It seems more probable that four of the six coördinating positions of the metal atom are occupied by carboxyl oxygens from diazomalonate ions, while the diazo groups cross-coördinate to other metal atoms. The simplest polymer thus formed would be a dimer, but the way would be open to higher polymerization. This might explain the gummy or tacky nature of the lanthanum precipitate described above, which is characteristic of some high polymers. It does not seem likely that the nature of the diazomalonate is essentially changed in the chelation process, as by formation of a bisdiazo compound.

There is no evidence as to why the aluminum chelate should be so much less subject to decomposition than the others. It is less dissociated into its parent ions, but dissociation is of minor importance with lanthanum and cerium ions, especially when these are present in excess. It is, of course, not unusual for chelates to be much more or much less reactive than the parent substances.[10]

We can conclude that chelate formation represses the general base catalysis, and in the presence of aluminum ion only the small amount of free diazomalonate in equilibrium with the complex can decompose. The lanthanum and cerium chelates, on the other hand, can react with acids, and the reaction may be subject to general acid catalysis.

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[10] Reference 7, p. 64, and Chap. 8.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY]

Spectrophotometric Investigation of the Copper(II) Ion–Triethanolamine Complex

BY JOHN M. BOLLING[1] AND JAMES L. HALL

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The deep blue complex ions existing in aqueous solutions of copper(II) ion and triethanolamine were studied, from *p*H 3 to *p*H 14 and at ionic strengths 0.03 and 0.120, by the methods of spectrophotometry and electrical migration. In dilute solutions copper(II) ion and triethanolamine form complex ions only in the ratio of 1:1. Variations in the light absorption with changes in *p*H are believed to be due to changes in the number of coördinated hydroxyl ions. At low values of *p*H migration experiments indicate a positively charged complex. As the *p*H is raised, a neutral complex is formed and at still higher values of *p*H, the complex becomes negatively charged. At *p*H 9.8 the colored complex does not migrate in the electric field and is assumed to be $Cu(OH)_2(H_2O)N(C_2H_4OH)_3$.

Introduction

Although a number of crystalline compounds have been prepared from aqueous solutions of triethanolamine and various copper(II) salts[2] there have been few attempts to determine the formulas of the complexes formed in aqueous solution. Yoe and Barton[3] studied the system copper(II) ion–triethanolamine in an attempt to develop a colorimetric analytical method for the determination of copper. They did not attempt to identify the entity that produced the deep blue color. Harvey, Tewksbury and Haendler[4] studied the system copper(II) ion–diethanolamine by the method of continuous variations as extended by Vosburgh and Cooper.[5] Their results were interpreted to indicate that ions are formed with copper to diethanolamine ratios of less than 1:3 and also with ratios greater than 1:3.

The present investigation was undertaken to obtain information regarding the composition of complexes formed between copper(II) ion and triethanolamine in aqueous solution.

Preliminary investigations showed that for solutions of copper(II) ion and triethanolamine the wave length of maximum optical density and the extinction coefficient at this wave length varied as the ratio of the two substances was changed. It was further found that at a fixed ratio of copper(II) ion to triethanolamine similar spectral variations occurred as acid or alkali was added. It was found that for corresponding copper(II) ion concentrations, the spectrum of a solution containing copper(II) ion and four equivalents of triethanolamine was almost identical with the spectrum of the compound $Cu(OH)_2 \cdot N(C_2H_4OH)_3$ prepared by the method of Duff and Steer.[2b] For solutions made by adding only copper(II) salt and triethanolamine to water, at ratios of copper(II) ion to triethanolamine below 1:2, the complex or complexes formed were not stable enough to prevent precipitation of copper hydroxide or other hydrolysis products. At higher ratios of the amine to copper(II) ion or with added alkali the solutions were stable. The spectra of solutions containing varying ratios of copper(II) ion to triethanolamine at various fixed *p*H values and ionic strengths are reported here. Since these data indicate that the charge of the complex varies as *p*H is changed, the results of a series of migration experiments are also reported.

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[1] This paper is based upon a portion of the thesis by John M. Bolling in partial fulfillment of the requirements for the Ph.D. degree, June, 1952.

[2] (a) J. R. Anderson, "The Use of Alkanolamines in the Separation of Cobalt from Nickel and the Determination of Cobalt," M.S. Thesis, West Virginia University, Morgantown, W. Va., 1941, p. 35; (b) J. C. Duff and E. H. Steer, *J. Chem. Soc.*, 2861 (1932); (c) G. Garelli, *Atti. accad. sci. Torino, Classe Sci. Fis., Mat. Nat.*, **68**, 398 (1933); (d) F. Garelli, *Congr. intern. quim. pura y aplicada, 9th. Congr. Madrid*, **3**, 295 (1934); (e) F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, **63**, 570 (1933); (f) F. Garelli and A. Tettamanzi, *Atti. accad. sci. Torino, Classe Sci. Fis., Mat. Nat.*, **69**, 89 (1934); (g) F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, **64**, 474 (1934); (h) W. Hieber and E. Levy, *Z. anorg. allgem. Chem.*, **219**, 225 (1934); (i) A. Tettamanzi and B. Carli, *Gazz. chim. ital.*, **63**, 566 (1933); (j) A. Tettamanzi and B. Carli, *ibid.*, **64**, 315 (1934).

[3] J. H. Yoe and C. J. Barton, *Ind. Eng. Chem., Anal. Ed.*, **12**, 456 (1940).

[4] J. E. Harvey, C. I. Tewksbury and H. M. Haendler, THIS JOURNAL, **71**, 3641 (1949).

[5] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).

Experimental

Apparatus.—Absorption measurements were made with a Beckman spectrophotometer, model DU. The optical densities of the solutions, D, are defined by the relationship $D = \log_{10} I_0/I$, where I_0 and I are the incident and transmitted intensities, respectively. All measurements were in 1.00-cm. silica cells.

The *p*H determinations were made with a Beckman Model H-2 meter. Glass electrodes were used. The migration experiments were made in an ordinary transference number apparatus of the Hittorf type.[6]

Materials.—An approximately 1 *M* aqueous solution of triethanolamine was made from Carbide and Carbon triethanolamine which had been vacuum distilled at approximately 170° at a pressure of 5 mm. This stock solution was standardized with hydrochloric acid; the titration being made potentiometrically, using the *p*H meter. Hydrochloric acid and sodium hydroxide stock solutions were prepared and standardized by the usual methods. A solution of copper(II) perchlorate was made by suspending 22 g. of C.P. malachite in 200 ml. of water and treating with slightly less than the theoretical amount of J. T. Baker C.P. 60% perchloric acid. The solution was filtered and standardized iodometrically.[7] The spectrum of the copper perchlorate solution was identical with those previously reported.[8] The 1 *M* solution of sodium perchlorate was made by neutralization of standardized perchloric and sodium hydroxide solutions.

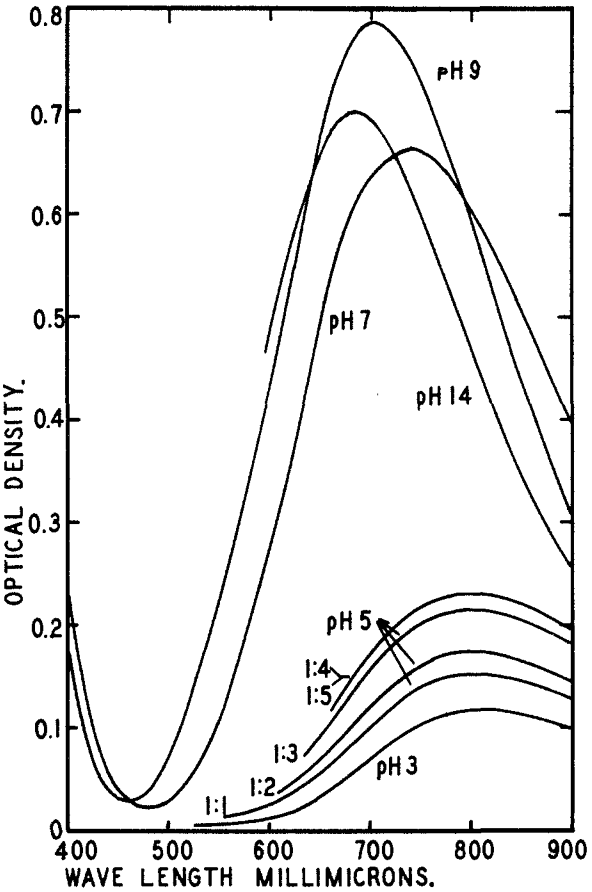

Fig. 1.—Spectra of copper(II) ion-triethanolamine system at various *p*H values. All data are for a copper(II) ion concentration of 0.01 *M*, and all are at an ionic strength of 0.03 except at *p*H 14, which is in an approximately 1.0 *N* solution of sodium hydroxide. At *p*H 3, the addition of amine to the solution does not alter the spectrum shown which is for 0.01 *M* copper ion. At *p*H 5 the addition of the amine increases the optical density of the solutions to a ratio of 1:4. At *p*H 7, the spectra of solutions at all ratios from 1:1 to 1:5 are identical. At *p*H 9, the curve shown is for a ratio of 1:3, the curve for ratio 1:2 is slightly higher and the curve for ratio 1:4 is slightly lower. The curve shown at *p*H 14 is for a ratio of 1:5.

Method.—The solutions for absorption measurements were made by diluting calculated quantities of the stock solutions so as to obtain previously calculated concentrations of copper(II) perchlorate and triethanolamine. Before the final dilution the *p*H values were adjusted and the ionic strength was fixed by addition of appropriate amounts of perchloric acid, sodium hydroxide, or sodium perchlorate.

The migration experiments were performed in order to determine the direction of movement of boundaries formed between a clear solution and a colored solution. In order to obtain pairs of solutions identical as nearly as possible in *p*H value and conductance, the following procedure was carried out: A buffer solution of the desired *p*H and triethanolamine concentration was prepared; this solution was divided into two parts, and to one part was added the minimum amount of copper(II) perchlorate to give a visible color. For each experiment reversible silver-silver chloride electrodes were immersed in a saturated solution of sodium chloride. Above this was the clear solution of triethanolamine filling the remainder of the apparatus except for the lower half of the central U-tube which contained the colored solution. A potential of about 200 volts was maintained across the electrodes.

Results

The spectra of solutions at *p*H values of 3.0, 5.0, 7.0, 8.0, 9.0, 10.0 and 11.0 were determined for ratios of copper(II) ion to triethanolamine varying from 1:2 to 1:5 at a copper(II) ion concentration of 0.01 *M* and an ionic strength of 0.120. Solutions with a ratio of 1:1 could not be studied because of the formation of a precipitate. Solutions of *p*H 7 or higher exhibited spectra independent of the copper(II) ion-triethanolamine ratio within the range 1:2 to 1:5, but differing markedly with changing *p*H. Typical results are shown in Fig. 1. For any fixed *p*H value above 7, these data indicate that no colored entity with a ratio above 1:2 is produced because addition of amine in greater proportion produces no further change in the spectra. Since these data do not include information which would show a difference in the position of the absorption maximum between solutions having a 1:1 and a 1:2 ratio, the presence of any complex greater than 1:1 is not proved.

The method of continuous variations was used at *p*H 8 and ionic strength of 0.03 with a maximum copper(II) ion concentration of 0.0025 *M*. Under these conditions ratios below 1:2 could be obtained as clear solutions. For solutions with a fixed copper(II) ion concentration of 0.0025 *M* with varying amounts of triethanolamine, above the ratio 1:1.5, the spectra were identical, indicating an unstable 1;1 complex and no higher ratio complex. For the solutions of constant total copper(II) ion and triethanolamine concentration, a plot of optical density as a function of mole fraction at 715 mμ yielded a broad maximum at mole fraction 0.52, supporting the conclusion that a 1:1 complex is present.

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(6) F. Daniels, J. H. Mathews, J. W. Williams and Staff, "Experimental Physical Chemistry," 4th Ed., McGraw-Hill Book Co., New York, N. Y., 1949, p. 174.

(7) W. T. Hall, "Textbook of Quantitative Analysis," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 130.

(8) R. Bastian, *Anal. Chem.*, **21**, 972 (1949); A. V. Kiss, P. Csokan and G. Nyiri, *Z. physik. Chem.*, **A190**, 65 (1942).

Since the spectrophotometric evidence indicated that copper(II) ion and triethanolamine form complex ions only in the ratio 1:1, it was assumed that the variation of the spectra with *p*H could be accounted for by interaction of the complex with the hydroxyl ion. If this assumption is correct a positive ion, a neutral molecule, and a negative ion should be formed as the *p*H is increased, thus: $Cu(OH)(H_2O)_2N(C_2H_4OH)_3^{+1}$, $Cu(OH)_2(H_2O)N(C_2H_4OH)_3$, and $Cu(OH)_3N(C_2H_4OH)_3^{-1}$. These assumptions were confirmed by a series of migration experiments performed at *p*H values of 8.0, 9.0, 9.5, 9.8 and 10.0. The boundaries moved toward the negative electrode at *p*H values of 8.0, 9.0 and 9.5; they moved toward the positive electrode at a *p*H value of 10.0. The boundaries showed no movement over a period of two hours for the experiment at *p*H 9.8.

For the data obtained at *p*H 8.0 and an ionic strength of 0.03 the dissociation constant of the copper(II) ion–triethanolamine complex was calculated and found to be given by $\log_{10} K_{\text{equilib}} = 4.3 \pm 1$.

MORGANTOWN, W. VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

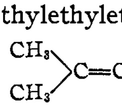
Rates and Temperature Coefficients in the Hydration of Two Gaseous Pentenes by Dilute Aqueous Nitric Acid[1]

BY JOSEPH B. LEVY, ROBERT W. TAFT, JR., DAVID AARON AND LOUIS P. HAMMETT

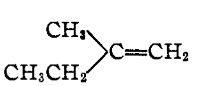
RECEIVED MAY 2, 1953

Although the hydrations of the isomeric pentenes trimethylethylene and *as*-methylethylethylene are measurably reversible and lead to the same alcohol, the specific rates of the hydrations may be determined to a useful precision from the decrease with time of the vapor pressure of the olefin over the solution in which the hydration is occurring. These specific rates do not differ largely from that of isobutene, yet the data obtained offer a strong indication that both enthalpies and entropies of activation are significantly lower for the pentenes than for isobutene.

The isomeric olefins trimethylethylene (I) and methylethylethylene (II)



I



II

hydrate in an essentially quantitative fashion to a single product *t*-amyl alcohol.[2] At temperatures of 25° or more the hydration is, we find, measurably reversible, and the reverse reaction must, in the case of at least one, and possibly of both of these olefins, lead to the formation of the isomer. Evidence which we have previously reported[2c] shows that no facile interconversion of the olefins occurs independently of the formation of the alcohol by way, for instance, of the mobile and reversible formation of a single carbonium ion. The reaction system with which we have to deal is therefore

$$\text{Olefin I} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Alcohol} \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} \text{Olefin II}$$

Nevertheless we find with I at 35° and lower and with II at 30° and lower that the quantity $s = -\mathrm{d}\ln(P - P^e)/\mathrm{d}t$ (where P is the partial pressure of gaseous olefin over a solution in which the hydration is proceeding and P^e is the partial pressure at equilibrium) is independent of time to excellent precision up to as much as 80% completion of reaction, just as it was in the simpler cases which we have studied previously.[3]

For this reaction system we have by virtue of a development which closely parallels that of eq. 3 of article I[3a]

$$(h_1 + r/RT)\frac{\mathrm{d}P_1}{\mathrm{d}t} = -k_1P_1 + k_{-1}C_a \qquad (1)$$

$$(h_2 + r/RT)\frac{\mathrm{d}P_2}{\mathrm{d}t} = -k_2P_2 + k_{-2}C_a \qquad (2)$$

k_1 and k_2 are rates of reaction at unit pressure of olefin (the k_p quantity of articles I and II), P_1 and P_2 are the partial pressures of olefin I and II, r is the ratio (volume of gas phase)/(volume of solution), h_1 and h_2 are the distribution constants of olefin between gas and liquid, C_a is concentration of alcohol. If alcohol and olefin II are absent at time 0 and the partial pressure of olefin I is P^0 at that time we can eliminate C_a by material balance considerations, obtaining after substitution of the definitions

$$k_1' = k_1/(h_1 + r/RT),\ k_2' = k_2/(h_2 + r/RT) \qquad (3)$$

and

$$Q = \frac{h_2 + r/RT}{h_1 + r/RT} \qquad (4)$$

the equations

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = -k_1'P_1 + k_{-1}(P^0 - P_1) - k_{-1}QP_2 \qquad (5)$$

$$\frac{\mathrm{d}P_2}{\mathrm{d}t} = -k_2'P_2 - k_{-2}P_2 + \frac{k_{-2}}{Q}(P^0 - P_1) \qquad (6)$$

These may be integrated by the method of Rakowski[4] to yield

$$P_1 - P_1^e = \frac{\lambda_1(P^0 - P_1^e - \lambda_2P_2^e)}{\lambda_1 - \lambda_2}e^{-\rho_1t} - \frac{\lambda_2(P^0 - P_1^e - \lambda_1P_2^e)}{\lambda_1 - \lambda_2}e^{-\rho_2t} \qquad (7)$$

$$P_2 - P_2^e = -\frac{P^0 - P_1^e - \lambda_2P_2^e}{\lambda_1 - \lambda_2}e^{-\rho_1t} + \frac{(P^0 - P_1^e - \lambda_1P_2^e}{\lambda_1 - \lambda_2}e^{-\rho_2t} \qquad (8)$$

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (a) H. J. Lucas and Yun-Pu Liu, THIS JOURNAL, **56**, 460 (1934); (b) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936); (c) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, THIS JOURNAL, **75**, 1253 (1953).

[3] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); (b) R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

[4] **Rakowski**, *Z. physik. Chem.*, **57**, 321 (1907).