Electronic Remarks on the Origin of the Anomalous Color of Some Organic Iron. III. Complex Salts

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Introduction

The absorption spectra of chelate compounds of Fe (II) were studied by the present author[1] and he came to the conclusion that unsaturated intramolecular chelate rings formed between Fe and chelating organic compound would probably act as the new chromophore to produce the new absorption bands in the visible region. The several compounds of Fe (III) containing ligands such as acetylacetone[2] or 8-quinolinol were found also to show a similar intense absorption band as Fe (II) compounds. Other examples of such an intense absorption bands, those of Fe (III) chelate compounds of 1-nitroso-2-naphthol and nitrosophenylhydroxylamine will be reported in this paper.

The Fe (III) complexes of NCS^- and N_3^- ions[3] and the enolic and phenolic substances[4] all show intense, distinct bands in the visible region and from the fact that these bands are also completely different from the band of Fe^{+++} ion or from those of the ligands, it is likely that these bands also belong to the

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[1] K. Sone, This Bulletin, **25**, 1 (1952); *J. Am. Chem. Soc.* in press.

[2] K. Sone, I. Miyake, H. Kuroya, K. Yamasaki, *J. Chem. Soc. Japan*, **69**, 70 (1948).

[3] A.v. Kiss et al., *Z. anorg. allg. Chem.*, **244**, 98 (1940); J. Badoz-Lambling, *Bull. soc. chim. France*, **1950**, 1195.

[4] F. Wesp and W.R. Brode, *J. Am. Chem. Soc.*, **56**, 1037 (1934); H. Henecka, *Ber.*, **81**, 179 (1948); see also H. Henecka, "Chemie der Beta-Dicarbonyl-Verbindungen", p. 110, Springer-Verlag, Berlin, 1950.

same kind as those absorption bands of the above mentioned chelate complexes.

From all these facts it seems clear that the Fe^{+++} ion posesses a peculiarly high ability to produce anomalously deep-colored organic complexes. Indeed it was pointed out by Yoe⁵⁾ that among about 5000 organic substances studied, about 1200 were found to produce intensely colored complexes with iron, while no other metal showed such a high ability for color production.

In the present article, discussions will be made on this problem from the standpoint of the electronic theory of organic chemistry and it will be shown that by the application of this theory a number of features of these colorations can be explained satisfactorily.

Experimental

A Beckman model DU spectrophotometer and a Coleman universal spectrophotometer were used in the spectral measurements. The results of absorption spectra were shown in Fig. 1 in which the ordinate expresses the value of molecular extinction coefficient ε calculated by the familiar formula $\varepsilon = \frac{\log I_c/I}{c.d.}$

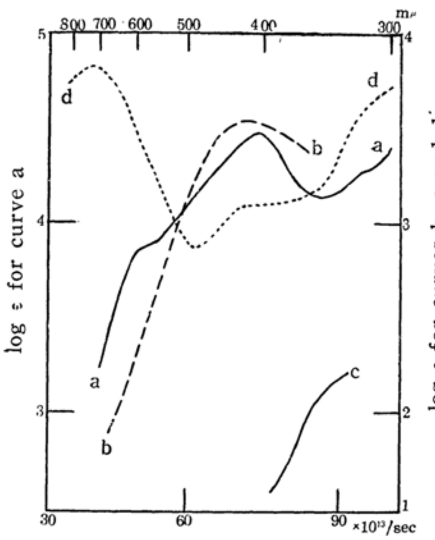

Fig. 1.—Curve a: Tris (1-nitroso-2-naphthol) iron in chloroform, b: Tris (nitrosophenylhydroxylamine) iron in chloroform, c: Ammonium salt of nitrosophenylhydroxylamine (cupferron) in water, d: Colloidal solution of Prussian blue.

The tris (1-nitroso-2-naphthol) iron (III) was prepared after Ilinsky and Knorre⁶⁾. Chloroform solutions of the above complex and of tris (nitrosophenylhydroxylamine) iron (III) were used for spectral measurements. Concentrations used were 1/1500 mole for tris (1-nitroso-2-naphthol) iron and 1/5000 mole for tris (nitrosophenylhydroxylamine) iron respectively.

Colloidal solution of Prussian blue prepared by mixing aqueous solutions of $K_4[Fe(CN)_6]$ and iron alum was also studied. The final concentration of Fe^{++} and Fe^{+++} were 1/2000 and 1/4000 mole respectively. The ε value was calculated for one atom of Fe^{+++}.

Discussion

The tris (nitroso-naphthol) iron has a band at 407 mμ. The longer wave length side of this band shows a hump at ca. 600 mμ. This means the probable existence of a new band in this region which is responsible for the dark color, almost black of this iron complex. This color is in contrast with the nitrosonaphtholates of other metals such as Co, Cu and Pd which are mostly red or brown.

The iron (III) complex of nitrosophenylhydroxylamine which contains 3 molecules of the ligand shows a strong band at 420 mμ which is quite different from the absorption of the ligand itself (Fig. 1, curve c.). The color of this iron complex is red which is in contrast with complexes of other metals. For example, complexes of Cr, Ni and Co are green and pink⁷⁾ and similar to their hydrated ions in the color.

The number and shapes of the anomalous absorption bands in the above-mentioned Fe (III) complexes are considerably different in each case, and therefore it will be rather difficult to give a general treatment to explain their origins. In addition, it is also known from magnetochemical observations⁸⁾ that the Fe-ligand coordinate bonds in the dipyridyl and phenanthroline complexes are of covalent character, while most of the other complexes with anomalous absorption only contain ionic linkage. Therefore there certainly exists a considerable difference between the electronic structures of these two types of complexes. Nevertheless, it is fairly clear that by the combination of the Fe (III) ion and all these organic ligands some completely new electron transitions which were absent beforehand become possible.

In regard to the origin of the appearance of such transition, it can be pointed out that the redox transition between the Fe^{++} and

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5) J. H. Yoe, *Anal. Chem.*, **20**, 393 (1948).

6) M. Ilinsky and J. Knorre, *Ber.*, **18**, 2728 (1885).

7) V. Anger, L. Lafontaine, C. Caspar, *Compt. rend.*, **180**, 376 (1925).

8) B. Werbel, V.H. Diebler and W.C. Vosburgh, *J. Am. Chem. Soc.*, **65**, 2329 (1943); A.E. Martell and M. Calvin " Chemistry of the Metal Chelate Compounds ", **1952**, p. 214

Fe^{++} ions occurs with relative ease in contrast with the other heavy metals, such as Co, Ni and Cu which have strong tendencies to keep their most stable valence states. This indicates that the energy difference between these two valence states is relatively small.

Now if an organic ligand which can cause the anomalous absorption with Fe (III) and which generally contains conjugated double bonds and is therefore rich in the mobile π-electrons, approaches the Fe^{+++} ion, the electronic structure (B) shown below becomes possible,

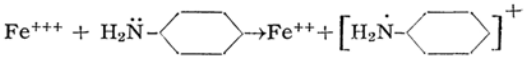
$$\underset{(A)}{Fe^{+++} + :R} \longleftrightarrow \underset{(B)}{Fe^{++} + .R} \qquad (1)$$

i.e., one electron is partially transferred from $:R$ to Fe^{+++}, producing a Fe^{++} ion and a free radical $\cdot R$ derived from the ligand.

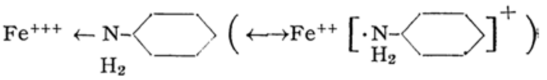
These two structures (A) and (B) will make possible the condition of mutual resonance and therefore the structure (B) will, to a certain extent, contribute to the resonance of the whole system containing Fe^{+++} and R^- together.

The present author assumes that the establishment of this resonance system (1) and the occurrence of electron transitions between the new energy states produced by such resonance could be the true origin of the anomalous absorption bands of the above-mentioned Fe (III) complexes.

The assumption of the existence of such a resonance system may be supported by the following facts of organic chemistry. Dewar⁽⁹⁾ described that when some aromatic amines are oxidized by $FeCl_3$, the first step is the reaction of the type

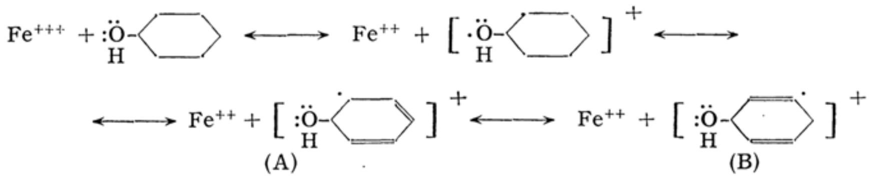


which looks quite analogous to the above mentioned resonance formula, and from this fact it is also very probable that this reaction proceeds through the formation of an intermediate complex,



in which the two electronic states corresponding to the (A) and (B) given above are in resonance. Similar assumption of the one-electron transfer is generally accepted also to explain the oxidation and oxidative decomposition of phenols, facts which are important for the later discussions.

From these considerations, it will be quite reasonable to assume that, in the well-known reaction of the Fe^{+++} ion and phenol, the Fe^{+++} ion will show some properties of the Fe^{++} ion, and the phenol molecule will acquire some properties of the free radicals as shown schematically in (1′). Under this assumption, a number of experimental data on the Fe^{+++} ~phenol reaction can be explained satisfactorily.



(1′)

(1) When an anionoid, or electron-donating group (alkyl, halogens, NH_2, OH etc.) is substituted in the benzene nucleus of phenol, the electron transfer from the phenolic OH to the Fe^{+++} ion will be more or less facilitated, thus promoting the contribution of the structure (B) in the resonance system (1′), and therefore increasing the mobility of the whole π-electron system, shifting the absorption band to the longer wave length, and making the phenol molecule highly reactive owing to its free-radical character enhanced by the substituted group.

(2) When a cationoid, or electron-attracting group (CHO, COOH, NO_2 etc.) is substituted, the electron transfer from OH to Fe^{+++} will become rather difficult, shifting the band towards the shorter wave length and thereby stabilizing the ligand molecule from reacting away.

These conclusions coincide completely with the experimental data of Wesp and Brode⁽⁴⁾. According to them,

(1) In the alkyl-, halogen-, NH_2- and OH-substituted phenols, the position of the band is generally shifted to longer wave length from the position found for the unsubstituted phenol and, in the case of its *o*- and *p*-derivatives, the produced colored complexes are very unstable, changing rapidly into the Fe^{++}

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9) M.J.S. Dewar, "The Electronic Theory of Organic Chemistry", 1949, p. 248; L. Fieser and M. Fieser, "Organic Chemistry", 1950, p. 677.

ion and resinous substances which are formed from the oxidative polymerization of the respective phenols. With *m*-derivatives the band shifts are much less, or even in the opposite direction and the complexes are somewhat more stable.

These facts can be explained if the following two assumptions are made. Namely, (i) the coordinated phenol molecule with some enhanced free radical character polymerizes into the resinous matter, leaving the iron which is now in the Fe (II) state; (ii) since the m-substituent is difficult to resonate with the OH group, it cannot greatly influence the resonance of the whole system in such a way as the o- and p-substituents do.

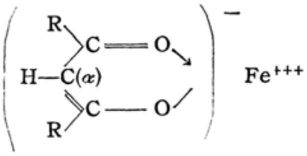
It might be added that the same kind of band shift and instabilization of complexes occurs in the case of thiophenol, whose SH group is much more deformable than the OH group of phenol.

(2) In the case of the CHO-, COOH- and NO_2-substituted phenols the band is shifted to the shorter wave length than in the case of phenol, and the resulting complexes become very stable.

Wesp and Brode also observed that the Fe (III) complexes of naphthols are generally colored in blue or green, and thus absorb light at longer wave length than phenols, and this fact is explained easily if the greater mobility of the π-electrons in the naphthalene ring compound with benzene ring is taken into account.

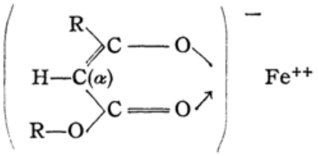
Recently Henecka⁴⁾ measured the absorption spectra of the color reactions of two series of enolic substances with Fe^{+++}. The structures of their complexes are, respectively,

(A) acetylacetone type,



and

(B) acetoacetate type.



From his experimental data it can be observed that: (1) the absorption maximum for a compound of type (A) is generally located at a shorter wave length than that of the corresponding compound of type (B) with silmilar substituent groups, (2) when the H atom on the α-position in both types is replaced by alkyl, Cl-, or OR-group (i.e. anionoid group), the band is shifted to the longer wave length, while RCO-, RO_2C- or CN-group (i.e. cationoid groups) shifts the band in the opposite direction. It is very remarkable that these relationships are quite analogous to those observed by Wesp and Brode for the phenols. The relationship (1) can be readily understood because the compound of type (B) is that of type (A) substituted with an anionoid OR group.

In this way, the general characteristics of the Fe^{+++}~phenol and enol colorations can be explained adequately, and other anomalous colorations of the Fe (III) complexes can be considered in analogous manners. There exist some experimental evidences which support this point of view; for example, Linhard and Weigel⁽¹⁰⁾ indicated that the strong absorption band at 300~330 mμ shown by the rhodanato- and azido-complexes of Co (III) originates from the following electron transition:

$$\left[Co^{(+++)}\ X^{(-)}A_5\right]^{++} \xrightarrow{h\nu} \left[Co^{(++)}\ X\ A_5\right]^{++}$$
$$(A = NH_3,\ X^- = NCS^- \text{ or } N_3^-)$$

which is virtually an electron transfer from the ligand to the central metal. If their arguments are correct it will be fairly probable that the strong bands at 450~500 mμ of the Fe^{+++}~NCS^- and Fe^{+++}~N_3^- complexes are also of the same origin, i.e., they are derived from the electron transfers which are closely related to the resonance of type (1). The change between the Fe (III) and Fe (II) in this case, however, would occur much more easily than that between the Co (III) and Co (II) in the ammine complexes, and this will cause the absorption band of Fe^{+++} complex appear in the longer wave length, as is observed experimentally.

It is also conceivable that the anomalous colors of the Fe (II) chelates, which the author formerly considered to be due to the special ring formation⁽¹⁾, might be in fact, due to the resonance of the type

$$Fe^{++} + :R \text{ —— } Fe^{+++} + :R^{\cdot -}$$

i.e. the reverse of that assumed for the Fe (III) complexes⁽¹¹⁾. The possibility of the

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10) M. Linhard and M. Weigel, *Z. anorg. allg. Chem.*, **267**, 113, 121 (1951).

11) Interesting remarks concerning such colorations were made by P. Krumholz (*Nature*, **167**, 570 (1951).

production of deep colors as the result of the resonance between the metallic complex ion and the organic molecules was also indicated by the study of Kröhnke[12] on some deeply colored organic ferrocyanides, and further examples of similar anomalous colorations of iron complexes are found in the books of Feigl[13].

It may be added that some of the absorption spectra of anomalously colored complexes such as $Fe^{+++}\sim NCS^-$ or $Fe^{++}\sim$phenanthroline complexes show apparent similarities to that of the Prussian blue solution, which certainly contains a resonance system between the Fe^{++} and Fe^{+++} ions through the coordinated CN^- ions. (cf. Fig. 1, curved). These apparent similarities seem to give further support to the point of view discussed throughout this article.

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[12] F. Kröhnke, *Ber.*, **83**, 35 (1950).

[13] F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions", New York, 1949.