Ligand Oxidation in Iron Diimine Complexes. II.[1a] Rate and Mechanism of the Oxidation of Tris(glyoxal bis(methylimine))iron(II) by Cerium(IV)[1b]

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The rate of oxidation of tris(glyoxal bis(methylimine))iron(II) ($Fe(GMI)_3{}^{2+}$) by cerium(IV) in $4.07 M$ H_2SO_4 at $25°$ has been investigated in *open* and *closed* systems by potentiometric and photometric techniques. The primary reaction step is the oxidation of $Fe(GMI)_3{}^{2+}$ to $Fe(GMI)_3{}^{3+}$, with a second-order rate constant of $(4 \pm 1) \times 10^3$ M^{-1} sec^{-1} and an equilibrium constant of 400 ± 50. This step is followed by a disproportionation of $Fe(GMI)_3{}^{3+}$ into $Fe(GMI)_3{}^{2+}$ on the one hand and ligand-oxidized complexes on the other. Experimental data are consistent with the rate expression $-d[Fe(GMI)_3{}^{3+}]/dt = k_a[Fe(GMI)_3{}^{3+}]^2 + k_b[Fe(GMI)_3{}^{3+}]$, with $k_a = (2.2 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}, and $k_b = (2.5 \pm 1) \times 10^{-3}$ sec^{-1}. A reaction scheme, compatible with product analysis and kinetic results, is proposed. Participation of free radical intermediates in the disproportionation of $Fe(GMI)_3{}^{3+}$ is postulated.

Introduction

In part I of this study,[1a] it was concluded, on the strength of general chemical arguments, that oxidation of tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3{}^{2+}$, by Ce(IV) proceeds *via* the Fe(III) complex $Fe(GMI)_3{}^{3+}$, which then disproportionates regenerating $Fe(GMI)_3{}^{2+}$ and forming two new ligand-oxidized complexes. We now report on a kinetic investigation of this system which confirms the earlier results and provides new information on the mechanism of the reaction. In addition to conventional spectrophotometric techniques, a new combination of electrochemical measurements in both *closed* and *open* systems has been applied successfully to the kinetic analysis of the aforementioned reaction.

Experimental Section

Materials. The chemicals used in this study are described in part I.[1a]

Electrochemical Rate Measurements. Unless otherwise stated, all measurements were made at $25 \pm 0.1°$ in deoxygenated solutions $4.07 M$ in H_2SO_4. At acidities lower than $2 M$, the reproducibility of potential measurements becomes poor, reaction rates become inconveniently fast, and results cannot be explained in simple terms.

Two different, and complementary, potentiometric techniques were used. In the first, a solution of Ce(IV) is allowed to flow continuously at a constant rate into a vigorously stirred solution of Fe-$(GMI)_3{}^{2+}$, while the potential of a platinum indicator electrode *vs.* sce is recorded. This technique, known as automatic titration,[2] is described in part I.[1a] Automatic titrations represent an *open* experimental system. Any simple treatment of the kinetics in this system depends on the assumption that mixing is practically instantaneous. In the present case, this requirement appears to be closely approximated. Reduction of the stirring speed, which was generally kept at the maximum stable value (*ca.* 800 rpm), by one half caused a decrease of the potential by only 0.5–1 mV, which is comparable with the average experimental error (± 0.5 mV). It is further required that enough time is allowed to elapse so that the rate of change of the potential becomes steady, or nearly so. This occurs in the present case when 0.2–0.5 mol Ce(IV) per mole of $Fe(GMI)_3{}^{2+}$ has been added (see Figure 1).

The second technique[3] differs from the first one in that addition of the reagent is interrupted so that *closed* system conditions are established and conventional kinetic treatments can be applied. Addition of Ce(IV) was stopped at 0.45 mol (in some cases 0.9 mol) per mole of $Fe(GMI)_3{}^{2+}$. Potential readings were taken in intervals of 0.1 min for a period of 2.5 min (corresponding to 3–5 half-lives). On the average, measurements were reproducible within 1 mV. Readings were corrected, whenever necessary, for the slow response of the meter. For the first readings, this may introduce an additional uncertainty of *ca.* ± 1 mV. Measurements were made at two quite different concentrations of Ce(III), 4.75×10^{-2} and 8.0×10^{-4} M, subsequently referred to as *high* and *low* Ce(III). All potentials are referred to sce and contain the unknown liquid junction potential H_2SO_4, $4.07 M$ |KCl, saturated.

Spectrophotometric Rate Measurements. I. Oxidation of $Fe(GMI)_3{}^{2+}$ by Cerium(IV). Since $Fe(GMI)_3{}^{3+}$ is practically nonabsorbing at the absorption maximum of $Fe(GMI)_3{}^{2+}$ (554 nm), oxidation of the iron(II) to the iron(III) complex can be followed photometrically. In a typical experiment, 8.0 ml of a 2.00×10^{-5} M solution of $Fe(GMI)_3{}^{2+}$ in $4.07 M$ H_2SO_4 was injected, with a syringe, into a cell of 40-mm optical path containing 8.0 ml of 2.00×10^{-5} M Ce(IV) in $4.07 M$ H_2SO_4 and which was placed in the cell compartment of the spectrophotometer,[4] thermostated at $25.0°$. Absorbance readings were taken, at 554 nm, in intervals of 5 sec.

II. Disproportionation of $Fe(GMI)_3{}^{3+}$. The rate of disproportionation of $Fe(GMI)_3{}^{3+}$ was measured by following the increase of the absorbance at 554 nm caused by the formation of $Fe(GMI)_3{}^{2+}$ and other absorbing species. A 1.0×10^{-3} M solution of $Fe(GMI)_3{}^{3+}$ in $10.2 M$ H_2SO_4 was prepared by oxidizing $Fe(GMI)_3{}^{2+}$ with the stoichiometric amount of Ce(IV).[1a] Four tenths of a milliliter of this solution was blown, by air pressure, into the absorption cell containing 16 ml of $3.92 M$ H_2SO_4. Mixing was complete within 1 sec. Absorbance readings were taken over a period of 2 min (*ca.* 3 half-lives) at intervals of 5 sec.

Treatment of Data. I. Electrochemical Measurements. In the following, $Fe(GMI)_3{}^{2+}$ and $Fe(GMI)_3{}^{3+}$ will be abreviated as G^{2+} and G^{3+}, respectively. It is assumed that the potential of the indicator electrode is determined by the G^{3+}/G^{2+} couple. Since the formal potential of this couple was not known in the beginning, only relative values of $[G^{3+}]$ were accessible by experiment. Therefore, measured potentials were related to the auxiliary quantities R and S defined as
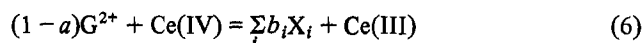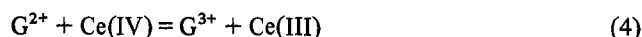
$$R = 10^{(E - E')/0.0591} = f[G^{3+}]/[G^{2+}] \tag{1}$$

$$S = R[G^{2+}] = f[G^{3+}] \tag{2}$$

with

$$f = 10^{(E_0' - E')/0.0591} \tag{3}$$

E is the measured potential, E_0' the (unknown) formal potential, and E' an arbitrary reference potential (0.800 V) introduced for convenience of calculations.

$[G^{2+}]$, which varies with the progress of the reaction, can be calculated from the formal stoichiometry of the reaction sequence[1a]

$$G^{2+} + Ce(IV) = G^{3+} + Ce(III) \tag{4}$$

$$G^{3+} = aG^{2+} + \sum_i b_i X_i \tag{5}$$

$$(1 - a)G^{2+} + Ce(IV) = \sum_i b_i X_i + Ce(III) \tag{6}$$

(1) (a) Part I, H. L. Chum and P. Krumholz, *Inorg. Chem.*, **13**, 514 (1974). (b) Presented in part in *Proc. Int. Conf. Coord. Chem., 14th*, 230 (1972); (c) taken in part from the doctoral thesis of H. Li Chum at the University of Sao Paulo, 1972.

(2) R. E. Cover and L. Meites, *J. Phys. Chem.*, **67**, 1528 (1963).

(3) J. Janata and J. Zyka, *Collect. Czech. Chem. Commun.*, **30**, 1723 (1965).

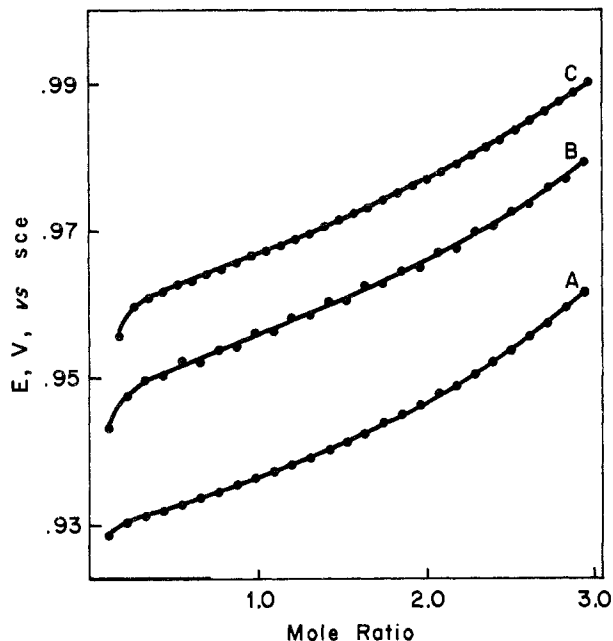(4) P. Krumholz, *Spectrochim. Acta*, **10**, 269 (1957).

Figure 1. Automatic titrations of $Fe(GMI)_3^{2+}$ with $Ce(IV)$: $[Ce(III)]_0 = 4.75 \times 10^{-2}$ M; 4.07 M H_2SO_4; $25 \pm 0.1°$; (A) $[Fe(GMI)_3^{2+}]_0 = 8.33 \times 10^{-4}$ M; $\rho_0 = 1.52 \times 10^{-6}$ M sec^{-1}; (B) $[Fe(GMI)_3^{2+}]_0 = 4.16 \times 10^{-4}$ M; $\rho_0 = 1.52 \times 10^{-6}$ M sec^{-1}; (C) $[Fe(GMI)_3^{2+}]_0 = 8.33 \times 10^{-4}$ M; $\rho_0 = 1.22 \times 10^{-5}$ M sec^{-1}. The abscissa gives the moles of $Ce(IV)$ added per mole of $Fe(GMI)_3^{2+}$ present.

where a and b_i are stoichiometric coefficients and X_i products of the disproportionation reaction, other than G^{2+}. One obtains

$$[G^{2+}] = [G^{2+}]_0 - (1-a)([Ce(IV)]_0 - [Ce(IV)]) + a([G^{3+}]_0 - [G^{3+}]) \qquad (7)$$

$[G^{2+}]_0$ is the initial concentration of $Fe(GMI)_3^{2+}$. $[Ce(IV)]_0$ is the total concentration of added $Ce(IV)$ if no reaction would have occurred. In all experiments, $[G^{3+}]_0$ is zero. Whenever necessary, initial concentrations as well as the values of the rate of addition of $Ce(IV)$, ρ (expressed in mol $liter^{-1}$ $second^{-1}$), were corrected for the change of volume in the course of a titration. The coefficient a has been determined previously[1a] as *ca.* 0.66. It is assumed that for $[Ce(IV)]_0 \leq [G^{2+}]_0$, a remains at least approximately constant.

In the preliminary treatment of the *open* system kinetics (automatic titrations), the lesser terms in $[Ce(IV)]$ and $[G^{3+}]$ in eq 7 were neglected. For a constant ratio $[Ce(IV)]_0/[G^{2+}]_0$, one obtains then from eq 1 and 7

$$(^2E - {}^1E) = \log ({}^2[G^{3+}]/{}^1[G^{3+}]) - \log ({}^2[G^{2+}]_0/{}^1[G^{2+}]_0) \qquad (8)$$

Equation 8 was used to obtain an approximate functional relation between the concentration of $Fe(GMI)_3^{3+}$ and ρ, from the measured potentials ^iE.

In the *closed* system, rates were expressed in terms of S as follows

$$-dS/dt = k_a * S^2 + k_b * S \qquad (9)$$

The equivalent expression

$$d(1/S)/dt = k_a * + k_b *(1/S) \qquad (10)$$

allows one to obtain the rate constants $k_a *$ and $k_b *$ from a linear least-squares plot of $d(1/S)/dt$ *vs.* $1/S$. The second right-hand term in eq 10 is a lesser correction term. Thus, if a sufficiently small time interval, Δt, is chosen (in the present case 0.2 min), $d(1/S)/dt$ can be set equal to $\Delta(1/S)/\Delta t$ for $1/S$ equal to the value at the midpoint of the time interval. Initially, $[G^{2+}]$, necessary to calculate S, was obtained from eq 7 neglecting the terms in $[Ce(IV)]$ and $[G^{3+}]$. The first values of $k_a *$ and $k_b *$ were then used to calculate f from the expression for the *open* system kinetics (*vide infra*)

$$f = (k_a * S_{00}^2 + k_b * S_{00})/\rho_{00} \qquad (11)$$

The subscript 00 denotes values at the moment when addition of cerium(IV) is interrupted. For reasons to be explained later, this procedure is only correct for the experiments at *low* Ce(III). The average value of f from those experiments was now used in the following expression, deduced from eq 1 and 7, to obtain better values of

$$[G^{2+}] = \frac{[G^{2+}]_0 - (1-a)([Ce(IV)]_0 - [Ce(IV)])}{1 + aR/f} \qquad (12)$$

$[G^{2+}]$. At *low* Ce(III), the term in $[Ce(IV)]$ in eq 12 is negligibly small. At *high* Ce(III), $[Ce(IV)]$ is close to the equilibrium value of eq 4, $[Ce(IV)] = R[Ce(III)]/fK$. The equilibrium constant K can be obtained from the formal potential of the G^{3+}/G^{2+} couple, E_0', now accessible from f with the help of eq 3, and that of the Ce(IV)–Ce(III) couple, determined by experiment.

Successive values of f, S, and of the rate constants converge after few iterations.

Alternatively, the right-hand side of eq 9 can be replaced by a single term, $k * S^n$, with a fractional exponent n. Modifying eq 11 accordingly, the rate constant $k *$ can be obtained by a similar iterative procedure.

II. Spectrophotometric Rate Measurements. It is assumed that under the experimental conditions of the disproportionation reaction, $[G^{2+}]_0$ and all concentration terms in Ce(IV) are negligibly small. It is further assumed that the stoichiometric coefficients of eq 5 remain constant during the course of the reaction. The measured absorbance per unit optical path, A, can then be expressed as follows

$$A = \epsilon_{G^{2+}} [G^{2+}] + \sum_i \epsilon_i[X_i] = \text{constant} \times [G^{2+}] \qquad (13)$$

With $[G^{3+}]_\infty = 0$, one obtains from eq 13 and 7

$$\frac{[G^{3+}]_0 - [G^{3+}]}{[G^{3+}]_0} = \frac{[G^{2+}]}{[G^{2+}]_\infty} = \frac{A}{A_\infty} \qquad (14)$$

Subscripts ∞ denote values for $t \to \infty$. Experimentally, one finds[1a]

$$A_\infty = 0.83\epsilon_{G^{2+}}[G^{3+}]_0 \qquad (15)$$

which leads to the desired relation between A and $[G^{3+}]$

$$[G^{3+}] = \frac{A_\infty - A}{0.83\epsilon_{G^{2+}}} \qquad (16)$$

The rate of disproportionation of $Fe(GMI)_3^{3+}$ can now be directly expressed in terms of $[G^{3+}]$. The rate expression has the same form as that of eq 9 and can be solved by the same procedure without the need of iteration.

Results

Electrochemical Rate Measurements. The results presented in part I of this study[1a] suggest that oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV), which eventually leads to ligand-oxidized products, proceeds *via* the iron(III) complex $Fe(GMI)_3^{3+}$. Now, it is known that the rate of electron exchange between iron(III) and iron(II) diimine complexes,[5] such as $Fe(phen)_3^{3+}$-$Fe(phen)_3^{2+}$, is much faster than the Ce(IV)–Ce(III) exchange.[6] Thus, there is good reason to believe that the potential of a platinum indicator electrode immersed in a reacting mixture of $Fe(GMI)_3^{2+}$ and Ce(IV) is determined by the $Fe(GMI)_3^{3+}$-$Fe(GMI)_3^{2+}$ couple and not by the Ce(IV)–Ce(III) couple, as long as the complex iron species are present in finite concentration.

Automatic titrations of $Fe(GMI)_3^{2+}$ with cerium(IV) in 4 M H_2SO_4 provided the first information on the underlying rate law. Once sufficient cerium(IV) has been added to reach stationary or quasistationary conditions, titration curves for different rates of addition of Ce(IV), ρ, and different con-

(5) M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, 38, 1591 (1963).

(6) P. B. Sigler and B. J. Masters, *J. Amer. Chem. Soc.*, 79, 6353 (1957).

centrations of $Fe(GMI)_3^{2+}$ run virtually parallel, until at least 2 equiv of Ce(IV) per mole of $Fe(GMI)_3^{2+}$ has been added (*cf.* Figure 1). Within those limits, changing the concentration of Ce(III) from 4.75×10^{-2} to 3×10^{-3} M causes no significant change of the measured potentials. At constant concentration of $Fe(GMI)_3^{2+}$, an eightfold increase in ρ displaces the titration curves by *ca.* 30 mV toward more positive potentials, *i.e.*, causes a *ca.* threefold increase of the concentration of $Fe(GMI)_3^{3+}$. At constant ρ, a twofold increase (or decrease) of the concentration of $Fe(GMI)_3^{2+}$ results in a decrease (or increase) of the potentials by *ca.* 19 mV, *i.e.*, causes little change in the concentration of $Fe(GMI)_3^{3+}$.

Thus, in first approximation, the open system rate law can be written as follows

$$\rho = k[Fe(GMI)_3^{3+}]^n \tag{17}$$

with n somewhat less than 2. Using eq 8, a value of $n = 1.85 \pm 0.1$ was obtained from a series of titration experiments similar to those of Figure 1.

Meites and coworkers[7,8] have shown that under certain limiting conditions, a simple rate law of the form of eq 17 with $n = 2$ is valid in terms of the intermediate species A' for the reaction sequence

$$A + T' \rightleftharpoons A' + T$$

$$2A' \xrightarrow{k} A + A'' \tag{18}$$
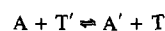
where the reagent T', introduced at constant rate, oxidizes (or reduces) the substrate A to A', which then disproportionates regenerating A and yielding A'' which is in a still higher (or lower) oxidation state. Since $Fe(GMI)_3^{3+}$ undergoes disproportionation into $Fe(GMI)_3^{2+}$ and ligand-oxidized products, a similar reaction sequence might well apply to the reaction between $Fe(GMI)_3^{2+}$ and Ce(IV).

More direct information on the rate law, which governs the disproportionation of $Fe(GMI)_3^{3+}$, is obtained from the modified automatic titrations with interrupted addition of the reagent. In terms of the quantity $S = f[Fe(GMI)_3^{3+}]$, data can be satisfactorily fitted over a period of 3-5 half-lives using the expression

$$-\frac{dS}{dt} = k^*S^n \tag{19}$$

with $n = 1.85 \pm 0.05$. An equally satisfactory rate expression that eliminates the fractional exponent[9] is

$$-\frac{dS}{dt} = k_a^*S^2 + k_b^*S \tag{9}$$

In terms of $[Fe(GMI)_3^{3+}]$, the *closed* system rate expression becomes

$$-\frac{d[Fe(GMI)_3^{3+}]}{dt} = k_a[Fe(GMI)_3^{3+}]^2 + k_b[Fe(GMI)_3^{3+}] \tag{20}$$

with $k_a = f k_a^*$ and $k_b = k_b^*$. The proportionality factor f, necessary to calculate the true second-order rate constant k_a, can now be obtained from the expression for the *open* system kinetics. To be compatible with the *closed* system

(7) R. E. Cover and L. Meites, *J. Phys. Chem.*, **67**, 2311 (1963).

(8) P. W. Carr and L. Meites, *J. Electroanal. Chem.*, **12**, 373 (1966).

(9) For the purpose of elucidating a reaction mechanism, it is preferable to express the data in the latter form; see D. Margerison in "Comprehensive Chemical Kinetics," Vol. I, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1969, Chapter 5.

expression in the form of eq 20, the former expression must be modified, *viz.*[10]

$$\rho = k_a[Fe(GMI)_3^{3+}]^2 + k_b[Fe(GMI)_3^{3+}] = \frac{1}{f}(k_a^*S^2 + k_b^*S) \tag{21}$$

Substitution of the values k_a^* and k_b^*, obtained from an analysis of the *closed* system data in terms of eq 9, into eq 21 allows one to calculate f from ρ and the value of S at the instant when addition of cerium(IV) has been interrupted. As a matter of fact, proper evaluation of S requires the knowledge of f. Thus, calculation of the rate constants requires, actually, an iterative procedure (*cf.* Experimental Section).

Table I lists values of the rate constants k_a and k_b obtained by a least-squares treatment of the data from a series of automatic titrations with interrupted addition of the reagent. Standard deviations for single experiments are *ca.* $\pm 0.1 \times 10^3$ M^{-1} sec^{-1} for k_a and $\pm 0.5 \times 10^{-3}$ sec^{-1} for k_b. Values from duplicate measurements agree, on the average, within ± 2 and $\pm 10\%$, respectively. It is to be noted that the term in k_b is a lesser correction term which only becomes important when most of $Fe(GMI)_3^{3+}$ has already reacted.

Within the experimental uncertainty, values of k_a at *low* Ce(III) show no significant dependence, either on ρ or on the concentration of $Fe(GMI)_3^{2+}$. Similarly, the presence of atmospheric oxygen (expt 7 and 8) has no significant influence on k_a but causes a *ca.* twofold increase of k_b. The average values of the rate constants from the experiments at *low* Ce(III) in 4.07 M H_2SO_4 at 25°, calculated with $f = (4.6 \pm 0.3) \times 10^3$, are: $k_a = (2.1 \pm 0.3) \times 10^3$ M^{-1} sec^{-1} and $k_b = (2.5 \pm 1) \times 10^{-3}$ sec^{-1}. At *high* Ce(III), values of k_a show a marked decrease with decreasing concentration of $Fe(GMI)_3^{2+}$, which will be commented on later.

With the help of eq 3, one obtains from the listed value of f the formal potential of the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ couple in 4.07 M H_2SO_4 at 25°, $E_0' = 1.017$ V (*vs.* sce). Under the same conditions, the formal potential of the Ce(IV)/Ce(III) couple is 1.171 V (*vs.* sce). From those values, one obtains the equilibrium constant of reaction 4, $K = 400 \pm 50$.

Spectrophotometric Rate Measurements. The reliability of the numerical values listed above depends on the validity of several assumptions which has not been definitively established. In particular, (a) that potentials are determined by the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ couple and (b) that the *open* system rate law can be written in the form of eq 21. Therefore, it seemed advisable to obtain confirmation by an independent method. For that purpose, solutions of yellow $Fe(GMI)_3^{3+}$ in 10 M H_2SO_4 were brought to an acidity of 4.07 M and formation of the red disproportionation products was followed photometrically. Because of the technical difficulties of working in an inert atmosphere, the experiments were performed in air. Using eq 16, concentrations of $Fe(GMI)_3^{3+}$ can now be directly calculated from the measured absorbances.

In fact, it was found that the concentration-time data fit, satisfactorily, a rate expression of the form of eq 20 over a period of 3 half-lives. The average values of the rate constants from a series of photometric experiments are: $k_a = (2.35 \pm 0.2) \times 10^3$ M^{-1} sec^{-1} and $k_b = (5 \pm 1.5) \times 10^{-3}$ sec^{-1}. It is seen that the value of k_a agrees, within the experimental error, with that from the electrochemical experiments at *low* Ce(III). For k_b, agreement with the electrochemical value ($\approx 7 \times 10^{-3}$ sec^{-1}, in the presence of

(10) Experimental data are insufficient and not precise enough to permit a direct test of eq 21.

Table I. Rate Constants of Eq 20 from Automatic Titrations of $Fe(GMI)_3{}^{2+}$ with Ce(IV) with Interrupted Addition of the Reagent[a]

Expt no.	[Fe-(GMI)$_3{}^{2+}$]$_\infty$ × 10^3	10^6ρ, M sec^{-1}	10^{-3}k_a, M^{-1} sec^{-1}	10^{-3} × k_a,[b] M^{-1} sec^{-1}	10^3 × k_b, sec^{-1}
1	1.35	1.41	2.15		3.0
2	1.34	5.62	2.15		2.5
3	1.33	11.2	2.1		2.8
4	0.68	1.43	2.0		2.0
5	0.65	5.70	2.05		2.7
6	0.13	1.50	2.05		3.0
7[c]	1.35	1.41	2.0		7.0
8[c]	1.34	5.62	2.05		7.0
9	1.33	5.60	1.8	1.95	3.5
10	1.33	11.2	1.75	1.9	3.5
11	0.68	1.43	1.7	2.0	2.5
12	0.66	5.70	1.6	1.9	2.3
13	0.52	5.62	1.7	2.1	2.3
14	0.34	1.51	1.4	1.95	2.5
15	0.14	1.51	1.1	2.0	2.2

[a] 0.45 mol of Ce(IV) added per mole of $Fe(GMI)_3{}^{2+}$, except in expt 6, 13, and 15 where the ratio is 0.9; [Ce(III)] = 8 × 10^{-4} M (expt 1-8) and 4.75 × 10^{-2} M (expt 9-15), [H$_2$SO$_4$] = 4.07 M, 25.0°. [b] Values corrected in accord with eq 29. [c] Presence of atmospheric O$_2$.

atmospheric oxygen) is poorer but still at the limit of the (larger) experimental error.

Considering that the two methods used to establish the empirical rate law for the disproportionation of $Fe(GMI)_3{}^{3+}$, eq 20, are completely independent, the agreement between the numerical values of the rate constants, k_a in particular, is certainly gratifying.

Finally, photometric measurements permit a direct visualization of the sequence of reactions 4 and 5, oxidation of $Fe(GMI)_3{}^{2+}$ to $Fe(GMI)_3{}^{3+}$ followed by disproportionation of the latter. Figure 2 displays the change of the absorbance at 554 nm (absorption maximum of $Fe(GMI)_3{}^{2+}$), with time, of an equimolecular mixture of $Fe(GMI)_3{}^{2+}$ and Ce(IV), 1 × 10^{-5} M, 4.07 M in H$_2$SO$_4$. The initial decrease of the absorbance reflects the disappearance of $Fe(GMI)_3{}^{2+}$ and formation of the nonabsorbing $Fe(GMI)_3{}^{3+}$. From this part of the curve, the rate constant for the forward reaction 4 can be estimated as $(4 \pm 1) \times 10^3$ M^{-1} sec^{-1}. As the concentration of $Fe(GMI)_3{}^{3+}$ builds up, disproportionation of the latter into $Fe(GMI)_3{}^{2+}$ and other absorbing species becomes more and more important. After a certain time, the rates of disappearance and of formation of the absorbing species become equal and the absorbance becomes stationary. Finally, the disproportionation reaction 5 assumes control and the absorbance starts to increase.

Under the conditions of the aforesaid experiments, the reverse reaction 4, reduction of $Fe(GMI)_3{}^{3+}$ by Ce(III), is of little importance. However, when $Fe(GMI)_3{}^{3+}$ is allowed to disproportionate in the presence of a higher concentration of Ce(III), the rate of disappearance of $Fe(GMI)_3{}^{3+}$ becomes larger. At [$Fe(GMI)_3{}^{3+}$]$_0$ = 2.0 × 10^{-5} M, an increase of the concentration of Ce(III) from 2 × 10^{-5} to 3 × 10^{-3} M causes an increase of the initial rate of approximately 100%. This leads to a crude estimate of the rate constant for the back reaction 4 as *ca.* 15 M^{-1} sec^{-1}, which compares favorably with the value of 10 ± 3 M^{-1} sec^{-1}, calculated from the rate constant of the forward reaction and the equilibrium constant K (*vide supra*).

The rate of disproportionation of $Fe(GMI)_3{}^{3+}$ decreases strongly with increasing acidity. At 5 M H$_2$SO$_4$, the rate constants k_a and k_b decrease by a factor of 3. At 10 M H$_2$SO$_4$, the rate decreases at least by a factor of 10^3.
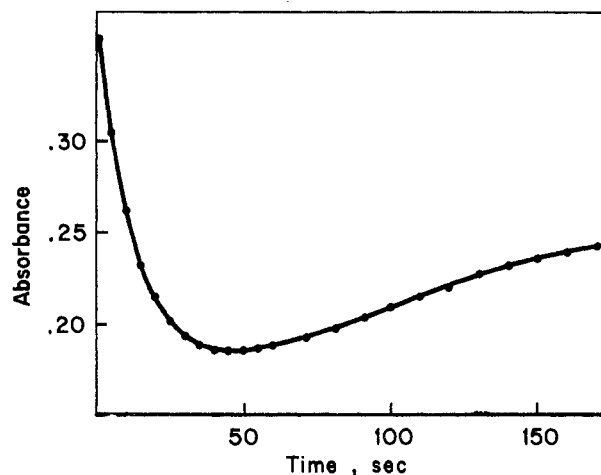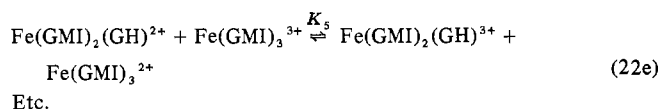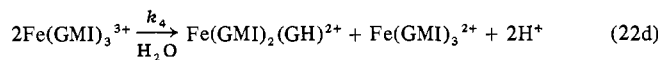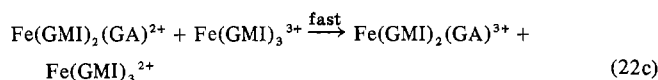

Figure 2. Plot of the absorbance *vs.* time for the oxidation of $Fe(GMI)_3{}^{2+}$ by Ce(IV): [$Fe(GMI)_3{}^{2+}$]$_0$ = [Ce(IV)]$_0$ = 1.0 × 10^{-5} M; 4.07 M H$_2$SO$_4$; 25 ± 0.1°; λ 554 nm.

Discussion

The main conclusions from the current kinetic study are (a) that $Fe(GMI)_3{}^{3+}$ is the first product of the oxidation of $Fe(GMI)_3{}^{2+}$ by Ce(IV), (b) that $Fe(GMI)_3{}^{3+}$ subsequently undergoes rapid disproportionation, and (c) that the rate of disappearance of $Fe(GMI)_3{}^{3+}$ obeys eq 20 with a *dominant* second-order term. Kinetic results, together with product analysis (*cf.* part I), suggest the following reaction mechanism

$$Fe(GMI)_3{}^{2+} + Ce(IV) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(GMI)_3{}^{3+} + Ce(III) \tag{22a}$$

$$2Fe(GMI)_3{}^{3+} \underset{H_2O}{\overset{k_2}{\longrightarrow}} Fe(GMI)_2(GA)^{2+} + Fe(GMI)_3{}^{2+} + 2H^+ \tag{22b}$$

$$Fe(GMI)_2(GA)^{2+} + Fe(GMI)_3{}^{3+} \overset{fast}{\longrightarrow} Fe(GMI)_2(GA)^{3+} + Fe(GMI)_3{}^{2+} \tag{22c}$$

$$2Fe(GMI)_3{}^{3+} \underset{H_2O}{\overset{k_4}{\longrightarrow}} Fe(GMI)_2(GH)^{2+} + Fe(GMI)_3{}^{2+} + 2H^+ \tag{22d}$$

$$Fe(GMI)_2(GH)^{2+} + Fe(GMI)_3{}^{3+} \overset{K_5}{\rightleftharpoons} Fe(GMI)_2(GH)^{3+} + Fe(GMI)_3{}^{2+} \tag{22e}$$
Etc.
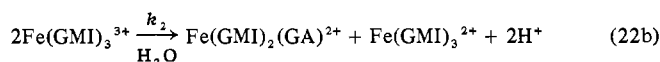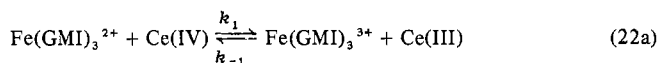
Equations 22b and 22d represent two parallel disproportionation paths which lead to complexes in which one of the original glyoxal bis(methylimine) ligands has been oxidized to $H_3CN=CNC(OH)=NCH_3$ (GA) or to $H_3CN=CHCH=NCH_2OH$ (GH), respectively (*cf.* part I). Redox reactions of the type of eq 22c and 22e are known to be very fast.[11] Since the formal potential of the $Fe(GMI)_2(GA)^{3+}/Fe(GMI)_2$-$(GA)^{2+}$ couple[1a] is *ca.* 0.3 V less positive than that of the $Fe(GMI)_3{}^{3+}/Fe(GMI)_3{}^{2+}$ couple, reaction 22c must nearly go to completion. Therefore, $Fe(GMI)_2(GA)^{2+}$ can be treated as a stationary intermediate. On the other hand, one may expect that the equilibrium constant K_5 is close to 1, as oxidation of a single =NCH$_3$ group in $Fe(GMI)_3{}^{2+}$ to =NCH$_2$OH is unlikely to cause a major change in the oxidation potential (and other properties) of the complex. For this same reason, one may also expect that $Fe(GMI)_2(GH)^{3+}$, just as $Fe(GMI)_3{}^{3+}$, will be subject to disproportionation yielding products such as $Fe(GMI)(GH)(GA)^{2+}$, etc. How-

(11) B. M. Gordon, L. L. Williams, and N. Sutin, *J. Amer. Chem. Soc.*, 83, 2061 (1961).

ever, as long as $Fe(GMI)_3^{2+}$ is allowed to react with not more than 1 equiv of cerium(IV), the concentration of $Fe(GMI)_2$-$(GH)^{2+}$ is much smaller ($\leqslant 1/5$) than that of $Fe(GMI)_3^{2+}$ (*cf.* part I). Thus, the contribution of reactions beyond eq 22d will be small and $Fe(GMI)_2(GH)^{2+}$, together with $Fe(GMI)_2$-$(GA)^{3+}$, will be the main reaction products. This is borne out by experiment.[1a] Therefore, kinetic treatment will be restricted to the reaction sequence eq 22a-d. To avoid repetition, equations will be written in a form valid for the *open* system kinetics. For the *closed* system, the term in ρ is omitted.

The following differential rate equations are considered.[12]

$$\rho - \frac{d[Ce(IV)]}{dt} = k_1[Fe(GMI)_3^{2+}][Ce(IV)] -$$
$$k_{-1}[Fe(GMI)_3^{3+}][Ce(III)] \qquad (23)$$

$$-\frac{d[Fe(GMI)_3^{3+}]}{dt} = (3k_2 + 2k_4)[Fe(GMI)_3^{3+}]^2 -$$
$$k_1[Fe(GMI)_3^{2+}][Ce(IV)] +$$
$$k_{-1}[Fe(GMI)_3^{3+}][Ce(III)] \qquad (24)$$

Adding up eq 23 and 24, one obtains

$$\rho - \frac{d[Fe(GMI)_3^{3+}]}{dt} - \frac{d[Ce(IV)]}{dt} =$$
$$(3k_2 + 2k_4)[Fe(GMI)_3^{3+}]^2 \qquad (25)$$

From the slope of the automatic titration curves in the quasi-stationary region, one finds that $|d[Fe(GMI)_3^{3+}]/dt| \ll |\rho|$. It is most likely that this also applies to $|d[Ce(IV)]/dt|$. Under those conditions, eq 25 is reduced to

$$\rho = (3k_2 + 2k_4)[Fe(GMI)_3^{3+}]^2 \qquad (26)$$

which is analogous to Meites's[7,8] expression and differs from eq 21 by the absence of the linear term in $Fe(GMI)_3^{3+}$.

In the case of a *closed* system ($\rho = 0$), the set of eq 23 and 24 has no explicit solution unless (a) $d[Ce(IV)]/dt$ is zero or (b) eq 22a can be treated as a preequilibrium. It will be shown that those conditions are approached (a) when the concentration of Ce(III) is *low* ($<10^{-3}$ M) or (b) when it is *high* ($\approx 5 \times 10^{-2}$ M).

The concentration of Ce(IV) in the course of an automatic titration, where $d[Ce(IV)]dt \ll \rho$, can be estimated from eq 23 as

$$[Ce(IV)] \approx \frac{\rho}{k_1[Fe(GMI)_3^{2+}]} + \frac{[Fe(GMI)_3^{3+}][Ce(III)]}{K[Fe(GMI)_3^{2+}]} \qquad (27)$$

Equation 27 is valid until the moment when addition of Ce-(IV) is interrupted. It is found, that for the experiments at *low* Ce(III) listed in Table I, the first (dynamic) term in eq 27 is *ca.* 10-20 times larger than the second (equilibrium) term. Nevertheless, in all experiments, except expt 6, the total concentration of Ce(IV) is only a few per cent of that of $Fe(GMI)_3^{3+}$. At the moment when *closed* system conditions are established, $d[Ce(IV)]/dt = -\rho$. Numerical integration[13] of the set of eq 23 and 24 (using $3k_2 + 2k_4 \approx k_a$) shows that $d[Ce(IV)]/dt$ decreases within 1-2 sec to a

negligibly small value (except in expt 6). Even in the latter experiment, neglect of the differential term in Ce(IV) causes an error in k_a of only 5 to 10%.

At *high* Ce(III), the second term in eq 27 is the dominant term and the total concentration of Ce(IV) is only 10-30% higher than the equilibrium concentration. It can again be shown by numerical integration that, when addition of the reagent is interrupted, the concentration of Ce(IV) approaches rapidly the equilibrium concentration (except in expt 15).

In the photometric experiments, where preformed Fe-$(GMI)_3^{3+}$ is allowed to disproportionate, the initial concentration of Ce(IV) is smaller than the equilibrium concentration. Reaction 22a proceeds thus from the right to the left. However, unless excess Ce(III) is added (*vide supra*), $d[Ce(IV)]/dt$ is negligibly small.

Thus, at *low* Ce(III), eq 25 becomes

$$-\frac{d[Fe(GMI)_3^{3+}]}{dt} = (3k_2 + 2k_4)[Fe(GMI)_3^{3+}]^2 \qquad (28)$$

which again differs from eq 20 by the absence of the linear term in $Fe(GMI)_3^{3+}$.

At *high* Ce(III), Ce(IV) is supposed to stay in equilibrium with its reaction partners in eq 22a. Neglecting minor differential terms in $Fe(GMI)_3^{2+}$ and Ce(III), eq 25 becomes

$$-\frac{d[Fe(GMI)_3^{3+}]}{dt} =$$
$$\frac{3k_2 + 2k_4}{1 + [Ce(III)]/K[Fe(GMI)_3^{2+}]}[Fe(GMI)_3^{3+}]^2 \qquad (29)$$

Thus, the apparent value of the rate constant is now $(1 + [Ce(III)]/K[Fe(GMI)_3^{2+}])^{-1}$ times the value for *low* Ce(III). This correction factor was tentatively applied to the values of the second-order rate constant k_a of the empirical rate law, eq 20, obtained from the experiments at *high* Ce(III). Corrected values of k_a are listed in the penultimate column of Table I. Agreement with the (uncorrected) values obtained in the experiments at *low* cerium(III) is indeed quite satisfactory.

Theory and experiment agree thus rather well in what concerns the squared term in $[Fe(GMI)_3^{3+}]$. However, the presence of the minor linear term in eq 20 and 21 is unexplained. A possible explanation is the occurrence of some unidentified, first-order side reaction (or reactions) such as reduction[1a] of $Fe(GMI)_3^{3+}$ by organic decomposition products, accidental impurities, or even by solvent water.[14] Systematic errors caused, for example by the slow response of the electrode or of the indicating instrument, might also cause an apparent deviation from the straight second-order rate law. Finally, the reaction mechanism of eq 22a-d is probably oversimplified.

It is difficult to see how the disproportionation reactions 22b and 22d could proceed in a single step. Those reactions can be considered as a limiting case of an *induced electron transfer* extensively studied by Taube and coworkers[15] in which two-electron oxidation of a ligand occurs by the concomitant action of an internal and of an external one-electron oxidant. The internal oxidant is the higher valent metal ion bound to the ligand to be oxidized and the external oxidant

(12) For a general treatment of the *open* system kinetics in automatic (and coulometric) titrations, see J. Janata and H. B. Mark Jr., in "Electroanalytical Chemistry," Vol. 3, A. J. Bard Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 1.

(13) Using the Runge-Kutta Method (4th order) programmed for a IBM 1130 computer.

(14) Actually, a free-radical intermediate in equilibrium with $Fe(GMI)_3^{3+}$ (*vide infra*) might be more easily reduced than the latter complex.

(15) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970, Chapter 4.

another (complexed) higher valent metal ion. The partic-ularity of the present system is that the two metal ions as well as their ligand systems are identical. The uniqueness of that system may justify some speculation about the intrinsic reaction mechanism.

It is generally conceded[15,16] that induced electron transfer proceeds in two consecutive one-electron steps; *viz.*, the co-ordinated ligand first reacts with the external oxidant to form a free-radical intermediate which then transfers the odd electron to the internal oxidant, *i.e.*, the central metal ion. In the present case, however, one rather would expect the internal electron transfer to occur more readily than the electron transfer to another, *identical* complex. Thus, un-less the internal and external oxidants act in concert, the primary, radical-forming step in reaction 22b and 22d should be an *intramolecular* electron transfer assisted by a nucleo-philic attack by solvent water,[17] as shown schematically in reaction 30. The so formed free-radical intermediates may
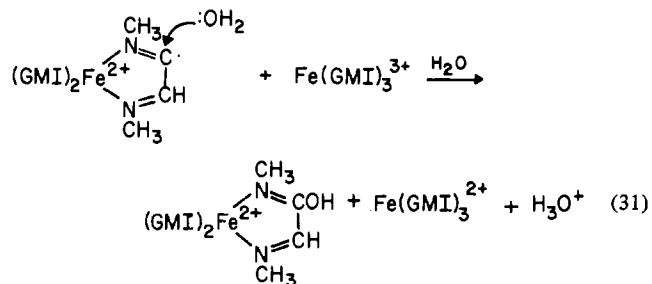

(30)
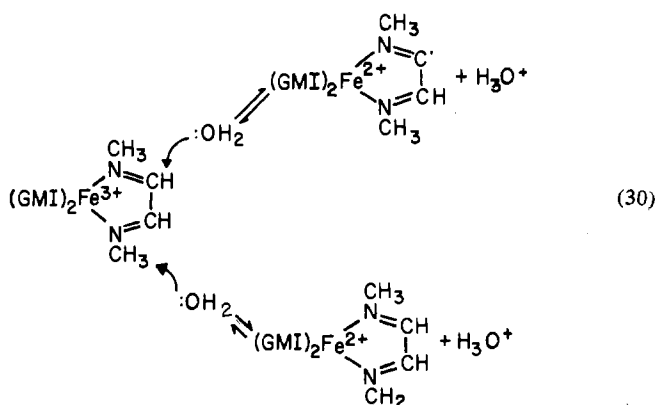
then react with another Fe(GMI)$_3{}^{3+}$ complex and with solvent water to form the stable two-electron oxidation products, as

shown for the reaction path of eq 22b in reaction 31. The

(31)

observation that the rate constant k_b of eq 20 increases in the presence of oxygen supports the postulated free-radical mechanism.

If the radical-forming steps, eq 30, are considered as pre-equilibria,[18] the disproportionation of Fe(GMI)$_3{}^{3+}$ follows a second-order rate law. Whichever is the correct mechanism, water must participate actively in both the bond-breaking (eq 30) and the bond-making (eq 31) steps. The strong decrease of the disproportionation rate at high acid concen-tration, mentioned earlier, can be connected with the de-crease of the water activity and the increase of the activity of the acid which displaces the equilibria of eq 30 to the left. Ion pair formation[19] may further contribute to the lowering of the reaction rate by excluding water from the vicinity of the complex ions and facilitating the approach of a proton.

(16) J. P. Candlin and J. Halpern, *J. Amer. Chem. Soc.*, **85**, 2518 (1963).

(17) See C. G. Swain and K. Hedberg, *J. Amer. Chem. Soc.*, **72**, 3373 (1950).

(18) See A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 2456 (1954).

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