REACTIONS OF TERTIARY ALIPHATIC AMINES

WITH COPPER HALIDES

by

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THE UNIVERSITY OF ARIZONA

1964
I hereby recommend that this dissertation prepared under my direction by Joseph F. Weiss entitled Reactions of Tertiary Aliphatic Amines with Copper Halides be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy.

After inspection of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:

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SIGNED: Joseph F. Weiss
The research problem described in this dissertation derived from an original problem of much larger scope. The original problem was to investigate the chemical compounds and reactions occurring between transition metal halides and tertiary amines. The purpose of this investigation was to gain a better understanding of the nature of such compounds and their reactions with a view to clarifying the factors controlling complex formation and electron transfer processes in these systems. Modifications of such systems may have biochemical significance. As work on the original problem progressed, it quickly became apparent that unexpected complications may arise in transition metal halide-amine reaction systems. Little had previously been done on the study of possible oxidation-reduction reactions in such systems because of the intractable nature of some of the reaction products. Therefore it was decided to limit the area of this investigation to a study of the copper halides and their reactions with tertiary aliphatic amines, particularly triethyl and trimethyl amines.

The author wishes to express his gratitude for the friendly encouragement, instruction, and countless valuable discussions provided by Dr. J. T. Yoke III, who served as research advisor to this project.
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ABSTRACT

Triethylamine complexes of copper(I) and copper(II) halides were prepared for the first time in this work. With copper(I) halides, a series of complexes of the type CuX·NEt₃ were prepared. The stability sequence Cl > Br > I was observed, with relation to decomposition into the components. With copper(II) chloride, the complex CuCl₂·2NEt₃ was prepared. It does not decompose reversibly into its components, but undergoes irreversible internal oxidation-reduction on warming. Vacuum line techniques were used in preparing the solid complexes, and phase studies and a variety of spectral techniques were used in their study.

The direct reaction of triethylamine and copper(II) chloride was observed at elevated temperatures, and shown to correspond to the equations:

(1) \[ \text{CuCl}_2 + 2\text{Et}_3\text{N}(l) \rightarrow A \text{ (dark solid)} \]  
(2) \[ A \xrightarrow{\text{6 mm}} \frac{25^\circ C.}{6 \text{ mm}} \text{ B (dark oil) + Et}_3\text{N(g)} \]

Of the two moles of triethylamine bound in step (1), half is recovered reversibly in step (2). Alkaline hydrolysis of B liberates an additional ca. 0.85 mole of triethylamine. Only a small fraction of a mole of
triethylamine is oxidized per mole of copper(II) reduced; this is attributed to repeated steps of oxidative deprotonation of the amine. In reaction products A and B, the triethylamine and the oxidation and reduction products are bound in complex form. Information about these forms was obtained by study of the model system:

\[
(3) \text{CuCl} \cdot \text{NEt}_3 + \text{Et}_3\text{NH}^+\text{Cl}^- \xrightarrow{\text{6 mm, } 25^\circ \text{C.}} \text{Et}_3\text{NH}^+\text{CuCl}_2^- + \text{Et}_3\text{N} (g)
\]

The solid-oil interconversion and pressure-composition behavior suggest that the system in equation (2) corresponds to the model system in equation (3), differing only by the presence of the non-volatile polymeric amine derived from oxidation of ca. 0.15 mole of triethylamine. This was confirmed by comparison of the n.m.r. spectra of B and of triethylammonium dichlorocuprate(I).

At -45°C., triethylamine and copper(II) chloride undergo coordination, rather than oxidation-reduction. The product, CuCl₂·2NEt₃, contains the components in the same molar proportions as are involved in the oxidation-reduction reaction at higher temperatures. An electron paramagnetic resonance study was made of the thermal decomposition of this green crystalline complex. At 0°C., internal oxidation-reduction occurs, giving a diamagnetic orange solid intermediate. This darkens on further warming, giving new paramagnetic transient species and finally the same diamagnetic product shown in equation (1). Excitation
in the charge-transfer band of the complex had no effect on the rate of its decomposition.

A mechanism is proposed for the oxidation-reduction reaction between triethylamine and copper(II)-chloride, starting with the 2:1 coordination complex. Disproportionation of the radical cation formed on one-electron oxidation of triethylamine is postulated to account for the diamagnetic intermediate and for the subsequent ability of the initial oxidation product to reoxidize copper(I). Such disproportionation gives protonated starting material and diethylvinylamine. The presence of diethylvinylamine in the diamagnetic intermediate was confirmed by isolation of its hydrolysis products, acetaldehyde and diethylamine. Continued oxidative deprotonation to a polymer derived from trivinylamine is postulated to account for the stoichiometry and for the nature of the final oxidation product.

The initial steps of the reaction may be related to the metabolic path of oxidative dealkylation of amines by the copper-containing enzyme, amine oxidase, under aqueous aerobic conditions. That copper may play an electron carrying catalytic role was demonstrated by the regeneration of the transient paramagnetic species seen in the final stages of the reaction by admission of oxygen.

Oxidation of trimethylamine and several other amines by copper(II) was observed. The redox reactions were found to occur
in a number of non-aqueous solvents. The stoichiometry of the reaction in ethanol, where red products are formed, was shown to be the same as in the absence of solvent. The kinetics of the reaction in acetonitrile were studied briefly, and found not to correspond to any simple order.
I. INTRODUCTION

The objective of this research was to study the nature of the chemical reactions and compounds formed between tertiary aliphatic amines and copper(I) and copper(II) halides. The information so obtained should contribute to a better understanding of the nature of the bonding and electron transfer processes occurring in such compounds.

Complexes of metal halides with simple tertiary aliphatic amines have been little studied in the past, and even in recent times some workers have supposed that such complexes did not exist. Decreasing polarity and increasing steric hindrance with increasing degree of alkyl substitution on nitrogen are factors contributing to the well known decrease in donor ability in the sequence ammonia, primary, secondary, and tertiary amines. Also the lack of energetically available orbitals on saturated nitrogen for double bonding through back donation places the amines at a disadvantage relative to the analogous phosphorus and arsenic compounds. However, recent work has shown that stable tertiary amine complexes of metal halides are formed in a number of systems. Oxidation-reduction reactions have been observed in a number of such systems, but the nature of such reactions and of the oxidation products have not been studied. The extreme sensitivity to
temperature, water, oxygen, and the often slow rate of formation of complexes in such systems have probably contributed to the little attention they have received to date.

In the past many copper complexes of ammonia and a number of primary and secondary alkyl substituted amines have been prepared and studied. Except for one investigation employing trimethylamine (1), there have been no reports of copper(II) halide complexes with tertiary alkyl amines. Simon and coworkers have shown that a series of copper(II) chloride and bromide complexes of ethyl and mono-, di-, and trimethylamines could be prepared at low temperatures (1). Such complexes were shown to undergo irreversible decomposition on warming.

Accordingly in this work the preparation of tertiary amine complexes of copper(I) and copper(II) halides was undertaken so that a study of coordination and oxidation-reduction could be made. A study of the factors affecting complex formation in these systems could shed light on the fairly general phenomenon of oxidation-reduction observed in related systems.

Addition of triethylamine to aqueous solutions containing copper(II) ion results simply in the precipitation of hydrous copper(II) oxide, which shows no tendency to redissolve in excess of amine (2). The use of modern vacuum line techniques has made
possible much of the work described in this research. Oxygen and moisture sensitivity no longer pose insurmountable problems, and relatively unstable compounds may be easily prepared and studied by these methods. In this work an excess of pure amine was usually condensed directly onto the halide and isothermal pressure-composition measurements made on the materials resulting from the interaction. The triethylamine copper(I) halide systems were studied in this manner at several temperatures. The triethylamine copper(II) halide systems were similarly studied when applicable.

Electron paramagnetic resonance spectrometric methods have proved to be a valuable means of studying many systems involving paramagnetic species and electron transfer reactions. Data obtained by this technique may shed light on the nature of coordinate bonding and on the mechanism of electron transfer reactions in complex copper(II) amine systems. The copper(II) ion is strongly polarizing, and when not strongly stabilized has a tendency to attain the $3d^{10}$ configuration of the cuprous ion by means of ligand oxidation. This tendency has been substantiated in this work. Information of this kind regarding the stabilities of such coordination compounds has had a profound influence on the formulation of modern theories of the chemical bond.
II. HISTORICAL BACKGROUND

A. Tertiary Aliphatic Amine Complexes

Complexes of copper(I) and copper(II) halides with tertiary aliphatic amines have not been reported prior to this work, except for one study of the copper(II) chloride-trimethylamine system by Simon and coworkers. These investigators found a series of plateaus in an isobaric temperature-composition phase diagram of the system, indicating complex formation. The corresponding copper(II) bromide system gave no evidence of such interaction (1).

It is well known that in general the coordinating abilities of the alkylamines decrease in the series \( \text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N} \) (3). It has been stated that tertiary alkylamines have virtually no tendency to coordinate to metal salts (4) unless stabilized by chelation (5). This has been attributed (4) to the fact that amines, unlike phosphines cannot participate in pi bonding with transition metal cations, since no low energy orbitals of suitable symmetry are available on nitrogen, and to a decreased basicity of tertiary amines arising from steric effects (6). On the other hand a number of complexes of trimethylamine and/or triethylamine with metal halides have been reported; this work has been summarized by Yoke and Hatfield (7). Recently these workers have prepared triethylamine
complexes of cobalt(II) halides, and have discussed the ability of simple tertiary aliphatic amines, such as triethylamine, to form coordination compounds.

It has been indicated (7) that the maximum coordination numbers exhibited by substituted amines to metal cations generally decreases with the degree of alkyl substitution on the nitrogen atom. This is partially apparent in the specific case of the copper halides; the previously reported complexes of the copper halides with ammonia and the methyl and ethylamines are given in Table 1.

TABLE 1.--Previously Reported Complexes of Copper Halides with Ammonia and the Methyl and Ethylamines.

<table>
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<tr>
<th>Amine</th>
<th>CuCl</th>
<th>CuBr</th>
<th>CuI</th>
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a Structures of the analogous CuBr·2n-C₆H₁₂NH₂ and CuBr·2n-C₁₂H₂₅NH₂ are halogen bridged dimers (16).

b Structures of the analogous CuX·n-C₁₂H₂₅NH₂ are tetrameric (16).
The stoichiometries of coordination of amines to copper halides thus follows rather closely the trend exhibited by other ions of both the transitional and non-transitional groups (7), in that a general decrease in coordination tendency with degree of alkyl substitution on nitrogen is observed. The structures of the copper-amine complexes having $3\frac{1}{3}$ moles of amine per copper(II) halide are unknown, but are probably poly-nuclear.

It has been shown that the coordinating ability of tertiary amines is not outstanding. Another reason for their lower tendency to coordinate to Lewis acids, which has been suggested, is the inability of the nitrogen atom of such ligands to dispose of the positive charge developed on it after complex formation (17). Such a mechanism is open to primary and secondary amines and involves hyperconjugated resonance forms, in which the hydrogen on nitrogen assumes a positive charge. Parry and Keller (18) have attributed the apparent decrease in coordinating ability of amines with increasing degree of alkyl substitution to the decrease of both permanent and induced dipole contributions to the total dipole moment. Brown (6) has shown that the basicity of a substituted amine depends on the Lewis acid in question and that triethylamine in particular owes its poor coordinating ability to its highly sterically hindered nitrogen atom. He has interpreted this in terms of his well known $F$ and $B$ strains.
Reasons for this effect of alkyl substitution on the stabilities of coordination complexes can also be rationalized in terms of the change in lattice energies in going from the simple halide to the coordination complex. Qualitative considerations of these energy factors can be based on the sizes of the halide ions, of the amine molecules, and on the metal ion-amine dipole interactions, as well as on the anion polarization terms in the respective lattices. Thus one reason for the variation in the maximum number of ligand molecules bound per metal ion, decreasing in the series $\text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$, may be the relative degree of expansion of the metal halide lattices needed in order to incorporate the amine ligands.

The steric factor involved in lattice expansion could explain the extreme slowness of reaction observed in the formation of certain triethylamine complexes such as chlorotriethylaminocobalt(II) (7) and dichlorobis(triethylamine)copper(II) (this research), where large positive volume changes on complex formation are observed. Such behavior would suggest that the diffusion of the amine into the halide lattice at low temperatures and consequent lattice expansion may be the rate limiting steps in the formation of such complexes. The extreme slowness of the transformation from the simple to the complex salt in similar systems has been attributed by Fairbrother (19) to a reorganization of the lattice from a multidimensional ionic type to a molecular type.
B. Amine Oxidations

Biltz (9) noticed that when dichlorodiamminecopper(II) was heated, irreversible decomposition occurred producing among other products a sublimable solid. He did not identify the materials thus produced. Later Simon (1) repeated this work and identified the decomposition products as nitrogen, ammonium chloride, copper(I) chloride, and ammonia. A mechanism for the decomposition involving chlorine atoms was presented.

\[
\begin{align*}
\text{CuCl}_2 \cdot 2\text{NH}_3 & \rightarrow \text{CuCl}_2 + 2\text{NH}_3 \\
\text{CuCl}_2 & \rightarrow \text{CuCl} + \text{Cl}^- \\
6\text{Cl}^- + 2\text{NH}_3 & \rightarrow \text{N}_2 + 6\text{HCl} \\
\text{HCl} + \text{NH}_3 & \rightarrow \text{NH}_4\text{Cl}
\end{align*}
\]

The overall decomposition can be represented by the equation,

\[
6\text{CuCl}_2 \cdot 2\text{NH}_3 \rightarrow 6\text{CuCl} + 4\text{NH}_3 + \text{N}_2 + 6\text{NH}_4\text{Cl}.
\]

According to Biltz this decomposition takes place at 110°C. Simon et al. (1) noticed that in every case when copper(II) halide complexes of various primary, secondary, and tertiary amines were warmed sufficiently, an oxidation-reduction reaction occurred. This general reaction was one of the criteria of stability employed by these workers as a means of characterizing the complexes. Their 20 mm. isobaric
pressure-composition studies indicate that dichlorobis(methylamine)-
copper(II) begins to undergo irreversible decomposition at approximately
110°C., while dibromobis(methylamine)copper(II) begins to decompose
irreversibly at approximately 90°C. Dichlorobis(ethylamine)copper(II)
undergoes irreversible decomposition on heating to 70°C. The same was
found to be true for the copper(II) bromide-ethylamine system, although
an intermediate complex of composition, one-half mole ethylamine per
copper(II) bromide, was indicated by these workers. The complex
dichlorobis(dimethylamine)copper(II) undergoes irreversible decomposi-
tion at 60°C. Also dichlorobis(trimethylamine)copper(II) begins to
decompose at about 60°C. The redox decomposition of dichlorobis-
(methylamine)copper(II) was studied qualitatively. It was noted that
the decomposition gave mostly methylammonium chloride, but also
smaller amounts of copper(I) chloride, methane, nitrogen, and ethylene.
A mechanism involving atomic chlorine was presented for the decomposition.

\[
\begin{align*}
\text{CuCl}_2 \cdot 2\text{MeNH}_2 & \longrightarrow \text{CuCl}_2 + 2\text{MeNH}_2 \\
\text{CuCl}_2 & \longrightarrow \text{CuCl} + \text{Cl}^-
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{NH}_2 + \text{Cl}^- & \longrightarrow \text{HCl} + \text{CH}_3\text{NH}^-
\end{align*}
\]

\[
\begin{align*}
2\text{CH}_3\text{NH}^- & \longrightarrow 2\text{CH}_4 + \text{N}_2
\end{align*}
\]

\[
\begin{align*}
\text{HCl} + \text{CH}_3\text{NH}_2 & \longrightarrow \text{CH}_3\text{NH}_3\text{Cl}
\end{align*}
\]

The over-all reaction can be represented by the equation,
\[ 2\text{CuCl}_2 \cdot 2\text{MeNH}_2 \rightarrow 2\text{CuCl} + 2\text{MeNH}_3\text{Cl} + 2\text{CH}_4 + \text{N}_2. \]

Formation of ethylene was attributed to the thermal decomposition of methylammonium chloride,

\[ 2\text{CH}_3\text{NH}_3\text{Cl} \rightarrow \text{C}_2\text{H}_4 + 2\text{NH}_4\text{Cl}. \]

However, the temperature necessary for this reaction to proceed was not indicated and the salt is known to be sublimable at much higher temperatures. No studies were made of the nature of the decomposition reaction in the trimethylamine-copper(II)-chloride system. In all cases studied, the higher complexes indicated lose a portion of their base content reversibly on warming, but the lower ones, on reaching a specified temperature, under a constant pressure of 20 mm. undergo irreversible decomposition on further heating. It can be seen from an observation of the decomposition temperatures noted above that dichlorodiamminecopper(II) is the most stable complex with respect to internal oxidation-reduction. Generally the copper(II) chloride complexes were found to be more stable in this respect than the copper(II) bromide complexes. This can be explained in terms of the strong polarizing power of copper(II) and the greater polarizability of bromide ion, than of chloride ion. The greater stability of the chloride complexes over that of the bromide complexes can also be interpreted in terms of a greater degree of covalency of the copper(II)-bromide bond over that of the copper(II)-chloride bond, and consequent lowered dipolar
attraction for the amine ligands in the bromide complexes. It also appears that the order of stability with respect to thermally induced internal oxidation-reduction in copper(II) complexes is tertiary < secondary < primary < ammonia. It should be noted here that the isobaric temperature-composition method of study is unsuitable for this kind of stability determination. It will be shown in this work, that electron transfer occurs in dichlorobis(triethylamine)copper(II) at 0°C. with no loss of gaseous material. On these grounds there is strong reason to cast doubt upon the quantitative validity of this phase of the work reported by Simon et al. (1), although the placement of the copper(II) triethylamine complex reported in this work as being the least stable of the series of complexes is compatible with the results of these workers.

Fowles and coworkers (20-24) have shown that nitrogen bases frequently react with metal halides in which the metal is in a high oxidation state to form complexes which are unstable with respect to dehydrohalogenation or to oxidation-reduction. Zirconium(IV) chloride reacts with methylamine forming the compound ZrCl$_2$·2NHCH$_3$·CH$_3$NH$_2$ (20). 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 (25, 26). and triethylamine seems to behave similarly (26). It has also been observed that the major product on formation of tetrachlorotrimethylaminevanadium(IV) is the vanadium(III) complex, trichlorobis(trimethylamine)vanadium(III)
Fowles and coworkers (27) have studied the reactions of amines with tungsten(VI) chloride. It is found that secondary and tertiary amines initially coordinate to the halide, and that this then is followed by reduction of the tungsten(VI) to tungsten(IV) and formation of complex salts such as bistrialkylammoniumhexachlorotungstate(IV) and trialkylammonium halides. The formation of these compounds indicates that carbon-hydrogen bond cleavage rather than carbon-nitrogen bond cleavage occurs in these systems.

In these investigations no study of the nature of the oxidation-reduction reaction or of the products of amine oxidation were reported.

Eley and Watts (28) prepared triethyl and trimethylamine complexes of the aluminum halides. Aluminum chloride, bromide, and iodide formed trimethylamine complexes. All of these appeared to be far more stable to redox decomposition than the triethylamine complex of aluminium chloride. Aluminum bromide and iodide did not form complexes, but rather underwent immediate irreversible decomposition reactions with triethylamine. The tarry products of the decomposition reactions were not characterized. The stability sequence with respect to redox decomposition of the complexes appeared to be CI > Br > I.

In 1907 (2) Tschugaeff reported that platinum(II) species, such as tetrachloroplatinate(II) ion, oxidize triethylamine in aqueous solution. He noticed the formation of elemental platinum and the odor of an
aldehyde. Oxidations of tertiary amines by highly charged species have also been observed by Holmes (29). The reaction of trimethyl or of triethylamine with phosphorus(V) chloride resulted in oxidation-reduction producing phosphorus(III) chloride, rather than in complex formation. It was also observed that antimony(III) chloride was reduced to elemental antimony by trimethylamine.

Triethylamine has been subjected to oxidation by a variety of reagents. Several workers have postulated that upon one electron oxidation of triethylamine a triethylamine radical cation would result. This species may lose a proton from an α-carbon atom and thereby become a neutral free radical. Such a species has been postulated in the initial step of the oxidative deprotonation of triethylamine by 7,7,8,8-tetracyanoquinodimethane and by other oxidizing agents (30-32). 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 (33). Rosenblatt, et al., then postulate a second step of electron transfer and deprotonation leading to intermediate diethylvinylamine. The hydrolysis of this species leads to acetaldehyde and diethylamine, which were subsequently identified in the reaction mixtures. Horner and Schwenk (34) studied the oxidation of triethylamine by benzoyl peroxide. They found that approximately six moles of benzoic acid were formed per mole of triethylamine oxidized, and interpreted this
to mean that the six α-hydrogen atoms of triethylamine were abstracted in successive electron transfer and deprotonation steps.

Watters and coworkers (35) have shown that the two electron polarographic reduction wave of copper(II) ion is separated into two one electron steps if certain amines are present to stabilize the copper(I) state. Fernando (36) has shown that a chelate ligand in a copper(II) complex may be oxidized by the copper(II) when a specific complexing agent for copper(I) is added.

If a suitable reducing agent were present it would be possible to regenerate the amine, and in aerobic systems oxygen would serve to reoxidize the copper(I). Such a combination of circumstances would allow the copper-amine system to serve as an electron carrier in aerobic oxidations. Such systems are of biological significance. The copper-containing enzyme, amine oxidase, is known to oxidatively dealkylate amines to aldehydes, and amines of a lower order of substitution under aqueous aerobic conditions. It has been shown that enzymic activity is associated with the copper(II) content of this material (37, 38). It is also known that copper-amine complex systems are effective catalysts for the oxidative polymerization of phenols (39).

C. Electron Paramagnetic Resonance Studies of Copper Amine Systems

Electron paramagnetic resonance methods, hereafter referred to as e.p.r., have proven to be a valuable tool for the study of electron
transfer processes and for investigating the nature of the environment of paramagnetic species. Quite recently several authors have applied this method to study copper-amine complexes and to reacting systems involving the reduction of copper(II) by various substrates. E.p.r. studies have been employed to investigate the bonding of transition metals in a variety of compounds. Certain copper(II) complexes exhibit anisotropic behavior in their e.p.r. spectra (40-43). This is often interpretable in terms of structural and bonding factors. Along these lines, the work on copper complexes was most highly developed by Maki and McGarvey (44) in their analysis of the e.p.r. spectra of the copper(II) salicylaldimine and acetonylacetonate complexes. The e.p.r. spectrum of single crystals of ethylenediamine copper(II) nitrate dihydrate is discussed in terms of the bonding in the complex by R. Rajan (45). The hyperfine structure of the spectrum is interpreted as indicating a high degree of covalency in the bonding of the copper to the nitrogen atoms of the base. H. Rein et al. (43) have investigated the change in anisotropic g values in a homologous series of copper(II) complexes with pyridine, the picolines, and the lutidines, as well as with cyanide, cyanate, and thiocyanate. They find that the g factor decreases with increasing basicity of the pyridine homologs. B. G. Malmström et al. (46) have employed e.p.r. methods to study the course of the denaturation of copper containing oxidases. They
indicate that the immediate environment of the copper atom in these enzymes is altered from that of the native material upon denaturation.

Gersmann and Swalen (42) report the presence of a nitrogen free radical signal arising from the copper(II) chloride-triethylamine system, but this is not interpreted. Walaas and coworkers (47) have followed the reduction of copper(II) to copper(I) by various catecholamines in the oxidase ceruloplasmin. The copper(II) signal reappears in the reduced enzyme on admission of oxygen, indicating the presence of a steady state quantity of oxidized enzyme until all of the catecholamine is oxidized, whereupon the enzyme becomes fully paramagnetic again. These results indicate that a cupric-cuprous couple involving the enzyme is associated with the oxidation of the substrate by atmospheric oxygen. This work thus definitely shows that copper serves in an electron carrying capacity in the aerobic oxidation of these substrates.
A. Stability of Metal Halide-Amine Complexes

In coordination chemistry, the term stability commonly is used in reference to the energetics of interaction of the Lewis acid and base. Thus, attention may be given to the energy of the coordinate bond, or to the free energy change and related equilibrium constant of the coordination reaction. The fact of existence is the most fundamental qualitative criterion of stability, and this may be related not only to the energetics of the coordination reaction but also to any other decomposition reactions a potential complex may be able to undergo, such as elimination or oxidation-reduction reactions (48). In this regard, it is necessary to state the conditions of temperature, pressure, states of matter, and presence of other potential reagents such as moisture, oxygen, or solvents. The most meaningful criterion of stability of a complex under specified conditions is then its free energy of formation from the elements relative to the free energies of products of all possible decomposition reactions. In addition, kinetic factors may result in the apparent stability of thermodynamically unstable complexes, or in the failure to observe complexes in systems where interactions take place only very slowly. Such slow interactions
may be important, for example, in systems where a major reorganization of a solid lattice takes place (19).

In the specific case of the interaction of metal halides with alkylamines, a wide variety of reaction types is known, including coordination reactions between the pure components or between the components in solution, the latter being often complicated by solvent competition in coordination and competing protic acid-base reactions. With ammonia and primary and secondary amines, elimination of hydrogen halide (aminolysis) often occurs, leading to metal amide or imide formation. With tertiary amines, elimination of an alkyl group is a possibility. Oxidation-reduction reactions have also been observed in such systems.

The coordinate bond energy between a metal ion and a ligand is the enthalpy change for the reaction

\[ M^{+n} \quad (g) \quad + \quad L_{(g)} \quad \longrightarrow \quad ML^{+n} \quad (g) \]

(suitably modified in case of charge on the ligand). When more than one ligand is involved, only an average coordinate bond energy can be determined. In the case where the metal ion or donor atom bear substituents, additional energy factors, e.g., rehybridization energies, may contribute to the enthalpy of the reaction. There are relatively few cases where the coordination reaction may be studied in the gas phase (6). For work involving liquids, solids, or solutions, it is
necessary to make use of thermochemical cycles. Coordinate bond energies are not easily obtainable from such work, since a number of other terms in the energy cycle are commonly unknown and not easily determined.

For the case of a solid complex formed from a non-volatile solid metal halide and a volatile amine, the coordinate bond energy is related to the enthalpy cycle (assuming a monovalent cation and a 1:1 complex for simplicity)

\[
\begin{align*}
MX(g) + L(g) & \rightarrow MX\cdot L(g) \\
MX(c) + L(l) & \rightarrow MX\cdot L(c)
\end{align*}
\]

Here \(U_1\) and \(U_2\) are lattice energies of the solid simple and complex salts referred to idealized gaseous species, \(\Delta H_V\) is the latent heat of vaporization of the amine, \(\Delta H_C\) is the heat of coordination, and \(\Delta H_R\) is the heat of reaction observable in practice. The heat of coordination is given by \(\Delta H_C = \Delta H_R - \Delta H_V - (U_1 - U_2)\) and cannot be evaluated unless the difference in lattice energies of the simple and complex salt is known, which is not usually the case. From the practical standpoints of the synthesis of such a complex from the pure components and of the temperature-pressure behavior of such a complex
in the case of a reversible reaction, both entropy and enthalpy terms must be considered. A similar free energy cycle can be written, and in such a cycle the term $\Delta F_R$ would be a measure of the stability of the complex relative to its dissociation into its components. The quantities $\Delta H_R$, $\Delta S_R$, and $\Delta F_R$ may be evaluated by measurement of the equilibrium dissociation pressures of the complex at a number of temperatures. The temperature variation of the vapor pressure of the free base must also be known. The Clausius-Clapeyron and Gibbs-Helmholz relations may be used for such a calculation.

Factors influencing the stability of metal halide-alkylamine complexes, with respect to dissociation into their components, have been discussed by Hatfield (7) in terms of the polarized ion-dipole model of coordination including ligand field effects. The effect of variation of the metal cation, the halide anion, the Group V donor atom, and the degree of alkyl substitution of the donor atom, were also discussed. In the present study the oxidation number of the metal cation serves as a potential variable, i.e., a comparison of copper(I) and copper(II) complexes of tertiary alkylamines is undertaken.

In terms of the idealized gas phase electrostatic model of coordination energetics (49), the charge on the copper ion appears in the ion-ligand total dipole term $-q\mu_{tot}/r^2$ and also in the expression for the induced contribution to the total dipole moment. The potential energy of a coordination complex is given by the equation,
\[ E = -nq(\mu_{\text{tot}})/r^2 + nk(\mu_{\text{tot}})^2/r^3 + n(\mu_1)^2/2a + \frac{6B}{r^m} - \text{CFSE} \]

where

- \( n \) = coordination number
- \( k \) = geometric constant
- \( m \) = a larger power (e.g., 9) to which the distance is raised in the Van der Waal's repulsion term
- \( q \) = charge on the cation
- \( \mu_{\text{tot}} = \mu_{\text{permanent}} + \mu_{\text{induced}} \)
- \( \mu_1 = \mu_{\text{induced}} \)
- \( a \) = ligand polarizability

Moreover, the higher the charge on the copper ion, the smaller would be the value of \( r \), the equilibrium internuclear distance between copper and nitrogen. Still another effect of the charge on copper would result from the influence of charge on the induced dipole moment and the internuclear distance, this additional effect being on the magnitude of the crystal field stabilization energy for a given ligand geometry. (For example, it is well known that in the hexaquo complexes of the first series of transition metals, an increase in the cation charge from +2 to +3 approximately doubles the magnitude of the ligand field.)

Such comparisons of the effect of the oxidation number of the copper cation on stabilities of complexes are not applicable in the probable case that coordination numbers and geometries of copper(I) and copper(II) complexes are dissimilar. Common coordination numbers
and geometries are discussed by Wells (50) and are: for copper(I) bi-coordinate (linear) and tetracoordinate (tetrahedral); for copper(II) hexacoordinate (with extreme Jahn-Teller distortion, leading to apparent tetracoordinate square-planar structures) and tetracoordinate (square-planar or markedly distorted tetrahedral). In addition, in the case that the amine ligand does not displace the halide anion from the coordination sphere of the copper, variation in the charge on copper would also result in variation in the number of halide ions present in the complexes.

Further complicating the comparison of copper(I) and copper(II) complexes would be reactions of the components other than coordination, such as oxidation-reduction reactions. While considerable information about oxidation-reduction mechanisms in aqueous solution, such as electron transfer or atom or group transfer processes, has been obtained recently (51), little is known about the mechanism of oxidation-reduction reactions in pure systems of metal salts and neutral polar ligands.

B. Electron Paramagnetic Resonance Studies of Copper Complexes

Electron paramagnetic resonance studies may yield information both about the nature of electron transfer reactions and about the nature of the bonding in transition metal complexes. The results of a number of such studies have been reviewed recently (52). The technique involves measurement of the resonance absorption of radiant energy in the microwave
region corresponding to the splitting between energy states of a system containing a net non-zero electron angular momentum. The splitting is induced by the presence of a strong external magnetic field. The number of energy states is given by \(2S + 1\), where \(S\) is the spin angular momentum of the system. For \(d^9\) copper(II), \(S = 1/2\) and two states exist; for \(d^{10}\) copper(I) the system is diamagnetic, i.e., \(S = 0\), and there is no splitting. Therefore, e.p.r. measurements are useful in the study of copper(II) complexes, and in the study of the reduction of copper(II) to copper(I).

The energy splitting and condition for resonance is given by the relations

\[
\Delta E = g\beta H = h\nu
\]

where \(g\) is the gyromagnetic ratio of the spinning electron, \(\beta\) is the Bohr magneton, and \(H\) is the magnetic field strength. For simple free radical systems containing one unpaired electron, \(g = 2.0\), and for applied fields of the order of 3000 gauss the resonance frequency lies in the \(10^{10}\) c.p.s. region. Such frequencies are obtained by use of klystron tubes developed for radar work in the 3 cm. wavelength region.

The magnetic moment of a transition metal complex is often first approximated by the "spin-only" formula,

\[
\mu_{\text{eff}} = g[S(S + 1)]^{1/2} = 2[S(S + 1)]^{1/2}.
\]

If the system possesses orbital angular momentum, the value of \(g\)
will differ from 2.0 in a manner depending upon the magnitude of orbital momentum and its coupling with electron spin. The orbital contribution may be reduced or eliminated (quenched) by a decrease in the orbital degeneracy through the action of a ligand field. The ligand field may be asymmetric, as is particularly common in copper(II) complexes. In such a case, the sample will be magnetically anisotropic, and the $g$ tensor may be resolved into three components, one parallel to the unique axis of the applied field and two in the plane perpendicular to this axis. 

This may be expressed in the relation $<g>^2 = \frac{1}{3} [g_{||}^2 + 2g_{\perp}^2]$.

Under conditions of high resolution, additional details of the structure and bonding of a complex may be revealed by hyperfine structure in the resonance signal arising from further splitting of the energy states through coupling of the electron angular momentum with the nuclear moments. Copper has two principal isotopes, both of which possess nuclear moments, and nitrogen and halide nuclear moments may also potentially contribute structure to the resonance signal. Actually, nitrogen hyperfine contributions to copper(II) signals are often observed, while chloride nuclear coupling is not energetically significant.

The extent to which the magnetic moment of a copper(II) complex exceeds the "spin-only" value of 1.73 Bohr magnetons, i.e., the extent to which $<g>$ differs from 2.0, is inversely related to the strength of the ligand field. Comparison of different copper(II) complexes is rendered difficult, however, by variations in the degree of distortion.
from simple symmetry. However, particular values of the anisotropic $g$ factors are characteristic, and changes in these $g$ values are indicative of changes in the coordinative environment of copper(II) in a chemical reaction. A decrease and disappearance of the e.p.r. signal is characteristic of reduction to diamagnetic copper(I).

A knowledge of $<g>$ for a complex allows calculation of the magnetic moment from the equation,

$$\mu_{\text{eff.}} = g[S(S + 1)]^{1/2}$$

when the value of $S$ or the number of unpaired electrons is known. For copper(II) systems, the amount by which the value of $\mu_{\text{eff}}$ exceeds the spin only value of $\mu_0 = 1.73$ B.M., is related to the strength of the ligand field $\Delta$ (or $10Dq$) by the relation,

$$\mu_{\text{eff}} = \mu_0(1 - 2\lambda /\Delta) \quad (53)$$

where $\lambda$ is the spin orbit coupling constant. The value of $\Delta$ obtained from the magnetic data may be correlated with the electronic spectrum of a particular complex.
IV. STATEMENT OF THE PROBLEM

This research is concerned with the study of the interactions of tertiary aliphatic amines with copper halides. Reactions occurring in such systems involve donation of electrons from the nitrogen atom of the amine to the metal cation. Coordination reactions and oxidation-reduction reactions are included in this category. Studies of the products of such reactions will yield information about the nature of the processes occurring and of the factors influencing the course of such reactions under a variety of conditions. Mechanistic implications drawn from the data obtained will be of value to a more complete understanding of the general phenomena of both coordination and electron transfer reactions occurring in these systems and their many analogues. Differences in the behavior of copper(I) and copper(II) halides towards the amines as well as factors favoring complex formation or electron transfer may be interpreted in terms of modern theories of the chemical bond.

The purpose of the research is to investigate specifically the nature of the chemical reactions and of the compounds formed by such interactions, with the end in view of obtaining information about the mechanisms which describe the reacting systems. Such information
may contribute to our knowledge of this kind of interaction in terms of current theories of bonding and electron transfer.
V. EXPERIMENTAL

A. Materials

1. Purification of the Amines

   a. Trimethylamine. --Trimethylamine (Eastman, anhydrous, White Label grade) was stirred for 24 hours with barium oxide, decanted and stirred again as before with phosphorus(V) oxide (54). It was then distilled from trap to trap in the high vacuum system until the material was tensiometrically homogeneous and exhibited a vapor pressure of 682 mm. at 0°C. The vapor pressure-temperature data observed for trimethylamine are shown in Table 2. The value observed at 0°C. is in excellent agreement with the values of 681.2 mm. and 679.9 mm. reported by Holmes (55a) and Holmes and Bertaut (55a). The vapor pressure values observed in this work were combined with the previously reported values (55, 55a) to calculate the equation:

   \[
   \log p = -1380.7/T + 7.9082.
   \]

   From this equation, the average heat of vaporization, 6.3 kcal./mole of trimethylamine was calculated. This value leads to a Trouton constant of 23.0 e.u. A plot of \( \log p \) vs. \( 1/T \) for the purified material produced a straight line. This plot is shown in Figure 1. The purified trimethylamine was stored in the gas phase in a storage bulb affixed to the high vacuum system.
Figure 1. Purified Trimethylamine
TABLE 2. --Pressure-Temperature Data for Trimethylamine.

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Pressure mm.</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>682</td>
<td>water-ice mixture</td>
</tr>
<tr>
<td>-22.9</td>
<td>255</td>
<td>carbon tetrachloride slush</td>
</tr>
</tbody>
</table>

b. Triethylamine. --Triethylamine (Eastman, anhydrous, White Label grade) was refluxed over phosphorus(V) oxide for three hours and then distilled from the residue in a system fitted with a calcium hydride drying tube. The fraction boiling between 89°C. and 90°C. was collected and stored over phosphorus(V) oxide until used. No trace of impurity could be detected by gas chromatography with a carbowax on firebrick column, on a Wilkins Aerograph instrument. The triethylamine so obtained exhibited a vapor pressure of 66 mm. at 25.0°C. and 50.0 mm. at 18.4°C. These values were combined with the previously reported values (7) and with values of 89.4°C. and 89.5°C. for the normal boiling point (55) to give the equation:

\[
\log p = -1788/T + 7.8154
\]

The triethylamine was found to be tensiometrically homogeneous in the vacuum system.

Triethylammonium chloride was prepared from the purified triethylamine and anhydrous hydrogen chloride (Matheson) in absolute ethanol. The product crystallized readily and was recrystallized from
absolute ethanol, m.p. (sealed tube) 254°C., lit. (55) 254°C. The material was dried under vacuum at room temperature and stored in a vacuum desiccator over phosphorus(V) oxide.

c. Tri-n-propylamine. --Tri-n-propylamine (Eastman, anhydrous, White Label grade) was refluxed over barium oxide and then distilled from the residue. The material boiling between 153-155°C. (ca. 700 mm.) was collected and allowed to stand over phosphorus(V) oxide for 24 hours. This was followed by distillation from the residue. The fraction boiling between 153-154°C. was collected and stored over phosphorus(V) oxide until used, lit. (55) b.p. 154°C.

d. Tri-n-butylamine. --Tri-n-butylamine (Eastman, anhydrous, White Label grade) was refluxed over barium oxide for two hours and then distilled from phosphorus(V) oxide. The fraction boiling between 210-212°C. (ca. 700 mm.) was collected and stored over phosphorus(V) oxide until used, lit. (55) b.p. 214°C. No trace of impurity could be detected by gas chromatography at 250°C. using the vapor phase chromatographic instrument and column described earlier.

2. Preparation of Anhydrous Metal Halides

a. Copper(I) Chloride and Copper(I) Bromide. --These salts were prepared from Reagent grade copper(II) halides by the sulfite reduction technique (56), washed with acetone and dried at room temperature.
in vacuo. The halides were stored in a vacuum desiccator over phosphorus(V) oxide until ready for use.

b. Copper(I) Iodide.--Copper(I) iodide (Baker and Adamson, purified grade) was dried at 200°C. under a stream of dry nitrogen. The material was stored in a vacuum desiccator over phosphorus(V) oxide until used.

c. Copper(II) Chloride.--Copper(II) chloride dihydrate (Baker's Reagent Grade) was dehydrated by heating at 110°C. until all of the blue dihydrate had become brown (57). This material was stored in a vacuum desiccator over phosphorus(V) oxide until used. Just prior to use the material was heated to 100°C. for one-half hour under high vacuum on the vacuum line.

d. Copper(II) Bromide.--Copper(II) bromide (Baker's Reagent Grade) was dried by heating to 200°C. under a stream of dry nitrogen. The material was stored in a vacuum desiccator over phosphorus(V) oxide until used.

e. Chromium(III) Chloride.--Chromium(III) chloride (Diamond Alkali Corp., anhydrous, sublimed) was heated to 350°C. under a stream of hydrogen chloride, which was dried by passage through concentrated sulfuric acid, to ensure its anhydrous condition. The
material was cooled under an atmosphere of dry nitrogen. It was stored in a stoppered flask in a desiccator over phosphorus(V) oxide.

3. Solvents

a. Acetonitrile. --Acetonitrile (Matheson, practical grade) was purified by the method of Edward J. Cokal (58) with some modifications. The practical grade material was washed three times with ice cold 50 percent sodium hydroxide solution in a separatory funnel. This was followed by shaking with anhydrous sodium sulfate and filtration. These operations removed the acidic impurities and most of the water. The basic impurities and the remaining water were removed by shaking the acetonitrile with phosphorus(V) oxide. The lumps that formed were discarded, more phosphorus(V) oxide was added, and the mixture shaken. This was continued until a suspension of the oxide in the liquid was obtained. The excess of oxide was allowed to settle as a powder, and the suspension poured off from the settled material. The suspension was distilled in an apparatus that was preflushed with dry nitrogen and open to the atmosphere only through a calcium hydride-filled drying tube. The fraction boiling in the range 79-80°C. (ca. 700 mm.) was collected and stored in a stoppered flask in a nitrogen-filled dry box, lit. (55) b.p. 82°C.

b. γ-Butyrolactone. --γ-Butyrolactone (Matheson, Coleman and Bell, b.p. range 91-93°C. at 17 mm.) was shaken with anhydrous
sodium sulfate, filtered, and distilled. The fraction boiling in the range 198-199°C. (ca. 700 mm.) was collected. The material was stored in a stoppered flask in a nitrogen filled dry box, lit. (55) b.p. 206°C. at 760 mm.

c. Water Used in Hydrolysis Studies. -- Distilled water was boiled for one-half hour to remove dissolved oxygen. The water was then cooled under a nitrogen gas cover, the flask stoppered, and the water stored for short periods of time until used.

All other chemicals used in this study were of Reagent grade quality unless otherwise stated.

B. Technique for the Pressure-Composition Isotherms

A glass high vacuum system such as that described by Sanderson (59) was used both in the synthesis and in the study of the pressure-composition isotherms of the various complexes. Dow Corning silicone high vacuum grease was used on the stopcocks and ground glass joints. In certain parts of the work, a combination of a mechanical oil fore-pump and mercury diffusion pump was used, with residual non-condensable gas pressures of the order of 10^{-5} mm. being attained. In most of the work with triethylamine, however, a simpler vacuum system equipped only with the mechanical oil vacuum pump was used, the residual pressures being approximately 10^{-2} mm. Dissociation and vapor
pressures of the volatile amines were measured with sufficient precision (ca. 0.6 mm.) using mercury manometers and a meter stick. A cathetometer was used for the triethylamine vapor pressure-temperature relation studies.

The sample of anhydrous metal halide was transferred in a nitrogen-filled dry box to a tared reaction assembly, consisting of a reaction flask containing a Teflon coated magnetic stirring bar, and fitted through ground glass joints with a connecting tube having a stopcock, permitting attachment to and removal from the vacuum system. The usual procedure was to attach the empty reaction assembly to the vacuum system and evacuate the entire unit. The assembly was then detached from the system, the inner, $\mathbb{F} 10/30$, connecting joint was wiped free of grease, and the assembly was then weighed to obtain the tare weight. The evacuated assembly was subsequently placed into a nitrogen-filled dry box and opened. A small amount of copper halide was transferred to the reaction tube through a powder funnel. Care was taken to insure that the funnel did not touch the greased walls of the reaction tube joint. The connecting tube, with stopcock, was then replaced and the reaction assembly removed from the dry box and reattached to the vacuum system. The reaction assembly was then re-evacuated for one-half hour, while the reaction tube was heated to 100°C., in a water bath. This was done to insure the anhydrous condition of the copper halide. After this operation the stopcock in the
connecting tube was closed and the reaction assembly was removed from the vacuum system. The attachment tube joint was again wiped free of grease and the evacuated assembly containing the copper halide weighed. In this manner the exact weight of the copper halide taken for study was determined.

The reaction assembly was then reattached to the vacuum system, and the fore-part of the assembly evacuated. A considerable excess of the volatile amine was allowed to distill under its own vapor pressure, through the vacuum system, into the reaction tube, which was cooled in a Dry Ice or similar cold bath. The stopcock in the reaction assembly was then closed. With the reaction tube now containing both reactants isolated from the vacuum system, the mixture was stirred to permit interaction of the components. At this stage the reaction tube could be either heated or kept cold at specified temperatures by the use of various baths. When reaction was complete the excess of amine was distilled from the reaction system back into the amine storage vessel. With the temperature of the reaction tube maintained at the desired value by means of a constant temperature water bath or an appropriate cold slush bath, the pressure of the volatile amine in equilibrium with the complex reaction product could be determined by opening the system to a manometer. In this manner it was possible to remove the excess of amine from a complex and to measure the equilibrium pressures. In this way it could readily be determined when all of
the excess of volatile amine had been removed from a complex, this being indicated by a sharp drop in the equilibrium pressure. If a complex possessed a measurable dissociation pressure, this could be determined in like manner. At the point corresponding to complete removal of the excess of amine, the stopcock in the reaction assembly was closed, the assembly removed from the vacuum system, and reweighed. The increase in weight representing combined amine was thus determined. The mole ratios of copper halide to amine retained, so obtained represent the stoichiometry of the coordination or other reaction.

Most of the complexes thus prepared had negligible (i.e., <1 mm. and not detectable on the manometer) equilibrium dissociation pressures of the volatile amine, and complex formation was readily detected by the sudden drop in the pressure exhibited by the reaction system.

C. Spectrometric Techniques

1. E.P.R. Spectra

All e.p.r. spectra were recorded on a model V-4501 Varian 100 kc. modulation e.p.r. spectrometer. Sample tubes were attached to the vacuum system and evacuated prior to spectral study. A V-4547 variable temperature accessory was used to regulate the temperature of the sample.
2. Visible and Ultraviolet Spectra

All such spectra were taken on a Cary model 14 double beam recording spectrophotometer using a set of 1 cm. quartz cells.

3. Nuclear Magnetic Resonance Spectra

Proton n.m.r. spectra were recorded on a Varian A-60 n.m.r. spectrometer. Sample tubes were loaded in a nitrogen-filled dry box and closed with plastic caps sealed with wax.

4. Infrared Spectra

A Perkin-Elmer Infracord, double beam recording infrared spectrophotometer was employed for all of the spectral work.

5. Reflectance Spectra

A Beckmann model D. U. single beam spectrophotometer fitted with a standard reflectance attachment was used to obtain the reflectance spectra. Samples were loaded into the sample holder at low temperature in a nitrogen-filled dry box. Reagent Grade magnesium carbonate was used as the reflectance standard.

D. Analytical Methods

1. Copper(I) Halide Triethylamine Complexes

a. Triethylamine Content. --Samples were removed in a nitrogen-filled dry box and placed into a known amount of standard hydrochloric
acid solution. This decomposed the complex and produced triethyl-
ammonium chloride. These solutions were back-titrated with standard
sodium hydroxide solution to a methyl red endpoint.

b. Copper Content. --A sample of a particular complex was
removed from the reaction assembly in a nitrogen-filled dry box and
dissolved in dilute nitric acid solution, leading to decomposition of the
complex and oxidation of the copper(I) to the divalent state. Copper
was then determined iodimetrically according to the procedure of Kolthoff
and Sandell (60).

c. Halide Content

i. Chloride. --The chloride content was determined by
the adsorption indicator method. A measured portion of the solution
obtained by dissolving a known amount of the complex in nitric acid
solution was neutralized with dilute sodium hydroxide solution, acidi-
fied with dilute acetic acid solution, and titrated with standard silver
nitrate solution using dichlorofluorescein as the indicator. The sus-
pension that resulted was stabilized by the addition of dextrin to the
solution prior to titration (61).

ii. Bromide and Iodide. --Bromide and iodide were deter-
mined gravimetrically. Portions of the complex were removed as indi-
cated and fused with solid sodium hydroxide in a platinum crucible. The
residue was dissolved in water and filtered to remove the copper(I) oxide formed. The solution was then neutralized with dilute acetic acid solution and adjusted to pH 4-5, prior to precipitation of the halide with 0.1 molar silver nitrate solution.

2. Product B
   
a. Copper(I) Chloride. --Hydrolysis of product B results in the precipitation of a white substance. This material was dissolved in dilute nitric acid solution and the copper content determined iodimetrically as previously described. A known volume of the nitric acid solution was taken and the chloride content determined by titration as described.

   b. Triethylammonium Chloride. --Hydrolysis of product B also results in the formation of a water soluble, white crystalline material. A known weight of this material was taken and treated in a distillation assembly with concentrated sodium hydroxide solution. Distillation of the solution was commenced and the distillate caught in a known volume of standard hydrochloric acid. This solution was then back-titrated with standard sodium hydroxide solution to a methyl red endpoint. Chloride content was determined gravimetrically by precipitation with silver nitrate solution.

   c. Triethylamine Oxidation Product. --Hydrolysis of product B also produces a dark solid material. Carbon and hydrogen content were
determined by the C. F. Geiger Co., Ontario, California. Nitrogen content was determined by the micro-Kjeldahl method allowing two to three hours for digestion of the sample with concentrated sulfuric acid. Micro-Kjeldahl analyses were performed with the aid of Dr. William McCaughey and staff, Department of Agricultural Biochemistry, University of Arizona. Copper content was determined by the iodine-thiosulfate method, following oxidation of the copper by digestion of the sample with nitric-perchloric acid mixtures. Chloride content was determined gravimetrically by addition of silver nitrate solution to solutions obtained by digesting a known amount of sample in concentrated nitric acid.

E. Copper(I) Halide-Trialkylamine Systems

1. Copper(I) Chloride-Triethylamine System

Anhydrous copper(I) chloride was placed into the tared reaction assembly as described previously and the system evacuated and heated to 100°C. The assembly was removed from, and after weighing, reattached to the vacuum system. Purified anhydrous triethylamine was distilled onto the copper(I) chloride by cooling the reaction tube in a Dry Ice bath. The reactants were stirred magnetically for 24 hours at room temperature (ca. 30°C.) and then for one hour at 80°C. Reaction was indicated by a large change in volume of the copper(I) chloride as it was being stirred with the amine. The solid phase in equilibrium with the supernatant
liquid changed from a granular to a pasty appearance as the reaction progressed. The excess of triethylamine was removed, and pressure-composition measurements were made as described previously. These are given in Table 3. A time period of 24 hours was allowed to establish dissociation equilibrium. When the reaction vessel containing the sample at a mole ratio value of 1.0 was opened directly to the pump for 24 hours a negligible loss of weight occurred. The solid phase appeared to be essentially insoluble in an excess of triethylamine as indicated by qualitative observations as the excess of amine was removed. The reaction assembly was removed from the vacuum system to a nitrogen-filled dry box where it was opened and samples of the white product were taken for analysis. The analytical results listed in Table 5 support the conclusions drawn from the isotherm regarding the composition of the product.

2. Copper(I) Bromide-Triethylamine System

Using the same technique, pressure-composition data were obtained for this system. The data are given in Table 3. The dissociation pressure of the product was too small to be measured with the mercury manometer. A period of 24 hours was allowed for the establishment of dissociation equilibrium. However, when the reaction tube containing the product was opened directly to the pump a significant loss of weight occurred over a period of five hours. The product at a
mole ratio value of 1.0 is white, and like the chloro analogue appeared to be essentially insoluble in an excess of triethylamine. A sample was taken for analysis and the results are listed in Table 5.

3. Copper(I) Iodide-Triethylamine System

The pressure-composition isotherm of this system indicates the formation of a product of 1:1 stoichiometry. It was found that the dissociation pressure of the product was appreciable, and equilibrium dissociation pressure measurements were made at several temperatures.
The data are given in Table 4. The measurements were made using water from a constant temperature (±0.1°C.) bath. Water was pumped from the bath through a coil placed in a Dewar flask surrounding the reaction tube containing the sample. The Dewar flask was suspended under the vacuum system in a manner such that the reaction assembly could be connected through the vacuum system to the manometer, and pressure readings taken at specified temperatures. A calibrated mercury in glass thermometer graduated in tenths of a degree was employed. Measurements were made at 25.0, 35.0, and 45.0°C. Dissociation pressure equilibrium in this system was established in one and one-half to two days at 25.0°C., while somewhat shorter periods sufficed at the higher temperatures. The product was white but on warming to 95°C. it became yellow. On cooling to temperatures below 80°C. it became white again. This color change resembles that observed with pure copper(I) iodide when it is heated to approximately 250°C. During the heating phase of the synthesis it was observed that the solid phase was appreciably soluble in warm triethylamine; and that upon cooling it separated from the solution in the form of small well-formed crystals. A sample of the product was taken for analysis. The results are shown in Table 5.

It was observed that the chloride complex darkened rapidly on exposure to the laboratory atmosphere. The bromide complex darkened also, but not as rapidly, while the iodide complex exhibited
<table>
<thead>
<tr>
<th>$\text{Et}_3\text{N/CuI}$</th>
<th>Pressure mm. (25.0°C.)</th>
<th>$\text{Et}_3\text{N/CuI}$</th>
<th>Pressure mm. (35.0°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.20</td>
<td>65.0</td>
<td>2.20</td>
<td>62.0</td>
</tr>
<tr>
<td>1.04</td>
<td>31.0</td>
<td>1.75</td>
<td>65.0</td>
</tr>
<tr>
<td>1.00</td>
<td>27.0</td>
<td>1.64</td>
<td>42.0</td>
</tr>
<tr>
<td>0.93</td>
<td>7.0</td>
<td>1.28</td>
<td>35.0</td>
</tr>
<tr>
<td>0.90</td>
<td>10.0</td>
<td>1.13</td>
<td>38.0</td>
</tr>
<tr>
<td>0.83</td>
<td>6.0</td>
<td>1.06</td>
<td>23.0</td>
</tr>
<tr>
<td>0.82</td>
<td>6.0</td>
<td>0.90</td>
<td>14.0</td>
</tr>
<tr>
<td>0.78</td>
<td>6.0</td>
<td>0.86</td>
<td>14.0</td>
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<td>0.74</td>
<td>6.0</td>
<td>0.80</td>
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<tr>
<td>0.73</td>
<td>6.0</td>
<td>0.73</td>
<td>15.0</td>
</tr>
<tr>
<td>0.71</td>
<td>6.0</td>
<td>0.61</td>
<td>14.0</td>
</tr>
<tr>
<td>0.70</td>
<td>6.0</td>
<td>0.55</td>
<td>15.0</td>
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<td>0.69</td>
<td>6.0</td>
<td>0.46</td>
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<tr>
<td>0.61</td>
<td>6.0</td>
<td>0.21</td>
<td>14.0</td>
</tr>
<tr>
<td>0.53</td>
<td>6.0</td>
<td>0.08</td>
<td>6.0</td>
</tr>
<tr>
<td>0.39</td>
<td>6.0</td>
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<td>&lt;1</td>
</tr>
<tr>
<td>0.21</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$At 45.0°C. pressures of 34.0 mm. were read at mole ratios, 0.71 and 0.57.

no tendency to darken even over periods of relatively long exposure. Qualitative solubility studies of the complexes in benzene solution were made. All of the complexes exhibited far greater solubility in benzene than the cuprous halides themselves. Evaporation of the
benzene solutions resulted in visible residues, while no residues were visible when similar solutions of the cuprous halides themselves were evaporated.

TABLE 5. --Analysis of Copper(I) Halide-Triethylamine Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mole ratio Et₃N/CuX</th>
<th>% Et₃N Found</th>
<th>Theory</th>
<th>% Halide Found</th>
<th>Theory</th>
<th>% Copper Found</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl·NEt₃</td>
<td>0.923</td>
<td>43.35ᵃ</td>
<td>52.58</td>
<td>18.16</td>
<td>18.01</td>
<td>33.82</td>
<td>33.03</td>
</tr>
<tr>
<td>CuBr·NEt₃</td>
<td>0.970</td>
<td>42.77</td>
<td>41.88</td>
<td>32.92</td>
<td>33.09</td>
<td>26.54</td>
<td>26.30</td>
</tr>
<tr>
<td>CuI·NEt₃</td>
<td>0.990</td>
<td>33.62</td>
<td>34.81</td>
<td>42.88</td>
<td>43.66</td>
<td>21.53</td>
<td>21.86</td>
</tr>
</tbody>
</table>

ᵃ Of questionable validity.

4. Copper(I) Bromide-Trimethylamine System

Purified trimethylamine was distilled onto an anhydrous sample of copper(I) bromide, and the mixture was stirred at 0°C. for 24 hours. The excess of trimethylamine was removed in the vacuum system as described earlier. The gain in weight upon reaction indicates the formation of a product with 1:1 stoichiometry. The dissociation pressure of the product was not measurable on the mercury manometer at 30°C., when 24 hours were allowed for its development. Very little loss in weight was observed on opening the sample directly to the mercury diffusion pumping system for 9 hours. The preparation of analogous trimethylamine complexes of the other cuprous halides was not attempted.
5. The System Copper(I) Chloride-Triethylammonium Chloride-Triethylamine

When 5.03 mmoles (0.498 grams) of anhydrous copper(I) chloride was added to 5.09 mmoles (0.700 grams) of pure anhydrous triethylammonium chloride, a clear amber oil formed rapidly. When this oil, which is taken to be triethylammonium dichlorocuprate(I) by analogy with previously reported alkylammonium chlorocuprate(I) complexes (62), was treated with an excess of triethylamine and stirred in a reaction unit attached to the vacuum system, the oil rapidly became a white crystalline solid. Identical behavior was noted when copper(I) bromide was substituted for copper(I) chloride in this system. In the triethylammonium dichlorocuprate(I)-triethylamine system, the excess of triethylamine was removed by distillation at its vapor pressure of 66 mm. at 25°C. The pressure of the system was found to drop suddenly to an equilibrium value of 6.0 mm. at 25.0°C. The weight of the reaction product corresponded to the retention of 5.02 mmoles of triethylamine at this point. On further removal of triethylamine at 6 mm., the solid product was transformed back to the original non-volatile oil. Pressure-composition data for the system at 25.0°C. are given in Table 6. When triethylamine was distilled back onto the oil and again removed, the same solid-oil transformation and stepwise pressure-composition behavior was observed, proving reversibility and establishment of equilibrium.

In another experiment the existence of the equilibrium,

$$\text{CuCl} \cdot \text{NEt}_3^{(c)} + \text{Et}_3\text{NHCl}^{(c)} \xrightleftharpoons[{25^\circ\text{C.}}]{6 \text{ mm.}} \text{Et}_3\text{N}^{(g)} + \text{Et}_3\text{NHCuCl}_2^{(1)}$$

was demonstrated.
TABLE 6. --Pressure-Composition Data for the System; Triethylammonium Dichlorocuprate(I)-Triethylamine at 25.0°C.

<table>
<thead>
<tr>
<th>Mole ratio $\text{Et}_3\text{N}/\text{Et}_3\text{NHCuCl}_2$</th>
<th>Pressure mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.24</td>
<td>66.0</td>
</tr>
<tr>
<td>0.99</td>
<td>6.0</td>
</tr>
<tr>
<td>0.79</td>
<td>6.0</td>
</tr>
<tr>
<td>0.28</td>
<td>6.0</td>
</tr>
<tr>
<td>0.24</td>
<td>6.0</td>
</tr>
<tr>
<td>0.16</td>
<td>6.0</td>
</tr>
<tr>
<td>0.00</td>
<td>0.0</td>
</tr>
</tbody>
</table>

was verified. Triethylammonium chloride in the amount of 10.11 mmoles (1.390 grams) was added to 10.11 mmoles (2.022 grams) of solid chlorotriethylaminecopper(I). Operations were performed in a nitrogen-filled dry box. Neither component exhibited a measurable vapor pressure at 25.0°C., when tested on the vacuum system prior to mixing. When the two solids were pressed together, the mixture developed an equilibrium vapor pressure of 6.0 mm. at 25.0°C., some darkening being observed. As triethylamine was pumped off at this equilibrium pressure, oil formation occurred. Continued removal of triethylamine eventually resulted in complete transformation of the sample to an oil. A sharp drop in the equilibrium pressure of the system from 6.0 mm. to a negligible value occurred at a point where the loss in weight of the system corresponded to removal of 10.10 mmoles of triethylamine. An
experiment employing only triethylamine and triethylammonium chloride was performed. Pressure-composition measurements indicated no interaction between these materials at 25°C. This behavior differs from that of the ammonia-ammonium chloride system (63).

When a sample of triethylammonium dichlorocuprate(I) was poured into water, it was decomposed into its components giving a precipitate of copper(I) chloride and a solution of triethylammonium chloride.

6. The System Copper(I) Chloride-Triethylammonium Chloride-Tri-n-butylamine

Triethylammonium dichlorocuprate(I) in the amount of 10.06 mmoles (2.380 grams) was treated with an excess of purified tri-n-butylamine (vapor pressure < 1 mm. at 25.0°C.) in the manner previously described and the mixture stirred for two hours. No solid material could be detected, two liquid phases being present. The system developed an equilibrium pressure of 8 mm. on stirring overnight at 28°C. Volatile material was removed at this pressure and isolated in a Dry Ice-cooled trap. It was characterized as triethylamine by preparation of the hydrochloride, which was recrystallized from ethanol, m.p. (sealed tube) 254°C., mixed m.p. with authentic triethylammonium chloride (sealed tube) 254°C.
F. Copper(II) Halide-Trialkylamine Systems

1. Preliminary Studies

   a. Early Observations of Amine Oxidation. - At an early stage of the work, an attempt was made to prepare a complex of chromium(III) chloride and triethylamine. To effect this, purified anhydrous chromium(III) chloride was placed in a reaction vessel and attached to the high vacuum system. Pure triethylamine was condensed onto the halide and the mixture was stirred at 25°C. for 24 hours. No interaction of the components was apparent. The reaction tube was heated to 85°C. and stirring continued for another hour. Subsequently the excess of triethylamine was removed by distillation in the vacuum system. No appreciable quantity of triethylamine was retained by the halide. A study of possible interaction of the components under conditions of prolonged refluxing was undertaken. In a system preflushed with dry nitrogen and open to the atmosphere only through a calcium hydride filled drying tube, a mixture of anhydrous chromium(III) chloride and triethylamine was maintained under reflux for three days. During this time it was observed that the violet chromium(III) chloride was slowly transformed into a dark gray mass, while the supernatant triethylamine became dark in color. It was concluded that simple complex formation had not occurred, and that the chromium(III) chloride had decomposed some of the triethylamine, the products of the reaction being unknown.
Subsequent to this an attempt was made to prepare a triethylamine complex of copper(II) bromide. This resulted in a very apparent decomposition reaction. The copper(II) bromide and the triethylamine were transformed into a black oily tar and a dark brown liquid. It was concluded that the copper(II) bromide had oxidized the triethylamine. No free bromine was observed. The system was not studied further.

b. Copper(II) Chloride-Triethylamine System. — In a reaction assembly affixed to the high vacuum system, an excess of purified trimethylamine was distilled onto 7.65 mmoles (1.03 grams) of anhydrous copper(II) chloride. The technique described earlier of measuring the pressure of the system as a function of composition was employed. Some brown copper(II) chloride dissolved in the excess of trimethylamine at 0°C. forming a blue solution. The mixture was stirred for an hour at 0°C. without any noticeable change, other than a slow change in the initial blue color of the solution to a greenish cast. The trimethylamine was removed by distillation in the vacuum system leaving behind a greenish brown solid residue, which consisted of mostly unreacted copper(II) chloride, as judged from its appearance. The liquid trimethylamine was kept in a storage bulb at a temperature just below 0°C., so that its vapor, at a pressure of 635 mm., was in contact with the copper(II) chloride in the reaction assembly. The pressure in the system remained constant as the reaction assembly was warmed
to 25°C. It did not change after the copper(II) chloride sample had remained at room temperature in contact with the vapor for one hour. The reaction tube was heated in a water bath. Very suddenly at 85°C, the solid sample absorbed trimethylamine rapidly causing the pressure in the system to drop and trimethylamine to distill back into the reaction tube. The absorption of the amine was accompanied by a rapid transformation of the solid copper(II) chloride to a clear amber oil. The excess of amine was removed from the product by distillation in the vacuum system. At this point the presence of a non-condensable gas was tentatively indicated. The product was opened directly to the vacuum line pumping system and all volatile material was removed. The gain in weight of the sample corresponded to the retention of 11.0 mmoles of trimethylamine (on an original basis) in the reaction product. This would correspond to an amine to copper(II) chloride mole ratio of 1.14 in the product. Pumping over the sample for extended periods of time resulted in further loss of material from the product. It was concluded that a thermally induced oxidation-reduction reaction had occurred. The system was not investigated further.

c. Copper(II) Chloride-Triethylamine System. --In a preliminary experiment it was noted that the behavior of the copper(II) chloride-triethylamine system closely resembled that observed in the copper(II) bromide-triethylamine system. When anhydrous copper(II) chloride was
treated with an excess of highly purified triethylamine for short periods of time at 25°C. in a reaction assembly attached to the high vacuum system, with rigorous exclusion of moisture, nearly all of the amine could be recovered at its equilibrium vapor pressure by distillation in the vacuum system. Some discoloration of the halide was apparent. An obvious reaction did occur when such systems were warmed to about 50°C., with the development of a red-black tarry reaction product. The reaction was observed to be markedly exothermic, and when once initiated in any part of the reaction mixture the heat given off proved sufficient to spread reaction throughout the mass.

On addition of water a discolored whitish precipitate was formed together with black tarry material. Some of the white precipitate was separated and identified as copper(I) chloride. The solution remaining after filtration of the copper(I) chloride and black tarry material was evaporated to dryness. The reddish residue remaining was extracted with 95 percent ethanol and a colorless crystalline product was isolated on evaporation of the ethanol. This was recrystallized from absolute ethanol-ether mixtures and identified as triethylammonium chloride, m.p. (sealed tube) 254°C., authentic sample 254°C., mixed m.p. 254°C.

When a solution of copper(II) chloride dihydrate in 95 percent ethanol was treated with triethylamine a green gelatinous precipitate formed immediately. When this mixture was heated on a steam bath the entire reaction mixture was transformed to a clear red solution.
Exposure of this solution to the atmosphere for one month resulted in slow precipitation of a green substance. This material was isolated and analyzed. It contained no chloride or nitrogen and agreed with the composition of malachite, CuCO$_3$·Cu(OH)$_2$, if it is supposed that two percent of the hydroxide was replaced by ethoxide. Anal. calculated for such a composition: copper, 56.4%; carbon, 6.36%. Found: copper, 56.4%; carbon, 6.39%. The behavior of the material on ignition clearly indicated the presence of some organic constituent. This indicates reoxidation of the reduced copper species by atmospheric oxygen. Similarly, when a solution of anhydrous copper(II) chloride in absolute ethanol was treated with pure anhydrous triethylamine, operations being carried out in a nitrogen-filled dry box, a blue gelatinous precipitate was formed. When the mixture was warmed a red color developed and on further heating the entire mixture transformed into a clear red solution. This solution was covered with dry nitrogen and sealed in a stoppered flask with wax. The solution was stable for one month but on opening and subsequent passage of oxygen through the solution it became turbid and precipitation of a light green substance occurred. Analysis of this material showed it to be primarily copper(I) chloride. The supernatant solution, which contained no copper, was evaporated to dryness yielding a red tarry material. This material was leached with ethanol, the ethanol was evaporated, and the crystalline
material obtained was identified as triethylammonium chloride in the manner previously described.

Under anhydrous conditions 10 ml. of triethylamine were added to a solution of two grams of anhydrous copper(II)-chloride in 50 ml. of absolute ethanol. The deep blue gelatinous precipitate which formed was separated by centrifugation and washed with anhydrous ethanol by decantation. The supernatant solution was colored red indicating that oxidation-reduction had occurred to a limited extent. The precipitate was placed in a tared weighing bottle and dried at room temperature in vacuo. Analysis of this material indicated that it was primarily copper(II) ethoxide with a trace of chloride present. Anal. calculated for copper(II) ethoxide: copper, 41.36%. Found: copper, 44.10%. The red filtrate was evaporated and triethylammonium chloride was shown to be present in the manner indicated previously.

In another experiment hydrochloric acid was added with stirring at 0°C. to a mixture of one gram of anhydrous copper(II) chloride and 5 ml. of triethylamine in 25 ml. of water until the green gelatinous precipitate initially formed had just dissolved. The pH of the solution was found to be 3.5, as indicated by pH Hydrion paper. The mixture was refluxed for one week under nitrogen. The color of the reaction mixture became slightly darker green and upon the passage of oxygen through the solution a small amount of a white precipitate was formed. This material was identified as copper(I) chloride by qualitative tests. Apparently reaction under these conditions is almost negligible.
A reaction between 65 grams of anhydrous copper(II) chloride and 35 ml. of purified triethylamine was carried out in an apparatus which was preflushed with dry nitrogen and contained 200 ml. of anhydrous chlorobenzene. The insoluble copper(II) chloride was dispersed in the chlorobenzene by mechanical stirring. Triethylamine was added dropwise to the agitated mixture, which was kept cool in an ice-bath. As the reaction progressed lumps of dark oil appeared as a distinct phase. No gas evolution during the reaction occurred. This was tested for by placing a delivery tube from the apparatus into a solution of bromine in carbon tetrachloride.

It was shown (64), that when anhydrous copper(II) chloride was ground or fused at 110°C. with triethylammonium chloride in 1 to 2 mole proportions respectively, a golden colored material was obtained, which exhibited a definite melting point without decomposition, m.p. 125.5-127.5°C. When a mixture of the components in 1:1 mole proportions was heated, hydrogen chloride was lost and the remaining material underwent the oxidation-reduction reaction, with attendant formation of the black tarry oxidation product previously observed to be characteristic of this system. A number of such alkylammonium tetrachlorocuprate(II) complexes have been reported to decompose on heating (65).
2. Pressure-Composition Study of the Copper(II)-Chloride-Triethylamine System

a. Stoichiometry of the Oxidation-Reduction Reaction: Products A and B. --An excess of pure triethylamine was added to 16.59 mmoles (2.220 grams) of anhydrous copper(II) chloride in a reaction assembly attached to the vacuum system in the manner described previously. The mixture was warmed to induce the oxidation-reduction reaction to take place. The reaction mixture was then cooled to 30°C. and stirred magnetically for 24 hours. The reaction product was a gray-brown solid powder, finely dispersed in, and apparently insoluble in the supernatant liquid phase of triethylamine. The excess of triethylamine was removed at 25.0°C. by distillation in the vacuum system. Removal of triethylamine was continued until the vapor pressure suddenly dropped. The gray-brown solid reaction product remained as a residue. At this point the reaction assembly was removed from the vacuum system and weighed. The gain in weight of the system corresponded to 33.10 mmoles of triethylamine (original component basis).

The reaction assembly was then reattached to the vacuum system, more triethylamine removed, and the assembly subsequently reweighed. These operations were repeated and the pressure composition data so obtained are listed in Table 7. The data indicate that at a mole ratio value of 2:1, triethylamine/copper(II) chloride, the pressure drops
from the value for the vapor pressure of triethylamine, 66 mm. at 25.0°C., to a new equilibrium value of 6.0 mm. at 25.0°C. The solid reaction product of mole ratio 2:1 will be hereafter referred to as product A.

Upon further removal of triethylamine at the 6 mm. equilibrium pressure, transformation of the gray-brown solid residue to a black oil occurs. Triethylamine was removed at 6 mm. pressure until the composition of the system corresponded to a mole ratio of 1:1 (on the basis of the original components). At this point the equilibrium vapor pressure dropped to a negligibly small value, and the product was entirely in the form of a black viscous oil. Exposure of this material directly to the vacuum line pumping system for extended periods of time failed to cause further loss in weight. The liquid reaction product of mole ratio 1:1 will be hereafter referred to as product B.

Triethylamine was distilled onto product B and the mixture stirred for 6 hours. It was observed that as a result of this operation, product B slowly changed into the original gray-brown solid product A. The excess of triethylamine was again removed and the same solid-oil transformation and stepwise pressure composition relations were observed, indicating the reversible nature of the process, and proving the establishment of equilibrium between products A and B.

The reaction was repeated exactly as above except that the material removed at 6 mm. pressure, during the conversion of product A into product B, was isolated in a Dry Ice cooled trap. This material
TABLE 7. -- Pressure-Composition Data: Copper(II) Chloride-Triethylamine System at 25.0°C.

<table>
<thead>
<tr>
<th>Mole ratio Et₃N/CuCl₂ (original)</th>
<th>Pressure mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.11</td>
<td>65.5</td>
</tr>
<tr>
<td>3.11</td>
<td>65.5</td>
</tr>
<tr>
<td>2.58</td>
<td>63.0</td>
</tr>
<tr>
<td>2.09</td>
<td>53.0</td>
</tr>
<tr>
<td>1.95</td>
<td>23.0</td>
</tr>
<tr>
<td>1.82</td>
<td>6.0</td>
</tr>
<tr>
<td>1.74</td>
<td>6.0</td>
</tr>
<tr>
<td>1.69</td>
<td>6.0</td>
</tr>
<tr>
<td>1.56</td>
<td>6.0</td>
</tr>
<tr>
<td>1.34</td>
<td>6.0</td>
</tr>
<tr>
<td>1.30</td>
<td>6.0</td>
</tr>
<tr>
<td>1.26</td>
<td>6.0</td>
</tr>
<tr>
<td>1.15</td>
<td>6.0</td>
</tr>
<tr>
<td>1.04</td>
<td>4.7</td>
</tr>
<tr>
<td>0.96</td>
<td>1.7</td>
</tr>
<tr>
<td>0.95</td>
<td>a</td>
</tr>
</tbody>
</table>

*Pressure too low to be read on Hg manometer.*

was subjected to gas chromatographic analysis and was found to consist of pure triethylamine, i.e., the sample exhibited only one peak, whose retention time was identical to that exhibited by an authentic sample of triethylamine (1 min. 38 sec. at 75°C., 5 ft. carbowax on firebrick column, Wilkins Aerograph Instrument). In addition the
sample was characterized as triethylamine by preparation of the hydro-
chloride salt, m.p. 254°C. (sealed tube).

b. Stoichiometry of the Reaction in Ethanol. --A 1.760-gram
(13.13 mmole) quantity of anhydrous copper(II) chloride was dissolved in
30 ml. of absolute ethanol. The operations were performed in a nitrogen-
filled dry box. The reaction assembly containing the solution was
attached to the vacuum system and triethylamine distilled into the solu-
tion. The reaction was allowed to proceed. The previously mentioned
red solution was formed, and this was heated to 85°C. to insure complete
reaction. Solvent and the excess of triethylamine were rapidly removed
by distillation in the vacuum system, until a significant drop in pressure
occurred. At this point the product was a red-brown solid with a mole
ratio value of 2:1, triethylamine:copper(II) chloride (original component
basis), and exhibited a 6 mm. equilibrium vapor pressure at 25.0°C.
With further removal of volatile matter at 6 mm. pressure the solid
material was transformed to a non-volatile red oil of composition
corresponding to a 1:1 mole ratio of the components on an original
basis. As before, the solid-oil interconversion at mole ratio values
between 2:1 and 1:1 was completely reversible. The only effect of
running the reaction in ethanol solution was on the color of the
product.
3. Hydrolysis Studies of the Copper(II) Chloride-Triethylamine Reaction Product

a. Qualitative Studies. - - It was noted previously that copper(I) chloride, triethylammonium chloride, and a dark tarry material were established as being among the products obtained when the copper(II) chloride-triethylamine oxidation-reduction product B was treated with water. More detailed hydrolysis studies were made to determine the nature of any other products formed. A series of reactions were run, in which fairly large amounts of copper(II) chloride (0.6-0.8 mole) were allowed to react with triethylamine. In these reactions an approximate 1:2 mole ratio of amine to copper(II) chloride was employed. This ratio was chosen to insure the complete reaction of triethylamine and to prevent formation of triethylamine complexes of the reaction products as noted in the previous section.

The viscous oily product of the oxidation-reduction reaction formed from 0.63 mole (84 grams) of anhydrous copper(II) chloride and 0.30 mole (53 ml.) of triethylamine, after heating at 100°C. for one hour, was treated with 300 ml. of water. After refluxing for one hour, distillation was commenced and a fore-run of a few ml. collected. The presence of two organic components in the distillate was demonstrated by vapor phase chromatography on a Wilkins Aerograph model no. A-100-C instrument fitted with a carbowax on firebrick column. Retention times at 55°C. indicated that neither substance was triethylamine. The
distillate gave a positive test with 2, 4-dinitrophenylhydrazine reagent. The material remaining in the reaction flask was treated with strong sodium hydroxide solution and distilled. The fore-run of this distillate contained triethylamine, as indicated by a comparison of the retention time of the major organic component with that of pure triethylamine at 55°C. (retention time, 1 min. 30 sec. under the conditions described above).

A similar reaction between 0.70 mole (94 grams) of anhydrous copper(II) chloride and 0.35 mole (50 ml.) of triethylamine was performed. After hydrolysis the mixture was distilled and a fore-run collected. The distillate gave positive tests with sodium hypoiodate and Fehling's solution. Manganese dioxide was precipitated from an alkaline potassium permanganate solution of the distillate. The excess of permanganate was destroyed with sulfite, the manganese dioxide removed by filtration, and the filtrate evaporated to dryness. The residue was acidified with sulfuric acid, the solution distilled, and the distillate characterized as containing acetic acid; p-bromophenacyl ester, m.p. 86°C., lit. (66) 85°C. It appears that the original reaction mixture gave a slight amount of acetaldehyde on hydrolysis. Additional evidence for this is that the fore-run on distillation of the hydrolyzed reaction mixture gave a vapor phase chromatogram with two peaks preceding the water peak; one of these was matched with an authentic
sample of acetaldehyde under the same conditions (Wilkins Aerograph instrument, five feet carbowax on firebrick column, retention time, 48 sec., when a helium gas pressure of 7 lbs. was employed).

A similar experiment using 0.74 mole (99 grams) of copper(II) chloride, mechanically dispersed in 200 ml. of anhydrous chlorobenzene and 0.37 mole (53 ml.) of triethylamine was performed. As the reaction mixture was warmed, dark masses of oil separated and collected at the bottom of the flask. Hydrolysis followed by distillation gave a material which again gave tests for a carbonyl component. Attempts at preparation of standard carbonyl derivatives resulted in materials which had no definite melting points or could not be crystallized.

b. Quantitative Determination of Triethylammonium Ion in Product B. --The product obtained from 13.93 mmoles (1.870 grams) of anhydrous copper(II) chloride, from which the excess of triethylamine had been removed after reaction, contained 13.92 mmoles of triethylamine (original). The reaction tube containing this material was dropped into several hundred ml. of concentrated sodium hydroxide solution in a distillation apparatus. The distillate was caught in a measured volume of standard hydrochloric acid and this solution was back-titrated with standard sodium hydroxide solution to a methyl red end point. Recovery amounted to 91.95 percent of the total 13.92 mmoles present. The tarry product was decomposed by the boiling
sodium hydroxide solution producing a yellow precipitate of copper(I) oxide and a yellow solution.

To avoid the possibility that some of the volatile amine was formed by degradation of the tarry product, milder hydrolytic conditions were employed in subsequent runs. Product B containing on an original basis 17.96 mmoles of copper(II) chloride and 17.26 mmoles of triethylamine was poured into water and triturated for one-half hour. The mixture was filtered to remove precipitated copper(I) chloride and gummy tar-like material and the solution thus obtained treated with sodium hydroxide solution and distilled. Recovery of 88.20 percent of the total 17.26 mmoles of triethylamine resulted. A sample of product B corresponding to a mole ratio value of 0.965 mole of amine per mole of copper, after treatment with water for five minutes, filtration and washing of the residue, and combination of solutions as before, released 84.80 percent of its triethylamine content. To prove that it was triethylamine and only triethylamine that was being titrated, the titration solutions were combined, treated with concentrated sodium hydroxide solution and distilled. 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 triethylamine by conversion to the hydrochloride, m.p. (sealed tube) 254°C.
In one run, product B containing on an original basis 18.08 mmoles of copper(II) chloride and 17.62 mmoles of triethylamine was decomposed and the volatile amine liberated by the addition of calcium oxide rather than alkaline hydrolysis. A fourfold mole excess of calcium oxide powder was added to the product by rotation of a side-arm addition tube about a joint in the system attached to the vacuum line. The mixture was stirred as well as possible and then heated to 150°C. The volatile amine was pumped off and collected in a cold trap; the loss in weight of the reaction assembly was equated with triethylamine removed, and corresponded to 92.95 percent of the original 17.62 mmoles of triethylamine present.

4. Studies on the Nature of the Triethylamine Oxidation Product
   a. Isolation and Polymeric Nature of the Triethylamine Oxidation Product. --Attempts to isolate the organic oxidation product of triethylamine in a pure form were unsuccessful. A sample of the triethylamine-copper(II) chloride oxidation-reduction product B was poured into water, resulting in the precipitation of large amounts of copper(I) chloride and separation of a black gummy material. On trituration, the white copper(I) chloride became mostly suspended in a finely divided state and could be separated by decantation. After repeated washing and decantation, the black material, which settled readily, was separated by filtration, washed repeatedly, and dried
at room temperature in vacuo. Elemental analysis of the sample gave the following results: C, 10.51, 10.67; H, 1.91, 1.92; Cu, 49.0, 49.6; N, 1.54, 1.60 (questionable validity); apparent remainder 36.6%; qualitative tests for chloride: trace. The black material was appreciably soluble in dimethylsulfoxide, dimethylformamide, and 6 N hydrochloric acid, only slightly soluble in water, and insoluble in dilute sodium hydroxide, alcohol, carbon tetrachloride, and chloroform. The material could be precipitated from dimethylformamide solutions by the addition of chloroform. All these properties suggest a basic polymeric nature for the organic oxidation product, which would explain the difficulty encountered in separating copper from the organic material. This material will hereafter be referred to as product 1.

A process for increasing the fraction of organic matter in the sample of oxidation product was suggested by the observation that partial decomposition of the black material took place in hydrochloric acid solution. When such a solution was made basic with sodium hydroxide, the black material did not reprecipitate but rather a yellow precipitate of copper(I)-oxide appeared.

A sample of the black material was warmed and triturated with a small amount of 4 N hydrochloric acid over a 2 hour period. A black residue and a brown solution were formed. The residue was washed with dilute hydrochloric acid and water; qualitative tests indicated a strong concentration of copper in the filtrates. The
residue was dried at room temperature in vacuo; elemental analysis indicated a large increase in the organic content of the sample:

C, 42.64, 42.46; H, 5.00, 4.97; N, 6.34, 5.60; apparent remainder 46.49%. The nature of the remainder is not clear; the sample gave a large ash on ignition, and yet digestion of a portion of the sample with mixed nitric and perchloric acids gave a solution which exhibited a negative qualitative test for copper(II). When this material was dissolved in dilute hydrochloric acid, it could be reprecipitated by the addition of dilute sodium hydroxide solution. This material will hereafter be referred to as product 2.

Qualitative studies of the apparent order of magnitude of the molecular weight of this polymeric material were made by measurements of the viscosities of solutions of the sample in dimethylsulfoxide. The material described above, product 2, and another sample obtained from an independent reaction, which was treated in a similar manner, were employed. Dimethylsulfoxide solutions of the samples ranging in concentration from 0.25 to 3.00 percent by weight of product 2 were prepared. The flow times of these solutions, as well as the flow time for pure dimethylsulfoxide, at 30.0°C. (constant temperature bath) and the number of the Ostwald viscometer used are listed in Table 8. All of the flow times were converted to values for viscometer number 3 by the use of time ratios.
The intrinsic viscosity of the material may be obtained from the data and does not require the determination of the actual viscosities of the solutions. At constant temperature,

\[ \frac{n_1}{n_2} = \frac{d_1 t_1}{d_2 t_2} \]

where \( n_1 \) and \( n_2 \) are the viscosities of solutions 1 and 2, while \( d_1 \) and \( d_2 \) are their respective densities, and \( t_1 \) and \( t_2 \) are their flow times as measured in the same viscometer. Assuming that the densities are equal,

\[ \frac{n_1}{n_2} = \frac{t_1}{t_2} . \]

By making use of the equations for the specific and intrinsic viscosities,

\[ n_{sp} = \frac{n}{n_0} - 1 \]

\[ (n) = \lim_{C \to 0} \frac{n_{sp}}{C} \]

where \( n \) is the viscosity of the solution, \( n_0 \) the viscosity of the solvent, \( n_{sp} \) the specific viscosity, \( (n) \) the intrinsic viscosity, and \( C \) the concentration of the solution in grams per 100 ml., it is possible to calculate a value of \( (n) \) for the sample (67). The values of \( n_{sp} \) for the various solutions were calculated and are given in Table 9. The density of dimethyl sulfoxide [25°C. lit. (68) 1.096 g./ml.] at 30°C. was found to be 1.086 gm./ml. Values of \( C \) were calculated by converting percent by weight to gms./100 ml. using this density factor.
TABLE 8. --Flow Times at 30.0°C. in Ostwald Viscometers.

<table>
<thead>
<tr>
<th>Solution %</th>
<th>Time sec.</th>
<th>Viscometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>101.5</td>
<td>1</td>
</tr>
<tr>
<td>DMSO</td>
<td>508.2</td>
<td>2</td>
</tr>
<tr>
<td>DMSO</td>
<td>452.1</td>
<td>3</td>
</tr>
<tr>
<td>0.25</td>
<td>465.4</td>
<td>3</td>
</tr>
<tr>
<td>0.50</td>
<td>530.8</td>
<td>2</td>
</tr>
<tr>
<td>1.00</td>
<td>107.3</td>
<td>1</td>
</tr>
<tr>
<td>1.50</td>
<td>504.6</td>
<td>3</td>
</tr>
</tbody>
</table>

product from second reaction

<table>
<thead>
<tr>
<th>Solution %</th>
<th>Time sec.</th>
<th>Viscometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>508.0</td>
<td>3</td>
</tr>
<tr>
<td>3.00</td>
<td>532.4</td>
<td>3</td>
</tr>
<tr>
<td>3.00</td>
<td>600.6</td>
<td>2</td>
</tr>
</tbody>
</table>

Above values converted to flow times for viscometer no. 3

<table>
<thead>
<tr>
<th>Solution %</th>
<th>Time sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>452.1</td>
</tr>
<tr>
<td>0.25</td>
<td>465.4</td>
</tr>
<tr>
<td>0.50</td>
<td>473.0</td>
</tr>
<tr>
<td>1.00</td>
<td>478.5</td>
</tr>
<tr>
<td>1.50</td>
<td>504.6</td>
</tr>
<tr>
<td>2.00</td>
<td>508.0</td>
</tr>
<tr>
<td>3.00</td>
<td>533.5</td>
</tr>
</tbody>
</table>

A plot of \( n_{sp}/C \) vs. \( C \) gives the intrinsic viscosity (n), when extrapolated to zero concentration (67). In this manner the intrinsic viscosity of the organic triethylamine oxidation product was determined; see Figure 5. A knowledge of this quantity allows an estimate of the average molecular weight of the material to be made.
TABLE 9. --Calculated Viscosity Data.

<table>
<thead>
<tr>
<th>C. % by wt.</th>
<th>C. gms./100 ml.</th>
<th>n&lt;sub&gt;sp&lt;/sub&gt;</th>
<th>n&lt;sub&gt;sp&lt;/sub&gt;/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.27</td>
<td>0.029</td>
<td>0.1065</td>
</tr>
<tr>
<td>0.50</td>
<td>0.54</td>
<td>0.046</td>
<td>0.0847</td>
</tr>
<tr>
<td>1.00</td>
<td>1.09</td>
<td>0.058</td>
<td>0.0532</td>
</tr>
<tr>
<td>1.50</td>
<td>1.63</td>
<td>0.114</td>
<td>0.0700</td>
</tr>
<tr>
<td>2.00</td>
<td>2.18</td>
<td>0.122</td>
<td>0.0560</td>
</tr>
<tr>
<td>3.00</td>
<td>3.26</td>
<td>0.180</td>
<td>0.0552</td>
</tr>
</tbody>
</table>

b. Spectra of the Oxidation-Reduction Product. --The infrared spectrum of product B taken between sodium chloride discs shows absorptions characteristic of a tertiary alkylammonium ion. The presence of ethyl groups is indicated by the characteristic shape of the absorption bands at 770 cm<sup>-1</sup> through 900 cm<sup>-1</sup>. Other weak absorptions listed in Table 10 are probably due to the organic oxidation product of triethylamine. These absorptions do not lend themselves to ready interpretation in terms of structural factors and are thus unassigned. The infrared spectrum of product B differed from the spectrum of triethylammonium chloride (KBr disc) only by an absorption in the 1250-1260 cm<sup>-1</sup> region and three very weak absorptions in the 1500-1600 cm<sup>-1</sup> region. The absence of immonium absorption bands at 1800-2200 cm<sup>-1</sup> indicate the absence of eneamine species in either the protonated or free forms. Similarly the spectra indicate the absence of carbon-carbon unsaturation in product B.
TABLE 10. - Infrared Spectral Bands of Product B.

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>Assignment (83)</th>
</tr>
</thead>
<tbody>
<tr>
<td>770-900</td>
<td>m C₂H₅</td>
</tr>
<tr>
<td>1030</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1050</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1150</td>
<td>m probably C-C str.</td>
</tr>
<tr>
<td>1194</td>
<td>w probably C-C str.</td>
</tr>
<tr>
<td>1250-1260</td>
<td>s probably C-N str. (^a)</td>
</tr>
<tr>
<td>1278</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1430</td>
<td>w CH₂ bend., adjacent to N⁺</td>
</tr>
<tr>
<td>1450</td>
<td>s CH₃ assym. def.</td>
</tr>
<tr>
<td>1500</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1550</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1600</td>
<td>w unassigned</td>
</tr>
<tr>
<td>2700</td>
<td>m &quot;ammonium band&quot; N⁺-H str.</td>
</tr>
<tr>
<td>2870</td>
<td>m C-H str.</td>
</tr>
</tbody>
</table>

\(^a\)Not observed in triethylammonium chloride spectrum, KBr disc.

TABLE 11. - Infrared Spectral Bands of the Isolated Triethylamine Oxidation Products 1 and 2. \(^a\)

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>Assignment (83)</th>
</tr>
</thead>
<tbody>
<tr>
<td>880-970</td>
<td>w unassigned</td>
</tr>
<tr>
<td>1550</td>
<td>w (^b) unassigned</td>
</tr>
<tr>
<td>1665</td>
<td>w unassigned</td>
</tr>
<tr>
<td>2450</td>
<td>s &quot;ammonium band&quot; N⁺-H str.</td>
</tr>
<tr>
<td>3300</td>
<td>m associated N-H</td>
</tr>
</tbody>
</table>

\(^a\)Nujol mulls. \(^b\)Sharp closely spaced spikes.
The infrared spectra of the isolated triethylamine oxidation products can roughly be interpreted as being due to tertiary amine hydrochlorides. The absorptions characteristic of these materials are given in Table 11. The infrared spectra indicate the absence of vinylic hydrogen atoms as well as the absence of unsaturated carbon-carbon linkages in the oxidation product.

The visible spectrum of the reaction product in solution in various non-aqueous solvents was taken in connection with kinetic studies of the redox reaction between copper(II) chloride and triethylamine. The reagents were dissolved in separate solutions of the particular solvent under anhydrous conditions. These component solutions were then mixed and the oxidation-reduction reaction allowed to take place in solution in the spectrophotometer cell. The visible spectrum of an acetonitrile solution, which was $2.50 \times 10^{-3}$ molar in original copper(II) chloride, showed after reaction with triethylamine the following absorptions: a maximum at 416 μm, $\epsilon = 3.82$, with a shoulder at 440 μm, $\epsilon = 2.60$, this shoulder dropping to another maximum at 510 μm, $\epsilon = 0.8$. The absorption curve shown in Figure 7 displayed this general characteristic shape for reactions run over large concentration ranges in acetonitrile solution. The presence of water in other than trace amounts prevents reaction, and the reaction mixture shows instead a single sharp absorption band at 412 μm, $\epsilon = 1.04$, which does not change with time. This band
probably represents a shift of the copper(II) chloride absorption band at 463 m\(\mu\), \(\epsilon = 0.78\), in anhydrous acetonitrile brought about by the addition of the amine.

In \(\gamma\)-butyrolactone a different kind of behavior is observed. Copper(II) chloride solutions in anhydrous \(\gamma\)-butyrolactone are yellow having absorption bands at 475 m\(\mu\) and at 310 m\(\mu\) (64). On addition of triethylamine the color immediately becomes green and the solution exhibits absorption bands at 225 m\(\mu\), 303 m\(\mu\), and 676 m\(\mu\). Such solutions on standing overnight or on warming change color, becoming orange as the oxidation-reduction reaction takes place. The final solution of the redox product exhibits strong absorption bands at 200 m\(\mu\) and 305 m\(\mu\) and weak ones at 390 m\(\mu\) and 495 m\(\mu\).

The proton magnetic resonance spectrum of product B was taken. The sample tube was loaded in a nitrogen-filled dry box and closed with a plastic cap sealed with wax. The spectrum is shown in Figure 6. Triethylammonium dichlorocuprate(I) was prepared from equimolar amounts of triethylammonium chloride and chlorotriethylaminecopper(I). These were mixed in a bulb on the vacuum line and the triethylamine removed as described earlier. The n.m.r. spectrum of the authentic triethylammonium dichlorocuprate(I) was then obtained in a similar manner. The samples and hence the spectra were found to be sensitive to atmospheric oxygen.
5. Studies in Various Solvents

a. Triethylamine-Copper(II) Chloride Reaction in Various Solvents. --

Copper(II) chloride is insoluble in p-1, 4 dioxane, 2, 2-dimethoxypropane, and in 1, 2-dichloroethane. Copper(II) chloride is soluble in anhydrous acetone, glyme, diglyme, and triglyme, but precipitation of blue-green substances occurred on the addition of triethylamine. Copper(II) chloride was also found to be soluble in tetraglyme and ethyl acetate, but precipitation of a brown material resulted on the addition of triethylamine. The blue material precipitated from diglyme and triglyme solutions of copper(II) chloride turned brown on warming. Oxidation-reduction was thus indicated in these cases. No interaction between the two reagents was noted in pyridine solution even when heated.

Anhydrous copper(II) chloride forms a yellow solution in dry \(\gamma\)-butyrolactone (64). On addition of triethylamine a green color was formed immediately. On standing for 24 hours, or on warming, the solution became orange. When the blue solution was poured into water no copper(I) chloride was formed and the resulting solution gave a strong qualitative test for the copper(II) ion with ammonia. On similar treatment the orange solution gave a white precipitate, which was identified as copper(I) chloride. In this case the supernatant solution gave a negative test for the copper(II) ion with ammonia.

The addition of triethylamine to a solution of 0.5 gram of copper(II) chloride in 10 ml. of anhydrous acetonitrile resulted in
rapid formation of a red-brown solution. When such solutions were poured into water a white material was precipitated; this was identified as copper(I) chloride. The rate of the oxidation-reduction reaction in acetonitrile solution was found to be sensitive to traces of water, which retard the reaction. A study employing vacuum line techniques and rigorously anhydrous conditions showed that the redox reaction proceeds at -23°C. without the formation of intermediate blue or green colors.

The solution obtained on dissolution of one gram of copper(II) chloride in 10 ml. of dimethylsulfoxide gave a large green precipitate on standing (69). The addition of two ml. of triethylamine led to the disappearance of the precipitate and formation of a red solution. When the reaction mixture was poured into water, a white precipitate, which was identified as being copper(I) chloride was obtained.

b. Oxidation of Other Amines in Solution. - - When one ml. of tri-n-butylamine was added to a solution of copper(II) chloride in 15 ml. of dimethylsulfoxide, a deepening of the original green color of the solution was observed and on warming, the solution became red followed by separation of a dark red oil. Addition of water to the mixture resulted in the formation of a precipitate of copper(I) chloride. The addition of tri-n-butylamine to a solution of 0.1 gram of copper(II) chloride in 15 ml. of 95 percent ethanol resulted in the precipitation
of blue hydrous copper(II) oxide. No further reaction was observed on boiling the solution for several minutes. The behavior of tri-n-butylamine is thus different in this respect from that of triethylamine. When absolute ethanol was used as the solvent, oxidation of tri-n-butylamine by copper(II) chloride slowly took place when the solution was warmed. A dark red-brown opaque suspension was formed. When N-methyl-aniline or N, N-dimethylaniline was added to a solution of copper(II) chloride in absolute ethanol, immediate precipitation of violet to jet black solid materials resulted.

c. Kinetics of the Oxidation of Triethylamine by Copper(II) Chloride in Acetonitrile Solution. --The redox reaction was found to take place at an appreciable rate in acetonitrile at -23°C. forming a red-brown solution. The presence of traces of water retarded the reaction considerably, and completely inhibited it in solutions of ca. $10^{-4}$ molar copper(II) chloride. The green solvated copper(II) species formed in such solutions has a distinct spectrum, which does not change with time (see Figure 7) indicating that redox does not occur. With traces of moisture present redox does proceed in more concentrated solutions, e.g., $5 \times 10^{-3}$ molar copper(II) chloride. However, a small amount of material precipitated as the reaction proceeded in such solutions. Under rigorously anhydrous conditions reproducible reaction rates were obtained. It was observed that the
originally yellow, dilute solutions of copper(II) chloride in acetonitrile had become colorless over a period of 10 days, indicating instability and probable reduction of copper(II) to the copper(I) state with concurrent oxidation of acetonitrile. The solutions prepared for the kinetic study were therefore used immediately.

The copper(II) chloride and triethylamine solutions were prepared in pre-dried nitrogen-filled volumetric flasks. All operations were performed in a nitrogen-filled dry box. The kinetic work was done in 1 cm. quartz cells on the Cary model 14 double beam recording spectrophotometer. The cells were half filled with 1.6 ml. of copper(II) chloride solution in the dry box. The acetonitrile solutions of triethylamine were similarly prepared and placed into a bottle closed with a rubber serum bottle stopper. The materials were taken to the instrument and the cells placed in the compartments. In a typical run the triethylamine solution was removed from the container through the rubber serum bottle stopper with a hypodermic syringe, and 1.6 ml. was injected directly into the bottom of the Cary cell containing the copper(II) chloride solution. This filled the cell and the turbulence created by the forced injection of the triethylamine solution served to completely mix the solutions during the filling operations. As soon as this operation was completed, the spectrophotometer was activated and the rate of reaction was followed by measuring the absorbance of the solution at 416 m\(\mu\) with respect to time.
The color of a dilute solution of copper(II) chloride in acetonitrile is yellow. However as the redox reaction proceeded the color became pink-rose due to the formation of the product with consequent disappearance of the copper(II) chloride. An examination of the spectra of both reactant and product enabled a choice of wavelength with which to follow the progress of the reaction to be made. The product absorption band at 416 m\(\mu\) was found to be suitable for kinetic work. Tailing of the product absorption band at 440 m\(\mu\) into the region of the copper(II) chloride absorption band at 463 m\(\mu\) made it impossible to follow the rate of loss of copper(II) chloride. This was due largely to the high extinction of the product in this region, which is just about equal to that of the reactant at this wavelength. The high extinctions of both the reactant and product in the ultraviolet made utilization of this area of the spectrum unsuitable. Equal volumes of these solutions

<table>
<thead>
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<th>(\text{CuCl}_2)</th>
<th>(\text{Et}_3\text{N})</th>
</tr>
</thead>
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<tr>
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<td>(4.94 \times 10^{-2}) M</td>
</tr>
<tr>
<td>(7.92 \times 10^{-3}) M</td>
<td>(2.63 \times 10^{-2}) M</td>
</tr>
<tr>
<td>(5.00 \times 10^{-3}) M</td>
<td>(1.58 \times 10^{-2}) M</td>
</tr>
<tr>
<td>(2.50 \times 10^{-3}) M</td>
<td>(1.00 \times 10^{-2}) M</td>
</tr>
<tr>
<td>(9.91 \times 10^{-4}) M</td>
<td>(1.97 \times 10^{-3}) M</td>
</tr>
<tr>
<td>(5.07 \times 10^{-4}) M</td>
<td>(1.00 \times 10^{-3}) M</td>
</tr>
<tr>
<td>(1.01 \times 10^{-4}) M</td>
<td>(2.00 \times 10^{-4}) M</td>
</tr>
</tbody>
</table>
were brought into reaction in all possible combinations in the manner described. The final concentrations of the reacting solutions were one-half of the values listed because of the way in which they were mixed in the spectrophotometer cell.

A kind of rate behavior was observed which does not lend itself to ready interpretation. In Table 13 are listed the rate data representing typical behavior of the system observed in many kinetic runs. Figure 8 depicts the change in absorbance, \( \Delta A \), at 416 m\( \mu \) with respect to time for these three reaction systems.

An inspection of the absorption bands of the reactant and product in \( \gamma \)-butyrolactone indicates that it would be possible to follow the rate of loss of copper(II) chloride in this solvent spectrophotometrically at 676 m\( \mu \).


An excess of triethylamine was transferred by means of the high vacuum system into an e.p.r. sample tube containing degassed anhydrous copper(II) chloride. The tube was then sealed off in vacuo and placed into the cavity of an e.p.r. spectrometer. No interaction of the reagents was apparent, and only the broad resonance signal \( (g = 2.2) \) of paramagnetic \( d^9 \) copper(II) was observed. The tube was then heated to about 80°C. for about two minutes, allowed to cool,
# TABLE 13. --Representative Kinetic Data, 26°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>ΔA^a</th>
<th>Time</th>
<th>ΔA^a</th>
<th>Time</th>
<th>ΔA^a</th>
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<tr>
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<tr>
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<td>10</td>
<td>0.219</td>
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<td>0.562</td>
<td>28</td>
<td>0.932</td>
<td>26</td>
<td>0.760</td>
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</tbody>
</table>

^aΔA = change in absorbance at 416 mμ.
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-black tarry material. The e.p.r. spectra are shown in Figures 9 and 10. At intermediate stages of the reaction, sharp peaks appeared superimposed (at \( g \) values less than and greater than 2.2) on the diminishing copper(II) signal. These peaks first gained in intensity and subsequently diminished. After five such heating cycles, paramagnetism due to the intermediate as well as to the original \( d^9 \) copper(II) had disappeared. On admission of oxygen, the e.p.r. signal characteristic of the intermediate reappeared and on further heating disappeared again, the sample becoming fully diamagnetic. Re-admission of oxygen resulted in the reappearance of the resonances characteristic of the transient species. Electron paramagnetic resonance studies of the redox reaction in acetonitrile, dimethylformamide, and \( \gamma \)-butyrolactone solutions were attempted in order to obtain fine structural e.p.r. data, as well as to obtain rate information for purposes of comparison with the spectro-photometric kinetic data. In every case it was found that these solvents were good absorbers of microwave energy making e.p.r. study of their solutions by these techniques unsuitable.
7. Dichlorobis(triethylamine)copper(II)

a. Preliminary Observations. - The preparation of this complex grew out of an attempt to prepare the previously mentioned transient blue intermediate observed in the oxidation-reduction reaction between triethylamine and copper(II) chloride. Some attempts to do this are described, as they led to conditions for the preparation of dichlorobis(triethylamine)copper(II). Anhydrous copper(II) chloride was ground to a fine powder and spread in a film over the walls of a reaction flask, which was attached to the high vacuum system. The vapor of triethylamine in one case and of tri-n-propylamine in another was admitted to the reaction flask. In both cases redox occurred at 25°C. and at 10°C. when the system was allowed to stand overnight. No blue intermediate could be detected at any time and the reaction produced the usual tarry black material dispersed on the walls of the flask. In another attempt, triethylamine vapor was passed through copper(II) chloride at low pressures in a U tube attached to the vacuum system. At 25°C., 10°C., and 0°C. no intermediate could be detected and the copper(II) chloride eventually blackened as the redox reaction took place. An attempt to prepare an intermediate in acetonitrile solution at low temperatures also resulted only in the occurrence of the oxidation-reduction reaction. A final attempt employing two grams of copper(II) chloride in a reaction flask attached to the vacuum system resulted in a faint green surface coloration, when the vapor of triethylamine
impinged upon the solid at -46°C. It was thus decided that a large surface and low temperatures were necessary for the preparation of any intermediates, such as the green substance.

b. Preparation. ---Employing vacuum line techniques previously described, triethylamine was distilled onto very finely powdered anhydrous copper(II) chloride in a reaction flask, which had been precooled to -78°C. for one hour in a Dry Ice-acetone bath. The mixture was stirred at -78°C. for two hours to completely disperse the powder in the liquid amine. This step was necessary to avoid the formation of lumps of unreacted copper(II) chloride. The reaction mixture was warmed to -46°C. (chlorobenzene slush bath) with constant stirring. The mixture was stirred at -46°C. for one to four days, during which time a bright apple green color slowly developed and the copper(II) chloride became flocculent and puffy with consequent large increase in volume. When allowed to settle it was seen that the supernatant triethylamine was colored slightly orange indicating that redox had occurred to a very small extent. The sample was warmed to -23°C. in a carbon tetrachloride slush bath, stirring being maintained, and the excess of triethylamine removed by distillation in the vacuum system at its equilibrium vapor pressure of 4 mm. at -23°C. On complete removal of the excess of ligand, the pressure of the system dropped suddenly to less than 1 mm. The product was a bright green solid of much larger bulk than the original copper(II) chloride.
In various runs, from 2.00 to 2.02 moles of triethylamine were retained per mole of copper(II) chloride, as indicated by the gain in weight of the samples.

c. Thermal Stability. --Dichlorobis(triethylamine)copper(II) appeared to be stable indefinitely at -45°C or below. At -23°C, the complex showed signs of decomposition after several days, in that it became more yellow in color. As the complex was slowly allowed to warm to room temperature it became progressively more yellow. Upon remaining at 0°C for 12 hours the complex became completely yellow in color. When allowed to warm further it became progressively more orange. However, the original structure was retained. When warming was continued to 25°C, dark black spots suddenly appeared around the walls of the flask. These spots grew rapidly and spread through the mass of the complex, enough heat being liberated in the process to appreciably heat the flask. Within one minute of the appearance of the first spot, the process converted the entire mass of the complex to a dark black tar. During this process, the original structure of the material was completely lost.

The total decomposition behavior of the complex suggests that the complex decomposes to an intermediate material between the temperatures -23°C and 10°C. and that a second stage characterized by conversion to tar and evolution of heat converts the yellow-orange
intermediate to the final oxidation-reduction product of two to one
stoichiometry (product A), characteristic of the copper(II) chloride-
triethylamine system.

d. Reflectance Spectrum.--The reflectance spectrum of the
complex was obtained in the following manner. The movable sample
tray of the standard reflectance attachment to the Beckmann D. U.
spectrophotometer was modified by drilling a one-quarter inch hole
in the side. Through this hole were passed a blackened Tygon tube
and the leads of an iron-constantan thermocouple. The tube terminated
just under the sample, while the thermocouple junction was placed
directly adjacent to the sample dish.

In a typical run the sample, which had been cooled to -196°C.
with liquid nitrogen, was loaded in the dry box into a similarly pre-
cooled one inch Petrie dish and then placed into the sample holder of
the movable tray. A similar dish contained Reagent Grade magnesium
carbonate as a reflectance standard. The entire tray including the
sample and standard was placed into a plastic bag and carried to the
spectrophotometer. Another plastic bag had been carefully taped
around the sample housing of the instrument. During a run this bag
was opened in front and the sample tray was inserted into the instru-
ment housing. Then the bag was resealed, isolating the sample area
from the atmosphere. The Tygon tube and thermocouple leads were
led out of the enclosure through a small hole cut in the bag. The vapor from boiling liquid nitrogen was passed through the tube, this serving to cool the sample and adjacent area. This method of cooling the sample also provided a dry nitrogen atmosphere for the sample, and as most of the nitrogen exited through the instrument, it prevented frosting of the optical components as well as of the sample area by forcing the atmosphere from these places. In this manner, the sample temperature was maintained at about -15°C.

Position changes of the sample were seen to change the absorbance values by as much as 0.1 absorbance units. Since several samples were studied, the values listed in Table 14 are relative. The slit width was kept constant at 0.3 mm during the spectral determination unless otherwise indicated. A composite spectrum of dichlorobis(triethylamine)copper(II), in the range 300 μm to 1300 μm, was constructed from the data and is given in Figure 11.

8. E.P.R. Study of the Thermally Induced Internal Oxidation-Reduction of Dichlorobis(triethylamine)copper(II)

a. The Diamagnetic Intermediate. - Dichlorobis(triethylamine)-copper(II) was prepared as previously described and three quartz e.p.r. sample tubes, which were precooled to -196°C. with liquid nitrogen, were filled with samples of the complex in a nitrogen-filled dry box. The tubes were evacuated and stored at -78°C. until the e.p.r.
TABLE 14. Reflectance Data for Dichlorobis(triethylamine)copper(II).

<table>
<thead>
<tr>
<th>( \text{m} \mu )</th>
<th>O.D.</th>
<th>Slit mm.</th>
<th>( \text{m} \mu )</th>
<th>O.D.</th>
<th>Slit mm.</th>
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<td>790</td>
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spectra could be taken. An approximate value of the field strength was calculated from the observed signal of diphenylpicrylhydrazyl ($g = 2.004$) and the relation $h \nu = gBH$, using the value $9.5 \times 10^9$ c.p.s. as the klystron frequency. Subsequent estimations of $g$ values of other species were then based upon accurate measurements of changes in field strength from the point of approximate calibration. Such $g$ values are of high accuracy relative to each other, but of lower absolute accuracy. The sample and cavity temperatures were controlled with a V-4547 variable temperature accessory. The temperature was measured with an iron-constantan thermocouple, the output of which was measured on a Leeds and Northrup standard potentiometer.

The e.p.r. spectrum of dichlorobis(triethylamine)copper(II) shows resolution of the $d^9$ copper(II) resonance according to the anisotropy in the $g$ values, $g_\perp = 2.06$, $g_\parallel = 2.27$, as shown in Figure 12. As the sample was allowed to warm from $-40^\circ C$ to $0^\circ C$, there was a slow decrease in the intensity of this signal. In the temperature range $0^\circ C$ to $20^\circ C$, the rate of decrease in intensity became much greater, while at $20^\circ C$, the sample became completely diamagnetic in a few minutes. The loss of paramagnetism of the sample in this manner was not accompanied by the appearance of transient paramagnetic species as noted earlier, nor was the solid structure of the complex lost. The green solid paramagnetic complex simply transformed into a yellow-orange diamagnetic solid.
It was decided to attempt to promote the observed thermally induced electron transfer and consequent loss of paramagnetism of the sample by use of radiation of the appropriate wavelength, namely in the region of the charge transfer band of the complex as determined from the reflectance spectrum. In one experiment the effect of irradiation of the sample on the rate of disappearance of paramagnetism was investigated with light from a 500 watt tungsten filament projection lamp equipped with a blue-green filter (Corning 4-71, maximum transmittance at 464 μ) and lens system focused on the sample within the e.p.r. cavity. Such irradiation with blue light had no noticeable effect on the rate of disappearance of the copper(II) signal in the temperature range -40°C. through 20°C. Also irradiation did not initiate the second phase of the decomposition of the complex, namely the formation of the dark tarry polymeric final product.

b. The Final Product. - When the sample tube containing the yellow-orange diamagnetic material was hand warmed or immersed in warm water for a few moments, a new paramagnetic resonance signal exhibiting the values $g_\perp = 2.04$ and $g_\parallel = 2.18$ rapidly developed. The differences in the new signal from the signal of the original complex can be seen in Figure 12. The appearance of this new signal in the diamagnetic material was accompanied by rapid darkening of the sample followed by loss of solid structure, as tar formation took
place. The sample tube was removed from the spectrometer, immersed in boiling water for 30 seconds, cooled to room temperature, and returned to the spectrometer, this process being repeated in a number of cycles. The new paramagnetic resonance signal developed rapidly reaching a maximum intensity and then diminished and disappeared, this being associated with complete transformation of the yellow-orange diamagnetic solid to the final dark tarry diamagnetic oxidation-reduction product. During the course of these changes, the intensity (peak to peak height) of the second resonance signal never amounted to as much as five percent of the intensity of the signal due to the original complex. Dry oxygen gas was admitted to the final diamagnetic product and the sample allowed to stand overnight. On replacement of the sample tube in the e.p.r. cavity, the resonance signal for which the values $g \perp = 2.04$ and $g \parallel = 2.18$ were observed was again seen to be present. This signal was characterized by slow redevelopment followed by slow diminution until the sample was again fully diamagnetic. Readmission of oxygen repeatedly brought redevelopment of this signal with anisotropic $g$ values identical to those observed in the second stage of the decomposition reaction.


a. Anaerobic Conditions. -- A 50.0 mmole (16.8 grams) sample of dichlorobis(triethylamine)copper(II) was prepared and allowed to
convert to the yellow-orange diamagnetic intermediate by maintaining the sample in an ice bath for 13 hours. Care was taken to achieve complete reaction of the copper(II) chloride with the triethylamine in this run, as the presence of copper(II) chloride is known to oxidatively chlorinate carbonyl compounds in aqueous solution. To insure complete reaction the components were stirred together for four days at -23°C. before the excess of triethylamine was removed from the reaction vessel.

To effect the hydrolysis, ice cold deoxygenated water was allowed to be drawn into the evacuated reaction vessel containing the yellow-orange diamagnetic solid. The mixture was stirred for 10 minutes at 0°C. The color of the reaction mixture at this point was apple green. The reaction assembly was then reattached to the vacuum system and volatile material removed from the reaction in vacuo. The volatile material was caught in a Dry Ice cooled trap. Approximately 40 ml. of material were collected. It was treated with an alcoholic hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The yellow precipitate that formed on addition of the reagent was recrystallized from ethanol-water mixtures, m.p. 142°C. -143°C. An authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone was prepared, m.p. 146°C., lit. (70) 146°C. The mixed melting point of the two materials was found to be 145°C. The material melting at 142°C. -143°C. was boiled in an alcoholic
solution of 2, 4-dinitrophenylhydrazine reagent (71) to try to effect the osazone reaction if the material was glycolaldehyde 2, 4-dinitrophenylhydrazone, which melts at 155-158°C. (72, 73). The material that precipitated on addition of water to the alcoholic solution melted at 140°C. after recrystallization. The glyoxal 2, 4-dinitrophenylosazone derivative has a much higher melting point, lit. (70) 328°C. In addition, the solubility behavior of the material was unlike that exhibited by the glyoxal derivative.

The acid solutions containing an excess of 2, 4-dinitrophenylhydrazine, from which the acetaldehyde derivative had been removed by filtration, were evaporated to dryness. The amine hydrochloride residue was taken up in a minimum amount of water and this solution added quickly to a strong solution of sodium hydroxide in a distillation apparatus. The mixture was distilled employing an ice water-cooled condenser and receiver. The first 5-ml. portion of distillate obtained was set aside for vapor phase chromatographic analysis. An additional 50-ml. sample of distillate was collected.

Using an F and M model no. 609 flame ionization vapor phase chromatograph with a carrier of helium gas at a flow rate of 50 ml./min. and a two ft. column packed with silicone rubber at 35°C., the amine fraction was separated into two peaks having retention times of 2.48 min. and 5.45 min., respectively. The substance responsible for the second peak was present in larger amounts, as determined from an
inspection of peak areas. The observed peaks were exactly matched by a prepared mixture of authentic di- and triethylamines, and the second of the two peaks was shown to be identical with that produced by pure triethylamine under identical instrument conditions.

The remainder of the first fraction of the distillate was added to the second fraction and a Hinsberg reaction with benzenesulfonyl chloride performed on the combined amine distillate. The reaction mixture was worked up in the usual manner and the sample was found not to contain any primary amines. Diethylamine was characterized as the benzene sulfonate, m.p. 41-42°C., lit. (74) 42°C. A mixed melting point with an authentic sample of diethylamine benzenesulfonate was not depressed (m.p. 42°C.). The large tertiary amine fraction present was characterized as triethylamine by preparation of the hydrochloride (m.p. and mixed m.p. with authentic material in sealed tubes, 254°C.).

b. Aerobic Conditions.--A 22.4 mmole (7.54 grams) sample of dichlorobis(triethylamine)copper(II) was prepared and allowed to warm to 0°C. The sample was kept at 0°C. for six hours and then allowed to warm to 20°C. It was kept at 20°C. for 15 minutes to insure complete conversion of the complex to the diamagnetic yellow-orange solid intermediate. At this point the sample was cooled to 0°C., ice cold water added, and the mixture stirred for one hour at 0°C. During this operation the mixture became a dull green suspension.
Hydrochloric acid was added until the mixture was acid to litmus paper and stirring was continued in a stoppered flask at 0°C. for another hour. Volatile material from the reaction mixture was then distilled off in a system with an ice water cooled condenser and receiver. Distillate in the amount of 100 ml. was collected.

The distillate was treated with 2, 4-dinitrophenylhydrazine reagent (71). This resulted in the formation of a large amount of yellow precipitate. The derivative was recrystallized from ethanol, m.p. 326°C. with decomposition. An authentic sample (Fisher 30% aqueous, Cat. no. G-49) of glyoxal was obtained and its 2, 4-dinitrophenyllosazone prepared, m.p. 324°C. with decomposition [lit. (70) 328°C., mixed m.p. 323°C. with decomposition].

Another sample of dichlorobis(triethylamine)copper(II) in the amount of 37.2 mmoles (12.5 grams), was prepared and converted to the yellow-orange intermediate as described. This material was hydrolyzed and the reaction mixture distilled as before. A portion of the distillate was heated in a stoppered test tube with o-phenylenediamine, as was a control sample of a drop of glyoxal in water solution. o-Phenylenediamine condenses specifically with a-dicarbonyl compounds. The tube containing the known sample of glyoxal readily showed the presence of a yellow solid condensation product, while the tube containing the hydrolysis reaction distillate remained clear. Another
portion of the distillate was used to prepare a semicarbazide derivative. This was recrystallized from ethanol-water mixtures, dried, and a melting point determination attempted. The material did not melt until 340°C. at which point it charred away. Glyoxal disemicarbazide has a definite melting point [lit. (70) m.p. 270°C.]. Portions of the distillate were tested with orcinol and with phloroglucinol (75), which give specific color tests for glycolaldehyde and for other \( \alpha \)-hydroxy aldehydes. A small amount of glyoxal was similarly tested with these reagents in equal volumes of solution. With both test reagents glyoxal gave negative tests, while the distillate gave color sequences specific for glycolaldehyde with each reagent. There are no derivatives of either functionality of glycolaldehyde described in the literature except for two reports of a difficultly preparable 2, 4-dinitrophenylhydrazone (72, 73).

The acidic solution of the hydrolysis reaction mixture remaining after distillation was evaporated to 200 ml. This mixture was then made basic with strong sodium hydroxide solution and the volatile amine component distilled away from the remaining mass of copper oxides using an ice-water cooled condenser and receiver. A Hinsberg reaction using benzenesulfonyl chloride was performed as described earlier. The presence of a secondary and a tertiary amine was indicated. These amines were characterized as being diethylamine and triethylamine as previously described: triethylammonium chloride, m.p. 254°C. (sealed tube), lit. (55) 254°C., mixed m.p. with authentic material.
254°C.; the diethylamine benzenesulfonate was recrystallized from ethanol-water mixtures, m.p. 36°C., lit. (74) 42°C. A mixed melting point with authentic prepared diethylamine benzenesulfonate was taken (m.p. 38°C.).
VI. RESULTS

A. Copper(I) Halide Complexes

The pressure-composition isotherms at 25°C. for the triethylamine-copper(I) chloride and bromide systems are shown in Figure 2. A sharp break at mole ratio 1.0 was observed in each case. The synthesis of the copper(I) halide triethylamine complexes was accompanied by a great taking up of liquid amine. The volume of the complexes themselves was much greater than that of the solid finely divided reactant halides, indicating that appreciable lattice expansion probably occurs on their formation.

The dissociation pressures of the 1:1 complexes at 25°C. 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. Analytical data support the conclusions drawn from the isotherms regarding the composition of the complexes. The pressure-composition isotherms for iodo triethylamine copper(I) at 25.0, 35.0 and 45.0°C. are given in Figure 3. The dissociation pressures of the iodide complex are
Figure 2. Isotherms for the Systems CuCl-Et$_3$N and CuBr-Et$_3$N at 25.0°C.
Figure 3. Isotherms for the System CuI + Et$_3$N at 25.0, 35.0, and 45.0°C.
appreciable. From the vapor pressure of triethylamine and the measured values of the dissociation pressure of the complex, the following thermodynamic quantities can be calculated for the process,

\[ \text{CuI} \ (c) + (C_2H_5)_3N \ (l) \rightarrow \text{CuI} \cdot (C_2H_5)_3 \ (c) \]

at 25°C., \( \Delta F^\circ = -1.42 \text{ kcal./mole} \), \( \Delta H^\circ = -8.21 \text{ kcal./mole} \), \( \Delta S^\circ = -22.8 \text{ e.u.} \). The values of the thermodynamic quantities thus calculated include lattice and vaporization energy terms as well as the coordinate bond energy.

The quantity \( \Delta H^\circ \) is equivalent to the term \( \Delta H_R \) in the equation,

\[ \Delta H_C = \Delta H_R - \Delta H_V - (U_1 - U_2) \]

derived from the thermochemical cycle given on page 19. A knowledge of the other terms in this equation would allow the calculation of \( \Delta H_C \) between triethylamine and copper(I) iodide. The methods of calculation of the thermodynamic quantities are outlined below. The equilibrium vapor pressures of iodotriethylaminecopper(I) at various temperatures are given in Table 5. The vapor pressure of triethylamine as a function of temperature is given by the equation,

\[ \log p = -1822/T + 12.7906. \]

For the process,
\[
\text{CuI} \cdot \text{N(C}_2\text{H}_5)_3 \rightarrow \text{CuI} + \text{N(C}_2\text{H}_5)_3
\]

the change in free energy is given by,

\[
\Delta F^\circ = -RT \ln K_1 = -RT \ln P_{\text{Net}_3}
\]

For the vaporization of triethylamine the free energy is given by the equation,

\[
\Delta F^\circ = -RT \ln K_2 = -RT \ln P_{\text{Net}_3}
\]

For the process,

\[
\text{CuI} \cdot \text{Net}_3 \rightarrow \text{CuI} + \text{Et}_3\text{N}
\]

the free energy is given by,

\[
\Delta F^\circ = \Delta F^\circ_1 - \Delta F^\circ_2 = -RT (\ln K_1 - \ln K_2) = -RT \ln \left( \frac{K_1}{K_2} \right)
\]

\[
\Delta F^\circ = -RT \ln \left( \frac{P_{\text{Net}_3}}{P_{\text{Net}_3}^\circ} \right)
\]

On substituting the experimental values we also have, at 35°C.,

\[
\Delta F^\circ = 1.999 \text{ kcal./mole and at 45°C.}, \Delta F^\circ = 0.970 \text{ kcal./mole.}
\]

The value, \[\Delta F^\circ = 1.42 \text{ kcal./mole at 25°C. was similarly calculated.}\]

For the formation process,

\[
\text{CuI} + \text{Et}_3\text{N} \rightarrow \text{CuI} \cdot \text{Net}_3
\]
the signs of the calculated free energy values are reversed. To calculate
\( \Delta H^\circ \), the relation,

\[
\log \left( \frac{P_{T_2}}{P_{T_1}} \right) = \frac{\Delta H^\circ}{2.3R} \left( \frac{T_2 - T_1}{T_2 T_1} \right),
\]

is employed. This quantity however contains the heat of vaporization
of triethylamine. Thus, 8.181 kcal./mole, the heat of vaporization of
triethylamine, must be subtracted from the calculated quantity. To
calculate \( \Delta S^\circ \), the relation,

\[
\Delta S^\circ = \frac{(\Delta H^\circ - \Delta F^\circ)}{T},
\]

is employed.

A brief study of the copper(I) bromide-triethylamine system
indicated the formation of a stable 1:1 complex by a similar sharp drop
in the equilibrium pressure of the system to a negligibly small value,
at a mole ratio of 1.0 of the components.

B. Copper(II) Halide-Trialkylamine Systems

Anhydrous copper(II) halides will oxidize trialkylamines
under a variety of conditions. Primary and secondary amines will
also be oxidized (1). The oxidation-reduction reaction between tertiary
amines and such halides results in the reduction of copper(II) to copper(I).
Large amounts of trialkylammonium halide as well as dark tarry polymeric
amine oxidation products are formed. The presence of trialkylammonium halide, as opposed to quaternary ammonium species in the product, indicates that carbon-hydrogen bond breakage rather than carbon-nitrogen bond breakage occurs.

The reaction between copper(II) chloride and triethylamine was studied in detail. Pressure-composition studies of this reaction system indicate an over-all stoichiometry of two moles of triethylamine bound per mole of original copper(II) chloride. In Figure 4 is shown the 25.0°C. pressure-composition isotherm for this system. The flat at 6.0 mm., between mole ratio values of 2.0 and 1.0, corresponds to the reversible removal of one mole of triethylamine. The equilibrium removal of one mole of triethylamine results in the transformation of the gray solid product A to a dark black oil, product B. The volatile material lost at 6 mm. pressure was collected and shown to be pure triethylamine by gas chromatography. On readmission of triethylamine the oil was converted back to the solid product A.

Very similar phase transformation behavior was observed in the system, copper(I) chloride-triethylamine-triethylammonium chloride. When pure anhydrous copper(I) chloride and triethylammonium chloride were placed together in equimolar amounts, even without mixing of the white powders, an amber colored oil was quickly formed. Apparently triethylammonium dichlorocuprate(I) is a non-volatile
Figure 4. 25.0°C. Isotherm for the CuCl₂ + Et₃N Reaction Mixture After Heating for 1 Hour at 90°C. (Redox).
liquid at room temperature. When this oil was treated with an excess
of triethylamine, and the excess of triethylamine then removed by
distillation at its vapor pressure of 66 mm. at 25°C., one mole of
triethylamine was retained per mole of each of the starting materials.
The solid so obtained lost triethylamine at an equilibrium pressure of
6 mm. at 25°C. giving back the original oil. The process was found
to be completely reversible, as was the accompanying solid-oil
transformation. The same kind of behavior was observed on mixing
chlorotriethylaminecopper(I) and triethylammonium chloride, each of
which independently is non-volatile at 25°C. This system therefore
is described by the equation,

\[
\text{CuCl} \cdot \text{NEt}_3 + \text{Et}_3\text{NHCl} \xrightleftharpoons{6 \text{ mm.}}{25 \degree \text{C.}} \text{Et}_3\text{N} + \text{Et}_3\text{NHCuCl}_2
\]

When triethylammonium dichlorocuprate(I) was treated with
an excess of tri-n-butylamine at 28°C., triethylamine was displaced
at a pressure of 8 mm., indicating that a less volatile amine can
participate in this kind of equilibrium. The triethylamine oxidation
product has been shown to be polymeric amine species. Apparently
its conjugate acid can replace a part of the triethylammonium ion shown
in the above equation. This accounts for the 2:1 and 1:1 stoichiometric
relations of the oxidation-reduction product as well as for the phase
changes and pressure-composition behavior observed.
The oxidation-reduction reaction between copper(II) chloride and trimethylamine was observed to produce an amber colored oil, derived from 1.14 moles of trimethylamine (original) per mole of copper(II) chloride.

C. Hydrolysis of the Reaction Product

Product B was hydrolyzed under a variety of conditions. In every case on working up the mixture, a large amount of crystalline white triethylammonium chloride was obtained. All of the copper(II) was reduced to copper(I) and hydrolysis resulted in the release of copper(I) chloride. The exact amount of unoxidized triethylamine bound in product B was determined by hydrolysis and analysis. The results were somewhat variable depending on the hydrolysis conditions. Values ranging between 84.80 percent and 92.95 percent were obtained. The recovered amine was shown to be pure triethylamine by vapor phase chromatography and by the melting point of the amine hydrochloride. Hence, although exactly 1.0 mole of triethylamine is bound per mole of copper in the non-volatile reaction product B, only a minor portion of it has been oxidized, although all of the copper(II) originally present is reduced to copper(I).

Hydrolysis of large amounts of product B, followed by acidification and distillation, produced only trace amounts of a carbonyl compound identified as acetaldehyde by conversion to acetic acid and characterization.
as the p-bromophenacyl ester, and also by a comparison of the retention time of the material with that of authentic acetaldehyde in a vapor phase chromatogram.

D. Nature of the Oxidation Product

Thus far it has been shown that about 85 to 90 percent of the material in the reaction product B consists of triethylammonium dichlorocuprate(I). On hydrolysis a dark black solid material is also obtained. This material represents largely the organic oxidation product, and being itself an amine it strongly binds copper(I). This makes it extremely difficult to completely free this material of copper. However, by repeated treatment with hydrochloric acid solutions a sample was obtained in which the organic material was concentrated. Analysis, spectra, and chemical behavior of this material indicate that it is a polymeric substituted amine.

Viscosity measurements of solutions of this material in dimethylsulfoxide were made. In Figure 5 is shown a plot of the quantity \( n_{sp}/C \) vs. \( C \). This plot was found to be linear in the low concentration range, in agreement with theory. Extrapolation of the plot to zero concentration gives the intrinsic viscosity of the material, which was found to be 0.122. On substitution of this value into the Staudinger equation, \( (n) = kM^a \) (67), a rough estimate of the average molecular weight, \( M \), was obtained. Values for the empirical constants \( k \) and \( a \),
Figure 5. Triethylamine Oxidation Product.
were selected on the basis of model polymers of similar type and composition. A choice of $k = 3.18 \times 10^{-4}$ and $a = 0.65$ gives a value for $M$ of $9.5 \times 10^3$, suggesting at least an order of magnitude for the average molecular weight.

A comparison of the nuclear magnetic resonance spectrum of product B with that of pure triethylammonium dichlorocuprate(I) is given in Figure 6. The spectra indicate a very close correspondence between the two materials and also indicate the absence of any other kind of protonic function in the product of the oxidation-reduction reaction. This is in agreement with the infrared spectral data. The two n.m.r. spectra are identical in exhibiting resonances characteristic of ethyl groups and of the tertiary alkylammonium proton moiety. However, the spectrum of product B exhibits no fine structure as does the sample of triethylammonium dichlorocuprate(I). The presence of small amounts of paramagnetic copper(II) species are known to have this effect. A spectrum of the reaction product was taken with no precautions being observed to exclude oxygen during the filling of the sample tube. The spectrum was of similar character except that all of the resonances were very much broadened out, the alkylammonium proton resonance being so broad as to be hardly visible. This broadening is due to the greater concentration of paramagnetic species present, caused by atmospheric oxidation of diamagnetic copper(I) species to paramagnetic
Figure 6. Proton Magnetic Resonance Spectra.
copper(II) species. A high magnification study of the spectrum of product B in the regions $T = 6.0$ through $7.5$ and $T = 2.0$ through $5.0$ failed to indicate the presence of any other kind of hydrogen atom in the product. The absence of vinylic hydrogen atoms is thus indicated, corroborating the conclusions drawn from the infrared spectrum. The functionalities present in the product appear at the following $T$ values: methyl, 9.07; methylene, 8.1; and the alkylammonium proton at 5.6. The areas under the resonances appear in the correct integral ratio for the triethylammonium ion, namely $1:6:9$. The sharp resonance of the alkylammonium proton indicates the absence of any other exchangeable proton in the reaction product.

The formation of triethylammonium ion in the oxidation-reduction reaction is not dependent on the presence of an hydroxylic solvent, as shown by its presence in product B and the earlier finding that triethylammonium chloride could be isolated from the redox reaction when run in ethanol solution.

The visible spectrum of the oxidation-reduction reaction product in acetonitrile is given in Figure 7. The product exhibits this characteristic spectrum both when the reaction product is dissolved in acetonitrile and when the redox reaction is run, over a wide range of reactant concentrations, in acetonitrile solution.
Figure 7. A - Visible Spectrum of CuCl₂ + Et₃N Reaction Product in Acetonitrile Solution, CuCl₂ Originally 2.5 x 10⁻³ M.

B - Spectrum of Reaction Mixture as in A, But With Some H₂O Present (No Redox).

C - Spectrum of 5 x 10⁻³ M CuCl₂.
E. Oxidation-Reduction in Various Solvents

The stoichiometry of the reaction between triethylamine and copper(II) chloride, when run in alcohol solution, was found to be identical to that observed between the pure components. The redox reaction proceeds in 95 percent ethanol, dimethylsulfoxide, acetonitrile, γ-butyrolactone, dimethylformamide, and in absolute ethanol. Traces of water were found to decrease the rate of reaction in acetonitrile solution. When the reagents were mixed in absolute ethanol a blue material found to be copper(II).ethoxide was initially precipitated. On warming this mixture the redox reaction proceeded with the formation of a red solution. Copper(I) chloride and triethylammonium chloride were isolated from such solutions. The ethanol solution of the reaction product was attacked by oxygen, with release of copper(I) chloride, indicating possible further oxidation of the tarry product which, as noted previously, strongly binds copper(I). Reaction in dimethylsulfoxide and in acetonitrile solution resulted in the formation of copper(I)-chloride and triethylammonium chloride, as indicated by analysis of the products obtained on hydrolysis of such solutions. Tri-n-butylamine, N-methylaniline, and N,N-dimethylaniline were also oxidized by copper(II).chloride in various solvents with concurrent formation of copper(I) chloride as determined by analysis following hydrolysis.
The kinetics of the reaction between copper(II) chloride and triethylamine in acetonitrile solution was studied spectrophotometrically. The rate of appearance of the product was followed by measurement of the absorption band of the product at 416 μm. It was not feasible to follow the rate of loss of copper(II) by measurement of the copper(II) chloride band at 463 μm, due to overlap of the product absorption at this wavelength. The kinetic measurements indicate that the rate of product formation does not follow a simple reaction order. The rate of the reaction was found to be highly dependent on the concentration of copper(II) chloride, and was not very sensitive to the triethylamine concentration, as long as triethylamine was present in excess. However, if one equates the rate of product formation with the rate of loss of copper(II) chloride, a log-log plot of fractional life periods versus copper concentration leads to a reaction order of 1.6 with respect to copper(II) chloride. The spectrophotometric reaction curves shown in Figure 8 are typical of those exhibited by the reaction under a variety of concentration conditions.

P. Electron Paramagnetic Resonance Study of the Redox Reaction Between Copper(II) Chloride and Triethylamine

When triethylamine and copper(II) chloride were brought together under anhydrous anaerobic conditions in an e.p.r. sample tube, no interaction was immediately evident, and only the broad copper(II) d9
Figure 8. Representative Kinetic Behavior in Acetonitrile Solution.
resonance \( g = 2.2 \) of paramagnetic copper(II) was observed. When the tube was heated and then cooled a transient blue coloration became evident, this being followed by the appearance of a red-black tarry material. The tube was returned to the spectrometer and the results after a number of such cycles are shown in Figures 9 and 10. At intermediate stages of the reaction sharp resonances were observed superimposed on the diminishing copper(II) signal. After five such heating cycles, all paramagnetism had virtually disappeared, demonstrating reduction of \( d^9 \) copper(II) to \( d^{10} \) copper(I) and also demonstrating the intermediate nature of different paramagnetic species produced during the course of the reaction. Admission of oxygen to the diamagnetic final product resulted in redevelopment of the same transient paramagnetic species having \( g \) values greater and less than 2.2.

G. Dichlorobis(triethylamine)copper(II)

At low temperatures triethylamine and copper(II) chloride form a coordination complex, which contains the reagents in the same 2:1 mole proportion as is involved in the oxidation-reduction reaction at higher temperatures. Like the copper(I) halide triethylamine complexes, the formation of this complex was accompanied by a large volume change relative to the volume of anhydrous copper(II) chloride. This complex was found to be unstable with respect to thermally induced internal electron transfer, followed by total decomposition to the previously
Figure 9. I - The e.p.r. Signal of Cu(II) in the CuCl₂ + Et₃N Mixture Before Reaction.
II-VI - Effect on the Signal of Successive Heating Cycles. Relative Signal Magnification at Right.
Figure 10. E.S.R. Signal Intensities of Species Present in CuCl₂ + Et₃N Reaction as a Function of Heating Cycles.
described oxidation-reduction reaction product A. The final products formed are identical to those obtained in the direct reaction of copper(II) chloride and triethylamine at higher temperatures. The green complex undergoes decomposition in two stages. It becomes yellow-orange at 0°C., and on standing at room temperature for a short time it suddenly and rapidly loses its solid structure and transforms into the black tarry final redox product with the evolution of considerable heat.

The reflectance spectrum of the complex given in Figure 11 shows a very broad absorption in the near infrared region, corresponding to d-d transitions localized on copper (76), while the more intense absorption centered at $26.6 \times 10^3 \text{ cm}^{-1}$ (360 μ) would be ascribed to ligand to metal charge transfer bands of the complex. Since ligand to metal charge transfer would be related in a formal sense to electron transfer within the complex and would correspond to the first step of copper(II) reduction and amine oxidation, it was attempted to promote the thermally induced electron transfer and consequent loss of paramagnetism of the complex by irradiation with blue light. However, irradiation had no effect on the rate of loss of paramagnetism of the complex as studied by e.p.r. techniques. Thus, charge transfer excitation is not sufficient to promote the rate of the actual electron transfer process. The thermally induced decomposition of the complex was followed by repeated sweeping of the paramagnetic resonance signal of the complex as its temperature was slowly raised in the
Figure 11. Reflectance Spectrum of CuCl$_2$·2Et$_3$N at Approximately -15°C.
cavity of the e.p.r. spectrometer. The e.p.r. signal of dichlorobis(triethylamine)copper(II) shows resolution of the $d^9$ copper(II) resonance according to the anisotropy in the $g$ values, $g_\perp = 2.06$, $g_{||} = 2.27$, as shown in Figure 12. These values allow an approximate ligand field treatment of the complex to be made.

As the sample was allowed to warm from -40 to 0°C., there was a slow decrease in the intensity of this signal. This can be completely accounted for by a $1/T$ (Curie) dependence. In the temperature range 0°C. to 20°C., the rate of decrease in intensity of the signal due to the complex became much greater and at 20°C. the complex became completely diamagnetic within a few minutes. The diamagnetic material was a yellow-orange powder at this point. Slowly at room temperature, or more rapidly if the sample tube was warmed slightly, the second phase of the decomposition began as was made evident by formation of a black tarry mass. This stage of the reaction was characterized by the appearance of a new paramagnetic resonance signal, for which the values $g_\perp = 2.04$ and $g_{||} = 2.18$ were observed. The differences in the new signal from that of the original complex can be seen in Figure 12. When the sample was subjected to a number of heating cycles followed each time by cooling to room temperature and sweeping over the resonance signal in the e.p.r. spectrometer, the new signal arising from the originally diamagnetic orange intermediate developed rapidly and then
Figure 12. E.p.r. Spectrum of CuCl$_2$·2Et$_3$N at -40°C. (Dashed Line) and of the Intermediate Reaction Mixture (Full Line Magnified 63.5X).
diminished and totally disappeared. The disappearance of the signal was accompanied by the total transformation of the yellow-orange solid to the final dark tarry diamagnetic oxidation-reduction product. At no time during the course of these changes did the intensity of the second resonance signal amount to as much as five percent of the intensity of the signal due to the original complex. Admission of dry oxygen to the final diamagnetic system resulted in the slow redevelopment of a copper(II) resonance signal with anisotropic $g$ values identical to those observed in the second stage of the decomposition reaction.

H. Hydrolysis of the Diamagnetic Intermediate

When deoxygenated water was added to the diamagnetic yellow-orange solid under anaerobic conditions, and volatile material then removed from the hydrolyzed reaction mass, acetaldehyde was shown to be the carbonyl component of the distillate. The remainder of the hydrolysis reaction mass was made basic and distilled. The amine component distilling was shown to contain both diethylamine and triethylamine. The amines were identified by comparison of retention times with authentic samples by vapor phase chromatography. In addition, derivatives of both were prepared and compared with derivatives of the authentic materials. Acetaldehyde and diethylamine are the hydrolysis products of diethylvinylamine, which is the product of the two electron oxidation of triethylamine (33).
When a similar hydrolysis was carried out on a sample of the material under aerobic conditions, and the hydrolysis reaction mass made acid, stirred for two hours, and then distilled, glycolaldehyde was shown to be present in moderate amounts in the aqueous distillate. When the hydrolysis reaction mass was made basic and distilled, an amine fraction was obtained. This fraction was shown to contain large amounts of triethylamine and a smaller amount of diethylamine. Apparently under aerobic conditions, copper(II) chloride present in the hydrolysis reaction mass oxidatively chlorinated the initially produced acetaldehyde to α-chloroacetaldehyde, which underwent subsequent hydrolysis to glycolaldehyde. Such processes are known to occur in aqueous solutions containing copper(II) chloride and carbonyl compounds (77, 78).
VII. DISCUSSION

A. Tertiary Amine Complexes

It has been shown (7) that anhydrous $d^{10}$ zinc halides do not interact with triethylamine at $25^\circ$C. It is now found that moderately stable 1:1 triethylamine complexes of $d^{10}$ copper(I) halides do exist. The stability sequence observed was Cl > Br > I. Also, bromotriethylaminecopper(I) appeared to be fairly stable with respect to loss of trimethylamine. However, the chloro analogue was not prepared for a direct comparison in this regard. The stability order, with respect to dissociation into the components, observed in the series of copper(I) halide triethylamine complexes, can be explained in terms of the polarizing power of the cation and the polarizability sequence $I^-$ > $Br^-$ > $Cl^-$. If one equates higher polarizability with a greater degree of covalency, the copper(I)-iodide bond is more covalent than the copper(I)-bromide or chloride bonds. Consequently one would expect a lowered degree of dipolar attraction for the amine ligand in the series, CuCl > CuBr > CuI. That $d^{10}$ copper(I) is coordinated by triethylamine, while the more highly charged $d^{10}$ zinc(II) cation is not, may be attributed to differences in the lattice energies of the respective halides. These energy factors, involved in the Born-Haber energy
expression (page 19), may preclude the coordination of triethylamine to zinc(II), although undoubtedly, in the gas phase, zinc(II) would exhibit a larger heat of coordination with a halide ion or with triethylamine, than would copper(I), this being inferred from the relative electrostatic interactions (page 21). In this particular case, however, the differences in the lattice energies between the simple halides and the coordination complexes may be the controlling factors, as the total enthalpy of the coordination reaction depends on differences in lattice energies as well as on the coordinate bond energy. The syntheses of the copper(I) halide-triethylamine complexes was accompanied by a great expansion of volume on complex formation. This suggests that lattice energy factors are appreciable for these systems.

It has been noted 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, primary, and secondary amine systems.

In considering the ion dipole interaction energy, the importance of shielding of the nuclear charge of the cation is clearly reflected in the coordinating ability of triethylamine to the series of cations Ca(II), Zn(II), Co(II) (7), and Cu(I) and Cu(II). Triethylamine, the largest and least polar of the ethylamines, will coordinate to Co(II) (7) and to Cu(I) and Cu(II), but not to Zn(II) or to Ca(II). Increasing the degree
of alkyl substitution on nitrogen is unfavorable, both in lowering the permanent and induced contributions to the total dipole moment and consequently the terms involving these quantities in the potential energy expression, and increasing the molar volume and hence the energy required for expansion of the metal halide lattice. In this respect, it was found (7) that with two ethyl groups on nitrogen, Co(II) and Zn(II) halides still form stable 2:1 complexes, but that calcium(II) chloride no longer reacts. With triethylamine only 1:1 complexes are formed with Co(II) and Cu(I). The fact that copper(II) chloride forms a 2:1 complex with triethylamine, while copper(I) forms only a 1:1 complex is consistent with this interpretation.

B. Oxidation of Triethylamine by Copper(II) Chloride

The oxidation-reduction reaction between amines and d^9 copper(II) halides may be accounted for in terms of extreme polarization of the donor atom by the poorly shielded d^9 copper(II) ion, which would be similar to the interaction of copper(II) and iodide ions. Complete transfer of one or more electrons may be regarded as an extreme case of electron donation in Lewis acid base theory.

Similar redox reactions involving trialkylamines have been observed previously with more highly charged ions, specifically Ti(IV) (25, 26); V(IV) (21); and P(V) (29); and with Pt(II) (2). The
results at room temperature in the absence of solvent suggest that there may be an appreciable activation energy for the formation of the unstable dichlorobis(triethylamine)copper(II), or for the actual electron transfer. A contribution to the favorable enthalpy change observed (the reaction is quite exothermic) in the reduction of copper(II) by triethylamine may involve both stabilization of copper(I) in the product by coordination and the protonation of large amounts of triethylamine.

Only a small fraction of a mole of triethylamine is oxidized per mole of copper(II) reduced. It is reasonable to postulate that the room temperature reaction is initiated by the formation of unstable dichlorobis(triethylamine)copper(II), which in a one electron transfer process gives dichlorocuprate(I) and a radical cation. The dichlorocuprate(I) would be in equilibrium with copper(I) chloride and a chloride ion.

The triethylamine free radical ion may disproportionate and with accompanying proton transfer produce triethylammonium ion and the conjugate acid of diethylvinylamine. The latter species may lose a proton to triethylamine, which was normally present in excess, and thereby become neutral diethylvinylamine (79, 80). One of the hydrolysis products of this material, namely acetaldehyde, was detected in trace amounts after hydrolysis of product B. Repeated steps of electron loss followed by disproportionation and proton
transfer would explain why, even when an excess of amine was present during the room temperature redox reaction, only a small fraction of a mole of triethylamine was oxidized per mole of copper(II) reduced. 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 in the manner postulated serves to reduce one mole of copper(II) chloride to copper(I) chloride, one mole of triethylammonium chloride also being formed.

Horner and Schwenk (34) studied the oxidation of triethylamine by benzoyl peroxide. They concluded that six moles of the reduction product, benzoic acid, were formed per mole of triethylamine oxidized, and interpreted this in terms of abstraction of the six α-hydrogen atoms of 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 the results in the present work on the observed quantity of unrecoverable amine.

It is further postulated that the equilibrium in the system copper(I) chloride-triethylammonium chloride-triethylamine is closely related to the relationship between products A and B of the triethylamine oxidation-reduction reaction. The former model system
exhibits an equilibrium pressure of 6 mm. of triethylamine at 25.0°C.,
with a reversible solid-oil transformation phenomenon. This resembles
exactly the reaction in which reaction product A is transformed to
product B with the loss of one mole of triethylamine. This behavior
may be accounted for in terms of the equilibrium:

\[
\text{Et}_3\text{NHCl}_{(c)} + \text{CuCl}:\text{NEt}_3 \rightleftharpoons \frac{6 \text{ mm.}}{25^\circ\text{C.}} \Rightarrow \text{Et}_3\text{N}_{(g)} + \text{Et}_3\text{NHCuC}_{(c)}\text{Cl}_2
\]

The 6 mm. pressure would then 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 (62). In this work, it was found that the triethyl-
ammonium compound is a non-volatile liquid at room temperature.
Triethylammonium chloride and chlorotriethylaminecopper(I), by them-
selves, have negligible vapor pressures at 25°C.

When triethylammonium dichlorocuprate(I) was treated with
an excess of tri-n-butylamine, the triethylamine was displaced, showing
that a less volatile amine can participate in this type of equilibrium:

\[
\text{Bu}_3\text{N} + \text{Et}_3\text{NHCuC}_{(c)} \rightleftharpoons \frac{8 \text{ mm.}}{28^\circ\text{C.}} \Rightarrow \text{Et}_3\text{N} + \text{Bu}_3\text{NHCuC}_{(c)}\text{Cl}_2
\]

Since this equilibrium involves competition of a proton with copper(I)
for the amine, differences in base strengths are partly compensated.
To account for the pressure-composition breaks of Figure 4, coming at
exactly 2.0 and 1.0 moles of triethylamine per copper, it is necessary to suppose that the non-volatile 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 polymeric amine, which has been shown to strongly bind copper(I). When the reaction product in ethanol solution was exposed to the atmosphere the catalytic electron carrying role of copper(I)-copper(II) was accompanied by slow removal of the copper(II) as the basic carbonate. That oxygen can bring about the reformation of d⁹ copper(II) species in the diamagnetic product B has been shown in the e.p.r. work. The development of the transient d⁹ species reaches a maximum and then decreases again as more triethylamine is oxidized. In proposing such a copper-catalyzed oxidation of amines by oxygen, one may suppose that if a suitable reducing agent were present, it would be possible to regenerate the amine from its initial oxidation product, while oxygen would serve to reoxidize the copper(I). Such a combination of circumstances would allow the copper-amine system to serve as an electron carrier in aerobic oxidations. Copper-amine complex systems have been found to
be effective catalysts for the oxidative polymerization of phenols (39).

C. Internal Electron Transfer in Dichloro-
 bis(triethylamine)copper(II)

The formation of dichlorobis(triethylamine)copper(II) was accompanied by a large increase in volume relative to the volume of anhydrous copper(II) chloride. Large volume changes on complex formation are indicative of a reorganization or expansion of the original metal halide lattice. Anhydrous copper(II) chloride exists in the solid state in the form of infinite chains in which each metal atom is attached to four chlorine atoms lying in the same plane. The arrangement of the chains is such that each copper atom has two more chlorine neighbors in neighboring chains at greater distances than the four nearest in a particular chain. Thus the structure is a distorted octahedral arrangement of six bonds from each copper atom (50). Diffusion of triethylamine into the copper(II) chloride followed by the breakdown of this polymeric lattice on reaction, or the steric factor involved in lattice expansion necessary to incorporate the ligand molecules may be responsible for the slow rate of formation of the triethylamine complex of copper(II) chloride.

The e.p.r. signal of dichlorobis(triethylamine)copper(II) shows resolution of the d^9 copper(II) resonance according to the anisotropy in
the $g$ values, $g_\perp = 2.06$, $g_{\parallel} = 2.27$. These results are typical for copper(II) systems in tetragonally distorted octahedral ligand fields. Such Jahn-Teller distortion along the four-fold axis leads in the extreme to apparent square-planar four coordination. From the magnetic observations, $g_{\parallel} = 2.27$ and $g_\perp = 2.06$, the average value $<g>$ may be calculated from the equation,

$$<g>^2 = \frac{1}{3} (g_{\parallel}^2 + 2g_\perp^2),$$

to be $<g> = 2.20$. Since the $d^9$ system contains one unpaired electron, $S = \frac{1}{2}$ and the magnetic moment is given by,

$$\mu_{\text{eff}} = g \sqrt{S(S+1)}.$$

Substitution of the numerical values gives the result $\mu_{\text{eff}} = 1.91 \text{ B. M.}$, which exceeds the spin-only value of $1.73 \text{ B. M.}$ due to some orbital contribution arising from the mixing of higher energy levels of proper symmetry into the ground state. For Cu(II) systems, the amount by which the value of $\mu_{\text{eff}}$ exceeds the spin-only value $\mu_o$ is related to the strength of the ligand field $\Delta$ (or $10 Dq$) by the relation,

$$\mu_{\text{eff}} = \mu_o (1 - 2\lambda/\Delta) \quad (53),$$

where $\lambda$ is the spin-orbit coupling constant. The value of $\lambda$ is usually taken to be a few percent lower than the field-free value for Cu(II) of $-829 \text{ cm}^{-1}$, and specifically the value $-800 \text{ cm}^{-1}$ is suggested by Dunn.
Substitution of the numerical values gives $\Delta = 10 \text{Dq} = 1.54 \times 10^4 \text{cm}^{-1}$. This value, obtained from the magnetic data, may be correlated with the observed electronic spectrum (obtained by reflectance) for the complex. Assuming the "average ligand field" approximation and taking the square-planar sequence of orbital energies (82), a transition between states corresponding to the configurations $d_{xz}^2$, $d_{yz}^2$, $d_{z^2}$, $d_{xy}^2$, $d_{x^2-y^2}$ and $d_{xz}^2$, $d_{yz}^2$, $d_{z^2}$, $d_{xy}^2$, $d_{x^2-y^2}$ may be expected. These states arise first from the splitting of the free ion term, $^2D$, by an octahedral field into $^2E_g$ and $^2T_{2g}$, and then further decomposition of these states due to distortion along the z axis. The energy of the transition would then correspond to the energy of promotion of an electron from $d_{xy}$ to $d_{x^2-y^2}$, and would equal the difference in ligand field stabilization energy of these orbitals; 2.28 and 12.28 Dq respectively. Hence a transition corresponding to $10 \text{Dq} = 1.54 \times 10^4 \text{cm}^{-1}$, or absorption at 650 mµ, is predicted from the magnetic data. The experimentally determined spectrum of the complex shows that this wavelength corresponds to the beginning of a broad absorption which is only partly resolved and which extends well into the infrared. Thus, even the crudest type of ligand field model indicates internal consistency between the magnetic and spectral data. In quantitative detail, however, such a model is inapplicable.

In general the e.p.r. and visible (reflectance) spectra of dichlorobis(triethylamine)copper(II) indicate four coordinate copper
with strong distortions. The e.p.r. results suggest a highly distorted square planar structure, while the visible spectrum suggests a distorted tetrahedral structure. Distortion in complexes having $T_d$ or $D_{4h}$ symmetry approach the same structure of relatively low order symmetry from opposite directions.

Dichlorobis(triethylamine)copper(II) is unstable with respect to thermally induced internal electron transfer followed by total decomposition to the final diamagnetic product A. Regarding progressively greater sensitivity to thermally induced redox decomposition with greater degree of alkyl substitution of the coordinated amine, a comparison of the results of this investigation with those reported by Simon et al. (1), correctly place dichlorobis(triethylamine)copper(II) as the least stable member of a series of copper(II) complexes. The theory advanced (page 10) to explain the stability sequence $\text{Br}^- < \text{Cl}^-$ would allow prediction that dibromobis(triethylamine)copper(II) would be found to be less stable to redox decomposition than the chloro analogue. Facile oxidation-reduction between copper(II) bromide and triethylamine was observed in a preliminary portion of this research.

Dichlorobis(triethylamine)copper(II) was indicated by e.p.r. studies to decompose in two stages. Electron transfer slowly occurs in the temperature range -10 to $0^\circ\text{C.}$ and rapidly at temperatures just below room temperature. The product at this point is a diamagnetic
yellow-orange solid. The reflectance spectrum of dichlorobis(triethylamine)copper(II) shows a strong absorption centered at 360 m\(\mu\). This absorption can be ascribed to ligand to metal charge transfer bands of the complex. Since ligand to metal charge transfer is related in a formal sense to electron transfer within the complex and consequent oxidation of triethylamine and reduction of copper(II), it was attempted to promote the thermally induced electron transfer and consequent loss of paramagnetism by use of radiation of the appropriate wavelength. The inability to promote the actual charge transfer process in dichlorobis(triethylamine)copper(II), at low temperatures, by irradiation with light of wavelength corresponding to the charge transfer band of the complex indicates that charge transfer excitation is not sufficient to promote the rate of the actual electron transfer process.

The diamagnetic yellow-orange solid intermediate rapidly transforms to product A, identical to that obtained in the direct reaction of copper(II) chloride and triethylamine at higher temperatures, when allowed to stand at room temperatures for a short while or when warmed slightly. This stage of the decomposition reaction was characterized by the appearance of new transient paramagnetic species, as was shown by e.p.r. signals arising from the previously completely diamagnetic material. The magnetic behavior exhibited by the reaction was complex. The complexity observed provided the means of following the course of
the reaction, as well as a basis for a mechanistic interpretation of the reaction path. The following discussion of the mechanism of electron transfer and decomposition applies specifically to dichlorobis(triethylamine)copper(II). However, much of the discussion would apply to the room temperature reaction where no intermediate complex or diamagnetic intermediate material can be isolated.

The one electron oxidation product of triethylamine would be a highly reactive radical cation. Rapid disproportionation of this species may be postulated to account for the fact that the intermediate stage of the reaction is diamagnetic, and to explain the ability of the oxidation product to reoxidize copper(I) on subsequent warming. Proton transfer accompanying disproportionation would prevent excessive charge build-up on any species.

(1) $[(\text{Et}_3\text{N} \longrightarrow)_2\text{CuCl}_2] \rightarrow [\text{Et}_3\text{N} \longrightarrow \text{CuCl}] + [\text{Et}_3\text{N}^\cdot]^+ + \text{Cl}^-$

(2) $2[\text{Et}_3\text{N}^\cdot]^+ \rightarrow \text{Et}_3\text{N}: + \text{Et}_3\text{N}^{\cdot\cdot\cdot} \rightarrow \text{Et}_3\text{NH}^+ + \text{Et}_2(\text{CH}_3\text{CH}=)\text{N}^+$

The doubly oxidized species shown is written as one of the tautomeric forms of the conjugate acid of diethylvinylamine. The presence of this substance at this stage in the reaction mixture was proved by the hydrolysis experiments, in which the hydrolysis products of diethylvinylamine, acetaldehyde and diethylamine, were obtained.
A consideration of the subsequent reaction steps must account for reoxidation of copper(I), for the fairly low concentration of transient species containing copper(II) in a different coordination environment than in the original complex, and for the stoichiometry of the over-all reaction.

Competition between diethylvinylamine and triethylamine for the proton and copper(I) would result in formation of some chloro(diethylvinylamine)copper(I), as is shown by the acid-base equilibrium:

\[
(3) \text{Et}_2(CH=CH)N^+ + [\text{Et}_3N \rightarrow \text{CuCl}] \leftrightarrow \text{Et}_3\text{NH}^+ + [\text{Et}_2(CH_2=CH)N \rightarrow \text{CuCl}]
\]

Warming could then induce electron transfer from d^{10} copper(I) to the coordinated diethylvinylamine, with accompanying proton transfer and coordination of copper(II) by chloride ion.

\[
(4) [\text{Et}_2(CH_2=CH)N \rightarrow \text{CuCl}] + 2\text{Et}_3\text{NH}^+ + 2\text{Cl}^- \rightarrow 2\text{Et}_3\text{N}^- + [\text{Et}_3\text{N}^+] + \text{CuCl}_3^-
\]

Immediate disproportionation of the triethylamine cation radical so regenerated, with two accompanying proton transfer steps promoted by the presence of an excess of triethylamine in the reacting mixture would liberate diethylvinylamine.

\[
(5) 2[\text{Et}_3\text{N}^+] + \text{Et}_3\text{N}^- \rightarrow 2\text{Et}_3\text{NH}^+ + \text{Et}_2(CH_2=CH)N:
\]

Both copper(I) and copper(II) species would now be present in the sample.
Steps 1-5 can be summed up in a bookkeeping sense in the balanced equation.

\[
(6) \quad 4[(\text{Et}_3\text{N} \rightarrow)\text{CuCl}_2] = 2[\text{Et}_3\text{NH}^+\text{CuCl}_3^-] + 2[\text{Et}_3\text{N} \rightarrow \text{CuCl}] + 3\text{Et}_3\text{N}: + \text{Et}_2(\text{CH}_2=\text{CH})\text{N}:
\]

It has been shown (64) that triethylammonium trichlorocuprate(II) is not stable. A mixture of triethylammonium chloride and copper(II) chloride in a 1:1 mole ratio undergoes loss of hydrogen chloride followed by oxidation-reduction. The trichlorocuprate(II) ion is known (64) in certain solvents where the fourth coordination position is filled by solvent. In the reacting system described above, the coordinatively unsaturated trichlorocuprate(II) species shown would be further coordinated by either of the two amines present, triethylamine and diethylvinylamine. The trichloro(tertiary amine)cuprate(II) ion so formed would be responsible for the second paramagnetic resonance signal shown in Figure 12. Formation of the trichloro(triethylamine)cuprate(II) ion would result in the amine oxidation-copper(II) reduction reaction sequence starting all over again, in steps similar to those shown above. Formation of the trichloro(diethylvinylamine)cuprate(II) ion, on the other hand, followed by oxidation-reduction, would lead to progressively unsaturated tertiary amines such as ethyldivinylamine and trivinylamine. This accounts for the stoichiometry observed. For example, oxidation of one-sixth of a
mole of triethylamine to trivinylamine would bring about reduction of one mole of copper(II). Of the two moles of triethylamine involved in the reaction per mole of copper(II) chloride, 1.84 moles would be subsequently recoverable unoxidized. This is in excellent agreement with the data. Eneamine polymerization reactions, perhaps similar to the aldol condensation, then account for the formation and the chemical and physical properties of the final non-volatile red-black tarry oxidation product.

The data lead to the conclusion that the final product of the reaction is chloro(triethylamine)copper(I) plus the hydrochlorides of triethylamine and the oxidized polymeric tertiary amine. After removal of triethylamine from this mixture (at 6 mm. pressure at 25°C.) a residue of triethylammonium dichlorocuprate(I) and small amounts of a saturated polymeric alkylammonium dichlorocuprate(I) remain.

In general terms, the type of mechanism postulated seems to be the simplest possible to account for the experimental observations. The initial steps of this mechanism may be related to the metabolic path of oxidative dealkylation of amines catalyzed by the copper-containing enzyme amine oxidase. Similarities may be noted between observations on the sequence Cu(II) → Cu(I) → Cu(II) → Cu(I), the ability of oxygen to regenerate the Cu(II), and the e.p.r. spectra of the reacting mixture, with the results of other workers on copper(I)-copper(II) containing oxidases (46, 47) (pages 14-16). The non-aqueous conditions involved in this work promoted repeated oxidation steps
leading to a highly unsaturated amine. The diethylvinylamine formed on disproportionation of the initial triethylamine oxidation product at the first intermediate stage of the reaction was found to be subject to hydrolysis to diethylamine and acetaldehyde. The initial steps of the above mechanism, postulated largely on the basis of magnetic behavior exhibited by the system, was thus tested successfully. Under anaerobic conditions, the copper(I) reduction product was subject to atmospheric reoxidation. Such a reaction under aqueous aerobic conditions would correspond to the enzymic process, in which copper plays a catalytic role in the oxidative dealkylation of an amine to an aldehyde and an amine of one lower degree of substitution (pages 14-16).
VIII. CONCLUSIONS

It is found that tertiary aliphatic amines, in particular triethylamine, do have an extensive and interesting coordination chemistry. Stable complexes can be prepared with the copper(I) halides. Several new and interesting equilibria involving these substances have been uncovered. Triethylamine complexes of copper(II) halides are stable at low temperature with respect to dissociation. Such complexes decompose by internal electron transfer above 0°C., rather than by dissociative mechanisms. Oxidation-reduction reactions may occur in these systems particularly when the reduced form of the metal can be stabilized by complex formation with species liberated or present during the course of the reaction. The products of such reactions are themselves involved in a series of complex equilibria. Such processes can occur both in solution and in the solid state.
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