

The Thermodynamics of Formation of tris-*o*-Phenanthroline-Iron Complexes in Solution

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From spectrophotometric measurements the thermodynamic functions for the formation of *o*-Phenanthroline ion and tris-*o*-Phenanthroline-Iron(II) complex have been determined. Using the present values for tris-*o*-Phenanthroline-Iron(II) complex and E° of the Fe^{II} - and Fe^{III} -Phenanthroline couples from literature, the thermodynamic functions for the ferric complex has been calculated. These are:

	ΔF at 25°C in kcal · mole ⁻¹	ΔH in kcal · mole ⁻¹	ΔS in e.u.
$H^+ + oPh \rightleftharpoons o-PhH^+$	- 6.90 (± 0.02)	- 4.07 (± 0.25)	9.5 (± 1.5)
$Fe^{2+} + 3 o-Ph \rightleftharpoons FePh_3^{2+}$	-27.94 (± 0.05)	-31.32 (± 0.66)	-11.3 (± 3.5)
$Fe^{3+} + 3 o-Ph \rightleftharpoons FePh_3^{3+}$	-18.81 (± 0.11)	- 9.9 (± 0.8)	29.0 (± 4.0)

The complexes of iron with *o*-Phenanthroline, Ferroin and Ferri-in, are well-known for their use in analytical chemistry. The dissociation constants of the ligand *o*-Phenanthroline ion, ferroin and also ferri-in have been determined by a number of workers using different techniques. The values are so very different from one another that it becomes difficult to choose the best one. Recently IRVING and MELLOR¹ have determined the stability constants of the complexes of *o*-Phenanthroline with a number of metal ions. In view of the discrepancies in the earlier determinations they have given a list of preferred values. No attempt, however, appears to have been made to determine the other thermodynamic properties (dissociation constant gives only ΔF at that temperature) of the complexes.

¹ H. IRVING and D. H. MELLOR, J. chem. Soc. [London] 1962, 5222.

NASANEN and UUSITALO², using a glass and a $Ag-AgCl$ electrode, have determined ΔH and ΔS for *o*-Phenanthrolium ion.

In the present communication, we report the ΔH and ΔS for ferroin, *o*-Phenanthrolium ion, and Ferriin. The stability constants of *o*-Phenanthrolium and ferroin have been determined spectrophotometrically at three different temperatures. As direct evaluation of the stability constant of Ferriin is not possible, for getting ΔH and ΔS for ferroin, we have used the data of GEORGE, HANANIA and IRVINE³ who from the measurement of e.m.f.'s at different temperatures of Ferroin—Ferriin couple, report a value for $\bar{S}_{\text{Ferroin}} - \bar{S}_{\text{Ferriin}}$.

Experimental

Ferrous-perchlorate was prepared by dissolving Ironwire (A.R.Riedel) in about .5 to .7 M solution of perchloric acid (G.R.-E. Merck) in an atmosphere of Nitrogen. The iron-content was determined in the usual way with standard dichromate.

o-Phenanthroline perchlorate was prepared by direct weighing and dissolving *o*-Phenanthrolinehydrate (G.R.-E. Merck) in more than one equivalent of $HClO_4$.

For the determination of dissociation constant of Phenanthrolium ion, Sodium-acetate—Acetic acid (WALPOLE⁴) buffers were used. All other chemicals were of reagent grade.

For the determination of dissociation constant of Phenanthrolium ion, the optical densities (o.d.) of various solutions of Phenanthrolium ion were measured in the u.v. and visible regions. No absorption was found to occur in the visible region.

The u.v. spectra of the anion and that of neutral molecule were measured in excess acid ($HClO_4$) solution and in excess alkali ($NaOH$) solution.

To ascertain the effect of different anions on Phenanthrolium ion, o.d. measurements of Phenanthroline in $N/10 HClO_4$, $N/10 HCl$, $N/10 H_2SO_4$ and $N/10 CH_3COOH$ were made. The nature of the curves were same and the optical density at the peak did not change.

At first an approximate value of pK is obtained by measuring o.d. at different pH 's at 255 $m\mu$ and 260 $m\mu$, o.d.'s of ionic and molecular

² R. NASANEN and E. UUSITALO, *Soumen Kemistilehti*, **29B**, No. 2 (1956) 11.

³ P. GEORGE, G. I. H. HANANIA and D. H. IRVINE, *J. chem. Soc. [London]* **1959**, 2548.

⁴ H. T. S. BRITTON, *Hydrogen Ions Vol. I*, Fourth Ed., p. 357, Van Nostrand Inc. N. Y., 1956.

species being known. This gave a value of pK about 4.8. For an accurate determination of pK the o.d.'s of *o*-Phenanthroline ($2 \times 10^{-5}M$) in a number of buffers with pH 's ranging from 4.4 to 5.4 and in $N/10 HClO_4$ and $N/10 NaOH$ were measured. The blank solutions were of the same composition as in the experimental solutions except *o*-Phenanthroline. Optical densities of the solutions were measured at three different temperatures, viz., 25°C, 33°C and 45°C and at wavelengths 255 m μ and 260 m μ with cells interchanged. Although cells were matched this was done to be sure that no error crept in due to the cell becoming dirty during the course of work.

No attempt has been made to determine the composition of the complex in the mixture since it was established by BLAU⁵ that in Ferriin three Phenanthroline molecules were bound to Fe^{2+} ion. It was established by GOULD and VOSBURGH⁶ that $FePh^{2+}$ and $FePh_2^{2+}$ were not present in spectrophotometrically detectable amounts. KOLTHOFF and co-workers⁷ also report that $FePh_2^{2+}$ is very unstable and $FePh^{2+}$ is formed only in presence of large excess of Fe^{2+} having a broad absorption maximum between 400 to 460 m μ and having no absorption in 510 to 520 m μ region and beyond.

The extinction coefficients, ϵ , of the Ferrous-orthophenanthroline complex were determined from the measurement of o.d.'s of solutions containing 6 to 50 fold excess of Phenanthroline to different amounts of Fe^{2+} ion at those wavelengths. Under the condition the concentration of the complex could be taken equal to the Ferrous ion. This was further confirmed by the fact that for the same concentration of ferrous ion and 6 to 30 fold excess of *o*-Phenanthroline, the o.d. reading were same.

For the determination of stability constants, o.d.'s of solutions containing different amounts of Ferrous perchlorate and *o*-Phenanthroline perchlorate were measured. The pH 's ranged from 2.0 to 3.5. Measurements were made at 25°C, 33°C and 45°C respectively (where 33°C represents average room temperature). Since " ϵ " at 510 and 520 m μ were known, concentrations of Ferriin could be determined from the o.d. of the mixtures.

Extinction coefficient measurements in presence of excess $NaClO_4$ concentrations as well as determinations of o.d. of solutions containing

⁵ F. BLAU, *Monatsh.* **19** (1898) 666.

⁶ R. K. GOULD and W. C. VOSBURGH, *J. Amer. chem. Soc.* **64** (1942) 1630.

⁷ I. M. KOLTHOFF, D. L. LEUSSING and T. S. LEE, *J. Amer. chem. Soc.* **72** (1950) 2173.

$Fe(ClO_4)_2$ and *o*-Phenanthroline ($10^{-3}M$) in high perchloric acid concentrations could not be performed as red-precipitates of ferrous-*o*-phenanthroline perchlorate were formed.

All optical density measurements were taken with a Beckmann-D.U. Quartz spectrophotometer fitted with thermostated cell-holder and the *pH*-measurements with a Cambridge-bench type *pH*-meter.

Results

Dissociation constant of Phenanthrolium ion

The thermodynamic dissociation constant K_T for the equilibrium, $PhH^+ \rightleftharpoons Ph + H^+$ (where *Ph* is *o*-Phenanthroline) is represented by

$$K_T = \frac{\alpha_{Ph} \cdot \alpha_{H^+}}{\alpha_{PhH^+}} = \frac{c_{Ph} \cdot c_{H^+}}{c_{PhH^+}} \cdot \frac{f_{Ph} \cdot f_{H^+}}{f_{PhH^+}} \quad (1)$$

or

$$pK_T = pH + \log \frac{c_{PhH^+}}{c_{Ph}} + \log f_{PhH^+} \quad (2)$$

(Since *Ph* is uncharged)

This becomes,

$$pK_T = pH + \log \frac{d - d_M}{d_1 - d} + \log f_{PhH^+} \quad (3)$$

or

$$pK_T = pK + \log f_{PhH^+} \quad (3a)$$

in case of *o*-Phenanthroline where $d =$ o.d. of the mixture of ion and molecule at the analytical wavelength,

$d_M =$ o.d. of the molecule at the same wavelength

and

$d_1 =$ o.d. of the ion at the same wavelength.

Since the *pH*'s of the buffer solutions are known and do not vary with temperature, thus from measurements of d_M , d_1 and d at different *pH*'s at the analytical wavelengths, the pK values can be calculated.

The thermodynamic values pK_T were calculated using DEBYE-HÜCKEL limiting law as well as the DEBYE-HÜCKEL equation containing the ionic radius term taking $\alpha^\circ = 9 \text{ \AA}$ (the highest value of α° from KOLTHOFF's data⁸ on f_{PhH^+} for *o*-Phenanthroline ion using DEBYE-HÜCKEL equation). These values are given in Table 1.

⁸ T. S. LEE, I. M. KOLTHOFF and D. L. LEUSSING, J. Amer. chem. Soc. **70** (1948) 2348.

Determination of Dissociation Constants of Ferroin

As was observed by KOLTHOFF⁸ et al. Phenanthroline may be regarded as a monoacid-base and in *pH*'s less than 3, Phenanthroline is present mainly as PhH^+ . The equilibrium between Ferroin and a strong acid may be represented as,



Thus,

$$K_a = \frac{\alpha_{Fe^{2+}} \cdot (\alpha_{PhH^+})^3}{\alpha_{FePh_3^{2+}} \cdot (\alpha_{H^+})^3} = \frac{(c_{Fe^{2+}})(c_{PhH^+})^3}{(c_{FePh_3^{2+}})(c_{H^+})^3} \cdot \frac{f_{Fe^{2+}} \cdot f_{PhH^+}^3}{f_{FePh_3^{2+}} \cdot f_{H^+}^3} \quad (5)$$

If $f_{Fe^{2+}} = f_{FePh_3^{2+}}$ and $f_{PhH^+} = f_{H^+}$, K_c becomes equal to K_a . But since PhH^+ is likely to have much larger size, it may be that $f_{PhH^+} \neq f_{H^+}$ which would need an accurate determination of f_{PhH^+} .

In order to avoid this, we have worked in solutions of μ of the order of $10^{-3}M$, where it is reasonable to assume $f_{Fe^{2+}} = f_{FePh_3^{2+}}$ and $f_{PhH^+} = f_{H^+}$. Thus K_c becomes equal to thermodynamic equilibrium constant K_a . In our experiments we get the activity of hydrogen ion from direct measurements. So the equation we use, will be:

$$K_a = \frac{c_{Fe^{2+}} \cdot (c_{PhH^+})^3}{c_{FePh_3^{2+}} \cdot (\alpha_{H^+})^3} \cdot f_{PhH^+}^3 \quad (6)$$

The concentration of Phenanthrolium ion is calculated from

$$\begin{aligned} Ph_t &= 3(FePh_3^{2+}) + PhH^+ + Ph \\ \text{i.e. } PhH^+ &= Ph_t - 3(FePh_3^{2+}) - Ph \end{aligned} \quad (7)$$

where Ph_t = Total concentration of Phenanthroline,

PhH^+ = Phenanthroline present as Phenanthrolium ion.

Ph = unionized Phenanthroline.

Ph is calculated where necessary using the relation

$$pK = pH + \log \frac{(PhH^+)}{(Ph)} \quad (8)$$

taking appropriate pK values given in Table 1. The concentration of Fe^{2+} is calculated from the relation $(Fe^{2+}) = (Fe^{2+})_t - (FePh_3^{2+})$ (9)
 Fe_t^{2+} = Total initial concentration of Fe^{2+} .

The H^+ ion activity is determined from *pH*-measurements. The activity coefficient of Phenanthrolium ion is calculated from DEBYE-HÜCKEL limiting law as well as from DEBYE-HÜCKEL equation using the value of $\alpha^\circ = 9A^\circ$.

Table 1

System	Temp. °C	Thermodynamic Equilibrium Constant	
		Using Limiting DEBYE-HÜCKEL equation	Using DEBYE-HÜCKEL equation with $\alpha^\circ = 9A^\circ$
$PhH^+ \rightleftharpoons Ph + H^+$	25	$1.099 (\pm 0.048) \times 10^{-5}$	$0.889 (\pm 0.05) \times 10^{-5}$
	33	$1.291 (\pm 0.03) \times 10^{-5}$	$1.039 (\pm 0.04) \times 10^{-5}$
	45	$1.702 (\pm 0.08) \times 10^{-5}$	$1.377 (\pm 0.11) \times 10^{-5}$
$*FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+$	25	$4.495 (\pm 0.34) \times 10^{-6}$	$4.565 (\pm 0.35) \times 10^{-6}$
	33	$12.29 (\pm 0.61) \times 10^{-6}$	$12.59 (\pm 0.63) \times 10^{-6}$
	45	$34.34 (\pm 2.8) \times 10^{-6}$	$34.86 (\pm 2.9) \times 10^{-6}$
$*FePh_3^{3+} \rightleftharpoons Fe^{2+} + 3Ph$	25	5.96×10^{-21}	3.20×10^{-21}
	33	26.44×10^{-21}	14.1×10^{-21}
	45	169.2×10^{-21}	91.0×10^{-21}

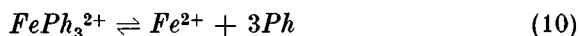
* The values are average from at least 10 measurements at wavelength 510 m μ as well as 520 m μ .

Table 2

System	ΔF at 25° in Kcal/mole	ΔH in Kcal/mole	ΔS in e.u.
$Ph + H^+ \rightleftharpoons PhH^+$	- 6.90 (± 0.02)	- 4.07 (± 0.25)	9.5 (± 1.5)
$Fe^{2+} + 3PhH^+ \rightleftharpoons FePh_3^{2+} + 3H^+$	- 7.28 (± 0.04)	- 19.27 (± 0.5)	- 40.2 (± 2.8)
$3Ph + Fe^{2+} \rightleftharpoons FePh_3^{2+}$	- 27.94 (± 0.05)	- 31.32 (± 0.66)	- 11.3 (± 3.5)
$Fe^{3+} + 3Ph \rightleftharpoons FePh_3^{3+}$	- 18.81 (± 0.11)	- 9.9 (± 0.80)	29 (± 4.0)
$H^+ + Dipy \rightleftharpoons HDipy^+$	- 6.09	- 2.0	13
$Fe^{2+} + 3Dipy \rightleftharpoons FeDipy_3^{2+}$	- 23.28	- 24.3	- 4.3
$Fe^{3+} + 3Dipy \rightleftharpoons FeDipy_3^{3+}$	- 15.4	- 2.9	41.9

From o.d. measurements concentrations of Ferroin were calculated using the extinction coefficients of Ferroin at 510 and 520 $m\mu$'s which are $1.1342 (\pm 0.0015) \cdot 10^4$ and $1.0765 (\pm 0.0019) \cdot 10^4$ respectively at average temperature 33°C . (It has been assumed that the extinction coefficient are unaltered at the ionic strengths of solution studied in the range of 10^{-3}M and in the temperature range studied though the extinction coefficient changes slightly about 0.5% for the temperature range 15°C).

The equilibrium constants for the reaction (4) at different temperatures are given in the Table 1. If the equilibrium is written as



the dissociation constant is given by

$$K \text{ dissociation of Ferroin} = K_a \cdot K_T^3. \quad (11)$$

The equilibrium constants are included in the same Table.

Evaluation of other Thermodynamic Properties

The ΔH 's for the reactions (1), (4) and (10) have been determined from the slope of the plot of $-\log K$ against $1/T$.

The values of ΔF 's of the reactions (1), (4) and (10) at different temperatures are calculated on the basis of the equation.

$$\Delta F = -RT \ln K. \quad (12)$$

Using these values of ΔF 's and assuming that ΔH is constant over the temperature range studied, ΔS values of the reactions (1), (4) and (10) have been calculated. The values are given in Table 2.

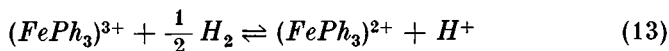
Evaluation of the Thermodynamic Properties of Ferriin

The analogous Ferric-compound of *o*-Phenanthroline known as Ferriin cannot be obtained directly. It can only be obtained by oxidising the analogous iron(II) complex⁹.

GEORGE, HANANIA and IRVINE³ determined the e.m.f. of the tris-*o*-Phenanthroline Ferrous and tris-*o*-Phenanthroline-Ferric couple. By plotting the e.m.f. at different μ 's against $\frac{\mu^{1/2}}{1 + \mu^{1/2}}$ they obtained

⁹ F. BLAU, *Monatsh.* **19** (1898) 647.

a value, of E_0 for the system. They measured also the variation of E.M.F. with temperature. Thus, for the reaction,



they give for ΔF , $-26.5 (\pm 0.1)$ Kcal/mole, ΔH , $-32.7 (\pm 0.5)$ Kcal mole $^{-1}$ and ΔS a value of $-20.8 (\pm 2.0)$ e.u. using the values of ΔF , ΔH and ΔS for $\frac{1}{2} H_2 \rightarrow H^+$, they got for $\bar{S}_0(FePh_3)^{2+} - \bar{S}_0(FePh_3)^{3+}$ a value of $-5.2 (\pm 2.0)$ e.u.

They did not have the ΔF , ΔH and ΔS for ferrous-orthophenanthroline available at hand. Now if we combine these with our values for ferrous-orthophenanthroline complex, we can have the ΔF , ΔH and ΔS for ferric orthophenanthroline complex. These are also given in the Table.

We have included in the Table, the thermodynamic functions for Ferrous and Ferric dipyridyl complexes for comparison^{3,10}.

Discussions

It is seen that in the case of PhH^+ ion, spectrophotometric value obtained agrees well with the value obtained by KOLTHOFF and co-workers⁸ from conductometric methods and ΔH and ΔS values of the present determination agree well with the values obtained by potentiometric method² although the values of $-\log K$ at $25^\circ C$ is little too low (4.857).

The value of $\log K_{stab.}$ we report in the present work is 5.05 at $25^\circ C$.

The stability constant of $FePh_3^{2+}$ at $25^\circ C$ has been determined by a number of workers. KOLTHOFF and co-workers⁸ give a value of 21.301 for $\log K_{stab.}$ of $FePH_3^{2+}$ complex. These investigators worked in a medium of high ionic strength. To get the thermodynamic constant they used the activity coefficients of PhH^+ which they determined from pH -measurements of 1:1 mixture of Ph and PhH^+ in varying concentration of KCl . These workers themselves admit that this is subject to liquid-junction potential. We examined these data more critically as, surprisingly enough, f_{PhH^+} is reported to be much smaller than f_{H^+} . The Phenanthroline being a large molecule, we would expect larger $a_{PhH^+}^\circ$ (ion-size parameter) values for Phenanthroline

¹⁰ J. H. BAXENDALE and P. GEORGE, Trans. Faraday Soc. **55** (1950) 46.

than Hydrogen and as such a larger f on the basis of the equation $-\log f_i = \frac{Az_i^2 \cdot \mu^{1/2}}{1 + Ba^\circ \mu^{1/2}}$. To have an idea about a° , we calculate a° on the basis of the above equation using KOLTHOFF and co-workers' values of f_{PhH^+} . These values give for a° values varying between $1.5A^\circ$ to $8.5A^\circ$. So we prefer to use the assumption $f_{H^+} = f_{PhH^+}$.

In their calculation of the thermodynamic K_a for PhH^+ , KOLTHOFF and co-workers themselves preferred to use the assumption that activity co-efficient of PhH^+ ion is equal to that of H^+ ion in dilute solution.

If this assumption is used, their results give 20.64 for $\log K_{stab}$, although the standard deviation is high.

COOK and LONG¹¹ determined the constant by radioactive tracer method. They used the activity coefficient values of KOLTHOFF and co-workers and reported for the $\log K_{stab}$, a value 21.155. If these are recalculated on the basis of assumption that $f_{H^+} = f_{PhH^+}$, it becomes 20.77.

IRVING and co-workers¹ determined the stability constant by partition technique and report a value of 21.15 for $\log K_{stab}$, at ionic strength of 0.1M *KCl*. On the basis of the present assumption $f_{H^+} = f_{PhH^+}$, this becomes 20.90. for $\log K_{stab}$, (thermodynamic).

Thus on the basis of the same assumption regarding the activity coefficient, we have 20.90 (IRVING et al.), 20.77 (COOK and LONG), 20.64 (KOLTHOFF et al.) and 20.55 in the present determination for the value of $\log K_{stab}$, at $25^\circ C$ by a different technique. Although we would be happy to get better agreement between determinations by different techniques and also between workers, considering the various limitations, we would take the agreement to be good.

The thermodynamic functions given in the Table show some generalisations. Like the dipyriddy complexes of Fe^{2+} and Fe^{3+} , the formation of $FePh_3^{2+}$ is highly exothermic while the entropy factor is unfavourable and in the case of Ferric complexes the main factor is the entropy effect. Entropy change in complex formation as is known due to decrease in number of ions, partial neutralisation of electric charge and displacement of water from the hydration sphere. This last factor is apparently the cause of difference in the entropy of formation of $FePh_3^{2+}$ and $FePh_3^{3+}$. If we picture it by means of thermochemical cycle, we get:

$$\Delta S_{complex} = \Delta S_{g\ complex} + \Delta S_{h\ complex} - S_{hM} - n \Delta S_L \quad (14)$$

¹¹ C. M. COOK and F. A. LONG, J. Amer. chem. Soc. **73** (1951) 4119.

Thus the entropies of hydration of Fe^{2+} , Fe^{3+} , $FePh_3^{2+}$ and $FePh_3^{3+}$ cause this difference.

IRVING and co-workers¹ while correlating the stability of dipyridyl and *o*-Phenanthroline complexes of Fe^{2+} , have suggested that since, in terms of the proton affinity of dipyridyl and *o*-Phenanthroline, a difference to the extent of 2Kcals would be expected, the rest of the free energy in excess of 2Kcals is due to the resonance stabilization possible in *o*-Phenanthroline. It may be interesting to analyse the enthalpy data in light of the suggestion. The enthalpy of formation of PhH^+ is -4.07 Kcal/mole and that for dipy H^+ -2.0 Kcal/mole.

In the formation of both these compounds a $\geq N \rightarrow H$ bond is involved and as such we would expect the same enthalpy change. This difference may be due to the possibility of greater resonance in the *o*-Phenanthroline. Now, in case of $FePh_3^{2+}$ and $FeDipy^{2+}$ we have similar $Fe-N$ bonding and three ligand molecules. If we assume the same type of resonance stabilisation, a difference of about 6Kcals would be expected. The difference in the experimental values of enthalpy values for $FeDipy^{2+}$ and $FePh^{2+}$ is very nearly the same, about 7.0Kcals.

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