electrical energy when required to the resistance wire around the copper block. At equilibrium the temperature of the copper block and the temperature in the thermocouple well near the sample do not differ by more than the limits of error of the potentiometer used to measure the emf of the copper–constantan thermocouples placed at these two points.

Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard[14] and diamagnetic corrections were estimated from Pascal's constants.[15] A value of 60×10^{-6} cgs unit was assumed for the temperature-independent paramagnetism per copper ion.

Spectral Measurements.—The spectra of butanol solutions were obtained using a Cary Model 14 recording spectrophotometer. Reflectance spectra of solid samples were measured with a Beckman DU spectrophotometer equipped with the standard reflectance attachment and employing a block of magnesium carbonate as standard. In order to suppress the dissociation

$$[Cu(R-C_6H_4CO_2)_2 \cdot C_4H_9OH]_2 \rightleftharpoons$$
$$[Cu(R-C_6H_4CO_2)_2 \cdot {}^1\!/{}_2C_4H_9OH]_2 + C_4H_9OH$$

the samples were filtered from the mother liquor and placed in a sample cell with traces of butanol adhering to the surface of the sample. The cell was then sealed and the reflectance spectrum measured.

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
(15) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

Analyses.—Microanalyses for carbon and hydrogen were performed by Triangle Chemical Laboratories, Inc., Chapel Hill, N. C. Copper analyses were determined by EDTA titration following the method developed by Guerrin, *et al.*[16] The complexes were decomposed in nitric acid and the mixture neutralized with sodium hydroxide and, after the addition of sodium acetate buffer, titrated with standardized EDTA solution using Snazox as an indicator. The analytical data are presented in Table IV.

TABLE IV
ANALYTICAL DATA

Compound		Analyses		
		% C	% H	% Cu
$Cu(C_6H_5CO_2)_2 \cdot C_4H_9OH$	Found:	56.63	5.33	16.77
	Calcd:	56.89	5.27	16.73
$Cu(p\text{-}CH_3C_6H_4CO_2)_2 \cdot C_4H_9OH$	Found:	58.09	6.09	15.33
	Calcd:	58.84	5.88	15.58
$Cu(p\text{-}CH_3OC_6H_4CO_2)_2 \cdot C_4H_9OH$	Found:	54.31	5.82	14.48
	Calcd:	54.56	5.46	14.45
$Cu(p\text{-}BrC_6H_4CO_2)_2 \cdot C_4H_9OH$	Found:	40.82	3.66	11.82
	Calcd:	40.18	3.35	11.82
$Cu(p\text{-}NO_2C_6H_4CO_2)_2 \cdot C_4H_9OH$	Found:	46.22	4.35	13.39
	Calcd:	46.01	3.83	13.53

(16) G. Guerrin, M. V. Sheldon, and C. N. Reilley, *Chemist-Analyst*, **49**, 36 (1960).

The Oxidation Reactions of Peroxydiphosphate. I. The Kinetics and Mechanism of the Reaction with Tris(1,10-phenanthroline)iron(II)

By Sr. Agnes Ann Green,[1a] John O. Edwards, and Peter Jones[1b]

The rate of the reaction of lithium peroxydiphosphate with tris(1,10-phenanthroline)iron(II) perchlorate has been studied in neutral, aqueous solutions at 35° and ionic strength 1.00. The observed rate law can be represented by the equation

$$-\frac{d[Fe(phen)_3{}^{2+}]}{dt} = \frac{k_1 k_2 [Fe(phen)_3{}^{2+}][P_2O_8{}^{4-}]}{k_{-1}[phen] + k_2[P_2O_8{}^{4-}]}$$

which leads to the conclusion that the rate-determining step, when $P_2O_8{}^{4-}$ is in large excess, is the dissociation of the iron(II) complex ion. The reactions of $Fe(phen)_3{}^{2+}$ with Cu^{2+}, Ni^{2+}, EDTA, and $P_2O_7{}^{4-}$ were studied under similar conditions and were found to have similar rate-determining steps. The observed rate constant, k_{obsd}, for all these reactions approached 4×10^{-4} sec^{-1} at concentrations for which first-order behavior was found.

Introduction

A study of the reaction of peroxydiphosphate with tris(1,10-phenanthroline)iron(II) complex ion (hereafter $Fe(phen)_3{}^{2+}$) in aqueous, neutral solutions was undertaken to begin the investigation of the oxidation reactions of this peroxide. While reactions involving $Fe(phen)_3{}^{2+}$ as a reducing agent have been studied,[2–6]

(1) (a) Public Health Service Fellow, 1965–1966; on leave from Immaculate Heart College, Los Angeles, Calif. 90027. (b) On leave from the University of Newcastle upon Tyne, England.
(2) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 2348 (1948); *ibid.*, **70**, 3596 (1948).
(3) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).
(4) J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, **85**, 3328 (1963).
(5) (a) P. George and D. H. Irvine, *J. Chem. Soc.*, 587 (1954); (b) P. George, G. I. H. Hanania, and D. H. Irvine, *ibid.*, 2548 (1959).
(6) G. Gordon, private communication, 1966.

very little work has been done on the peroxydiphosphate ions as oxidizing agents.[7–9] The reaction with $Fe(phen)_3{}^{2+}$ should be of interest as a basis for the comparison of the peroxydiphosphate reaction with the peroxydisulfate reaction which was studied by Irvine.[10]

Experimental Section

Materials.—Potassium peroxydiphosphate was synthesized by anodic oxidation of alkaline phosphate solution and converted to the lithium salt for purification according to the method of Chulski.[7,8] Other peroxydiphosphate salts were obtained by

(7) T. Chulski, Doctoral Thesis, Michigan State University, 1953.
(8) C. H. Chong, Doctoral Thesis, Michigan State University, 1958.
(9) A. Indelli and P. L. Bonora, *J. Am. Chem. Soc.*, **88**, 924 (1966).
(10) D. H. Irvine, *J. Chem. Soc.*, 2977 (1959).

the ion-exchange method of Crutchfield.[11,12] Since some kinetic measurements using potassium peroxydiphosphate indicated that the cation did not affect the rate of the reaction significantly, the more readily purified lithium salt was used throughout these measurements. All other reagents were analytical grade laboratory chemicals. Most of the experimental work was done with the perchlorate salt of $Fe(phen)_3^{2+}$ which was purchased from City Chemical Corp., New York, N. Y. However, identical results were obtained with the sulfate compound which was prepared in solution by adding ferrous ammonium sulfate to 1,10-phenanthroline monohydrate in a 1:3 molar ratio.

Methods and Measurements.—The kinetic experiments were carried out at 35° in a thermostated water bath. The reaction was followed by removing and chilling samples to 0° to retard the reaction, immediately bringing them to room temperature, and measuring the concentration of $Fe(phen)_3^{2+}$ colorimetrically at 500 mμ in 1-cm cells in a Beckman Model B spectrophotometer. Some check runs made under prepurified nitrogen with solutions which were deaerated before mixing showed no effect of atmospheric oxygen on the reaction rates; thus, all subsequent measurements were made in simple, glass-stoppered flasks. Spectra were obtained on a Bausch and Lomb Spectronic 505 recording spectrophotometer in the range 250–650 mμ using 1-cm silica cells, and pH measurements were made on a Beckman Model G pH meter.

The peroxydiphosphate preparations were analyzed gravimetrically for total phosphate and volumetrically for active oxygen content, owing to the peroxide bond. The latter was done by adding a weighed lithium peroxydiphosphate sample to a measured excess of ferrous ammonium sulfate, which was 1 N in H_2SO_4, and back titrating with a standard ceric solution. At room temperature this reaction is rapid enough for analytical purposes and the equivalency of ferrous ion to peroxydiphosphate is 2 to 1. Ferroin can be used for the indicator, if added just before the final titration, since at room temperature the reaction of peroxydiphosphate with $Fe(phen)_3^{2+}$ is very slow, while the reaction of cerium(IV) sulfate with $Fe(phen)_3^{2+}$ is very rapid.[2] Both analyses yield the same results, based on the stoichiometry, $Li_4P_2O_8 \cdot 4H_2O$, for the tetrahydrate.

All of the kinetic experiments were carried out in solutions in which the ionic strength was adjusted to 1.00 ± 0.05 with sodium sulfate. Sodium sulfate was chosen because of the limited solubility of the $Fe(phen)_3(ClO_4)_2$ in high concentrations of added perchlorate salts. The reaction is slower in solutions of higher ionic strength, although this negative effect is relatively small, as shown in Table I. A preliminary observation indicated that nitrate salts produce a somewhat larger negative ionic strength effect.

TABLE I

EFFECT OF Na_2SO_4 ON THE RATE OF THE REACTION OF $Li_4P_2O_8$[a] WITH $Fe(phen)_3(ClO_4)_2$[b] AT 35°

[Na₂SO₄], M	I[c]	10^4k_{obsd}, sec⁻¹ [d]
0.040	0.17	4.3
0.133	0.45	4.0
0.333	1.05	3.8
0.865	2.65	3.2

[a] $[Li_4P_2O_8]_0 = 5 \times 10^{-3}\ M$. [b] $[Fe(phen)_3^{2+}]_0 = 10^{-4}\ M$. [c] I = total ionic strength. [d] $k = 4.65 \times 10^{-4}\ sec^{-1}$ at $I = 0$, by extrapolation.

Results

Using initial concentrations of $Fe(phen)_3^{2+}$ of 10^{-4} M and excess concentrations of peroxydiphosphate, ranging from 20- to 200-fold greater than that of the

(11) M. M. Crutchfield and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 3533 (1960).

(12) M. M. Crutchfield in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 46 ff.

ferrous complex, the reaction is first order in $Fe(phen)_3^{2+}$ and zero order in the peroxydiphosphate total ionic species. At concentrations below 2 × 10^{-3} M peroxydiphosphate, curvatures in the pseudo-first-order plots of the data appear, and the initial first-order rate constants show dependence upon the initial concentrations of the peroxydiphosphate. This is shown in Figure 1, in which line E represents the
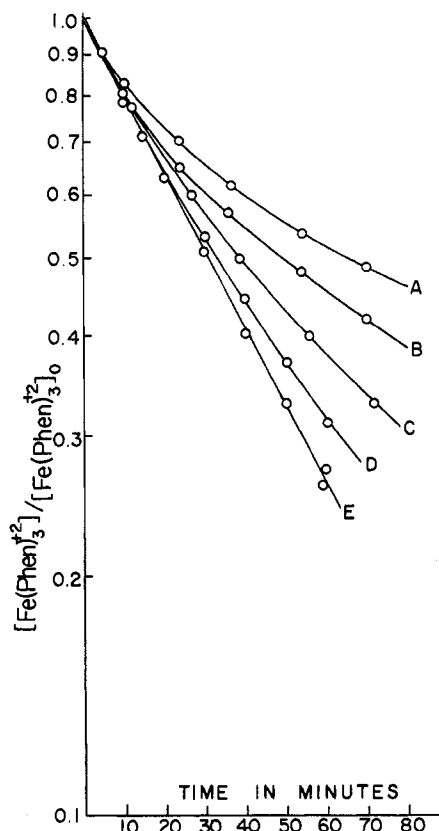

Figure 1.—Effect of peroxydiphosphate concentration on the rate of the reaction with $Fe(phen)_3^{2+}$ at $t = 35.0°$ and $I = 1.00 ±$ 0.05. $[Fe(phen)_3^{2+}]_0 = 10^{-4}\ M$; $[P_2O_8^{4-}]_0$: A, $10^{-4}\ M$; B, 2 × $10^{-4}\ M$; C, 5 × $10^{-4}\ M$; D, $10^{-3}\ M$; E, all concentrations greater than 2 × $10^{-3}\ M$.

reaction for all concentrations of peroxydiphosphate greater than 2 × 10^{-3} M. The first-order rate constants reported in Table II are for 75% of the reaction for the high concentrations of peroxydiphosphate and for the initial 25% of the reaction for the low concentrations, marked b, since deviation from first-order behavior occurred thereafter. Varying the initial concentration of $Fe(phen)_3^{2+}$ from 4 × 10^{-5} to 1.5 × 10^{-4} M in the presence of excess peroxidiphosphate, 5 × 10^{-3} M, established the first-order dependence of the reaction on $Fe(phen)_3^{2+}$; the variation produced no change in the observed first-order rate constant, which was 3.8 × 10^{-4} sec⁻¹. The reaction appeared insensitive to variation of pH from 6 to 9, the range in which these measurements were made. Atmospheric oxygen did not affect the reaction. Reproducible results were obtained without excluding air and without doubly distilling the water used. However, a slight photoeffect was observed which necessitated

Table II

Reaction of Peroxydiphosphate and Some Substances with Tris(1,10-phenanthroline)iron(II) in Neutral Solutions[a]

Substance	Concn, M_0	$10^4 k_{obsd}$, sec^{-1}
Li$_4$P$_2$O$_8$	1.0×10^{-2}	3.8
	6.0×10^{-3}	3.8
	5.0×10^{-3}	3.8
	2.4×10^{-3}	3.8
	2.0×10^{-3}	3.7
	1.0×10^{-3}	3.6[b]
	5.0×10^{-4}	3.5[b]
	3.0×10^{-4}	3.3[b]
	2.0×10^{-4}	2.9[b]
CuSO$_4$	2.0×10^{-3}	4.0
	1.0×10^{-3}	4.0
	5.0×10^{-4}	4.0
NiSO$_4$	1.0×10^{-2}	3.9
	5.0×10^{-3}	3.9
Na$_4$P$_2$O$_7$	5.0×10^{-2}	3.8
	2.5×10^{-2}	3.8
	1.0×10^{-2}	3.8[b]
	5.0×10^{-3}	2.8[b]
	2.5×10^{-3}	2.4[b]
EDTA	5.0×10^{-3}	2.3[b]
	2.5×10^{-3}	2.1[b]

[a] $t = 35°$; $I = 1.00$; pH range 6–8; $[Fe(phen)_3{}^{2+}]_0 = 10^{-4} M$. [b] Initial first-order constants, based on first 25–35% of reaction.

precautions in making concentration measurements at 500 mμ and also required that the samples be measured within 3–5 min after quenching.

The unusual observation of zero order for an oxidant, as the reaction in higher concentrations of peroxydiphosphate appeared, led to some rate measurements of the reductant with other substances under the same conditions of temperature and concentration ranges. These results are included in Table II. Copper(II) sulfate, nickel(II) sulfate, sodium pyrophosphate, and the disodium salt of EDTA produced the same kind of rate process and almost the same rate constant as observed with peroxydiphosphate ion. For example, above a certain concentration, when used in excess, the reactions appear independent of their concentration and dependent on the $[Fe(phen)_3{}^{2+}]$ alone.

Copper(II) sulfate was also added to the reaction of peroxydiphosphate with $Fe(phen)_3{}^{2+}$ to look for a possible catalytic effect. However, the amounts required to produce a significant effect did not indicate catalysis but rather a parallel or a competing reaction. The results, included in Table III, show that the copper(II) salt did cause a slight increase in the rate of the reaction. The addition of excess 1,10-phenanthroline, on the other hand, decreased the rate of the reaction, as shown both in Table III and in Figure 2. Also shown in Figure 2 is the fact that the presence of excess ligand increases the absorbance of the initial solutions slightly. Repetitive spectral scans taken during the course of the reaction of peroxydiphosphate with $Fe(phen)_3{}^{2+}$ showed the disappearance of the strong absorption band with peak at 510 mμ, characteristic of the ferrous complex, and the appearance of two absorption bands at 345 and 360 mμ and an isosbestic

Table III

Effect of Copper(II) Sulfate and Excess 1,10-Phenanthroline on the Reaction of Peroxydiphosphate with Fe(phen)$_3{}^{2+}$ [a]

Additive	Concn of additive, $10^4 M_0$	Concn of P$_2$O$_8{}^{4-}$, $10^3 M_0$	$10^4 k_{obsd}$, sec^{-1}
None	. . .	2	3.7$_5$
CuSO$_4$	5	2	4.4$_5$
None	. . .	5	3.8
phen	4	5	2.7$_5$
phen	8	5	1.8

[a] $[Fe(phen)_3{}^{2+}]_0 = 10^{-4} M$; $t = 35°$; $I = 1.00$.
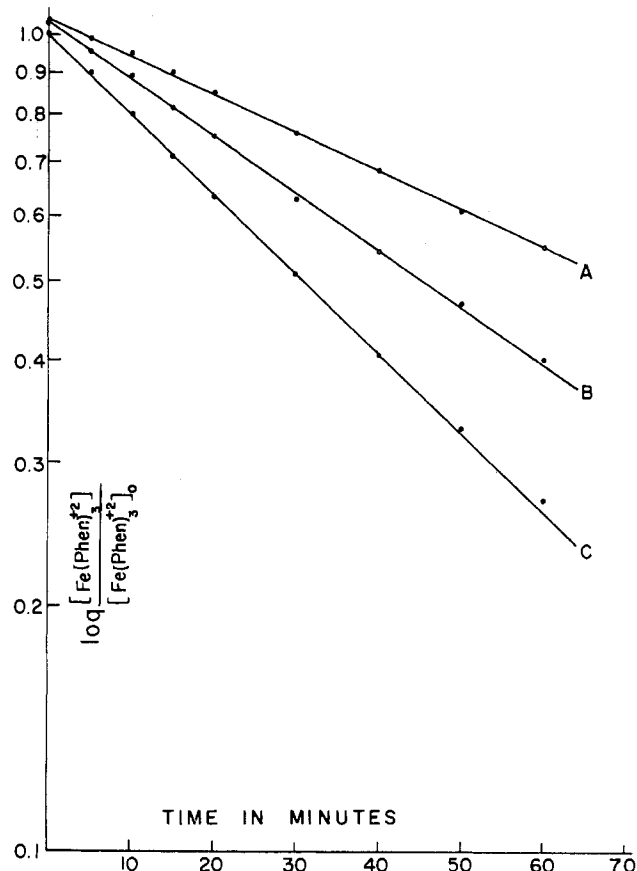

Figure 2.—The effect of excess 1,10-phenanthroline on the rate of the reaction of peroxydiphosphate with Fe(phen)$_3{}^{2+}$ at $t = 35°$ and $I = 1.00 \pm 0.05$. $[P_2O_8]_0 = 5 \times 10^{-3} M$; $[Fe(phen)_3{}^{2+}] = 10^{-4} M$; [phen]$_0$: A, $8 \times 10^{-4} M$; B, $4 \times 10^{-4} M$; C, no excess phenanthroline was added.

point near 375 mμ. No band appeared at 600 mμ, where Fe(phen)$_3{}^{3+}$ should absorb in the longer wavelengths of the visible spectrum.[13] This is consistent with the visual observations that the solutions after 8 or more half-lives were pale yellow and that no blue appeared at any time during the course of the reaction. It has been reported[14] that the blue Fe(phen)$_3{}^{3+}$ is not formed by the direct mixing of a ferric salt with 1,10-phenanthroline, but only by the oxidation of the corresponding ferrous complex, Fe(phen)$_3{}^{2+}$, usually by a very acidic cerium(IV) solution. Direct mixing of ferric ion and 1,10-phenanthroline solutions in a 1:3

(13) J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **79**, 1286 (1957).

(14) W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

molar ratio produces a yellow solution with an absorption band around 360 mμ, which has been shown[15] to be similar to the product of the decomposition of the blue form upon standing. We have compared the spectrum of this form with that of the product of the oxidation of $Fe(phen)_3^{2+}$ by peroxydiphosphate and find that they are similar but not identical, since the latter shows two discrete peaks at 345 and 360 mμ. This may indicate some ligand oxidation in the post-rate-determining steps following those in the proposed mechanism. The observations, however, support the initial steps postulated for the present reaction, since these steps do not lead to $Fe(phen)_3^{3+}$ in the products.
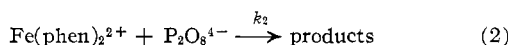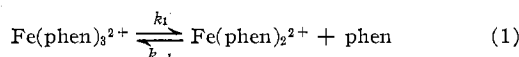
Discussion

It was our intention to investigate the oxidation of the complex cation: $Fe(phen)_3^{2+} \rightarrow Fe(phen)_3^{3+}$, in neutral aqueous solution. We found, instead, that the ferric complex is not a product of the reaction and that, in fact, the reaction proceeds by dissociation of the ferrous complex. It is possible that the oxidation potential of the peroxydiphosphate is not sufficient to allow the oxidation to proceed as expected. Of relevance to this point is the fact that $Fe(phen)_3^{3+}$ is unstable toward reduction by hydroxide ion in neutral solution.[16] The instability of $Fe(phen)_3^{3+}$ under these conditions is important for it indicates that even if the oxidant is sufficiently powerful (as is peroxydisulfate) to accomplish the desired oxidation, a step of the type

$$Fe(phen)_3^{3+} + OH^- \longrightarrow Fe(phen)_3^{2+} + OH \cdot$$
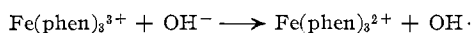
will inevitably lead to side reactions such as oxidation of the phenanthroline ligands. It would be of interest to measure the oxidation potential for peroxydiphosphate on a system with less complication.

The rate behaviors for the reactions of peroxydiphosphate and of a number of other species with $Fe(phen)_3^{2+}$ are similar. Thus, it appears reasonable to assume that the rate step is identical for all reactions and that the oxidation of this complex ion is dependent upon its first dissociation step, which is known to be slow.[2] A mechanism which is consistent with the data reported here is

$$Fe(phen)_3^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(phen)_2^{2+} + phen \qquad (1)$$

$$Fe(phen)_2^{2+} + P_2O_8^{4-} \overset{k_2}{\longrightarrow} products \qquad (2)$$

By considering $Fe(phen)_2^{2+}$ an intermediate which comes to a steady-state balance, the following relationship is derived

$$-\frac{d[Fe(phen)_3^{2+}]}{dt} = \frac{k_1k_2[Fe(phen)_3^{2+}][P_2O_8^{4-}]}{k_{-1}[phen] + k_2[P_2O_8^{4-}]} \qquad (3)$$

This rate law explains the apparent first-order behavior observed for high concentrations of $P_2O_8^{4-}$ and low concentrations of free phenanthroline. Under these conditions, eq 3 approaches the simple form, $-d[Fe-$

(15) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **74**, 4744 (1952).
(16) G. Lawler and N. Sutin, unpublished observations; N. Sutin, private communication.

$(phen)_3^{2+}]/dt = k_1[Fe(phen)_3^{2+}]$, and k_{obsd} should approach k_1. At low concentrations of the peroxide, on the other hand, eq 3 indicates a dependence on $P_2O_8^{4-}$ with the kind of variation observed. The decrease in the rate of the reaction produced by the addition of excess 1,10-phenanthroline, shown in Figure 2, is also predicted by this equation. Using the data from Table III ($k_{obsd} = 3.8 \times 10^{-4}$ sec^{-1} when no phenanthroline is added and $k_{obsd} = 1.8 \times 10^{-4}$ sec^{-1} when $[phen] = 8 \times 10^{-4}$ M and $[P_2O_8^{4-}]_0 = 5 \times 10^{-3}$ M) plus an estimate of 2×10^6 M^{-1} sec^{-1} for k_{-1} from ref 17, it is calculated that $k_2 \simeq 3 \times 10^5$ M^{-1} sec^{-1} under the conditions of our experiments. At high concentrations of peroxydiphosphate, the rate should be and is independent of pH. The value of k_2 should, on the other hand, be a function of pH because of the secondary phosphate ionizations which occur in this range. Our data at low peroxydiphosphate concentrations were not sufficiently detailed to show this.

To explain the results with copper(II) sulfate, shown in Table II, at least the first step in the formation of the copper(II) phenanthroline complexes must be considered

$$Cu^{2+} + phen \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Cu(phen)^{2+} \qquad (4)$$
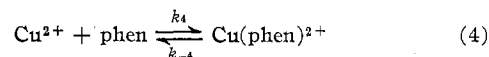
Then a mechanism for this reaction would consist of eq 1 and 4. If the reverse step of eq 4 is assumed to be initially unimportant to the rate and if the 1,10-phenanthroline concentration is assumed to reach a steady state, then a somewhat similar rate law results

$$-\frac{d[Fe(phen)_3^{2+}]}{dt} = \frac{k_1k_4[Fe(phen)_3^{2+}][Cu^{2+}]}{k_{-1}[Fe(phen)_2^{2+}] + k_4[Cu^{2+}]} \qquad (5)$$

which approximates the experimentally observed rate law in which the reaction appeared first order in $Fe(phen)_3^{2+}$ and zero order in copper(II) concentration. By using the rate constants for k_{-1} and k_4 from Holyer, *et al.*,[17] it can be shown that for the concentration ranges studied here, $k_4[Cu^{2+}]$ is more than 10^8 times larger than $k_{-1}[Fe(phen)_2^{2+}]$; thus, k_{obsd} should equal k_1.

A similar mechanism applies to nickel(II) sulfate, in which eq 1 would be followed by

$$Ni^{2+} + phen \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Ni(phen)^{2+} \qquad (6)$$
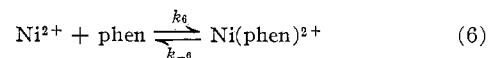
This kind of displacement reaction, which effects the dissociation of one metal complex by another metal ion (which reacts more rapidly and forms a more stable complex with the ligand), has been used to study the mono complexes of a number of metals.[17] From these two present cases, it is seen that the method is applicable to the study of the rates of dissociation of some higher complexes and is especially feasible for the study of the dissociation of $Fe(phen)_3^{2+}$.
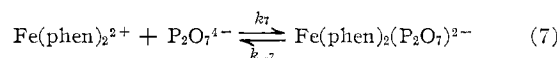
The other two substances shown in Table II, although similar in rate behavior, showed greater deviation from first-order behavior at lower concentrations. However, an explanation of their reaction with Fe-

(17) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

(phen)$_3^{2+}$ must invoke the other product of the dissociation, the Fe(phen)$_2^{2+}$ ion. Thus, for sodium pyrophosphate, the formation of an inner-sphere ion pair could compete with the k_{-1} step

$$\text{Fe(phen)}_2^{2+} + \text{P}_2\text{O}_7^{4-} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \text{Fe(phen)}_2(\text{P}_2\text{O}_7)^{2-} \qquad (7)$$

A mechanism for the reaction would then consist of eq 1 followed by eq 7 and would yield a similar rate law expression to that derived for the peroxydiphosphate reaction. Such a mechanism predicts that excess phenanthroline would also reduce the rate of the pyrophosphate reaction, and, indeed, it was found to have an even greater effect than in the peroxydiphosphate case. A 4×10^{-4} M excess of phenanthroline, for example, completely repressed the reaction in a 5×10^{-3} M Na$_4$P$_2$O$_7$ solution, while in a tenfold more concentrated solution (5×10^{-2} M Na$_4$P$_2$O$_7$) the same concentration of phenanthroline reduced the rate, changing the reaction half-life from 30 to 55 min. Using these data in a similar estimation to that above, it becomes evident that k_7 is much smaller than k_2. This is also supported by the higher concentrations of pyrophosphate necessary to achieve the same first-order behavior observed for all concentrations of peroxydiphosphate above 2×10^{-3} M.

The rate process of the peroxydiphosphate reaction similar to that of the pyrophosphate suggests that it, too, forms an ion pair (acts as a ligand) in the second step, eq 2, and that this step is then followed by other steps in which the oxidation occurs.

The rate process for the reaction of Fe(phen)$_3^{2+}$ with the sodium salt of EDTA is slower and deviates after the first 35% of the reaction from the first-order behavior found in the other reactions. While EDTA anion is an effective complexing agent as a hexadentate ligand, it may not compete effectively with phenanthroline in this rate case since four of the coordination sites are still blocked in Fe(phen)$_2^{2+}$.

The dependence of the peroxydiphosphate oxidation of Fe(phen)$_3^{2+}$ on the first dissociation step of the latter is interesting in that other of the Fe(phen)$_3^{2+}$ reactions show this same dependence. For example, the reaction with acids[18] and bases[19,20] and the racemiza-

tion processes[18] may be cited. The dissociation of Fe(phen)$_3^{2+}$ in 1 M HCl was measured by Basolo, *et al.*,[18] who found k_1 to be 3.7×10^{-4} sec^{-1} at 34.6°. Thus, H$^+$ acts remarkably as Cu^{2+} and Ni^{2+} in competing for the free phenanthroline produced in the first dissociation step.

It was expected that more pronounced rate effects due to outer-sphere ion pairing of Fe(phen)$_3^{2+}$ with both P$_2$O$_7^{4-}$ and P$_2$O$_8^{4-}$ would be observed, since both these anions are known to form strong ion-pair complexes.[11,12,21] The data, as shown in Tables I and II, show only slight evidences for such complexes. However, the mechanism is such that small effects can be rationalized for the first, rate-determining step. For the second step, complexing is undoubtedly important, especially in the pyrophosphate reaction for which no other driving force for breakdown of Fe(phen)$_3^{2+}$ seems plausible.

One interest in this study was the possible comparison of the reaction of P$_2$O$_8^{4-}$ and S$_2$O$_8^{2-}$ with Fe(phen)$_3^{2+}$. Irvine[10] reported that the peroxydisulfate reaction with Fe(phen)$_3^{2+}$ was a second-order reaction but that there were deviations after about 25–30% of the reaction. Since the peroxydiphosphate reaction was not second order, some measurements were made on the persulfate reaction under the same conditions of the other measurements in this study. These experiments confirmed the fact that the two reactions are different; also, the dependence on Fe(phen)$_3^{2+}$ when peroxydisulfate is present in 50-fold excess is not simple pseudo first order. Thus, the rate process is not adequately described by a second-order equation, nor is the rate process controlled by the first dissociation step of the Fe(phen)$_3^{2+}$ entirely since it can be either faster or slower than the rate predicted by k_1 alone. More work is needed to clarify the mechanism of the peroxydisulfate reaction mechanism and to evaluate the electrode potential for peroxydiphosphate before a meaningful comparison can be made.

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