

has a value of $4 \times 10^{+41}$. The analogous constant for the formation of $Zn_2DMP_3^-$ is equal to the product $q_0qQ_2^2ZnDMP_3^-$ and calculation yields a value of $4 \times 10^{+40}$ for this constant. Although this latter value can be considered to be only an estimate, the relative difference between it and the value for the nickel(II) complex is sufficiently great to be significant. Further evidence that the polynuclear nickel(II) complexes are more stable is suggested by the relative solubilities of the neutral species. The solid phase can be considered to be a polynuclear complex with an infinite value of n . The species $ZnDMP$ has a solubility product of about 10^{-18} and even dissolves to a slight extent as the undissociated species. With $NiDMP$, on the other hand, the solubility product is of the order 10^{-20} – 10^{-21} , and there is no evidence that the undissociated species is soluble to an appreciable extent under equilibrium conditions. And finally, mercaptoacetate ions form a "core plus links" polynuclear series with nickel(II), but there is no evidence that this ligand forms polynuclear complexes with zinc(II).

Spectral evidence^{3,6,8,9} indicates that $dd-\pi$ bonding is important in the polynuclear nickel(II) complexes. The π bonding acts to reduce the positive charge that would otherwise exist on the multiply bonded sulfur atoms and apparently has and the complex is probably present as $Ni_2DMP_3^-$. Recalculating the data on this basis gives a value of $4 \times 10^{+41}$ for the formation constant of this species.

a greater effect on the square planar nickel(II) complexes than in the (presumably) tetrahedral zinc(II) complexes. Both platinum(II) and palladium(II) ions, which like nickel(II) also have the d^8 electron configuration, form sulfur bridged complexes and π bonding has been suggested to be important in these complexes.^{21,22} Indeed, the MS_2M ring is probably an "inorganic aromatic ring".²²

The manganese(II)-DMP system does not form polynuclear complexes, at least under the present experimental conditions. Also, it was found that the neutral species, $MnDMP$, has quite high solubility. These observations give further support to the suggestion that π bonding is important in the polynuclear species. With the manganese(II) ion, the d shell is only half filled and the tendency for dative π bonding is much less.

It is interesting that complexes with such a large number of zinc ions are stable in solution. Preliminary experiments indicate that the alcohol group of the DMP molecule is important in bringing about the solution stability of these polynuclear zinc(II) species. With ethanedithiol as the ligand the benefit of the solvation of the OH group is not had and the solid phase remains dissolved to much higher n values than are observed with DMP.

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(22) J. Chatt and F. A. Hart, *ibid.*, 2807 (1960).

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The Kinetics of the Oxidation of the Iron(II) Ion by the Tris-(1,10-phenanthroline)-iron(III) Ion¹

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The kinetics of the oxidation of the iron(II) ion by tris-(1,10-phenanthroline)-iron(III) ion in 0.50 F $HClO_4$ has been studied using a rapid-mixing and flow technique. The reaction was shown to be first order with respect to each reagent and the specific rate constant determined to be $3.70 \times 10^4 F^{-1} \text{sec.}^{-1}$ at 25.0°. The rate constant increased slightly with decreasing acid concentration. The activation energy calculated from the temperature dependence of the rate constant is 0.8 ± 0.2 kcal./mole and the entropy of activation is -37.2 cal./mole deg. The oxidation of ferrous ion by the tris-(1,10-phenanthroline)-iron(III) ion is compared with other ferrous ion oxidations and the existence of a linear relation between the free energies of activation and the standard free energy changes of the oxidation-reduction reactions is shown.

Introduction

The iron(II)-iron(III) exchange reaction has been studied extensively in an attempt to elucidate some of the features of electron transfer in aqueous solution. Silverman and Dodson² studied the reaction between the uncomplexed cations and found the bimolecular rate constant to be $4.0 F^{-1} \text{sec.}^{-1}$ at 25.0°. The complexing of the ferric ion by halides^{2,3} increases the specific rate of exchange by a factor of ten, while complexing by hydroxide ion increases the specific rate a thousandfold. The results do not yield a satisfactory interpretation of the reaction mechanism. There is also some

doubt as to whether the ferric halides are inner or outer sphere complexes.

Eichler and Wahl⁴ used both radioactive tracers and optical activity methods in a study of the tris-(1,10-phenanthroline)-iron(II)-tris-(1,10-phenanthroline)-iron(III) electron transfer reaction. Both ions of this system are definitely inner sphere complexes in which the ligands are not readily substituted. The optical activity method resulted in a lower limit of $k = 10^2 F^{-1} \text{sec.}^{-1}$ for the exchange at 25°. The tracer experiments are more ambiguous because of the possibility of separation-induced exchange. Assuming 50% separation-induced exchange, Eichler and Wahl placed a lower limit of $k = 10^6 F^{-1} \text{sec.}^{-1}$ on the bimolecular rate constant at 0°.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(3) J. Hudis and A. C. Wahl, *THIS JOURNAL*, **75**, 4153 (1953).

(4) E. Eichler and A. C. Wahl, *ibid.*, **80**, 4145 (1958).

The oxidation of ferrous ion by hexachloroiridium(IV), tris-(1,10-phenanthroline)-ruthenium(III) and tris-(1,10-phenanthroline)-iron(III) has been studied by George and Irvine.⁵ They followed these reactions by observing the color changes in ordinary mixing experiments. The reactions were complete in the time required to mix the reactant solutions. From an estimate of this time they set a lower limit of $k = 10^5 F^{-1}\text{sec.}^{-1}$ for the reactions.

Rapid-mixing and flow techniques combined with a spectrophotometric means of analysis have been used with considerable success in several investigations of fast reactions.⁶⁻⁸ The ferrous-tris-(1,10-phenanthroline)-iron(III) system can readily be studied with such a technique by following the production of the intensely colored tris-(1,10-phenanthroline)-iron(II). Our interest in this system derives from both the similarities and differences with the systems involving ferrous ion reacting with ferric ion, complexes of ferric ion and other oxidizing agents.

Experimental

Chemicals.—Tris-(1,10-phenanthroline)-iron(II) perchlorate was prepared by adding an equivalent amount of ferrous perchlorate to 1,10-phenanthroline (G. Frederick Smith). Tris-(1,10-phenanthroline)-iron(II) perchlorate was precipitated with sodium perchlorate, redissolved in dilute sulfuric acid and oxidized to tris-(1,10-phenanthroline)-iron(III) perchlorate with lead dioxide. Excess lead dioxide and the lead sulfate produced were removed by filtration. Tris-(1,10-phenanthroline)-iron(III) perchlorate was precipitated from the filtrate by adding perchloric acid and was purified by recrystallization from dilute perchloric acid. A stock solution of tris-(1,10-phenanthroline)-iron(III) perchlorate was prepared by dissolving the crystals in concentrated perchloric acid and was stored in a dark container at -15° . Such stock solutions appeared stable over a period of several months.

Ferrous perchlorate (G. Frederick Smith) was purified by recrystallization from perchloric acid.

Sodium perchlorate was prepared by neutralizing sodium carbonate (Baker and Adamson) with perchloric acid (Baker Analyzed Reagent).

Triply-distilled water was used in preparing the solutions for the kinetic measurements.

Apparatus.—The apparatus consisted of two 100 ml. syringes which were mounted in a pushing block and connected *via* two three-way stopcocks to the mixing chamber. The reagents were kept in volumetric flasks and could be drawn into the syringes through the three-way stopcocks when required. Both the volumetric flasks and the syringes were kept in a constant temperature bath.

The mixing chamber was constructed from a cylinder of Lucite, 25 mm. in diameter and 25 mm. long, and consisted of four jets of 0.7 mm. bore which were tangentially arranged around a 2 mm. hole drilled into one face of the Lucite. A 21-cm. long 2-mm. quartz capillary observation tube was aligned with this hole and cemented into place.

The quartz observation tube was held firmly in a channel between two aluminum blocks, each 3 cm. \times 3 cm. \times 20 cm., held 1 mm. apart. This unit, together with the mixing chamber, fitted tightly into a jacket which replaced the cell compartment of a Beckman Model DU spectrophotometer. This assembly is similar to that described by Dalziel.⁹ The jacket was placed between two metal plates through which water from the constant temperature bath was circulated. The light from the monochromator traversed a short length of the observation tube at a distance of 5 cm. from the mixing chamber. The width of the light beam was controlled by means of the adjustable slit in the spectrophotometer.

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(6) B. Chance, *Rev. Sci. Instr.*, **22**, 619 (1951).

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(9) K. Dalziel, *Biochem. J.*, **55**, 79, 90 (1953).

The outlet of the observation tube was connected to one arm of a three-way stopcock. The second arm was connected to a vertically-mounted 100 ml. syringe and the remaining arm to a container for the reacted solutions.

The spectrophotometer was modified to allow direct measurement of the intensity of the transmitted light using a linear energy recording adapter (Beckman #5800). The output from this adapter was recorded on a Leeds and Northrup Speedomax recorder, which had a chart speed of up to 4 inches/sec. and a pen response time of two hundred milliseconds full scale.

The mixing efficiency was measured by flowing together a 0.1 *F* NaOH solution containing phenolphthalein indicator and a hydrochloric acid solution which was 1% more concentrated than the basic solution. At a flow rate of 8 ml./sec. the indicator color disappeared within five millimeters from the inlet to the mixing chamber indicating a mixing efficiency of better than 99% in two milliseconds.

Procedure.—The reagent solutions were drawn into the syringes through the three-way stopcocks. The syringes were driven by placing several lead bricks on the pushing block. Flow rates of up to 12 ml./sec. could be obtained by varying the number of bricks used. By suitable combinations of the positions of the three-way stopcocks either the ferrous solution or the ferric phenanthroline solution or both could be pushed through the observation tube. When the piston of the receiving syringe reached a stopping block, the flow was instantly halted. The course of the reaction was followed by measuring the absorbance of the solution at 510 $m\mu$ as a function of time from the stoppage of the flow. The extinction coefficient ($\epsilon = 11,100$) of ferrous phenanthroline is a maximum at this wave length.¹⁰ Neither ferrous ion nor ferric ion absorbs at this wave length, while the extinction coefficient of ferric phenanthroline is 300 at 510 $m\mu$. Corrections were made for the change in the total absorbance due to the disappearance of ferric phenanthroline during the reaction.

In a typical run the transmittance was recorded first with the ferrous solution in the observation tube. Then both reagents were pushed through the observation tube until the piston of the receiving syringe hit the stop and halted the flow. After the reaction was complete, the ferrous solution was again put through the observation tube. A typical trace is shown in Fig. 1.

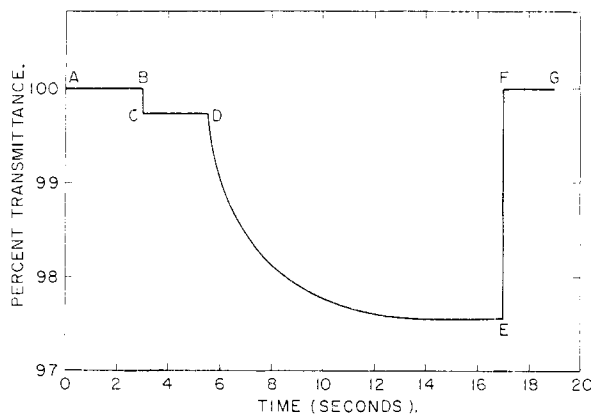


Fig. 1.—Example of a typical trace.

AB and CD measure the intensity of the light transmitted by the ferrous solution and the flowing reaction mixture respectively. Since the time required for the reaction mixture to reach the point of observation is very small compared to the half-time of the reaction, the reaction mixture contains practically no ferrous phenanthroline at this stage. The increase in the absorbance of the flowing solution over that of the ferrous solution can be accounted for quantitatively in terms of the absorption by the ferric phenanthroline. The flow was stopped at D and the subsequent decrease in the transmittance is caused by the production of ferrous phenanthroline. FG measures the intensity of the light transmitted by the ferrous solution put through at the end of the run. The difference between AB and FG

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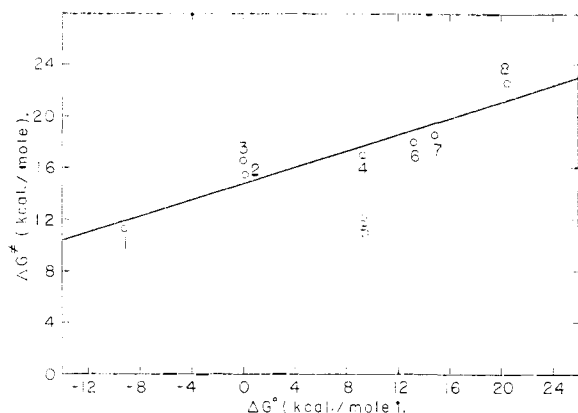


Fig. 2.—Free energy of activation plotted against the standard free energy change for the oxidation of ferrous ion by various oxidizing agents: 1, $\text{Fe}(\text{phen})_3^{+3}$; 2, FeCl^{+2} ; 3, Fe^{+3} ; 4, 2,6-dichlorosemiquinone; 5, FeOH^{+2} ; 6, benzosemiquinone; 7, tolusemiquinone; 8, durosemiquinone.

reflects the stability of the instrument during the run, which was in general excellent.

In view of the low concentration of the product formed ($<5 \times 10^{-6} F$) the intensity of the transmitted light decreased by less than 2.5% during the run, and thus the decrease in intensity could be assumed to be directly proportional to the concentration of ferrous phenanthroline without appreciable error.

Results and Discussion

Order of the Reaction.—The order of the reaction was determined by varying the concentration of the reactants. If the reaction is first order with respect to each of the reactants then a plot of $\log [b(a-x)/a(b-x)]$ versus t should give a straight line with zero intercept, where a and b are the initial concentrations of ferrous and ferric phenanthroline and x is the concentration of ferrous phenanthroline at time t . Rate constants calculated from the slopes of these lines are presented in Table I. It will be seen that the rate constants are independent of the initial concentrations of ferrous and ferric phenanthroline over a wide range, thus confirming that the reaction is first order with respect to each of the reactants. The rate constants were also independent of the flow rates, which ranged from 4 to 10 ml./sec.

TABLE I
DETERMINATION OF THE ORDER OF THE REACTION AT 25.0°
(HClO_4) = 0.50 F ; μ = 0.50

(Fe^{+2}) $F \times 10^6$	$(\text{Fe}(\text{phen})_3^{+3})$ $F \times 10^6$	$F^{-1} \text{ sec.}^{-1} \times 10^{-4}$
2.14	5.38	3.76
2.14	10.76	3.65
2.14	16.14	3.76
2.14	21.52	3.64
2.14	26.90	3.80
4.28	15.67	3.56
4.28	26.25	3.67
8.56	4.98	3.77
8.56	4.85	3.77
17.12	4.77	3.65
17.12	4.38	3.66

The mean value of the second order rate constant at 25.0° and at (HClO_4) = 0.50 F is $3.70 \times 10^4 F^{-1} \text{sec.}^{-1}$.

Acid Dependence.—The effect of the perchloric acid concentration on the rate constant was studied by varying the acid concentration and adding sufficient sodium perchlorate to maintain a constant ionic strength of 0.50. The results are presented in Table II. It will be seen that the rate of the reaction increases with decreasing acidity. Reliable rate measurements could not be made at lower acid concentrations because of the rapid decomposition of ferric phenanthroline in solutions of low acidity.

TABLE II
THE RATE DEPENDENCE ON PERCHLORIC ACID CONCENTRATION

(HClO_4) F	k_1 $F^{-1} \text{ sec.}^{-1} \times 10^{-4}$
0.50	3.70
.37	3.80
.24	4.05
.12	4.16
.048	4.30

The acid dependence may be explained in terms of the reversible association of $\text{Fe}(\text{phen})_3^{+3}$ with H^+ to yield $\text{HFe}(\text{phen})_3^{+4}$. This could account for the increase in the rate observed at lower acidities, if $\text{HFe}(\text{phen})_3^{+4}$ reacts more slowly with Fe^{+2} than does $\text{Fe}(\text{phen})_3^{+3}$. The existence of $\text{HFe}(\text{phen})_3^{+4}$ has been postulated by a number of investigators.^{5,11} However, the effect is small and may well be a salt effect.

Temperature Dependence.—The rate of the reaction in 0.50 F HClO_4 was also measured at 15.0 and 35.0°. The activation energy calculated from a plot of $\log k$ vs. $1/T$ is 0.8 ± 0.2 kcal./mole. The entropy of activation calculated from the equation¹²

$$k = \frac{eRT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-E_{\text{act.}}/RT}$$

is -37.2 cal./deg.-mole, which is considerably more negative than the values reported for other iron(II)-iron(III) reactions.^{2,3}

Rates of Ferrous Ion Oxidations.—Since there is some evidence that the rates of oxidation-reduction^{13,14} reactions may be related to their standard free energy changes, it is possible that the rapid rate of the $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{Fe}(\text{phen})_3^{+3}$ reaction is related to its favorable standard free energy change.¹⁵ It is therefore of interest to compare the rates of a variety of reactions in which $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ acts as a reducing agent, with their corresponding standard free energy changes. A considerable amount of data is available on the rate of oxidation of ferrous by ferric ions and ferric complexes.^{2,3,16} The rate of the reaction between ferric and several hydro-

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quinones has also been measured.^{17,18} One mechanism which is consistent with the acid-dependence observed in the latter studies involves the ionization of QH_2 to QH^- followed by the oxidation of QH^- by $\text{Fe}(\text{H}_2\text{O})_6^{+3}$. The standard free energy change of this reaction has been calculated,¹⁹ and this value, combined with the free energy of activation of the reaction can be used to calculate the free energy of activation of the $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - QH reaction. The free energy of activation calculated in this way, together with the appropriate data on some $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{Fe}(\text{III})$ reactions, is plotted in Fig. 2.

A linear relation appears to exist between ΔG^* and ΔG^0 for the reactions of $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ with $\text{Fe}(\text{phen})_3^{+3}$, $(\text{H}_2\text{O})_5\text{FeCl}^{+2}$ and the semiquinones. On this basis, the reaction of $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ with $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ seems somewhat slower than expected, while its reaction with $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$ seems considerably faster. The work required to bring the reactants from infinity to the distance they occupy in the activated complex is different in the various reactions. While the amount of this work is probably small at the distances and ionic strengths involved, it may be partly responsible for the relative slowness of the $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ reaction. In addition, the free energy required to reorganize the inner coordination shell of the $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ ion before electron transfer can occur²⁰ is probably larger than that required for the other species.

The very rapid rate of the $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ - $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$ reaction may indicate that this reaction proceeds by a different type of mechanism. Such a mechanism may involve hydrogen atom transfer as has been suggested.²¹ However, measurements of the rates of the exchange reactions of $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ with $\text{Fe}(\text{H}_2\text{O})_6^{+3}$, $(\text{H}_2\text{O})_5\text{FeOH}^{+2}$ and $(\text{H}_2\text{O})_5\text{FeCl}^{+2}$

in D_2O ,^{22,23} as well as those of other oxidation-reduction reactions in this solvent, do not support the interpretation that the hydroxide-catalyzed exchange proceeds uniquely *via* a hydrogen atom transfer mechanism.

In view of the above linear relation between ΔG^* and ΔG^0 for the oxidation-reduction reactions, it is likely that a similar relation exists between the ΔH^* and ΔH^0 for the oxidation-reduction reactions. The small value of the heat of activation (0.2 kcal./mole) found for the ferrous-ferric phenanthroline reaction suggests that the ΔH^0 of this reaction has a large negative value. Unfortunately the value of ΔH^0 has not been determined, but it may be estimated from the known value of ΔG^0 and an estimate of ΔS^0 for the reaction. The difference in the entropies of $\text{Fe}(\text{H}_2\text{O})_6^{+2}$ and $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ is 43.0 cal./deg. mole with that of $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ more negative.²⁴ Irvine¹³ has measured the difference in the entropies of the tris-(4,4'-dimethylbipyridyl)-iron(II) and tris-(4,4'-dimethylbipyridyl)-iron(III) ions to be 1.9 cal./deg. mole with that of the tripositive ion more positive. Because the sizes of the 4,4'-dimethylbipyridyl and 1,10-phenanthroline complexes are similar, the entropy difference of 1.9 cal./deg. mole measured for the 4,4'-dimethylbipyridyl complexes will be assumed also for the 1,10-phenanthroline complexes. This assumption is supported by unpublished measurements on a number of bipyridyl and phenanthroline complexes.¹³ The value of ΔG^0 for the oxidation-reduction reaction is -9.2 kcal./mole.¹⁵ This, together with the ΔS^0 estimate, gives a value of $\Delta H^0 = -22.6$ kcal./mole.

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Stabilities of Bivalent Metal Complexes of Some β -Ketoimines

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Acid dissociation constants of several β -ketoimines and formation constants of some of their metal derivatives have been determined.

Introduction

The chelating tendencies of β -diketones have been studied extensively.¹ However, the properties of β -ketoimines, Schiff-base derivatives of β -diketones, are less well known. Cromwell² has written an excellent review of the organic chemistry of β -

ketoimines. More recently, Holtzclaw, *et al.*,³ described the synthesis and infrared spectra of these ligands and their copper derivatives. Hovey, *et al.*,⁴ have reported the preparation and absorption spectra of analogs of bisacetylacetonethylenediimine and its metal chelates. The dissociation

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