Inorganica Chimica Acta, 30 (1978) L329–L330

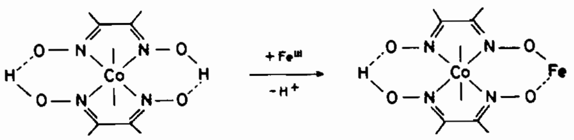
Complexation of Iron(III) at Oxime Oxygens in Cobaloximes

ANDREJA BAKAČ† and JAMES H. ESPENSON*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.

Received August 11, 1978

The basicity of the oxime oxygens in dimethylglyoxime complexes [1–3] as well as in similar complexes [4–9] has been recognized in several instances, but we are not aware of any studies relating to equilibrium constants and reaction rates. Since the characterization of these adducts is important in its own right as well as of considerable utility in the study of organocobalt(IV) complexes, a study was undertaken of adduct formation between iron(III) and bis(dimethylglyoximato)cobalt(III) complexes. These reactions result in the transformation of the internally hydrogen-bonded $(dmgH)_2$ pseudo-macrocycle to a form in which a hydrogen-bonded proton has been replaced by Fe(III):



Results

The visible–UV absorption spectrum of solutions of methyl(aquo)cobaloxime ("cobaloxime" is the trivial name given [10] to bis(dimethylglyoximato-cobalt complexes) is sharply altered upon addition of iron(III) perchlorate. The reaction is not unique to the alkyl-cobalt system, however, and similar adduct formation is observed between Fe^{3+} and the inorganic complex diaquocobaloxime(III) ion, $(H_2O)_2Co(dmgH)_2^+$. Both reactions occur reversibly and the extent of adduct formation depends upon $[H^+]$ as well as $[Fe^{3+}]$ in accord with the following equations for the principal equilibrium in each system:

$$\underset{(\mathbf{1a})}{CH_3Co(dmgH)_2H_2O} + Fe^{3+}_{aq} = \underset{(\mathbf{1b})}{[CH_3Co(dmg_2HFe)H_2O]^{2+}} + H^+ \quad (1)$$

$$\underset{(\mathbf{2a})}{(H_2O)_2Co(dmgH)_2^+} + Fe^{3+}_{aq} = \underset{(\mathbf{2b})}{[(H_2O)_2Co(dmg_2HFe)]^{3+}} + H^+ \quad (2)$$

The equilibrium constants were determined spectrophotometrically at 525 nm, at 25 °C and constant ionic strength 1.00 mol dm^{-3} with variable $[H^+]$, 0.02–0.90 (1) or 0.02–0.10 (2). Proper allowance was made for other protonation equilibria pertinent to this range of $[H^+]$, namely formation of $CH_3Co(dmg_2H_3)H_2O^+$ [11] and $FeOH^{2+}$ [12]. The resulting values of the equilibrium constants and molar absorptivities are: $K_1 = 16.2$, $\epsilon_{1b}^{525} = 1.62 \times 10^3$ $dm^3 mol^{-1} cm^{-1}$; $K_2 = 2.6$, $\epsilon_{2b}^{525} = 1.36 \times 10^3$. Adduct **1b** has absorption maxima at 450 (ϵ $3.0_5 \times 10^3$ sh), 390 ($3.9_3 \times 10^3$), and 240 nm (2.2×10^4 sh) as shown in Figure 1.

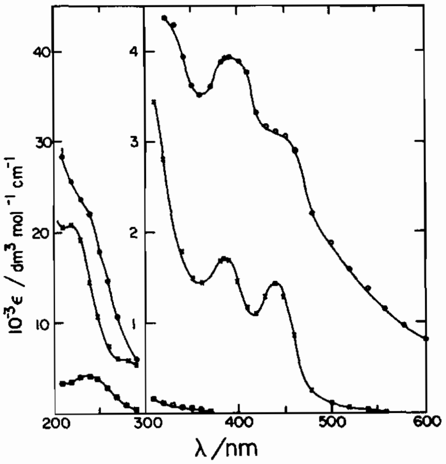


Figure 1. Absorption spectra for $CH_3Co(dmgH)_2H_2O$ (x), Fe^{3+}_{aq} (□), and the adduct $CH_3Co(dmg_2HFe)H_2O^{2+}$ (○).

Kinetics determinations were carried out under the same conditions using the range $0.020 < [H^+] < 0.90$ mol dm^{-3} for both reactions. The data for each correspond to a scheme of opposing first-order reactions.

Analysis of the data for adduct **1b** (again with due allowance other equilibria) results in the rate law given by eq. 3, where Q_{Fe} represents the acid ionization constant of Fe^{3+}_{aq}.

$$\frac{d[\mathbf{1b}]}{dt} = \left(k_1 + \frac{k_2Q_{Fe}}{[H^+]}\right)[\mathbf{1a}]\ [Fe^{3+}] - (k_{-1}[H^+] + k_{-2})\ [\mathbf{1b}] \quad (3)$$

The rate constants were evaluated subject to the restraint $K_1 = k_1/k_{-1} = k_2Q_{Fe}/k_{-2}$; values/$dm^3 mol^{-1} s^{-1}$ are $k_1 = 1.90$ and k_2 (using $Q_{Fe} = 1.65 \times$

---

†On leave from "Ruder Bosković" Institute, Zagreb, Croatia, Yugoslavia.

*To whom correspondence should be addressed.

10^{-3} mol dm^{-3}) = 4.41 × 10^2 (the form in which the rate law is written suggests that the k_2 pathway consists of the bimolecular reaction of $CH_3Co(dmgH)_2H_2O$ and $FeOH^{2+}$, a reasonable interpretation but not a mandatory one). The reverse reaction has k_{-1} = 0.117 dm^{3}mol^{-1}s^{-1} and k_{-2} = 0.045 s^{-1}.

A similar expression was found for adduct **2b**, except that the pathway represented by the terms k_1, k_{-1} is negligible within experimental error. The rate constants for 2b are k_2 = 1.18 × 10^2 dm^{3}mol^{-1}s^{-1}, k_{-2} = 0.075 s^{-1}.

Discussion

Evidence that these observations correspond to oxime oxygen substitution (and not, for example, to axial substitution) can be summarized as (a) the comparable values of the rate constants k_2 for the reactants **1a** and **2a**, whose rate constants for *axial* substitution [13, 14] differ by $>10^5$, (b) the loss of one H^+ upon coordination of Fe^{3+}; and (c) similar adduct formation [3] (and comparable spectral changes) between transition metal ions and $Co(dmg)_3^{3-}$, albeit in a fashion utilizing three oxime oxygens to substitute on an octahedral face.

The reaction pathway corresponding to the rate constants k_2, k_{-2} is common to both cobaloximes. Values of k_2 are comparable for the two adducts (4.4 × 10^2 and 1.2 × 10^2 dm^{3}mol^{-1}s^{-1} for **1a** and **2a**, respectively). The values are lower than those usually found for substitution of other ligands into the inner coordination sphere of iron by reaction with $FeOH^{2+}$, for which typical values are 10^4 – $10^{5.2}$. The lower rate is not surprising considering the structural changes in reaction 4 involving the strong intramolecular hydrogen bond of the cobaloximes. Relatively slow deprotonation of the O–H···O moiety in other $XYCo(dmgH)_2$ complexes has been noted [15].

An alternative preparation [16] of the adduct **1b** is the reduction of $[CH_3Co^{IV}(dmgH)_2H_2O]^+$ by Fe^{2+}, the former prepared from oxidation of **1a** by $Br_{2(aq)}$. In this case a nonequilibrium mixture of **1a** and **1b** is obtained very rapidly, followed by equilibration in reaction 1 at the same rate found here.

Acknowledgment

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

References

1 G. N. Schrauzer, *Chem. Ber.*, *95*, 1438 (1962).
2 D. R. Boston and N. J. Rose, *J. Am. Chem. Soc.*, *90*, 6859 (1968).
3 R. S. Drago and J. H. Elias, *J. Am. Chem. Soc.*, *99*, 6570 (1977).
4 E. Sinn and G. M. Harris, *Coord. Chem. Rev.*, *4*, 391 (1969).
5 M. D. Hobday and T. D. Smith, *J. Chem. Soc. A*, 1453 (1971).
6 M. D. Hobday and T. D. Smith, *J. Chem. Soc. Dalton*, 2287 (1972).
7 E. Sinn and W. T. Robinson, *Chem. Comm.*, 359 (1972).
8 S. Kokot, C. M. Harris, and E. Sinn, *Aust. J. Chem.*, *25*, 45 (1972).
9 G. R. Tauszik, G. Pellizer, and G. Costa, *Inorg. Nucl. Chem. Lett.*, *9*, 717 (1973).
10 G. N. Schrauzer, *Accounts Chem. Res.*, *1*, 97 (1968).
11 A. Adin and J. H. Espenson, *Chem. Comm.*, 653 (1971).
12 R. M. Milburn, *J. Am. Chem. Soc.*, *79*, 537 (1957).
13 D. Dodd and M. D. Johnson, *J. Organomet. Chem.*, *52*, 1 (1973).
14 N. M. Samus' and T. S. Luk' yanets, *Russ. J. Inorg. Chem.*, *17*, 390 (1972).
15 J. P. Birk, P. B. Chock, and J. Halpern, *J. Am. Chem. Soc.*, *90*, 6959 (1968).
16 A. Bakač and J. H. Espenson, unpublished results.