS, AND GORDON TOLLIN

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Triethylamine forms 1:1 complexes with anhydrous copper(I) halides, for which the stability sequence $\text{Cl} > \text{Br} > \text{I}$ is observed. Similarly, a 1:1 complex is formed by trimethylamine and copper(I) bromide. Triethylamine and anhydrous copper(II) chloride and bromide undergo an oxidation-reduction reaction. Oxidation of amines by copper(II) appears to be quite general and is found to occur under a variety of conditions. Stoichiometric measurements, e.p.r. spectra, and studies on related amine-triethylammonium chlorocuprate(I) systems permit a proposal for the course of the oxidation-reduction reaction in general terms.

Introduction

The ability of simple tertiary aliphatic amines such as triethylamine to form metal coordination compounds has been discussed recently.² Complexes of triethylamine with copper(I) or copper(II) halides have not been reported. Addition of triethylamine to aqueous solutions containing Cu^{+2} ion results in the precipitation of hydrous copper(II) oxide, which shows no tendency to redissolve in excess amine.³ Simon and co-workers⁴ have studied copper(II) chloride and bromide systems with ethyl- and mono-, di-, and trimethylamines. Their 20-mm. isobaric temperature-composition phase diagrams indicate in general formation of a series of complexes at temperatures below 0°. Such complexes lose part of the base reversibly on warming to about room temperature. The resulting lower complexes undergo irreversible decomposition on further heating.

We have studied the interaction of triethylamine with anhydrous copper(I) and copper(II) halides by isothermal measurement of the pressure of the systems as a function of composition, in the manner previously described.²

Results and Discussion

A. Copper(I) Halides.—The pressure-composition isotherms at 25.0° for the triethylamine systems with copper(I) chloride and bromide are shown in Fig. 1. A sharp break at mole ratio 1.0 was observed in each case. The dissociation pressures of the 1:1 complexes at 25.0° were too small to be measured on a mercury manometer. The chloride complex lost weight very slowly at room temperature when the tube containing it was opened directly to the vacuum line pumping system, while the bromide complex was clearly less stable by this criterion. Copper(I) iodide formed a similar 1:1 complex with triethylamine. The pressure-composition isotherms at 25.0, 35.0, and 45.0° are given in Fig. 2. The dissociation pressures of the iodide

complex are appreciable. In a brief study of the copper(I) bromide-trimethylamine system a similar sharp decrease in pressure at mole ratio 1.0 was observed.

It has been shown² that anhydrous zinc halides do not interact with triethylamine at 25°. It is now found that moderately stable 1:1 triethylamine complexes of copper(I) halides do exist. That $d^{10} \text{Cu}^+$ is coordinated while the more highly charged $d^{10} \text{Zn}^{+2}$ is not may be attributed to the fact that copper(I) commonly exhibits a coordination number of two (colinear) while zinc normally requires a coordination number of four or six. It has been noted² that while tertiary aliphatic amines may form stable metal complexes, the coordination numbers shown by metals are commonly smaller than are observed in analogous ammonia and primary and secondary amine systems.

From the vapor pressure of triethylamine and the measured values of the dissociation pressure of the triethylamine complex of copper(I) iodide, the following thermodynamic values can be calculated for the process $\text{CuI (solid)} + (\text{C}_2\text{H}_5)_3\text{N (liquid)} \rightarrow \text{CuI} \cdot \text{N}(\text{C}_2\text{H}_5)_3 \text{ (solid)}$ at 25.0°: $\Delta F^\circ = -1.42 \text{ kcal./mole}$, $\Delta H^\circ = -8.21 \text{ kcal./mole}$; $\Delta S^\circ = -22.8 \text{ e.u.}$ These values include lattice and vaporization energy terms as well as coordinate bond energy. It seems probable that the bonding between Cu^+ and triethylamine is not very strong. Complex stability increases with decreasing size of the anion.

B. Copper(II) Halides. Pressure-Composition Measurements.—When anhydrous copper(II) chloride or bromide was treated with an excess of highly purified triethylamine at 25.0° with rigorous exclusion of moisture, nearly all the amine could be recovered at its equilibrium vapor pressure by distillation in the vacuum system, although some discoloration is apparent. An obvious reaction does occur when such small-scale systems are warmed to about 50°, with the development of a reddish black tarry reaction product. Since the reaction is markedly exothermic, when once started in bulk the heat given off is sufficient to spread reaction throughout the mass. Thus, autogenous reaction between 84 g. of anhydrous copper(II) chloride and 40 ml. of triethylamine under a nitrogen atmosphere in a round-bottom flask resulted in sudden intense heating of the flask in an almost violent process.

(1) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962. Aided in part by a grant from the American Cancer Society.

(2) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

(3) L. Tschugaeff, *Ber.*, **40**, 173 (1907).

(4) A. Simon, H. Hamann, and F. Arnold, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 531 (1962).

The reaction between triethylamine and copper(II) chloride was investigated in some detail. In Fig. 3 is shown the 25.0° isotherm displaying pressure as a function of the mole ratio of triethylamine to copper(II) chloride *originally* taken. Pressures were measured after the reaction mixture had first been heated to 90° for 1 hr. and then cooled to 25.0°. The reaction products did not appear to be soluble in the excess of triethylamine, which was removed at its equilibrium vapor pressure (66 mm.) down to a mole ratio of 2.0. This indicates that the over-all stoichiometry of the oxidation-reduction reaction involves two moles of triethylamine per mole of copper(II). The flat at 6 mm. pressure between mole ratio values of 2.0 and 1.0 corresponds to the reversible removal of one mole of triethylamine. The volatile material lost at 6 mm. was collected and shown to be pure triethylamine by gas chromatography. At mole ratio 2.0 the sample was a dark reddish gray solid; on removal of triethylamine down to mole ratio 1.0 the sample liquefied to a viscous dark red-brown oil.

Hydrolysis of Product.—The reaction product at mole ratio 1.0 was hydrolyzed and on working up gave a considerable amount of a crystalline white solid, identified as triethylammonium chloride.

The exact amount of unoxidized triethylamine bound in the oily product at the point corresponding to mole ratio 1.0 of the reactants was determined in a number of runs by hydrolysis of the reaction mixture and distillation of the volatile amine into an excess of standard hydrochloric acid. The results were somewhat variable, depending on the hydrolysis conditions. Digestion of the entire reaction product for several hours with strong sodium hydroxide liberated 91.95% of the original amine. If the unrecovered amine all corresponded to material which has been oxidized, then 0.0805 mole of amine was oxidized per mole of copper(II) chloride reduced. In two other runs, milder hydrolysis by trituration of the tarry product with water for 5 min. and for 30 min. and subsequent treatment of the aqueous portion with strong base liberated somewhat smaller fractions of the original oxidized per mole of copper(II) reduced. Recovery of unoxidized amine was probably incomplete for the shorter time of hydrolysis. The liberated alkylamine portions were isolated after the titrations. The amine was shown to be pure triethylamine by vapor phase chromatography and by melting point of the amine hydrochloride. Similar results were obtained when, in place of hydrolysis, the oxidation-reduction product was warmed with an excess of quicklime. Hence, although exactly 1.0 mole of triethylamine is bound per mole of copper in the nonvolatile reaction product, only a minor portion of it has been oxidized and most is bound in such a way that it is set free on hydrolysis.

E.p.r. Study.—Further elucidation of the nature of the reaction was obtained in an e.p.r. study of the copper(II) chloride-triethylamine system. An excess of triethylamine was transferred by means of the high vacuum system into a tube containing degassed an-

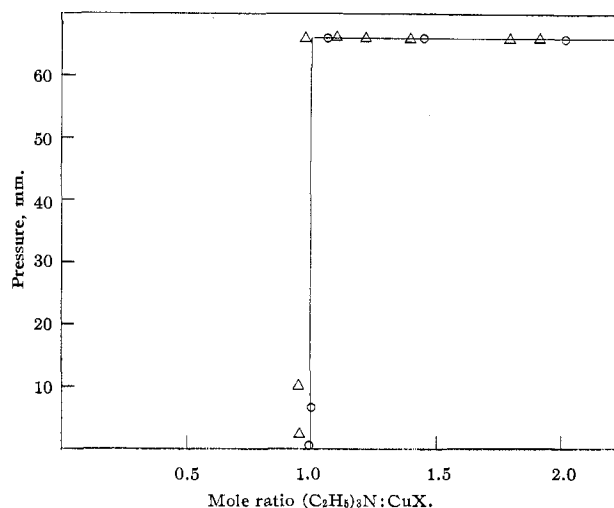


Fig. 1.—Isotherms (25°) for the systems CuX + (C₂H₅)₃N: Δ, CuCl; O, CuBr

hydrous copper(II) chloride. The tube was then sealed off *in vacuo* and placed in the cavity of the e.p.r. spectrometer. No interaction of the reagents was apparent, and only the broad resonance signal ($g = 2.2$) of paramagnetic d⁹ Cu(II) was observed. The tube was then heated to about 80° for about 2 min., allowed to cool, and returned to the spectrometer, this process being repeated several times. The initial action of the liquid triethylamine on the solid copper(II) chloride resulted in the appearance of a transient blue color, this being followed by the appearance of the dark red tarry material. The e.p.r. results are shown in Fig. 4. At intermediate stages of the reaction, sharp peaks were observed superimposed on the diminishing Cu(II) signal. This is consistent with a previous report of a free radical signal arising from this system.⁵ The superimposed peaks would also be consistent with species present in the reaction mixture in which the copper(II) ion is placed in a cubic crystalline field with a trigonal component.⁶ After five such heating cycles, paramagnetism had virtually disappeared, demonstrating reduction of d⁹ Cu(II) to d¹⁰ Cu(I), and also demonstrating the intermediate character of any other possible paramagnetic species.

Studies in Various Solvents.—Additional information concerning the oxidation-reduction reaction was obtained by a study of the copper(II) chloride-triethylamine system in alcohol. When a solution of copper(II) chloride dihydrate in alcohol was treated with excess triethylamine, a green gelatinous precipitate was formed at once. After being heated for 15 min. on a steam bath, the entire mixture formed a clear red solution. Exposure of this solution to the atmosphere at room temperature caused precipitation of a green crystalline substance identified as basic copper(II) carbonate, indicating reoxidation of the reduced copper species by air. When an excess of triethylamine was added to a solution of anhydrous copper(II) chloride in absolute alcohol in a nitrogen-filled drybox at room

(5) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(6) The authors are indebted to a referee for calling their attention to this point.

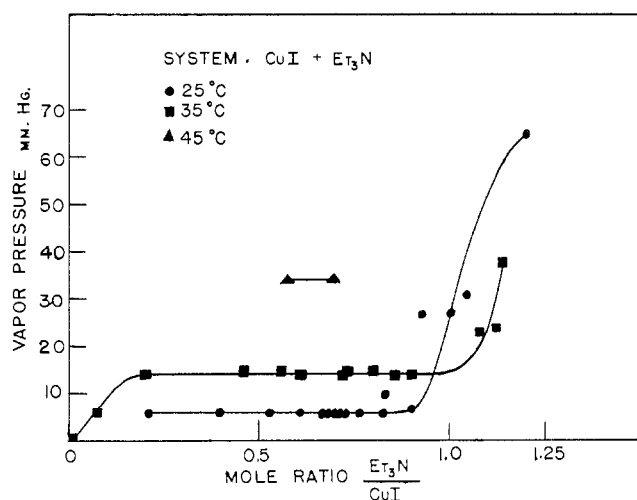


Fig. 2.—Isotherms for the system $\text{CuI} + (\text{C}_2\text{H}_5)_3\text{N}$.

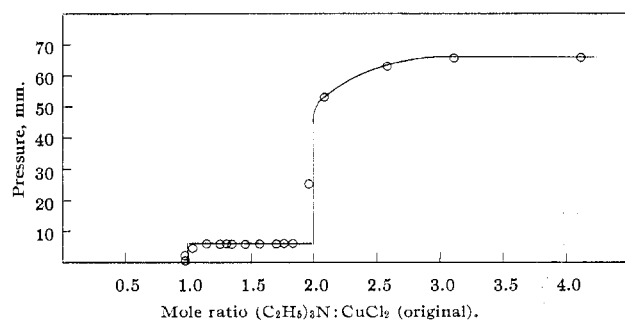


Fig. 3.—Isotherm (25°) for the $\text{CuCl}_2 + (\text{C}_2\text{H}_5)_3\text{N}$ oxidation-reduction reaction mixture (after heating at 90° for 1 hr.).

temperature, a red color slowly developed. Upon heating the mixture, a clear red solution was quickly formed. When pure oxygen gas was bubbled through this solution, a light green precipitate was formed, which was found to be primarily copper(I) chloride.

In an aqueous system, under nitrogen, excess triethylamine was added to copper(II) chloride and the minimum amount of hydrochloric acid was added to dissolve the hydrous oxide precipitate. The solution was maintained under reflux for 1 week. A slight amount of light green precipitate, identified as copper(I) chloride, was recovered. Apparently interaction of the reagents is almost negligible under these conditions. Triethylammonium tetrachlorocuprate(II) can be obtained from a triethylamine-copper(II) chloride-hydrogen chloride mixture in methanol, but not from aqueous systems.⁷

The oxidation-reduction reaction was carried out by adding triethylamine to a suspension of anhydrous copper(II) chloride in chlorobenzene. Copper(I) chloride was precipitated from the oily product by addition of water. Similarly, the tarry product from the reaction of the components in the absence of a solvent released copper(I) chloride on addition of water. When distillation of the water was undertaken at this point, the fore-run was found to contain slight amounts of more volatile material, which in part apparently was acetaldehyde.

(7) R. D. Whealy, D. H. Bier, and B. J. McCormick, *J. Am. Chem. Soc.*, **81**, 5900 (1959).

Triethylamine and copper(II) chloride undergo the oxidation-reduction reaction in homogenous solution in dimethyl sulfoxide and acetonitrile to give reddish solutions from which copper(I) chloride is precipitated on addition of water. The oxidation of amines by copper(II) appears to be very general and goes readily with trimethylamine, tri-*n*-butylamine, *N,N*-dimethylaniline, and *N*-methylaniline.

Role of the Metal Ion.—The oxidation-reduction reaction between amines and the d^9 copper(II) halides may be accounted for in terms of extreme polarization of the donor atom. The results in the absence of solvent suggest that there may be an appreciable energy of activation for the formation of an unstable copper(II) complex, or for the electron transfer, or both. Similar oxidation-reduction reactions involving trialkylamines have been observed previously with more highly charged metal ions. Instability of the titanium(IV) chloride-trimethylamine complex with respect to an oxidation-reduction reaction giving the titanium(III) chloride-trimethylamine complex has been reported,^{8,9} and triethylamine seems to behave similarly.⁹ Also, it has been noticed that on formation of the vanadium(IV) chloride-trimethylamine complex, some reduction to the vanadium(III) complex occurred.¹⁰

Course of the Reaction.—The experimental observations permit a general outline of the nature of the oxidation-reduction reaction to be drawn. The pressure-composition measurements show that the over-all stoichiometry of the reaction involves exactly two moles of triethylamine per mole of copper(II) chloride. Exactly one mole of triethylamine is subsequently recoverable at an equilibrium pressure of 6 mm. at 25° . Most of the remaining triethylamine can be liberated from the reaction mixture at this point by hydrolysis. Only a small fraction of a mole of triethylamine is oxidized per mole of copper(II) reduced.

The e.p.r. results show that the initially paramagnetic system containing d^9 Cu(II) is converted into a diamagnetic final product. The growth and decay of sharp peaks superimposed on the broad resonance are consistent with the presence of paramagnetic intermediates in the reacting mixture.

It is reasonable to postulate that the reaction is initiated by the formation of some sort of intermediate copper(II) chloride-amine complex, which in a one-electron-transfer process gives dichlorocuprate(I) and a positive radical ion. The dichlorocuprate(I) would be in equilibrium with copper(I) chloride and chloride ion. The triethylamine free radical ion may lose a proton from an α -carbon, triethylamine being the acceptor, this giving triethylammonium ion and a neutral radical, for which several electronic forms may be written. Such a species has been postulated previously in the initial step of oxidative deprotonation of triethylamine by copper(II), by 7,7,8,8-tetracyanoquino-

(8) M. Antler and A. W. Laubengayer, *ibid.*, **77**, 5250 (1955).

(9) G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 33 (1963).

(10) G. W. A. Fowles and C. M. Pleass, *ibid.*, 1674 (1957).

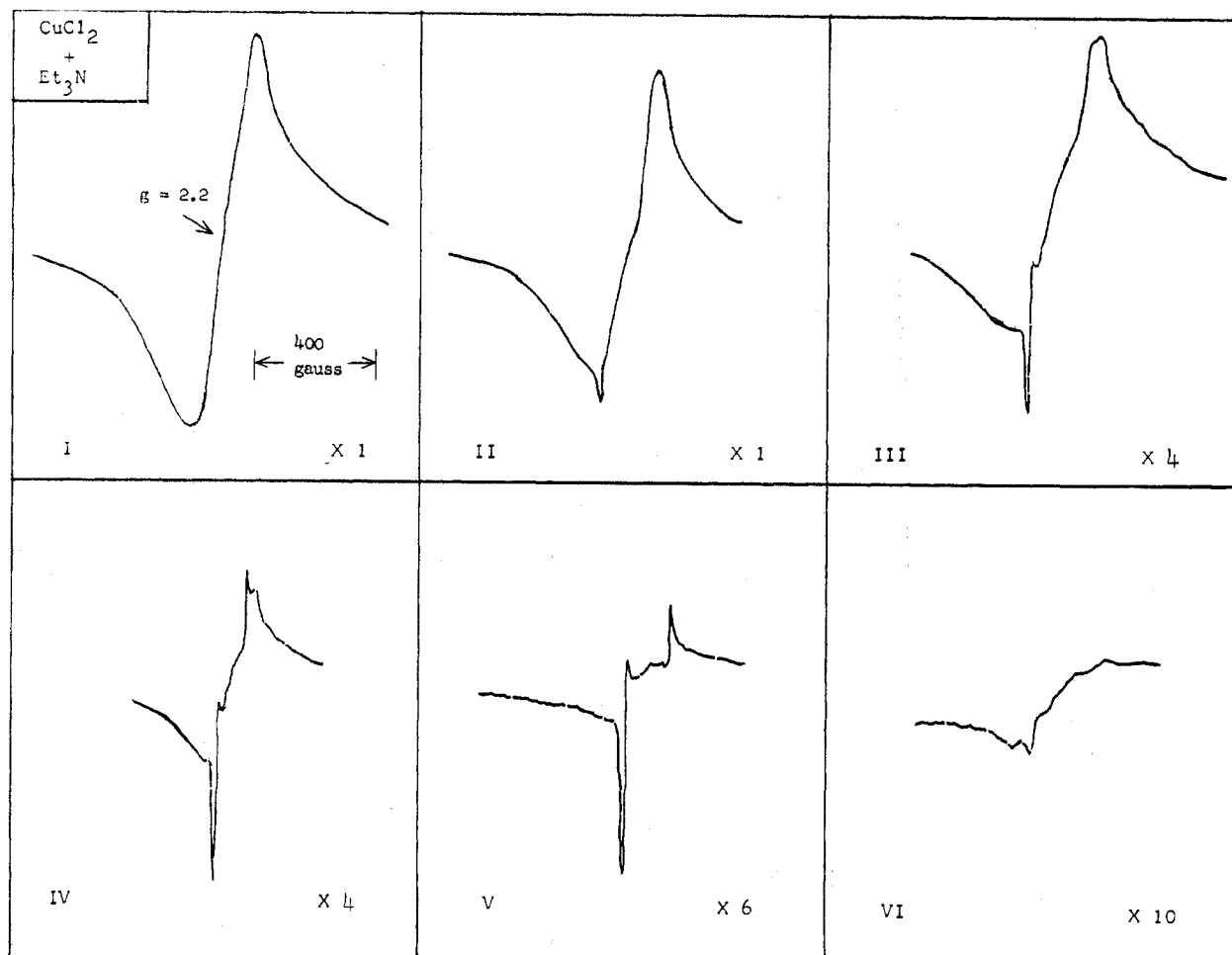


Fig. 4.—I: The e.p.r. signal of Cu(II) in the $\text{CuCl}_2 + (\text{C}_2\text{H}_5)_3\text{N}$ mixture before reaction. II–VI: Effect on the signal of successive heating cycles (see text). After five heating cycles the reaction mixture is nearly diamagnetic. The relative magnification of each signal is indicated.

dimethan, and by other oxidizing agents.¹¹ An identical species has been postulated to arise from the first step of the oxidation of triethylamine in aqueous solution by an excess of the paramagnetic oxidizing agent chlorine dioxide.¹² A second step of electron transfer and deprotonation then led to diethylvinylamine, the hydrolysis products of which, diethylamine and acetaldehyde, were isolated. In the copper(II) system, despite the fact that an excess of amine was commonly present, it appears that the product of initial oxidation is more sensitive to further oxidation, so that repeated steps of electron loss and deprotonation occur. Since each step of electron transfer reduces one copper(II) ion, and each step of deprotonation converts a triethylamine molecule into a triethylammonium ion, only a fraction of a mole of triethylamine undergoing oxidation serves to reduce one mole of copper(II) chloride to copper(I) chloride, one mole of triethylammonium chloride also being formed. Attempts to characterize the oxidation product are in progress.

Strong support for this postulate is found in the

(11) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); S. Dunstan and H. B. Henbest, *ibid.*, 4905 (1957); L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

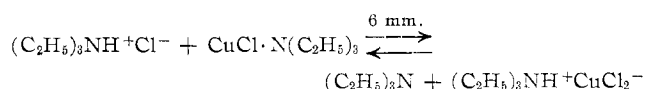
(12) D. H. Rosenblatt, *et al.*, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

work of Horner and Schwenk,¹³ who studied the oxidation of triethylamine by benzoyl peroxide. They concluded that six moles of the reduction product, benzoic acid, was formed per mole of triethylamine oxidized, and interpreted this in terms of abstraction of the six α -hydrogens in triethylamine. However, their actual experimental values ranged from 3.6 to 7.9 moles of benzoic acid formed per mole of triethylamine oxidized. The latter value would correspond closely to our results on unrecoverable amine.

Further support for the postulated course of the reaction is derived from the following additional experimental evidence. When pure anhydrous copper(I) chloride and triethylammonium chloride were placed together in equimolar amounts, even without mixing of the white powders a slightly discolored oil was quickly formed. When this oil was treated with an excess of triethylamine, and the excess of triethylamine then was removed by distillation at its vapor pressure of 66 mm. at 25°, one mole of triethylamine was retained per mole of each of the starting materials. The solid product so obtained lost the triethylamine at an equilibrium pressure of 6 mm. at 25°, giving back the original oil.

(13) L. Horner and E. Schwenk, *Ann.*, **566**, 69 (1950).

This behavior may be accounted for in terms of the equilibrium



The 6 mm. pressure then could correspond to the equilibrium constant of a reaction in which triethylamine is displaced from its copper(I) chloride complex by chloride ion. Alkylammonium dichlorocuprate(I) complexes have been reported previously.¹⁴ Apparently the triethylammonium compound is a nonvolatile liquid at room temperature. Triethylammonium chloride and the triethylamine copper(I) chloride complex by themselves have negligible vapor pressures at room temperature. A similar experiment using only triethylammonium chloride and triethylamine showed that there is no interaction between these two compounds at 25.0°. This behavior differs from that of the ammonium chloride-ammonia system.

When the triethylammonium dichlorocuprate(I) was treated with an excess of tri-*n*-butylamine, the triethylamine was displaced at a pressure of 8 mm. at 25°, showing that a less volatile amine can participate in this type of equilibrium. Since the equilibrium involves competition of a proton with copper(I) for the amine, differences in base strength are partly compensated. To account for the pressure-composition breaks of Fig. 3, coming at exactly 2.0 and 1.0 moles of amine per copper, it is necessary to suppose that the nonvolatile oxidation product, presumably a polymeric amine, can participate in this same alkylammonium chloride-dichlorocuprate(I) equilibrium at 6 mm. pressure.

In alcohol solution, the reaction product was attacked by oxygen, with release of copper(I) chloride. This may correspond in part to oxidation of the triethylamine bound in the reaction product, and in part to further oxidation of the tarry product. When the reaction product in alcohol is exposed to the atmosphere, the catalytic electron-carrying role of copper(I)-copper(II) is accompanied by slow removal of the copper(II) as the basic carbonate. In proposing such a copper-catalyzed oxidation of amines by oxygen, one may suppose that if some additional substance were present, which was a suitable reducing agent, the amine could be regenerated from its initial oxidation product. Indeed, copper-amine complex systems have been found to be effective catalysts for the oxidative polymerization of phenols¹⁵ and may be of biochemical importance in view of the finding that the activity of an amine oxidizing enzyme is associated with its copper(II) content.¹⁶

Experimental

The apparatus and techniques for the pressure-composition measurements have been described previously.² A Model V-

(14) H. Remy and G. Laves, *Ber.*, **66**, 571 (1933).

(15) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polymer Sci.*, **58**, 469 (1962).

(16) P. J. G. Mann, *Biochem. J.*, **79**, 623 (1961); H. Yamada and K. T. Yasunobu, *J. Biol. Chem.*, **237**, 3077 (1962).

4501 Varian 100 kc. modulation e.p.r. spectrometer was used in the paramagnetic resonance work. Vapor phase chromatograms were obtained using a Wilkens Aerograph instrument.

Materials.—Triethylamine was dried over phosphorus(V) oxide and further purified as previously described.² No trace of impurity could be detected by gas chromatography. A vapor pressure of 50.0 mm. was determined at 18.4°, and this was combined with the previously reported values³ and with values of 89.4 and 89.5° for the normal boiling point¹⁷ to give the equation

$$\log p = -1788/T + 7.8154$$

Trimethylamine was stirred at 0° with phosphorus(V) oxide and purified by trap to trap distillation in the vacuum system to give a tensiometrically homogeneous sample whose vapor pressures over a range of temperatures agreed with the literature values. Tri-*n*-butylamine was distilled from phosphorus(V) oxide, b.p. 210–212° (ca. 700 mm.). Triethylammonium chloride was prepared from pure triethylamine and anhydrous hydrogen chloride (Matheson) in absolute alcohol and recrystallized from alcohol; m.p. (sealed tube) 254°, lit. 254°. The material was stored in a vacuum desiccator over phosphorus(V) oxide. Copper(II) chloride dihydrate, reagent grade, was dehydrated by heating for 1 hr. at 110°, and copper(II) bromide, reagent grade, was dried by heating to nearly 200° in a stream of dry nitrogen.¹⁸ The anhydrous salts were stored in a vacuum desiccator. A commercial sample of copper(I) iodide, purified grade, was dried at 250° for 0.5 hr. in a stream of dry nitrogen. Copper(I) chloride and bromide were prepared from the copper(II) salts by the sulfite reduction technique,¹⁹ washed with acetone, and dried at room temperature *in vacuo*.

Copper(I) Halide-Triethylamine Complexes.—At the point corresponding to the removal of the excess of triethylamine from the systems equilibrated at 25.0° shown in Fig. 1 and 2, the samples were removed from the vacuum line to a nitrogen-filled drybox. The sample bulbs were opened and the contents were taken for analysis. Chloride was determined by the absorption indicator method, bromide and iodide were determined gravimetrically following sodium hydroxide fusion, and copper was determined by the iodine-thiosulfate method following oxidation of the copper by digestion of the complex with nitric acid.²⁰ Calculated values for copper and halide are based on the mole ratio of triethylamine to copper(I) halide determined by weighing the reaction tube at the point where all easily removable amine had been distilled off. *Anal.* Calcd. for $\text{CuCl} \cdot 0.93\text{N}(\text{C}_2\text{H}_5)_3$: Cu, 32.95; Cl, 18.38. Found: Cu, 33.00; Cl, 18.14. Calcd. for $\text{CuBr} \cdot 0.97\text{N}(\text{C}_2\text{H}_5)_3$: Cu, 26.30; Br, 33.09. Found: Cu, 26.54; Br, 32.92. Calcd. for $\text{CuI} \cdot 0.99\text{N}(\text{C}_2\text{H}_5)_3$: Cu, 21.86; I, 43.66. Found: Cu, 21.53; I, 42.88. From the values of the dissociation pressure of $\text{CuI} \cdot \text{N}(\text{C}_2\text{H}_5)_3$ (6.0, 14.5, and 34.0 mm. at 25.0, 35.0, and 45.0°, respectively), the following relation was calculated: $\log p = -3583/T + 12.7906$.

Copper(I) Bromide-Trimethylamine Complex.—In the same manner, it was observed that when a large excess of trimethylamine was distilled onto copper(I) bromide, the pressure of the system corresponded to the equilibrium vapor pressure of trimethylamine (682 mm. at 0°). Removal of the excess of amine gave a residue containing 1.017 moles of amine per mole of salt with a pressure of 7 mm. at room temperature. Further pumping gave a sample containing 0.95 mole of amine per mole of salt with a pressure of ca. 1 mm. at room temperature.

Hydrolysis of the Copper(II) Chloride-Triethylamine Oxidation-Reduction Product.—Material corresponding to the point at

(17) Lange's Handbook, 9th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1956; Handbook of Chemistry and Physics, 38th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1956.

(18) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., London, 1923, pp. 168, 197.

(19) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

(20) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., Macmillan Co., New York, N. Y., 1952, pp. 308, 544, 603.

mole ratio 1.0 in Fig. 3 was stirred with water and the mixture allowed to stand for 1 week. The discolored copper(I) chloride precipitate and much tarry polymer were separated by filtration and the filtrate was evaporated to dryness. The reddish residue was treated with alcohol and the mixture filtered. On crystallization a white solid was obtained. This was recrystallized and characterized as triethylammonium chloride m.p. (sealed tube) 254°.

Quantitative analysis of the material corresponding to mole ratio 1.0 of the reactants was undertaken by hydrolysis and distillation of volatile amine into an excess of standard acid, followed by back titration with standard base. Oxidation-reduction product obtained from 13.93 mmoles of copper(II) chloride, from which the excess of triethylamine was removed until no more could be pumped off, showed an increase in weight corresponding to 13.92 mmoles of triethylamine. The reaction tube was dropped into several hundred ml. of concentrated sodium hydroxide solution in a distillation assembly, and after distillation for several hours 91.95% of the amine was recovered. The tarry product was attacked extensively by the strong base, giving a yellow solution and yellow solid. To avoid the possibility that some of the volatile amine was formed by degradation of the tarry product, milder hydrolytic conditions were used in subsequent runs. The tarry reaction product was triturated with water, which caused some separation of copper(I) chloride. The aqueous phase was separated by filtration from the gummy mixture of precipitate and tarry oxidation product, the residue was washed several times with water, and the combined aqueous portions were added to strong base for analysis of volatile amine. A sample of oxidation-reduction product corresponding to 0.961 mole of amine per mole of copper, after treatment with water for 30 min., released 88.2% of its content of amine. A sample corresponding to a mole ratio value of 0.965, after treatment with water for 5 min., released 84.8% of its amine content.

After the volatile amine was distilled into standard hydrochloric acid, and the excess of acid determined by titration with sodium hydroxide, the resulting solutions were reacidified and evaporated to dryness. The residues so obtained were treated with strong lye and the pure volatile amine was recovered by distillation into a Dry Ice-cooled trap. The amine so obtained showed only one peak, identical with authentic triethylamine, in its vapor phase chromatogram, and was further shown to be pure triethylamine by conversion to the hydrochloride, m.p. (sealed tube) 254°. In one run, the reaction product corresponding to 0.975 mole of amine per mole of copper was decomposed and the volatile amine liberated by addition of calcium oxide rather than by alkaline hydrolysis. A fourfold excess of calcium oxide powder was added to the oxidation-reduction product by rotation of a side-arm addition tube about a joint in the system attached to the vacuum line. The mixture was then heated to 100°. The volatile amine was pumped off and collected in a cold trap; 92.95% of the amine content was set free.

The viscous oily product of the oxidation-reduction reaction under nitrogen between 94 g. of anhydrous copper(II) chloride and 50 ml. of triethylamine in a flask, formed after heating at 85° for 1 hr., was treated with 400 ml. of water. Distillation of the water was commenced, and a fore-run of a few ml. collected. The sample gave positive tests with 2,4-dinitrophenylhydrazine, sodium hypiodite, and Fehling's solution. Manganese dioxide was precipitated from an alkaline solution of the sample with potassium permanganate. The excess of permanganate was destroyed with sulfite, the manganese dioxide was removed by filtration, and the filtrate was evaporated to dryness. The residue was acidified with sulfuric acid, the solution was distilled, and the distillate was characterized as acetic acid; *p*-bromophenacyl ester, m.p. 86°, lit. 85°. It appears that the original reaction mixture gave a slight amount of acetaldehyde on hydrolysis. Additional evidence for this is that the fore-run of the distillation of water from the hydrolyzed reaction mixture gave a vapor phase chromatogram with two peaks preceding with water peak; one of these was matched by an authentic sample of acetaldehyde under the same conditions.

Copper(II) Chloride-Triethylamine Reaction in Various Solvents.—Evolution of heat and immediate formation of a gelatinous green precipitate occurred on the addition of 4.5 ml. of triethylamine to 1.5 g. of copper(II) chloride dihydrate in 20 ml. of absolute ethanol. An additional 20-ml. quantity of alcohol was added and the mixture was heated on a steam bath. After about 15 min. the reaction mixture had changed to a clear red solution. This solution showed no change over a period of 2 months when kept under nitrogen. After the reaction mixture had been exposed for several days to the atmosphere at room temperature, a green solid was removed by filtration, 95% alcohol being used for washing. Removal of additional amounts of precipitate was repeated several times until after 3 weeks no further precipitation was observed. The red filtrate was evaporated to dryness to give a residue which contained no copper. Analysis of the green precipitate shows that it contains no chlorine or nitrogen, and agrees with the composition of malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$, if it is supposed that 2% of the hydroxide is replaced by ethoxide. *Anal.* Calcd. for such a composition: Cu, 56.4; C, 6.36. Found: Cu, 56.4; C, 6.39. The behavior of the material on ignition clearly indicated the presence of some organic constituent. The red residue from the evaporation of the filtrate was extracted in a Soxhlet extractor with toluene. Most of the red material was insoluble. On cooling, discolored white needles were obtained, which were recrystallized from a toluene-1-butanol mixture. Qualitative tests indicated the presence of chloride ion and volatile amine, and chloride analysis agrees with the composition of triethylammonium chloride. *Anal.* Calcd. for $(\text{C}_2\text{H}_5)_3\text{NHCl}$: Cl, 25.76. Found: Cl, 25.33.

Under anhydrous conditions, 10 ml. of triethylamine was added to a solution of 2 g. of copper(II) chloride in 50 ml. of absolute alcohol. A deep blue precipitate of copper(II) ethoxide was formed at once, but before it could be completely removed by filtration at room temperature, a red color developed in the mixture. The filtrate was evaporated to give a red solid product, which was leached with a small amount of alcohol. Triethylammonium chloride was crystallized from the alcohol on addition of ether and was purified by recrystallization; m.p. and mixture m.p. (sealed tube) 253–254°.

Addition of 75 ml. of triethylamine to a suspension of 100 g. of anhydrous copper(II) chloride in 200 ml. of chlorobenzene resulted in progressive darkening of the reaction mixture and then separation of a dark oily phase. When a small amount of the dark oil was added to water, a slightly greenish precipitate of copper(I) chloride was formed (the insoluble salt reacted with nitric acid and the solution so formed gave positive tests for Cl^- and Cu^{+2}).

The solution obtained on dissolution of 1 g. of anhydrous copper(II) chloride in 10 ml. of dimethyl sulfoxide gave a copious green precipitate on standing. Addition of 2 ml. of triethylamine led to disappearance of the precipitate and the formation of a red solution. The reaction mixture was poured into water, and a white precipitate was formed, which was identified as before as copper(I) chloride.

When about 0.5 g. of copper(II) chloride was dissolved in 10 ml. of acetonitrile, a brown solution was formed. On addition of 1 ml. of triethylamine, darkening was observed, and on warming a clear red-brown solution was obtained. When this was poured into water, copper(I) chloride was precipitated as above.

Hydrochloric acid was added with stirring at 0° to a mixture of 1.0 g. of copper(II) chloride and 5 ml. of triethylamine in 25 ml. of water until the green gelatinous precipitate just dissolved. The mixture was refluxed for 1 week under nitrogen. Little change was noted. The reaction mixture became slightly darker in color, and upon addition of oxygen a very small amount of copper(I) chloride, identified as described above, precipitated from solution.

Oxidation of Other Amines.—Using the technique for measurement of pressure as a function of composition of the system, an excess of trimethylamine was distilled onto 9.65 mmoles of anhydrous copper(II) chloride in a tube on the vacuum system. A small portion of the copper(II) chloride dissolved, giving a

blue-green solution. The mixture was stirred magnetically for 1 hr. at 0.0° without any noticeable change. The trimethylamine was removed by distillation to another trap on the vacuum line, where it was kept at a temperature slightly below 0° so that its vapor, at an equilibrium pressure of 635 mm., was in contact with the copper(II) chloride in the reaction tube. The reaction tube was then heated in a water bath to 85°. Very suddenly the brown solid copper(II) chloride absorbed trimethylamine, causing the pressure in the system to drop and amine to distill back into the reaction tube. The product was a clear amber oil. Any excess of trimethylamine swept into the reaction tube was removed by pumping at room temperature; the gain in weight of the tube corresponded to the retention of 11.0 mmoles of trimethylamine in the reaction product; mole ratio 1.14.

When 1 ml. of tri-*n*-butylamine was added to a mixture of 1 g. of copper(II) chloride and 10 ml. of dimethyl sulfoxide, a deepening of the green color of the system was observed, and on warming a dark red oil slowly separated. On addition of water to the oil, a precipitate of copper(I) chloride was formed. Tri-*n*-butylamine caused precipitation of hydrous oxide when added to a solution of copper(II) chloride in 95% alcohol, and no reaction was observed on boiling this mixture for several minutes. When absolute alcohol was used, the solution darkened on addition of the amine, and on warming slowly took on a dark reddish brown opaque appearance.

Addition of *N*-methylaniline or *N,N*-dimethylaniline to a solution of copper(II) chloride in absolute alcohol led to immediate formation of violet to jet black solid products.

Reaction of Oxygen with the Copper(II) Chloride-Triethylamine Reaction Product.—When oxygen gas was bubbled through

the red solution obtained by the reaction of triethylamine with copper(II) chloride in mole ratio 2:1 in absolute alcohol, there was little change in the color of the solution but a precipitate was slowly formed. The dull green precipitate was removed by filtration and found, in the manner described above, to be mostly copper(I) chloride. Some oxidation to copper(II) had apparently occurred, but the major oxidative action was on the organic substance holding the copper(I) in solution. Evaporation of the filtrate gave a reddish product from which triethylammonium chloride was leached and identified as described previously.

Triethylammonium Dichlorocuprate(I)-Triethylamine System.—The liquid chlorocuprate(I) complex obtained from 5.03 mmoles of copper(I) chloride and 5.09 mmoles of triethylammonium chloride in a tube on the vacuum system was treated with triethylamine, and the excess of triethylamine was removed by distillation at 25° in the vacuum system. A sharp drop in pressure occurred at the point where 5.02 mmoles of triethylamine was retained in the reaction tube. The product was a white crystalline solid with a dissociation pressure of 6 mm. Triethylamine was then removed at this equilibrium pressure, this being accompanied by conversion of the solid back to an oil.

Triethylammonium Dichlorocuprate(I)-Tri-*n*-butylamine System.—Similarly, an excess of tri-*n*-butylamine was distilled in the vacuum system (vapor pressure < 1 mm. at 25°) onto the oil formed from triethylammonium chloride and copper(I) chloride. The system was not completely homogeneous. Volatile material was removed at an equilibrium pressure of 8 mm. at 25° and identified as triethylamine by conversion to the hydrochloride; m.p. and mixture m.p. (sealed tube) 254°.

CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN

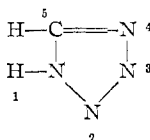
Complexes of Some 1-Substituted Tetrazoles and Cobalt(II), Nickel(II), Platinum(II), and Zinc(II) Chlorides

BY G. L. GILBERT AND C. H. BRUBAKER, JR.

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The compounds formed when zinc chloride, nickel chloride, and platinum(II) chloride react with 1-methyltetrazole, 1-cyclohexyltetrazole, and 1-phenyltetrazole in ethanol or tetrahydrofuran have the general formula MT_2Cl_2 (where T = 1-substituted tetrazole). The solids, with the exception of the zinc compounds, are insoluble in common solvents and decompose without melting upon heating. The complexes formed with zinc chloride are moderately soluble in tetrahydrofuran and ethanol and crystallize in clear, well-formed crystals from ethanol. Stability constant measurements with nickel in ethanol and cobalt in tetrahydrofuran yield similar values for the formation constants with 1-methyl- and 1-cyclohexyltetrazole.

Solid compounds resulting from the interaction of 5-substituted tetrazoles with silver, copper, iron(II), and cobalt have been reported¹⁻⁴ and the evidence indicated high stability due to anion formation by the tetrazole ring. Very little interaction occurs when both the 1 and 5 positions on the tetrazole are blocked. Examples of the formation of solid materials with 1-substituted



(1) N. A. Daugherty, Ph.D. Thesis, Michigan State University, 1961.

(2) N. A. Daugherty and C. H. Brubaker, *J. Am. Chem. Soc.*, **83**, 3779 (1961).

(3) C. H. Brubaker, Jr., *ibid.*, **82**, 82 (1960).

(4) H. Jonassen, J. Terry, and A. Harris, private communication.

tetrazoles are limited to the compound between platinum(IV) chloride and 1-ethyltetrazole.⁵ A formal similarity of the tetrazole ring to cyclopentadiene has prompted the further investigation of these ring systems. The present work concerns the preparation of solid complexes between zinc chloride, nickel chloride, and platinum(II) chloride and certain 1-substituted tetrazoles and studies of cobalt(II) and nickel(II) complexes in solution.

Experimental

Materials.—Reagent grade chemicals were used throughout this investigation. The tetrazoles used were prepared by the method of Herbst and Fallon,⁶ in the case of 1 phenyltetrazole, or

(5) E. Oliveri-Mandala and B. Alagna, *Gazz. chim. ital.*, **40**, II, 441 (1910).

(6) F. Fallon and R. M. Herbst, *J. Org. Chem.*, **22**, 933 (1957).