Spectrophotometric Studies of Empirical Formulas of Complex Ions[1]

BY AUBREY E. HARVEY, JR., AND DELMAR L. MANNING

The empirical formulas of the following complexes have been established: (1) the yellow complex of titanium(IV) and Tiron, (2) the blue complex of iron(III) and orthophenanthroline, (3) the yellow complex of iron(III) and orthophenanthroline. These formulas are, respectively: TiR_6, FeR_3 and Fe_2R_3. The data presented indicate that the blue complex of iron(III) and orthophenanthroline is probably in intermediate form which changes slowly to the yellow complex on standing.

Several of the existing methods for establishing the empirical formulas for colored complexes in solution[2] have been applied to a study of a complex of titanium(IV) and Tiron and two complexes of iron(III) and orthophenanthroline.

Experimental

Instruments.—Spectrophotometric measurements were made with a Beckman quartz spectrophotometer, Model DU, using 1-cm. Corex and Silica glass transmission cells. The instrument was operated at maximum sensitivity. A Beckman pH meter, model G, was used for all pH measurements.

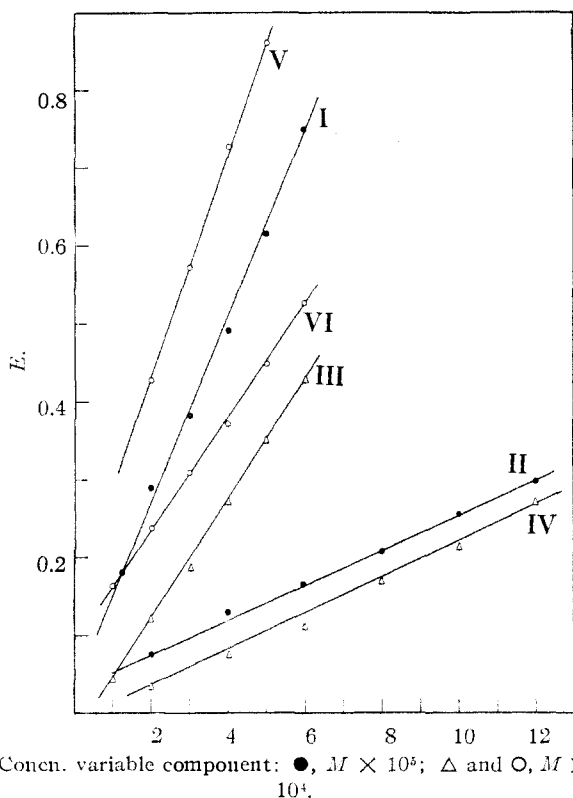Conen. variable component: ●, $M \times 10^5$; $\triangle$ and O, $M \times 10^4$.

Fig. 1.—Slope ratio method: ●, complex of Tiron and Ti- (IV); I, Tiron constant at $24 \times 10^{-4} M$; II, Ti constant at $4 \times 10^{-4} M$; pH 5.0, 380 mμ, ionic strength 0.2. $\triangle$, blue complex of orthophenanthroline and Fe(III); III, Fe varying; IV, orthophenanthroline varying; constant component $40 \times 10^{-4} M$, 0.7 M H, 590 mμ. O, yellow complex of orthophenanthroline and Fe(III); V, Fe varying; VI, orthophenanthroline varying; constant component $30 \times 10^{-4} M$, pH 3.0, 400 mμ.

Reagent Solutions.—Solutions of Tiron, 1,2-dihydroxy-benzene-3,5-disulfonate[3] and orthophenanthroline monohydrate were prepared in a concentration of 0.02 M by dissolving the commercial product in distilled water. A standard titanium(IV) solution was prepared by dissolving 2.7 ml. of 20% $TiCl_3$ in 25 ml. of 1 M H_2SO_4. Three per cent H_2O_2 was added until a faint yellow color persisted. The solution was then diluted to volume in a 500-ml. volumetric flask. Slight hydrolysis was evident but, after filtration, no further hydrolysis was observed. The solution was standardized by determining titanium as TiO_2 in two 75-ml. aliquots.

Solutions of iron(II) and iron(III) were prepared in a concentration of 0.02 M by dissolving reagent grade Fe-$(NH_4)_2(SO_4)_2\cdot6H_2O$ and $FeNH_4(SO_4)_2\cdot12H_2O$, respectively, in distilled water.

Buffer Solution.—An acetate buffer of pH 5.0 was prepared by directions already published.[2]

Electrolyte Solution.—A solution of 2.5 M NaCl was used to control ionic strengths.

Complex of Titanium(IV) and Tiron.—Tiron produces a lemon-yellow color with titanium(IV) in the pH range 1 to 6. Yoe and Armstrong[4] developed this reagent as the basis for the colorimetric determination of titanium. However, they did not investigate the formula of the complex.

Slope Ratio Method.[2]—For the study of the complex, two series of solutions were prepared. In one series the concentration of the titanium was varied in the presence of a constant excess of Tiron; in the other Tiron was the variable and titanium the constant component. The pH of the solutions was adjusted to 5.0 by adding 10 ml. of acetate buffer per 25 ml. of solution. The ionic strength of the solutions was adjusted to 0.2 by the addition of 2 ml. of 2.5 M NaCl per 25 ml. of solution.

Color formation is immediate. In solutions with excess Tiron, the color increases on standing, but there is no ap-
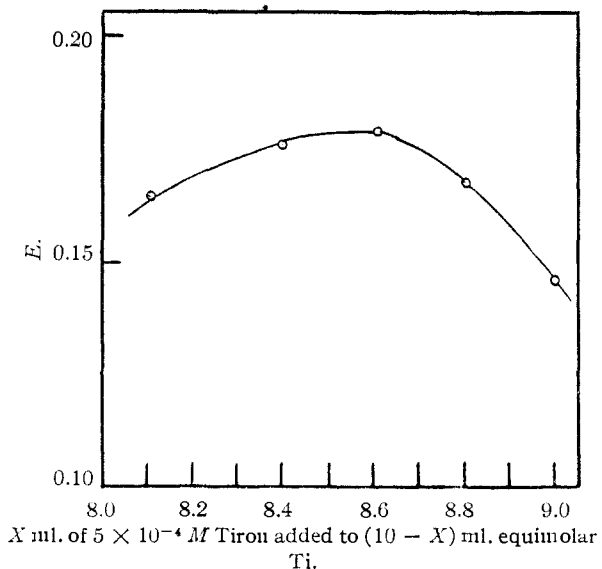

X ml. of $5 \times 10^{-4} M$ Tiron added to $(10 - X)$ ml. equimolar Ti.

Fig. 2.—Continuous variations: complex of Tiron and Ti(IV), pH 5.0, 380 mμ.

(1) Presented at the Seventh Southwest Regional Meeting, Austin, Texas.

(2) A. E. Harvey and D. L. Manning, THIS JOURNAL, 72, 4488 (1950).

(3) Obtainable from LaMotte Chemical Company, Baltimore, Maryland.

(4) J. H. Yoe and A. R. Armstrong, Anal. Chem., 19, 100 (1947).

preciable change in the slope of line I in Fig. 1. With titanium in excess, the solutions showed marked fading after 10 minutes and in the case of low Tiron concentrations, hydrolysis was evident after about 10 minutes standing.

Extinction measurements were made at the wave length of maximum absorption within 10 minutes after preparing the solutions. A slope ratio of 5.83:1 obtained from Fig. 1 (curves I and II) indicates a formula of TiR_6. Slope ratios varying from 5.8:1 to 6.1:1 were obtained on different series of solutions in which the ionic strength was not adjusted.

Method of Continuous Variations.—The curve in Fig. 2 results from the application of the method of continuous variations to the yellow complex. The function Y defined by Vosburgh and Cooper[5] becomes in this case equal to the measured extinction since titanium shows no appreciable absorption in the concentration range employed and Tiron is colorless. Preliminary measurements on prepared solutions showed the maxima to be in the range of X equal 8 to 9 ml. of Tiron to $(10 - X)$ ml. of equimolar titanium. Solutions were prepared with smaller intervals of X and the maxima obtained indicate a formula of TiR_6 for the complex. This is in agreement with the findings of the slope ratio method.

Blue Complex of Iron(III) and Orthophenanthroline.—The iron(III)-iron(II)-orthophenanthroline complex has been developed as a reversible oxidation–reduction indicator with a formal oxidation potential of 1.06 volts.[6,7] The red complex of iron(II) and orthophenanthroline was found to combine in the ratio of three moles of orthophenanthroline per mole of iron.[8] Although the oxidized form of this complex is assumed to have the same formula as the reduced form, it was of interest to test this assumption by applying the methods of formula proof to the oxidized complex.

Figures 3 (curve I), 4 and 1 (curves III and IV) result from the application of the method of continuous variation,[5] molar ratio method,[9] and the slope ratio method,[2] respectively, to the blue iron(III)-orthophenanthroline complex. In each case the complex was formed by combining the iron-(II) and orthophenanthroline solution to give the desired concentrations and oxidizing the red complex to the blue form with dilute cerium(IV) ion avoiding any excess of the oxidant. Dilute sulfuric acid was used to adjust the hydrogen ion concentration and each solution was diluted to a final volume of 25 ml.
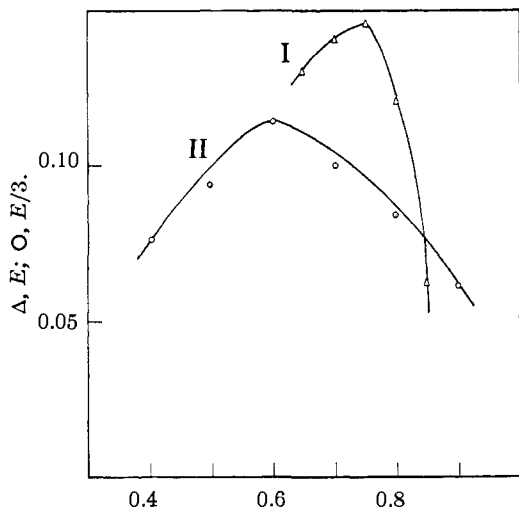
X ml. of 0.02 M orthophenanthroline added to $(1 - X)$ ml. equimolar Fe(III).

Fig. 3.—Continuous variations: I, blue complex, 0.7 M H$^+$, 590 mμ; II, yellow complex, pH 3.0, 400 mμ.

(5) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

(6) G. H. Walden, L. P. Hammett and R. P. Chapman, *ibid.*, **55**, 2649 (1933).

(7) D. N. Hume and I. M. Kolthoff, *ibid.*, **65**, 1895 (1943).

(8) R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

(9) J. H. Yoe and A. L. Jones, *Anal. Chem.*, **16**, 111 (1944).

Extinction measurements were made at the wave length of maximum absorption within 15 minutes after color formation. The color fades appreciably on standing.

The sharp break of the curve in Fig. 4 at a molar ratio of three moles orthophenanthroline per mole iron indicates a formula of FeR_3. The sharp break and rapid leveling off to become parallel to the molar ratio axis is indicative of a very slightly dissociated complex. A slope ratio of 3.1:1 is obtained from Fig. 1 (curves III and IV). The method of continuous variations indicates a formula of FeR_3 in agreement with the other findings.
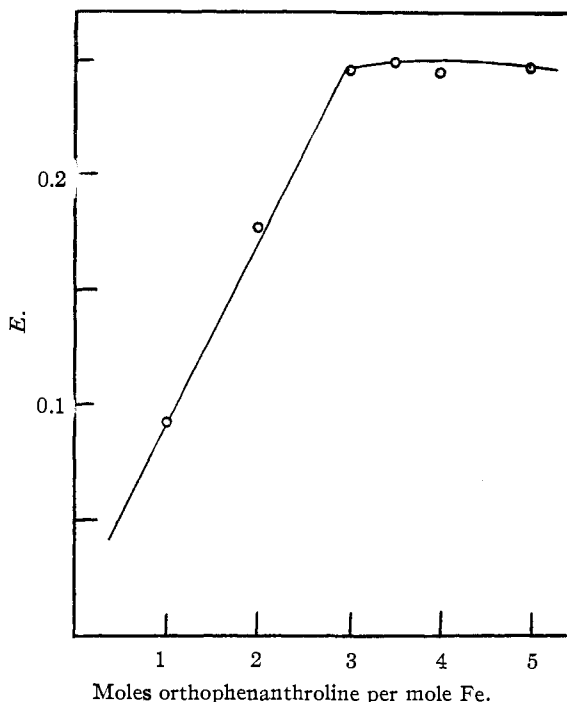

Fig. 4.—Molar ratio: blue complex of orthophenanthroline and Fe(III); C_{Fe} 4 × 10^{-4} M, 0.7 M H$^+$, 590 mμ.

Yellow Complex of Iron(III) and Orthophenanthroline.—Gaines, Hammett and Walden[10] upon mixing orthophenanthroline and iron(III) ions obtained a brown precipitate. It was concluded that this was a brown binuclear tetra-orthophenanthroline-diol-diferric ion, $[Fe_2(OH)_2(C_{12}H_8-N_2)_4]^{++++}$.

It has been found that in the concentration range of 10^{-4} molar, iron(III) ions and orthophenanthroline produce a lemon-yellow color when directly mixed, the color of the yellow complex is less intense below a pH of 3.0. Upon standing a short time at a pH 1.5, the color completely disappears. Apparently, the reaction is reversible since the yellow color reappears upon adjusting the pH of the solution to 3.0. No change in the color, that can be visually detected, occurs in the pH range of 3.0 to 8.0. Slight turbidity is evident at a pH of 9.0, indicating hydrolysis of the iron(III) ions. The optimum pH range for color development lies between 3.0 and 5.0.

In order to determine the wave length of maximum absorption, a solution of the complex was prepared from 0.5 ml. of 0.020 M Fe^{+3} and 1.5 ml. of 0.020 M orthophenanthroline in a total volume of 25.0 ml. The pH of the solution was adjusted to 3.0 by using dilute NaOH and H$_2$SO$_4$. An absorption curve was obtained for the complex in the range of 300 to 600 mμ. Results are shown in Fig. 5, curve I. Points plotted are the extinction of the complex minus the extinction of the same amount of orthophenanthroline used in complex formation. This correction is necessary since the orthophenanthroline absorbs heavily below 380 mμ; above 380 mμ the absorption is negligible. The wave length of maximum absorption of the yellow complex occurs at 360 mμ. Below 400 mμ, it was necessary to use 0.1-cm.

(10) A. Gaines, L. P. Hammett and G. H. Walden, *ibid.*, **58**, 1668 (1936).
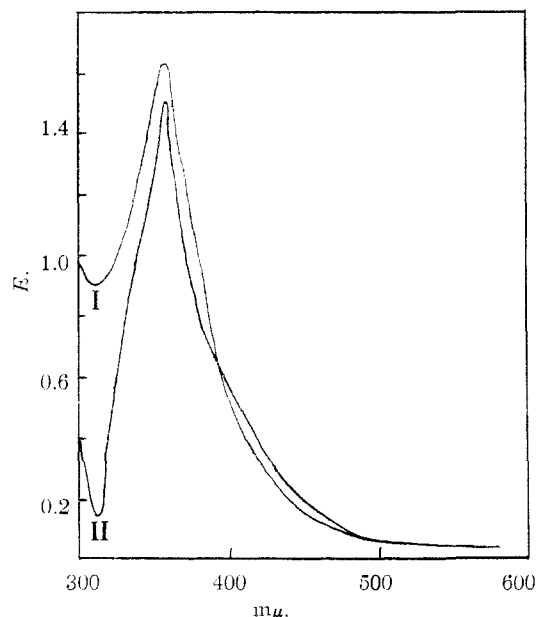
Fig. 5.—Yellow complex of orthophenanthroline and Fe(III): I, formed directly; II, formed by aging of blue complex; pH 3, Fe 4×10^{-4} M, orthophenanthroline 12×10^{-4} M.

cells due to the intense absorption of the complex. For graphical purposes, the extinction values are calculated on the basis of 1-cm. cells.

Further observations on the blue complex of iron(III) and orthophenanthroline have shown that on standing the color changes from a blue to a yellowish color. This change is first observed in about three days and is complete in a week. In order to test this further, a solution of the red complex was prepared from 0.5 ml. of iron(II) and 1.5 ml. of ortho-phenanthroline. This was oxidized to the blue form with dilute cerium(IV) ion solution, the solution was adjusted to pH 3.0 with dilute ammonium hydroxide, and diluted to 25 ml.

An absorption curve was obtained in the range 300 to 600 $m\mu$. The color at the time of measurement was yellow. Results are shown in Fig. 5, curve II. Points plotted are the extinction of the complex minus the extinction of the same amount of orthophenanthroline that was used in complex formation for previously stated reasons. The two curves in Fig. 5 show the same characteristics. This suggests the possibility that the blue complex, FeR_3, may be a stable intermediate slowly rearranging to the yellow form on standing.

Since the yellow color is apparently produced from a separate and distinct complex, it was of interest to make further studies of its empirical formula.

Slope Ratio Method.—Two series of solutions were prepared; in one series orthophenanthroline was the constant component in excess with variable concentrations of iron-(III). In the other series, iron was held constant and the concentration of the orthophenanthroline was varied. The pH of the solution was adjusted to 3.0 with a pH meter, using dilute H_2SO_4 and NaOH. Color formation is immediate and extinction measurements made even after 20 hours showed no appreciable fading, indicating a highly stable complex.

Extinction measurements were made at 400 $m\mu$. This wave length was chosen since the absorption of the ortho-phenanthroline at 400 $m\mu$ is negligible. The slope ratio obtained from Fig. 1 (curves V and VI) is 1.62:1 indicating an empirical formula of Fe_2R_3 for the yellow complex.

Method of Continuous Variations.—Curve II in Fig. 3, resulting from the application of this method, indicates a formula of Fe_2R_3 in agreement with the previous finding.

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Conductivities of Five Substances in Trifluoroacetic Acid

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An apparatus was constructed for producing and measuring conductances of substances in liquid trifluoroacetic acid. The conductivities over a range of dilutions at 25° in this apparatus were determined for H_2O, CF_3CO_2K, $(C_4F_9)_3N$, $(C_4H_9)_2O$ and $(C_4H_9)_3N$. Low conductivities were found for H_2O, $(C_4H_9)_2O$ and $(C_4F_9)_3N$ and moderate ones for CF_3CO_2K and $(C_4H_9)_3N$.

Trifluoroacetic acid has been shown to have a high dielectric constant with a value of about 40 at 25°[2] and to increase rapidly with a rise of temperature. It is also known to be a strongly acidic substance. The combination of high dielectric constant and high acidity gives rise to interest in its properties as a solvent for ionizable substances. It would be interesting, for example, to compare conductivities in it with similar measurements in hydrogen fluoride.[3]

A number of technical difficulties needed to be overcome before conductance measurements of value could be obtained. A sample of high purity was required from a relatively small sample of crude acid. Its purity needed to be maintained through several series of measurements. Due to the hygroscopic and corrosive nature of the material, exclu-

sion of laboratory air was necessary as well as freedom from contact with base metals or stopcock grease. Because of a great range of conductivities to be measured, cells of different cell constants were required. Four cells were arranged so that any one of the four could be used. The apparatus was constructed so that dilutions could be made without exposing the materials to the air or cause them to come into contact with contaminating substances. It was uncertain that electrode surfaces prepared in the usual manner in aqueous solutions would function satisfactorily, but no great difficulty was experienced.

Preparation of Materials.—Trifluoroacetic acid was produced electro-chemically from acetic acid.[4] The barium salt was prepared, dried and then treated with sulfuric acid to obtain the acid relatively free from water. After a further treatment with sulfuric acid, it was transferred to a recrystallization flask similar to one previously used for acetic acid.[5] The acid was recrystallized to constant freez-

(1) College of Engineering, University of Florida, Gainesville, Florida.

(2) J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **72**, 1426 (1950).

(3) J. H. Simons, Chem. Revs., **8**, 213 (1931).

(4) J. H. Simons and co-workers, J. Electrochem. Soc., **95**, 47 (1949).

(5) H. L. Ritter and J. H. Simons, THIS JOURNAL, **67**, 757 (1945).