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Ligand Oxidation in Iron Diimine Complexes. V. Kinetics of the Oxidation of Tris[2-pyridinal-α-methyl-(methylimine)]iron(II) by Cerium(IV)*

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At low acid concentration, e.g., <4 M H_2SO_4, the cerium(IV) oxidation of the iron(II) complex of the mixed-diimine ligand 2-pyridinal-α-methyl-(methylimine), PMM = $C_5H_4N{-}C(CH_3){=}NCH_3$, is a very complex reaction in which ligand-oxidized iron(II) and iron(III) complexes are formed and partly dissociated, with a total consumption of 10–11 equivalents of Ce(IV) per mole of $Fe(PMM)_3^{2+}$. The major oxidation product in ~50% yield is $Fe(PO)_3^{2+}$, where PO = $C_5H_4N{-}C(CHO){=}NCH_3$. The oxisation product has the α-methyl group oxidized to an aldehyde group. At the beginning of the reaction (<25% of the total Ce(IV) consumption) $Fe(PMM)_2PO^{2+}$ was identified as the major reaction product: $Ce(IV) + Fe(PMM)_3^{2+} = Ce(III) + Fe(PMM)_3^{3+} \rightarrow 0.75\ Fe(PMM)_3^{2+} + 0.25\ Fe(PMM)_2PO^{2+}$. At this stage the kinetics of the reaction was analyzed by two potentiometric techniques. From experiments of addition of $Fe(PMM)_3^{3+}$, prepared in 5 M H_2SO_4, to $Fe(PMM)_3^{2+}$, to a final 1 M H_2SO_4 concentration, the variation of the potential of the $Fe(PMM)_3^{3+}/Fe(PMM)_3^{2+}$ couple is recorded with time. This variation is associated with the rate of disproportionation of $Fe(PMM)_3^{3+}$ yielding $Fe(PMM)_2PO^{2+}$ and the original iron(II) complex. The rate law from these experiments is $-d[Fe(PMM)_3^{3+}]/dt = k[Fe(PMM)_3^{3+}]^{1.5}$. From automatic titration experiments, in which Ce(IV) is added to $Fe(PMM)_3^{2+}$ solutions at constant rate (ρ), at high $Fe(PMM)_3^{3+}$ concentration, the rate law is $\rho = k'[Fe(PMM)_3^{3+}]$. A mechanism, similar to that proposed for the oxidation of the aliphatic diimine complexes, is proposed. The first step is the formation of $Fe(PMM)_3^{3+}$ and Ce(III) with an equilibrium constant of 4.4×10^7. The iron(III) complex undergoes an intramolecular reduction to the iron(II) state with concomitant radical formation at the ligand, in a step assisted by solvent water and retarded by acid. Further oxidation of the iron(II) complex-ligand-radical by $Fe(PMM)_3^{3+}$ to the final production of $Fe(PMM)_2PO^{2+}$ leads to the derivation on the following rate law, $(\rho) - (d[Fe(PPM)_3^{3+}]/dt) = (3k_3k_7[Fe(PMM)_3^{3+}]^2)/(k_4 + k_7[Fe(PMM)_3^{3+}])$, which at high $[Fe(PMM)_3^{3+}]$ (automatic titrations) reduces to a first order reaction $[Fe(PMM)_3^{3+}]$ with $k_3 = 0.02\ s^{-1}$. Analysis of the potential variation experiments with time (low $[Fe(PMM)_3^{3+}]$) with the whole kinetic expression above leads to $k_3 = 0.02\ s^{-1}$.

Introduction

In parts I–IV [1–4] of this series the stoichiometry [1], reaction products [1], kinetics [2], acidity [4], and temperature [4] dependence of the oxidation of tris-[glyoxal-bis(methylimine)]iron(II), $Fe(GMI)_3^{2+}$, GMI = $H_3CN{=}CH{-}CH{=}NCH_3$ by cerium(IV) were presented and in part III [3], the electrochemical oxidation of this complex was investigated in detail. The oxidation of this iron(II) complex of an aliphatic diimine ligand is an example of a well studied reaction in which ligand-oxidation proceeds with the intermediate formation of the iron(III) complex, which then undergoes an intramolecular reduction to the iron(II) state, with concomitant oxidation of the organic ligands, yielding mostly stable ligand-oxidized complexes. This complex, $Fe(GMI)_3^{2+}$, first synthesized by Krumholz [5], is analogous to the well known complexes tris-(2,2-bipyridine)iron(II) [6] and tris(1,10-phenanthroline)iron(II) [6], presenting the common structure Fe(II) $(\dot{N}{=}\dot{C}{-}\dot{C}{=}\dot{N})_3$, the iron diimine chromophore [7], responsible for the similarity of spectral properties of these complexes. Busch and Bailar [8] synthesized the complexes which establish a structural link between the aromatic and aliphatic diimine complexes with the mixed diimine ligands, $C_5H_4N{-}C(R){=}N(R)$. This paper presents the investigation of the cerium(IV) oxidation of one of these complexes, with $R{=}R'{=}CH_3$, the title compound, $Fe(PMM)_3^{2+}$, which provides another example of a ligand-oxidation process.

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The aliphatic [9] and mixed diimine ligands make the resulting iron(II) complexes display acidity dependent oxidation properties. If the acid concentration is large enough, only the central metal ion is oxidized to the iron(III) state. At lower acidity, the iron(III) forms are less stable thermodynamically and kinetically and ligand-oxidation occurs [9]. This behavior contrasts markedly the acidity independent reversible oxidation of the aromatic diimine complexes of iron(II), well known redox indicators [10]. There are several examples in the literature of ligand-oxidation processes which proceed with the oxidation of the central metal ion prior to the oxidation of the ligands involving complexes of Ni [11], Fe [12] and Ru [13].

Experimental Section

Materials

The chemicals utilized in this investigation are described in ref. 1, with exception of the complex Fe(PMM)$_3^{2+}$, which was prepared as the perchlorate salt and purified according to a procedure by Krumholz [14].

Stoichiometry and Kinetics of Oxidation of Fe(PMM)$_3^{2+}$ by Cerium(IV) from Automatic Titrations

In order to characterize the stoichiometry and the kinetics of the reaction in its initial stages, the technique of automatic titration [16] was employed, in which cerium(IV) solutions were added to the complex compound solutions at constant rate, and the potential of a bright platinum indicator electrode *vs.* a calomel electrode was recorded as a function of time. The experimental procedure employed is described in ref. 1. The chemical pre-treatment of the platinum electrode was the following: the electrode was immersed for 5 min in a 0.1 *M* $FeSO_4$ and 1 *M* H_2SO_4 solution, and then for 5–3 min in a mixture of 1 ml of 0.2 *M* $Ce(SO_4)_2$ in 25 ml of concentrated H_2SO_4 at room temperature.

All experiments were carried out at 25.0 ± 0.1 °C, under nitrogen, and the concentration was 1–4 *M* H_2SO_4. The Ce(IV) solutions had identical acid concentration to that of the complex compound.

Photometric Determination of the Kinetics of Dissociation of the Complex Compounds

The double beam Zeiss DMR-10, with a digital readout and a six cell compartment was used. The kinetics of dissociation of Fe(PMM)$_3^{2+}$ in 1 *M* H_2SO_4 was followed at 30.0 ± 0.1 °C and at 50.0 ± 0.2 °C; samples of these solutions were transferred to a 1 cm optical path cell at 30.0 ± 0.5 °C during a period of 20 and 5 hours, respectively, and the absorbance at 558 nm (absorption maximum of Fe(PMM)$_3^{2+}$) was recorded. The kinetics of dissociation of the complex compound oxidized by varying amounts of cerium(IV), at 25 °C and under N_2, was also followed spectrophotometrically, at 30.0, 50.0, and 60.0 °C. The following ratios of equivalents of cerium(IV) per mol of complex were used: 1:1, 3:1, and 12:1.

Isolation of the Oxidized and non-Oxidized Ligands as 2,4-Dinitrophenyl-hydrazine Derivatives

Four solutions of Fe(PMM)$_3^{2+}$ (0.061 mol in 50 ml 1 *M* H_2SO_4) were oxidized with varying amounts of Ce(IV) (equiv Ce(IV): mol of complex: 0:1, 1:1, 3:1, 12:1). After 30 min, to these solutions 5–10 ml of 2% 2,4-dinitrophenylhydrazine in 5 *M* in H_2SO_4 were added and then 20–40 ml of H_2O. The resulting solutions were heated for 3 hours in a boiling water bath. All these procedures were carried out under nitrogen. After 3 hours the solutions were cooled down to ~3 °C for at least 4 hours. The yellow-brown precipitate was filtered off on a sintered-glass crucible, washed with 1 *M* H_2SO_4, water and dried *in vacuo*. The first solution, without prior oxidation yielded 95.0% of the 2,4-dinitrophenylhydrazone of 2-acetylpyrydine in the solid form and the 5% remaining were found to be the corresponding fraction of that compound solubilized in the amount of 1 *M* H_2SO_4 used (within 10%). This hydrazone has a melting point of 217–218 °C. Thin layer chromatography of this compound on a silica-gel Baker flex plate with the solvent benzene: petroleum ether (60–80 °C): ethyl acetate (34:5:1 v/v) [17] showed the presence of a single compound with $R_f = 0.152$. UV–visible absorption spectra in ethanol and ethylacetate solution gave maxima at 372 nm and 369 nm, respectively, with molar absortivities of 1.67×10^4 M^{-1} cm^{-1} and 1.81×10^4 M^{-1} cm^{-1}. *Anal.* Calcd. for $C_{13}H_{11}N_5O_4$: C, 51.83%; H, 3.68%; N, 23.25%. Found: C, 51.12%; H, 3.60%; N, 21.60%. This hydrazone was also prepared from Aldrich's 2-acetylpyridine following the same procedure with identical, within the experimental error, solubility, m.p., absorption spectra, R_f, and analytical data.

The solutions to which oxidizing agent was added, were treated as above. From the solutions with oxidizing agent in the 1:1 and 3:1 Ce(IV)/Fe(PMM)$_3^{2+}$ ratios, the solid precipitate was partly dissolved, first in cold ethyl acetate then in boiling ethyl acetate. The two solutions obtained were analyzed through thin layer chromatography with the same solvent described above. Three compounds were found, the first with $R_f = 0.152$, a second, present in trace amounts, with $R_f = 0.08$ (probably associated with the hydrazone of $C_5H_4N–C(CH_2OH)=O$), and another compound with $R_f = 0.00$. The last compound was identified with the insoluble fraction, with a melting point of 318 °C, and corresponds to the 2,4-dinitrophenylosazone of 2-glyoxylpyridine, $C_5H_4N–(CCHO)=O)$. *Anal.* Calcd. for: $C_{19}H_{13}N_9O_8 \cdot H_2O$: C, 44.43; H, 2.95; N, 24.57. Found: C, 43.42; H, 2.92; N, 23.0.

Estimates were made of the amount of non-oxidized ligand, PMM, and of the amount of ligand oxidized to the 2-glyoxylpyridine derivative by gravimetry and by quantitative extraction of the thin layer plates and photometric determination. For the 1:1 and 3:1 equivalents of Ce(IV)/mole of $Fe(PMM)_3^{2+}$, 90 ± 5% and 72 ± 5% respectively of the initial ligand concentration were found as non-oxidized ligand, and 8.3 ± 0.8% and 25 ± 1% respectively of the initial ligand concentration as the 2-glyoxylpyridine derivative. When the oxidation was carried out with a 12:1 Ce(IV) equivalents/mole of $Fe(PMM)_3^{2+}$, only the 2,4-dinitrophenylosazone of 2-glyoxylpyridine was identified and the amount found corresponded to 50 ± 2% of the initial ligand concentration. The thin layer chromatographic plates of the solubilized fractions indicated the presence of small amounts of other compounds with $R_f = 0.226$ and 0.116 which could not be identified. These R_f s do not correspond to the 2-pyridinecarboxaldehyde or formaldehyde derivatives of 2,4-dinitrophenylhydrazine, which were prepared and purified and showed R_f s = 0.292, and 0.278, respectively, under this experimental procedure.

Formal Electrode Potential of the $Fe(PMM)_3^{3+}$/$Fe(PMM)_3^{2+}$ Couple and Disproportionation Kinetics of $Fe(PMM)_3^{3+}$

The formal electrode potential of the complex couple was determined by injecting a known amount of the ferric complex prepared in 5 M H_2SO_4 at 2 °C under nitrogen into a ferrous complex solution such that the final acidity was 1.0 M. The concentration of ferric and ferrous forms following this procedure was known within 2–3%. The procedure utilized is described in the literature [4]. The ratios of the concentrations iron(III)/iron(II) complexes utilized varied in the $1–6 \times 10^{-3}$ range. The potential of the platinum indicator electrode was followed as a function of time. The potential extrapolated to zero time and the Nernst equation allowed the calculation of the formal electrode potential. The potential *vs.* time curve provided means to study the kinetics of the reaction. This procedure has been used previously and has been shown to give kinetic results in agreement with those of other potentiometric and photometric techniques [2, 4].

Isolation of the Final Oxidation Product and Iron and Nitrogen Determination

After oxidation with 12 equivalents of Ce(IV) per mole of complex, the blue oxidized product was precipitated off by addition of sodium polyiodide as described in ref. 1. The solid was analyzed for iron and nitrogen. The ratio of Fe:N, determined as described in ref. 1, was found to be 1:5.9 and the amount of iron in the polyiodide salt 50 ± 5% of the original iron complex submitted to oxidation.

Results and Discussion

Stoichiometry and Reaction Products

Automatic titration curves of $Fe(PMM)_3^{2+}$ by Ce(IV) in 4 M and 1 M H_2SO_4 at 25 °C, are shown in Fig. 1. The curve in 4 M H_2SO_4 corresponds essentially to the stoichiometric oxidation of $Fe(PMM)_3^{2+}$ to the corresponding iron(III) compound with an approximate rate constant of $\sim 10^9\ M^{-1}\ s^{-1}$ as calculated from the automatic titration curves [15, 16]. The solution color remains red but the intensity diminishes as Ce(IV) is added. The visible absorption spectra of these two complexes are shown in Fig. 2, normalized with respect to the absorbance maxima of these complexes. The iron(II) complex exhibits an absorbance maximum at 558 nm with $\epsilon = 1.25 \times 10^4\ M^{-1}\ cm^{-1}$ and a characteristic double structure towards smaller wavelengths. This band was assigned to an inverse charge transfer [18], $t_2 \rightarrow \pi^*$ and the structure to a vibrational progression of the electronic transition [19–21]. The iron(III) complex presents [22] an absorbance maximum at 535 nm and $\epsilon = 7.9 \times 10^2\ M^{-1}\ cm^{-1}$ in 10 M H_2SO_4. This broad band is associated to a direct charge transfer $\pi \rightarrow t_2$ [18, 21].

Inspection of Fig. 1 at 1 M H_2SO_4 and at two different flow rates of Ce(IV) reveals that the consumption of oxidation equivalents increases to 10–11 per mol of iron(II) complex and increases with decreased rate of additon of Ce(IV). During the course of the titration under these conditions, the solution turns from red to blue. Figure 2 also shows the visible absorption spectrum of the oxidation product, which consists of a very broad asymmetric band with maximum at 575 nm and $\epsilon \sim 2 \times 10^3\ M^{-1}\ cm^{-1}$. The molar absorptivity was calculated assuming the yield of the reaction as complexes of 50% as determined by isolation of a tarry polyiodide analyzed for Fe and N, and for which the ratio Fe:N = 1:5.9, which indicates that the oxidized complex retains the diimine chromophore. The broad asymmetric band resembles the spectrum of the ligand-oxidized product of the oxidation of tris-[glyoxal-bis(methylimine)]iron(II), $Fe(GMI)_3^{2+}$, in which one of the GMI ligands is transformed into $H_2CN{=}C(OH)CH{=}NCH_3$, with λ_{max} = 596 nm and ϵ_{max} $2.5 \times 10^3\ M^{-1}\ cm^{-1}$. In the present case, the final stable oxidation product in the iron(III) state has some interesting characteristics. Whereas the half-life of the original iron(II) complex is 120 hours at 30 °C (22.4 hours at 50 °C) with respect to the dissociative process, a first order process in $Fe(PMM)_3^{2+}$, which yields iron(II) ions and free ligands, the oxidized stable iron(III) complexes have a half-life of ~49.5 hours (50 °C), being therefore more inert than the original iron(II) compound. The presence of oxygen and dissociation products leads to the destruction of this product *via* probably free radicals as a result of

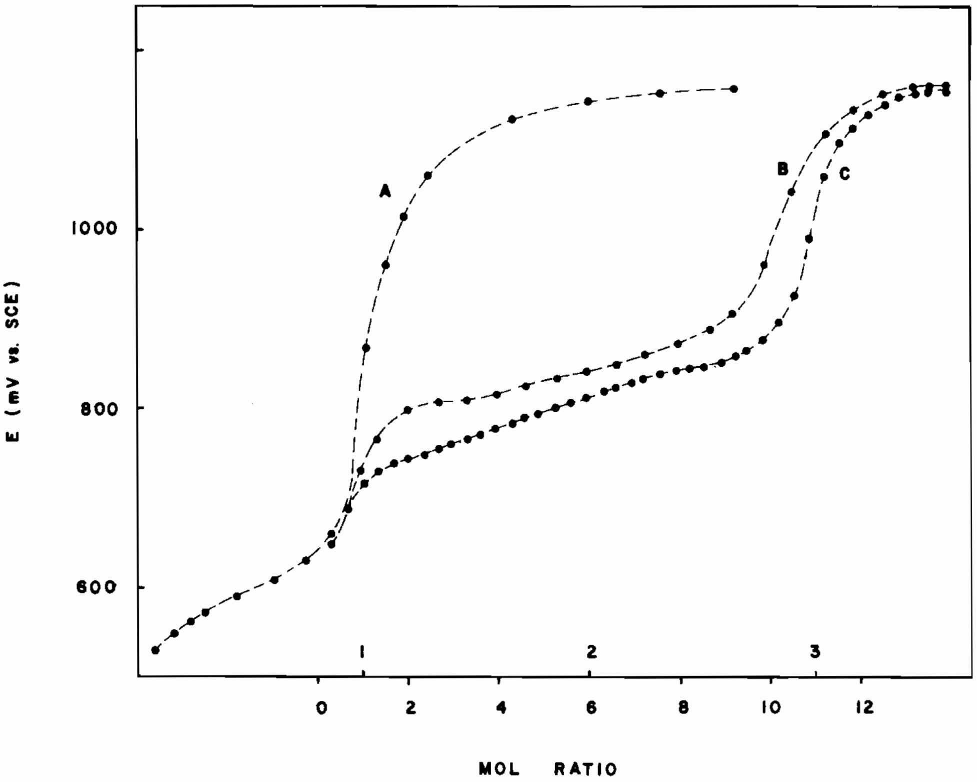

Fig. 1. Plots of potential *vs.* mol ratio of Ce(IV)/Fe(PMM)$_3^{2+}$,obtained in automatic titration of Fe(PMM)$_3^{2+}$ solutions by Ce(IV) at 25 °C. The molar concentrations of the complex and of H_2SO_4 and the rate of cerium(IV) addition in $M\,s^{-1}$ are respectively: (A) 2.6×10^{-4}; 4.0; 1.45×10^{-6}; (B) 5.2×10^{-4}; 1.0; 2.9×10^{-6}; and (C) 5.2×10^{-4}; 1.0; 1.45×10^{-6}.

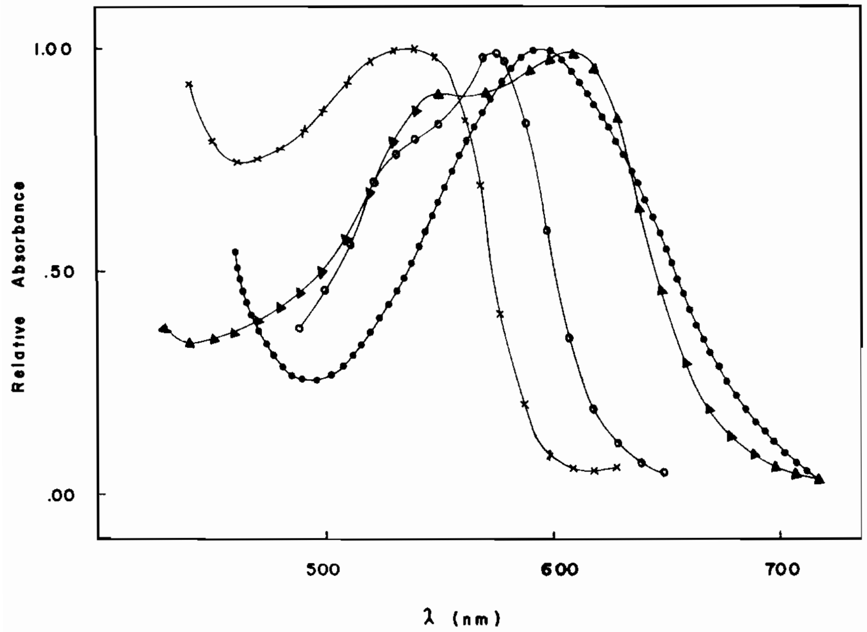

Fig. 2. Normalized absorption spectra of Fe(PMM)$_3^{2+}$ (○); cerium(IV) oxidation products of Fe(PMM)$_3^{2+}$ in a 11:1 mol ratio (●); and cerium(IV) oxidation products of Fe(PMM)$_3^{2+}$ in an 11:1 mol ratio reduced by Cr(II) (△) in 1 *M* H_2SO_4. Fe(PMM)$_3^{3+}$ (×) in 10 *M* H_2SO_4.

autoxidation reactions similar to those found with the tris[biacetyl-bis(methylimine)]iron(II) [23]. When the iron(III) complex, result of oxidation with $\geqslant 10$ eq. Ce(IV)/mol of complex, is reduced with iron(II) ions, very labile iron(II) complexes are formed (half life ~10 sec), thus explaining the low yield of final oxidation stable complexes. On the other hand, when Cr(II) ions are chosen as reducing agents, a much more inert ferrous complex is obtained. The visible absorption spectrum of this compound is also shown in Fig. 2, and one can observe that the same characteristics of the iron(II) diimine chromophore are present. It is very likely that Cr(II) ions reduce the oxidized ligands and the central metal.

In order to determine the nature of the oxidized ligands and the stoichiometry of the reaction, principally at its initial stages (~25% of the total Ce(IV) consumption), the hydrolized ligands were precipitated as 2,4-dinitrophenylhydrazine derivatives, as described in the Experimental Section. At the initial stages of the reaction, the two ligands: 2-acetylpyridine from the original ligand and 2-glyoxylpyridine are found in amounts which allow us to write the following stoichiometric reaction:

$$\begin{aligned} &\mathrm{Fe(PMM)_3^{2+} + Ce(IV) = Fe(\underset{\downarrow}{PMM})_3^{3+} + Ce(III)} \qquad (1)\\ &\mathrm{0.75Fe(PMM)_3^{2+} + 0.25Fe(PMM)_2PO^{2+}} +\\ &\qquad\qquad \mathrm{traces\ Fe(PMM)_2(POH)^{2+}} \end{aligned}$$

where PMM = $C_5H_4N{-}C(CH_3){=}NCH_3$; PO = $C_5H_9N{-}C(CHO){=}NCH_3$; and POH = $C_5H_4N{-}C(CH_2OH){=}NCH_3$.

As the oxidation proceeds, the possibility of oxidation of all the ligands should yield complex mixtures of $Fe(PMM)_2PO^{2+}$, $Fe(PMM)(PO)_2^{2+}$, $Fe(PO)_3^{2+}$ and their respective iron(III) complexes. The final stages of the reaction are very complex because they are coupled with the dissociation of labile intermediates and possibly further oxidation of PO, which could decarboxylate and yield CO_2; *ca.* 0.03 mol of CO_2 per mol of complex submitted to oxidation were obtained, according to the same procedure described in ref. 1. Oxidation at the ratio of 12:1 equivalents of Ce(IV) per mol of complex yields 2-glyoxylpyridine and no 2-acetylpyridine was detected. The amount of oxidized ligands, 50% of the total ligand concentration, agrees well with the amount of final stable oxidation complexes isolated as polyiodides, and indicates that the major oxidation product is $Fe(PO)_3^{3+}$. The fact that Cr(II) ions reduce this ligand-oxidized complex with a stoichiometry of 5 ± 1 mol of Cr(II) per mol of ligand oxidized complex, suggests that the free aldehyde groups at the oxidized ligands must be reduced to alcoholic groups to possibly mixtures of $Fe(PO)_2(POH)^{2+}$, $Fe(PO)(POH)_2^{2+}$ and $Fe(POH)_3^{2+}$. Cr(II) ions are known to be very appropriate reducing agents for complexation with available coordinating groups and most of these reactions proceed *via* inner sphere mechanisms.

Though the oxidation of $Fe(PMM)_3^{2+}$ by Ce(IV) in its final stages is a very complex reaction due to the lability of some of the intermediate reaction complexes, at the initial stages ($\leqslant 3$ equivalents of Ce(IV) per mol of $Fe(PMM)_3^{2+}$ (<25% of total oxidizing agent consumption), the reaction can be represented by eqn. (1) with only one major oxidation product. For this reason, the kinetics of this reaction during its initial stages was investigated.

Kinetics

The Ce(IV) oxidation of $Fe(PMM)_3^{2+}$ in its initial stages, *i.e.*, <20% stoichiometric Ce(IV) addition, in 1 *M* H_2SO_4, produces mostly one complex with oxidized ligand, as described by eqn. (1). The primary step of the reaction is the formation of $Fe(PMM)_3^{3+}$, as was shown in the $Fe(GMI)_2^{2+}$ oxidation by Ce(IV) [24]. Experiments in which $Fe(PMM)_3^{3+}$ was prepared at 5 *M* H_2SO_4 and a small aliquot of this solution injected in a $Fe(PMM)_3^{2+}$ solution of known concentration, and such that the final H_2SO_4 concentration was 10 *M*, allowed the determination of the $E^{0\prime}$ ($Fe(PMM)_3^{3+}/Fe(PMM)_3^{2+}$) under these conditions as 740 ± 5 mV *vs.* SCE (see Experimental). Analysis of the ligand composition agrees with the stoichiometry for the direct oxidation with 1 equivalent of Ce(IV) per mol of $Fe(PMM)_3^{2+}$. Under the same conditions, the $E^{0\prime}$ (Ce(IV)/Ce(III)) is 1192 ± 2 mV *vs.* SCE and therefore the reaction:

$$\mathrm{Fe(PMM)_3^{2+} + Ce(IV) \rightleftharpoons Fe(PMM)_3^{3+} + Ce(III)} \qquad (2)$$

has an equilibrium constant of 4.4×10^7, five orders of magnitude greater than that for the aliphatic complex $Fe(GMI)_3^{2+}$. The knowledge of $E^{0\prime}$ and the analysis of the potential *vs.* time curve allow use to write the following rate law (see Fig. 4):

$$\frac{-d[\mathrm{Fe(PMM)_3^{3+}}]}{dt} = k[\mathrm{Fe(PMM)_3^{3+}}]^{1.5} \qquad (3)$$

It is important to emphasize that in these experiments, the injected concentration of iron(III) complex did not exceed 1% of the iron(II) complex concentration, being typically in the 0.1–0.5% range. Therefore, the measured potential of the Pt electrode reflects changes in the $Fe(PMM)_3^{3+}/Fe(PMM)_3^{2+}$ concentrations, but there is no appreciable concentration of ligand oxidized products.

Kinetic information was also obtained from the automatic titration curves. Since this complex reaction generates several redox iron(III)/iron(II) complex couples, which can participate in the determination of the potential (mixed potentials), care was taken to interpret only potential regions where mixed potential participation was kept to a minimum. The

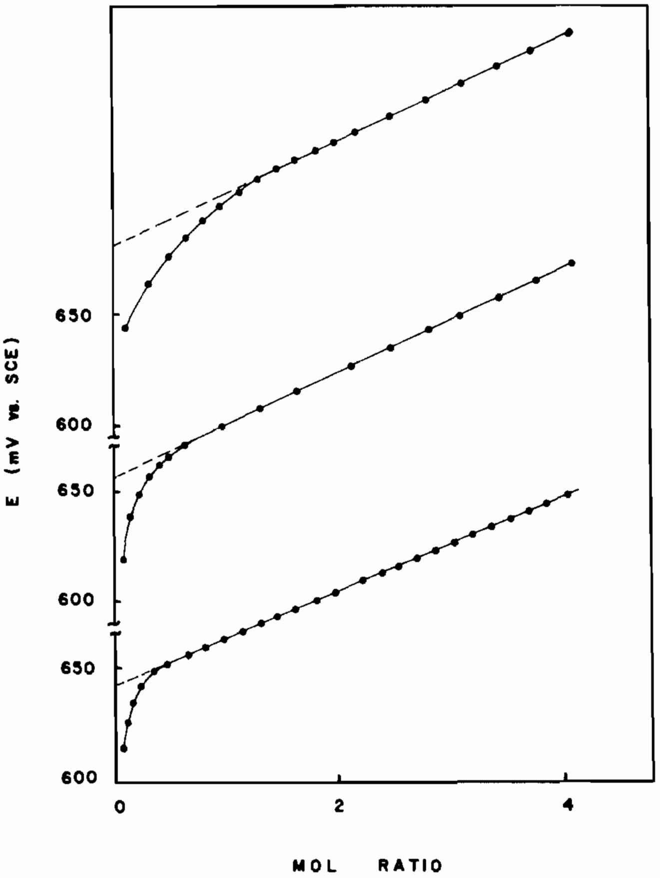

Fig. 3. Plots of potential *vs.* mol ratio of Ce(IV)/Fe(PMM)$_3^{2+}$ obtained in automatic titrations of 5.3 × 10^{-4} *M* solutions of Fe(PMM)$_3^{2+}$ in 1.0 *M* H_2SO_4 and at 25 °C as a function of the rate (ρ) of cerium(IV) addition: (a) 1.45 × 10^{-6}; (b) 2.9 × 10^{-6} and (c) 5.8 × 10^{-6} *M* s^{-1}.

best of such potentials is the potential extrapolated to zero time (E(t = 0)), for instance, in the curves of Fig. 3. Some examples of automatic titration curves at low conversion of Fe(PMM)$_3^{2+}$ into ligand oxidized products are shown in Fig. 3. These curves have a fixed concentration of Fe(PMM)$_3^{2+}$ and the rate of addition of Ce(IV), ρ, is varied. An increase in ρ by a factor of 2 causes an increase E(t = 0) of 25 mV, which corresponds to an increased Fe(PMM)$_3^{3+}$ concentration by a factor of ~3, (a factor of 2.0 corresponds to 17.8 mV at 25 °C). When the Fe(PMM)$_3^{2+}$ and ρ are increased by a factor of 2 the potential increases by ~18 mV, indicating an increase in Fe(PMM)$_3^{3+}$ concentration by a factor of two. At constant ρ (1.5 × 10^{-6} *M* s^{-1}) an increase in the concentration of Fe(PMM)$_3^{2+}$ by a factor of 2 causes a decrease of the E(t = 0) by 19 mV. If ρ is increased by a factor of 2 and the concentration of Fe(PMM)$_3^{2+}$ varied as above, the decrease of E(t = 0) is now 30 mV, thus indicating that the rate law is a function of Fe(PMM)$_3^{3+}$ concentration.

Table I lists the extrapolated E(t = 0) values and the Fe(PMM)$_3^{2+}$]$_0$, [Fe(PMM)$_3^{3+}$]$_0$ concentrations for some automatic titrations performed. These data suggest that the kinetics of oxidation of Fe(PMM)$_3^{2+}$ is very complex, with an approximate rate law:

$$\rho \simeq k'[\mathrm{Fe(PMM)_3^{3+}}]^n \qquad (4)$$

1 ⩽ n ⩽ 1.5 depending on the % of conversion of Fe(PMM)$_3^{2+}$ into Fe(PMM)$_3^{3+}$. The automatic titration curves are independent of the concentration of Ce(III) as one would expect based on the very large equilibrium constant for eqn. 2. Oxygen affects all the potentiometric experiments, and therefore care was taken to exclude oxygen from the reaction media, and also suggesting the participation of free radicals in the reaction mechanism.

Mechanism and Discussion

Based on the nature of the products, and on the similarity between the oxidation reaction of Fe(PMM)$_3^{2+}$ and that of aliphatic derivative, one can write the following mechanism:

$$\mathrm{Fe(PMM)_3^{2+} + Ce(IV)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(PMM)_3^{3+} + Ce(III)} \qquad (2)$$

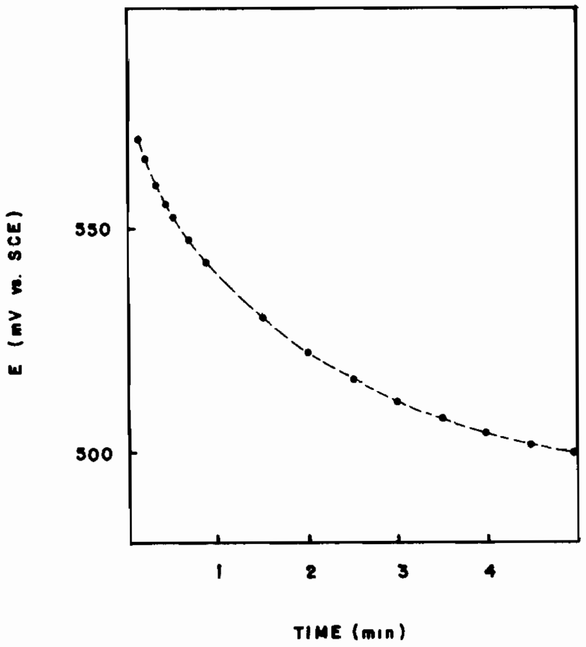

Fig. 4. Potential of the Fe(PMM)$_3^{3+}$/Fe(PMM)$_3^{2+}$ couple as a function of time in experiments of addition of Fe(PMM)$_3^{3+}$ prepared in 5 *M* H_2SO_4 to solutions of Fe(PMM)$_3^{2+}$. Final acid concentration 1 *M* H_2SO_4.

$$\mathrm{Fe(PMM)_3^{3+} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Fe(PMM)_2R^{\cdot 2+} + H_3O^+} \qquad (5)$$

$$\mathrm{Fe(PMM)_2R^{\cdot 2+} + Fe(PMM)_3^{3+} \underset{H_2O}{\overset{k_7}{\rightleftharpoons}} Fe(PMM)_2POH^{2+} + Fe(PMM)_3^{2+} + H_3O^+} \qquad (6)$$

$$\mathrm{Fe(PMM)_2POH^{2+} + 2Fe(PMM)_3^{3+} \underset{H_2O}{\overset{k_8}{\rightleftharpoons}} Fe(PMM)_2PO^{2+} + 2Fe(PMM)_3^{2+} + 2H_3O^+} \qquad (7)$$

The participation of water and acid in the reaction was firmly established for Fe(GMI)$_3^{2+}$ [4]. Since the reaction medium has another oxidant, Ce(IV), one can also propose:

$$\mathrm{Fe(PMM)_2R^{\cdot 2+} + Ce(IV) \underset{H_2O}{\overset{k_5}{\rightleftharpoons}} Fe(PMM)_2POH^{2+} + Ce(III) + H_3O^+} \qquad (8)$$

$$\mathrm{Fe(PMM)_2POH^{2+} + 2Ce(IV) \underset{H_2O}{\overset{k_6}{\rightleftharpoons}} Fe(PMM)_2PO^{2+} + 2Ce(III) + 2H_3O^+} \qquad (9)$$

Though k_5 and k_6 might be similar to k_7 and k_8, since [Fe(PMM)$_3^{3+}$]/[Ce(IV)] is of the order of 10^8–10^{14}, the rates v_5 (eqn. 8) and v_6 (eqn. 9), are negligible compared to v_7 (eqn. 6) and v_8 (eqn. 7). Clearly the reaction in eqn. 7 is composed of several intermediate steps, probably involving oxidation of the metal ion and internal reduction by the ligand. Considering only eqns. 5, 6 and 7, which correspond to the experiments of adding Fe(PMM)$_3^{3+}$ to Fe(PMM)$_3^{2+}$ and following its decay, and considering Fe(PMM)$_2$POH^{2+} and Fe(PMM)$_2$R$^{\cdot 2+}$ as steady state intermediates, one obtains:

$$\frac{-d[\mathrm{Fe(PMM)_3^{3+}}]}{dt} = \frac{3k_3k_7\,[\mathrm{Fe(PMM)_3^{3+}}]^2}{k_4 + k_7\,[\mathrm{Fe(PMM)_3^{3+}}]} \qquad (10)$$

Eqn. 10 can be rearranged as:

$$\frac{k_4}{3k_3k_7}\,\frac{d[\mathrm{Fe(PMM)_3^{3+}}]}{[\mathrm{Fe(PMM)_3^{3+}}]^2} + \frac{1}{3k_3}\,\frac{d[\mathrm{Fe(PMM)_3^{3+}}]}{[\mathrm{Fe(PMM)_3^{3+}}]} = dt \qquad (11)$$

which can be integrated. By using the method of multiple linear regression [25], one obtains $k_4/(k_3k_7) = 4.4 \times 10^{-6}$ and $1/(3k_3) = 14$, and therefore $k \simeq$

TABLE I. Extrapolated Values of E(t = 0); [Fe(PMM)$_3^{2+}$]$_0$, and [Fe(PMM)$_3^{3+}$]$_0$ Concentrations; ρ/[Fe(PMM)$_3^{3+}$]$_0$ Ratios from Automatic Titrations at Different Rates of Addition of Ce(IV), ρ, and Different Concentrations of the Complex.

Expt. No.	E(t = 0)	[Fe(PMM)$_3^{2+}$]$_0$, *M* × 10^4	[Fe(PMM)$_3^{3+}$], *M* × 10^5	10^6 ρ *M*, s^{-1}	ρ/[Fe(PMM)$_3^{3+}$]$_0$ s^{-1}
1	635.0	10.48	1.81	1.44	0.080
2	641.7	10.48	2.28	1.44	0.063
3	652.4	10.51	3.48	2.89	0.083
4	657.2	10.49	4.18	2.89	0.069
5	670.6	10.50	7.04	5.77	0.082
6	676.9	10.49	9.02	5.77	0.064
7	661.7	5.23	2.48	1.44	0.058
8	660.9	5.21	2.40	1.44	0.060
9	679.0	5.21	4.84	2.89	0.059
10	682.0	2.62	2.74	1.44	0.052

0.02 s^{-1}; from the experimental data of Fig. 4. One can write for the automatic titrations an analogous rate expression as:

$$\rho - \frac{d[\mathrm{Fe(PMM)}_3^{3+}]}{dt} = \frac{3k_3k_7[\mathrm{Fe(PMM)}_3^{3+}]^2}{k_4 + k_7[\mathrm{Fe(PMM)}_3^{3+}]} \quad (12)$$

for which at the initial stages of the reaction $\rho \gg d[\mathrm{Fe(PMM)}_3^{3+}]/dt$. If $k_4 < k_7[\mathrm{Fe(PMM)}_3^{3+}]$, the rate law is simplified to:

$$\rho \simeq 3k_3\,[\mathrm{Fe(PMM)}_3^{3+}] \quad (13)$$

a first order rate in $\mathrm{Fe(PMM)}_3^{3+}$. From the data in Table I, one can conclude that within the concentration ranges of experiments 1–10, $\rho/[\mathrm{Fe(PMM)}_3^{3+}]$ is approximately constant (within the experimental error) and that k_3 from these experiments is $k_3 \simeq 0.02 \pm 0.01$ s^{-1} in agreement with the data from the other potentiometric experiments in which $\mathrm{Fe(PMM)}_3^{3+}$ is added to $\mathrm{Fe(PMM)}_3^{2+}$. In the automatic titration experiments (1–10) eqn. 13 represents the observed rate law. The $\mathrm{Fe(PMM)}_3^{3+}$ concentrations are 2–3 orders of magnitude higher in these experiments than in the experiments illustrated in Fig. 4.

Conclusion

The oxidation of the iron(II) complex of the mixed-diimine ligand $C_5H_4N{-}C(CHO){=}NCH_3$ = PMM is a reversible stoichiometric reaction at high acid concentration, *e.g.*, $H_2SO_4 \geqslant 4$ *M*; at lower acid concentration, as observed for the apliphatic diimine complexes, ligand oxidation takes place *via* the Fe(III) complex, which undergoes internal reduction by the ligand. The rate of this reaction is dependent on the acid and water activities, as shown for the aliphatic derivatives. The ligand oxidized complexes in the iron(II) state are very labile, so that the maximum yield of ligand oxidized complexes is *ca.* 50%, and the product of the oxidation which consumes 10–11 Ce(IV) equivalents per mol of $\mathrm{Fe(PMM)}_3^{2+}$ is $\mathrm{Fe(PO)}_3^{3+}$. PO = $C_5H_4N{-}C(CHO){=}NCH_3$. The kinetics of the initial stages of this reaction (<25% total Ce(IV) consumption) is a first-order process in $\mathrm{Fe(PMM)}_3^{3+}$, at high $\mathrm{Fe(PMM)}_3^{3+}$ concentration. At lower iron(III) complex concentration, a more complex rate law is observed. The proposed reaction mechanism explains the order dependence on $\mathrm{Fe(PMM)}_3^{3+}$. The rate constant for the internal reduction of the $\mathrm{Fe(PMM)}_3^{3+}$, the rate determining step, is 0.02 s^{-1}, and $k_4/k_7 = 10^{-7}$, at 1.0 *M* H_2SO_4 and 25 °C. The rate determining step (k_3) is the rate of intramolecular reduction of $\mathrm{Fe(PMM)}_3^{3+}$ yielding the iron(II) complex-radical which can either be further oxidized (k_7) or return to the $\mathrm{Fe(PMM)}_3^{2+}$ state (k_4).

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