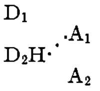
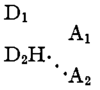
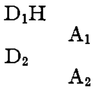
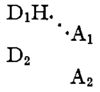
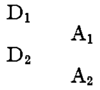
Series		x_1y
(G)		$K_{1j}K_1/[H^+]$
(H)		$K_{1j}K_1/[H^+]$
(I)		$K_1/[H^+]$
(J)		$K_{1j}K_1/[H^+]$
(K)		$(K_1/[H^+])^2$

From these, eq. (I-33) and (I-34) of the text are derivable in a manner similar to that shown in Appendix I.

NOTES

Metal–Amine Coördination Compounds.[1] II. The Iron(III)–1,10-Phenanthroline System in Glacial Acetic Acid[2]

By Warren W. Brandt and Wilfred B. Howsmon, Jr.

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The nature and uses of the ferrous–1,10-phenanthroline complex (ferroin) have been studied and are reviewed by Smith and Richter.[3] The corresponding ferric system (ferriin) is, however, not well understood. When ferroin is oxidized a blue complex results,[4] Fe(phen)$_3^{+++}$. This species is not obtained when ferric ion is mixed directly with 1,10-phenanthroline. Instead, a brown precipitate having the formula [Fe$_2$(phen)$_4$(OH)$_2$]Cl$_4$ is reported by Gaines, Hammett and Walden.[5] Manning and Harvey[6] have reported the formation of a soluble complex, Fe$_2$(phen)$_3$, under the same conditions. In addition, Simon and Knauer[7] obtained a precipitate, Fe(phen)Cl$_3$, by mixing ferric ion with 1,10-phenanthroline in both methanol and diethyl ether.

In the course of the present investigation, the reactions of chelating compounds containing the =N—C—C—N= grouping with various metallic ions in glacial acetic acid were studied. The purpose of this work was to determine the effects of this non-aqueous solvent on such chelation reactions. When 1,10-phenanthroline is mixed with ferric ion in this medium, a yellow complex is formed, the formula of which has been determined to be Fe(phen)$^{+3}$. A crystalline salt, Fe phen Cl$_3$, is precipitated from solutions in which [Fe^{+++}] exceeds 2.5×10^{-4}. When this behavior is contrasted with the analogous reaction in water, as mentioned above, it appears that the solvent effect is one of preventing the chelation of more than one 1,10-phenanthroline molecule. If this were due to coördination of the solvent, the latter would be expected to be present in the precipitate also. In this regard, it should be mentioned that the chelation of Fe(II) is apparently not altered in this solvent. A red complex is obtained, and the spectrophotometric curve is identical with the aqueous complex. The data obtained will be useful in future work on 1,10-phenanthroline systems, both from the standpoint of their analytical applications and for studies of their physical nature.

Apparatus and Reagents.—All absorbancy measurements were made on a Beckman model DU spectrophotometer. Matched one-centimeter cells were used. 1,10-Phenanthroline monohydrate was obtained from the G. Frederick Smith Chemical Company. Reagent grade glacial acetic acid and ferric chloride hexahydrate were used.

Experimental Work.—The complex forms immediately when ferric ion in glacial acetic acid is added to 1,10-phenanthroline in the same solvent. It is stable for several days. It has a wave length of maximum absorbance at 400 mμ. The blank contained the same concentration of iron as the sample but no 1,10-phenanthroline, since the absorbancy of the latter is negligible at the wave lengths used.

The formula for the complex was established by two methods, the molar ratio method of Yoe and Jones[8] and Job's method of continuous variations.[9] The result of the molar ratio method is shown in Fig. 1. For the method of continuous variations the blank was a solution containing ferric ion of a concentration equal to that in the sample in which the iron was most dilute. It was necessary to correct the absorbancy readings for the amount of free ferric ion in those solutions not cancelled by the blank.

If the concentration of iron is made greater than 2.5×10^{-4} *M*, an orange-yellow precipitate forms. When the solution is filtered and absorbancy measurements taken, it is found that the wave length of maximum absorbancy has shifted to about 425 mμ. This precipitate was analyzed for iron and chlorine with the results shown in Table I. The analysis shows the formula to be Fe(phen)Cl$_3$. This corresponds to the compound prepared by Simon and Knauer[7] in non-aqueous media. It is possible that this compound could be the monomer as represented by the formula, in which case iron has a coördination number of 5, or it could

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(1) Previous article in the series, R. T. Pflaum and W. W. Brandt, This Journal, **76**, 6215 (1954).

(2) Taken from the thesis presented by Wilfred B. Howsmon, Jr., to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, June, 1952.

(3) G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Co., Columbus, Ohio, 1944.

(4) G. H. Walden, Jr., L. P. Hammett and R. P. Chapman, This Journal, **55**, 2649 (1933).

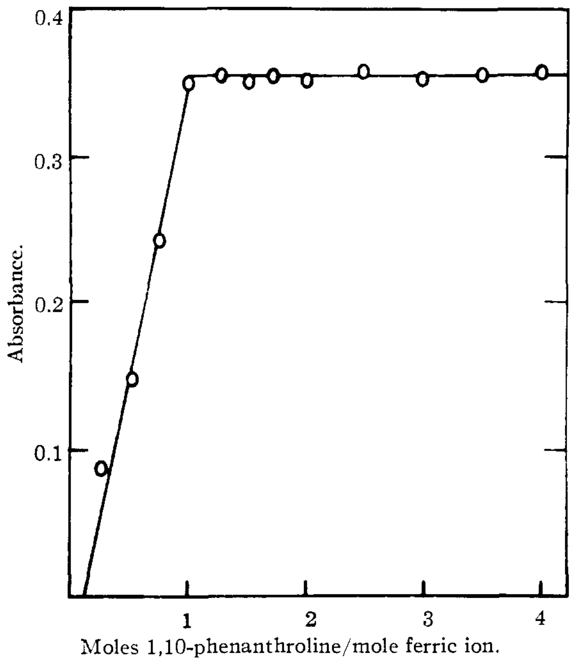
(5) A. Gaines, Jr., L. P. Hammett and G. H. Walden, Jr., *ibid.*, **58**, 3908 (1936).

(6) D. L. Manning and A. E. Harvey, Jr., *ibid.*, **74**, 4744 (1952).

(7) A. Simon and H. Knauer, *Z. Elektrochem.*, **45**, 678 (1939).

(8) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

(9) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).



ig. 1.—Molar ratio study: $(Fe^{+++}) = 2.5 \times 10^{-4}$ *M*, $\lambda = 400$ mμ.

be the dimer $Fe_2(phen)_2Cl_6$ wherein iron has the more common coördination number of 6.

TABLE I

RESULTS OF PRECIPITATE ANALYSIS

Element	$[Fe(phen)Cl_3]$, % Found	Calcd.
Fe	16.2	16.3
Cl	30.5	31.0

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The Oxidation–Reduction Potentials of Systems Involving the Bivalent and Tervalent Complexes of Iron, Ruthenium and Osmium with 2,2′2″-Terpyridyl

BY F. P. DWYER AND E. C. GYARFAS

RECEIVED SEPTEMBER 16, 1953

The bis-terpyridyl complexes of iron(III), ruthenium(III) and osmium(III) have not been prepared although the bivalent metal complexes have been known for some time,[1] nor has the potential for the reaction $M(trpy)_2^{++} \rightleftarrows M(trpy)_2^{+++} + e^-$ been determined save for the iron system, for which a single value, −1.10 ± 0.01 v. in 0.1 *f* H_2SO_4, is reported.[2]

The green ions $M(trpy)_2^{+++}$ were found to be much less stable than the corresponding $M(dipy)_3^{+++}$ and rapid reduction occurred in solution except in the presence of at least normal acid. At this acid concentration the iron(II) compound was rapidly destroyed. Whilst the green crystalline perchlorates could be precipitated with sodium perchlorate after oxidation of the bivalent complexes with ceric nitrate, they underwent reduction during filtration and washing. The complex osmium(III) perchlorate, however, was isolated as a pure compound following oxidation with chlorine.

The potentials of the iron and ruthenium systems were determined on solutions that had been exactly half oxidized with ceric ammonium sulfate. The potentials, developed on a smooth platinum electrode, rose rapidly on the addition of the oxidizing agent, and then fell at a variable rate depending on the acid concentration. Since equilibrium is never attained on an electrode under such conditions, the maximum potential was taken as the oxidation–reduction potential, and no attempt was made to extrapolate to zero time. The potential of the osmium system was measured by allowing the electrode to reach equilibrium for 15–20 min. in an initially equimolar solution of the oxidant and reductant, immediately determining the oxidation–reduction ratio spectrophotometrically, and applying the usual correction. The dark brown Os^{II} complex has a strong absorption maximum at 490 mμ and the green Os^{III} complex has a high transmission in this region with an absorption maximum at 650 mμ. Using two 1-cm. cells placed in front of each other, one containing the oxidant with a trace of chlorine, the other with the pure reductant, and a 490 mμ filter a calibration curve for various ratios was prepared. In the range 40–60% reductant this was a straight line and the oxidation–reduction ratio at equilibrium could be readily ascertained.

Although the color changes are favorable: Fe, violet to green; Ru, orange-red to green; Os dark brown to green, the instability of the oxidized form militates against the use of these compounds as oxidation–reduction indicators.

Experimental

Bis-2,2′,2″-terpyridylosmium(III) Perchlorate Dihydrate.—A warm aqueous solution of the bivalent complex iodide[1] was treated with dilute perchloric acid and the resulting sparingly soluble perchlorate recrystallized from hot water. The finely divided microcrystalline powder was suspended in ice-water and oxidized by shaking in a current of chlorine. After filtration from traces of unreacted material, the deep green solution was treated with a little 20% sodium perchlorate, the resulting green needles collected, washed with cold 2% perchloric acid, then purified ether containing a trace of chlorine and dried *in vacuo*. The dry substance was stable, but an aqueous solution at *p*H 6 rapidly became brown due to reduction. This behavior is characteristic of the tervalent ion, ruthenium and osmium complexes with dipyridyl and phenanthroline.[3]

Anal. Calcd. for $Os(C_{15}H_{11}N_3)_2(ClO_4)_3 \cdot 2H_2O$: Os, 19.19; N, 8.47. Found: Os, 19.3; N, 8.6.

Oxidation-Reduction Potentials.—The pure perchlorates of the iron(II) and ruthenium(II) complexes[1] in *M*/500 solution containing various concentrations of sulfuric acid were oxidized by the addition of the calculated volume of *N*/100 ceric ammonium sulfate, prepared in sulfuric acid of the same concentration, in the oxidation–reduction assembly previously described.[4] The potential of the saturated calomel half-cell, calibrated against the quinhydrone electrode at *p*H 4 in the same assembly was taken as 0.2423 v. at 25°. The oxidation–reduction mixture of the osmium complexes was prepared initially *M*/2000 with respect to each and $10^{-4}N$ with respect to nitric acid, and subsequently diluted to *M*/4000 with sulfuric acid. Higher

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(1) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 20 (1932).

(2) W. W. Brandt, THIS JOURNAL, **76**, 6215 (1954).

(3) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **74**, 4699 (1952).

(4) G. T. Barnes, F. P. Dwyer and E. C. Gyarfas, *Trans. Faraday Soc.*, **48**, 269 (1952).