It is of interest to compare the intermolecular attraction due to complex formation with that due to dispersion forces as developed by London.[11] Here the excited state is taken to be the ionization of both molecules in the interacting pair. This excited state lies $I_a + (e^2/r) + E_a$ higher than the excited state in the Mulliken complex. For the I_2–benzene system, the dispersion force excited state lies some 19 e.v. above the ground state; while for the complex, the excited state lies 3 e.v. above the ground state. Consequently, could the dispersion transition be observed, it would lie at much shorter wave lengths than those observed for the complex. It is of interest to note that both types of interaction are inversely proportional to the ionization energy of the base.[12] The matrix

(11) F. London, Z. Physik, **63**, 245 (1930).

(12) The inverse proportionality is obtained by assuming the approximate constancy of $\overline{r_A^2}$ and $\overline{r_B^2}$ in the expression

$$E = -\frac{2}{3}\frac{e^4 \overline{r_A^2} \text{ and } \overline{r_B^2}}{(I_A + I_B)R^6}$$

H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 354.

element in the dispersion force formulation is fairly large since it is, in effect, the sum over a large number of matrix elements for individual excited states. Consequently there is detectable attraction even though the separation of the excited state (states) from the ground state is large.

The excited state for the complex is stabilized against dissociation by the coulomb term. With a stable excited state, the electronic transition is usually well-defined and, transition probability permitting, so usually is the absorption spectrum.

Note Added in Proof.—McConnell, Hamm and Platt (J. Chem. Phys., 21, 66 (1953)) have also reported on regularities in the spectra of molecular complexes. These authors discuss the effect of variation in the Lewis acid as well as the base.

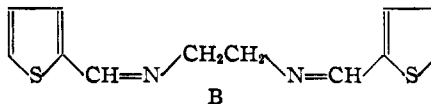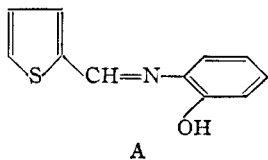[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Metal Ion Catalysis in the Hydrolysis of Schiff Bases[1,2]

By Gunther L. Eichhorn and John C. Bailar, Jr.

Received December 29, 1952

The action of metallic ions in enhancing the rate of many organic and physiological reactions has frequently been attributed to the formation of complex intermediates. The present work represents a study of the cleavage of bis-thiophenal–ethylenediamine in the presence of metal ions. Spectrophotometric measurements have yielded evidence for the transitory existence of the intermediate, and have made possible a study of its rate of decomposition. It is believed that the formation of bonds between the positive ion and nitrogen brings about a labilization of the nitrogen to carbon double bonds, which are thereby rendered more susceptible to hydrolytic cleavage.

The capacity of the azo and azomethine groups to act as coördinating donors to metal ions has been demonstrated by the work of many investigators during the last quarter century. Generally the presence of an auxochrome, such as a hydroxyl, amino or carboxyl group, or a heterocyclic nitrogen (as in pyridine and pyrrole) is required to stabilize the complex through chelate formation. In order to determine whether or not a heterocyclic sulfur atom would perform the same function, the following Schiff bases were synthesized by the condensation of 2-thiophenaldehyde[3] with o-amino-phenol (A) and ethylenediamine (B).

A

(1) Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951.

(2) Taken in part from the doctoral dissertation of G. L. Eichhorn, University of Illinois, 1950.

(3) The authors are indebted to Dr. Seymour Meisel and Dr. D. E. Badertscher, of the Socony–Vacuum Oil Co., Paulsboro, N. J., for furnishing the 2-thiophenaldehyde used in these studies, as well as for providing directions for its purification.

B

Although the participation of the sulfur atoms in these molecules during the coördination reactions would result in polycyclic chelation, a phenomenon usually associated with extraordinary stability, all attempts to isolate metal complexes of these compounds by the usual procedures were unsuccessful. However, an application of the method of continuous variation[4] to the system copper(II) sulfate–bis-thiophenal–ethylenediamine indicated the formation of 1:1 and 1:2 metal to base complexes. The striking resemblance of the absorption curves obtained in the continuous variation study to those reported by Jonassen and Dexter[5] suggested that the complexes in solution were those of ethylenediamine, rather than those of the Schiff base. This was corroborated by isolation of the ethylenediamine complexes from the solutions.

It had been observed during the preparation of the solutions for the continuous variation studies

(4) P. Job, Compt. rend., **180**, 928 (1925); Ann. chim., [10] **9**, 115 (1928); W. C. Vosburgh and S. R. Cooper, This Journal, **63**, 437 (1941).

(5) H. B. Jonassen and T. H. Dexter, ibid., **71**, 1553 (1949).

that the solutions in which the violet 1:2 ethylenediamine complex finally appeared were blue when first made up. The gradual color change was thereupon measured by the Cary recording spectrophotometer, which made it possible to obtain a complete visible spectrum every two minutes. The results are plotted in Fig. 1. The absorption
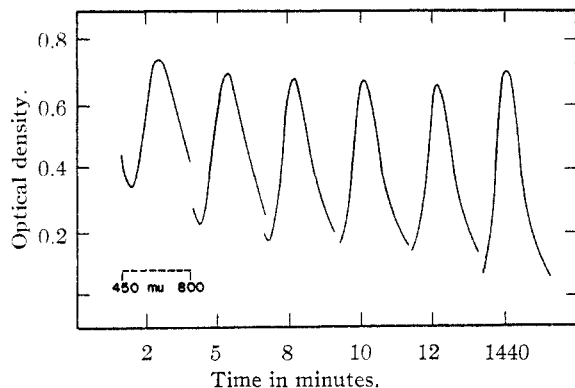

Fig. 1.—Change in absorption of a 1:2 mixture of copper(II) sulfate and bis-thiophenalethylenediamine in 50% alcohol.

characteristics of this system were found to be suitable for quantitative studies, but a similar change was discovered spectrophotometrically in 1:1 copper–base mixtures (Fig. 2), even though the
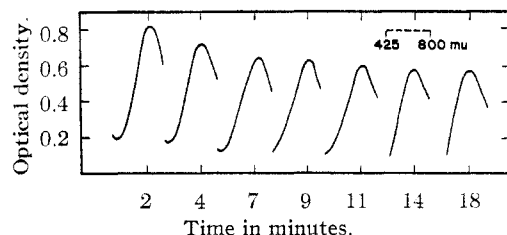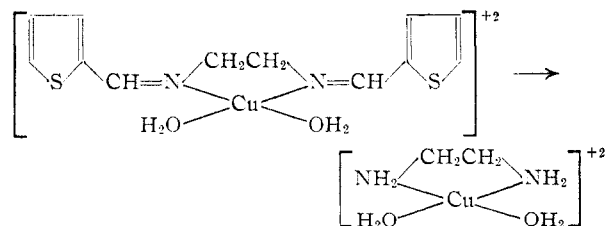

Fig. 2.—Change in absorption of an equimolar mixture of copper(II) sulfate and bis-thiophenalethylenediamine in 50% alcohol.

visual evidence for this transition is not striking. The following reaction presumably takes place

The presence of a substance more highly absorbing than $[\text{Cuen}(\text{H}_2\text{O})_2]^{+2}$ in the reaction mixture can be accounted for by the primary formation of $[\text{CuB-}(\text{H}_2\text{O})_2]^{+2}$, and the progressive diminution of the absorption can be explained by the conversion of this complex into $[\text{Cuen}(\text{H}_2\text{O})_2]^{+2}$.

Figure 3 is a plot of the change in absorption with time of a 1:1 copper–B mixture. At 425 mμ the ethylenediamine complex does not absorb, so the optical density at this wave length must be proportional to the concentration of the Schiff base complex. A plot of the logarithm of the optical density at this wave length against time gives a straight

line, thus providing evidence that the reaction is of the first order with respect to the decomposing molecule.
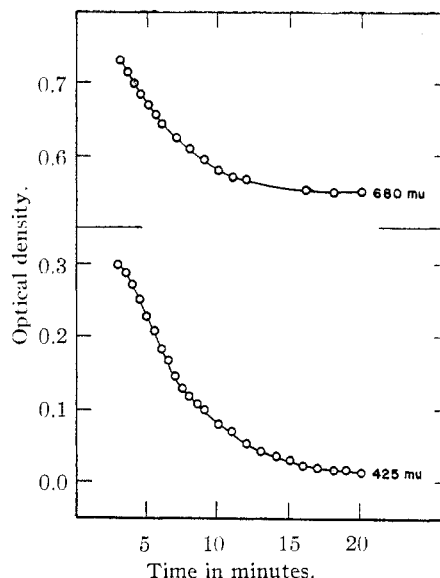

Fig. 3.—Change in absorption of an equimolar mixture of copper(II) sulfate and bis-thiophenalethylenediamine in 50% alcohol.

Solutions of copper(II) complexes of ethylenediamine maintain constant absorption from the moment of preparation, thus indicating that the formation of the bond between copper and nitrogen is practically instantaneous. In the absence of metal ions, solutions of the Schiff base decompose very slowly. Hydrogen ions, whose catalytic influence on the hydrolysis of Schiff base has been recognized for a long time, are not responsible for the decompositions reported in this paper; the pH in the dilute copper sulfate solutions is very close to 7. A similar dissociation occurs, incidentally, if acetate is substituted for sulfate.

From this evidence the following reaction mechanism may be postulated: The complex of copper and Schiff base is formed instantly. The resulting metal to nitrogen bond causes a distortion of the nitrogen electron cloud in the direction of the copper atom, and away from the carbon, thus weakening the carbon to nitrogen bond and rendering it more susceptible to cleavage. This mechanism bears a close resemblance to the interpretation by Smith[6] of the function of carboxypeptidase enzyme in the cleavage of peptide bonds. The reaction of Grignard reagent with β-diketones[7] has also been explained on the basis of cleavage as the result of coördination. Recently Kroll[8] has promulgated a similar theory to account for the catalytic hydrolysis of amino acid esters by heavy metal ions.

Experimental

2-Thiophenal-o-aminophenol (A).—Commercial 2-thiophenaldehyde was purified by washing with 50% hydrochloric acid, and distilling under reduced pressure; b.p. 106° (30 mm.). All experiments with this aldehyde were

(6) E. L. Smith, Proc. Natl. Acad. Sci. U. S., **35**, 80 (1949).

(7) T. A. Geissman and V. Tulagin, THIS JOURNAL, **63**, 3352 (1941).

(8) H. Kroll, ibid., **74**, 2036 (1952).

carried out with freshly distilled material, since it rapidly darkened on exposure to air.

A solution of 5.4 g. of o-aminophenol, 4.6 ml. of 2-thiophenaldehyde and two drops of glacial acetic acid, was refluxed on a hot-plate for ten minutes.[9] The insoluble brown residue was removed from the solution by filtration, and the brown filtrate was poured onto ice. The light brown precipitate that formed was filtered and recrystallized from 25 ml. of hot absolute alcohol by the addition of a drop of water. The brown crystalline product was collected by filtration, and dried in vacuo over phosphorus(V) oxide; m.p. 81°.

Anal. Calcd. for $C_{11}H_9ONS$: C, 65.0; H, 4.4; N, 6.9. Found: C, 64.66; H, 4.62; N, 6.60.

Bis-2-thiophenal–ethylenediamine (B).—A solution of 9.2 ml. of 2-thiophenaldehyde, 6.4 ml. of redistilled ethylenediamine monohydrate and two drops of glacial acetic acid in 125 ml. of absolute alcohol was refluxed for ten minutes, and poured onto ice. The white crystalline product was recrystallized by careful regulation of the solvent ratio. The material was suspended in a mixture of 40 ml. of water and 25 ml. of 95% alcohol which was brought to the refluxing temperature, and just enough additional alcohol was added dropwise to take the remainder of the solid into solution. Upon cooling, small white crystals were produced. The twice recrystallized product was dried *in vacuo* over phosphorus(V) oxide; m.p. 92°.

Anal. Calcd. for $C_{12}H_{12}N_2S_2$: C, 58.0; H, 4.8; N, 11.3. Found: C, 57.60; H, 4.97; N, 11.11.

The System Copper(II) Sulfate–Bis-thiophenal–Ethylenediamine.—The best solvent for the absorption studies proved to be 50% alcohol, since B is insoluble in water, and the copper(II) sulfate and the complexes formed are insoluble in alcohol. It was necessary to use dilute solutions in order to keep all of the components in the liquid phase.

Stock solutions of B in absolute alcohol and of copper(II) sulfate in water (each 0.02 molar) were prepared. The visible absorption spectra of solutions containing only copper sulfate, and copper sulfate and B in 1:1 and 1:2 proportions were measured with the Cary recording spectrophotometer. From these curves the wave lengths 556, 630 and 710 mμ were selected for the continuous variation studies. The stock solutions were then mixed in various proportions and diluted so that the sum of the concentrations of copper ion and B was always 0.006 molar; a 1:1 ratio of alcohol to water was maintained throughout. Solutions containing only copper or only B were colorless at this low concentration, these containing up to 0.533 mole per cent. B were blue-violet, and all others were violet. All solutions that eventually turned violet were initially blue.

Plots were made of the difference in the optical density observed and that calculated on the assumption of additive absorption, according to the method of Vosburgh and

Cooper.[4b] The absorption curves bear such a striking resemblance to those reported by Jonassen and Dexter[5] that they are not recorded here.

Isolation of the Solid Complexes.—0.1 molar copper(II) sulfate and 0.1 molar B were mixed in various proportions so as to produce concentrated solutions containing copper and complexing agent in 2:1, 1:1 and 1:2 ratios. After 24 hours, beautiful blue monoclinic crystals had separated from the 2:1 and 1:1 solutions. These were collected on a sintered glass filter, and dried in air for four hours.

Anal. Calcd. for $C_{12}H_{16}N_2O_6S_2Cu([CuB(H_2O)_2]SO_4)$: C, 32.4; H, 3.6. Calcd. for $C_2H_{12}N_2O_6SCu([Cuen(H_2O)_2]SO_4)$: C, 9.37; H, 4.7. Found, from 2:1 solution: C, 9.09; H, 4.73. From 1:1 solution: C, 9.38; H, 4.87.

The violet 1:2 complex is apparently much more soluble in 50% alcohol, since no crystals formed even after eight days standing. The complex was precipitated by the dropwise addition of ether, filtered on sintered glass, washed with ether and alcohol, redissolved in 50% alcohol, reprecipitated with ether, and again filtered and washed, with ether. It was dried *in vacuo* over phosphorus(V) oxide for 24 hours.

Anal. Calcd. for $C_{24}H_{24}N_4O_4S_6Cu([CuB_2]SO_4)$: C, 43.9; H, 3.7; N, 8.5. Calcd. for $C_4H_{16}N_4O_4SCu([Cuen_2]SO_4)$: C, 17.15; H, 5.7; N, 20.0. Found: C, 17.42; H, 5.92; N, 19.46.

Decomposition Studies.—A solution containing copper(II) sulfate and B (each 0.015 molar) in 50% alcohol was placed in a 1-cm. absorption cell immediately after the components had been mixed. Figure 2 records the spectral changes observed at 2-minute intervals. After 30 minutes the solutions became somewhat turbid because of the formation of $[Cuen(H_2O)_2]SO_4$ crystals. To gain an indication of the time required for the completion of the decomposition, the absorption of a 0.003 molar solution was measured in a 5-cm. cell. Comparison of the spectra obtained after one hour and after six hours showed them to be identical. The reaction therefore requires less than one hour to go to completion.

More precise measurements of changes in absorption were made at 680 mμ, the approximate peak of the $[CuB(H_2O)_2]^{+2}$ curve, and at 425 mμ, the minimum in the spectrum for $[Cuen(H_2O)_2]^{+2}$. In two separate runs the changes in absorption of a 0.003 molar 1:1 copper to B solution were determined at these wave lengths at a temperature of 28°, using a 5-cm. cell. The results are plotted in Fig. 3.

URBANA, ILLINOIS

(9) This procedure was adapted from a method suggested by Dr. H. B. Freyermuth, of the General Aniline and Film Corporation, for the preparation of the corresponding derivative of *m*-nitroaminophenol.