However, nitrito complexes have been isolated[14] and we have observed recently the rapid formation of the nitritonitro complex ($[Coen_2NO_2(ONO)]^+$) under our experimental conditions.[15] The kinetics of the rearrangement of nitrito complexes to the corresponding nitro compounds were the subject of extensive investigation by Adell.[16] The zero order dependence on nitrite ion at high concentrations of nitrite ion (Fig. 2) results from the very rapid formation of the nitritonitro complex and thus the observed change in optical density is due to the rearrangement of the nitritonitro compound to the dinitro complex. At the wave length used (440 mμ) the extinction coefficient of the nitritonitro complex is close to that of the aquonitro compound. The fact that the unstable nitrito intermediate is formed rapidly suggests the cobalt–oxygen bond is not broken.[15] Instead the attack occurs on the coördinated oxygen which thus accounts for the formation of the nitrito isomer (Co–ONO) rather than the more stable nitro form ($Co-NO_2$).

There is no sign of reaching a limiting rate in the reactions with thiocyanate or azide ions (Fig. 2). Unfortunately these reactions are complicated by ion-pair formation. The occurrence of ion-pair formation can be observed by a shift of the ultraviolet spectra toward longer wave lengths immediately upon addition of thiocyanate or azide ions.[17]

In the case of thiocyanate ion, apparently there is ion-pair formation occurring, since considerable spectral shifts are observed, but there is no indication of its being complete at 2.0 *M* thiocyanate. At this concentration, the highest used, the optical density at zero time increased from 0.322 to 0.475 at 275 mμ upon addition of 2.0 *M* thiocyanate ion to a 8.1×10^{-6} *M* solution of the *cis*-aquo complex. This observation is in agreement with the continued rate dependence on thiocyanate ion as shown in Fig. 2.

With azide ion, there is a much smaller change in the spectrum of the *cis*-aquonitro complex but here again one is limited by the absorption of the azide ion. Thus, it is not possible to say whether ion-pair formation occurs only slightly, or that it occurs extensively but with only small spectral changes. However, the general character of all the rate constant-concentration curves, shown in Fig. 2, indicates ion-pair formation. Thus, the data for azide ion and thiocyanate ion are approximately linear but do not extrapolate to zero rate at zero concentration.

In view of the possibility of stepwise formation of higher ion-pairs at high concentrations, and because each ion-pair and the free complex ion would have its own rate of reaction, it does not seem possible to resolve the rate data of Fig. 2 any further. Hence, no conclusions can be drawn concerning the molecularity of these reactions.

---

[14] A. Werner, *Ber.*, **40**, 285, 783 (1907).

[15] R. G. Pearson, P. Henry, J. G. Bergmann and F. Basolo, forthcoming publication.

[16] B. Adell, *Svensk. Kem. Tid.*, **56**, 318 (1944); **57**, 260 (1945); *Z. anorg. Chem.*, **252**, 272 (1944); **271**, 49 (1952); *Acta. Chem. Scand.*, **1**, 624, 659 (1947); **4**, 1 (1950); **5**, 54, 941 (1951).

[17] M. Linhard, *Z. Electrochem.*, **50**, 224 (1944); H. Taube and F. Posey, THIS JOURNAL, **75**, 1463 (1953).

EVANSTON, ILLINOIS

NOTES

The Iron–2,2′,2″-Terpyridine System[1]

BY WARREN W. BRANDT AND JACK P. WRIGHT

RECEIVED DECEMBER 4, 1953

The bis-2,2′,2″-terpyridine-ferrous ion has been utilized considerably in analytical procedures.[2] However, the system itself has received little study even though it is closely related to the iron–2,2′-bipyridine and iron–1,10-phenanthroline systems which have received considerable attention. This investigation was undertaken to provide some of the fundamental information concerning the terpyridine molecule and its complexes with iron.

Experimental

Reagents.—Ferrous ammonium sulfate was used in the preparation of the ferrous solutions. A small amount of hydroxylamine was added to the stock solutions to prevent air oxidation. The solution of perchloric acid in glacial acetic acid was standardized with diphenylguanidine, which had been recrystallized from toluene according to the method of Carlton.[3] The 2,2′,2″-terpyridine was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio.

Determination of the Oxidation Potential.—The oxidation–reduction potential of the bis-2,2′-2″-terpyridine-iron(II) complex was determined by potentiometric titration with cerium(IV) in 0.1 *F* sulfuric acid. The reactants were weighed directly into 0.1 *F* sulfuric acid in ratios varying from 2.0–2.4 moles of 2,2′,2″-terpyridine to 1.0 mole of iron(II). The graphically determined value of the formal potential[4] was 1.10 ± 0.01 volt.

The oxidation of bis-2,2′-2″-terpyridine-iron(II) to bis-2,2′,2″-terpyridine-iron(III) in 0.1 *F* sulfuric acid is accompanied by a vivid color change from deep wine red to a light green. The green solution changes very rapidly to a bright yellow upon standing a minute or two. In 1.0 *F* sulfuric acid the deep wine red changed directly to the yellow. No green form was observed. This phenomenon did not alter the potentiometric results.

Determination of the Acid Equivalency.—The reaction of the bis-terpyridine-iron(II) ion with hydrogen ion may be represented as

$$FeTerpy_2^{++} + 2nH^+ \longrightarrow Fe^{++} + 2TerpyH_n^{n+} \quad (1)$$

The value of *n* in this equation was evaluated by potentio-

---

[1] Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 3, 1953. Abstracted from a thesis submitted by Jack P. Wright to the Graduate School of Purdue University, 1952, in partial fulfillment of the requirements for the degree of Master of Science.

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

[3] C. A. Carlton, THIS JOURNAL, **44**, 1469 (1922).

[4] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, New York, N. Y., 1950, p. 109.

metric titrations. Terpyridine is too insoluble in water and too weak a base to permit its direct titration in this medium. The titrations were made using various solvents (glacial acetic acid, chlorobenzene, dioxane). Perchloric acid in glacial acetic acid was used as the titrant.

When titrated in this manner, terpyridine gave only one inflection point on the potentiometric curve in each solvent. This point occurred at a volume of titrant corresponding to exactly two equivalents of acid per mole of terpyridine. If terpyridine were taking up two protons per mole, two inflection points might be expected in the potentiometric curves. Since double inflection points were not obtained, a series of conductometric titrations were also carried out using the same solvents. Here, as in the potentiometric series, only one inflection point was obtained in each case at a volume of titrant corresponding to exactly two equivalents of acid per mole of terpyridine.

Determination of the Acid Dissociation Constant.—The acid dissociation constant for terpyridine was determined by sodium hydroxide titration of weighed samples of terpyridine dissolved in a hydrochloric acid solution containing an amount of acid exactly equivalent to the amount of terpyridine. Only one inflection point was observed.

The half-way point on the potentiometric curve obtained was taken as a measure of the geometric average value for the two acid dissociation constants involved. On this basis, the composite pK_a is 7.1.

Determination of the Instability Constant.—Solutions were prepared containing varying amounts of iron(II) and sulfuric acid. The equilibrium concentration of the complex was determined spectrophotometrically at 550 mμ. From the data, the equilibrium constant for the reaction of the bis-terpyridine-ferrous complex with hydrogen ion was calculated. The values from nine experiments varied from 1.3–3.4×10^{-4}. The average instability constant for the complex calculated from these values and the acid dissociation constant was 1×10^{-18}.

Discussion

A direct comparison of the instability constants of the ferrous complexes of 1,10-phenanthroline, 2,2′-bipyridine and 2,2′,2″-terpyridine is prevented by the difference in the number of organic molecules and the number of hydrogen ions involved. These differences may be resolved by calculating an "average basicity" for each nitrogen atom involved in the chelation. This then permits a comparison similar to the correlation of instability constant and basicity of the organic molecules which has been previously demonstrated for a series of substituted 1,10-phenanthroline complexes.[5] Table I contains the known instability constants and the calculated "average basicities." The graphical relationship is shown in Fig. 1. The position of bipyridine demonstrates the erroneous nature of a previous report.[5] The similarity between the juxtaposition of the bipyridine and terpyridine values indicates that it may be due to the dissimilarity of their ring systems from that of 1,10-phenanthroline.

TABLE I

AVERAGE NITROGEN BASICITIES

Compound	pK_a	Nitrogen atoms per molecule	Av. basicity per nitrogen atom	pK_D
2,2′,2″-Terpyridine	7.10	3	2.37	18.0
2,2′-Bipyridine[a]	4.35	2	2.18	17.3
1,10-Phenanthroline[b]	4.95	2	2.48	21.3
5-Methyl-1,10-phenanthroline[b]	5.23	2	2.62	22.3
5-Chloro-1,10-phenanthroline[b]	4.26	2	2.13	19.7
5-Nitro-1,10-phenanthroline[b]	3.57	2	1.79	17.8

[a] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N.Y., 1952. [b] Reference 5.

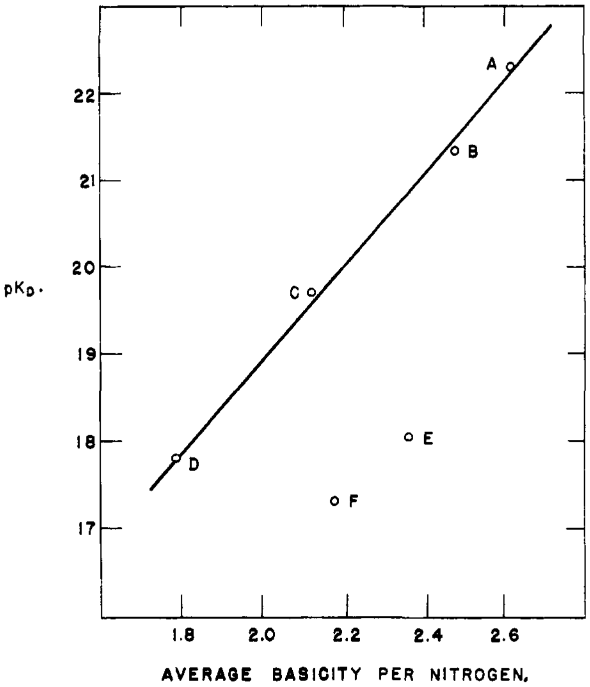

Fig. 1.—A comparison of the stabilities of several chelate complexes of iron(II): A, 5-methyl-1,10-phenanthroline; B, 1,10-phenanthroline; C, 5-chloro-1,10-phenanthroline; D, 5-nitro-1,10-phenanthroline; E, 2,2′,2″-terpyridine; F, 2,2′-bipyridine.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

---

[5] W. W. Brandt and D. K. Gullstrom, THIS JOURNAL, **74**, 3532 (1952).

Diffraction of X-Rays by the Ferric Chloride–Aniline Complex

BY E. VERNON BALLOU[1] AND HANS F. WINTERKORN

RECEIVED JANUARY 14, 1954

Previous preparations[2–5] of the ferric chloride–aniline complexes have involved acid reactions in aqueous solutions and no X-ray diffraction data have been reported. In order to form the reaction products characteristic of the bulk reaction of anhydrous ferric chloride and dry aniline, the complexes were made by the following methods.

(1) Addition of a 50% aniline in dry benzene solution to a solution of 0.56 g. per 100 ml. of anhydrous ferric chloride in dry benzene in the molar ratios of one to one, six to one, and twelve to one.

(2) Addition of aniline to a solution of 17% ferric

---

(1) Division of Applied Science, Harvard University. This research was initiated at the Winterhorn Road Research Institute, Princeton, N. J., and completed at the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York.

(2) J. L. C. Schoreder van der Kolk, *Z. anal. Chem.*, **35**, 301 (1896).

(3) R. M. McKenzie, *Am. Chem. J.*, **50**, 308 (1913).

(4) Y. Osaka, G. Shima and R. Yoshida, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **7**, 69 (1924).

(5) J. V. Dubsky and E. Wagenhofer, *Z. anorg. allgem. Chem.*, **230**, 112 (1936).