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Kinetics of the Oxidation Reactions of Iodide and Iron(II) Ions by Tris(1,10-phenanthroline)iron(III) Ion in Aqueous Mixtures of Methanol and Ethanol

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The rate constant of the oxidation reactions of iodide and iron(II) ions by tris(1,10-phenanthroline)iron(III) complex ion has been measured by using stopped-flow spectrophotometry in aqueous mixtures of methanol and ethanol at varied ionic strengths from 0.05 to 1.3 M at 10, 15, 20, and 25 °C. The ionic strength dependence and the permittivity (dielectric constant) dependence on the rate constant are examined. The linear relationships of log k vs. $\mu^{1/2}/(1+\mu^{1/2})$ and also those of log k vs. $1/D$ are well established for the reaction between iodide ion and tris(1,10-phenanthroline)iron(III) ion. On the contrary, the reaction kinetics of the reaction between iron(II) ion and tris(1,10-phenanthroline)iron(III) ion does not simply obey such relationships. The reaction mechanisms are discussed in terms of the sign of the ionic charge and the sizes of the reactants and the products.

Introduction

The usual form of the equation relating the rate constants with the ionic strength (μ) and the dielectric constant (D) of the reaction solution, obtained from the Brønsted–Bjerrum equation and the Debye–Hückel equation, is

$$\ln (k/k_0) = \frac{\epsilon^2 Z_a Z_b}{\kappa r T}\left(1 - \frac{1}{D}\right) + A\frac{Z_a Z_b \mu^{1/2}}{1+\mu^{1/2}} \tag{1}$$

as shown by Laidler and Eyring,[1] where z_a and z_b are the charges of reactants, ϵ is the electron charge, κ is the Boltzmann constant, r is the radius of the activated complex, k_0 is the rate constant at the ionic strength zero and at D = 1, and A is a parameter involving the absolute temperature (T), D, and so forth. Since eq 1 is deduced from the electrostatic-interaction model for the reactants only, when a neutral molecule or atom leaves from an activated complex to the product, eq 1 should hold, but when it is charged, eq 1 would be influenced relating to the size of the reactants and the products. From such points of view, the outer-sphere type of the oxidation reactions of iodide and iron(II) ions by tris(1,10-phenanthroline)iron(III) ion were investigated in the present paper. Further, it will be interesting to examine whether eq 1 holds at the relatively high ionic strength, and so the ionic strength was varied over a large range of 0.5–1.3 M. Sutin and Gordon[2] have reported the kinetics of the oxidation of iron(II) ion by tris(1,10-phenanthroline)iron(III) complex ion (ferriin) in 0.50 M perchloric acid at 15, 25, and 35 °C in aqueous solution. Therefore, only the ionic strength and permittivity dependencies on the reaction of iron(II) ion with ferriin are reported in this paper. On the reaction between iodide ion and ferriin, the stoichiometry and several effects of the ionic strength, permittivity, acidity, and temperature are more extensively studied. The rate of the oxidation reaction of the solvents by ferriin was also measured as a preliminary experiment for this investigation.

Experimental Section

Materials. Tris(1,10-phenanthroline)iron(III) perchlorate was prepared by oxidizing $Fe(phen)_3{}^{2+}$ with lead dioxide in dilute sulfuric acid aqueous solution; after removal of PbO_2 and $PbSO_4$ the perchlorate salt of $Fe(phen)_3{}^{3+}$ was precipitated by addition of sodium perchlorate. The solid obtained was recrystallized from perchlorate solution; it was dried at room temperature and stored in the dark. Stock solution of ferriin was prepared by dissolving 0.3 g of perchlorate salt into 70% (v/v) perchloric acid (100 mL). The blue solution having an absorption maximum at 600 nm is very stable in perchloric acid, and no appreciable decomposition occurred for at least 3 months at room temperature in the dark. Reagent grade sodium iodide was used without further purification. A perchlorate salt of iron(II) was prepared by dissolving pure iron wire in perchloric acid and recrystallizing it. Sodium perchlorate used for adjusting the ionic strength was recrystallized twice from aqueous solution. Methanol and ethanol were distilled in a glass still. Deionized water was further distilled through alkaline permanganate solution in a glass still.

Table I. Iodide Ion Concentration Dependence on the Pseudo-First-Order Rate Constants for the Reaction between Iodide Ion and Ferriin[a]

$10^4[NaI]_{added}$/M	k_{obsd}/s^{-1}	$10^{-4}k/M^{-1}\ s^{-1}$
2.0	11.9 ± 0.2	6.0 ± 0.1
2.5	16.3 ± 0.4	$6.5_2 \pm 0.1_6$
4.0	22.5 ± 0.6	$5.6_3 \pm 0.1_5$
6.0	36.3 ± 0.9	$6.0_5 \pm 0.1_5$
8.0	46.4 ± 1.0	$5.8_0 \pm 0.1_3$
10	57.0 ± 2.5	5.7 ± 0.25
12	75.6 ± 2.5	6.3 ± 0.2
	mean	$6.0 \pm 0.1_6$

[a] 0.05 M in $HClO_4$; 1 × 10^{-5} M in $Fe(phen)_3(ClO_4)_3$; ionic strength 1.0 M; 25 °C.

Kinetic Measurements. All the kinetic data were obtained using a Yanako SPS 1 stopped-flow spectrophotometer with MS-5019 memoriscope. Reactions with iodide ion or iron(II) ion in excess over ferriin in concentration were followed by means of the increase in absorption due to the ferroin at 510 nm. The cell housing was thermostated at a constant temperature (with ±0.2 °C) by a water bath.

Results

Stoichiometry. The stoichiometry for the reaction between iodide ion and ferriin was determined as follows. A total of 100 mL of the solution reacted was extracted twice by two 5-mL portions of tetrachloromethane and shaking each for 1 min, and the iodine concentration in the extracted solution was determined at 518 nm with ϵ_{max} 9.45 × 10^2 M^{-1} cm^{-1} in tetrachloromethane. The concentration of ferroin formed was determined at 510 nm with ϵ_{max} 1.1 × 10^4 M^{-1} cm^{-1} in aqueous solution. For the solutions of 5 × 10^{-5}, 1 × 10^{-4}, and 2 × 10^{-4} M in NaI, 0.12 and 1.2 M in $HClO_4$, and 2.15 × 10^{-5} M in ferriin, $[Fe(phen)_3{}^{2+}]_{formed}$ and $[I_2]_{formed}$ were, respectively, (2.15 ± 0.06) × 10^{-5} M and (1.05 ± 0.09) × 10^{-5} M for ten runs. The data show that the reaction is represented by the stoichiometric equation of

$$2Fe(phen)_3{}^{3+} + 2I^- \rightarrow I_2 + 2Fe(phen)_3{}^{2+} \tag{2}$$

The experiments on the stoichiometry for the reaction of iron(II) ion with ferriin were not made.

Order of Reaction. In concentration excess of iodide or iron(II) over ferriin, the rate law of the pseudo first order of $-d[Fe(phen)_3{}^{3+}]/dt = d[Fe(phen)_3{}^{2+}]/dt = k_{obsd}[Fe(phen)_3{}^{3+}]$ was well established for all the runs, and k_{obsd} obtained was

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Table II. Ionic Strength and Temperature Dependences on the Second-Order Rate Constants for the Reaction of Iodide Ion with Ferriin in Aqueous Solution[a]

ionic strength (μ)/M	$10^{-5}k/M^{-1}\ s^{-1}$ 10 °C	15 °C	20 °C	25 °C
0.05	5.80 ± 0.05	7.12 ± 0.05	8.9 ± 0.5	10.0 ± 2.0
0.10	3.09 ± 0.09	3.4 ± 0.3	5.0 ± 0.2	6.5 ± 0.7
0.15				5.2 ± 0.1
0.20	1.50 ± 0.06	1.95 ± 0.06	2.70 ± 0.05	3.9 ± 0.1
0.25				4.7 ± 0.1
0.30	1.01 ± 0.05	1.25 ± 0.08	1.93 ± 0.09	
0.35				2.40 ± 0.05
0.45				1.70 ± 0.05
0.50	0.52 ± 0.01	0.80 ± 0.02	1.00 ± 0.03	1.60 ± 0.02
0.50			1.24 ± 0.02[b]	
0.65			0.88 ± 0.22[b]	1.00 ± 0.02
0.70			0.75 ± 0.02[b]	
0.82			0.60 ± 0.01[b]	
0.85				0.73 ± 0.01
1.0	0.23 ± 0.01	0.29 ± 0.01	0.38 ± 0.01	0.60 ± 0.01
1.0			0.51 ± 0.01[b]	
1.3			0.33 ± 0.01[b]	

[a] 0.05 M in $HClO_4$; 5×10^{-6} M in $Fe(phen)_3(ClO_4)_3$; 2.5×10^{-4} M in NaI. [b] As in *a*; except 0.50 M in $HClO_4$.

proportional to the concentrations of iodide or iron(II). It is illustrated in Table I that $k_{obsd}/[I^-]$ holds a constant even in large range of the iodide ion concentration. The value of $k_{obsd}/[I^-]$ is of the second-order rate constant (k).

Acidity Dependence. The second-order rate constant of the reaction between iodide ion and ferriin increased slightly with increasing perchloric acid concentration in range the 0.05–1.0 M; the values of k at 25 °C at ionic strength 1.0 were 6.0×10^4, 6.5×10^4, 6.6×10^4, 7.4×10^4, 7.9×10^4, 8.5×10^4, and 9.3×10^4 $M^{-1}\ s^{-1}$ in 0.05, 0.1, 0.3, 0.4, 0.6, 0.7, and 1.0 M in $HClO_4$, respectively.

Ionic Strength and Temperature Dependences. The rate constants of the reaction of iodide ion with ferriin in 0.05 M $HClO_4$ were determined at varied ionic strengths at 10, 15, 20, and 25 °C, and also at several ionic strengths of 0.5–1.3 in 0.5 M $HClO_4$. These results are tabulated in Table II. The rate constants of the reaction of iron(II) ion with ferriin were also determined at varied ionic strengths at 20 °C in 0.05 M $HClO_4$, and the logarithmic values were plotted against $\mu^{1/2}/(1 + \mu^{1/2})$. The plots are shown in Figure 1 together with those of the corresponding iodide reaction at 20 °C.

All the plots of log k vs. $\mu^{1/2}/(1 + \mu^{1/2})$ for the data in Table II showed straight lines with negative slope even when perchloric acid was 0.5 M. The values of the slope in 0.05 M $HClO_4$ were −4.46, −4.34, −4.17, and −4.20 at 10, 15, 20, and 25 °C, respectively, and the slope in 0.5 M $HClO_4$ at 20 °C was −4.67. These absolute values are somewhat larger than those predicted from the usual equation of $\log (k/k_0) = 1.02z_az_b\mu^{1/2}/(1 + \mu^{1/2})$ at 25 °C. The corresponding plots for the reaction between iron(II) ion and ferriin do not show a straight line and reach a finite limit as seen in Figure 1.

Permittivity Dependence. The rate constant of the reaction of iodide ion with ferriin in 0.05 M $HClO_4$ was determined in aqueous mixtures of methanol and ethanol at ionic strength 0.2, 0.5, and 1.0 at 20 °C, and the logarithmic values were plotted against $1/D$, where the dielectric constant in the aqueous mixtures of methanol and ethanol was obtained from the data reported by Åkerlöf.[3] The plots are shown in Figure 2 together with those of the reaction of iron(II) ion with ferriin. The slopes were 640, 627, and 680 at the ionic strengths 0.2, 0.5, and 1.0, respectively. The values of r in eq 1 were calculated to be 1.2×10^{-8}, 1.2×10^{-8}, and 1.1×10^{-8} cm at the ionic strengths 0.2, 0.5, and 1.0, respectively. The positive slope in the reaction between iron(II) ion and ferriin was the reverse trend of the negative slope predicted from eq 1.

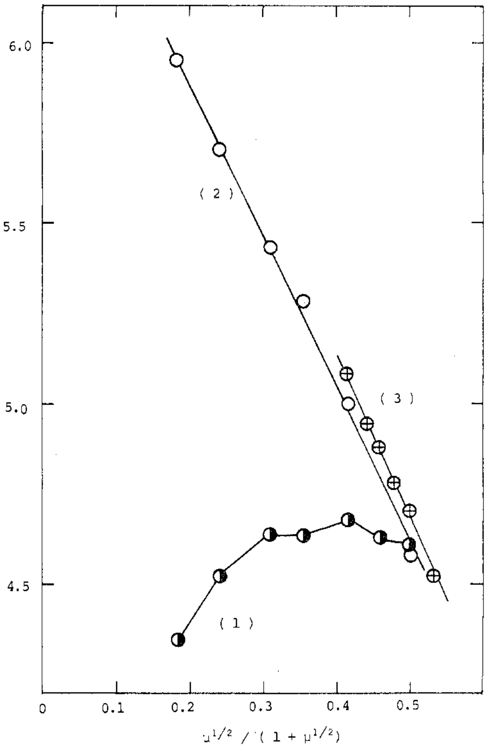

Figure 1. Plots of log k vs. $\mu^{1/2}/(1 + \mu^{1/2})$: (1) 0.05 M in $HClO_4$, 5×10^{-4} M in $Fe(ClO_4)_2$, 1×10^{-5} M in $Fe(phen)_3(ClO_4)_3$, 20 °C; (2) 0.05 M in $HClO_4$, 20 °C, other conditions as in Table II; (3) 0.50 M in $HClO_4$, 20 °C, other conditions as in Table II.

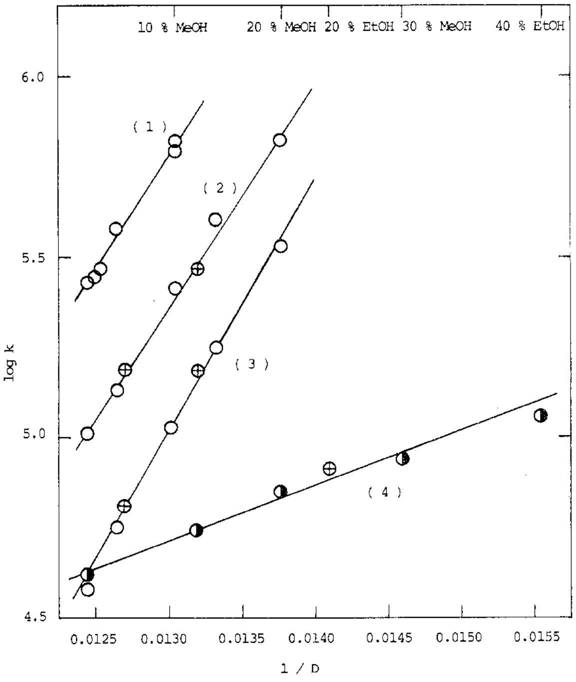

Figure 2. Plots of log k vs. $1/D$. Lines 1, 2, and 3 are for the reaction of iodide ion with ferriin, and line 4 is for the reaction of Fe(II) ion with ferriin: 20 °C; 0.05 M $HClO_4$; 0.15 M $NaClO_4$ for lines 1 and 4, 0.45 M for line 2, and 0.95 M for line 3; ○ and ◑ indicate the methanol–water mixture and ⊕ indicates the ethanol–water mixture.

Temperature Dependence. The rate constant for the reaction of iodide ion with ferriin in 0.05 M $HClO_4$ was measured at 10, 15, 20, and 25 °C at several ionic strengths. Activation energy calculated from the plot of log k vs. $1/T$ is 7.0 ± 0.2, 8.5 ± 0.5, 9.9 ± 0.4, 10.9 ± 0.5, 11.4 ± 0.5, and 11.0 ± 0.5 kcal mol^{-1} at ionic strength 0.05, 0.10, 0.20, 0.30, 0.50, and

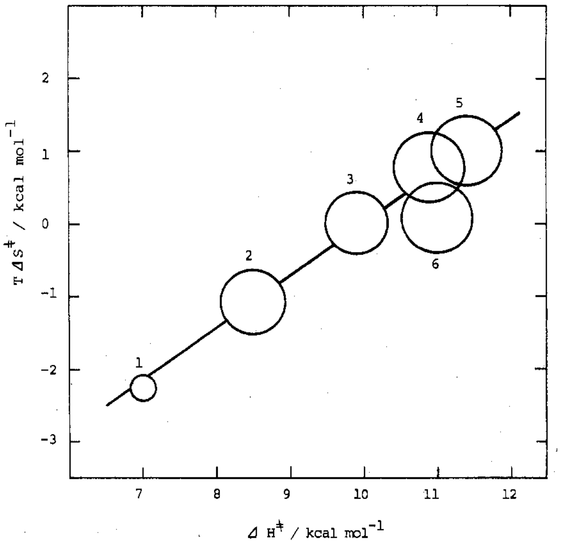

Figure 3. Plots of $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$. Ionic strengths are 0.05, 0.10, 0.20, 0.30, 0.50, and 1.0 M for the plots 1, 2, 3, 4, 5, and 6, respectively.

1.0 M, respectively. The entropy of activation calculated from the equation

$$k = \frac{\kappa T}{h} \exp[\Delta S^{\ddagger}/R] \exp[-\Delta H^{\ddagger}/RT]$$

is -7.6 ± 0.5, -3.6 ± 1.5, 0.03 ± 1.37, 2.8 ± 1.7, 3.4 ± 1.7, 0.17 ± 1.7 cal deg^{-1} mol^{-1} at ionic strength 0.05, 0.10, 0.20, 0.30, 0.50, and 1.0, respectively. It appears that a compensation rule for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is well established; a plot of $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$ shown in Figure 3. The slope is rather smaller than unity. The decrease of the rate of reaction between iodide ion and ferriin with increasing ionic strength is seen to be caused by the increase of the activation enthalpy.

Oxidation Rate of Solvents by Ferriin. The rate of decrease of ferriin concentration or the rate of increase of ferroin concentration was measured in aqueous mixtures of methanol and ethanol; in 0.3 M $HClO_4$ at 20 °C, the rate constants of the equation of $-d[Fe(phen)_3^{3+}]/dt = d[Fe(phen)_3^{2+}]/dt = k[Fe(phen)_3^{3+}]$ were 2.9×10^{-5}, 3.6×10^{-5}, 4.4×10^{-5}, 4.5×10^{-5}, 6.2×10^{-5}, 12×10^{-5}, and 14×10^{-5} s^{-1} for 0, 10, 20, 30, 40, 50, and 70% (v/v) ethanol, respectively, and were 4.3×10^{-5}, 5.3×10^{-5}, 5.9×10^{-5}, 8.5×10^{-5}, 13×10^{-5}, and 17×10^{-5} s^{-1} for 10, 20, 30, 40, 50, and 70% (v/v) methanol, respectively. These values decreased considerably with increasing the perchloric acid concentration. For example, the values in 2.4 M $HClO_4$ were 0.56×10^{-5}, 0.78×10^{-5}, 0.97×10^{-5}, and 0.97×10^{-5} s^{-1} for 0, 20, 40, and 60% (v/v) ethanol, respectively, and 0.94×10^{-5}, 1.7×10^{-5}, 2.2×10^{-5}, and 3.5×10^{-5} s^{-1} for 20, 40, 60, and 80% (v/v) methanol, respectively, and those in aqueous solution were 3×10^{-5}, 0.9×10^{-5}, 0.6×10^{-5}, 0.4×10^{-5}, 0.2×10^{-5}, 0.05×10^{-5}, 0.04×10^{-5}, and 0.006×10^{-5} s^{-1} in 0.3, 1.2, 2.4, 3.0, 6.0, 7.2, and 9.6 M $HClO_4$, respectively. Since the rate of dissociation of ferroin increases with increasing the alcohol concentration and with increasing acidity, the correction of the ferroin dissociation was made. The rate of reaction between iodide ion or iron(II) ion and ferriin is much faster than that of the oxidation reaction of solvents by ferriin and also that of the dissociation rate of ferroin, and so the former reaction rate was not disturbed by the latter reactions under the conditions of 0.05–1.0 M $HClO_4$ and 0–40% (v/v) alcohols in the present study.

Discussion

The stoichiometry of the reaction between iodide ion and tris(1,10-phenanthroline)iron(III) ion suggests that the oxidation reaction is first the production of atomic iodine followed by the rapid formation of iodine:

$$I^- + Fe(phen)_3^{3+} \xrightarrow{k} I + Fe(phen)_3^{2+} \qquad (3)$$

$$2I \rightarrow I_2 \qquad (4)$$

The large negative slope in the plot of log k vs. $\mu^{1/2}/(1 + \mu^{1/2})$ and the large positive slope in the plot of log k vs. $1/D$ indicate that a strong electrostatic force acts between I^- and $Fe(phen)_3^{3+}$ to form an activated intermediate complex. This is also revealed in the fact that the activation energy increased with increasing the ionic strength. The following mechanism for reaction 3 can be assumed.

$$I^- + Fe(phen)_3^{3+} \overset{K_a}{\rightleftarrows} [I^- \cdots Fe(phen)_3^{3+}] \overset{K_b}{\rightleftarrows} [I \cdots Fe(phen)_3^{2+}] \xrightarrow{k_c} I + Fe(phen)_3^{2+} \qquad (5)$$

One can write the following equation for the observed rate constant.

$$\frac{d \log k}{dD^{-1}} = \frac{d \log K_a}{dD^{-1}} + \frac{d \log K_b}{dD^{-1}} + \frac{d \log k_c}{dD^{-1}} \qquad (6)$$

Where K_a path indicates an ion association, K_b path the electron transfer, and k_c path the departure of each molecule. Since the leaving molecule from the intermediate is neutral, both the second and third terms on the right-hand side of eq 6 should be zero. Therefore, the permittivity dependence on the rate constant is controlled by the first association term only. This trend is well established in Figure 2. On the other hand, the kinetic trend of the reaction between iron(II) ion and ferriin is somewhat irregular and contrasts to that of the reaction of iodide ion with ferriin. The specific trend observed will not be rationally interpreted in terms of the formation of some complexes such as iron(II) perchlorate and hydroxoiron species which may not exist in a solution of 0.05 M $HClO_4$, 0.15 M $NaClO_4$, and 0–40% (v/v) alcohols (Figure 2). When Fe^{2+} is considered in place of I^- in the mechanism of reaction 5, the second term in the right-hand side of eq 6 would be zero as in the case of the iodide reaction; however, the first and third terms should be, respectively, of negative and positive signs because those two terms correspond to the associative and dissociative reactions between two ions of like signs. Therefore, when the absolute values of the first and third terms are equal to each other, the left-hand side of eq 6 should be zero and so the permittivity dependence should not be observed in this case. If the distance $(r_{Fe^{2+}} + r_{Fe(phen)_3^{3+}})$ is larger than $(r_{Fe^{3+}} + r_{Fe(phen)_3^{2+}})$, the absolute value of the third term could be larger than that of the first one, and the left-hand side of eq 6 could be positive as observed in the present study (see Figure 2). For ions such as $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, the corresponding $r_{Fe^{2+}}$ and $r_{Fe^{3+}}$ are 2.21 and 2.05 Å, respectively.[4] The sizes of ferriin and ferroin in aqueous solution are probably not so different as in the aqua ions of Fe(II) and Fe(III) because the phenanthroline complexes are extremely hydrophobic. If it is assumed that $r_{Fe(phen)_3^{2+}}$ is nearly equal to $r_{Fe(phen)_3^{3+}}$, the results obtained could be well-accounted for by eq 6. The rate of reaction between iodide ion and ferriin increased slightly with increasing acidity, and the values of the slope in the plot log k vs. $\mu^{1/2}/(1 + \mu^{1/2})$ in 0.5 M $HClO_4$ were to a small extent larger than that in 0.05 M $HClO_4$. The acid dependence may be explained in terms of the reversible association of $Fe(phen)_3^{3+}$ with H^+ to yield $HFe(phen)_3^{4+}$. This accounts for the increase in the rate observed at increasing acidities, because $HFe(phen)_3^{4+}$ would associate more easily with I^- ion than does $Fe(phen)_3^{3+}$. Since hydrogen iodide is so strong an acid that McCoubrey[5] calculated the dissociation constant to be 3×10^9 M which is larger than that of hydrochloric acid (10^7 M for HCl), the iodide ion would exist as I^- under the conditions of the present study. Sutin and

Gordon[2] studied the effect of the perchloric acid concentration of 0.05–0.5 M on the reaction of iron(II) ion with ferriin and found that the rate decreased with increasing acidities. They have also explained this effect by postulating the formation of $HFe(phen)_3^{4+}$. The rate of oxidation reaction of solvents of water, methanol, and ethanol by ferriin becomes sluggish with increasing acidities. In particular, it is of interest to note that ferriin becomes extremely stable in 11 M perchloric acid and only slowly oxidizes even iron(II) ion.[6] A strong association shell between $Fe(phen)_3^{3+}$ and ClO_4^- may inhibit iron(II) ion to approach to the ferriin molecule.

Registry No. $Fe(phen)_3^{3+}$, 13479-49-7; I^-, 20461-54-5; Fe^{2+}, 15438-31-0.

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Solution Chemistry of Silver Porphyrins. 1. Demetalation[1]

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Kinetics of the reaction between a water-soluble silver(II) porphyrin and nitric acid were investigated. In salt solutions, where the predominant species is dimeric, the reaction is first order in porphyrin concentration and first order in hydrogen ion concentration. In 25% methanolic solutions, where the predominant porphyrin species is monomeric, the reaction is found to be second order in porphyrin and first order in hydrogen concentration. Under both conditions, the product solution consisted of equimolar amounts of silver(III) porphyrin and dication of the metal-free porphyrin. A probable mechanism involving disproportionation of silver(II) is proposed.

Introduction

Chemistry of higher oxidation states of silver has been a subject of considerable interest to inorganic chemists. In aqueous solution the di- and trivalent states of silver are highly reactive and unstable. Many catalytic activities of silver(I) have been explained in terms of the involvement of these oxidation states.[2] Recently several coordination compounds of these higher states of silver with N-donor ligands have been synthesized and characterized.[3] Though the silver(II) complexes of porphyrins have been known for a long time, their aqueous solution chemistry has not been investigated. Results of such a study that we have undertaken comprise this series of articles.

Based on the ease with which a given metal ion is replaced by protons when the respective metalloporphyrin is placed in acids of varying concentration, an order of acid stability has been devised:[4] Pt(II) > Pd(II) > Ni(II) > Co(II) > Ag(II) > Cu(II) > Zn(II) > Mg(II) > (Na^{I}_2) > (Ag^{I}_2). Even those metalloporphyrins which are unstable toward acids undergo demetalation on reduction.[5] In aqueous solution zinc(II) and magnesium(II) porphyrins have been the subject of all the kinetic studies of this reaction.[6] The general rate law for this reaction in water appears to be rate = $k[MP]\cdot[H^+]^2$. A unique mode of demetalation observed for tetrakis(*p*-sulfonatophenyl)porhinatosilver(II) ($Ag^{II}TPPS$) (Figure 1) is reported here.

Experimental Section

Tetraphenylporphine was synthesized by the method of Adler et al.[7] and sulfonated.[8] Chemicals such as HNO_3 (AR Grade, Mallinckrodt), $NaNO_3$ (AlFA Products), methanol (North-Strong), silver acetate (reagent grade, Allied Chemical), and potassium persulfate (Baker Analyzed) were used as obtained.

A Beckman Model CIII Acta UV–visible spectrophotometer was used for spectral studies. Kinetic studies were carried out employing a Durrum Model D110 stopped-flow spectrophotometer, thermostated at 30.0 ± 0.1 °C. Kinetics of the disappearance of the silver porphyrin were monitored at 412 nm (λ_{max} of the dimer) for reactions in water solutions and at 421 nm (λ_{max} of the monomer) for reactions in 25% methanolic solutions. Pseudo-first-order rate constants were obtained either from the slope of a plot of ln $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances of the solution at time "t" and at the end of the reaction, or by using a nonlinear least-squares program. These plots were linear over at least 3 half-lives. The pseudo-second-order rate constants were obtained by computation from the slope of a plot of $1/A_t$ vs. time, where A_t is the absorbance of the solution at time "t". The rate constant, k_{obsd}, is equal to the product of the slope × light path length × change in molar extinction coefficient. The changes in molar extinction coefficients were 2.03×10^5 M^{-1} cm^{-1} at 421 nm in 25% methanolic solution and 9.02×10^4 M^{-1} cm^{-1} at 412 nm in water solutions. The rate constants for duplicate runs were found to deviate less than 5%. Magnetic susceptibilities were determined in solution by the method of Evans[9] and in the solid state by the Faraday method.

Synthesis of $Ag^{II}TPPS$. In a 150-mL beaker, 1.0 g Na_4TPPS was dissolved in 50 mL of water and heated. Little more than twice the stoichiometric amount of silver(I) acetate was added with stirring to the porphyrin solution, when it was about to boil and the solution was set aside to cool. In about 30 min, the solution was filtered, passed through a column (30 × 2 cm) of cation-exchange resin, Dowex 50W-X8 in sodium form, and evaporated to dryness. The crude product was Soxhlet extracted with methanol, precipitated from the methanolic solution by two volumes of acetone, filtered, and dried in an oven at 100 °C for 30 min. Anal. Calcd for $C_{44}H_{24}N_4S_4O_{12}Na_4Ag\cdot 10H_2O$: C, 40.37; H, 3.36; N, 4.28; S, 9.79. Found: C, 40.37; H, 3.07; N, 3.95; S, 9.92. Molecular weight calculated for the above formula is 1308. Molecular weight determined by demetalation after reduction is 1310. The number of water molecules was chosen to fit the analytical data. Magnetic moment is 1.76 μ_B.

Synthesis of $Ag^{III}TPPS$. In a 250-mL beaker, 1.2 g of pure $Ag^{II}TPPS$ was dissolved in 50 mL of water. The solution was made slightly alkaline with a few drops of dilute (0.1 M) sodium hydroxide solution. The solution was heated to boil, 0.15 g of potassium persulfate was added to the solution, and the mixture was constantly stirred while the heating continued. Intermittently a few drops of the solution were tested spectrophotometrically for completion of oxidation. Incomplete

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