[Contribution from the Chemistry Laboratories of Northwestern University]

Mechanism of Racemization of Complex Ions. III. Effect of Added Ions upon the Rates of Dissociation of Tris-(1,10-phenanthroline)-iron(II) and Tris-(1,10-phenanthroline)-iron(III) and upon the Rate of Racemization of Tris-(1,10-phenanthroline)-iron(III)[1,2]

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The rate of dissociation of tris-(1,10-phenanthroline)-iron(II) was found to be not acid independent, but affected both by the nature and the concentration of added anions and cations. The rate of dissociation of tris-(1,10-phenanthroline)-iron(III) was measured directly and showed a pronounced dependence upon the nature and concentration of added anions and cations. The behavior of tris-(1,10-phenanthroline)-iron(III) is attributed to ionic association, whereas that of tris-(1,10-phenanthroline)-iron(II) is regarded as being due only to a general ionic background effect. The rate of racemization of tris-(1,10-phenanthroline)-iron(III) was measured directly and again the effect of added ions is pronounced. Studies of the ultraviolet spectrum of the iron(III) complex indicate that it does form ion-pairs with anions whereas the iron(II) complex does not.

It is known that the presence of large cations and anions affects the rate of racemization of tris-(1,10-phenanthroline)-nickel(II)[3] and that the rates of both racemization[4] and dissociation[5] of tris-(1,10-phenanthroline)-iron(III) are acid-dependent. In the course of studying the effect of large ions upon the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) in this laboratory, it was observed that the rate of dissociation was not acid independent, although previous workers[1,5] had reported it to be so. A study of the rate of dissociation of the iron(II) complex at 25° in aqueous solutions of some mineral acids and their salts shows that small anions and cations including the hydrogen ion have specific salt effects. The iron(III) complex is more sensitive to the effect of added ions, possibly because of its higher charge, and therefore direct measurements were made of both its rates of racemization and dissociation. The acid dependence of the rate of dissociation of the iron(III) complex has been attributed to the hydrogen ion and to the possible resulting formation of the ion, $[Fe(ophen)_3 \cdot H]^{4+}$. Spectral studies were undertaken to determine whether or not such a species does exist, since it is known that the singly charged phenanthrolium ion forms a diprotonated species in strongly acidic solutions, and that the doubly charged complex, mono-(1,10-phenanthroline)-nickel(II) probably forms a protonated species, $[Ni(ophen) \cdot H]^{3+}$.[6]

Experimental

Rates of Dissociation.—Rates of dissociation of $[Fe(ophen)_3]^{2+}$ in chosen acid and salt solutions at 25° were determined spectrophotometrically by the method previously described.[1] The initial concentration of $[Fe(ophen)_3]^{2+}$ was 2.5×10^{-5} M and measurements of optical density at a wave length of 510 mμ were made at suitable time intervals over a period corresponding to several half-lives. Under all conditions, dissociations did not deviate from first-order dependence.

Tris-(1,10-phenanthroline)-iron(III) has an absorption band in the visible with a maximum intensity at 600 mμ. Products of dissociation have a negligible absorption at this wave length. Measurements of optical density were made at suitable time intervals. Solutions of $[Fe(ophen)_3]^{3+}$ can be prepared only by oxidation of $[Fe(ophen)_3]^{2+}$ solutions. Chosen solutions of $[Fe(ophen)_3]^{2+}$, (1.5×10^{-4} M), salt and acid were oxidized by the addition of a fourfold excess of solid cerium(IV) sulfate. The resulting concentration of cerium(IV) ion (1×10^{-3} M) does not absorb light at 600 mμ. Oxidation of the red iron(II) complex to the blue iron(III) complex was rapid in highly acidic solutions. In solutions of low acidity, the oxidation proceeded sluggishly and fine suspensions of white solid (basic cerium(IV) salts) formed slowly. Solutions of the iron(III) complex are instantly reduced to the iron(II) complex when passed through filter paper, and it was found that the solutions could be freed from solid satisfactorily by centrifuging. The continued separation of white solid in solutions of perchlorates and in high concentrations of potassium hydrogen sulfate made accurate measurements of the absorbancies of these solutions impossible. Solutions containing cerium(IV) ion, $[Fe(ophen)_3]^{3+}$, and hydrochloric acid evolved chlorine and for this reason no measurements were made in chloride solutions.

Rates of Racemization.—Tris-(1,10-phenanthroline)-iron(III) racemizes rapidly at room temperature and it was necessary to conduct experiments at 0–5°. Although the oxidation of a saturated solution of d-$[Fe(ophen)_3](ClO_4)_2$ at 0° produces a solution of iron(III) complex of low rotation (0.05° in a 1 dm. tube at 546 mμ), solutions of the iron(III) complex of concentration 5×10^{-4} M, with rotations of 0.5° in a 1 dm. tube at 546 mμ were prepared by the addition of solid d-$[Fe(ophen)_3](ClO_4)_2$[7] to a chosen solution at 0° containing dissolved excess cerium(IV) sulfate as oxidizing agent.

The ice-cold solution was poured into a 1 dm. jacketed polarimeter tube through which water from a refrigerating unit was circulating. Optical rotations were measured using a Bellingham and Stanley polarimeter with a photomultiplier attachment. Solutions of $[Fe(ophen)_3]^{3+}$ absorb sodium vapor light very strongly, and it was found to be more satisfactory to use a mercury vapor lamp. Measurements of optical rotation were taken when the solution reached the equilibrium temperature of the containing cell (3.5 ± 0.1°). Dry air was directed onto the windows to prevent misting.

Spectra of Complexes.—The ultraviolet and visible spectra of the iron(II) and iron(III) complexes were recorded using a Beckman DK spectrophotometer. In general form and optical density, the ultraviolet spectra of both complexes closely resemble the phenanthrolium ion. Solutions containing complex, 1×10^{-5} M, were examined in 1 cm. fused silica cells. Solutions of $[Fe(ophen)_3]^{3+}$ may not be prepared for spectral studies using cerium(IV) ion as the oxidizing agent, since the cerium(IV) ion has a very intense absorption band in the ultraviolet region. A more suitable oxidizing agent with a relatively small ultraviolet extinction

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(1) Previous paper is this series, F. Basolo, J. C. Hayes and H. M. Neumann, This Journal, **76**, 3807 (1954).

(2) This investigation was supported by a Grant-in-aid from the National Institutes for Health, Grant No. RG-4335(C).

(3) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 24 (1954).

(4) N. R. Davies and F. P. Dwyer, *ibid.*, **50**, 820 (1954).

(5) T. S. Lee, I. M. Kolthoff and D. L. Leussing, This Journal, **70**, 3596 (1948).

(6) D. W. Margerum, R. I. Bystroff and C. V. Banks, *ibid.*, **78**, 4211 (1956).

(7) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950).

coefficient is freshly prepared chlorine water. Chlorine gas was bubbled through selected solutions of background salts and acids for a short time. Sample solutions were prepared by adding 1 ml. of a stock solution of $[Fe(ophen)_3]^{2+}$ to 10 ml. of a particular chlorinated solution. Reference solutions were prepared by adding 1 ml. of water to 10 ml. of the chlorinated solution. Oxidation was slow in solutions of low acidity. Solutions were scanned immediately after preparation since gradual spectral changes occur as the complexes dissociate in the acidic solutions. Nitric acid could not be used because of the ultraviolet absorption band of the nitrate ion.

Results and Discussion

In each of the three acids chosen, nitric, sulfuric and hydrochloric, the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) decreases with increasing concentration of acid. In order to determine whether decreases in the rate were due chiefly to the influence of the hydrogen ion, rates of dissociation were measured in solutions where almost all the hydrogen ion was replaced by potassium or lithium ions. It is necessary for some small concentration of hydrogen ions to be present in solution in order that dissociation may proceed. Results are given in Tables I, II and III. Plots of the rate of dissociation (k_{diss}) against the concentration of anion present in solution (Fig. 1) give curves which are at the experimental concentrations, straight lines within the limits of experimental error. The same type of dependence of rate upon the concentration of added salts has been observed by Winstein and co-workers[8] in the solvolysis of certain organic compounds in acetic acid, but it is not apparent whether there is a common feature that accounts for the linear dependence in the two cases.

TABLE I

DISSOCIATION OF $[Fe(ophen)_3]^{2+}$ IN SOLUTIONS OF HCl AND OTHER CHLORIDES

Initial $[Fe(ophen)_3]^{2+}$ concn., 2.5 × 10^{-5} mole/l.; temp., 25.00 ± 0.05°

[HCl], *M*	[KCl], *M*	[LiCl], *M*	[Cl⁻], *M*	k_{diss}, min.$^{-1}$ × 10^3 ±0.05
0.0505	...	...	0.0505	4.50
.202	...	...	.202	4.45
.463	...	...	.463	4.34
.926	...	...	.926	4.12
1.85	...	...	1.85	3.64
0.101	0.455	...	0.556	4.45
.101	1.01	...	1.11	4.40
.101	1.82	...	1.92	4.33
.020	...	0.454	0.474	4.40
.020	...	0.909	0.929	4.28
.020	...	1.37	1.39	4.14
.020		2.36	2.38	3.78

TABLE II

DISSOCIATION OF $[Fe(ophen)_3]^{2+}$ IN SOLUTIONS OF H_2SO_4 AND OTHER HYDROGEN SULFATES

Initial $[Fe(ophen)_3]^{2+}$ concn., 2.5 × 10^{-5} mole/l.; temp., 25.00 ± 0.05°

[H_2SO_4], *M*	[$KHSO_4$], *M*	[$LiHSO_4$], *M*	[HSO_4^-], *M*	k_{diss}, min.$^{-1}$ × 10^3 ±0.05
0.080	...	...	0.08[a]	4.50
.402	...	...	.402	4.18
.804	...	...	.804	3.83
1.64	...	...	1.64	3.26
0.080	0.364	...	0.444	4.38
.080	0.727	...	0.807	4.24
.080	1.45	...	1.53	3.90
.080	2.18	...	2.26	3.60
.080	...	0.680	0.760	4.00
.080	...	1.02	1.10	3.79
.080	...	1.45	1.53	3.46

[a] In this solution, the hydrogen sulfate ion is 10% dissociated into [$SO_4^=$] + [H^+].

TABLE III

DISSOCIATION OF $[Fe(ophen)_3]^{2+}$ IN SOLUTIONS OF HNO_3 AND OTHER NITRATES

Initial $[Fe(ophen)_3]^{2+}$ concn., 2.5 × 10^{-5} mole/l.; temp. 25.00 ± 0.05°

[HNO_3], *M*	[KNO_3], *M*	[$LiNO_3$], *M*	[NO_3^-], *M*	k_{diss}, min.$^{-1}$ × 10^3 ±0.05
0.010	...	...	0.010	4.54
.448	...	...	.448[a]	4.35
.895	...	...	.895[a]	4.15
1.79	...	...	1.79[a]	3.68
0.010	0.364	...	0.374	4.56
.010	0.727	...	0.737	4.60
.010	1.454	...	1.464	4.63
.010	2.18	...	2.19	4.69
.010	...	0.364	0.374	4.41
.010	...	0.727	.737	4.27
.010	...	1.454	.464	4.00
.010	...	2.18	2.19	3.72

[a] Sufficient hydroxylamine hydrochloride was added to prevent oxidation of $[Fe(ophen)_3]^{2+}$ to $[Fe(ophen)_3]^{3+}$.

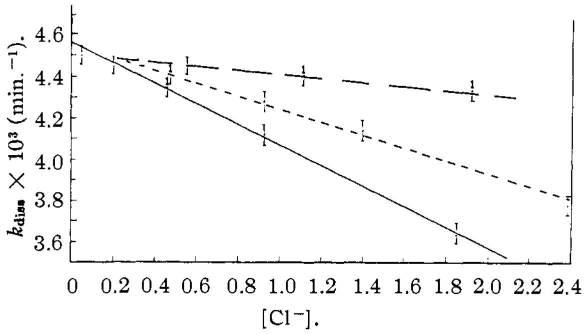

Fig. 1.—Dissociation of $[Fe(ophen)_3]^{2+}$ at 25° in aqueous solutions containing: HCl, ———; KCl + 0.1 *M* HCl, — —; LiCl + 0.02 *M* HCl, - - - -.

Some of the retardation may be due to a decrease in the activity of water in these solutions, but this cannot be the sole effect. The activity of water in the H_2SO_4 solutions was calculated utilizing the densities of the solutions and the data in Harned and Owen,[9] and compared with the rates in these solutions. No simple dependence of the rate on the activity of water was found. Comparison between H_2SO_4 and HCl solutions leads to the same conclusion. The activity of water is the same in 1.64 *M* H_2SO_4 as in 2.07 *M* HCl; the rate constant in the H_2SO_4 solution is 3.26 × 10^{-3} min.$^{-1}$, while a rate constant of 3.55 × 10^{-3} min.$^{-1}$ is indicated by Fig. 1 for the HCl solution.

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(8) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2763, 2767, 2780 (1956); S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y. 1954, p. 436.

The general observation may be made that the ions occur in the following orders with respect to their effectiveness in retarding the rate.

$$HSO_4^- > Cl^- \sim NO_3^-$$

$$H^+ > Li^+ > K^+$$

It is likely that the anions have at least two effects, one a direct effect resulting from the general negative field formed around the complex ion, and the second an indirect effect resulting from the anions causing a decrease in the activity of water. The principal effect of the cations may well be of the second type; the order of their effectiveness is consistent with this view.

There is a very sharp decrease in the rate of dissociation of tris-(1,10-phenanthroline)-iron(III) with increasing acid concentration (Tables IV and V).

TABLE IV

DISSOCIATION OF $[Fe(ophen)_3]^{3+}$ IN SOLUTIONS OF SULFURIC ACID AND OTHER HYDROGEN SULFATES

Initial $[Fe(ophen)_3]^{3+}$ concn., 1.5×10^{-4} *M*; temp., 25.00 ± 0.05°

$[H_2SO_4]$, *M*	$[KHSO_4]$, *M*	$[LiHSO_4]$, *M*	$[HSO_4^-]$, *M*	k_{diss}, $\times 10^3$ min.$^{-1}$ ±0.05
0.0296	...	...	0.0296	5.88
.0442	...	...	.0442	5.44
.082	...	...	.082	4.50
.296	...	...	.296	2.56
.443	...	...	.443	2.09
.820	...	...	.820	1.64
2.08	...	...	2.08	1.07
0.082	0.212	...	0.294	3.98
.082	.314	...	.396	3.76
.082	.500	...	.582	3.31
.082	...	0.251	.333	3.82
.082	...	.377	.460	3.50
.082	...	.755	.837	2.54
.082	...	1.17	1.25	1.76
.082	...	1.64	1.72	1.41

TABLE V

DISSOCIATION OF $[Fe(ophen)_3]^{3+}$ IN SOLUTIONS OF NITRIC ACID AND OTHER NITRATES

Initial $[Fe(ophen)_3]^{3+}$ concn., 1.5×10^{-4} mole/l.; temp. 25.00 ± 0.05°

$[HNO_3]$, *M*	$[KNO_3]$, *M*	$[LiNO_3]$, *M*	$[NO_3^-]$, *M*	k_{diss}, $\times 10^3$ min.$^{-1}$ ±0.05
0.0197	...	...	0.0197	3.03
.044	...	...	.044	2.14
.098	...	...	.098	1.56
.492	..	..	.492	0.54
.985	..	..	.985	0.41
.044	0.50	..	.54	1.45
.044	1.00	..	1.04	1.00
.044	1.50	..	1.54	0.85
.044	2.00	..	2.04	0.77
.044	..	0.50	0.54	1.19
.044	..	1.00	1.04	0.75
.044	..	1.50	1.54	0.64
.044	..	2.00	2.04	0.44

This observation was made by Lee, Kolthoff and Leussing,[5] who followed rates of dissociation by a potentiometric method. The results obtained by their method and by our method diverge considerably. Possibly processes at the electrodes in the oxidation–reduction measurements involve species other than $[Fe(ophen)_3]^{2+}$.

It has been suggested that the decrease in rate may be due to a specific interaction between the complex and the hydrogen ion, with the resulting formation of $[Fe(ophen)_3H]^{4+}$.[5] It is evident from the present results (Tables IV and V, Fig. 2) that large decreases in the rate of dissociation of the iron(III) complex may be obtained by the addition of simple salts to $[Fe(ophen)_3]^{3+}$ solutions containing low concentrations of hydrogen ion. As with the iron(II) complex, H^+, Li^+ and K^+ each have specific effects which lie in the order, $H^+ > Li^+ > K^+$. Thus it would appear that the decrease in rate of dissociation in acid is not due to a protonated species, since Li^+ and K^+ have much the same effect as H^+.

The effect of added ions upon the rate of dissociation is marked in the case of the iron(III) complex compared with the iron (II) complex. Davies and Dwyer[4] have suggested that the expanded or "ionic" transition states for dissociation and for intra-ionic racemization of tris-phenanthroline complexes may be very similar and the effect of added ions upon the rates of racemization of $[Fe(ophen)_3]^{2+}$ and $[Fe(ophen)_3]^{3+}$ would be expected to parallel the effects observed with rates of dissociation. Because of the intense color of these complexes, the probable error in the measured rates of racemization is ±5%. Under such conditions it would be impossible to detect small changes in the rate of racemization of the iron(II) complex and information available indicates that the rate constant is acid independent up to 3.0 *N* HCl.[4] Results for the racemization of the iron(III) complex (Table VI) show that the rate constant (k_{rac}) is dependent upon the concentration of the ionic background and that the specific catalytic effect of the lithium ion is less than that of the hydrogen ion (Fig. 3). Thus the effect of added ions upon the rate of racemization does parallel that of dissociation. Solubility difficulties at 3.5° prevented the use of potassium nitrate solutions. The racemization constant was derived from the slope *m*, of the first-order plot of log α *vs.* t(min.), $k_{rac} = -2.303m$. This racemization constant is directly comparable with k_{diss}, and double the inversion quoted by Davies and Dwyer.[4]

TABLE VI

RACEMIZATION OF $[Fe(ophen)_3]^{3+}$ IN SOLUTIONS OF NITRIC ACID AND LITHIUM NITRATE

Temp., 3.5 ± 0.1°

$[HNO_3]$, *M*	$[LiNO_3]$, *M*	$[NO_3^-]$, *M*	$k_{rac} \times 10^2$ min.$^{-1}$ ±5%
1.2	..	1.2	10.4
2.4	..	2.4	6.2
3.6	..	3.6	3.9
4.8	..	4.8	2.05
1.2	1.0	2.2	7.8
1.2	2.0	3.2	5.3

The results suggest that although the changes in rate constant observed with the iron(II) complex can be accounted for by the influence of the general ionic background, the much larger changes ob-

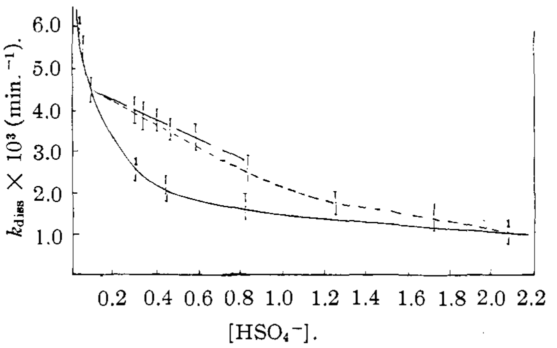

Fig. 2.—Dissociation of $[Fe(ophen)_3]^{3+}$ at 25° in aqueous solutions containing: H_2SO_4, ———; $KHSO_4$ + 0.08 M H_2SO_4, — —; $LiHSO_4$ + 0.08 M H_2SO_4, - - - -.

served with the iron(III) complex result from specific ionic interactions. N. Bjerrum[10] has shown that ion association would not be anticipated between a divalent ion and a monovalent ion in aqueous solution at 25° if the sum of the radii of the two ions is greater than 6.9 Å. The ionic radius of the chloride ion is 1.8 Å. in the solid lattice, and its effective radius in solution may be a little larger. The ionic radii of the ions, HSO_4^- and ClO_4^-, lie between 2 and 3 Å. From a Fischer–Hirschfelder model, the measured maximum radius of $[Fe(ophen)_3]^{2+ \text{ or } 3+}$ is approximately 7 Å. The ion is not spherical and its effective ionic radius may be somewhat less than 7 Å. The sums of the ionic radii of the complex ion and the anion used probably lie between the iron(II) complex ion and the surrounding anions. Trivalent ions tend to associate with monovalent ions if the sum of the ionic radii of cation and anion is less than 10.3 Å.[10] It would thus be anticipated that the iron(III) complex would form ion pairs to some extent with the anions used in this work.

Ion-pair formation of complex ions in solution can be detected by changes in the ultraviolet spectrum.[11] The spectra of $[Fe(ophen)_3]^{2+}$ was observed in solutions containing sulfuric, hydrochloric and perchloric acids, and the salts, lithium and potassium hydrogen sulfates, lithium and potassium chlorides and lithium and sodium perchlorates. Even in solutions of very high ionic strength, no change could be detected in the characteristic visible spectrum.[3] Only at extremely high background concentrations (>5 M) did a very slight shift toward the red in parts of the ultraviolet spectrum occur. No changes could be observed in the spectra of the complex ions $[Ni(ophen)_3]^{2+}$ and $[Ru(ophen)_3]^{2+}$ in solutions containing the ionic backgrounds used in the $[Fe(ophen)_3]^{2+}$ studies.

In solutions of sulfuric, hydrochloric and perchloric acids, changes occur in the ultraviolet spectrum of the $[Fe(ophen)_3]^{3+}$ ion, although none occurs in the visible region. The principal peak of absorption decreases slightly and its maximum shifts from 272 to 275 mμ. Distinctive shoulders appear at 243 and 303 mμ. These spectral modifications are not caused by the hydrogen ion, since in salt solutions containing no acid, the same spectral changes occur.

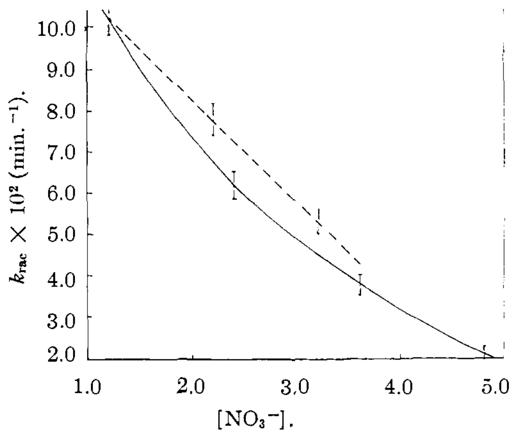

Fig. 3.—Racemization of $[Fe(ophen)_3]^{3+}$ at 3.5° in aqueous solutions containing: HNO_3, ———; $LiNO_3$ + 1.2 M HNO_3, - - - -.

Because of the instability of chlorine water, accurate measurements of the heights of the new peaks could not be made. Changes in spectra are detectable in solutions of acids or salts of concentration 1 × 10^{-2} M. Only very small changes in spectra occur over concentration ranges 2 × 10^{-1} to 10 M. These changes in the ultraviolet spectrum of the iron(III) complex may be attributed to ion-pair formation between it and the anions in solution with it, HSO_4^-, Cl^- and ClO_4^-. Qualitative observations show that ion-pair formation is virtually complete when the anion concentration is 2 × 10^{-1} M. Typical recorded spectra are shown in Fig. 4.

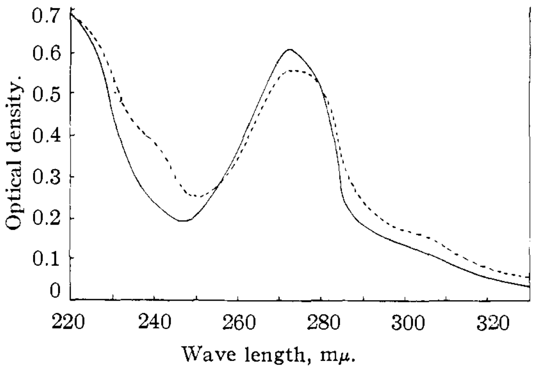

Fig. 4.—Absorption spectra of $[Fe(ophen)_3]^{3+}$, concentration 8 × 10^{-6} M; chlorine water, ———; chlorine water + 0.2 M $NaClO_4$, - - - -.

The rapid decrease in the rate of dissociation of $[Fe(ophen)_3]^{3+}$ would best be accounted for by this ion-pair formation, where the close approach of the anion places an intense electric field in the immediate vicinity of the complex ion. The nitrate ion is smaller than the hydrogen sulfate ion and so its tendency toward ion-pair formation is greater. This is probably the reason why nitric acid causes a greater decrease in the rate of dissociation of $[Fe(ophen)_3]^{3+}$ than does an equal concentration of sulfuric acid.

The Bjerrum[10] criterion for ion-pair formation, based on the charge and size of the ions, which satisfactorily accounts for the differences in behavior of the Fe(II) and Fe(III) complexes, is also consistent

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[10] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[11] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

with kinetic studies on other complex ions. Taube and Posey[12] present both spectral and kinetic evidence for ion pairs between $[Co(NH_3)_5H_2O]^{3+}$ and $SO_4^=$, a system where ion pairs would be expected. Garrick[13] measured the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in the presence of $SO_4^=$ and NO_3^-. The Bjerrum criterion would predict ion pairs with $SO_4^=$, but not with NO_3^-. The observed kinetic results are consistent with this; 0.1 M $SO_4^=$ approximately doubles the rate, 0.1 M NO_3^- increases the rate by approximately 4%.

Acknowledgment.—Helpful suggestions regarding the Bjerrum criterion were made by Dr. Ralph G. Pearson, and the authors wish to acknowledge this assistance.

EVANSTON, ILLINOIS

[12] H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

[13] F. J. Garrick, *Trans. Faraday Soc.*, **34**, 1088 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Stepwise Mixed Complex Formation

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The formation constants for a mixed complex composed of copper(II) ion, the negative ion of iminodiacetic acid ($I^=$) and ethylenediamine (en) are determined. The reactions studies were $CuI + en = CuIen$, $Cuen^{++} + I^= = CuIen$ and $2CuIen = Cu(en)_2^{++} + CuI_2^=$. The log K values for these reactions are 8.8, 8.2 and −2.0, respectively. The conditions are 30° and an ionic strength of 0.1.

Introduction

Previous work on the formation of mixed complexes of the type MAB, where M is a metal ion and A and B are ligands, has been carried out by Watters and co-workers.[1] These workers have determined the constants for the reaction

$$MA_2 + MB_2 = 2MAB \qquad (1)$$

utilizing such ligands as oxalate and ethylenediamine. One cannot determine from such a constant the constants for reactions such as

$$MA + B = MAB \qquad (2)$$

and

$$MB + A = MAB$$

These reactions are of interest because one can determine the influence one bound ligand has upon the ability of metal ion to combine with another.

The purpose of this work is to determine constants for reactions of type 2.

Experimental

An apparatus was designed such that potentiometric titrations and spectrophotometric studies could be made on the same solutions. This apparatus consisted in part of a titration vessel in a constant temperature-bath. This vessel contained a glass electrode, calomel electrode, stirring apparatus and a nitrogen inlet tube. The titrated solution was continuously pumped through a 10 cm. absorption cell in a Cary recording spectrophotometer. For maintaining a near constant temperature, the tubes leading to and from the absorption cell were jacketed and constant temperature fluid was pumped between the inner and outer tubes. A peristaltic pump, in which liquid is forced through a Tygon tube, was used to circulate the titrated solution.

The pH was measured with a modified design of a Beckman GS meter which was standardized before each titration with buffers at pH 4.01 and 9.14. The pH readings were reproducible to within 0.01 pH unit.

In all solutions constant ionic strength was maintained at 0.1 with the use of KCl. During titrations the ionic strength was maintained constant to within ±0.002 unit. Carbonate-free potassium hydroxide was prepared by the method of Schwarzenbach and Biedermann.[2] A nitrogen atmosphere was maintained over the titrated solutions.

Copper solutions were standardized by electro-deposition. Ligand solutions were prepared from commercially available iminodiacetic acid and ethylenediamine which were purified by recrystallization. The ethylenediamine was recrystallized as the dihydrochloride.

Calculations

The constants for the combination of protons with ethylenediamine and the iminodiacetic acid anion are expressed in terms of hydrogen ion activity and of the concentrations of other species. The metal complex formation constants are in terms of concentrations of species.

In the calculation of the constants there occurs a charge balance relationship. In some cases the hydrogen ion concentration is appreciable as compared to other species and so, in order to obtain consistent K values, a relation between pH and hydrogen ion concentration is necessary. To determine concentration of hydrogen ion a value of 0.8 for its activity coefficient is used.

In the remainder of the paper the following abbreviations will be used

en = ethylenediamine
$I^=$ = iminodiacetic acid anion
K^{H}_{Hen} = constant for $Hen^+ + H^+ = H_2en^{++}$
K^{H}_{en} = constant for $en + H^+ = Hen^+$
K^{H}_{HI} = constant for $HI^- + H^+ = H_2I$
K^{H}_{I} = constant for $I^= + H^+ = HI^-$
K^{en}_{Cu} = constant for $Cu^{++} + en = Cuen^{++}$
K^{en}_{Cuen} = constant for $Cuen^{++} + en = Cu(en)_2^{++}$
K^{I}_{Cu} = constant for $Cu^{++} + I^= = CuI$
K^{I}_{CuI} = constant for $CuI + I^= = CuI_2^=$
K^{en}_{CuI} = constant for $CuI + en = CuIen$
K^{I}_{Cuen} = constant for $Cuen^{++} + I^= = CuIen$
K^{CuIen}_{CuIen} = constant for $2CuIen = Cu(en)_2^{++} + CuI_2^-$

The absorption spectra of the species $Cuen^{++}$, $Cu(en)_2^{++}$, CuI and $CuI_2^=$ were determined by titration of mixtures of Cu^{++} and the ligand with KOH. From the usual relationships at each point in the titration curve, the concentration of each complex species can be determined. The absorption spectrum of each can then be determined from the composite spectrum of the mixture.

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[2] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 339 (1948).