tural Experiment Station, P. O. Box 1106, New Haven, Conn., for furnishing us with the dimethyl ester of isocitric lactone and the directions by which we converted it to the free acid. Dr. B. Vennesland of the Department of Biochemistry, University of Chicago, very kindly gave us a specially purified sample of oxalacetic acid.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE PURDUE UNIVERSITY DEPARTMENT OF CHEMISTRY]

Studies on Some Ferrous Complexes of Substituted 1,10-Phenanthrolines[1]

BY WARREN W. BRANDT AND DELORA K. GULLSTROM

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The stabilities of some 5-substituted 1,10-phenanthroline–iron(II) complexes were determined using rate data and equilibrium studies. The stability decreases in this order: 5-methyl, 1,10-phenanthroline itself, 5-phenyl, 5-chloro, 5-nitro. The stability of these complexes appears to be dependent only upon the acid dissociation constant for the organic molecule. A correlation was shown to exist between K_a, K_d and the formal potential of the $[Fe(Phen)_3]^{++}$–$[Fe(Phen)_3]^{+++}$ half-cell reaction, and calculations were made of the stability of the ferric complex utilizing this relationship. The change of formal potential with hydrogen ion concentration tends to support the 1:1 combination of $[Fe(Phen)_3]^{+++}$ and hydrogen ion postulated by Lee, Kolthoff and Leussing. A relationship was observed between stability and wave length of maximum absorption in the case of the ferric complexes, but not the ferrous.

Introduction

The factors affecting the stability of complex ions have been of interest for many years. Most of the early work was only qualitative or semi-quantitative in nature. In recent years, however, workers have attempted to control the variables and to measure in a quantitative manner the effect of changing the metal or substituents in the complexing group. Generalizations have been made upon complex stability of certain metals.

Because the tris-1,10-phenanthroline iron(II) ion is of considerable analytical interest, a study of this system might give further impetus to a theory which would enable the analytical chemist to predict in advance the properties of a given chelate. With data of this nature, he could order a tailor-made complex for a particular use.

Investigations have been carried out on the stability of the tris-1,10-phenanthroline–iron(II) complex itself by Lee, Kolthoff and Leussing.[2] They also determined the kinetics of complex formation and decomposition, the effect of acid concentration and the stabilities of the corresponding ferric complex. It would then appear to be of general and analytical interest to examine these same properties for a number of substituted phenanthrolines. From such an investigation information could be obtained as to the effects of substitution upon the properties of the complex and insight could be gained in predicting what changes in the molecule might enhance its use for a particular purpose.

The compounds studied were four substituted 1,10-phenanthrolines as well as the parent compound. The substituents were in every case in the 5-position.

Experimental

Materials Used.—1,10-Phenanthroline (ortho phenanthroline) monohydrate, 5-nitro-1,10-phenanthroline and 5-methyl-1,10-phenanthroline were obtained from the G. Frederick Smith Chemical Company. The 5-phenyl-1,10-phenanthroline was furnished by Professor Francis Case, Temple University, and the 5-chloro-1,10-phenanthroline was furnished by Professor G. Frederick Smith, University of Illinois.

Standard solutions of the following compounds were prepared from analytical reagent chemicals and standardized by accepted procedures: sulfuric acid, hydrochloric acid and ceric sulfate.

Spectrophotometric Data.—A Beckman DU spectrophotometer was used to obtain spectrophotometric curves of the various complexes studied. Values for the molar absorbancy index were based on the amount of iron present.

Determination of K_a.—K_a, the acid dissociation constant of the organic molecule, was determined by measuring the hydrogen ion activity in a solution containing 25 mg. of the substituted 1,10-phenanthroline and enough hydrochloric acid to react with approximately three-fourths of the phenanthroline present. Because of the insolubility of the substituted compounds it was necessary to determine the apparent *p*H in water–dioxane mixtures. The total volume used in all cases was 50 ml. 1,10-Phenanthroline itself was measured in solutions containing from 0 to 14 ml. of dioxane.

Determination of k_{diss}.—Suitable amounts of ferrous ammonium sulfate and the substituted phenanthroline to be studied were weighed out and mixed in a 100-ml. volumetric flask. From 5 to 50 ml. of 2 *M* sulfuric acid was added and the solution made up to volume using iron-free distilled water. Zero time was taken when half of the acid had been added. At intervals the amount of complex present was determined by measurements of the absorbancy at the previously determined wave length of maximum absorbancy. These measurements were made on a Beckman DU spectrophotometer.

Rates of Formation.—Reaction mixtures were prepared by mixing together sulfuric acid of the desired molarity and an appropriate amount of ferrous ammonium sulfate in a 100-ml. volumetric flask. A weighed amount of the substituted phenanthroline dissolved in a known amount of sulfuric acid was added and the solution was made up to volume. After various reaction periods, the mixtures were analyzed spectrophotometrically for the amount of complex formed. In the determination of the rate of formation of the complexes, the concentrations of all the reactants were kept large relative to the amount of complex formed.

Determination of $k_{diss.}$ from Equilibrium Data.—Equilibrium values were obtained on iron(II)–phenanthroline solutions by taking spectrophotometric readings on solutions of the complex until the value was constant for 12 hours.

Oxidation–Reduction Potentials.—Potentiometric curves were run on a Leeds–Northrup student-type potentiometer using a calomel reference electrode and a platinum indicator electrode. Ceric sulfate was used as the titrant in all cases and all solutions were 1 *F* in sulfuric acid.

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[1] An abstract of a thesis submitted by Miss Delora K. Gullstrom to the Graduate School of Purdue University, 1951, in partial fulfillment of the requirements for the Degree of Master of Science.

[2] (a) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); (b) **70**, 3598 (1948).

Discussion

Spectrophotometric Data.—The values for molar absorbancy index (a_m) and the wave length of maximum absorption are listed in Table I.

TABLE I

EXPERIMENTAL DATA ON THE TRIS-1,10-PHENANTHROLINE–IRON(II) COMPLEXES

5-Substituted-1,10-phenanthroline	Oxidation–reduction potential 1 F H_2SO_4	Wave length of maximum absorption Ferrous	Ferric	Molar absorbancy index
Methyl	1.02	515	600	12,200
Hydrogen	1.06	510	590	11,100
Phenyl	1.08	515	588	11,000
Chloro	1.12	512	578	11,700
Nitro	1.25	510	...	11,500

In the work of Brandt a relationship was established between substitution of the methyl groups on the phenanthroline nucleus and the wave length of maximum absorption of the complex.[3] It was possible to predict the wave length of maximum absorption from the position and number of methyl groups substituted. In the present study no correlation was discovered in the complexes of phenanthroline substituted in the five position. This may be due to the small differences in the wave length of maximum absorption. With the ferric complexes, which exhibit greater differences both in absorption maxima and stability, such a correlation is possible. The wave length of maximum absorption increases with increasing stability.

TABLE II

EQUILIBRIUM DATA FOR THE 5-SUBSTITUTED PHENANTHROLINE–IRON(II) COMPLEXES

	Initial concn. of Fe^{++}, $M \times 10^5$	Initial concn. of phen., $M \times 10^5$	Concn. of complex found $M \times 10^6$	Concn. of H^+ calcd.	Activ. equil. constant $\times 10^7$
5-Methyl	202	142	2.96	0.474	2.6
	204	96.5	1.05	.474	2.2
	202	126	2.13	.474	2.4
	408	121	3.86	.474	2.3
5-Hydrogen	254	201	3.64	.592	6.7
	11.7	1010	5.65	.592	3.0
	483	201	6.28	.592	2.9
5-Phenyl	510	137	4.10	.592	1.3
	382	137	2.90	.592	1.8
	204	78	2.21	.369	1.7
	204	39	0.22	.369	2.7
	127	39	3.38	.138	1.5
	127	58	7.02	.138	1.6
	187	39	3.63	.138	1.4
5-Chloro	510	163	11.70	.592	1.3
	255	163	5.86	.592	1.3
	255	163	0.57	1.420	0.9
	255	96	0.78	0.592	1.7
5-Nitro	255	163	5.15	.828	5.1
	255	163	5.22	.712	6.6
	255	117	3.95	.592	6.6
	255	163	1.59	1.377	3.3
	255	96	3.48	0.369	4.4
	255	117	3.77	.592	5.1

Acid Dissociation Data.—Acid constants were calculated using the formula $K_a = (H^+)(B)/(BH^+)$ where H^+ is the observed pH corrected to zero milliliters of dioxane, BH^+ is the amount of phenanthrolium ion (calculated from the amount of acid added) and B is the amount of phenanthroline used minus BH^+. Table III shows the acid constants for the compounds studied.

Kinetics of Dissociation.—If the decomposition follows a first-order mechanism a plot of log c_0 *versus* c (where c_0 is the initial concentration of complex, obtained by extrapolation to zero time and c is the concentration after time t) should give a straight line relationship. Figure 1 shows the decomposition curves obtained. The rate constant was independent of the acid concentration used within experimental error. Table III gives the rate constants which were calculated from a series of determinations.

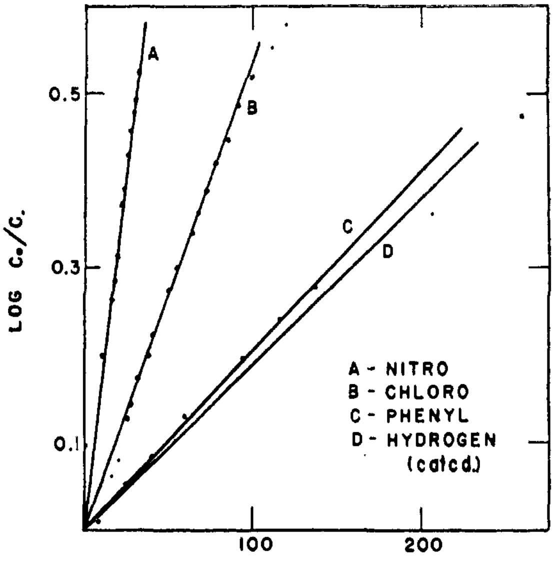

Fig. 1.—Rate of dissociation of some 5-substituted-1,10-phenanthroline–iron(II) complexes in 0.5 M sulfuric acid.

Kinetics of Formation.—Because of the large excess of all the reactants relative to the amount of complex formed, the concentration of reactants may be considered constant. Under such experimental conditions, a zero-order formation results. The expression for the zero-order formation must be modified by an expression for the first-order decomposition which is occurring simultaneously. The equation for a zero-order reaction of this type would be $dc/dt = A - k_{diss}\,c$ where A is a constant. Integration of this equation gives

$$c = A\left[\frac{1 - e^{(-k_{diss}\,t)}}{k_{diss}}\right]$$

If the data for the formation are plotted using this expression they should fall on a straight line whose slope is equal to A. Figure 2 shows the experimental data plotted in this manner. As was shown by Lee, Kolthoff and Leussing[2] $k_{form} = A\,(Fe^{++})(Phen)^3$ where A is the slope of the zero-order plot of the formation, (Fe^{++}) is the concentration of ferrous iron added and $(Phen) = K_a a_{(Phen \cdot H^+)}/a_{(H^+)}$. Values for the activity coefficients of the substituted organic complexing agents were assumed to be equal to those of 1,10-phenanthroline.

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(3) W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

TABLE III

SUMMARY OF STABILITY DATA OBTAINED ON THE TRIS-1,10-PHENANTHROLINE–IRON(II) COMPLEXES

5-Substituted-1,10-phenanthroline	pk_{form}	pk_{diss}	pk_{diss} from rate data	pk_{diss} from equil. data	pK_a	log of the equilibrium constant $Fe(Phen)_3^{++} + 3H^+ = Fe^{++} + 3Phen\ H^+$ From rate data	From equil. data
Methyl	....	..	..	22.3	5.23	..	6.62
Hydrogen	−18.9	2.36	21.5	21.3	4.96	6.64	6.40
Phenyl	−18.9	2.36	21.4	21.1	4.80	7.03	6.74
Chloro	−17.8	1.93	19.7	19.7	4.26	6.94	6.89
Nitro	−16.7	1.42	18.1	17.8	3.57	7.38	7.12

The latter were taken from the work of Lee, Kolthoff and Leussing who estimated them by the individual ion activity method. The average results from a series of experiments are shown in Table II.

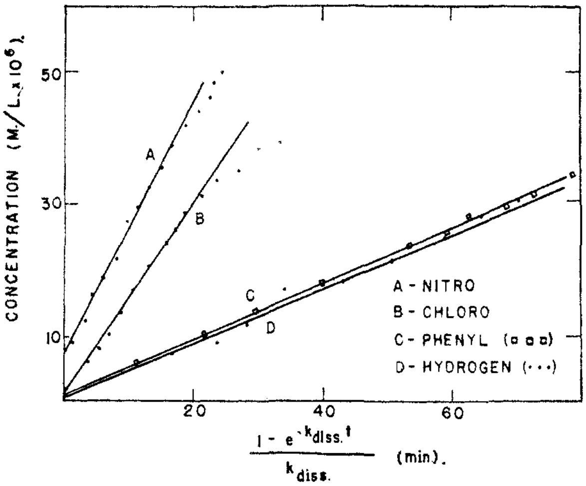

Fig. 2.—Rate of formation of some 5-substituted-1,10-phenanthroline–iron(II) complexes in 0.5 M sulfuric acid.

As can be seen in Fig. 2, 1,10-phenanthroline itself and the 5-phenyl-1,10-phenanthroline complexes give a good straight line plot for a zero-order formation. However, as the stability decreases as in the case of the chloro and nitro compounds, the function deviates from a straight line after 40 or 50% of the reaction is completed. It is possible to calculate the slope from the straight line portion of the curve and these are the results used in the calculations reported. The causes and nature of these deviations are now under consideration.

K_{diss} from Rate Data.—According to the mass action law, $K_{diss} = k_{diss}/k_{form}$. From the experimental data on rates the values for K_{diss} were calculated. Table II gives the values for K_{diss} obtained in this manner.

K_{diss} from Equilibrium Data.—Hydrogen ion concentration and order of addition were varied and proved to have no effect on the equilibrium constant (Table II). K_{diss} was then calculated from the following equation: $K_{diss} = a_{Fe^{++}}(Phen)^3/a_{FePhen_3^{++}}$. Activity coefficients for the Fe^{++} and $FePhen_3^{++}$ were assumed to be equal and so cancel. Phen is equal to $[a_{(PhenH^+)}/a_{H^+}]K_a$. Values for K_{diss} obtained in this manner are given in Table II. It is of interest to note that the value of K_a appears to the same power in both expressions given for K_{diss}. Agreement of these two expressions is thus independent of errors in K_a. It is also of interest to calculate K_d for the reaction

$$Fe(Phen)_3^{++} + 3H^+ = Fe^{++} + 3Phen{\cdot}H^+$$

from both sets of data. This value was essentially a constant for all of those compounds studied (Table III) indicating that for at least this series of compounds the acid dissociation constant is the only effect governing the difference in stability of the iron(II) complexes.

If log K_a is plotted against log k_{diss} in the manner described by Calvin and Wilson[4] a single straight line is obtained (Fig. 3). This same dependence upon K_a can be shown to be true for tris-bipyridine–iron(II) complex. If the tris-bipyridine–iron(II) complex is included on the same graph,[5,6] the plotted point falls within experimental error of the same straight line of the substituted phenanthrolines. In the work in which Calvin and Wilson plotted log K_a vs. log k_{diss} for a series of complexes with copper they obtained four straight lines having the same slope but different intercepts. They

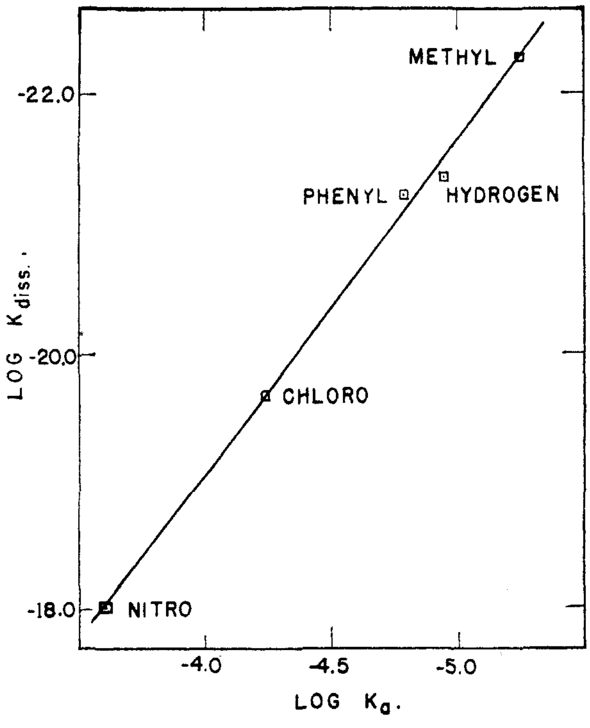

Fig. 3.—The correlation between log K_a and log K_{diss} of some 5-substituted-1,10-phenanthrolines.

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[4] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[5] P. Krumholz, *Nature*, **163**, 724 (1949).

[6] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

postulated that these different straight lines were obtained because of the differences in double bonded character of the chelating groups. Such a difference in intercepts is not found for the corresponding phenanthroline–bipyridine complexes. The difference in double bonded character does not appear to be a factor in this case.

Oxidation–Reduction Potentials.—The linear dependence of log k_{diss} upon log K_a suggests that other relationships between various properties of the series of compounds studied might add to the understanding of related systems. Since the series studied included only the 5-substituted phenanthrolines, the question naturally arises as to the possibility of extending the observed generalizations to other related compounds. The extent to which this type of approach can be extended will ultimately determine their usefulness. Data for the oxidation–reduction potentials are given in Table I.[7] The logarithms of the oxidation–reduction potentials may be plotted against log k_{diss} for the complexes and a straight line results. It has been observed that in many of the iron(II)–phenanthroline complexes a change in hydrogen ion concentration from 0.1 F to 1.0 F causes approximately a 0.03–0.04 volt change in formal potential. If one substitutes the expressions for the appropriate dissociation constants into the Nernst equation, it is possible to calculate the stabilities of the ferric complexes. The calculated values for 1,10-phenanthroline agree approximately with those obtained by Lee, Kolthoff and Leussing[2b] from potentiometric measurements only if a 1:1 combination of $Fe(Phen)_3^{+++}$ and H^+ is assumed. However, the assumption of a protonated ferric complex does not appear to be logical when this is not postulated for the ferrous complex. It does not seem reasonable, either, that the ferric ion with its higher charge would need an extra proton to ensure stability while the ferrous complex is apparently unaffected by hydrogen ion.

It is noted that if the data for the bipyridine complex are included on the graph of the oxidation–reduction potential against log k_{diss} the resulting point does not fall on the line obtained for the 5-substituted phenanthrolines.

Work by Mellon and Hale on the 3-carbethoxy-4-hydroxyphenanthroline complex with iron(II) points to another apparent exception.[8] Although the oxidation–reduction potential would indicate that this latter complex would be more stable than any of the complexes studied here, it was reported to be relatively unstable. In these cases other factors which were unimportant in the 5-substituted compounds, may influence the stability of the complexes.

[7] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Company, Columbus, Ohio, 1944.

[8] M. N. Hale and M. G. Mellon, THIS JOURNAL, **72**, 3217 (1950).

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereoisomerism of Complex Inorganic Compounds. XIV. Studies upon the Stereochemistry of Saturated Tervalent Nitrogen Compounds[1]

BY JOHN R. KUEBLER, JR., AND JOHN C. BAILAR, JR.

RECEIVED APRIL 9, 1952

The reactions of N,N-diethylglycine and N-methyl-N-ethylglycine with cobalt(III) and platinum(II) have been studied. A satisfactory synthesis for potassium dinitro-(N-methyl-N-ethylglcyine)-platinate(II) has been developed. That an asymmetric nitrogen atom exists in this compound was demonstrated through its resolution by fractionation with *l*-quinine and treatment with optically active quartz powder.

The problem of resolving into optically active antipodes compounds containing properly substituted nitrogen atoms has attracted interest for many years. Early investigators worked chiefly with organic compounds, and many resolutions of quaternary ammonium salts and tertiary amine oxides have been reported.[2]

In 1924, Meisenheimer and his co-workers[3] claimed to have shown the existence of the required four optical isomers of sarcosine-bis-ethylenediaminecobalt(III) chloride, $[Co\ en_2sarc]Cl_2$,[4] by fractional crystallization of the bromocamphorsulfonate salt. The interpretation of this work is complicated by the fact that the activity due to the cobalt ion is very large relative to that of the nitrogen atom and by the fact that when the resolving agent was removed, no nitrogen activity was detectable, but only that due to the cobalt ion; both of these factors cast doubt on the validity of the work. In addition, Basolo[5] was unsuccessful in an attempt to repeat Meisenheimer's procedure.

Later, Mann[6] prepared tetrachloro-(diethylenetriamine monohydrochloride)-platinum(IV) monohydrate $[Pt(dien{\cdot}HCl)Cl_4]{\cdot}H_2O$, but was not able to resolve it.

In these previous attempts to resolve inorganic

[1] The work reported in this article was taken from the doctorate thesis of J. R. Kuebler, Jr., 1951.

[2] R. L. Shriner, Roger Adams and C. S. Marvel, "Organic Chemistry," Ed. 2, Vol. 1, H. Gilman, ed., John Wiley and Sons, Inc., New York, N. Y., pp. 413–418.

[3] J. Meisenheimer, L. Angermann, H. Holsten and E. Kiderlen, *Ann.*, **438**, 269 (1924).

[4] Abbreviations used herein include dien = diethylenetriamine, en = ethylenediamine, amac = N,N-diethylglycinate ion, AMAC = N-methyl-N-ethylglycinate ion, glyc = glycinate ion, quin = quinine ion, sarc = sarcosinate ion, stry = strychnine ion, *d* = dextrorotatory, and *l* = levorotatory. D- and L- represent the observed rotatory behavior of the complex ions. All rotations were measured at the D line of sodium.

[5] F. Basolo, Thesis, Doctor of Philosophy, University of Illinois, 1943.

[6] F. G. Mann, *J. Chem. Soc.*, 466 (1934).