[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, UNIVERSITY OF MASSACHUSETTS]

Composition of the Complexes of Iron(III) with Phenols and Enols[1]

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The colored complexes which iron(III) forms with phenols, naphthols and enols in dilute solution at low *p*H have been investigated spectrophotometrically by the method of continous variations. With the monohydric phenols *m*-nitrophenol, *p*-nitrophenol, salicylaldehyde and salicyclic acid, iron(III) was found to form a single complex of 1:1 composition which may be represented by the type formula $Fe(OAr)^{++}$. Similar results were obtained with ethyl acetoacetate and 2-naphthol-3,6-disulfonic acid (sodium salt). Migration studies made with the salicylaldehyde, salicylic acid and *p*-nitrophenol complexes indicate that the colored ions are positively charged, consistent with the 1:1 formula. Data obtained with the dihydric phenol, resorcinol, indicate a 2:1 as well as a 1:1 complex, and there are indications that as many as three ferric ions combine with each molecule of the trihydric phenol, phloroglucinol.

Though the red to blue color produced by the reaction of ferric ion with phenols and enols has long been used as a qualitative test for these compounds, little is known of the nature of the colored complexes formed. Wesp and Brode[3] have summarized the results of earlier investigations and reported absorption spectra of the colors produced by ferric chloride with forty-four phenols and ten naphthols in water solutions. Wesp and Brode found that the anion of the iron(III) salt takes no part in the production of the color. This they regarded as evidence against the Weinland and Binder[4] formula, Cl_2FeOAr,, which had been widely accepted as responsible for these colors.

Hantzsch and Desch have shown[5] that an active hydroxyl group is essential for the color reaction, and the work of Wesp and Brode on the reaction of salicylic acid with ferric chloride in forty-eight solvents showed that color is produced only in polar solvents which are derivatives of water or ammonia. On the basis of very limited evidence Wesp and Brode postulated that "the ferric iron–phenol colors are due to the formation of complex coördinated negative ions of the type $Fe(OR)_6^{\equiv}$, wherein OR^- represents the ionized phenol." This has since been generally accepted as the type formula for the colored complexes. The 1:6 composition of the complex was assumed largely on the basis of analogy with other iron(III) complexes, particularly the red thiocyanate complex, which was then thought to be $Fe(SCN)_6^{\equiv}$ but which has since been shown to be predominately $Fe(SCN)^{++}$, at least at low concentrations.[6,7]

In a recent note, which appeared after the work here reported was essentially completed, Banerjee and Haldar[8] reported a 1:3 complex of iron(III) and phenol itself.

In view of the lack of evidence and the uncertainties involved, the nature of the colored complexes of iron(III) with typical phenols, enols and napthols, has been investigated spectrophotometrically by the method of continuous variations.[9,10,11]

Experimental

Materials.—All chemicals used were C.P. grade. Solid phenols were recrystallized twice and liquid compounds were twice distilled. The C.P. ferric salts were used without recrystallization. Though ferric nitrate was preferred to the chloride, because of the lower complexing tendency of the nitrate, ferric chloride is frequently used in practice and it was therefore used for part of the investigation.

Procedure.—The solutions of ferric chloride and nitrate were standardized by gravimetric determination of iron as ferric oxide. The phenol solutions were prepared by direct weighing of the purified compounds and used without standardization. The *p*H of the solutions was adjusted to the desired value by the addition of either concentrated nitric or hydrochloric acid, depending upon the iron(III) salt used. All solutions were filtered to remove suspended particles.

Fading occurs in many cases, while in others an increase in absorption was observed upon standing. Accordingly, it was necessary to adopt a standardized procedure in order that all measurements on the solutions of a series could be taken after the same period following preparation. Measurements were made within a few minutes of the time the solutions were mixed. In general systems involving rapid change, like phenol itself, were avoided.

All measurements were taken at a temperature kept nearly constant at 25°, though in the early determinations there was no provision for careful control. In later work the temperature was kept constant at 25.0 ± 0.2°.

Apparatus.—All *p*H measurements were made with a Beckman *p*H meter, model G, which was adjusted with standard buffer solutions before each measurement.

Light absorption measurements were made with a Beckman DU quartz spectrophotometer. The band widths used in the measurements ranged from 0.5 $m\mu$ of spectrum at wave length of 400 to 4 $m\mu$ of spectrum at a wave length of 600 $m\mu$ according to data supplied by the manufacturer. Matched square cuvettes of optical thickness 1.000 ± 0.002 cm. were used throughout.

Migration studies were made by carefully introducing the highly colored complex at the bottom of a U-tube which contained nitric acid at *p*H 1.2. Platinum electrodes were inserted in each nitric acid layer and with a potential of 6.5 volts a current of 2–4 milliamp. was passed for a period of from one to four days. The charge of the complex was inferred from the movement observed at the boundaries.

Results and Discussion

The complexes of iron(III) with a number of typical phenols and an enol have been investigated, using Job's method of continuous variations.[5,6,7] With consideration given to the solubility of the phenols or enol in water, and the stability as well as color intensity of the complexes, the following phenols, enol and naphthol were chosen for investiga-

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(2) From a thesis submitted in June, 1950, by Hormoz Broumand to the graduate school of the University of Massachusetts in partial fulfillment of the requirements for the degree of Master of Science.

(3) E. F. Wesp and W. R. Brode, THIS JOURNAL, **56**, 1037 (1934).

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(6) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

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tion as suitable and representative[12]: (a) monohydric phenols—*m*-nitrophenol, *p*-nitrophenol, salicylaldehyde, salicylic acid; (b) dihydric phenol—resorcinol; (c) trihydric phenol—phloroglucinol; (d) enol—ethyl acetoacetate; (e) naphthol—2-naphthol-3,6-disulfonic acid (sodium salt).

Following the method of continuous variations, absorption curves were obtained for several iron(III)-phenol systems in which the concentrations were adjusted to ratios which might be expected in probable complexes. For example, Fig. 1 gives plots for the iron(III)-salicylaldehyde system for solutions in which the iron(III) concentration was held constant while the salicylaldehyde concentration was varied in such a way that the iron(III)-phenol ratio was 1:0, 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6. There is no apparent shift in the wave length of maximum absorption, and therefore no indication from these data that more than one complex is formed. Similar evidence was obtained with other monohydric phenols. Since the absorption spectra given by Wesp and Brode obviate to some extent the necessity for obtaining these curves, they were not determined for all phenols. Wave lengths at and near the maxima were selected arbitrarily for further study of the systems.

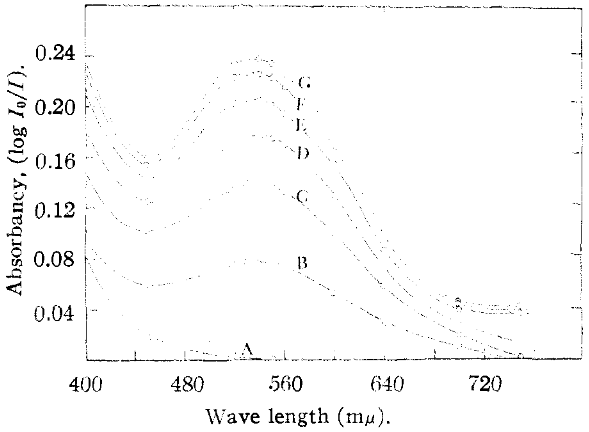

Fig. 1.—Absorption spectra of 0.005 *M* iron(III) chloride and 0.005 *M* salicylaldehyde and water mixed in such a way that while the iron(III) concentration was constant at 0.0005 *M* the ratio to salicylaldehyde concentration was 1:0 (A), 1:1 (B), 1:2 (C), 1:3 (D), 1:4 (E), 1:5 (F), 1:6 (G). The *p*H was 2.9.

Continuing the method of continuous variations, equimolar solutions of iron(III) and the phenols were mixed in proportions such that while the total number of moles present was constant the ratio was varied from iron(III) alone to substituted phenol. Absorption measurements were made on each of the solutions thus obtained at the several selected wave lengths. Data obtained are plotted[13] in Figs. 2, 3, 4 and 5, for the substituted monohydric phenols, salicylaldehyde, salicylic acid, *m*-nitrophenol and *p*-nitrophenol, respectively. It is apparent that in every case the maximum falls at 0.5, which corresponds to a 1:1 ratio of iron(III) to the monohydric phenols in the colored complexes formed. The results at all wave lengths agree, and no evidence was found to indicate complexes other than the 1:1 for iron(III) and the substituted monohydric phenols under these conditions.

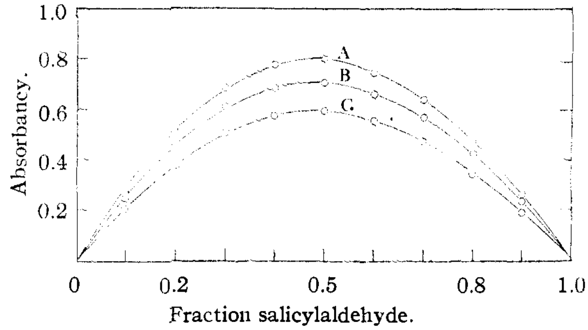

Fig. 2.—Continuous variations studies using 0.005 *M* iron(III) chloride and 0.005 *M* salicylaldehyde at *p*H 2.9: A, 530 mμ; B, 450 mμ; C, 600 mμ. Similar data were obtained at 550 mμ.

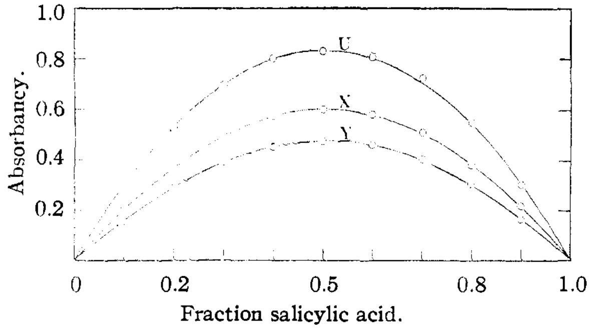

Fig. 3.—Data obtained using 0.005 *M* iron(III) nitrate and 0.005 *M* salicylic acid at *p*H 1.2: U, 530 mμ; X, 600 mμ; Y, 450 mμ. Similar data were obtained at 500 mμ.

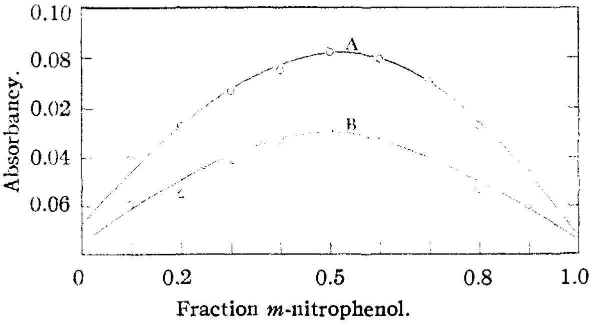

Fig. 4.—Data obtained using 0.025 *M* iron(III) nitrate and 0.025 *M* *m*-nitrophenol at *p*H 1.2: A, 510 mμ; B, 600 mμ. Similar data were obtained at 450 mμ.

Since iron(III) forms 1:1 colored complexes with the monohydric phenols it was of interest to study

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[12] The iron(III) complex of phenol itself was found to be so unstable as to make investigation difficult and the results uncertain. Rapid color change and precipitation effects were observed. Accordingly this system was not intensively investigated.

Resorcinol was selected as the most suitable dihydric phenol since the pyrocatechol complex shows maximum absorption in the ultraviolet region where the iron(III) absorption is high and hydroquinone is rapidly oxidized by iron(III).

Of the trihydric phenols, phloroglucinol was selected since it seemed most suitable in terms of resistance to oxidation, complex stability, and relative distance between -OH groups.

[13] Strictly speaking, a correction should have been made by subtracting the absorption due to iron(III) which had not reacted. At the wave lengths used the iron(III) absorption is not great, however, and the result is not altered by this correction.

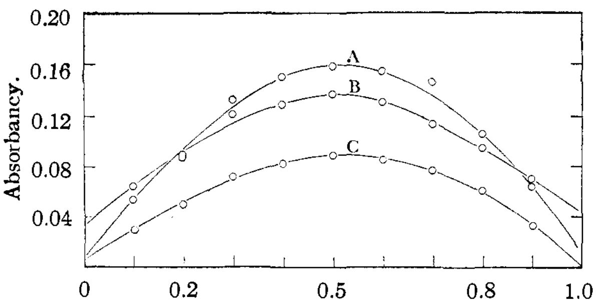

Fig. 5.—Data obtained using 0.025 M iron(III) chloride and 0.025 p-nitrophenol at pH 1.5: A, 515 mμ; B, 450 mμ; C, 600 mμ. Similar data were obtained at 500 and 550 mμ.

the complexes of the polyhydric phenols. For the resorcinol system some shift in the wave length of maximum absorption was observed as the iron(III)–resorcinol ratio was altered with the iron(III) concentration held constant. This suggests that more than one colored complex is formed. This is confirmed by data such as are plotted in Fig. 6 for solutions in which the total moles of iron(III) and resorcinol were constant while the ratio of the two was varied continuously. At 550 mμ the maximum occurs at 0.5 corresponding to a 1:1 complex such as was found with the monohydric phenols. A similar result was obtained at 500 mμ. On the other hand at 450 mμ the maximum absorption falls at 0.33, which corresponds to an iron(III)–resorcinol ratio of 2:1. Similar results were obtained at 426 mμ and 400 mμ. In these plots a correction has been made for the iron(III) absorption which is rather high at these short wave lengths. The data indicate, therefore, that two colored complexes of iron(III) to resorcinol ratios 1:1 and 2:1, respectively, are present at pH of 1.15. At a pH of 0.9 the 400 and 450 mμ maxima are nearer to 0.5, indicating that the 1:1 complex becomes relatively more important at low pH. This is to be expected since the dissociation of the resorcinol is suppressed by acid, and hence the concentration of the complexing ion is decreased.

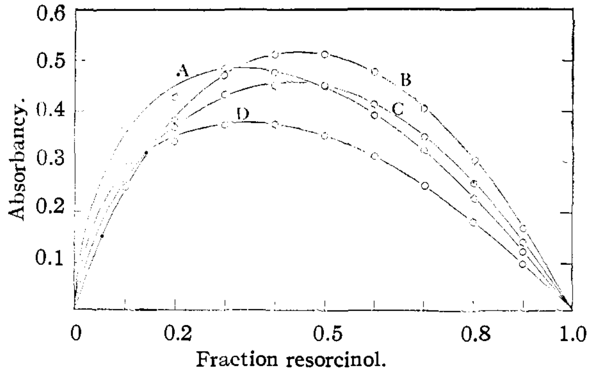

Fig. 6.—Data obtained using 0.0909 M iron(III) nitrate and 0.0909 M resorcinol at pH 1.15 and ionic strength 0.545: A, 400 mμ; B, 550 mμ; C, 500 mμ; D, 450 mμ.

In view of the results found with the mono- and dihydric phenols the complexes formed with the trihydric phenols are of particular interest and accordingly an attempt was made to investigate them in spite of their instability. Methods similar to those used with the mono- and dihydric phenols were followed in studying the phloroglucinol system. Evidence for a 1:1 complex was again found at long wave lengths, and there was some indication of other complexes of iron(III)–resorcinol ratios, perhaps 2:1 or 3:1, though the data obtained do not warrant a definite decision primarily because of the uncertainties due to instability. The data obtained on this system are not consistent, and accordingly any conclusions must be regarded as tentative.

It appears that each active –OH group in the phenol is capable of complexing a single ferric ion. The fact that only the 1:1 complex was found with the substituted monohydric phenols suggests that under the conditions used the iron(III) does not complex appreciably with more than one phenolic –OH group. That two ferric ions combine with a resorcinol molecule, despite the coulombic repulsion between the ferric ions, lends further support to this conclusion as does the indication of higher complexes of the 1,3,5-trihydroxybenzene.

The recent note by Banerjee and Haldar[8] indicates that they have found a 1:3 iron(III)–phenol complex, but they did not indicate concentrations, pH, ionic strength or other conditions. Due to the instability of the complex the phenol system was not thoroughly investigated, but a 1:1 complex was found at pH 1.68 with 0.1 M solutions at ionic strength of 0.6. Evidence for higher complexes, perhaps 1:2 or 1:3, was found at lower pH though the instability caused uncertainty.

Ethyl acetoacetate was chosen for investigation as representative of the enols which give colored complexes with ferric ion. The data obtained by procedures similar to those used with the monohydric phenols are presented in Fig. 7. It is apparent that, as with the monohydric phenols, a single colored complex of 1:1 composition is formed.

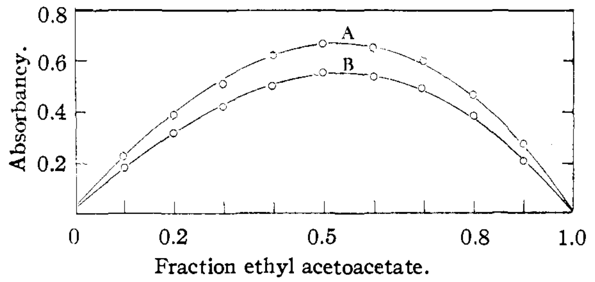

Fig. 7.—Data obtained using 0.1 M iron(III) chloride and 0.1 M ethyl acetoacetate at pH 1.2: A, 500 mμ; B, 550 mμ. Similar data were obtained at 480, 450 and 530 mμ.

Similar investigation of the complex formed with 2-naphthol-3,6-disulfonic acid (sodium salt) as a representative naphthol gave the data shown plotted in Fig. 8. It is evident that here again a 1:1 colored complex is formed when 0.01 M solutions are mixed.

The rather broad maxima at 0.5 for the monohydric phenols, the enol, and the naphthol indicate 1:1 complexes of rather low stability at the low concentrations and pH's used. The possible exist-

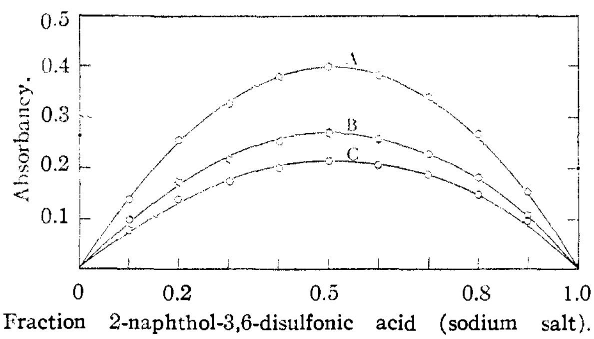

Fig. 8.—Data obtained using 0.01 *M* iron(III) nitrate and 0.01 *M* naphthol at *p*H 1.17: A, 600 mμ; B, 500 mμ; C, 450 mμ.

ence of higher complexes should be considered. As J. Bjerrum[14] has shown, concentration is a very important factor and higher complexes may be found in a more concentrated range than was studied. For many of the substituted phenols, however, solubility is a factor which limits investigation to the range used. Moreover, the tests are commonly made in practice at high dilution in view of their sensitivity. Hence it seems reasonable to conclude that the color reaction commonly observed for identification purposes is due primarily to the 1:1 complex. All measurements were made at low *p*H, in the range 0.9 to 2.8 to avoid hydrolysis effects which were encountered when attempts were made to work at high *p*H. If, as seems likely, the complex involves the OAr group it is possible that the nature of the complex may be different at high *p*H since the OAr^- concentration should increase with *p*H. Babko[15] has recently investigated the iron(III)–salicylic acid system and reported a violet 1:1 complex of possible formula FeR^+ at low *p*H. At higher *p*H he found FeR_2^- and at a *p*H of 10 a possible complex $FeR_3^{=}$. Foley and Anderson[16] have studied the complex formation of sulfosalicylic acid with iron(III) by the method of continuous variations. They found a 1:1 complex up to a *p*H of 2.4, and observed that the stability of the complex is a function of acidity. Their measurements at higher *p*H values were first interpreted to indicate complexes of other mole ratios, but the formulas could not be determined, and later work indicated a 1:1 complex up to *p*H of 7.5 in phthalate and bicarbonate buffers. Recent polarographic study by Banks and Patterson[17] has shown a 1:3 sulfosalicylate complex in neutral and alkaline solution.

The 1:1 composition found for the monohydric phenol complexes suggests a formula such as $Fe(OAr)^{++}$, and raises the question of the charge on the ion. Wesp and Brode stated that the iron(III)–salicylic acid complex is negatively charged since it was found to migrate toward the anode, but they failed to give any details or indicate the conditions under which the migration study was made. Accordingly, it was impossible to duplicate the conditions of the Wesp and Brode investigation, but their observation was not confirmed by the results of migration studies made with the solutions prepared by mixing equal volumes of 0.01 *M* ferric nitrate and salicylic acid. The purple complex was observed to move toward the negative electrode and away from the positive, thus indicating a positively charged ion. A similar result was observed when a saturated (at 21°) salicylic acid solution was used in place of the 0.01 *M* solution. Similar evidence for positively charged colored complexes was found with the salicylaldehyde complex at 0.005 *M* and *p*H of 1.2 and the *p*-nitrophenol complex at 0.0125 *M* and *p*H of 1.2. All data obtained indicate a positively charged complex and are consistent with the 1:1 composition found and some such formula as $Fe(OAr)^{++}$.

Throughout this investigation it was observed that the color of the complexes decreased with *p*H, and virtually disappeared at very high acidity. This effect has been observed rather generally for iron(III) solutions, particularly those in which the iron(III) forms complexes with the negative ion of a very weak acid, as was the case here. The color was returned by the addition of alkali to the solution, and intensified until colloidal hydrous iron oxide begins to appear at *p*H about 3.5 under the conditions used. Tests for colloidal properties of the solutions were negative in the low *p*H range (below *p*H 2.8).

The study of iron(III) complexes of these and similar compounds is being continued and extended.

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