proposed to explain the weight loss anomalies encountered in the reaction of UF_4 with dry oxygen.

The extent to which this side reaction occurs during a UF_4 oxidation may be obtained from chemical analyses and weight losses. Since UO_2F_2 was found to be quite stable at the temperatures of interest, it was used as a measure of the UF_4 consumed by the reaction $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$. However, more UF_4 was consumed during an experiment than could be accounted for by UO_2F_2 formation. Hence, the amount of UF_4 involved in the side reaction was obtained by difference. Table III contains data for oxidations at various temperatures calculated on this basis. As seen from these data a considerable fraction of UF_4 is consumed by the side reaction. The scatter at each temperature is perhaps due to differences in packing of the individual powdered UF_4 samples.

TABLE III

EFFECT OF THE SIDE REACTION $UF_4 + UF_6 \rightarrow 2UF_5$ AT VARIOUS TEMPERATURES

Run	Temp. (°C.)	Initial UF_4 (g.)	UO_2F_2 produced (g.)	UF_4 consumed by reaction with O_2 (g.)	Total UF_4 consumed (g.)	UF_4 consumed by side reaction Grams	%
1	900	12.1122	4.1491	8.4310	10.8205	2.3895	22.1
2	800	6.4019	0.8789	1.7859	2.1064	0.3205	15.2
3	800	12.5406	3.0497	6.1970	8.8085	2.6115	29.6
4	800	11.0964	3.5233	7.1593	9.4626	2.3033	24.3
5	800	12.3706	1.8925	3.8456	7.8283	3.9827	50.9
6	800	18.4868	5.1336	10.4315	15.3103	4.8788	31.9
7	800	9.8120	2.7951	5.6796	7.7115	2.0319	26.3
8	800	17.2728	2.0876	4.2420	6.4917	2.2497	34.6
9	750	9.8170	2.8849	5.8621	7.8402	1.9781	25.2
10	750	5.9361	0.1186	0.2410	0.3582	0.1172	32.7
11	700	4.1478	0.3303	0.6712	0.7009	.0297	4.2
12	700	14.4736	4.5541	9.2539	9.9503	.6964	7.0
13	700	11.9810	2.9116	5.9164	8.3630	2.4466	29.2
14	700	5.9359	0.3701	0.7520	0.9977	0.2457	24.6
15	650	5.9325	.0142	0.0288	0.0924	.0636	68.8
16	600	12.9860	.6108	1.2411	1.7171	.4760	27.7
17	600	8.6912	.1089	0.2213	0.3297	.1084	32.9
18	600	10.0843	.1114	0.2264	0.7544	.5280	70.0
19	600	10.9064	.3773	0.7667	1.5500	.7833	50.5

Material balances show that neither of the following reactions accurately describes the consumption of the UF_4.

$$2UF_4 + O_2 \longrightarrow UO_2F_2 + UF_6 \qquad (1)$$

$$3UF_4 + O_2 \longrightarrow 2UF_5 + UO_2F_2 \qquad (2)$$

The observed stoichiometry lies somewhere between the case of no side reaction (eq. 1) and that of a complete back reaction with UF_6 (eq. 2).

It is also seen from Fig. 3 that UF_5 is expected to be relatively unstable in the region of 600°. Its disproportionation has been reported previously.[11] This property of UF_5 can help explain the observed deposits of uranium compounds inside a reaction vessel. UF_5 formed at high temperature by the postulated side reaction apparently decomposes at a fairly rapid rate as it is being swept out of the reaction vessel. UF_4 is deposited initially by this mechanism. However, at temperatures greater than 600°, UF_4 may be reoxidized[3] to UO_2F_2. Use of a thermocouple probe indicated that little UO_2F_2 was deposited in regions where the temperature was lower than 600°.

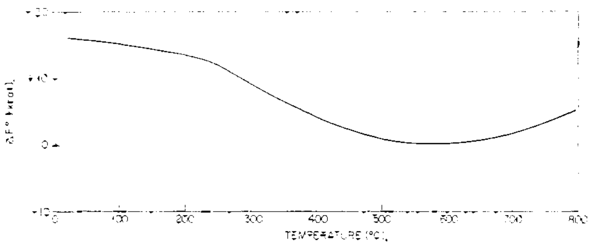

Fig. 3.—Estimates of the temperature dependence of standard free energy change for the reaction $2UF_5 \rightarrow UF_4 + UF_6$.

Deposition of UF_4 as a result of the dissociation of UF_6 is a thermodynamic impossibility.[12]

The U_3O_8 found in the system was a product of the reaction of UF_6 with quartz. This was verified by oxidizing UF_4 in a quartz reaction vessel which was lined with a protective Pt tube. In these experiments only traces of U_3O_8 were found.

Acknowledgment.—The author is indebted to Dr. R. G. Wymer and to Mr. R. E. Blanco for their helpful suggestions and discussions, and to Mr. J. F. Land and Mr. J. F. Talley who performed much of the experimental work.

[12] L. Brewer, *et al.*, USAEC Report MDDC-1543 (1945).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Cyanide–1,10-Phenanthroline Complexes of Iron(II)

BY ALFRED A. SCHILT

RECEIVED JUNE 21, 1957

Iron(II) has been shown to form the tetracyano-mono-(1,10-phenanthroline)-ferrate(II) ion and the neutral dicyano-bis-(1,10-phenanthroline)-iron(II) complex. The visible absorption characteristics of these complexes have been determined, and a spectrophotometric investigation of the equilibria involved in their formation has been made.

Introduction

The interference of cyanide ion in the colorimetric determination of iron by 1,10-phenanthroline and related compounds[1,2] constitutes a limitation to such applications. The following investigation was carried out in order to establish the nature of this interference and to provide information useful for the development of analytical procedures suitable for the determination of iron and cyanide ions in the presence of each other.

Experimental

Apparatus and Materials Used.—All spectrophotometric measurements were made employing a Cary Recording Spectrophotometer (Model 11), matched silica stoppered cells of path length 1.000 ± 0.001 cm., and slit widths ranging from 0.01 to 0.02 mm. over the wave length region scanned.

The 1,10-phenanthroline monohydrate was obtained from the G. Frederick Smith Chemical Company. Eastman Kodak Company (white label) *m*-dinitrobenzene and hydroxylamine hydrochloride were used without further purification. All other chemicals were reagent grade.

Identification of Dicyano-bis-(1,10-phenanthroline)-iron (II).—Preliminary studies disclosed that a dark violet precipitate is gradually produced from aqueous solutions con-

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[1] W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

[2] A. A. Schilt and G. F. Smith, *Anal. Chem.*, **28**, 809 (1956).

taining cyanide ion and ferroin (tris-(1,10-phenanthroline)-iron(II) ion). The rate of precipitation is quite slow at room temperature; however if the solutions are kept at elevated temperatures before cooling to room temperature the precipitation time is diminished appreciably. These observations indicate that a complex between iron(II), cyanide ion and 1,10-phenanthroline is produced rather than an insoluble cyanide salt of ferroin. In order to confirm this, as well as to establish the identity of the insoluble complex, a continuous variation study was made to determine the stoichiometry involved in the formation of the complex. In addition, the molecular weight of the complex was measured cryoscopically to distinguish between the several possible forms.

The method employed for determining the stoichiometry of the reaction was that of Vosburgh and Cooper.[3] Freshly prepared solutions of 5.00×10^{-4} *M* ferroin sulfate and 5.00×10^{-4} *M* potassium cyanide, each containing 0.01 mole of hydroxylamine hydrochloride and one mole of ammonium hydroxide per liter, were used. 10.0 ml. samples, prepared by mixing measured volumes of these two solutions, were heated in a boiling water-bath for one hour to promote reaction. After cooling, each sample was extracted three times with 3-ml. portions of chloroform, the extracts were combined in 10-ml. volumetric flasks, and the contents were diluted to volume with ethanol. The spectrophotometric measurements obtained of the chloroform solutions (refer to Fig. 1) indicate that two moles of cyanide ion react with one mole of ferroin to produce the complex. The formation of $\mathrm{Fe(CN)_6^{-4}}$ also appears to be indicated by the data shown in Fig. 1 since the curves intercept the abscissa at a mole fraction of KCN equal to 0.85.

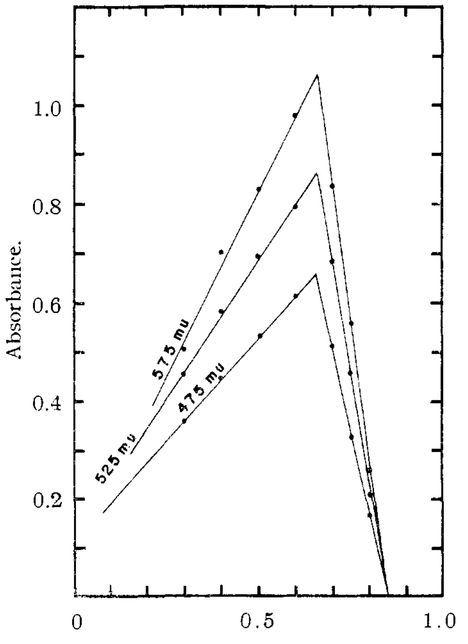

Fig. 1.—Identification of $\mathrm{FePh_2(CN)_2}$ by continuous variations applied to KCN and $\mathrm{FePh_3^{++}}$.

A sample of the solid complex was prepared and purified for subsequent studies. 0.02 mole of solid potassium cyanide was dissolved in one liter of 0.01 *M* ferroin sulfate and after standing overnight the mixture was filtered to obtain the product. No attempt was made to obtain a quantitative yield. The product proved to be only moderately soluble in ordinary solvents. It was dissolved in hot ethanol and precipitated by a several fold dilution with water. It was then subjected to continuous extraction with chloroform in a Soxhlet apparatus. The extracted product, which recrystallized in the flask during the reflux period, was filtered off and dried at 110°.

The most suitable solvent found for the cryoscopic molecular weight determination of the insoluble complex was *m*-dinitrobenzene. Other solvents, commonly employed for such determinations, either did not dissolve sufficient quantities of the complex or caused apparent dissociation as evidenced by the dark violet colored solid giving rise to red solutions. A differential thermometer, calibrated in 0.01°, was used to measure the small changes in freezing point (limited solubility precluded greater freezing point depressions). In 30.0-g. samples of the solvent 76.0, 60.0 and 30.0 mg. of the complex caused respective freezing point depressions of 0.056, 0.045 and 0.030°. The average value of the molecular weight, using 10.6 as the molal freezing point constant,[4] is 435.

Although the experimental value of the molecular weight is based upon measurements subject to rather large relative error, the reliability of its use to distinguish between various possible formulas of the complex should be satisfactory. The formula $\mathrm{[FePh_2(CN)_2]}$ corresponding to a molecular weight of 468 more closely agrees with the data and other observations than does either $\mathrm{[FePh_3][FePh(CN)_4]}$ or $\mathrm{[FePh_3](CN)_2}$.

Identification of the Tetracyano-mono-(1,10-phenanthroline)-ferrate(II) Ion.—The identification of this complex ion was accomplished by a continuous variation study.[3] Fresh solutions of 1.00×10^{-3} *M* potassium hexacyanoferrate(II) and 1.00×10^{-3} *M* 1,10-phenanthroline, each containing 0.1 mole of hydroxylamine hydrochloride and one mole of ammonium hydroxide per liter were employed. 10.0-ml. samples, prepared by mixing measured volumes of these two solutions, were heated in a boiling water-bath for one hour to promote reaction. After cooling and readjusting their volumes to 10.0 ml. with distilled water the samples were examined spectrophotometrically. The data plotted as shown in Fig. 2 indicate the stoichiometry

$$\mathrm{Fe(CN)_6^{-4} + Ph = FePh(CN)_4^{-2} + 2CN^-}$$

The reactions given below also were shown to occur; however, the data relating to these have been omitted here since the identity of the complexes involved is not in question.

$$\mathrm{Fe(CN)_6^{-4} + 2Ph = FePh_2(CN)_2 + 4CN^-}$$
$$\mathrm{Fe(CN)_6^{-4} + 3Ph = FePh_3^{++} + 6CN^-}$$

Visible Absorption Characteristics of Dicyano-bis-(1,10-phenanthroline-)-iron(II).—Known concentrations of the complex could be prepared directly from weighed quanti-

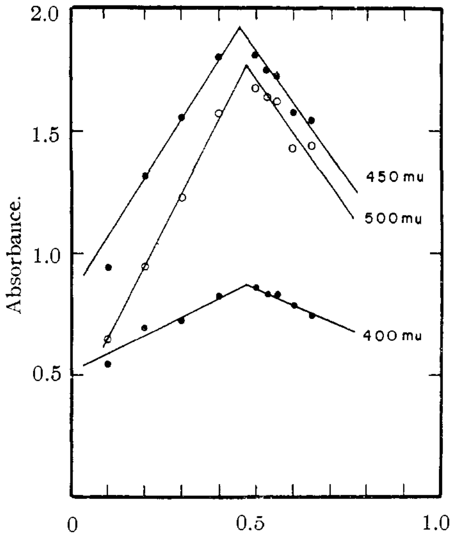

Fig. 2.—Identification of $\mathrm{FePh(CN)_4^{=}}$ by continuous variations applied to $\mathrm{K_4Fe(CN)_6}$ and 1,10-phenanthroline.

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

[4] W. T. Smith and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 68.

ties of the solid material as a result of its isolation and purification. The visible absorption spectra of the complex were found to be considerably influenced by the nature of the solvent, as illustrated in Fig. 3. Such behavior appears to be related to the dielectric strength of the solvent rather than to its acidic character.

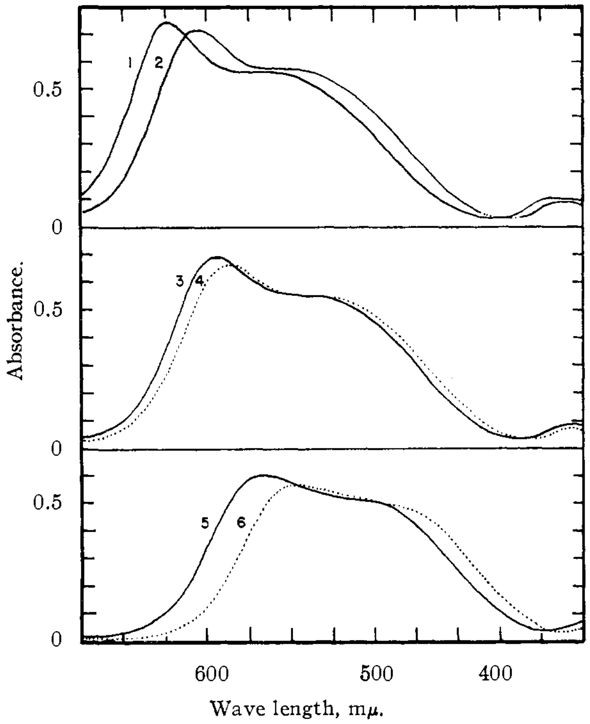

Fig. 3.—Spectra of equal formal concentrations (1.04 × 10^{-4} mole per liter) of $FePh_2(CN)_2$ in chloroform (curve 1), in 4 vol. chloroform and 1 vol. ethanol (curve 2), in 2 vol. chloroform and 3 vol. ethanol (curve 3), in ethanol (curve 4), in 3 vol. ethanol and 2 vol. water (curve 5), and in 1 vol. ethanol and 4 vol. water (curve 6).

The molar absorptivities of the complex as a function of wave length were determined in chloroform and also in absolute ethanol. Beer's law was found to govern the absorbance of the complex in both solvents throughout the concentration range (0–10^{-4} mole per liter) and the wave length region (400–650 mμ) employed. The results presented in Fig. 4 are average values taken from the Beer's law study.

Visible Absorption Characteristics of the Tetracyano-mono-(1,10-phenanthroline)-ferrate(II) Ion.—Standard solutions of the complex were prepared for spectrophotometric examination in the following manner. Measured volumes of 1.00 × 10^{-3} *M* 1,10-phenanthroline and 1.0 × 10^{-3} *M* potassium hexacyanoferrate(II) (both solutions contained one mole of ammonium hydroxide and 0.1 mole of hydroxylamine hydrochloride per liter) were mixed and then heated in a boiling water-bath for two hours to promote complete reaction. The solutions were cooled, diluted to 25.0 ml. with distilled water and measured spectrophotometrically.

The data are given in Table I. Concentrations of FePh-$(CN)^-_4$ in the final solutions are based upon the amount of 1,10-phenanthroline added, assuming the reaction to be essentially quantitative. To encourage this end an excess of hexacyanoferrate(II) ion was employed. The measured absorbancies were corrected for the absorbancies due to the known excesses of hexacyanoferrate(II) ion. The conformance of the results in Table I to Beer's law is evidence for the essentially quantitative nature of the reaction and for the validity of the absorbance corrections employed. The molar absorptivity of $FePh(CN)_4^=$ as a function of wave length is shown in Fig. 5; each point shown is the average value of the six determinations.

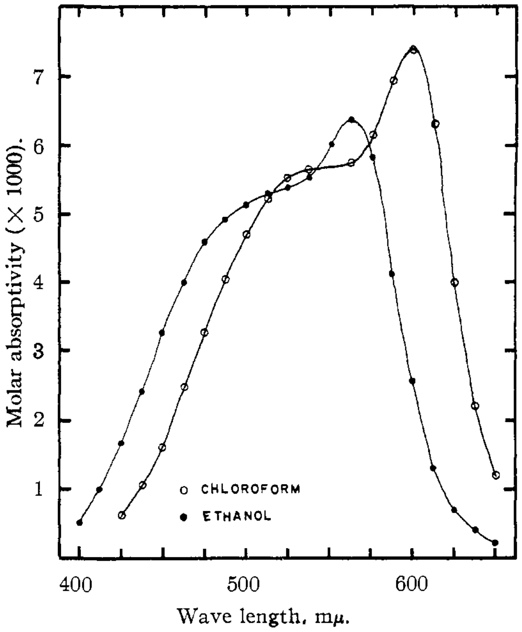

Fig. 4.—Molar absorptivity of $FePh_2(CN)_2$ as a function of wave length and solvent.

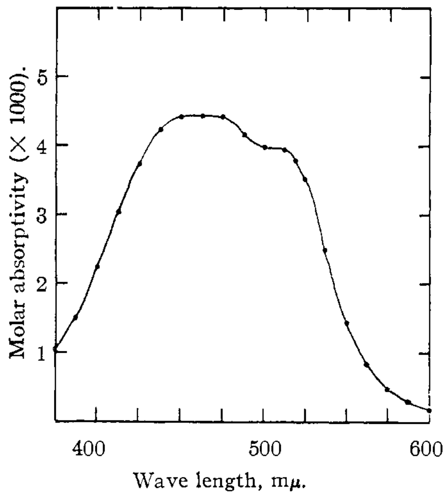

Fig. 5.—Molar absorptivity of $FePh(CN)_4^=$ as a function of wave length.

The Solubility Product (or Disproportionation Constant) of Dicyano-bis-(1,10-phenanthroline)-iron(II).—The dark violet complex $FePh_2(CN)_2$ is only slightly soluble in aqueous solutions giving rise to light orange colored solutions. An examination of the absorption spectra indicates that the

TABLE I

SPECTRAL DATA ON THE TETRACYANO-MONO-(1,10-PHENANTHROLINE)-FERRATE(II) ION

Molar concn. × 10^4		Measd. absorbancies		Molar absorptivities of $FePh(CN)_4^=$	
FePh-$(CN)_4^{-2}$	$Fe(CN)_6^{-4}$	At 450 mμ	At 510 mμ	At 450 mμ	At 510 mμ
0.00	10.00	0.535	0.100	..	..
2.80	4.40	1.462	1.150	4393	3950
2.40	5.20	1.343	1.010	4450	3991
2.00	6.00	1.270	0.870	4775	4050
1.60	6.08	1.070	.710	4456	4013
1.20	7.60	0.895	.542	4142	3900
0.80	8.40	0.793	.400	4412	3950
			Av.	4438	3976

TABLE II

VERIFICATION OF THE SOLUBILITY PRODUCT RELATIONSHIP

Soln. satd. with $FePh_2CN_2$ at 25°	Absorbancies At 450 mμ	At 510 mμ	Molar concn. × 10^6 of $FePh_3^{++}$	$FePh(CN)_4^{=}$	Ion product × 10^{10}
0.1 *M* KCl	0.151	0.170	0.92	1.70	1.6
.1 *M* KCN	.187	.207	1.05	2.27	2.4
.1 *M* NaOH	.137	.153	0.80	1.60	1.3
.1 *M* NH_4OH (*p*H 11.3)	.140	.156	.81	1.65	1.3
.1 *M* NH_4OH + 0.1 *M* NH_4Cl (*p*H 9.7)	.130	.149	.86	1.30	1.1
.1 *M* $NH_4C_2H_3O_2$ (*p*H 7.0)	.151	.170	.92	1.70	1.6
.1 *M* $HC_2H_3O_2$ + 0.1 *M* $NaC_2H_3O_2$ (*p*H 4.6)	.175	.205	1.28	1.58	2.0
.1 *M* NaOH + 0.01 *M* Ph	.225	.264	1.65	2.02	3.3
.1 *M* NaOH + 0.1 *M* KCN	.140	.158	0.86	1.56	1.3
.1 *M* NaOH + 0.010 *M* KCN + 0.002 *M* Ph	.138	.161	0.99	1.28	1.3
.1 *M* NaOH + 0.001 *M* KCN + 0.002 *M* Ph	.132	.161	1.13	0.89	1.0
.1 *M* NaOH + 0.001 *M* KCN + 0.010 *M* Ph	.235	.258	1.26	2.96	3.7
.1 *M* $NH_4C_2H_3O_2$ + 0.01 *M* KCN + 0.001 *M* Ph	.140	.158	0.86	1.56	1.3

following disproportionation reaction occurs on dissolution of the complex in water

$$2FePh_2(CN)_2 = FePh_3^{++} + FePh(CN)_4^{=}$$

Quantitative verification of this reaction was possible by spectrophotometric means since the two complex ions in question exhibit different absorption characteristics.

Saturated solutions of $FePh_2(CN)_2$ were prepared by adding an excess of the solid complex to various aqueous solutions which were then agitated at 25° for several hours. A simultaneous determination of the $FePh_3^{++}$ and $FePh(CN)_4^{=}$ concentrations was achieved by measuring the absorbancies of the solutions at 510 and 450 mμ. These values are related to the individual concentrations and molar absorptivities of the complexes. The molar absorptivities of $FePh_3^{++}$ were determined at 450 mμ and 510 mμ: they are 8150 and 11100, respectively. Corresponding values for $FePh(CN)_4^{=}$ are given in Table II. Concentrations of the complex ions were calculated using the following expressions, which can be derived from the molar absorptivities of the complexes.

$$[FePh_3^{++}] = 2.62 \times 10^{-4} A_{510m\mu} - 2.34 \times 10^{-4} A_{450m\mu}$$

$$[FePh(CN)_4^{=}] = 6.54 \times 10^{-4} A_{450m\mu} - 4.81 \times 10^{-4} A_{510m\mu}$$

The data of these experiments, given in Table II, indicate that the solubility of $FePh_2(CN)_2$ in aqueous solutions is governed by the product of the concentrations of $FePh_3^{++}$ and $FePh(CN)_4^{=}$.

Measurements of the solubility of $FePh_2(CN)_2$ in pure water at 10, 25 and 40° were made to determine the solubility product and its temperature dependence. The data are given in Table III. These measurements were taken after prolonged agitation periods at constant temperature. The reversibility of the dissolution reaction was tested by approaching the equilibrium at 25° from 0° and also from 40°; it was found to be reversible within the sensitivity of the measurements.

TABLE III

SOLUBILITY PRODUCT DETERMINATION FOR DICYANO-BIS-(1,10-PHENANTHROLINE)-IRON(II) IN WATER

Absorbance At 10° 450 mμ	 510 mμ	 At 25° 450 mμ	 510 mμ	 At 40° 450 mμ	 510 mμ	K_{sp} × 10^{10} 10°	 25°	 40°
0.091	0.100	0.150	0.168	0.243	0.275	0.55	1.54	4.07
.085	.095	.151	.168	.244	.277	.50	1.54	4.04
.066	.074	.143	.160	.237	.262	.30	1.41	3.83
.074	.080	.141	.157	.238	.269	.36	1.35	3.89
.065	.083	.139	.159	.263	.297	.17	1.31	4.73
.059	.067	.125	.140	.243	.275	.26	1.07	4.04
					Av.	0.4	1.4	4.1

Discussion

It would be possible to deduce the equilibrium constants of the following reactions from the solubility data obtained in this investigation provided that all equilibria conditions were satisfied at the time of measurement.

$$FePh_2(CN)_2 + Ph = FePh_3^{++} + 2CN^- \qquad (K_1) \quad (1)$$

$$FePh_2(CN)_2 + 2CN^- = FePh(CN)_4^{=} + Ph \qquad (K_2) \quad (2)$$

$$2FePh_2(CN)_2 = FePh_3^{++} + FePh(CN)_4^{=} \qquad (K_3) \quad (3)$$

$$FePh_3^{++} + 4CN^- = FePh(CN)_4^{=} + 2Ph \qquad (K_4) \quad (4)$$

$$FePh(CN)_4^{=} = Fe^{++} + Ph + 4CN^- \qquad (K_5) \quad (5)$$

$$FePh_2(CN)_2 = Fe^{++} + 2Ph + 2CN^- \qquad (K_6) \quad (6)$$

The equilibrium constants of these reactions show the relationships

$$[FePh_3^{++}]/K_1 = [Ph]/[CN^-]^2 = K_2/[FePh(CN)_4^{=}] \quad (a)$$

$$K_3 = K_1K_2 \quad (b)$$

$$K_4 = K_2/K_1 \quad (c)$$

$$K_5 = \frac{K_i \text{ for } FePh_3^{++}}{K_4} \quad (d)$$

$$(K_i \text{ for } FePh_3^{++} \text{ at } 25° = 5 \times 10^{-22})^5$$

$$K_6 = K_1K_i \text{ for } FePh_3^{++} \quad (e)$$

Reactions 1, 2 and 4 were observed to be sluggish indicating that 1,10-phenanthroline and cyanide ligands undergo exchange reactions very slowly at room temperature. The lack of conformity to expression (a) of the data obtained on solutions of known concentrations of 1,10-phenanthroline and cyanide ion is another indication of slow exchange processes. Equilibrium in reaction 3, however, can be attained independently of equilibria in reactions 1 and 2; this is particularly true if some mechanism is involved in the disproportionation of $FePh_2(CN)_2$ other than that represented by equations 1 and 2. Since dissolution of the complex occurs quite rapidly and because precautions were observed to attain saturated conditions the solubility (or disproportionation) constants obtained are considered to be reliable equilibrium constants.

TABLE IV

APPROXIMATED EQUILIBRIUM CONSTANTS

Constant	Approximated values At 10°	 At 25°	 At 40°
K_1	6×10^{-6}	1×10^{-5}	2×10^{-5}
K_2	6×10^{-6}	1×10^{-5}	2×10^{-5}
K_3	4×10^{-11}	1.4×10^{-10}	4.1×10^{-10}
K_4	1	1	1
K_5	....	5×10^{-22}	....
K_6	....	5×10^{-27}	....

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(5) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948)

Insofar as this is true, the mechanism of the disproportionation reaction does not appear to involve either 1,10-phenanthroline or the cyanide ion.

Attempts to measure the equilibrium constants for reactions 1, 2 and 4 directly were unsuccessful. In view of the experimental difficulties involved in the study of these equilibria it seems justifiable to make use of an approximation to at least obtain the order of magnitude of their equilibrium constants. The approximation is based on the assumption that the $FePh_3^{++}$ and $FePh(CN)_4^-$ ions are the predominating ionic species produced when pure water is saturated with respect to $FePh_2(CN)_2$. In this event their concentrations are approximately equal because of electrical neutrality considerations, and K_1 and K_2 are approximately equal. Values for the various constants approximated in this manner are presented in Table IV.

The possible analytical applications of the reactions revealed by this investigation are receiving further attention and will be described at an early date.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM U. S. GEOLOGICAL SURVEY]

A Fluorimetric Study of the Thorium-Morin System

BY ROBERT G. MILKEY AND MARY H. FLETCHER

RECEIVED MAY 23, 1957

Thorium reacts with morin to yield a yellow complex that fluoresces when irradiated with ultraviolet light. The effect on the fluorescence of such variables as concentration of acid, alcohol, thorium, morin, and complex; time, temperature and wave length of exciting light are studied to determine experimental conditions yielding maximum fluorescence. The effects of Zr^{+4}, Al^{+3}, Fe^{+3}, Ca^{+2} and La^{+3} are discussed. The fundamental relationships between light absorption and fluorescence are expressed in a general equation that applies to a three-component system when the fluorescence is measured in a transmission-type fluorimeter. This general equation is used to obtain an expression for the fluorescence of the thorium-morin system. Equations, derived from experimental data, relate both the fraction of thorium reacted to form complex and the fraction of unquenched fluorescence to the concentration of uncombined morin. These functions, when combined with the general equation, give an expression which relates the total net fluorescence to the amount of uncombined morin in the solution. This last equation can be used to determine the one region for the concentration of uncombined morin that gives maximum sensitivity for the system. Calculated standard curves are in good agreement with experimental curves.

Introduction

Morin reacts with thorium in weakly acid solutions[1-4] to form a stable yellow complex that fluoresces yellow-green when its solutions are irradiated with ultraviolet light. Both the color and fluorescence of this complex have been investigated.

The results of the spectrophotometric study have been presented in an earlier paper[5] which evaluates the color system as a basis for the quantitative determination of trace amounts of thorium.

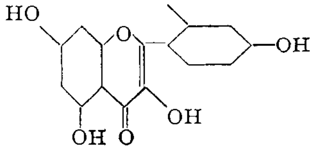
This paper evaluates the fluorescent system as a basis for the quantitative determination of trace amounts of thorium. Some of the theoretical and mathematical relationships between fluorescence and light absorption, as exhibited in the thorium-morin system, are also included. This report is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

Characteristics of Thorium-Morin System

The reaction between thorium and morin occurs in slightly acid solution according to the equation

$$ThX_4 + 2M{\cdot}H \rightleftarrows ThM_2X_2 + 2HX \qquad (1)$$

where M·H is morin (5,7,2′,4′-flavanol) having the structure



and X is a univalent negative ion such as Cl^- or NO_3^-. The reaction is instantaneous and results in the formation of a single, yellow, stable complex having a molar ratio of Th:M of 1:2.

The equilibrium constant for the reaction, according to the equation

$$K_{\text{equil}} = \frac{[ThM_2^{+2}][H^+]^2}{[Th^{+4}][M{\cdot}H]^2} \qquad (2)$$

is approximately 1×10^6 (5).

Solutions of the complex fluoresce a bright green when irradiated with long wave length ultraviolet light.[1-4] The wave length band of the fluorescent light ranges from approximately 488 to 555 mμ, with peak intensity between 513 and 533 mμ, as determined by visual inspection with a spectroscope (personal communication, H. Jaffe, U. S. Geological Survey, and C. E. White, Univ. of Maryland, 1952).

Absorption spectra for solutions of the complex (curve B) and for pure morin (curve A) are presented in Fig. 1. The region between the dotted lines in this figure indicates the wave length band of the fluorescent light. The fluorescence occurs in that part of the spectrum in which light is transmitted virtually completely by both the complex and morin. Moreover, solutions with thorium concentrations as large as 50 mg. of ThO_2 per 50 ml. also completely transmit all light in this spectral region. The spectra indicate that light having a wave length near 410 mμ would be advantageous for the production of fluorescence, and such light (404.7 mμ) was used to establish the experimental conditions.

Experimental Data

Apparatus and Reagents. **Transmission Fluorimeter.**—The transmission fluorimeter, especially built for this study, is arranged so that the light source, sample cell and photo-

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(1) H. Gôto, *J. Chem. Soc. Japan*, **59**, 625 (1933).

(2) H. Gôto, *Tohoku Imp. Univ. Sci. Repts.*, **1st ser.**, 287 (1940–1941).

(3) H. H. Willard and C. A. Horton, *Anal. Chem.*, **22**, 1190 (1950).

(4) H. H. Willard and C. A. Horton, *ibid.*, **22**, 1194 (1950).

(5) M. H. Fletcher and R. G. Milkey, *ibid.*, **28**, 1402 (1956).