

Kinetics and Equilibrium of Complexation of Iron(III) Ions by Methylaquorhodoxime¹

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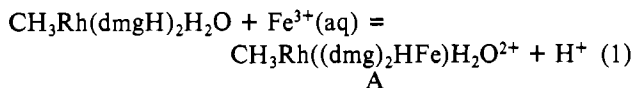
The species referred to in the title react reversibly to form $[\text{CH}_3\text{Rh}((\text{dmg})_2\text{HFe})\text{H}_2\text{O}]^{2+}$ (A) in which one O-H...O unit has been replaced by O-Fe-O according to the equilibrium $\text{CH}_3\text{Rh}((\text{dmgH})_2\text{H}_2\text{O}) + \text{Fe}^{3+} \rightleftharpoons \text{A} + \text{H}^+$. The equilibrium constant is 68.8 ± 4.0 (in water at 25.0 °C), with due allowance for the protonation equilibrium $\text{CH}_3\text{Rh}((\text{dmgH})_2\text{H}_2\text{O}) + \text{H}^+ \rightleftharpoons \text{CH}_3\text{Rh}((\text{dmg})_2\text{H}_3)\text{H}_2\text{O}^+$ ($K = 5.66 \text{ M}^{-1}$). The rate law for the forward reaction is $d[\text{A}]/dt = (k_{1f} + k_{2f}/[\text{H}^+])[\text{CH}_3\text{Rh}((\text{dmgH})_2\text{H}_2\text{O})][\text{Fe}^{3+}]$ with $k_{1f} = 2.08 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2f} = 0.620 \pm 0.010 \text{ s}^{-1}$. The reaction proceeds by parallel paths, in which it is proposed that the mechanism consists of "neutralization" of the hydrogen-bonded proton of O-H...O by $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$, as a result of which iron(III) is substituted in its place and an O-Fe-O unit is incorporated into the rhodoxime.

Introduction

An increasing number of examples are being found wherein one metal chelate complex can incorporate another Lewis acid, sometimes a metal ion. Many of these adducts are formed when the complex is of the bis(salicylaldehyde) type.²⁻⁷ A similar phenomenon has been noted for a number of dimethylglyoxime complexes, the general process being one in which the bridging hydrogen of the O-H...O group linking two ligands is replaced. Simple examples include complexes containing one or two O-BF₂-O units such as the compounds⁸⁻¹⁰ $\text{RCo}((\text{dmgBF}_2)_2\text{L})$ and $\text{ClCo}((\text{dmg})_2\text{HBF}_2)\text{PBu}_3$ as well as the cobaloxime adducts^{11,12} with iron(III) ions derived from organometallic as well as inorganic complexes such as $\text{CH}_3\text{Co}((\text{dmg})_2\text{HFe})\text{H}_2\text{O}^{2+}$ and $(\text{H}_2\text{O})_2\text{Co}((\text{dmg})_2\text{HFe})^{3+}$.

More complex examples of such interactions are the adducts formed from $\text{K}_3[\text{Co}(\text{dmg})_3]$, wherein boron trifluoride¹³ and selected metal complexes¹⁴ are bound to oxime oxygens. In addition, a most intriguing product is formed upon addition of silver nitrate to $\text{Ni}(\delta\text{-cqdH})_2$ (where $\delta\text{-cqdH}^-$ is the monoanion of δ -camphorquinone dioxime).^{15,16} This product is a hexanuclear metal cluster $[\text{Ni}(\delta\text{-cqd})_2\text{HAg}]_3$, in which three individual $[\text{Ni}(\delta\text{-cqd})_2\text{H}]^-$ units act as multidentate ligands coordinating a linear chain of three silver ions such that the central silver ion is coordinated to six oxime oxygens.

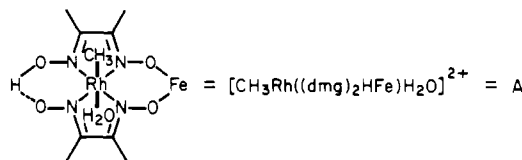
We have now extended our earlier studies^{11,12} of cobaloximes to the rhodium analogue, which reversibly forms a 1:1 adduct with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (eq 1, 2). The product is inferred to contain



$$K_1 = \frac{[\text{CH}_3\text{Rh}((\text{dmg})_2\text{HFe})\text{H}_2\text{O}^{2+}][\text{H}^+]}{[\text{CH}_3\text{Rh}((\text{dmgH})_2\text{H}_2\text{O})][\text{Fe}^{3+}]} \quad (2)$$

a pseudomacrocyclic unit in which one of the O-H...O groups has been converted to a new pseudomacrocyclic containing one

O-H...O and one O-Fe-O group:

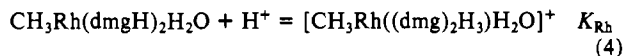
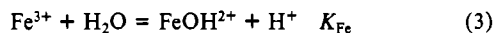


Our studies consist of a study of the equilibrium, kinetics, and mechanism of this transformation in water at 25.0 °C in solutions containing perchloric acid and lithium perchlorate to control $[\text{H}^+]$ in the desired range at a constant ionic strength of 1.00 M.

Experimental Section

Materials. Methylaquorhodoxime¹⁷ was prepared by reduction of $\text{Cl}_2\text{Rh}((\text{dmg})_2\text{H}_3)^{17b}$ in water-methanol (1:1) by sodium borohydride in the presence of sodium hydroxide and methyl iodide. The product was purified by passage through a Bio-Gel P-4 gel filtration column, from which it is readily eluted by water and obtained as a yellow crystalline solid by evaporation. Alternatively, methyl(pyridine)rhodoxime can be readily precipitated from the original preparation and converted in aqueous methanol to the aquo derivative, which crystallizes in pure form upon addition of water and perchloric acid and evaporation of methanol. Methylaquorhodoxime is stable toward acids, heat, and light both as a solid and in solutions. The UV-visible spectrum in 0.1 M perchloric acid shows maxima at 400 nm ($\epsilon = 4.65 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 329 (6.30×10^3), 262 (7.69×10^3), and 225 (1.19×10^4). The ¹H NMR spectra were identical in methanol-*d*₄, alkaline D₂O, and acidic (HClO₄)D₂O: doublet δ 0.65 (3 H, CH₃-Rh), $J_{\text{Rh-H}} = 2.6 \text{ Hz}$; singlet δ 2.3 (12 H, CH₃-dmgH). Other reagents were prepared and analyzed as described previously.^{12,18}

Equilibrium Data. The equilibrium constant was evaluated from spectrophotometric measurements using a Cary Model 219 spectrophotometer having a cell compartment thermostated at 25.0 °C. Most measurements were made at λ 500 nm, where the 1:1 adduct absorbs strongly ($\epsilon = 3.59 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) compared to iron(III) ions and methylaquorhodoxime (ϵ 11.5 $\text{M}^{-1} \text{ cm}^{-1}$). Analysis of the data required provision be made for two additional equilibria:



where $K_{\text{Fe}} = 1.65 \times 10^{-3} \text{ M}$ ($\mu = 1.0 \text{ M}$, $T = 25.0 \text{ °C}$).¹⁹ The value of K_{Rh} was unknown, although one might take as a provisional value that for methylaquocobaloxime, $K_{\text{Co}} = 3.2 \text{ M}^{-1}$.²⁰ Thus K_{Rh} was treated as an unknown parameter in this work.

Kinetics Data. The measurements were also made spectrophotometrically by monitoring the absorbance increase at 500 nm that occurs upon mixing prethermostated solutions of the reactants. The reaction was studied under pseudo-first-order conditions in which the half-times varied from 6.0 to 62 s, permitting the use of conventional techniques.

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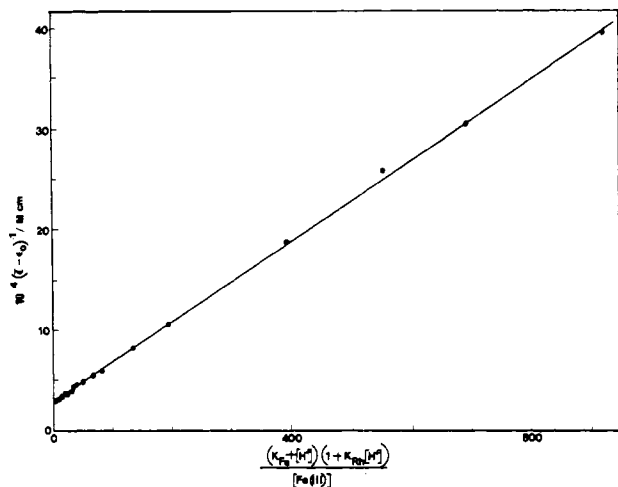


Figure 1. Evaluation of the equilibrium constant at 25 °C for the reaction of methylaquorhodoxime and Fe^{3+} (eq 1) plotted as suggested by eq 6 with $K_{\text{Rh}} = 5.66 \text{ M}^{-1}$. The line drawn through the points corresponds to a least-squares fit of all the data.

The rate constants were evaluated from the slopes of the usual plots of $\log(D_\infty - D_t)$ vs. time ($D = \text{absorbance}$).

Results

Equilibrium Constants K_1 and K_{Rh} . The equilibrium absorbance, expressed per 1-cm optical path and symbolized as D_∞ , provides an apparent molar absorptivity, $\bar{\epsilon} = D_\infty/[\text{Rh}]_{\text{tot}}$. It is related to the molar absorptivities of the parent complex, ϵ_0 (known, $11.5 \text{ M}^{-1} \text{ cm}^{-1}$), and of the product, ϵ_1 (unknown), by the equation

$$\bar{\epsilon} = \frac{\epsilon_0 P + \epsilon_1 K_1 [\text{Fe(III)}]_f}{P + K_1 [\text{Fe(III)}]_f} \quad (5)$$

where $[\text{Fe(III)}]_f = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}]$ and is very nearly²¹ equal to $[\text{Fe(III)}]_{\text{tot}}$, and the protonation parameter P , based on eq 3 and 4, is $(K_{\text{Fe}} + [\text{H}^+])(1 + K_{\text{Rh}}[\text{H}^+])$. Rearrangement affords eq 6, which contains three unknowns, ϵ_1 , K_1 , and K_{Rh} ,

$$\bar{\epsilon} - \epsilon_0 = \frac{(\epsilon_1 - \epsilon_0)K_1 [\text{Fe(III)}]_f}{P + K_1 [\text{Fe(III)}]_f} \quad (6)$$

the latter contained in P . A nonlinear least-squares computer program was used to fit the data to eq 6 on the basis of provisional values of K_1 and K_{Rh} , which were then used to reevaluate P and $[\text{Fe(III)}]_f$. Convergence was obtained in two iterations, giving the values $\epsilon_1 = (3.59 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm, $K_1 = 68.8 \pm 4.0$, and $K_{\text{Rh}} = 5.66 \pm 0.43 \text{ M}^{-1}$. These parameters fit the experimental values of $\bar{\epsilon}$ to within an average deviation of 2.2% and a maximum deviation of 5.3%. The fit of the data is shown by the plot in Figure 1, which depicts $(\epsilon_{\text{obsd}} - \epsilon_0)^{-1}$ vs. $P/[\text{Fe(III)}]_f$. The data fit this relationship over the entire concentration range without any systematic deviations, substantiating that the principal equilibrium conforms to the stoichiometry given by eq 1. The spectrum of the adduct A is shown in comparison with those of the species from which it forms in Figure 2.

Kinetics. The reaction does not go to completion even when an excess of one reactant is used; for that reason k_{obsd} refers to the rate of approach to equilibrium and is thus a sum of apparent forward and reverse rate constants. The situation is further complicated by the protonation equilibria of eq 3 and 4. At constant $[\text{H}^+]$, however, k_{obsd} is given by

$$k_{\text{obsd}} = k_f' [\text{Fe(III)}]_{f,\text{av}} + k_r' \quad (7)$$

in which the apparent rate constants k_f' and k_r' are dependent

(21) Because of the considerable excess of iron(III) present, $[\text{Fe(III)}]_f$ was nearly equal to the total. An iterative method based on provisional values of K_1 and K_{Rh} was used to allow for this effect.

Table I. Summary of Kinetic Data

concn range, M		no. of runs	Y^a/s^{-1}
$[\text{H}^+]$	$10^3 [\text{Fe(III)}]_{f,\text{av}}$		
0.015	0.108–2.92	5	44.8 ± 2.7
0.020	0.083–4.41	6	31.7 ± 2.4
0.025	1.68	1	31.0
0.033	5.96	1	18.8
0.050	0.278–6.91	5	14.1 ± 0.5
0.067	1.97	1	12.7
0.100	0.981–8.91	7	8.72 ± 0.40
0.200	9.97	1	5.42
0.500	4.97–44.94	5	3.32 ± 0.10
0.900	5.99–15.98	5	2.73 ± 0.11

^a The quantity Y is defined by eq 9; the uncertainty shown is the standard deviation of individual values from the mean. Experimental conditions: 25.0 °C; 1.00 M ionic strength, maintained by lithium perchlorate.

Table II. Rate Constants for Rhodoxime and Cobaloxime Reactions^a

rate or equil const	$\text{CH}_3\text{Rh}(\text{dmgH})_2\text{H}_2\text{O}^b$	$\text{CH}_3\text{Co}(\text{dmgH})_2\text{H}_2\text{O}^c$
$k_{1f}/\text{M}^{-1} \text{ s}^{-1}$	2.08 ± 0.06	1.80 ± 0.04
k_{2f}/s^{-1}	0.620 ± 0.010	0.702 ± 0.007
$10^2 k_{1r}/\text{M}^{-1} \text{ s}^{-1} d$	3.02 ± 0.27	11.8 ± 0.8
$10^2 k_{2r}/\text{s}^{-1} e$	0.90 ± 0.07	4.6 ± 0.3
K_1	68.8 ± 4.0	15.3 ± 0.8
$K_{\text{H}}/\text{M}^{-1} f$	5.66 ± 0.43	3.2 ± 0.2
$k_1/\text{M}^{-1} \text{ s}^{-1} g$	2.2×10^2	3.4×10^2
$k_2/\text{M}^{-1} \text{ s}^{-1} g$	3.8×10^2	4.3×10^2

^a At 25.0 °C, ionic strength is 1.00 M in water. ^b This work. ^c References 11 and 12. ^d Calculated as k_{1f}/K_1 . ^e Calculated as k_{2f}/K_1 . ^f For the protonation equilibrium of eq 4, designated K_{Rh} in the text. ^g Calculated bimolecular rate constants for the elementary reactions of eq 10 and 11: $k_1 = k_{1f}/K_{\text{Fe}}K_{\text{Rh}}$, $k_2 = k_{2f}/K_{\text{Fe}}$.

on $[\text{H}^+]$ because of the protonation equilibria as well as the direct involvement of hydrogen ions in mechanistic steps. Figure 3 depicts the variation of k_{obsd} with $[\text{Fe(III)}]$; at each $[\text{H}^+]$ it is linear as expected from eq 7.

Provided the rhodoxime reaction follows the same rate law as the cobaloxime, in which there are two kinetic terms for the rate of adduct formation differing by one power of $[\text{H}^+]$ (eq 8), the expression²² for k_{obsd} can be converted to a simple function of $[\text{H}^+]$ (eq 9).

$$\frac{d[\text{A}]}{dt} = \left(k_{1f} + \frac{k_{2f}}{[\text{H}^+]} \right) [\text{Fe}^{3+}] [\text{CH}_3\text{Rh}(\text{dmgH})_2\text{H}_2\text{O}] - (k_{1r}[\text{H}^+] + k_{2r})[\text{A}] \quad (8)$$

$$Y = \frac{k_{\text{obsd}} P K_1}{[\text{H}^+] P + K_1 [\text{Fe(III)}]_{f,\text{av}}} = k_{1f} + \frac{k_{2f}}{[\text{H}^+]} \quad (9)$$

The kinetic data depicted in Figure 3 are summarized in Table I. Figure 4 depicts the plot of the quantity Y of eq 9 vs. $1/[\text{H}^+]$, which defines a straight line. Nonlinear least-squares analysis of values of k_{obsd} as a simultaneous function of the two concentration variables was used to provide the final values for the rate parameters, which are summarized in Table II.

Discussion

As is readily apparent from Table II, the equilibrium and kinetic parameters describing the reaction of methylaquo-

(22) The system is exactly analogous to that treated in ref 12, and the derivations are not repeated here. Equation 10 of that reference is incorrect and should read $k_r' = k_r/P/K$; the subsequent equations and data analysis are correct.

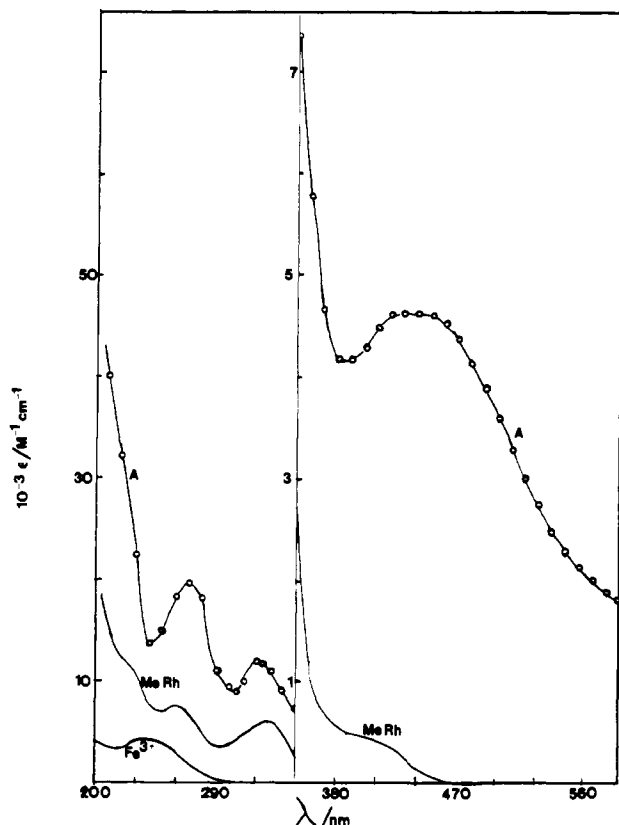


Figure 2. UV-visible absorption spectra for Fe^{3+} , $\text{CH}_3\text{Rh}(\text{dmgH})_2\text{H}_2\text{O}$, and the adduct A. The last is based on the measured spectrum of an equilibrium mixture with due allowance for the position of equilibrium, with $K_1 = 68.8$.

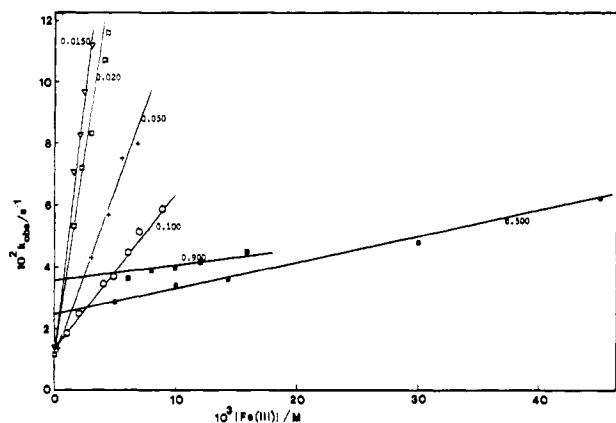


Figure 3. Plot of k_{obs} at 25 °C against the average concentration of iron(III) in runs at different $[\text{H}^+]$, according to eq 7. The lines drawn are the least-squares values based on the final fit of all the data.

rhodoxime are very similar to those of the previously studied^{11,12} cobaloxime. (That was by no means a foregone conclusion as instances are known where they react *very* differently; for example, the former is virtually unreactive toward Hg^{2+} under conditions where the cobaloxime reacts readily to cleave the cobalt-carbon bond, forming HgCH_3^+ .) Considering the strong similarity of the two cases, and our earlier extensive discussion of the chemistry, elaboration of our results

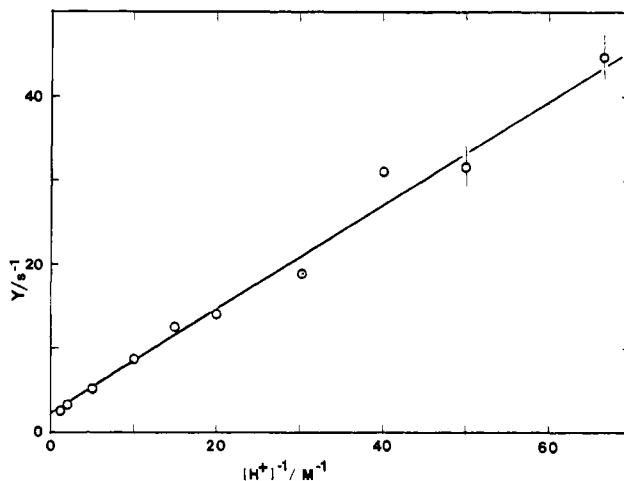
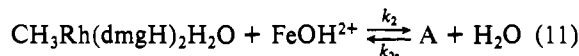
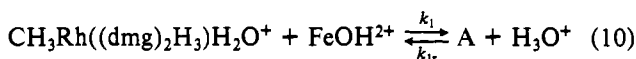


Figure 4. Analysis of the kinetic data at 25 °C by the linear plot of Y vs. $1/[\text{H}^+]$ according to eq 9.

is not called for. There are several ways, as noted earlier,^{11,12} that the proton ionization steps might be formulated. These mechanisms differ by what is termed a "proton ambiguity", in that a different pair of species is involved in the elementary rate-limiting bimolecular reaction. We do note that these results substantiate our earlier mechanistic assignment,¹² made in an effort to resolve this proton ambiguity, in which the reactivity is controlled by substitution on iron(III) together with O-H...O activation. Indeed, it is possible to regard this as a neutralization reaction between H^+ (of O-H...O) and OH^- (of FeOH^{2+}); that such reactions would occur much more slowly than diffusion control is consistent with results²³ in which cobaloximes react with OH^- in reactions having $k = 10^5$ – $10^6 \text{ M}^{-1} \text{ s}^{-1}$. As such the elementary reactions are believed to be



for which calculated values of the bimolecular rate constants k_1 and k_2 for adduct formation are also given in Table II.

The adduct has intense visible absorption bands, suggesting a considerable reduction of symmetry may accompany adduct formation. Incorporation of the O-Fe-O unit would tend to greatly compress the O-H...O group on the other side of the ring. For this reason not only is there no tendency to incorporate a second iron even at forcing concentrations but the closely related²⁴ complex $\text{CH}_3\text{Co}(\text{dpmH})\text{H}_2\text{O}^+$, which has a macrocyclic ligand much less amenable to distortion, fails¹² to form a detectable concentration of an analogous adduct.

Acknowledgments. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021 under Contract W-7405-ENG-82. We gratefully acknowledge helpful discussion with Dr. Andreja Bakač.

Registry No. $\text{CH}_3\text{Rh}(\text{dmgH})_2\text{H}_2\text{O}$, 26026-41-5; Fe^{3+} , 20074-52-6.

(23) Birk, J. P.; Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* 1968, 90, 6959.

(24) The ligand dpmH^- is related to $(\text{dmgH})_2^{2-}$ by the replacement of one O-H...O ligand by $\text{CH}_2\text{CH}_2\text{CH}_2$; it is also known as (DO)(DOH) pn^- .