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

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Tris(glyoxal bis(methylimine))iron(II) ($Fe(GMI)_3^{2+}$) (where GMI is $H_3CN{=}CHCH{=}NCH_3$) is oxidized stoichiometrically by Ce(IV) in 10 *M* H_2SO_4 to $Fe(GMI)_3^{3+}$. On dilution to lower acidities, the latter complex disproportionates regenerating $Fe(GMI)_3^{2+}$ and yielding two new, ligand-oxidized complexes, $Fe(GMI)_2(GA)^{3+}$ and $Fe(GMI)_2(GH)^{2+}$ (where GA is $H_3CN{=}CHCONHCH_3$ or $H_3CN{=}CHC(OH){=}NCH_3$, and GH is $H_3CN{=}CHCH{=}NCH_2OH$). The same products are formed when $Fe(GMI)_3^{2+}$ is allowed to react in 1–4 *M* H_2SO_4 with 1 equiv of Ce(IV). This proves that the reaction proceeds *via* the formation and disproportionation of $Fe(GMI)_3^{3+}$. Eventually, $Fe(GMI)_3^{2+}$ consumes about 4.5 oxidation equivalents yielding, in addition to $Fe(GMI)_2(GA)^{3+}$, further ligand-oxidized Fe(III) complexes formed, apparently, from $Fe(GMI)_2(GH)^{2+}$ by a succession of oxidations to the Fe(III) form and disproportionations of the latter.

Introduction

It has long been known that low-spin iron(II) complexes of aromatic diimine ligands, such as tris(2,2′-bipyridine)iron(II), can be oxidized to the corresponding stable iron(III) complexes.[2] One-electron oxidation of the iron(II) complexes of aliphatic diimine ligands, such as tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3^{2+}$, to $Fe(GMI)_3^{3+}$ by Ce(IV), has only been observed in strongly acid media (10 *M* H_2SO_4).[3] At lower acidities, $Fe(GMI)_3^{3+}$ undergoes spontaneous reduction to the iron(II) state with concomitant ligand oxidation, without disruption of the metal–ligand bonds. When oxidized directly at lower acidities, $Fe(GMI)_3^{2+}$ was shown to consume 4–4.5 oxidation equivalents, forming a ligand-oxidized iron(III) complex (or complexes).[3]

More recently, various other oxidation reactions of transition metal complexes which generate new complexes with oxidized forms of the ligands have been reported.[4] Complexes in which the metal has been oxidized to a higher state appear to be intermediates in these oxidations. In two cases (Ni(III)[5] and Fe(III)[6]) the supposed intermediates have been isolated and shown to spontaneously undergo an internal metal–ligand redox process which, eventually, leads to ligand-oxidized complexes. The tentatively proposed reaction models were not further supported by more detailed mechanistic or kinetic studies.

We report now the results of a detailed study of the oxidation of tris(glyoxal bis(methylimine))iron(II) by Ce(IV). This paper is concerned with the stoichiometry of the reaction and the nature of the reaction products. Part II will deal with the kinetics and the mechanism of the oxidation process.

Experimental Section

Materials. Solutions of cerium(IV) sulfate and cerium(III) sulfate were prepared from reagent grade materials and standardized according to accepted procedures. The sulfuric acid was Merck reagent grade which is low in reducing impurities. All solutions were made up using water redistilled from $KMnO_4$.

Tris(glyoxal bis(methylimine))iron(II) Perchlorate. The complex salt was prepared by a modification of the procedure reported earlier[7] for the preparation of the corresponding iodide. To a deaerated mixture of 20 ml (0.1 mol) of 30% glyoxal in water and 25 ml (0.03 mol) of 1.2 *M* aqueous $FeCl_2$ was added, in one portion and with vigorous stirring, 30 ml (0.3 mol) of 10 *M* aqueous methylamine. The mixture was kept under nitrogen at 25° for 1 hr and filtered and enough 1 *M* $HClO_4$ was added to bring the pH to 5. After addition of 20 g of $NaClO_4 \cdot H_2O$, the mixture was kept for 2 hr at 0°. The crystallized perchlorate salt was filtered off, washed with a small amount of cold water, and dried *in vacuo*, yield 5 g. The crude product was twice recrystallized by dissolving, at 60°, in 0.5 *M* acetic acid (14 ml/g), filtering, and cooling for 2 hr at 0°, yield, 3–3.5 g. *Anal.* Calcd for $FeC_{12}H_{24}N_6Cl_2O_8$: Fe, 11.01; N, 16.57. Found: Fe, 10.98; N, 16.52. Determination of glyoxal by acid hydrolysis of the complex in the presence of 2,4-dinitrophenylhydrazine (*vide infra*) yielded 99–99.5% of the theroretically expected amount.

Stoichiometry of the Oxidation of Tris(glyoxal bis(methylimine))iron(II) by Cerium(IV) from Automatic Titrations: In the automatic titrations,[8] a solution of cerium(IV) sulfate was allowed to flow at constant rate into a well-stirred solution of $Fe(GMI)_3^{2+}$ while the potential of a platinum indicator electrode *vs.* sce was recorded. A Corning Model 12 expanded scale pH meter, the scale of which was recalibrated to within ±0.1 mV, was used. The titration vessel is a jacketed glass jar, 35 × 100 mm, closed with a tightly fitting Lucite cover which holds the platinum electrode, the salt bridge, the polyethylene tip of a motorized syringe buret, a 10 mm wide glass baffle, and the gas inlet and outlet tubes. The salt bridge is an inverted U-tube closed with medium porosity glass frits and filled with a solution of H_2SO_4 of the same concentration as that in the titrated solution. The bridge solution was allowed to flow slowly (0.1–0.2 ml/hr) through the glass frits. One leg of the bridge and the tip of the reference electrode (sce) dip into a saturated KCl solution. The platinum electrode (coiled wire, diam 0.7 mm, length 8 cm) was pretreated before each titration by first immersing for 5 min in a solution, 0.1 *M* in $FeSO_4$ and 0.5 *M* in H_2SO_4, and then for 15 min in a mixture of 1 ml of 0.2 *M* $Ce(SO_4)_2$ and 25 ml of concentrated H_2SO_4, at 60°. The electrode was immersed into the test solution shortly *after* the addition of Ce(IV) was started. The solution was magnetically stirred (Teflon coated bar, 8 × 25 mm) at *ca.* 800 rpm. All experiments were made at 25.0 ± 0.1° in 0.50–4.07 *M* aqueous H_2SO_4. In order to maintain constant acid concentration throughout the titration experiment, the concentration of H_2SO_4 in both the reagent (Ce(IV)) and the test solutions was kept equal. The Ce(IV) concentration in the reagent solution was 4.75×10^{-2} *M*.

To correct for minor variations of the response of the platinum indicator electrode as well as of the liquid junction potential, the electrode was calibrated after each experiment using a solution containing fixed amounts of Ce(IV) and Ce(III) and having an acidity equal to that of the test solution. Titrations were usually performed under nitrogen.

At acidities equal to, or greater than, 2 *M*, titration experiments were reproducible within 1–2 mV. At 0.5 *M* H_2SO_4, deviations were two times larger.

(1) (a) Presented in part in, *Proc. Int. Conf. Coord. Chem., 14th*, 230 (1972); (b) abstracted from the doctoral thesis of H. Li Chum, University of Sao Paulo, 1972.

(2) F. Blau, *Ber.*, 21, 1077 (1888); *Monatsh. Chem.*, 19, 647 (1898).

(3) P. Krumholz, *Proc. Int. Conf. Coord. Chem., 7th*, 280 (1962).

(4) See V. L. Goedken and D. H. Busch, *J. Amer. Chem. Soc.*, 94, 7355 (1972); G. C. Christoph and V. L. Goedken, *ibid.*, 95, 3869 (1973); O. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 10, 463 (1971).

(5) N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).

(6) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).

(7) P. Krumholz, *J. Amer. Chem. Soc.*, 75, 2163 (1953).

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

Photometric Determination of the Stoichiometry. To a stirred, 10^{-3} *M* solution of $Fe(GMI)_3^{2+}$ in 1 *M* H_2SO_4, kept at 25°, was added Ce(IV) in amounts varying from 4 to 5 equiv per mole of complex. After 5 min, $FeSO_4$ was added to reduce the ligand-oxidized Fe(III) complexes to the Fe(II) state. The solution was transferred into a 1-cm absorption cell and placed in the thermostated (25°) cell compartment of the spectrophotometer (Hitachi Perkin-Elmer, Model 139). Absorbances were read in suitable time intervals at 554 nm (absorption maximum of $Fe(GMI)_3^{2+}$). The labile, ligand-oxidized Fe(II) complexes were found to decay completely within 1 hr. Thereafter, the absorbance decreased only slowly and practically linearly with time. Extrapolation of this linear part of the decay curve to zero time yields the absorbance of the less labile species. A plot of the latter *vs.* equivalents of Ce(IV) yields the stoichiometry as intercept with the zero absorbance line.

Disproportionation of Tris(glyoxal bis(methylimine))iron(III). A solution of $Fe(GMI)_3^{3+}$ was prepared by adding, at 0°, enough Ce(IV) to a 2.0×10^{-3} *M* solution of $Fe(GMI)_3^{2+}$ in 11 *M* H_2SO_4 to turn the red color to yellow. The consumption of Ce(IV) was within ±0.5% of the theoretical amount. At 0°, the solution was stable for at least 10 min. One milliliter of this solution was added to 25 ml of deaerated water at 25°, containing enough H_2SO_4 to bring the final acidity to the desired value. After a time necessary to complete the reaction (5 min for 1 *M* H_2SO_4, 30 min for 4 *M* H_2SO_4), a few crystals of $FeSO_4 \cdot 7H_2O$ were added and the absorbance at 554 nm (absorption maximum of $Fe(GMI)_3^{2+}$) was read as a function of time. The residual absorbance, extrapolated to zero time (*vide supra*), was referred to that of a solution of $Fe(GMI)_3^{2+}$ in H_2SO_4 of the same molarity.[9]

Rates of Acid Hydrolysis of Tris(glyoxal bis(methylimine))iron(II) and of Its Oxidation Products. Acid hydrolyses of Fe(II) and Fe(III) trisdiimine complexes are known to be first order in the complex.[10] Therefore, any major deviation of the plot of log *A* (absorbance) *vs.* time indicates that more than one complex is present. This method of *kinetic analysis*[11] has been extensively used in this investigation. Measurements were made in 1.00 *M* H_2SO_4. For $Fe(GMI)_3^{2+}$ and the inert Fe(II) complexes resulting from its partial oxidation, or from the disproportionation of $Fe(GMI)_3^{3+}$, solutions were kept in a thermostat at 35 ± 0.05° for periods of 100–200 hr; in suitable time intervals, absorbances were measured at several wavelengths. To measure the faster rate of the hydrolysis of the Fe(III) complexes resulting from the complete oxidation of $Fe(GMI)_3^{2+}$, the solution was kept for the time of the experiment (12 hr) in the thermostated (25 ± 0.1°) cell compartment of the photometer. Finally, to measure the still faster rate of the acid hydrolysis of the corresponding Fe(II) complexes, a solution containing the complex in the Fe(III) state was injected, with a thermostated syringe, into the cell which contained an acid solution of $FeSO_4$. Readings were started at 15 sec after injection of the complex and continued for 30 min.

Determination of Glyoxal in the Oxidation Products of Tris(glyoxal bis(methylimine))iron(II). Glyoxal was determined as its bis(2,4-dinitrophenylhydrazone) following the procedure of Neuberg and coworkers.[12] In a typical experiment, 0.102 g (0.2 mmol) of $Fe(GMI)_3^{2+}$ dissolved in 100 ml of 1 *M* H_2SO_4 at 25° was oxidized with 4.6 equiv of Ce(IV). After 5 min, the Fe(III) complexes were reduced with SO_2 and the solution kept until the red color had completely disappeared. Then 20 ml of a 2% solution of 2,4-dinitrophenylhydrazine in 5 *M* H_2SO_4 and 40 ml of water were added, and the mixture was heated for 1 hr in a boiling water bath. The solution was kept for 4 hr at 20°, the precipitate was filtered off on a sintered-glass crucible, washed with water, and dried *in vacuo*. Finally, the dried precipitate was extracted in the crucible with three successive 20-ml portions of boiling ethanol and dried to constant weight, mp 323–325°. There was no mp depression on mixture with an authentic sample of glyoxal bis(2,4-dinitrophenylhydrazone). *Anal.* Calcd for $C_{14}H_{10}N_8O_8$: C, 40.20; H, 2.41; N, 26.66. Found: C, 40.03; H, 2.49; N, 26.66. The yield of glyoxal was 1.96 (1.94) mol per mole of $Fe(GMI)_3^{2+}$.

***N*-Methylglyoxylamide 2,4-Dinitrophenylhydrazone. A. Isolation from the Oxidation Products of Tris(glyoxal bis(methylimine))iron(II).** $Fe(GMI)_3^{2+}$ (0.255 g (0.5 mmol) in 100 ml of 1 *M* H_2SO_4) was oxidized with 4.6 equiv of Ce(IV). The 2,4-dinitrophenylhydrazones were precipitated as in the preceding experiment. The crude precipitate was extracted with two 50-ml portions of boiling ethanol. On cooling to −10° for 4 hr, the first extract yielded a crop of 86 mg of a yellow, crystalline material. On recrystallization from 50 ml of boiling ethanol, the yield was 58 mg, mp 244–245° (no mp depression in mixture with an authentic sample of *N*-methylglyoxylamide 2,4-dinitrophenylhydrazone (*vide infra*)). *Anal.* Calcd for $C_9H_9N_5O_5$: C, 40.45; H, 3.39; N, 26.21. Found: C, 40.35; H, 3.36; N, 26.04.

From the combined mother liquors, another 20 mg of a slightly less pure product, mp 241–245°, was obtained. The total yield of *N*-methylglyoxylamide was 0.58 mol per mole of $Fe(GMI)_3^{2+}$. The mother liquor from the 2,4-dinitrophenylhydrazone precipitate was found to contain glyoxylic acid (as its 2,4-dinitrophenylhydrazone), which was determined photometrically after extraction with ethyl acetate and reextraction into aqueous Na_2CO_3.[13] The yield was *ca.* 0.1 mol of glyoxylic acid per mole of $Fe(GMI)_3^{2+}$. The acid is likely to result from the hydrolysis of the *N*-methylglyoxylamide.

B. Synthesis of *N*-Methylglyoxylamide 2,4-Dinitrophenylhydrazone. Diethoxyethyl acetate (0.175 g (1 mmol)) (Aldrich) was mixed with 2 ml of 10 *M* aqueous methylamine (20 mmol) and kept for 2 hr at 35°. The solution was evaporated under reduced pressure and the residue was extracted with 5 ml of petroleum ether. After evaporation of the solvent, the oily residue was dissolved in water (80 ml) and added to 20 ml of a 2% solution of 2,4-dinitrophenylhydrazine in 5 *M* H_2SO_4. The mixture was heated to boiling and allowed to cool slowly. Subsequently, the mixture was kept for 2 hr at 0°; the crystalline precipitate was filtered off, washed with water and recrystallized from boiling ethanol (100 ml): yield 0.20 g; mp 244–245°. *Anal.* Calcd for $C_9H_9N_5O_5$: C, 40.45; H, 3.39; N, 26.21. Found: C, 40.25; H, 3.35; N, 26.09.

Determination of Formaldehyde in the Disproportionation Products of Tris(glyoxal bis(methylimine))iron(III). Disproportionation of $Fe(GMI)_3^{3+}$ was allowed to occur in a 3×10^{-3} *M* solution in 1 *M* H_2SO_4 at 25°. After reduction with Fe(II), the solution was heated in a boiling water bath until the red color had disappeared. Formaldehyde was determined in this solution by the chromotropic acid method.[14] The glyoxylic acid derivatives present in the solution interfered slightly with the test because of the formation of a brownish color. The amount of formaldehyde found corresponds to 0.115 ± 0.01 mol per mole of $Fe(GMI)_3^{3+}$.

To determine the amount of formaldehyde present *before* hydrolysis of the inert Fe(II) complexes had occurred, the solution of the reduced disproportionation products was distilled *in vacuo* (24 Torr) until 50% had come over. In a separate experiment, the distillate from a 10^{-4} *M* solution of formaldehyde was found to contain *ca.* 30% of the aldehyde present in the original solution. Only trace amounts of formaldehyde were detected in the destillate of the main experiment. Approximately 0.005 mol of formaldehyde per mole of $Fe(GMI)_3^{3+}$ was found to have been formed.

Determination of Formaldehyde in the Blue Oxidation Product of Tris(glyoxal bis(methylimine))iron(II). $Fe(GMI)_3^{2+}$ was oxidized, as described earlier, with Ce(IV) and the products, after reduction with Fe(II), were allowed to decompose. The glyoxylic acid derivatives present interfered appreciably with the chromotropic acid test. Approximately 0.1 mol of formaldehyde per mole of $Fe(GMI)_3^{2+}$ was detected.

Results and Discussion

Figure 1 shows typical results of automatic titrations of $Fe(GMI)_3^{2+}$ with Ce(IV) in sulfuric acid media. Concentrations were varied as follows: $Fe(GMI)_3^{2+}$, 2.1×10^{-4}–8.35×10^{-4} *M*; H_2SO_4, 0.5–4.07 *M*; Ce(III), 3.0×10^{-3}–4.75×10^{-2} *M*. The rate of addition of Ce(IV) was varied from *ca.* 0.1 to 1 mol per mole of $Fe(GMI)_3^{2+}$ per minute. Under those conditions and at 25°, the equivalence point, taken as the point of steepest slope of the titration curves, was found between 4.2 and 4.7 oxidation equivalents per mole of $Fe(GMI)_3^{2+}$. The consumption of Ce(IV) increases with increasing acidity and, less regularly, when the rate of addition of Ce(IV) is increased. The concentration of Ce(III) has no significant influence on the position of the equivalence point nor on the potentials prior to equivalence. Titrations performed in the

(9) The molar absorptivity of $Fe(GMI)_3^{2+}$ at 554 nm increases slightly with increasing concentration of the acid.

(10) P. Krumholz, *Struct. Bonding (Berlin)*, 9, 139 (1971), and references therein.

(11) P. Krumholz, *Inorg. Chem.*, 4, 609 (1965).

(12) C. Neuberg and M. Kobel, *Biochem. Z.*, 256, 457 (1932); C. Neuberg and H. Simon, *ibid.*, 256, 485 (1932).

(13) T. E. Friedemann and G. E. Haugen, *J. Biol. Chem.*, 147, 415 (1943).

(14) D. A. Mac Fadyen, *J. Biol. Chem.*, 158, 107 (1945).

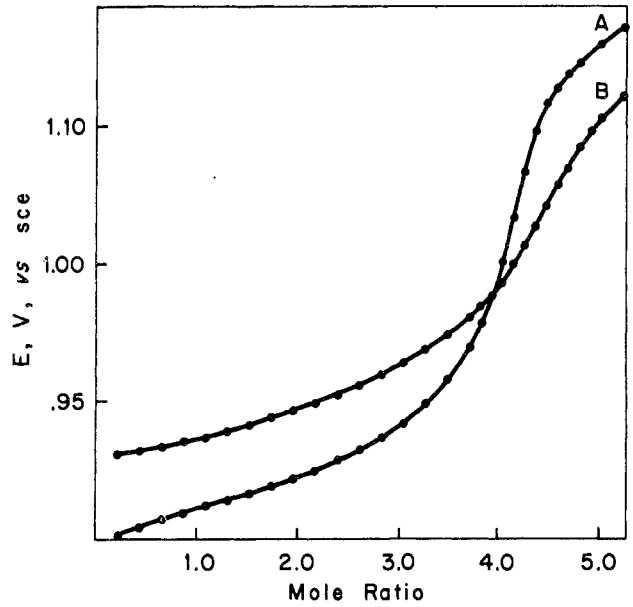


Figure 1. Automatic titrations of $Fe(GMI)_3^{2+}$ with Ce(IV). [$Fe(GMI)_3^{2+}]_0 = 8.33 \times 10^{-4}$ *M*; $[Ce(III)]_0 = 4.75 \times 10^{-2}$ *M*; $\rho_0 = 1.52 \times 10^{-6}$ *M* sec^{-1}; 25.0 ± 0.1°. (A) 0.5 *M* H_2SO_4; (B) 4.0 *M* H_2SO_4. The abscissa gives the moles of Ce(IV) added per mole of $Fe(GMI)_3^{2+}$ present.

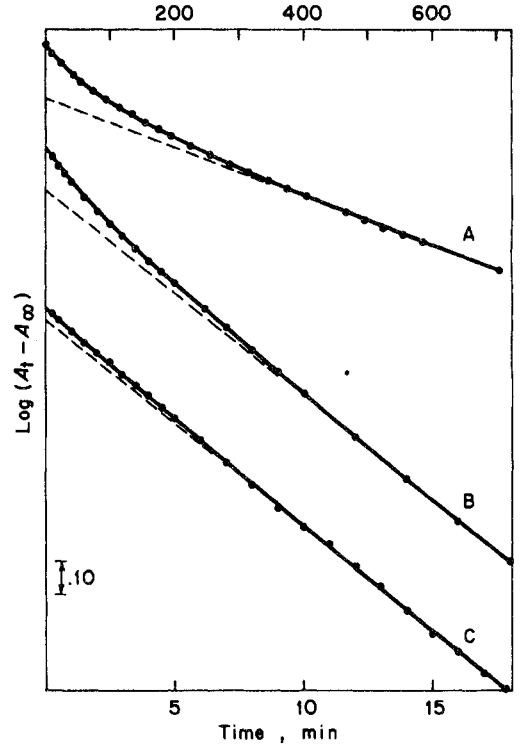


Figure 2. Log ($A_t - A_\infty$) *vs.* time for the acid hydrolysis of ligand-oxidized complexes derived from $Fe(GMI)_3^{2+}$. 1 *M* H_2SO_4; 25.0 ± 0.1°. (A) Oxidation product of $Fe(GMI)_3^{2+}$ by 5.0 equiv of Ce(IV) (Fe(III) form), λ 595 nm; (B) same (Fe(II) form), λ 560 nm; (C) disproportionation product of $Fe(GMI)_3^{3+}$ (labile Fe(II) form), λ 560 nm. Curve A, upper abscissa scale, curves B and C, lower abscissa scale.

presence and absence of atmospheric oxygen give, within the experimental error, the same results.

In the course of the titration, the color of the solution changes gradually from red to blue. On addition of a reducing agent such as Fe(II), the blue color turns almost instantaneously to red which fades away in less than 1 hr.

The stoichiometry of the oxidation reaction was determined independently by determining the amount of Ce(IV) just sufficient to transform $Fe(GMI)_3^{2+}$ completely into the blue oxidation product (see Experimental Section). In 1 *M* H_2SO_4 and at 25°, the consumption of Ce(IV) was 4.55 equiv per mole of $Fe(GMI)_3^{2+}$.

On rapid addition (*ca.* 30 sec) of Ce(IV), the blue oxidation product is formed in a yield of *ca.* 85%, as determined by oxidizing $Fe(GMI)_3^{2+}$ with a slight excess of Ce(IV) and rapid back-titration at 3° (to minimize decomposition) with Fe(II). The potential drops sharply when most of the excess Ce(IV) is reduced and then again when the blue Fe(III) species is reduced to the red Fe(II) form. At 50% reduction, the potential is close to 0.70 V *vs.* sce. Under the same conditions, the formal potential of the Ce(IV)-Ce(III) couple is 1.17 V *vs.* sce.

The absorption spectrum of the blue oxidation product displays a broad, structureless band centered at 596 nm, $\epsilon_{max} \approx 2.5 \times 10^3$. The spectrum of the reduced Fe(II) form in 1 *M* H_2SO_4 has a maximum at *ca.* 570 nm, $\epsilon_{max} \approx 7 \times 10^3$, and a broad shoulder toward shorter wavelengths, characteristic of the (low spin) iron(II) diimine chromophore.[10] On increasing the pH to *ca.* 4, the spectrum changes drastically, now displaying two distinct peaks at 600 and 515 nm, respectively. The increase of the pH causes, likewise, an increase of the half-life of the complex Fe(II) species by a factor of *ca.* 50.

When the blue oxidation product is allowed to partly decompose, slight but distinct changes in the shape of the absorption band are observed which indicate that more than one complex is present. This was confirmed by an analysis of the rate of acid hydrolysis of the oxidation product in the original Fe(III) form, as well as after its reduction to the red Fe(II) form (see Figure 2, curves A and B). Extrapolation of the final linear part of the logarithmic decay curves to zero time provides a rough measure of the mole fraction in the least labile component of the mixture. On the assumption that the molar absorptivities of all components are the same, mole fractions of 0.68 and 0.74 were obtained from the decay curves of the complex mixtures in the Fe(III) and the Fe(II) forms, respectively. The first-order rate constants for the acid hydrolysis of the least components are: Fe(III) form, $(2.8 \pm 0.5) \times 10^{-5}$ sec^{-1}; Fe(II) form, $(2.5 \pm 0.1) \times 10^{-3}$ sec^{-1} (1 *M* H_2SO_4, 25°).

The complexes which result from the oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV) could only be isolated as tarry polyiodides (with simultaneous reduction to the Fe(II) state). In several preparations, the Fe:N ratio varied between 1:5.9 and 1:5.95. Thus, the original FeN_6 chromophore of $Fe(GMI)_3^{2+}$ is substantially preserved in its oxidation products.

To obtain further information on the nature of those products, the amount of glyoxal formed in the acid hydrolysis of the labile Fe(II) form was determined as its bis(2,4-dinitrophenylhydrazone);[15] 1.95 mol of glyoxal per mole of $Fe(GMI)_3^{2+}$ submitted to oxidation was recovered. In addition, another hydrazone was isolated and identified by analysis and comparison with an authentic sample as the 2,4-dinitrophenylhydrazone of *N*-methylglyoxylamide, OHC-$CONHCH_3$. The yield of this material which must have been originally present as the methylimine, *i.e.*, methylimino-

(15) Precipitation of the bis-2,4-dinitrophenylhydrazone from the solution of the hydrolysis products occurred only very slowly at 25°. This indicates that glyoxal is still present as the methylimine which, in analogy to other aliphatic aldimines, is expected to hydrolyze slowly in strongly acid media; see J. Hine, J. C. Craig, Jr., J. G. Underwood, and F. A. Via, *J. Amer. Chem. Soc.*, 92, 5194 (1970).

N-methylacetamide, $H_3CN{=}CHCONHCH_3$, or the tautomeric form $H_3CN{=}CHC(OH){=}NCH_3$ (=GA), was *ca.* 0.6 mol per mole of $Fe(GMI)_3^{2+}$. Finally, presence of *ca.* 0.1 mol of glyoxilic acid, resulting probably from the hydrolysis of the amide, was detected.

In view of those findings, we now identify the least labile component of the blue oxidation product of $Fe(GMI)_3^{2+}$ with an Fe(III) complex in which one of the original glyoxal bis(methylimine) ligands has been oxidized to methylimino-*N*-methylacetamide, *i.e.*, $Fe(GMI)_2(GA)^{3+}$.

Formation of the latter complex from $Fe(GMI)_3^{2+}$ requires only 3 oxidation equiv while *ca.* 4.5 equiv has actually been consumed. However, as we have shown, the blue oxidation product contains *ca.* 30% of more labile complexes in which ligand oxidation might have proceeded further. Since the yield of ligand-oxidized Fe(III) complexes is only *ca.* 85%, the most labile components may have decomposed in the course of the oxidation process. Finally, the organic decomposition products may have consumed additional oxidant. A clue to the nature of the more labile oxidation products, as well as to the mechanism of the oxidation process of $Fe(GMI)_3^{2+}$, was provided by a study of the "disproportionation" of $Fe(GMI)_3^{3+}$.

In 10 *M* or stronger H_2SO_4, $Fe(GMI)_3^{2+}$ is oxidized by the stoichiometric amount of Ce(IV) to $Fe(GMI)_3^{3+}$. Oxidation is accompanied by a color change from red to yellow. On prolonged standing, the yellow color changes gradually back to red. On dilution with water, this color change becomes more rapid the lower the final acidity. In deoxygenated 1 *M* H_2SO_4 at 25°, the absorbance at 554 nm (absorption maximum of $Fe(GMI)_3^{2+}$) approaches, within 5 min, a constant value which amounts to *ca.* 83% of that which would obtain if all of the $Fe(GMI)_3^{3+}$ were reconverted into $Fe(GMI)_3^{2+}$. On addition of Fe(II), the absorbance increases almost instantaneously to *ca.* 95% of the latter value, then decreases rapidly and becomes, after *ca.* 1 hr, practically constant at 78.8%. In 4 *M* H_2SO_4, this value is reduced to 78.2%; a further reduction to 77.5% occurs in the presence of air. The normalized[16] absorption spectra of those final solutions display only very minor differences when compared with the normalized spectrum of $Fe(GMI)_3^{2+}$. It seems thus that $Fe(GMI)_3^{3+}$ undergoes a kind of a disproportionation reaction yielding $Fe(GMI)_3^{2+}$ on the one hand and ligand-oxidized Fe(III) complexes on the other. The properties of the latter are, apparently, very similar to those of the blue oxidation product of $Fe(GMI)_3^{2+}$, *viz.*, low absorptivity and easy reduction to a more strongly absorbing and more labile Fe(II) form. Measurements of the rate of acid hydrolysis proved, finally, that the ligand-oxidized product from the disproportionation reaction consists, to at least 90%, of a complex which, in its reduced form, dissociates at the same rate as the least labile component of the reduced form of the blue oxidation product of $Fe(GMI)_3^{2+}$, identified earlier as $Fe(GMI)_2(GA)^{3+}$ (see curves B and C in Figure 2).

However, if $Fe(GMI)_2(GA)^{3+}$ and $Fe(GMI)_3^{2+}$ were the sole products of the disproportionation reaction, the two complexes should have been formed in a proportion of 1:2, which seems inconsistent with the experimental results. Now, it was mentioned before that there exist minor differences between the spectrum of $Fe(GMI)_3^{2+}$ and that of the inert Fe(II) fraction from the disproportionation reaction which, originally, were not considered significant.

(16) Spectra brought to the same height at the absorption maximum; this makes detection of minor spectral differences possible even if concentrations and/or molar absorptivities are not known.

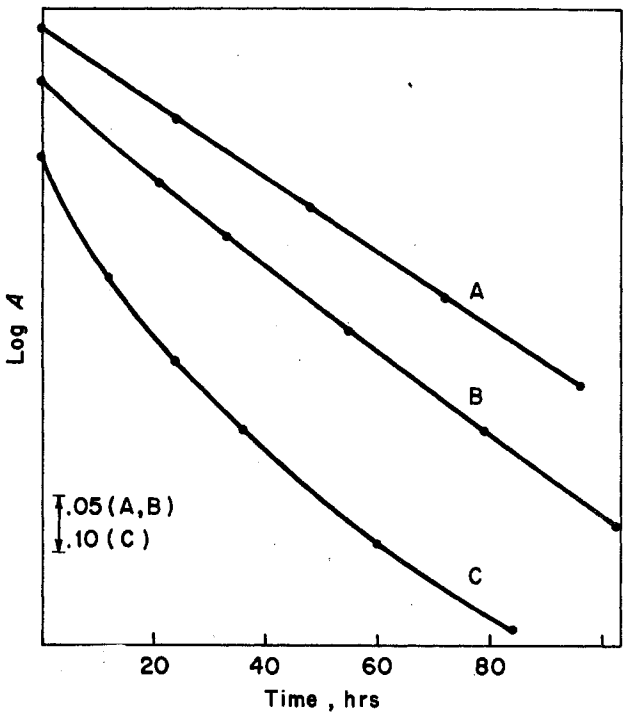


Figure 3. Log *A* *vs.* time for the acid hydrolysis of $Fe(GMI)_3^{2+}$ and its inert oxidation products (Fe(II) forms). 1 *M* H_2SO_4; 35.1 ± 0.05°. (A) $Fe(GMI)_3^{2+}$; (B) disproportionation product of $Fe(GMI)_3^{3+}$ (after the decay of the labile Fe(II) complexes); (C) oxidation product of $Fe(GMI)_3^{2+}$ by 4.0 equiv of Ce(IV) (after the decay of the labile Fe(II) complexes), λ 550 nm.

However, it was found later that the rate of acid hydrolysis of the latter fraction deviates significantly from that of $Fe(GMI)_3^{2+}$ (see Figure 3, curves A and B). Analysis of the experimental data in terms of two parallel first-order reactions yields a value of 0.15 ± 0.02 for the mole fraction of a second complex with a rate constant three to four times larger than that of $Fe(GMI)_3^{2+}$ (presuming equal molar absorptivities of the two complexes at 530–550 nm).

Formation of the new complex must have involved oxidation of a ligand. The rather moderate difference in the rates of the acid hydrolysis and the similarity of the absorption spectra of the two complexes indicate that the basic ligand functions of $Fe(GMI)_3^{2+}$ have not been substantially altered on oxidation. There is only one possibility of oxidizing a glyoxal bis(methylimine) ligand without causing a major structural change: oxidation of a $=NCH_3$ group to $=NCH_2OH$. Detection of formaldehyde (0.115 ± 0.01 mol per mole of $Fe(GMI)_3^{3+}$) among the products of the disproportionation reaction (after acid hydrolysis of the products) definitively supports this conclusion. The measured spectral intensities of the disproportionation products indicate that the new complex is predominantly formed in its Fe(II) state.[17]

Consequently, we identify this compound with a Fe(II) complex in which one of the original glyoxal bis(methylimine) ligands has been oxidized to glyoxal (*N*-methyl-*N'*-hydroxymethyl)diimine, $H_3CN{=}CHCH{=}NCH_2OH$ (=GH), *i.e.*, $Fe(GMI)_2(GH)^{2+}$.

The formal stoichiometry of the disproportionation of $Fe(GMI)_3^{3+}$ can now be written approximately as follows.

(17) In analogy to $Fe(GMI)_3^{3+}$, the Fe(III) complex is expected to be nonabsorbing or only weakly absorbing at 554 nm. Under this assumption, the observed evolution of spectral intensities of the disproportionation products of $Fe(GMI)_3^{3+}$ becomes unintelligible.

$$Fe(GMI)_3^{3+} = 0.22Fe(GMI)_2(GA)^{3+} + 0.12Fe(GMI)_2(GH)^{2+} + 0.66Fe(GMI)_3^{2+} \quad (1)$$

It is noticed that there is still an imbalance of 0.1 oxidation equiv in eq 1, in favor of the reactant. The difference is larger than would be expected considering the probable error in the evaluation of the stoichiometric coefficients. It can, at least in part, be explained by the presence of lesser amounts of other complexes[18] in which ligand oxidation has proceeded further (*vide infra*). Reduction of $Fe(GMI)_3^{3+}$ to $Fe(GMI)_3^{2+}$, by organic decomposition products, is another possible reason for this imbalance.

If $Fe(GMI)_3^{2+}$ is allowed to react in 1-4 *M* H_2SO_4 with 1 equiv of Ce(IV), the composition of the reaction products is substantially the same as that of the products of the disproportionation of preformed $Fe(GMI)_3^{3+}$. This proves that in both cases the course of the reaction is the same: $Fe(GMI)_3^{2+}$ is primarily oxidized to $Fe(GMI)_3^{3+}$ which, in turn, undergoes disproportionation in accord with eq 1.

If the amount of Ce(IV) allowed to react with $Fe(GMI)_3^{2+}$ is increased, the concentration of the latter will decrease while that of $Fe(GMI)_2(GH)^{2+}$ should tend to increase. However, the latter complex is certainly capable of being oxidized to $Fe(GMI)_2(GH)^{3+}$ and will thus increasingly compete with $Fe(GMI)_3^{2+}$ for the oxidizing agent. Once formed, $Fe(GMI)_2(GH)^{3+}$ is expected to disproportionate just like $Fe(GMI)_3^{3+}$, *i.e.*, regenerating $Fe(GMI)_2(GH)^{2+}$ and yielding further ligand-oxidized complexes. Because of the presence of two different ligands, a number of different ligand-oxidized complexes can now be formed. One expects (*cf.* eq 1) the formation of Fe(III) complexes, such as $Fe(GMI)(GH)(GA)^{3+}$ on the one hand, and of Fe(II) complexes, such as $Fe(GMI)(GH)_2^{2+}$ on the other. In addition, a Fe(II) complex may have been formed in which the $H_3CN{=}CHCH{=}NCH_2OH$ ligand has been further oxidized to $H_3CN{=}CH{-}CH{=}NCHO$.

Evidence for the formation of such intermediate Fe(II) species was obtained by a kinetic analysis of the inert Fe(II) fraction of the oxidation products of $Fe(GMI)_3^{2+}$ by 4 equiv of Ce(IV) (*i.e., ca.* 10% less than required for total transformation into the blue Fe(III) product). From curve C in Figure 3, one can infer the presence of a considerable amount of a complex which dissociates several times faster than $Fe(GMI)_2(GH)^{2+}$ (but still *ca.* 500 times more slowly than $Fe(GMI)_2(GA)^{2+}$). Apparently, $Fe(GMI)_3^{2+}$ is now only a minor component of the complex mixture.

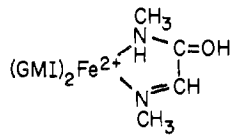
Oxidation of the various intermediate Fe(II) species to the Fe(III) state, followed by disproportionation of the latter, may, in principle, go on still further. Eventually, all of the $Fe(GMI)_3^{2+}$ originally present will be oxidized to $Fe(GMI)_2(GA)^{3+}$ and to other Fe(III) complexes in which additional oxidation of one (or more) $=NCH_3$ group to $=NCH_2OH$ or =NCHO (or even =NCOOH[19]) has occurred. There are good reasons to believe that the latter complexes, formed at the expense of 5 or more oxidation equiv, represent the bulk of the more labile fraction of the final (blue) oxidation product of $Fe(GMI)_3^{2+}$. Since the yield of formaldehyde from this product is only about one-third of that of the more labile fraction, complexes containing a =NCHO (or =NCOOH) group are more likely to be present than complexes with two (or more) $=NCH_2OH$ groups.

(18) As mentioned earlier, the Fe(III) fraction from the disproportionation reaction may contain, in addition to $Fe(GMI)_2(GA)^{3+}$, up to 10% of other, more labile complexes (*cf.* curve C in Figure 2).

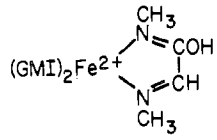
(19) Approximately 0.03 mol of CO_2 was detected in the products of the acid hydrolysis of the blue oxidation product of $Fe(GMI)_3^{2+}$.

Conclusions

In spite of the complexity of the oxidation reaction of tris(glyoxal bis(methylimine))iron(II) by Ce(IV) in its more advanced stages, the basic features of this reaction seem reasonably well established. It can be rather safely concluded that ligand oxidation does not proceed *via* a direct attack on a ligand by Ce(IV) but involves the intermediate formation of the Fe(III) complex $Fe(GMI)_3^{3+}$. The latter disproportionates yield, in addition to $Fe(GMI)_3^{2+}$, the complexes $Fe(GMI)_2(GA)^{3+}$ and $Fe(GMI)_2(GH)^{2+}$ in which a two-electron oxidation has occurred at the methine carbon and methyl carbon centers of a ligand, respectively. It is likely that further oxidation of $Fe(GMI)_2(GH)^{2+}$ proceeds basically by the same mechanism. It is also evident that the disproportionation reactions, such as that of eq 1, must involve several parallel and consecutive steps. This aspect will be explored in part II of this study. Since the yield of ligand-oxidized products in the disproportionation reaction of $Fe(GMI)_3^{3+}$ was found to increase slightly (by *ca.* 3%) in the presence of atmospheric oxygen, the possibility of the participation of free-radical intermediates must be acknowledged. $Fe(GMI)_2(GA)^{3+}$ is the main product of the total oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV). In its Fe(II) form, this complex undergoes profound spectral changes with change of the pH. In strongly acid solution, the complex may have one of the two structures shown below.



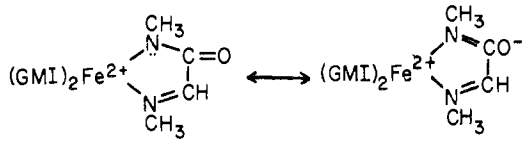
1



2

Preference is given to structure **2** because it preserves the iron(II) trisdiimine chromophore.

At pH 3, or higher, the complex apparently looses a proton. The resulting structure may, perhaps, be best represented as a resonance hybrid of forms **3** and **4**.



3 4

In addition to $Fe(GMI)_2(GA)^{3+}$, other Fe(III) complexes are formed in which additional ligand oxidation at one of the $=NCH_3$ groups to $=NCH_2OH$, =NCHO, and possibly =NCOOH may have occurred.

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Registry No. $Fe(GMI)_3(ClO_4)_2$, 43211-75-2; cerium(IV) sulfate, 13590-82-4; $Fe(GMI)_2(GA)^{3+}$, 49564-89-8; $Fe(GMI)_2(GH)^{2+}$, 43211-74-1.