[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

A Colorimetric Study of Two Derivatives of 1,10-Phenanthroline

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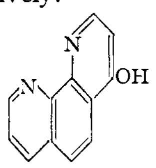
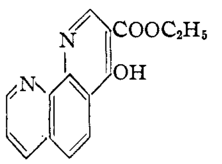
The compound 1,10-phenanthroline reacts with iron(II) to form a five-membered chelate ring involving the metal and the cyclic N–C–C–N grouping. It has been widely used as a color reagent for ferrous iron,[2,3,4] and its ferrous complex as an internal indicator in certain oxidimetric titrations.[5,6] As would be expected, similar complexes may be formed with derivatives of 1,10-phenanthroline. Although the effect of various substituents is usually unpredictable, a reasonable guess may sometimes be made. Case[7] studied the complexes formed by iron(II) with 2,2′-bipyridine derivatives and found that color formation depends upon the position, the type, and the number of the substituent groups. Wesp and Brode[8] reported that phenols containing –COOH, –CHO, –COOR, $-NO_2$, or $-SO_3H$ groups in any position produce colors with ferric chloride which are more stable than those with the unsubstituted phenol itself.

In the present research two derivatives of 1,10-phenanthroline have been investigated with respect to their reactions with iron, and also, to a limited extent, with copper, cobalt, nickel, and molybdenum. These two derivatives were 4-hydroxy-1,10-phenanthroline and 3-carbethoxy-4-hydroxy-1,10-phenanthroline. Hereafter these compounds will be referred to as I and II, respectively.



Compound I



Compound II

A number of derivatives of 1,10-phenanthroline have been investigated,[9] but I and II are unique in that substitution is in the three and the three, four positions.

Experimental

Apparatus.—All transmittancy measurements were made with a General Electric recording spectrophotometer set for a spectral band width of 10 mμ and with one-centimeter absorption cells. Measurements of *p*H were made with a Beckman glass electrode *p*H meter, and oxidation–reduction potentials with a Leeds and Northrup hydrogen ion potentiometer against a normal calomel electrode.

Materials.—Compounds I and II were prepared and supplied by Dr. C. S. Hamilton of the University of Nebraska. A 0.1% aqueous solution of I and a 0.1% ethanolic solution of II were used.

A standard iron solution was prepared from reagent grade ferrous ammonium sulfate and sufficient sulfuric acid to prevent hydrolysis. The theoretical iron content of the ferrous ammonium sulfate used was confirmed by titration with standard potassium dichromate solution.

Standard copper sulfate solution was prepared from copper wire. The standard molybdate solution was prepared by the dissolution of molybdic oxide in sodium hydroxide. Reagent grade cobaltous nitrate hexahydrate was used to prepare the standard cobalt solution. The standard nickel solution was prepared from reagent grade nickel sulfate hexahydrate.

A 10% solution of hydroxylamine hydrochloride was used as reducing agent. The relative merits of hydroxylamine hydrochloride as compared with other less expensive reducing agents has been established.[3] A solution of chlorostannous acid was prepared by dissolution of reagent grade stannous chloride in concentrated hydrochloric acid.

Procedure.—Although the order in which reagents are added is limited only by possible hydrolysis of iron, the same procedure for color development was followed throughout the study. First the hydroxylamine hydrochloride solution was added to approximately 30 ml. of distilled water in a 100-ml. volumetric flask. Then the appropriate volume of phenanthroline solution was added. The *p*H was measured and adjusted to 7.0 or 7.5 depending upon which derivative was being used as the color reagent. Thirty minutes before the transmittancy measurement was to be made, the desired volume of standard iron solution was added and the sample was diluted to volume.

The procedure followed for color development with copper and molybdenum was that recommended by Moss and co-workers.[9,10] The cobalt-phenanthroline complex of both I and II was formed by the addition of 10 ml. of the reagent solution to the desired amount of cobalt. The *p*H was adjusted to 9.5 with dilute aqueous ammonia and the solution was diluted to 50 ml.

A blank solution of the reagents with no iron or other metallic ion added was placed in the reference beam of the spectrophotometer for all transmittancy measurements.

Discussion

1,10-Phenanthroline Derivatives as Color Reagents for Iron.—Solutions of both I and II are colorless and form intense colors with iron(II). The hue of the ferrous complex formed by I is not materially different from that formed by 1,10-phenanthroline. The wave length of maximum absorption is 544 mμ for I and 561 mμ for II, as compared with 510 mμ for the unsubstituted base. The characteristic forms of the transmittancy curves for the complexes developed by these three compounds with 4 p. p. m. of iron are shown in Fig. 1.

Effect of *p*H.—Unlike the parent compound, the development of the colored ferrous phenanthroline complex with either I or II is greatly

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(1) Present address: Esso Laboratories, Baton Rouge, Louisiana.

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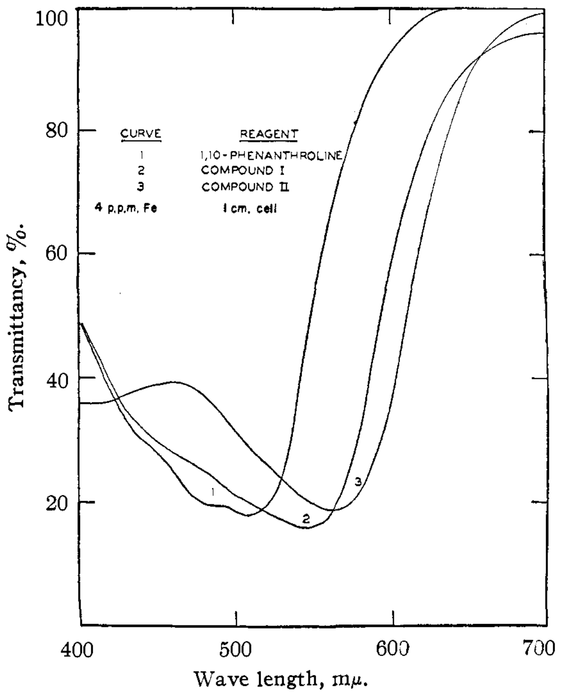

Fig. 1.—Spectral transmittancy curves for ferrous complexes of 1,10-phenanthroline and derivatives.

influenced by the *p*H of the system. The colored complex between II and iron(II) is not formed below *p*H 4 and maximum color develops between *p*H 7 and 8. A study of the stability of a number of solutions containing 4 p. p. m. of iron and 6 ml. of reagent at varying *p*H values indicated that least fading occurs at *p*H 7. The complex between I and iron(II) is developed above *p*H 5 and minimum transmittancy is at *p*H 7.5. The stability study with varying *p*H indicated that this colored system is most stable at *p*H 7.5. The increased sensitivity to *p*H of the complexes with I and II over the parent 1,10-phenanthroline is probably the effect of the substituted hydroxyl groups.

TABLE I

STABILITY STUDY OF FERROUS COMPLEXES OF 1,10-PHENANTHROLINE DERIVATIVES

Time after development of color	Transmittancy,[a] % Soln. 1	Soln. 2	Soln. 3
Compound I (544 mμ)			
10 min.	17.4	16.8	17.5
60 min.	16.6	16.8	17.2
21 hours	19.4	21.5	18.2
53 hours	25.8	29.0	18.8
85 hours	31.8	34.5	19.5
173 hours	34.8	36.3	21.1
293 hours	36.0	37.5	25.5
Compound II (561 mμ)			
10 min.	18.8	18.8	18.8
60 min.	18.6	18.8	18.7
21 hours	19.0	19.0	18.7
53 hours	21.0	20.5	19.1
85 hours	25.0	23.5	21.1
173 hours	34.9	30.8	22.0
293 hours	48.0	48.0	22.9

[a] Solution 1 was allowed to stand with no special treatment; solution 2 was bubbled with air for approximately thirty seconds after each reading; and solution 3 was bubbled with inert gas for approximately thirty seconds after each reading.

Since several solutions showed a change in *p*H of only 0.1 after the color had been developed for 280 hours, no buffer was considered necessary in any of this work.

Effect of Reagents and Iron Concentration.—Concentration of the reagent is not a critical factor in the development of the ferrous complex with either I or II, provided that sufficient is present for completion of the complex formation. When insufficient phenanthroline is present to form the complex, excess ferrous iron precipitates as the hydroxide, as shown by a decrease in transmittancy in the red region of the spectrum.

Reliable determinations may be made with I or II over a range of 0.2 to 6 p. p. m. of iron when 1-cm. absorption cells are used. The range for 1,10-phenanthroline is the same with 1-cm. absorption cells. The sensitivity of I is slightly greater than that of either II or the unsubstituted phenanthroline. The colored systems obtained with I and with II conform to Beer's law at 544 and 561 mμ, respectively.

Stability of the Colors.—The colored ferrous phenanthroline complexes were developed in three samples with both I and II. The two sets of three samples each were allowed to stand under ordinary laboratory conditions, and transmittancy measurements at the wave lengths of maximum absorption were made at various time intervals, as shown in Table I. After each reading, Sample 1 was stoppered and allowed to stand and Samples 2 and 3 were bubbled for a few seconds with air and inert gas, respectively. The ferrous complexes exposed to air were much less stable than those which were kept under an inert atmosphere, the transmittancy decreasing several per cent. after only twenty hours in the system containing I. The ferrous complexes which were kept under an inert atmosphere showed only slight changes visually and fading of only a few per cent. spectrophotometrically after 293 hours. The characteristic colors formed by ferrous iron with I and II had changed after 293 hours to gray-green in the solutions bubbled with air and in those allowed to stand without inert scrubbing.

The instability of the complexes in the presence of air appears to be due to the formation of some new compound by oxidation. The presence of a new compound in each system is indicated by the change in color and by the appearance of an isosbestic point at 590 mμ for the system containing I and at 607 mμ for the system containing II (Figs. 2 and 3). More careful measurements would probably have shown a second isosbestic point in each case.

After the stability studies had been made over a period of 394 hours, an attempt was made to restore the characteristic color of the complexes. To determine whether fading was caused merely by oxidation of iron(II) to iron(III), portions of the faded solutions were acidified, more hydroxylamine hydrochloride was added, and the *p*H was again brought to the appropriate range with dilute sodium hydroxide. The characteristic colors were not restored. Either the iron and phenanthroline originally present were tied up in new, stable complexes or the phenanthroline originally present had been destroyed and was no longer present to form the colored complex with ferrous iron. The former seems the more likely since the isosbestic points shown in Figs. 2 and 3 indicate the formation of new compounds. However, in order to eliminate the second possibility, more phenanthroline was added to samples of the faded solutions and the solutions were again acidified, reduced, and adjusted to the proper *p*H range. The characteristic colors were not restored. Since the excess phenanthroline originally added was not accounted for, other portions of the faded solutions were acidified, 2 ml. of the standard iron solution added, the solutions reduced, and the *p*H readjusted. Since the colors of the ferrous–phenanthroline complexes were not formed, the excess phenanthroline originally present was either oxidized or used in the formation of the new complex. It may be concluded, thus, that the ferrous complexes formed by both I and II are converted by standing for long periods of time in the presence of air to more stable complexes which are gray-green in color.

The addition of a few drops of hydrogen peroxide to freshly prepared samples of the ferrous complexes destroys the characteristic colors immediately to form colorless solutions. Hydrogen peroxide also destroys the green color of the faded solutions. The green complexes formed by air oxidation may represent intermediate stages in the complete oxidation of the ferrous–phenanthroline complexes.

The ferrous complex formed by either I or II is much less stable than is the complex formed by the parent compound. One source of instability may be the presence of the hydroxyl group in both I and II. It is a generally accepted fact that a phenol is more or less ionized to form RO^- and H^+ depending upon the basicity of the solution. Assuming that the presence of the hydroxyl group on the ring actually does lend phenolic properties to the two phenanthroline derivatives, the ionization which is characteristic of phenols may influence the stability of the complexes formed by iron(II). This would explain the increased sensitivity of the ferrous complexes toward changes in hydrogen ion concentration.

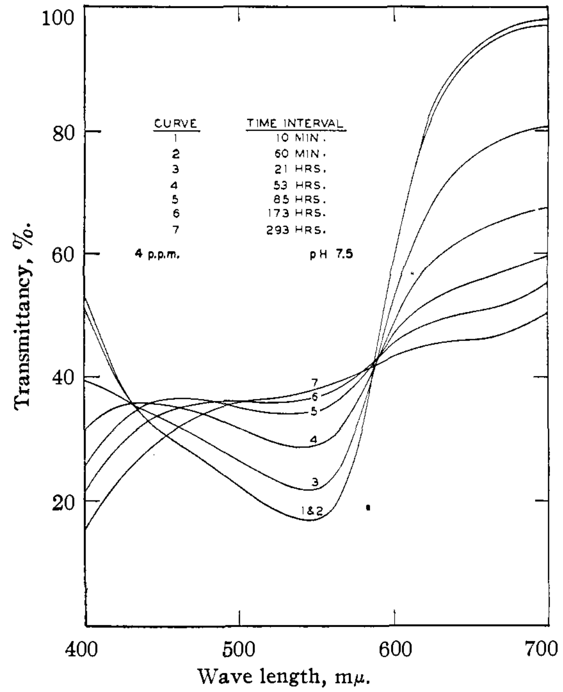

Fig. 2.—Curves showing stability of ferrous complex compound I (bubbled with air).

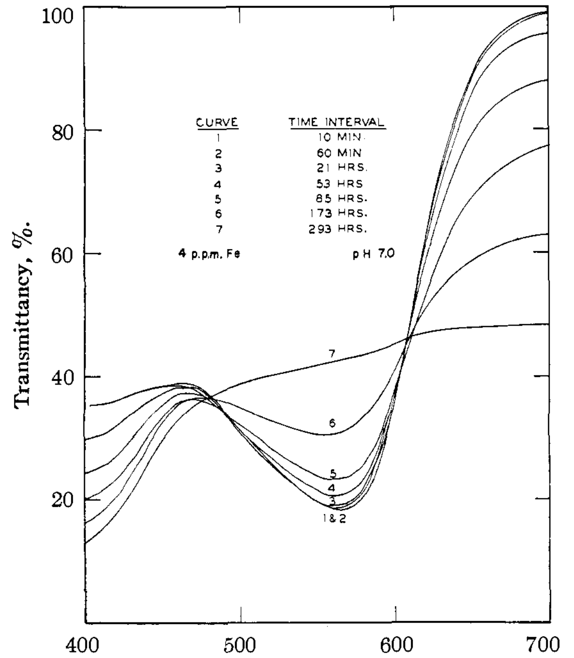

Fig. 3.—Curves showing stability of ferrous complex of compound II (bubbled with air).

It may also be significant to note that the colored complex formed by II with iron(II) is more stable than that formed by I. Apparently, the substituted ester in II lends stability to the colored system. This stabilizing influence was also noted by Wesp and Brode in their work with substituted phenols. From their work, it might be predicted that substitution of -COOH, -CHO, $-NO_2$, and $-SO_3H$ groups into I would also lend stability.

Effect of Ammonia.—Adjustment of the hydrogen ion concentration with aqueous ammonia produced erratic results with either I or II as evidenced by a peculiar crossing of transmittancy curves in the red and the violet regions of the spectrum. When the *p*H of the solutions was adjusted with sodium hydroxide, the crossing of transmittancy curves was decreased, and both colored systems showed straight line relationships between iron concentration and log transmittancy. A straight line relationship was not shown by I when *p*H adjustment was made with aqueous ammonia. A straight line was obtained, however, with II, although the line was slightly displaced below 100% transmittancy. No satisfactory explanation for these irregularities in the presence of ammonia is evident. It is of interest, however, to note that the complex formed by I appears to be more susceptible to this influence than is the complex formed by II. Possibly the presence of the carbethoxy group in II stabilizes the complex to such an extent that the influence of ammonia on the system is decreased.

2. **Other Color Reactions of 1,10-Phenanthroline Derivatives.**—An investigation was made of the possibility of the formation of colored complexes of I and II with ions known to form complexes with 1,10-phenanthroline. Three such ions are copper, molybdate and nickel.

According to Moss,[9] a color is developed by copper with 1,10-phenanthroline only if the copper is present as the copper–ammonia complex before addition of the phenanthroline itself. Therefore, this procedure was followed in the study of the color developed by copper with both phenanthroline derivatives. Neither I nor II was found to be a satisfactory color reagent for copper. Compound I forms a precipitate immediately with as little as 5 p. p. m. of copper. Compound II forms a pale green solution with copper in absence of ammonia which is too unstable to be of any analytical significance.

The molybdate ion, when reduced with chlorostannous acid in the presence of an excess of I or II forms a pink to purple color which fades and then precipitates. This reaction is similar to that reported by Moss[9] with 1,10-phenanthroline.

The nickel ion does not develop a color with I or II over a *p*H range of 4 to 9. Formation of the nickel–ammonia complex before the addition of phenanthroline has no apparent effect.

Hammett, Walden and Edmonds[5] reported that 1,10-phenanthroline does not form a colored complex with cobalt. Fortune[11] noted that cobalt develops a colorless complex with 1,10-phenanthroline above *p*H 6. Compounds I and II also form complexes with cobalt at this *p*H, but the complexes are intensely colored. The yellow color developed by I appears to be quite stable, but the transmittancy curve in the visual region does not show the maximum and minimum absorption bands which are desirable for quantitative work. The color developed by cobalt with II is quite similar to that developed by I, and the same general type of transmittancy curve is obtained. The minimum concentration of cobalt which gives a measurable color with I or II is 5 p. p. m.

3. **1,10-Phenanthroline Derivatives as Oxidation–Reduction Indicators.**—Solutions of the ferrous complexes of I and II as well as the complex of 1,10-phenanthroline with iron(II) were used as indicators in the titration of known weights of ferrous ammonium sulfate with approximately 0.1 *N* trisulfatoceric acid. The indicator solutions were prepared according to the procedure given by Walden, Hammett and Chapman.[12] The color change from red to blue-green observed with the complex of I is the same as that with the 1,10-phenanthroline complex. The end-point is very sharp and reversible on the addition of more ferrous ammonium sulfate. The color change of the complex with II is from pink to yellow. The end-point is not as sharp as those for the other two and does not appear to be reversible.

The oxidation–reduction potentials of 1,10-phenanthroline and compound II were measured and found to be 1.08 v. and 0.71 v., respectively. Hume and Kolthoff[13] reported the oxidation potential of ferrous–phenanthroline to be 1.06 v. The results obtained with I were erratic and the limited amount of material prevented further investigation.

Summary

A spectrophotometric study of the ferrous complexes of two derivatives of 1,10-phenanthroline indicates that stability is decreased and sensitivity to slight changes in *p*H increased by the presence of a substituted hydroxyl group. Introduction of a carbethoxy group ortho to the hydroxyl group appears to minimize the influence of a substituted hydroxyl group, stabilizing the colored system developed with iron(II).

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