

Anal. Calcd. for $C_{19}H_{36}O_3$: neut. equiv., 313. Found: neut. equiv., 313, 314.

A semicarbazone derivative¹⁴ prepared in 90% yield melted at 86–86.4° after three recrystallizations from methanol, petroleum ether and acetone in that order.

Anal. Calcd. for $C_{20}H_{38}N_2O_3$: N, 11.37. Found: N, 11.42.

Ethyl 10-Methyloctadecanoate (IV).—Using the general method of Schneider and Spielman¹⁵ for a Clemmensen reduction, 51 g. (0.15 mole) of ethyl 9-keto-10-methyloctadecanoate dissolved in 1 l. of absolute ethanol and mixed with 420 g. of amalgamated zinc¹² was saturated with dry hydrogen chloride. The mixture was refluxed for twenty-four hours, again saturated with hydrogen chloride, and then refluxed for a second twenty-four-hour period. After removal of the unreacted zinc, the volume of the solution was reduced to one-half and excess water added. The precipitated organic layer was removed by extraction with benzene and the benzene solution distilled to remove the volatile material. Distillation of the residue gave 40 g. (83%) of ester, b. p. 175–180° (2 mm.), n_D^{25} 1.4440. Prout, Cason and Ingersoll⁴ report n_D^{25} 1.4447 for this compound.

Anal. Calcd. for $C_{21}H_{42}O_2$: sapon. equiv., 326. Found: sapon. equiv., 322.

10-Methyloctadecanoic Acid (V).—A mixture of 17.5 g. (0.054 mole) of ethyl 10-methyloctadecanoate, 25 ml. of 40% aqueous sodium hydroxide solution and 100 ml. of ethanol was refluxed for twelve hours and worked up as described above for the saponification of ethyl 9-keto-10-methyloctadecanoate. There was obtained 15 g. (94%) of the acid, n_D^{25} 1.4513 (the literature^{3,4} records n_D^{25} 1.4512 for 10-methyloctadecanoic acid). In view of the fact that the product had a low melting point (around 5–10° compared with literature values of 20–21°³ and 25.4–26.1°⁴), and it was difficult to recrystallize without large loss, it was decided to convert the acid to its more easily handled amide, purify the amide by recrystallization, and hydrolyze the pure amide to the acid.

10-Methyloctadecanamide (VI).—Twelve and five-tenths grams (0.042 mole) of the 10-methyloctadecanoic acid isolated above was converted to the acid chloride by refluxing with excess thionyl chloride and the excess thionyl chloride removed by distillation. The residual acid

chloride dissolved in dioxane was added dropwise with rapid stirring to cold concentrated aqueous ammonia. The precipitated amide was recrystallized once from acetone and four times from petroleum ether (b. p. 30–60°) to give 8.8 g. (70%) of pure amide, m. p. 77–78° (the literature reports 76–77°³ and 77.5–79.2°⁴).

Hydrolysis of 10-Methyloctadecanamide.—The 8.8 g. of amide prepared above was hydrolyzed by refluxing for twelve hours with 50 ml. of 10% alcoholic sodium hydroxide. The mixture was treated as described above under saponification of ethyl 9-keto-10-methyloctadecanoate to give an essentially quantitative yield of 10-methyloctadecanoic acid, m. p. 23.5–25.8° (cor.), b. p. 200–203° (1 mm.), n_D^{25} 1.4512.

Anal. Calcd. for $C_{19}H_{36}O_2$: neut. equiv., 299. Found: neut. equiv., 301, 303.

Table I summarizes the physical constants of 10-methyloctadecanoic acid and its derivatives found in this work in comparison with those obtained by Spielman³ and by Prout, Cason and Ingersoll.⁴

TABLE I

PHYSICAL CONSTANTS OF 10-METHYLOCTADECANOIC ACID AND ITS DERIVATIVES

Physical constant	This work	Spielman ³	Prout, Cason and Ingersoll ⁴
Melting point of acid, °C.	23.5–25.8 (cor.)	20–21	25.4–26.1 (cor.)
Boiling point of acid, °C.	200–203 at 1 mm.
Index of refraction of acid n_D^{25}	1.4512	1.4512	1.4512
Melting point of amide, °C.	77–78	76–77	77.5–79.2
Melting point of 2,4,6-tri-bromoanilide, °C.	93.5–94	93–94	93.4–93.9

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Summary

A new and improved method of synthesis of tuberculostearic acid (10-methyloctadecanoic acid) is reported.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Soluble Complex of Ferric Iron and 8-Hydroxyquinoline

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In dilute mineral acid medium 8-hydroxyquinoline reacts with ferric ion to give a soluble green complex. A number of workers have made use of the formation of this green substance in the indirect colorimetric determination of magnesium by treating an acid solution of the magnesium hydroxyquinolate precipitate with a ferric salt. The present work deals with the composition of the green complex and its dissociation constant. The value of the dissociation constant is needed in calculating the solubility product of ferric hydroxyquinolate as well as in treating the problem of the extractability of ferric hydroxyquinolate by chloroform from aqueous solutions at various acidities.

The composition of the complex was established by applying the familiar method of continuous variations.¹ Solutions of ferric perchlorate and 8-hydroxyquinoline in perchloric acid were mixed in various ratios, the sum of molar concentrations of the two reactants being kept constant at $1.19 \times 10^{-3} M$. The transmittancy of the mixtures was determined at 645 $m\mu$, the approximate wave length of maximum absorption by the iron-hydroxyquinoline complex; at this wave length, absorption by hydroxyquinolinium ion (in which form hydroxyquinoline is chiefly present at the acidities used) and ferric ion is negligibly small, at least in the concentrations employed. Transmittancy

(1) P. Job, *Ann. chim.*, **9**, 113 (1928); **11**, 97 (1936).

(14) Shriner and Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

(15) Schneider and Spielman, *J. Biol. Chem.*, **142**, 345 (1942).

tancy measurements were made with a Coleman spectrophotometer, Model 10, at a band width of 5 $m\mu$. The mixtures were prepared at various pH 's, ranging from 1.1 to 2.6, and a glass electrode was used to obtain the pH .

The results are shown in Fig. 1. At pH 1.9 and below, the curves exhibit a maximum at the value 0.5 for the ratio $[Fe^{+++}]/([Fe^{+++}] + [HOx \cdot H^+])$ and are symmetrical. At pH 2.1 to 2.6, the ratio for the maximum color intensity is shifted slightly to the left and lies between 0.45 and 0.5. It can be calculated that the solubility product of ferric 8-hydroxyquinolate is exceeded in solutions of higher pH in which the maximum is displaced from 0.5. These experiments demonstrate that in the more acidic solutions the colored product is an equimolecular compound of iron and 8-hydroxyquinoline and is therefore the ion $FeOx^{++}$.

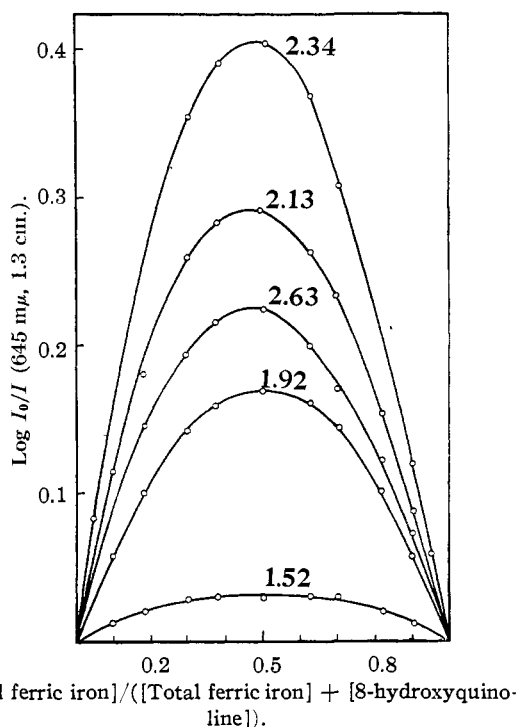


Fig. 1.—Continuous variation method applied to mixtures of ferric ion and 8-hydroxyquinoline; sum of concentrations of components $1.19 \times 10^{-3} M$ except in pH 2.63 series where concentration is one-half of others. pH values are given on curves.

The same species is no doubt predominantly formed at higher pH 's, but here the incipient formation of slightly soluble $FeOx_3$ is an obscuring factor. Even if the departure of the maximum color intensity from the ratio 0.5 is interpreted to mean formation of some $FeOx_2^+$, the amount of the latter is small compared to that of $FeOx^{++}$ if it can be assumed that the extinction coefficients of the two complex ions are similar in magnitude. Transmission curves of solutions in which ferric ion was present in excess, on the one hand, and 8-hydroxy-

quinoline in excess on the other, showed no significant difference in the range 450–700 $m\mu$. In aqueous medium $FeOx_2^+$ cannot be formed in appreciable concentration because the increase in the hydroxyquinolate ion (Ox^-) concentration by addition of more 8-hydroxyquinoline or by raising the pH , required to shift the equilibrium toward $FeOx_2^+$, precipitates ferric hydroxyquinolate. In an alcoholic medium it may be expected that $FeOx_2^+$ can be formed in appreciable amount.

The maximum color intensity of acidic mixtures of ferric ion and 8-hydroxyquinoline is attained very rapidly, constancy being reached before the transmittancy of the solution can be measured. The color is moderately stable, but decreases in strength on long standing.

Dissociation Constant of $FeOx^{++}$

The extinctions of a series of mixtures, at three different pH values, of ferric perchlorate and 8-hydroxyquinoline, in which the concentration of the latter was constant and the concentration of excess iron was varied, were measured at 645 $m\mu$ and 25° (Fig. 2). The value of the extinction coefficient of $FeOx^{++}$ and of the dissociation constant

$$a_{Fe^{+++}}a_{Ox^-}/a_{FeOx^{++}} = K_1$$

were obtained from the relations indicated below. It is not feasible to obtain the extinction coefficient of the complex directly by adding a large excess of ferric ion.

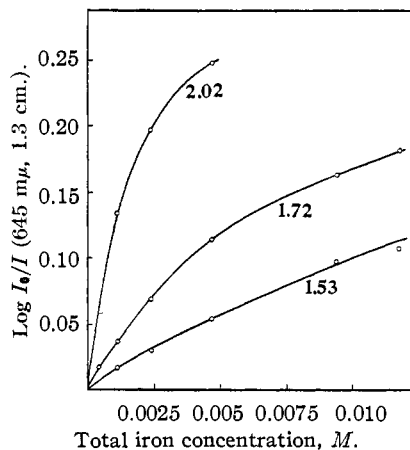


Fig. 2.—Extinction of ferric ion–8-hydroxyquinoline solutions with iron in variable excess; oxine concentration $2.38 \times 10^{-4} M$. pH values are given on curves.

The ionic strength of the mixtures was maintained constant at 0.073 by addition of sodium perchlorate. Buffer solutions were not used in the adjustment of the acidity because of the formation of complexes between ferric iron and anions. These experiments had to be carried out in a restricted range of acidity. If the solution is not sufficiently acidic, the hydrolysis of ferric ion becomes too extensive and introduces uncertainties; if the solution is too acidic, insufficient $FeOx^{++}$ is formed to allow measurement.

The following relations have been used to obtain the values of the constants mentioned

$$E = \log I_0/I = \epsilon l [\text{FeOx}^{++}] \quad (1)$$

$$K_1 = f_2 [\text{Fe}^{+++}] f_1 [\text{Ox}^-] / f_2 [\text{FeOx}^{++}], \text{ where } f = \text{activity coefficient, with valence of ion indicated by subscript} \quad (2)$$

$$\begin{aligned} \text{Let } b &= \text{total 8-hydroxyquinoline concentration} \\ &= [\text{HOx}\cdot\text{H}^+] + [\text{HOx}] + [\text{Ox}^-] + [\text{FeOx}^{++}] \end{aligned}$$

where HOx represents 8-hydroxyquinoline. When the pH is low, as in the present experiments, the concentration of undissociated 8-hydroxyquinoline and of hydroxyquinolate ion is small and can be neglected, and therefore

$$b = [\text{HOx}\cdot\text{H}^+] + [\text{FeOx}^{++}]$$

Now

$$[\text{HOx}\cdot\text{H}^+] = \frac{(a\text{H}^+)^2 [\text{Ox}^-]}{K_{\text{Ox}}}$$

where

$$\begin{aligned} K_{\text{Ox}} &= K_{1\text{Ox}} K_{2\text{Ox}} = \frac{a\text{H}^+ a\text{HOx}}{a\text{HOx}\cdot\text{H}^+} \times \frac{a\text{H}^+ a\text{Ox}^-}{a\text{HOx}} \\ &= \frac{(a\text{H}^+)^2 a\text{Ox}^-}{a\text{HOx}\cdot\text{H}^+} = \frac{(a\text{H}^+)^2 [\text{Ox}^-]}{[\text{HOx}\cdot\text{H}^+]} = 3.4 \times 10^{-16} \end{aligned}$$

The value 3.4×10^{-16} for K_{Ox} is based on the values 1.2×10^{-5} and 2.86×10^{-11} , respectively, for $K_{1\text{Ox}}$ and $K_{2\text{Ox}}$ at 25° .²

$$\therefore [\text{FeOx}^{++}] = b - [(a\text{H}^+)^2 [\text{Ox}^-] / K_{\text{Ox}}] \quad (3)$$

From (2) and (3)

$$[\text{Ox}^-] = \frac{K_1 f_2 [\text{FeOx}^{++}]}{f_1 f_2 [\text{Fe}^{+++}]} = \frac{f_2 K_1 K_{\text{Ox}} b}{f_1 f_2 K_{\text{Ox}} [\text{Fe}^{+++}] + f_2 K_1 (a\text{H}^+)^2} \quad (4)$$

From (1), (3) and (4)

$$E = \frac{\epsilon f_1 f_2 K_{\text{Ox}} [\text{Fe}^{+++}] b}{f_1 f_2 K_{\text{Ox}} [\text{Fe}^{+++}] + f_2 K_1 (a\text{H}^+)^2} \text{ when } l = 1 \quad (5)$$

Let C = sum of molar concentrations of ferric iron in all its forms in the solution

$$= [\text{Fe}^{+++}] + [\text{FeOH}^{++}] + [\text{FeOx}^{++}]$$

Taking $a\text{FeOH}^{++} a\text{H}^+ / a\text{Fe}^{+++} = 6 \times 10^{-3}$ (Bray and Hershey³) we find

$$C = [\text{Fe}^{+++}] + \frac{0.006 f_2 [\text{Fe}^{+++}]}{f_2 (a\text{H}^+)} + \frac{E}{\epsilon}$$

$$\therefore [\text{Fe}^{+++}] = \frac{C - E/\epsilon}{Q}, \text{ where } Q = 1 + \frac{0.006 f_2}{f_2 (a\text{H}^+)} \quad (6)$$

Substituting (6) into (5)

$$\begin{aligned} E &= \frac{\epsilon f_1 f_2 K_{\text{Ox}} b (C - E/\epsilon)}{f_1 f_2 K_{\text{Ox}} (C - E/\epsilon) + f_2 K_1 (a\text{H}^+)^2 Q} \\ \therefore K_1 &= \frac{(C - E/\epsilon) (\epsilon f_1 f_2 K_{\text{Ox}} b - E f_1 f_2 K_{\text{Ox}})}{Q E f_2 (a\text{H}^+)^2} \end{aligned}$$

(2) The value for K_2 is the converted concentration constant of K. G. Stone and L. Friedman, *THIS JOURNAL*, **69**, 209 (1947). The values for K_1 available when this work was begun were not considered reliable, and this constant was therefore determined by measuring the pH of mixtures of 8-hydroxyquinoline and hydrochloric acid. The value 1.2×10^{-5} was obtained. In the meantime, J. P. Phillips and L. L. Merritt, Jr., *THIS JOURNAL*, **70**, 410 (1948), reported the same value for K_1 ; their value was obtained spectrophotometrically.

(3) W. C. Bray and A. V. Hershey, *THIS JOURNAL*, **56**, 1889 (1934).

The values of K_1 and ϵ were obtained by fitting the equation to the curves. The following values were used for the activity coefficients⁴: $f_1 = 0.81$, $f_2 = 0.42$, $f_3 = 0.20$.

The following values for ϵ and K_1 were obtained at three different acidities

pH	ϵ	K_1
1.53	1120	3.2×10^{-15}
1.70	1020	3.2×10^{-15}
2.02	1120	2.0×10^{-15}

There appears to be no reason for giving greater weight to any particular set. The rounded averages are $\epsilon = 1090$ (645 m μ) and $K_1 = 3 \times 10^{-15}$. These figures cannot be regarded as very accurate, partly because of uncertainties in activity coefficients and the hydrolysis constant of ferric ion.

Solubility Product of Ferric Hydroxyquinolate

The approximate value of the solubility product of ferric hydroxyquinolate (needed to determine whether mixtures of ferric ion and 8-hydroxyquinoline were saturated in the experiments described above) was obtained by shaking dilute perchloric acid solutions with an excess of ferric 8-hydroxyquinolate and determining the amount of iron in solution. In some of these experiments, 8-hydroxyquinoline was added to the mixtures. The experimental work will not be described in detail, since the values obtained are considered preliminary, although adequate for the present purpose.

Difficulties were encountered in reaching equilibrium and the solid phase seemed to undergo aging which resulted in a decrease in solubility on long shaking. The values obtained varied from 1×10^{-48} to 6×10^{-47} . Account was taken of hydrolysis of ferric ion and the formation of FeOx^{++} . The figure 10^{-47} will be taken as an average value for $a\text{Fe}^{+++} (a\text{Ox}^-)^3$ in aqueous solution at 25° . Even though approximate, this value should be of use in analytical calculations, especially since the solubility products of the metal hydroxyquinolates vary over a wide range. The value of the solubility product of ferric hydroxyquinolate has not previously been reported. It is of interest that the solubility product of aluminum hydroxyquinolate has been reported as much larger (10^{-32}) than that of iron.⁵

Summary

1. 8-Hydroxyquinoline reacts with ferric ion in dilute mineral acid medium to give the green ion FeOx^{++} .

2. The dissociation constant of this complex ion is $a\text{Fe}^{+++} a\text{Ox}^- / a\text{FeOx}^{++} = 3 \times 10^{-15}$.

3. The approximate value of the solubility product of ferric hydroxyquinolate is 10^{-47} .

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(4) Interpolated from J. Kielland, *ibid.*, **59**, 1675 (1937).

(5) S. Lacroix, *Anal. Chim. Acta*, **1**, 269 (1947).