pentoxide) were unsuccessful. A saturated solution of the complex was treated with an equimolar amount of the gaseous diacid chloride (phosgene) or a solution of the diacid chloride in dry acetone. The solid product was isolated by pouring the reaction mixture into water, followed by washing with water and organic solvents to remove impurities. The elemental analysis and infrared spectra of the products obtained indicated slight polymerization and partial decomposition of the chelate.

Infrared Absorption Spectra.—All infrared spectra were obtained using a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. Samples were prepared as potassium bromide disks or hexachlorobutadiene mulls.

To avoid absorption of water, mulls of the azomethine derivatives were prepared in a drybox, after drying the sample at 110°, *in vacuo*.

Thermal Stability Measurements.—Measurements were performed under nitrogen or argon using a simple thermogravimetric balance similar to that described by Winslow and Matreyek.[25] The accuracy of the apparatus was checked using reagent grade $CuSO_4 \cdot 5H_2O$ as a standard. The weight losses observed at two different temperatures (125 and 270°) with a 200-mg. sample of $CuSO_4 \cdot 5H_2O$ heated under nitrogen for consecutive 12-hr. periods agree to within 2% of the expected values at these temperatures.[26]

The weight loss after 12 hr. at 150° was usually slight and presumed to be due to loss of water. The thermal stability data are reported in Tables IV and V as per cent weight loss at the designated temperature relative to the sample weight at 150°, after heating for 12 hr. at that temperature. Temperatures were constant to within ±5° and the weight of sample used was approximately 200 mg., except as noted. The reliability of these data has been checked in two cases by duplicate determinations which agree to within 5% of the given value for weight losses greater than 4%.

Acknowledgments.—The authors wish to thank Mr. J. Nemeth and his associates for analyses and molecular weight measurements, and Mr. D. H. Johnson and staff who provided most of the infrared spectra. We are indebted to the National Science Foundation for financial support, which was extended to Leonard V. Interrante through a fellowship.

---

[25] F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

[26] W. W. Wendlandt, *Anal. Chim. Acta*, **27**, 313 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA

Reactions of Triethylamine with Copper Halides. II. Internal Oxidation–Reduction of Dichlorobis(triethylamine)copper(II)[1,2]

BY JOSEPH F. WEISS,[3a] GORDON TOLLIN,[3b] AND JOHN T. YOKE III[3c]

Received May 11, 1964

Triethylamine and copper(II) chloride react at −45° to form the crystalline complex $CuCl_2 \cdot 2N(C_2H_5)_3$, characterized by composition and by its electronic and e.p.r. spectra. Upon warming to about 0° this complex undergoes internal electron transfer to give a diamagnetic solid. The hydrolysis products of diethylvinylamine are obtained from this diamagnetic product. A relation to the enzymic copper-catalyzed oxidative dealkylation of amines is suggested. Further warming of the anhydrous reaction mixture causes reappearance of the e.p.r. signal of Cu(II). A change in the coordination environment is indicated by a shift in the anisotropic g values from those of the original complex. The transient paramagnetic species react further to give the diamagnetic final product previously observed[1] in the direct reaction of triethylamine with copper(II) chloride at elevated temperatures. Some n.m.r. data offer additional evidence corroborating the previous suggestion[1] on the nature of the final product.

Introduction

In the previous work,[1] it was shown that an irreversible oxidation–reduction reaction is easily induced on warming a mixture of anhydrous copper(II) chloride and an excess of triethylamine. Pressure–composition phase studies and hydrolysis studies showed that the reaction corresponds to the equations

$$CuCl_2(c) + 2(C_2H_5)_3N(l) \longrightarrow A(\text{dark solid}) \qquad (1)$$

$$A \underset{25°}{\overset{6\text{ mm.}}{\rightleftharpoons}} B(\text{dark liquid}) + (C_2H_5)_3N(g) \qquad (2)$$

$$B \xrightarrow[(NaOH)]{H_2O} CuCl + (NaCl) + {\sim}0.85(C_2H_5)_3N + C(\text{tar}) \qquad (3)$$

The recovery of a total of *ca.* 1.85 moles of the original 2.00 moles of triethylamine bound in the reaction mixture suggests that the dark tarry product C is a polymeric amine derived from the oxidation of *ca.* $^1/_6$ mole of triethylamine. To account for the reduction of 1 mole of copper(II) to copper(I), repeated steps of oxidative deprotonation of triethylamine were postulated.

Using the pure components, the equilibrium reaction

$$(C_2H_5)_3NHCl(s) + CuCl \cdot N(C_2H_5)_3(s) \underset{25°}{\overset{6\text{ mm.}}{\rightleftharpoons}} (C_2H_5)_3NHCuCl_2(\text{oil}) + (C_2H_5)_3N(g) \qquad (4)$$

was observed. Both the pressure–composition behavior and the phase changes suggest a close relation between this system and the products A and B above.

---

[1] Paper I: J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

[2] This investigation was supported by P.H.S. grant GM from 11511-01 the National Institutes of Health, Public Health Service.

[3] (a) N.S.F. Summer Fellow, 1963. N.A.S.A. Fellow, 1963–1964. Abstracted from the Ph.D. dissertation of J. F. W., University of Arizona, 1964. (b) Alfred P. Sloan Foundation Fellow. (c) To whom inquiries should be addressed at the Department of Chemistry, Oregon State University, Corvallis, Ore.

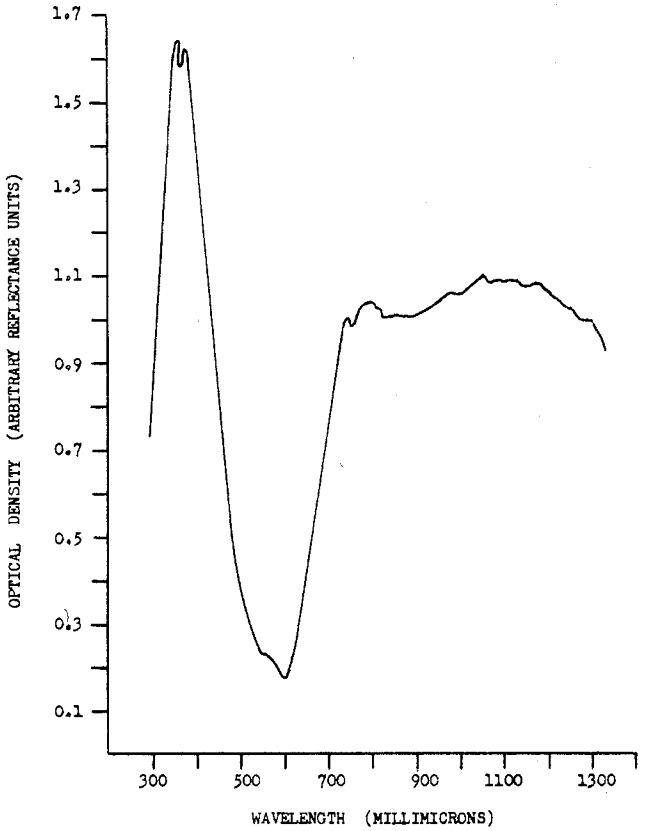

Fig. 1.—Reflectance spectrum (*ca.* −15°) of $CuCl_2 \cdot 2N(C_2H_5)_3$.

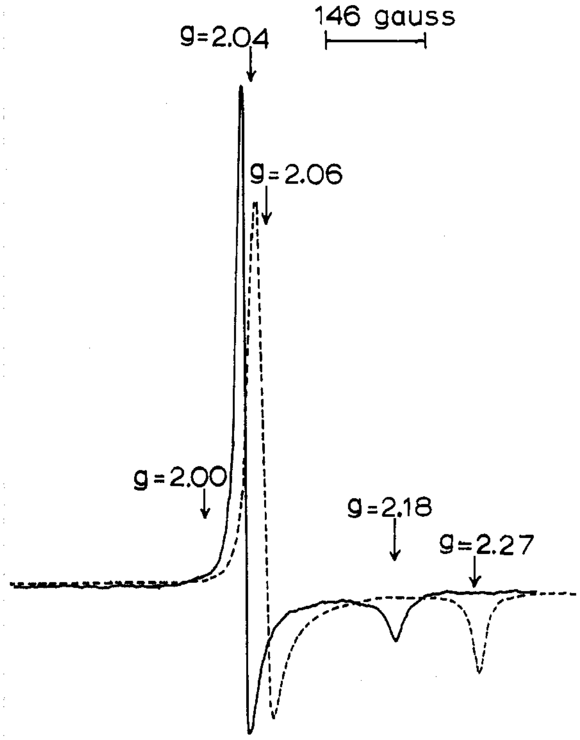

Fig. 2.—E.p.r. spectrum of $CuCl_3 \cdot 2N(C_2H_5)_3$ at −40° (dashed line) and of the intermediate reaction mixture (full line, magnified 63.5×).

It was postulated that eq. 2 and 4 correspond to systems differing only by the presence in the former case of the nonvolatile dark polymeric amine derived from oxidation of about $^1/_6$ mole of triethylamine. In the present work, some n.m.r. studies offer further corroborating evidence for this postulate.

The main purpose of the present work was to undertake the preparation of a pure triethylamine complex of copper(II) chloride, so that a study of the oxidation–reduction reaction could be made with the two reagents intimately placed in stoichiometric proportions within a coordination compound. That such a complex could be prepared at a low temperature was suggested by the work of Simon, *et al.*,[4] who studied systems of copper(II) chloride and bromide with ethyl- and mono-, di-, and trimethylamine. Their isobaric temperature–composition phase diagrams indicated formation of a series of complexes at low temperatures, such complexes undergoing irreversible decomposition at room temperature or above. They made no study of the nature or products of the decomposition reaction in the trimethylamine–copper(II) chloride system.

Results

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. The reflectance spectrum of the yellow-green complex (Fig. 1) shows a very broad absorption in the near-infrared region corresponding to d–d transitions localized on copper,[5] while the more intense absorption centered at 26.6×10^3 cm.$^{-1}$ would be ascribed to charge-transfer bands of the complex. Since ligand to metal charge transfer would seem formally related to the first step of copper(II) reduction and amine oxidation, it was of interest to see if irradiation of the complex would promote the thermally induced oxidation–reduction reaction.

The thermally induced reaction could be followed conveniently by repeated sweeping of the paramagnetic resonance signal of the complex as its temperature was raised slowly in the cavity of the e.p.r. spectrometer. In the previous work,[1] only the broad unresolved resonance of solid copper(II) chloride, centered at $\langle g \rangle = 2.2$, was observed in the initial mixture. The e.p.r. signal of the dichlorobis(triethylamine)copper(II) complex, however, shows resolution of the d^9 Cu(II) resonance according to the anisotropy in the g values, $g_\perp = 2.06$, $g_\| = 2.27$, as shown in Fig. 2. This behavior has often been observed previously in e.p.r. studies of copper(II) complexes.[6]

As the sample was allowed to warm from −40 to 0° there was a small decrease in the intensity of this signal which could be completely accounted for by a $1/T$ dependence. In the temperature range 0 to 20°

---

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

(5) C. Furlani and G. Morpugo, *Theoret. Chim. Acta*, **1**, 102 (1963).

(6) For example, see H. Beinert, D. E. Griffiths, D. C. Wharton, and R. H. Sands, *J. Biol. Chem.*, **237**, 2337 (1962); D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962); H. Rein, O. Ristau, and F. Jung, *Z. physik. Chem.*, **221**, 197 (1962).

this decrease in intensity became much greater and changed with time. At 20° the sample became completely diamagnetic within a few minutes as indicated by disappearance of the e.p.r. signal. Irradiation with blue light had no effect on the rate of disappearance of the copper(II) signal. Thus, charge-transfer excitation is not sufficient to promote the rate of the actual electron transfer and subsequent mass transfer and diffusion processes which probably limit the rate of oxidation–reduction. At the diamagnetic stage, the specimen had become an orange powder.

Slowly at room temperature, or more rapidly if the sample tube was hand-warmed for a few minutes, a new paramagnetic resonance signal developed in the sample, for which the values $g_\perp = 2.04$ and $g_\parallel = 2.18$ were observed. The differences in the new signal from the signal of the original complex can be seen in Fig. 2. The sample tube was removed from the spectrometer, immersed in boiling water for about 30 sec., 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 and diminished and disappeared, this being associated with transformation of the orange powder to the final dark diamagnetic oxidation–reduction product. At no time during the course of these changes did the intensity (peak to peak height) of the second resonance signal amount to as much as 5% of the intensity of the signal of 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 with those observed in the second stage of the reaction.

If water was added to the reaction mixture at the intermediate diamagnetic stage, *i.e.*, to the orange powder obtained by warming the original complex to a temperature just above 0°, acetaldehyde and diethylamine were liberated in large amounts and were characterized. These compounds are the hydrolysis products of diethylvinylamine, the product of two-electron oxidation of triethylamine.[7]

Discussion

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 buildup on any species.

$$[\mathrm{CuCl_2 \cdot 2N(C_2H_5)_3}] \longrightarrow [\mathrm{CuCl \cdot N(C_2H_5)_3}] + \{\mathrm{(C_2H_5)_3N\cdot^+}\} + \mathrm{Cl^-} \quad (5)$$

$$2\{\mathrm{(C_2H_5)_3N\cdot^+}\} \longrightarrow \mathrm{(C_2H_5)_3NH^+} + \mathrm{(C_2H_5)_2(CH_3CH{=})N^+} \quad (6)$$

That copper(I) chloride binds triethylamine in a 1:1 complex was shown in the previous work.[1] 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 is proven 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 previously established[1] 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

$$\mathrm{(C_2H_5)_2(CH_3CH{=})N^+} + [\mathrm{CuCl \cdot N(C_2H_5)_3}] \rightleftharpoons \mathrm{(C_2H_5)_3NH^+} + [\mathrm{CuCl \cdot N(C_2H_5)_2(CH{=}CH_2)}] \quad (7)$$

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.

$$[\mathrm{CuCl \cdot N(C_2H_5)_2(CH{=}CH_2)}] + 2\mathrm{(C_2H_5)_3NH^+} + 2\mathrm{Cl^-} \longrightarrow 2\mathrm{(C_2H_5)_3N} + \{\mathrm{(C_2H_5)_3N\cdot^+}\} + \mathrm{CuCl_3^-} \quad (8)$$

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.

$$2\{\mathrm{(C_2H_5)_3N\cdot^+}\} + \mathrm{(C_2H_5)_3N} \longrightarrow 2\mathrm{(C_2H_5)_3NH^+} + \mathrm{(C_2H_5)_2(CH_2{=}CH)N} \quad (9)$$

Both copper(I) and copper(II) species would now be present in the sample. Steps 5–9 can be summed up in a bookkeeping sense in the balanced equation

$$4[\mathrm{CuCl_2 \cdot 2N(C_2H_5)_3}] = 2\{\mathrm{(C_2H_5)_3NHCuCl_3}\} + 2[\mathrm{CuCl \cdot N(C_2H_5)_3}] + 3\mathrm{(C_2H_5)_3N} + \mathrm{(C_2H_5)_2(CH_2{=}CH)N} \quad (10)$$

It has been shown[8] 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[8] 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 Fig. 2. 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)-

---

(7) D. H. Rosenblatt, *et al.*, *J. Org. Chem.*, **28**, 2790 (1963).

(8) J. T. Yoke and G. L. McPherson, *J. Inorg. Nucl. Chem.*, **26**, 655 (1964).

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 $^1/_6$ mole of triethylamine to trivinylamine would bring about reduction of 1 mole of copper(II). Of the 2 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 formation of the final nonvolatile red-black tarry oxidation product.

The data presented here and in the previous work[1] 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°) a residue of triethylammonium dichlorocuprate(I) and small amounts of a saturated polymeric alkylammonium dichlorocuprate(I) remain. As is shown in Fig. 3, the proton magnetic resonance spectrum of the actual product obtained in this way corresponds exactly to the spectrum of authentic triethylammonium dichlorocuprate(I) as a pure liquid, except that the fine structure of the methyl and methylene resonances is lost. Possibly this is due to remaining traces of paramagnetic copper(II). No other types of protons can be detected in the n.m.r. spectrum of the product, nor are other types of functions apparent in the infrared spectrum of the product (one extra absorption at 1250–1275 cm.$^{-1}$ being unassigned).

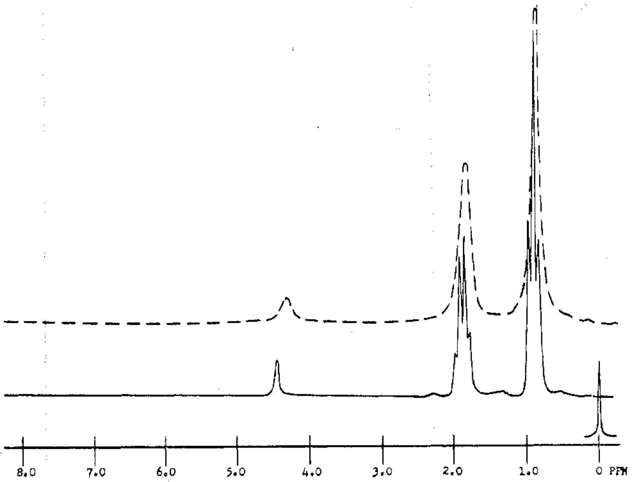

Fig. 3.—Proton magnetic resonance spectrum (relative to tetramethylsilane external standard) of triethylammonium dichlorocuprate(I) (full line) and the oxidation–reduction reaction product (dashed line).

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 our 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.[9] The nonaqueous conditions involved in the present 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. Under aerobic 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.

Experimental

Dichlorobis(triethylamine)copper(II).—The materials and techniques used have been described previously.[1] Triethylamine was distilled onto finely powdered copper(II) chloride in a trap on the vacuum line, the mixture was stirred magnetically at −45° (chlorobenzene slush bath) for 1–4 days, and the excess of triethylamine was then removed at its equilibrium vapor pressure of 4 mm. at −23° (carbon tetrachloride slush bath) until the pressure of the system suddenly dropped to much less than 1 mm. In various runs, from 2.00 to 2.02 moles of triethylamine was retained per mole of copper(II) chloride, as indicated by the gain in weight of the samples. The complex, a light green-yellow powder, appeared to be stable indefinitely at −45°, showed signs of very slight decomposition after several days at −23°, and was observed to decompose quickly on warming to give the dark oxidation–reduction product previously observed.[1]

Ultraviolet and Visible Spectra.—The reflectance spectrum of the complex was measured using a Beckman DU spectrophotometer in the manner previously described.[10] The sample holder was loaded at a low temperature in a nitrogen-filled drybox. The temperature of the sample was maintained at about −15° by passing the gas stream from boiling liquid nitrogen through a tube into the sample housing of the spectrophotometer, around which there was taped a plastic bag.

E.p.r. Spectra.—A Varian Model V 4501 e.p.r. spectrometer was used in the paramagnetic resonance work, as previously described.[1] An approximate value of field strength was calculated from the observed signal of DPPH ($g = 2.004$) and the relation $h\nu = g\beta H$, using the value 9.5×10^9 c.p.s. as the klystron frequency. Subsequent estimations of g values of other species are then based on accurate measurements of changes in field strength from the point of approximate calibration, and such g values are of high accuracy relative to each other, but of lower absolute accuracy. Actually, the determination of an unknown g value near to 2.0 in this way is not very sensitive to small errors in H. A V 4547 variable temperature accessory was used to regulate sample temperature. The photochemical sensitivity of the sample was studied using a 500-watt tungsten filament projection lamp with a blue-green filter (Corning 4–71, maximum transmittance at 464 mμ) focused on the e.p.r. cavity. The quartz sample tubes were loaded with chilled samples of complex in a nitrogen-filled drybox. The contents were degassed *in vacuo* at

---

(9) L. Broman, B. G. Malmstrom, R. Aasa, and T. Vanngard, *J. Mol. Biol.*, **5**, 301 (1962); E. Walaas, O. Walaas, and S. Haavaldsen, *Arch. Biochem. Biophys.*, **100**, 97 (1963).

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

−79° and the evacuated tubes were stored at this temperature until ready to run.

Hydrolysis of the Reaction Intermediate. (A) Anaerobic Conditions.—To the orange diamagnetic powder obtained on warming a sample of dichlorobis(triethylamine)copper(II) to a temperature just above 0° was added an excess of water. The mixture was stirred for 10 min., and the more volatile materials so liberated were removed by distillation in the vacuum system. In addition to a little water, the distillate was found to contain large amounts of acetaldehyde, diethylamine, and triethylamine. Acetaldehyde was characterized by precipitation of its 2,4-dinitrophenylhydrazone from a solution of the distillate in dilute hydrochloric acid (m.p. 142–143°, authentic sample m.p. 146°, m.m.p. 145°). The distillate was evaporated to dryness and the amine hydrochlorides were taken up in the minimum amount of water. Concentrated sodium hydroxide was added to the solution, and the amine fraction was obtained by distillation. Using an F. and M. flame ionization gauge vapor phase chromatograph with a helium carrier gas flow rate of 50 ml./min. and a 2-ft. column packed with silicone rubber at 35°, the amine fraction was separated into two peaks having retention times of 2.48 and 5.45 min., respectively. These peaks were identical with those shown by a 50:50 synthetic mixture of di- and triethylamines, and the second peak was identical with that of authentic triethylamine. Separation of the amine fraction by the Hinsberg method also permitted characterization of diethylamine as the benzenesulfonamide, m.p. 41–42°, authentic sample m.p. 42°, m.m.p. 42°.

(B) Aerobic Conditions.—A similar sample was hydrolyzed at 0° over a period of 2 hr. in a system open to the air. The mixture was made acidic, distillation of the water was commenced, and the aldehyde portion was found to be concentrated in the forerun. It gave the 2,4-dinitrophenylhydrazone of glyoxal (m.p. 326°, authentic sample m.p. 324°, m.m.p. 323°) and was in fact glycolaldehyde (the glyoxal derivative being formed by an osazone reaction). Thus, the aldehyde gave a negative test for glyoxal with *o*-phenylenediamine, and gave positive tests for glycolaldehyde with orcinol and phloroglucinol.[11] Formation of glycolaldehyde from the originally liberated acetaldehyde under aerobic conditions is attributed to air reoxidation of some copper(I) to copper(II) chloride, which is known[12] to convert carbonyl compounds to the α-chloro derivatives. Hydrolysis of chloroacetaldehyde would then yield glycolaldehyde.

After distillation of the aldehyde portion, the hydrolyzed reaction mixture was made alkaline and the amine portion was then obtained by distillation. In addition to triethylamine, it contained diethylamine which was separated and identified by the Hinsberg method, *p*-benzenesulfonamide m.p. 36°, authentic sample m.p. 42°, m.m.p. 38°.

N.m.r. and Infrared Spectra.—In the previous work,[1] the postulate was made that product B of eq. 2 corresponds to triethylammonium dichlorocuprate(I) (except that the alkylammonium moiety is about 85% triethylammonium ion and about 15% the conjugate acid of the polymeric amine derived from repeated steps of oxidative deprotonation of triethylamine). To obtain further evidence on this point, a sample of B was prepared in the manner previously given. The n.m.r. spectrum of this reaction product was compared with that of authentic triethylammonium dichlorocuprate(I), prepared as previously described,[1] using a Varian A-60 spectrometer. The sample tubes were loaded in a nitrogen-filled drybox and closed with plastic caps sealed with wax. The results are shown in Fig. 3. Carbon tetrachloride and carbon disulfide extracts of the dark liquid product were only slightly yellow, indicating fairly low solubility. A Perkin-Elmer Infracord was used to obtain infrared spectra of these solutions, but the results showed poor definition and differed from triethylamine and triethylammonium chloride spectra only by absorption in the 1250–1275 cm.$^{-1}$ region.

---

(11) E. Tommila, *Acta Chem. Fennica*, **7B**, 85 (1934); *Chem. Abstr.*, **28**, 4008 (1934).

(12) C. E. Castro, *J. Org. Chem.*, **26**, 4183 (1961); J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

CONTRIBUTION NO. 1672 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Kinetics of Aquation of Dibromo- and Bromoaquobis(ethylenediamine)chromium(III) Cations[1]

BY LAWRENCE P. QUINN AND CLIFFORD S. GARNER

Received April 20, 1964

The kinetics and products of aquation of *cis*- and *trans*-$\mathrm{Cr(en)_2Br_2^+}$ and *cis*- and *trans*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ have been investigated in acid solution at 24.8 ± 0.2°. In 0.01–0.1 F $\mathrm{HClO_4}$ (μ = 0.1, $\mathrm{LiClO_4}$) k_{aq} is $(2.8 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ for *cis*-$\mathrm{Cr(en)_2Br_2^+}$ and $(3.2 \pm 0.2) \times 10^{-4}$ sec.$^{-1}$ for *trans*-$\mathrm{Cr(en)_2Br_2^+}$. The directly-formed products of *cis*-$\mathrm{Cr(en)_2Br_2^+}$ aquation are *cis*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ (97 ± 3%) and *trans*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ (3 ± 3%). In *trans*-$\mathrm{Cr(en)_2Br_2^+}$ aquation 96% of the first-formed product is *trans*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$; the other 4% of first-formed product is either *cis*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ (aquation) or *cis*-$\mathrm{Cr(en)_2Br_2^+}$ (isomerization). In 0.06–0.14 F $\mathrm{HClO_4}$ or $\mathrm{HNO_3}$ *cis*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ has $k_{\mathrm{aq}} = (1.8 \pm 0.2).$ $\times 10^{-4}$ sec.$^{-1}$, the directly-formed products being *cis*-$\mathrm{Cr(en)_2(OH_2)_2^{+3}}$ (95 ± 5%) and *trans*-$\mathrm{Cr(en)_2(OH_2)_2^{+3}}$ (5 ± 5%) In 1.4 F $\mathrm{HNO_3}$ *trans*-$\mathrm{Cr(en)_2(OH_2)Br^{+2}}$ releases $\mathrm{Br^-}$ at an initial rate corresponding to $k = (3.0 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$; there is evidence for a faster competing reaction, probably involving loss of ligand ethylenediamine. Upper limits for the *cis–trans* isomerization rates have been estimated. Reaction paths consistent with the kinetic and stereochemical results are presented, and a comparison is made with the aquation behavior of the chloro analogs and the Co(III) analogs. The previously unreported visible absorption spectra of these Cr(III) species are given.

The hydrolysis of *cis*- and *trans*-dibromobis(ethylenediamine)chromium(III) cations and the related bromoaquo complexes apparently has not been investigated previously. We report here a study of the kinetics and products of aquation of these species in acid solution, undertaken to allow comparisons to be

---

(1) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University.