derived from these measurements are compiled in Table VII. It turned out, however, that thermostating of the commercial device is very unsatisfying[24] and that a precise control of the temperature at the syringes and at the cuvette is not possible. As described in the Experimental Section, a modified thermostating device was built, and special efforts were made to provide it with good temperature control. The reinvestigation of the temperature dependence (25–50 °C) led to distinctly greater activation energies (as it can be seen from Table VII) whereas the rate constants at 25 °C were identical. Hence, at higher temperatures there is a temperature gradient in the system which leads to activation energies that are 25–30% too low. By comparing k' (Table II and III) and $\Delta H^{\ddagger}$ (Table VII), one can see that the decrease in rate constants for the solvent path is paralleled by an increase in activation enthalpy. The plot of $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$ is reasonably linear with a slope of 0.8; i.e., both enthalpy and entropy changes are equally responsible for the variation in rate.

Acknowledgment. The cooperation with Miss Ursula Reiffer, who carried out the experiments leading to the data in Table VI, is gratefully acknowledged. The authors thank the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie e.V. for support. Salicylaldehyde was kindly provided by Bayer AG, Leverkusen.

Registry No. I, 36748-26-2; II, 72784-66-8; III, 72784-67-9; IV, 6852-54-6; V, 6852-58-0; HSA=*N*-Et, 5961-36-4; salicylaldehyde, 90-02-8; ethylamine, 75-04-7; Cu(SA=*N*-Et)$_2$, 26194-23-0; MeOH, 67-56-1.

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Contribution from the Instituto de Quimica,
Universidade de Sao Paulo, Sao Paulo, Brazil

Ligand Oxidation in Iron Diimine Complexes. 4. Temperature and Acidity Dependence of the Oxidation of Tris(glyoxal bis(methylimine))iron(II) by Cerium(IV)[1]

HELENA LI CHUM* and MARIA E. M. HELENE

Received August 3, 1979

The influence of acidity and temperature on the kinetics of the oxidation of tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3^{2+}$, by cerium(IV) was studied in the temperature range 10–30 °C and acidity 4–7 M H_2SO_4. The stoichiometry of the reaction is $Fe(GMI)_3^{2+} + Ce(IV) = Ce(III) + Fe(GMI)_3^{3+} \rightarrow 0.24Fe(GMI)_2(GA)^{3+} + 0.12Fe(GMI)_2(GH)^{2+} + 0.64Fe(GMI)_3^{2+}$; GMI = $H_3CN{=}CHCH{=}NCH_3$, GA = $H_3CN{=}CHC(OH){=}NCH$, and GH = $H_3CN{=}CHCH{=}NCH_2OH$. The primary step is the oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV) to the corresponding iron(III) complex. The thermodynamic parameters for this reaction are $\Delta H = -(2.1 \pm 0.6)$ kcal/mol and $\Delta S = 5 \pm 2$ eu, in 4.0 M H_2SO_4. The equilibrium constant for this reaction increases by a factor of approximately 2 in going from 4.0 to 6.0 M H_2SO_4. The iron(III) complex undergoes ligand oxidation, yielding the products above, in a reaction which is second order with respect to the iron(III) complex. The plot of $\log k_{obsd} - H_0$ vs. $\log a_{H_2O}$ is linear within the experimental error, where H_0 is the Hammett acidity function, essentially equal to the activity of acid in the medium. The slope is 1.9 ± 0.4. Therefore, the observed rate constant can be expressed as $k_{obsd} = k[H_2O]^2/[H_3O^+]$. The mechanism proposed to explain this dependence involves the iron(III) complex $Fe(GMI)_3^{3+}$, which undergoes an intramolecular reduction with concomitant ligand oxidation. This reaction is assisted by a reversible nucleophilic attack by solvent water. The products of this reaction are an iron(III)–ligand radical (on the methine or methyl carbons) complex and H_3O^+. The iron(III)–ligand radical complex undergoes oxidation by another molecule of iron(III) complex. This step is also assisted by solvent water. The rate law derived with this scheme reproduces the experimental rate law. The disproportionation of $Fe(GMI)_3^{3+}$ was also studied as a function of temperature, holding $\log([H_2O]^2/[H_3O^+])$ constant within 2.5%. Within the experimental error, plots of $\log k_{obsd}$ vs. T^{-1} are linear with an activation enthalpy of 10.5 ± 1 kcal/mol. The activation entropy is $-(8 \pm 2)$ eu.

Introduction

In parts 1[2] and 2[3] of this series, the stoichiometry, reaction products, and kinetics 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 studied at 25 °C in 4.0 M H_2SO_4. This reaction provides an example of a well-studied process 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 stable ligand-oxidized complexes. Several other examples of ligand oxidation proceeding via intermediate formation of the complex in a higher oxidation state prior to ligand oxidation are known.[4,5] More recently, ruthenium(II) derivatives[6] of ethylenediamine were shown to be oxidized to the corresponding ruthenium(II) diimine complex and then further oxidized at the ligands, via Ru(III) complexes. No detailed kinetic studies were described. The kinetics of the autoxidation of the iron diimine complex derived from biacetyl was studied in detail.[7] It has been suggested that the reaction proceeds via the iron(III) complex.[7] In part 2[3] of this series it was shown that the rate of ligand oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV),

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(1) (a) Abstracted in part from the M.Sc. thesis of M.E.M.H., University of Sao Paulo, 1978. (b) Presented in part in *Proc. Int. Conf. Coord. Chem., 18th*, 201 (1977).

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0020-1669/80/1319-0876$01.00/0

essentially, a second-order process in $Fe(GMI)_3^{3+}$, was strongly dependent upon the acid concentration. In fact, if the acid concentration is >10 M H_2SO_4, the simple stoichiometric oxidation to $Fe(GMI)_3^{3+}$ is observed, with no observable ligand oxidation for a period of about an hour. As the acid concentration is lowered, ligand oxidation takes place more rapidly, and its rate is inversely proportional to the acid concentration. This paper quantifies the rate of dependence of this reaction as a function of acid concentration and temperature, thus completing the detailed kinetic and mechanistic study of the oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV).

Experimental Section

Materials. The chemicals used in this study are described in part 1.[2]

Stoichiometry Measurements. The stoichiometry of the oxidation of $Fe(GMI)_3^{2+}$ by 1 equiv of Ce(IV) (initial stage of the reaction) was determined by spectrophotometry and by chemical analyses as a function of temperature and acidity, as described in part 1.[2] In the studied temperature range (10–30 °C) and acid concentration (4.0–7.0 M H_2SO_4) one can write for the stoichiometry of this reaction eq 1 where GMI = $H_3CN{=}CHCH{=}NCH_3$, GA = $H_3CN{=}CHC(OH){=}NCH_3$, and GH = $H_3CN{=}CHCH{=}NCH_2OH$.

$$Fe(GMI)_3^{2+} + Ce(IV) \rightleftarrows Ce(III) + Fe(GMI)_3^{3+} \rightarrow (0.24 \pm 0.03)Fe(GMI)_2(GA)^{3+} + (0.12 \pm 0.02)Fe(GMI)_2(GH)^{2+} + (0.64 \pm 0.06)Fe(GMI)_3^{2+} \quad (1)$$

Rate Measurements. In the present work, the disproportionation of $Fe(GMI)_3^{3+}$ as a function of acid concentration and temperature was followed potentiometrically, by using a platinum indicator electrode vs. SCE. The experimental setup is described in part 2,[3] as is the chemical pretreatment of the indicator electrode. Liquid junction potentials were estimated as 2 mV for acid concentrations smaller than 5 M H_2SO_4 and as 5 mV for 6 M H_2SO_4.[8] To confirm data at 6 M H_2SO_4 and obtain new data at 7 M H_2SO_4, we also carried out spectrophotometric determinations described in part 2.[3]

The rate of the disproportionation of $Fe(GMI)_3^{3+}$ measured potentiometrically was determined as follows. A solution of the iron(III) complex was prepared in 10 M H_2SO_4, by oxidation of the iron(II) complex with the stoichiometric amount of Ce(IV) (also in 10 M H_2SO_4), at 5 °C, under nitrogen. With a glass syringe refrigerated at 5 °C, 0.12 mL of this iron(III) complex solution was injected into a deoxygenated solution of the iron(II) complex, at a certain temperature (10–30 °C, known within ±0.1 °C), containing H_2SO_4, so that the final acid concentration would be 4, 4.5, 5, or 6 M. With this small volume of 10 M H_2SO_4 (at 5 °C) and vigorous stirring of the final solution, the temperature of the latter did not rise more than 0.05 °C, less than the experimental error in the temperature. A constant temperature circulator equipped with a compressor, Lauda Brinkmann K2/R, was employed. The real acid concentration and volume of acid and complex added at 5 °C were determined by titration of the same volume of acid with NaOH. The final sulfuric acid concentration was also determined by titration. Knowing the exact amount of acid added, the final molarity of the solution, and the density of sulfuric acid solutions,[9] one can calculate the final volume of the solution and, therefore, concentrations of iron(III) and iron(II) complexes within ±0.5%.

The measurements of potential (within 0.1 mV) were made with the Corning digital pH meter 112. The reproducibility of duplicate or triplicate measurements was 1 mV for experiments in the 4–5 M H_2SO_4 range and 2 mV at 6 M H_2SO_4. Time zero (±0.02 min) corresponded to the injection of the iron(III) complex solution into the iron(II) complex solution. Potential measurements started at 0.40–0.50 min and were made in intervals of 0.10 min (4–5 M H_2SO_4 over a period of 5 min) and 0.50 min (6 M H_2SO_4 over a period of 20 min).

As previously described,[3] minor variations of the response of the platinum indicator electrode as well as of the liquid junction potential were corrected by the measurement of a solution containing fixed amounts of Ce(IV) and Ce(III), having an acidity equal to that of the test solution. The reproducibility of the measured potential for the Ce(IV)/Ce(III) solution was 2 mV.

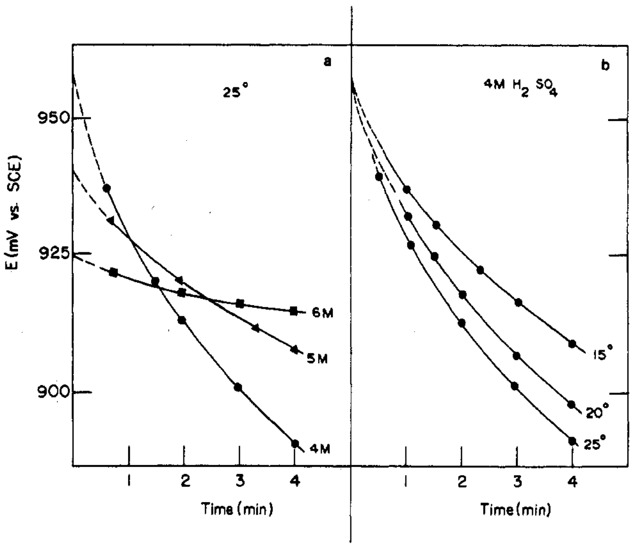

Figure 1. Potential of the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ couple measured with a platinum indicator electrode vs. SCE as a function of time: (a) with varying acid concentration at 25 °C (for concentration conditions, see Table I, experiments 7, 9, and 10); (b) with varying temperature at 4.0 M H_2SO_4 (for concentration conditions, see Table I, experiments 2, 5, and 7). The figures only show representative points. The average number of points in that time interval is 30.

All spectrophotometric rate measurements were performed on a Zeiss DMR-10 spectrophotometer, equipped with a Lauda Brinkmann K2/R constant temperature circulator.

Treatment of Data. Since the initial concentrations of iron(III) and -(II) forms are known, the potential extrapolated to zero time of the potential vs. time curves, combined with the Nernst equation (2), yields the formal electrode potential of the couple $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$, abbreviated as G^{3+}/G^{2+}. The precision of the extrapolation procedure is ±2 to ±1 mV. On the basis of the Nernst equation (2), the stoichiometry equation[3] (1), and the rate law[3] (4), where the second-order term is dominant, one obtains the combined equation (5). Plots of $-dE/dt$ vs. $e^{E/Q}$ are linear with

$$E = E^{\circ\prime} + Q \ln([G^{3+}]/[G^{2+}]) \quad (Q = RT/nF) \qquad (2)$$

$$[G^{2+}]_t = [G^{2+}]_{t=0} + 0.64([G^{3+}]_{t=0} - [G^{3+}]_t) \qquad (3)$$

$$-d[G^{3+}]_t/dt = k_a[G^{3+}]_t^2 + k_b[G^{3+}]_t \qquad (4)$$

$$-dE/dt = (e^{-E^{\circ\prime}/Q}Q(k_a([G_3^{2+}]_{t=0} + 0.64[G_3^{3+}]_{t=0}) + 0.64k_b))e^{E/Q} + k_bQ \qquad (5)$$

intercepts equal to k_bQ. Since k_b, the initial concentrations, and $E^{\circ\prime}$ are known, the slope yields k_a.

Results

The results presented in part 2[3] of this series indicated that the disproportionation reaction of $Fe(GMI)_3^{3+}$ according to eq 1 follows rate law 4 in which the second-order term is dominant. At 25 °C and 4.0 M H_2SO_4 the rate constants k_a and k_b have been determined by two independent techniques:[3] a photometric technique and a combination of open-system automatic titrations[10] and closed-system interrupted automatic titrations,[3] which provided the formal electrode potential of the complex couple and the rate constants.

In order to investigate the effects of temperature and acid concentration, and thus confirm the proposed reaction mechanism[3] with respect to acid and water participation, we em-

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Table I. Potentiometric and Photometric Rate Constants k_a and k_b for the Disproportionation of $Fe(GMI)_3^{3+}$, Equilibrium Constants K_{eq} for the Cerium(IV) Oxidation of $Fe(GMI)_3^{2+}$ to $Fe(GMI)_3^{3+}$, and Formal Electrode Potentials $E^{\circ\prime}$ of the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ Couple as a Function of Acid Concentration and Temperature

expt no.	temp, °C (±0.1 °C)	$[H_2SO_4]$, M (±0.02 M)	$[Fe(GMI)_3^{3+}]_{t=0}$, M	$[Fe(GMI)_3^{2+}]_{t=0}$, M	$10^{-3}k_a$, $M^{-1}\,s^{-1}$	10^3k_b, s^{-1}	$10^{-1}K_{eq}$	$E^{\circ\prime}$, V vs. SCE
1	9.9	4.01	7.5×10^{-6}	1.39×10^{-4}	0.82 ± 0.05	1.9 ± 0.2	48 ± 4	1.008
2	15.0	4.00	9.9×10^{-6}	1.01×10^{-4}	1.25 ± 0.07	2.1 ± 0.2	43 ± 4	1.012
3	15.0	4.00	9.9×10^{-6}	1.01×10^{-4}	1.16 ± 0.07	2.8 ± 0.3	43 ± 4	1.012
4	20.0	3.99	4.75×10^{-5}	3.42×10^{-4}	1.69 ± 0.05	5.2 ± 0.4	41 ± 3	1.015
5	20.0	3.99	1.01×10^{-5}	1.01×10^{-4}	1.66 ± 0.05	4.1 ± 0.4	41 ± 3	1.015
6	25.0	3.98	9.8×10^{-6}	1.03×10^{-4}	2.3 ± 0.2	5.1 ± 0.5	39 ± 3	1.017
7	25.0	3.98	9.8×10^{-6}	9.9×10^{-5}	2.2 ± 0.2	4.7 ± 0.5	39 ± 3	1.017
8	25.0	4.41	9.4×10^{-6}	1.01×10^{-4}	1.19 ± 0.06	3.0 ± 0.3	40 ± 4	1.011
9	25.0	4.96	9.3×10^{-6}	1.01×10^{-4}	0.62 ± 0.04	3.4 ± 0.3	51 ± 5	1.001
10	25.0	5.92	9.4×10^{-6}	1.02×10^{-4}	0.16 ± 0.03	0.30 ± 0.03	83 ± 6	0.986
11[a]	25.0	5.94	1.96×10^{-5}		0.14 ± 0.02	0.58 ± 0.05		
12[a]	25.0	6.81	5.5×10^{-5}		0.021 ± 0.003	0.45 ± 0.05		

[a] Photometric determinations in the presence of atmospheric oxygen.

ployed a different potentiometric technique, described in the Experimental Section, and the photometric technique. Plots of the potential of the platinum indicator electrode vs. time as a function of acid concentration and temperature are illustrated in Figure 1a,b, respectively. Extrapolation of the potential to zero time yields the formal electrode potential of the complex couple (see Experimental Section). The analysis of the E vs. time curve, described in the treatment of data, yields the rate constants k_a and k_b. Since the formal electrode potential of the couple Ce(IV)/Ce(III) has been determined under the same experimental conditions (within ±0.2 mV), one can calculate the equilibrium constant for the primary reaction step of the overall reaction which produces ligand-oxidized complexes represented by eq 1, which is the formation of the iron(III) complex[3] (eq 6) as a function of acid con-

$$Fe(GMI)_3^{2+} + Ce(IV) \rightleftarrows Fe(GMI)_3^{3+} + Ce(III) \quad (6)$$

centration and temperature. Table I assembles rate constants k_a and k_b, equilibrium constant K_{eq}, and the formal electrode potential of the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ couple as a function of acid concentration and temperature.

Discussion

(a) Equilibrium Constants for the Formation of $Fe(GMI)_3^{3+}$ (Eq 6). Inspection of Table I shows that K_{eq} decreases slightly with increased temperature in 4.0 M H_2SO_4. The errors in the equilibrium constants are large due to the 2 mV uncertainty of the extrapolation procedure of the $E^{\circ\prime}$ for the complex couple. Estimate of K_{eq} at 30.0 °C gave 370 ± 50. With these data one can calculate for the reaction represented by eq 6 $\Delta H = -(2.1 \pm 0.6)$ kcal/mol and $\Delta S = 5 \pm 2$ eu. These values indicate that the formation of $Fe(GMI)_3^{3+}$ is favored enthalpically and entropically. Due to the similarity between $Fe(GMI)_3^{2+}$ and the analogous tris(1,10-phenanthroline)-iron(II) complex,[11] it is very likely that this reaction proceeds via an outer-sphere mechanism.[12] Cerium(IV) oxidation of substituted iron phenanthroline complexes was shown to proceed via an outer-sphere mechanism by Dulz and Sutin,[13] obeying the Marcus equation:[14] $\Delta G^{\ddagger}_{12} = 0.5\Delta G^{\ddagger}_{11} + 0.5\Delta G^{\ddagger}_{22} + 0.5\Delta G^{\circ}_{12}$ (for symbols see ref 14). The rate constant (4×10^3 $M^{-1}\,s^{-1}$) and equilibrium constant (~400) values for $Fe(GMI)_3^{2+}$ fit well the correlation presented by Dulz and Sutin.[13] The dependence of the equilibrium constants on the acid concentration is also shown in Table I. K_{eq} increases by a factor of approximately 2 in going from 4.0 to 6.0 M H_2SO_4 at 25.0 °C. This increase is due to an increased thermodynamic stability of the iron(III) form with increased acidity, as shown by the pronounced decrease of the formal electrode potentials of the complex couple. This decrease is 3 times larger than that observed for the Ce(IV)/Ce(III) couple under the same experimental conditions. Within the experimental errors, the formal electrode potential decreases linearly with the Hammett acidity (H_0)[15] in the 4.0–6.0 M H_2SO_4 range. Such type of correlation had been also observed for the 1,10-phenanthroline and 2,2′-bipyridine complexes of iron[16] and for the aliphatic diimine complex tris(biacetyl bis(methylimine))iron.[17] Acidity exerts a controlling influence on the relationship between the electron affinity of the metal ion and that of the ligand.[18] As the acid concentration is lowered, the formal electrode potential of the $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$ couple increases, as well as the rate of intramolecular oxidation of the ligand by the metal ion.

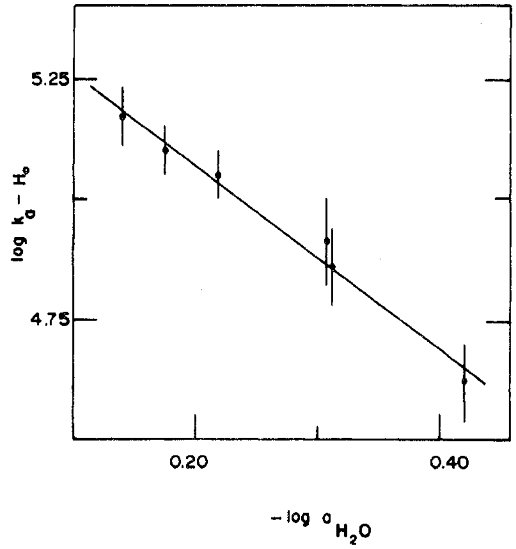

Figure 2. Plot of log $k_a - H_0$ (Hammett acidity function) vs. −log a_{H_2O} for the disproportionation reaction of $Fe(GMI)_3^{3+}$ at 25 °C.

(b) Rate and Mechanism of the Disproportionation Reaction as a Function of Hammett Acidity and Water Activity. The rate of the disproportionation reaction, k_a (eq 4), is inversely proportional to the acid concentration (see Table I). In going from 4 to 7 M H_2SO_4, k_a decreases by a factor of 100. Figure 2 shows a plot of log $k_a - H_0$ vs. log a_{H_2O},[19] where H_0 is the

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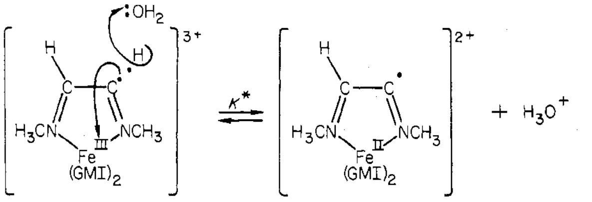
Hammett acidity function[15] ($-H_0$ is essentially equal to log $a_{H_3O^+}$). This plot is linear within the experimental error and the slope is 1.9 ± 0.4, indicating that

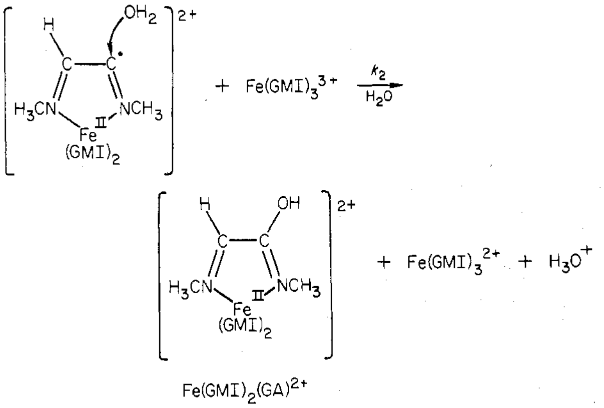
$$k_a = k a_{H_2O}^2 / a_{H_3O^+} \quad (7)$$

This experimental rate law clearly indicates that the reaction is retarded with increased acid activity and decreased water activity.

The detailed mechanism[3] proposed for this reaction, which accounts for the dominant second-order dependence of the rate as a function of the concentration of $Fe(GMI)_3^{3+}$, is shown in eq 8–10.



(8)



(9)

$$\mathrm{Fe(GMI)_2(GA)^{2+} + Fe(GMI)_3^{3+} \xrightarrow{k_3} Fe(GMI)_2(GA)^{3+} + Fe(GMI)_3^{2+}} \quad (10)$$

Step 8 represents the intramolecular reduction of the iron(III) complex assisted by solvent water, yielding an iron(II)–ligand radical complex and H_3O^+ reversibly. This complex radical undergoes oxidation by another molecule of the iron(III) complex (step 9) in a reaction which is also assisted by nucleophilic attack of solvent water. Solvation studies of this complex and several other complexes of iron with aliphatic, mixed (aliphatic–aromatic), and aromatic diimine ligands in sulfuric acid solutions from 4 to 10 M and in water reveal that these complexes are tightly solvated and the solvent molecules (H_2O and/or H_3O^+) fill up the pockets between the ligands[20] and suggest that reversible reactions involving the participation of H_2O and H_3O^+ (step 8) can occur.

A sequence of reactions analogous to (8) and (9) can be written for the formation of $Fe(GMI)_2(GH)^{2+}$, the corresponding constants being K^{**} and k_4. Since the couple $Fe(GMI)_2(GH)^{3+}/Fe(GMI)_2(GH)^{2+}$ has identical[21] formal electrode potential to that of the couple $Fe(GMI)_3^{3+}/Fe(GMI)_3^{2+}$, a reaction analogous to (10), in which the difference in electrode potentials of the complex couples is 0.3 V, is not important at the initial stages of the reaction. From this sequence of reactions one obtains the rate law

$$-\frac{d[\mathrm{Fe(GMI)_3^{3+}}]}{dt} = (3k_2K^* + 2k_4K^{**})\frac{[\mathrm{H_2O}]^2}{[\mathrm{H_3O^+}]}[\mathrm{Fe(GMI)_3^{3+}}]^2 \quad (11)$$

which reproduces the dominant term of the observed experimental law (eq 7) with respect to the water and acid activity dependence.

(c) Activation Parameters of the Disproportionation Reaction and the Mechanism of the Reaction. A plot of log k_a from the data in Table I (plus the rough datum at 30.0 °C, log k_a = 3.5 ± 0.15) vs. $1/T$ is linear within the experimental error. One should point out that in this range of temperature, there are variations in H_0 and in log a_{H_2O}. Considering the errors in H_0[22] and log a_{H_2O},[22] the term 2 log $a_{H_2O} + H_0$ has an intrinsic error of 2%. In the studied temperature range the term 2 log $a_{H_2O} + H_0$ remains constant within 2.5%. Therefore, the rate dependence of temperature does not appear to be masked by variations of acid and water activity. The activation parameters obtained for this reaction are $\Delta H^{\ddagger} = 10.5 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -(8 \pm 2)$ eu, at 4.0 M H_2SO_4.

In 1961, Bunnett[23] reviewed ca. 30 organic reactions catalyzed by acid and found that linear plots of log $k + H_0$ vs. log a_{H_2O} are obtained. The slope of this plot, w, was found experimentally to correlate with the entropy of activation of the reactions. The slope, w, corresponds to the differences between the average degree of hydration of the transition state and that of the substrate and incorporates differences in the average degree of hydration of the protonated and nonprotonated forms of the indicator used to determine H_0. According to Bunnett,[23] all water molecules attached to the substrate or to the transition state with enough energy to affect the reaction rate are considered hydration molecules. Bunnett[23] has shown that for a participation of water such that $w = 1$, which corresponds to the incorporation of a water molecule into the transition state, the reaction exhibits $\Delta S^{\ddagger} = -(4.1 \pm 0.7)$ eu.

In the mechanism of disproportionation of $Fe(GMI)_3^{3+}$ (see eq 8–10), where the assistance of two water molecules is postulated, one obtains a slope of the plot log $k_{obsd} - H_0$ (this reaction is retarded by acid) vs. log a_{H_2O}, which can be associated with the slope w of Bunnett's correlation, equal to 2 and $\Delta S^{\ddagger} = -(8 \pm 2)$ eu. Thus, with the assumption of Bunnett's correlation, the activation entropy and the "w" = 2 presently obtained corroborate the proposed reaction mechanism.

Conclusion

The cerium(IV) oxidation of the aliphatic diimine complex tris(glyoxal bis(methylimine))iron(II), which produces stable ligand-oxidized products, has a remarkable rate dependence on acid concentration, investigated in this work. The first step of this complex reaction is the formation of the iron(III) complex, in an equilibrium reaction, which is also strongly dependent on the acid concentration of the medium. The higher the acid concentration, the larger the equilibrium constant and the slower the overall rate of oxidation. This trend corresponds to that of increased thermodynamic and kinetic stability of the iron(III) form with increased acid concentration and exemplifies well the role of acid concentration in determining the relative electron affinity of the central metal ion and that of the ligand. The proposed reaction mechanism[3] involves the reduction of the iron(III) complex by the coordinated ligand, in an equilibrium reaction which is assisted by a nucleophilic attack of water and is retarded by acid, followed by the oxidation of the ligand-oxidized

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iron(II) complex radical by another iron(III) ion molecule in a step assisted by a nucleophilic attack by water. The rate law proposed by this mechanism generates an acid and water activity dependence of the form $a_{H_2O}^2/a_{H_3O^+}$ which was experimentally confirmed.

The temperature dependence of the reaction rate gives the parameters $\Delta H^{\ddagger} = 10.5 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -(8 \pm 2)$ eu obtained by maintaining $a_{H_2O}^2/a_{H_3O^+}$ essentially constant. The participation of two water molecules and an activation entropy of −8 eu are found in several acid-catalyzed organic reactions reviewed by Bunnett.[23] The kinetic data presented in this paper corroborate the mechanism[3] proposed for this complex reaction and point to an interesting correlation between water participation and entropy of activation common to acid-catalyzed organic reactions, which can be explored further.

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Kinetics and Mechanism of the Formation, Acid-Catalyzed Decomposition, and Intramolecular Redox Reaction of Oxygen-Bonded (Sulfito)pentaamminecobalt(III) Ions in Aqueous Solution[1]

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Dissolved sulfur dioxide reacts almost instantaneously with aqueous $Co(NH_3)_5OH^{2+}$ ion to form the oxygen-bonded sulfito complex ion $Co(NH_3)_5OSO_2^+$. This unstable product rapidly loses SO_2 when acidified, restoring the aquopentaammine species. However, at higher pH values, a relatively slow intramolecular redox decomposition can be observed, which produces $Co(aq)^{2+}$ and SO_4^{2-} in a 2:1 ratio. This is a stepwise process, probably involving the SO_3^- radical ion. The kinetics of the very rapid SO_2-uptake reaction was studied within the ranges $3.7 < pH < 7.7$, $10\ °C < t < 34\ °C$, and 0.01 M < [total sulfite] < 0.06 M. The formation of the complex ion $Co(NH_3)_5OSO_2^+$ is a second-order process for which $k = (2.6 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$ at 10 °C, $\Delta H^{\ddagger} = 9.8 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 14.0 \pm 0.4$ cal deg^{-1} mol^{-1}. The rather slow redox reaction was studied over the ranges $3.4 < pH < 6.7$, $15\ °C < t < 35\ °C$, and 0.02 M < [total sulfite] < 0.10 M. The rate-determining step appears to be an inner-sphere one-electron transfer between the Co(III) center and the ligand sulfite, with a rate constant (extrapolated to 10 °C) of $k = (1.3 \pm 0.3) \times 10^{-3}\ s^{-1}$, $\Delta H^{\ddagger} = 26.9 \pm 1.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 23.1 \pm 4.2$ cal deg^{-1} mol^{-1}. The rate of the moderately rapid SO_2-elimination process, studied in absence of excess sulfite, is directly proportional to $[H^+]$ within the range $3.3 < pH < 4.6$ and has a rate constant at 10 °C of $(2.2 \pm 0.4) \times 10^6\ M^{-1}\ s^{-1}$.

Introduction

Significant contributions have been made in recent years toward the understanding of the formation reactions and reactivity properties of S-bonded sulfito complex ions. Salts of $Co(NH_3)_5SO_3^+$ can only be prepared and purified in solutions containing free ammonia,[3] since this complex reacts with water (especially in acidic medium) to form *trans*-$Co(NH_3)_4(OH_2)(SO_3)^+$. The latter reaction has led to impurities in earlier reported preparations of the (sulfito)pentaamminecobalt(III) complex.[4-6] The extraordinarily strong trans-labilizing influence of the S-bonded sulfito ligand in octahedral Co(III) species has been studied in several laboratories. The studies have included complexes containing ammonia,[7-11] ethylenediamine,[12-16] cyanide,[17,18] and dimethylglyoximate[19-21] as the N-bonded ligands. It has also been reported[8,9] that the tetraammine(sulfito)cobalt(III) complexes undergo redox decomposition to Co^{2+} and the free radical HSO_3 in acidic medium, at rates of approximately $10^{-4}\ s^{-1}$ at 25 °C. More recently the preparation of some S-bonded sulfur dioxide complexes has been described.[22,23]

On the contrary, very little has been reported on the formation and reactivity of O-bonded sulfito complexes. Stranks

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