(en)$_3{}^{3+}$ [6]) in the *trans* case was about 1.9 times that of the *cis* which agrees quite well with the simple crystal field prediction for monodentate complexes of this type. The theory predicts that the *cis* compound due to a lack of an effective center of symmetry should have a greater intensity than the *trans* isomer. The greater intensity of the *trans* isomer as observed here agrees with the results of Legg and Cooke[11] on similar complexes with iminodiacetic acid. As discussed by Ballhausen[13] the d-d transitions in the *trans* case gain intensity through the dissymmetry introduced by asymmetrical ligand vibrations.

The acetate and ethylenediamine methylene proton resonance peaks for the two isomers are summarized in Table II. The amine protons exchanged too rapidly for these peaks to be observed. The substituted and unsubstituted ethylenediamine methylene protons exhibit a complicated resonance in the 2.3–3.7-ppm region. Owing to the positioning of the acetate rings, the two methylene protons are in different chemical environments and an ab quartet is expected for each different acetate ring. The structure of each of the isomers is given in Figure 1. In the *trans* isomers the two acetate rings are equivalent and one quartet appears in the acetate proton region. For the *cis* isomer both acetate rings are different and two overlapping quartets are observed. These quartets are separated somewhat in the 100-Mc spectrum.

TABLE II

RESONANCE FREQUENCY ASSIGNMENT AND INTEGRATION VALUES FROM THE PMR SPECTRA OF THE *trans*- AND *cis*-TETRADENTATE CHELATE COMPLEXES[a]

	trans-(Co(en)AIEDA)Cl·$3H_2O$		*cis*-(Co(en)AEIDA)Cl·$2H_2O$		
Assignment	Res freq, ppm	No. of H's	Res freq, ppm		No. of H's
-$(CH_2COO)_2$	4.61 4.34 4.15 3.87	4.23	4.43 4.15 4.12 3.82	4.43 4.12 4.08 3.76	4.25
$>NCH_2CH_2N<$	3.57 ↓ 2.5	7.77		3.74 ↓ 2.34	7.75

[a] All frequencies on low-field side of NaTMS.

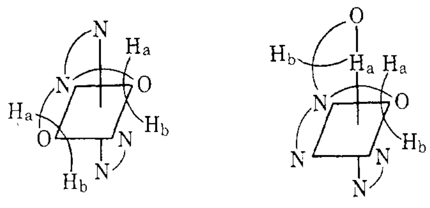

Figure 1.—Orientation of acetate ring protons in *trans*- and *cis*-Co(en)AEIDA.

The chemical shifts for the acetate ring protons for the two isomers calculated according to Jackman[14] are shown in Table III. For the *trans* isomer the acetate proton pointing upward toward the AEIDA ethylene backbond is designated H_b, and the other, H_a. The chemical shifts of these protons are comparable to the average values of 3.97 and 4.30 ppm found by Legg and Cooke[11] for *trans*-Co(dien)MIDA and can be explained by the anisotropy of the CN bond. The H_a will be shielded by the en ring of the tetradentate, and the H_b will be deshielded, so that H_a will occur at higher fields. For the *cis* isomer it is impossible to assign the different quartets to specific acetate rings. Apparently the different orientations of the neighboring groups result in each acetate group having similar chemical environment.

TABLE III

CHEMICAL SHIFTS (PPM) OF ACETATE RING PROTONS OF *trans*- AND *cis*-Co(en)AEIDA

trans-(Co(en)AEIDA)Cl		*cis*-(Co(en)AEIDA)Cl	
δ_a	δ_b	δ_a	δ_b
4.06	4.43	4.05	4.21
		4.02	4.18

Acknowledgments.—Financial support of this investigation by the National Institutes of Health is gratefully acknowledged.

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The Oxidation of Tris(1,10-phenanthroline)iron(II) Ion by Aqueous Chlorine[1a]

BY BASSAM Z. SHAKHASHIRI AND GILBERT GORDON[1b]

Received February 23, 1968

The oxidation of iron(II) species by chlorine may proceed through a two-electron step to form an iron(IV) intermediate

$$\mathrm{Fe(II)} + \mathrm{Cl_2} \rightleftarrows \mathrm{Fe(IV)} + 2\mathrm{Cl^-} \qquad (1)$$

$$\mathrm{Fe(IV)} + \mathrm{Fe(II)} \longrightarrow 2\mathrm{Fe(III)} \qquad (2)$$

or through a one-electron step to form a chlorine radical intermediate

$$\mathrm{Fe(II)} + \mathrm{Cl_2} \rightleftarrows \mathrm{Fe(III)} + \mathrm{Cl_2^-} \qquad (3)$$

$$\mathrm{Fe(II)} + \mathrm{Cl_2^-} \longrightarrow \mathrm{Fe(III)} + 2\mathrm{Cl^-} \qquad (4)$$

In this note we wish to report the results of our study of the oxidation of tris(1,10-phenanthroline)iron(II)

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[1] (a) Part of the thesis presented by B. Z. Shakhashiri to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1967. (b) Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.

ion, [Fe(phen)$_3$$^{2+}$], by aqueous chlorine in an attempt to differentiate between these two possibilities.

Experimental Section

Chemicals.—Solutions of tris(1,10-phenanthroline)iron(II) sulfate were prepared either by adding an equivalent amount of iron(II) sulfate heptahydrate to an aqueous solution of 1,10-phenanthroline monohydrate or by dissolving iron wire in warm dilute sulfuric acid solution and, after cooling to room temperature, adding an equivalent volume of a standard solution of 1,10-phenanthroline. The concentrations of 1,10-phenanthroline and Fe(phen)$_3$$^{2+}$ were determined spectrophotometrically at 2650 and 5100 Å, respectively. Chlorine(I) oxide, hypochlorous acid, and the chlorine solutions were prepared[2] and analyzed by standard methods.[3,4]

Procedure.—A known volume of the Fe(phen)$_3$$^{2+}$ solution was placed in a 1.0-cm cylindrical quartz cell. The temperature of the cell compartment of a Cary 14 recording spectrophotometer was measured by a Tele-Thermometer (YSI Model 42SC) and its output was followed on a Mosley 7101A strip chart recorder. In all kinetic experiments, the temperature control was maintained within 0.1°. A spring-powered syringe[5] was rinsed twice with the oxidant solution and carefully loaded. The syringe was secured in position on the Cary 14 such that a platinum hypodermic needle was inserted into the quartz cell through the serum cap. The reactants were mixed rapidly by triggering the cocked syringe and the course of the reaction was monitored by recording the change in absorbance due to Fe(phen)$_3$$^{2+}$ at 5100 Å as a function of time. The first absorbance value was read about 4 sec after mixing.

Aqueous chlorine solutions contain several species: Cl_2, HClO or ClO^-, and Cl_3^-. The relative concentrations of these species depend on the concentrations of chlorine, hydrogen ion, and chloride ion. The data of Zimmerman and Strong[6] are useful for solutions of chlorine in HCl–HClO$_4$ solutions of 1.00 M ionic strength at 25°. Variations of the data with ionic strength and changes in the medium are not known. These data[6] were used in calculating molar concentrations of the species Cl_2, HClO, and Cl_3^-. The method of calculation utilizes the equilibrium

$$Cl_2 + H_2O \rightleftharpoons Cl^- + H^+ + HClO \tag{5}$$

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^- \tag{6}$$

constants for reactions 5 and 6. At 3250 Å the molar absorptivities for Cl_2, HClO, and Cl_3^- are 75.3, 11.0, and 192.9 M^{-1} cm^{-1}, respectively.[6]

Results and Discussion

The extent of all reactions (90% completion) was determined spectrophotometrically by measuring the absorbance due to Fe(phen)$_3$$^{2+}$ at 5100 Å. Absorbance values were read at time intervals appropriate to the speed of each reaction. The kinetic data were analyzed by means of a nonlinear least-squares computer program with unit weights for each datum point. The square of the differences between the observed and calculated absorbance values in terms of the appropriate rate law is minimized and the corresponding standard deviations are calculated directly by means of this program.

Addition of aqueous chlorine to a dilute phenanthroline solution was found to change the ultraviolet spectrum of the latter. However, these changes were found to be similar to changes in the spectrum upon protonation of phenanthroline.[7] No evidence was found for either oxidation or chlorination of phenanthroline (free, protonated, or coordinated to iron) by the chlorine oxidants under the conditions of this investigation.

The oxidation of Fe(phen)$_3$$^{2+}$ by aqueous chlorine is known[8] to yield Fe(phen)$_3$$^{3+}$ as one product. In the kinetic study of the Fe(phen)$_3$$^{2+}$–$Cl_2$ reaction, a large excess of oxidant was used and pseudo-first-order kinetics were observed. The reaction is first order in each reactant and Fe(phen)$_3$$^{3+}$ is the major iron product. The absorbance due to Fe(phen)$_3$$^{3+}$ at 5100 Å is negligible and does not contribute to that of Fe(phen)$_3$$^{2+}$. Absorption spectra of the final products exhibit the characteristic band of Fe(phen)$^{3+}$ at 5900 Å and that of the iron(III)–phenanthroline dimer, (phen)$_2$Fe–O–Fe(phen)$_2$$^{4+}$ or (phen)$_2$Fe(OH)$_2$Fe(phen)$_2$$^{4+}$, at 3550 Å.[9,10] Formation of aquo- and chloroiron(III) species cannot be detected because of the large absorption band due to excess chlorine.

The major reaction path appears to be that represented by eq 3 and 4. The small amount of (phen)$_2$Fe(OH)$_2$Fe(phen)$_2$$^{4+}$ formed results from the decomposition of Fe(phen)$_3$$^{3+}$. The dependence of the rate of reaction on concentrations of Fe(phen)$_3$$^{2+}$ and chlorine is shown in Tables I and II.

TABLE I

REACTION BETWEEN Fe(phen)$_3$$^{2+}$ AND CHLORINE AT 25° AND IONIC STRENGTH 1.0 ± 0.1 M[a]

[H$^+$], M	[Cl$^-$], M	A_0[b]	[Total oxidant], mM	[Cl_2 species], mM	k_1,[c] M^{-1} sec^{-1}
1.0	1.0	0.48–1.36	2.9–13.8	2.5–11.6	1.9 ± 0.3
0.1	1.1	0.52–0.53	3.5–6.8	2.9–5.6	2.4 ± 0.1
0.01	1.0	0.50–0.57	2.0–8.0	1.7–6.6	2.3 ± 0.1
0.01–0.1	0.1	1.51–1.53	4.6–7.6	3.5–7.2	2.4 ± 0.1

[a] Ionic strength maintained with HCl, NaCl, NaNO$_3$, or a combination of the three. [b] Range of calculated initial absorbance values at 5100 Å. These values were in good agreement with measured values for the slower reactions (cell path length was 1.0 cm, and the molar absorptivity was 1.11 × 10^4 M^{-1} cm^{-1}). [c] Average rate constant with Cl_2 species concentration used in the rate law. The ± value corresponds to one standard deviation. The standard deviations for individual rate constants were less than 0.01.

At 25° and an ionic strength of 1.0 M and less than 0.1 M hydrogen ion, the average second-order rate constant is 2.4 ± 0.1 M^{-1} sec^{-1} when the concentration of the species Cl_2 is used. At an ionic strength of 0.1 M, or less, the average second-order constant is 1.17 ± 0.06 M^{-1} sec^{-1}. This variation in the rate constant with ionic strength is quite conspicuous, but is not understood.

In the reaction between aqueous chlorine species and Fe(phen)$_3$$^{2+}$, Cl_2 seems to be the most reactive. Although Cl_3^- may be expected to interact the most by forming an ion pair, the results of this investigation do

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TABLE II
REACTION BETWEEN $\mathrm{Fe(phen)_3^{2+}}$ AND CHLORINE AT 25° AND IONIC STRENGTHS LOWER THAN 1.0 M[a]

I, M	A_0[b]	[Total oxidant], mM	[$\mathrm{Cl_2}$ species], mM	k,[c] M^{-1} sec^{-1}
0.1	1.164	8.51	8.09	1.26
0.1	0.357	8.51	8.09	1.19
0.1	1.135	9.54	9.06	1.20
0.1	1.190	3.29	3.13	1.19
0.1	0.774	7.72	7.33	1.23
0.1	1.217	1.90	1.80	1.16
0.1[d]	1.250	7.39	5.75	1.10
0.1[d]	1.250	7.08	5.43	1.17
0.01[e]	1.237	9.12	3.76	1.06
0.01[e]	0.615	9.10	3.74	1.12

[a] Ionic strength maintained at 0.1 M with HCl. [b] Calculated initial absorbance. [c] Rate constant with $\mathrm{Cl_2}$ species concentration used in the rate law. [d] Hydrogen ion concentration was 0.01 M with HCl and the ionic strength was maintained with HCl and NaCl. [e] Hydrogen ion concentration was maintained at 0.01 M with HCl.

not reveal conclusively whether or not $\mathrm{Cl_3^-}$ is a significant reactant. The data reported in Tables I and II suggest that the $\mathrm{Fe(phen)_3^{2+}}$–$\mathrm{Cl_2}$ reaction rate is independent of both hydrogen ion and chloride ion concentration in the 0.01–1.0 M range. Under the conditions of these experiments and those of Crabtree and Schaefer,[11] the concentration of $\mathrm{Cl_3^-}$ changes from 2 to 16% of the total oxidant concentration while the concentration of $\mathrm{Cl_2}$ changes from 98 to 84% of the total oxidant by varying the concentration of either hydrogen or chloride ions. Thus more significant changes in concentrations of $\mathrm{Cl_3^-}$ occur when the chloride ion is varied over a wider range than that reported in this and other[11] works.

The species HClO was found to be less reactive than $\mathrm{Cl_2}$. In experiments where excess HClO was added to $\mathrm{Fe(phen)_3^{2+}}$ in dilute sulfuric acid (5×10^{-5} to 5×10^{-2} M) and at an ionic strength of 1.0 M, the decrease in absorbance due to $\mathrm{Fe(phen)_3^{2+}}$ at 5100 Å was found to be slower in the first few minutes than in the latter portion of reaction. Analyses of the absorbance–time data suggest that in the first portion of reaction where only about 2% of $\mathrm{Fe(phen)_3^{2+}}$ disappears, HClO reacts with $\mathrm{Fe(phen)_3^{2+}}$ to produce chloride ion which reacts rapidly with the excess HClO to form $\mathrm{Cl_2}$ in accordance with eq 5. Beyond the initially slow portion of reaction, deviation from linearity in absorbance–time plots occurs and the rate of disappearance of $\mathrm{Fe(phen)_3^{2+}}$ increases with time. The $\mathrm{Fe(phen)_3^{2+}}$–HClO reaction appears to be autocatalytic in that the $\mathrm{Cl_2}$ formed reacts faster with $\mathrm{Fe(phen)_3^{2+}}$ than does HClO. The kinetic details of the HClO–$\mathrm{Fe(phen)_3^{2+}}$ reaction will be reported elsewhere.

In conclusion, it should be pointed out that $\mathrm{Cl_2}$ reacts much faster than HClO with $\mathrm{Fe(phen)_3^{2+}}$ as in the case when $\mathrm{Fe(CN)_6^{4-}}$ is the reducing agent,[12] but HClO reacts more rapidly than $\mathrm{Cl_2}$ with $\mathrm{Fe^{2+}}$.[13] Furthermore, $\mathrm{Cl_2}$ reacts with $\mathrm{Fe(phen)_3^{2+}}$ *via* an outer-sphere path and involves a one-electron step. Formation of $\mathrm{FeCl^{2+}}$ as an initial product in the $\mathrm{Fe^{2+}}$–$\mathrm{Cl_2}$ and $\mathrm{Fe^{2+}}$–HClO reactions[13] strongly suggests that an inner-sphere path is involved. The mode of reaction seems to change significantly as iron(II) is complexed with phenanthroline or cyanide ion but, unfortunately, specific comparison of rates can be made only when all of the reactions proceed *via* the same path.

Acknowledgments.—The authors wish to express their appreciation to the United States Atomic Energy Commission for its financial support through Grant No. AT-(40)-2858.

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Substitution Reactions of the Bromo(1,1,7,7-tetraethyldiethylenetriamine)palladium(II) Cation in Nonaqueous Solvents

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Received May 13, 1968

It was found that substitution reactions (eq 1) in

$\mathrm{Pd(Et_4dien)}$[1]$\mathrm{Br^+ + Y^{n-} \longrightarrow Pd(Et_4dien)Y^{(2-n)+} + Br^-}$ (1)

water are first order in complex but zero order in Y, even for good ligands like $\mathrm{SO_3^{2-}}$, $\mathrm{SCN^-}$, and $\mathrm{I^-}$.[2,3] The mechanism was explained by a slow solvolysis step (eq 2) (S = $\mathrm{H_2O}$ in this case), followed by a rapid anation step (eq 3). The direct reagent path (eq 4), a parallel

$$\mathrm{Pd(Et_4dien)Br^+ + S \xrightarrow[k_1]{\text{slow}} Pd(Et_4dien)S^{2+} + Br^-} \qquad (2)$$

$$\mathrm{Pd(Et_4dien)S^{2+} + Y^{n-} \xrightarrow{\text{fast}} Pd(Et_4dien)Y^{(2-n)+} + S} \qquad (3)$$

$$\mathrm{Pd(Et_4dien)Br^+ + Y^{n-} \xrightarrow{k_2'} Pd(Et_4dien)Y^{(2-n)+} + Br^-} \qquad (4)$$

reaction so common in square-planar substitution kinetics in which a dependence of rate on nucleophile Y is found,[4] was observed[2,3] only for the ligands $\mathrm{OH^-}$ and $\mathrm{S_2O_3^{2-}}$. Hydroxide ion can remove the proton from the central amine nitrogen of $\mathrm{Et_4dien}$, creating the reactive conjugate-base species (SN1CB mechanism), and thiosulfate ion has a very large nucleophilic reactivity constant (n_{Pt})[5] toward a "soft" ion like Pd(II),[6] enabling it to form the necessary five-coordinate species even in this sterically hindered system.

In the present study, kinetics were carried out in $\mathrm{CH_3OH}$, $\mathrm{(CH_3)_2SO}$, and $\mathrm{CH_3CN}$ in an attempt to de-

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[1] $\mathrm{Et_4dien = HN[C_2H_4N(C_2H_5)_2]_2}$.

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