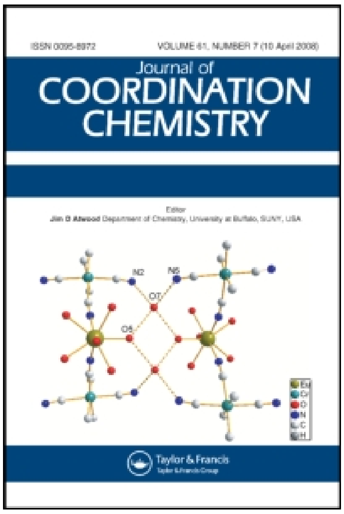

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REACTIONS OF METAL TERPYRIDINE COMPLEXES. I. THE DISPROPORTIONATION OF MONOTERPYRIDINECOBALT(II). ACID AND METAL ION EFFECTS

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The kinetics of the disproportionation of monoterpyridinecobalt(II), viz.,

$$2\,Co(trpy)(H_2O)_3^{2+} \rightleftharpoons Co(trpy)_2^{2+} + Co(H_2O)_6^{2+},$$

are reported. The reaction was studied as a function of added acid and metal ions at 25.0°C and I = 0.10 M (KNO_3). Added HNO_3 catalyzes the disproportionation. In the range studied (0.0010 – 0.0156 M HNO_3), the observed rate constant at first increases linearly with $[H^+]$ but later levels off. A mechanism consistent with the data is presented involving metal-nitrogen bond rupture and a protonation equilibrium of the unbound pyridine nitrogen. Added metal ions (Cd^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{2+}) retard the disproportionation with regard to both rate and extent of reaction. A mechanism involving formation of a metal chelate with a pendant terpyridine moiety (bound to cobalt(II) in a monodentate fashion) is presented to account for these results.

INTRODUCTION

Monoterpyridinecobalt(II) can serve as a template for the formation of mixed-ligand complexes according to the reaction

$$Co(tryp)(H_2O)_3^{2+} + AA \rightleftharpoons Co(tryp)(AA)\text{-}(H_2O)^{2+} + 2H_2O \quad (1)$$

where AA is a bidentate ligand such as 2,2′-bipyridine′ or 8-hydroxyquinoline, or possibly a terdentate ligand such as diethylenetriamine or terpyridine itself.[2] The rates and equilibria of these substitution processes have been measured as a prelude to oxygenation studies on the mixed-ligand species. Ignored in these studies is the possible disproportionation of monoterpyridinecobalt(II), i.e.,

$$2\,Co(trpy)(H_2O)_3^{2+} \rightleftharpoons Co(trpy)_2^{2+} + Co(H_2O)_6^{2+} \quad (2)$$

and the effect it might have on the substitution and oxygenation equilibrium constants.

As part of our research effort on the oxygenation and redox properties of these mixed-ligand systems, we chose to study the disproportionation reaction alone in aqueous media as well as in the presence of hydrogen ion and several metal ions. Those employed in this study were Cd^{2+}, Mn^{2+}, Zn^{2+} and Fe^{2+}.

EXPERIMENTAL SECTION

Materials.

Monoterpyridinecobalt(II) was prepared as the chloride salt $Co(trpy)Cl_2$ by sublimation of one mole of terpyridine per mole of bisterpyridinecobalt(II) chloride at 180° for 2 hours.[3] The terpyridine used in this study was purchased from G. F. Smith, Columbus, Ohio. Stock solutions of HNO_3 and metal ion salts were prepared from materials which were of reagent grade quality. Concentrations were determined by standard acid-base or other volumetric techniques such as those found in Vogel.[4]

Kinetics.

The disproportionation was followed by measuring the appearance of the 440 nm peak of the $Co(trpy)_2^{2+}$ product for all reaction studies except Fe^{2+}. For this system the reaction was followed at

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550 nm, the maximum absorbance wavelength for $Fe(trpy)_2^{2+}$. The procedure used involved dissolution of a small sample of $Co(trpy)Cl_2$ in a 0.10 M KNO_3 solution at pH = 3.0 followed by addition of H^+ or metal ion to the desired concentration level. For all reactions in the presence of metal ions (except Fe^{2+}) the pH was kept at 3.0 (and checked before and after each run). A Cary 15 spectrophotometer was used to measure all absorbance changes. The temperature of the cell compartment was maintained at 25.0°C with a Haake Model FK-2 temperature bath.

RESULTS AND DISCUSSION

Uncatalyzed and Hydrogen Ion Catalyzed Reaction

The rate data for the uncatalyzed (pH 3) disproportionation and the acid catalyzed (0.0010–0.0156 M) disproportionation are shown in Table I. A plot of k_{obs} *vs.* hydrogen ion concentration is shown in Figure 1. As seen from the figure, the plot is linear until about $[H^+]$ = 0.008 M and then begins to level off. The variation of k_{obs} with hydrogen ion was treated according to the mechanism presented by Farina, Hogg and Wilkins[5] for the $Fe(trpy)_2^+$ and $Co(trpy)_2^{2+}$ ions, as shown in Scheme I. Steady-state conditions are assumed for all intermediate species and the subsequent reaction of free terpyridine or the protonated terpyridine with $Co(trpy)(H_2O)_3^{2+}$ is taken as a very fast reaction.[6]

According to Scheme I, the observed first-order rate constant should show a complex dependence

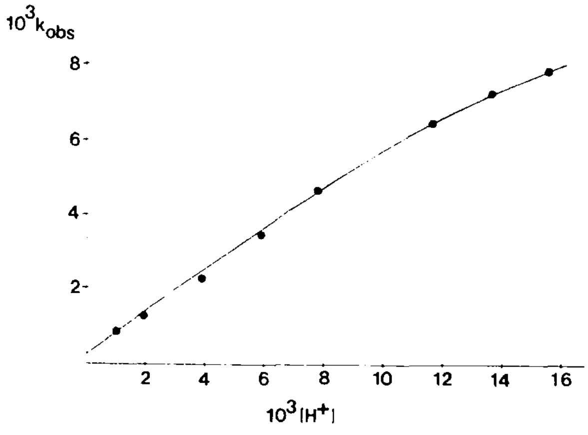


FIGURE 1 Dependence of the observed first-order rate constant on the concentration of added hydrogen ion.

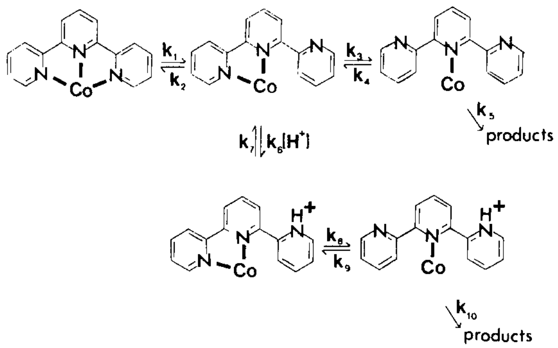
TABLE I

Rate data for acid and metal ion catalyzed disproportionation of monoterpyridinecobalt(II)[a,b]

HNO$_3$		M = Cd^{2+}		M = Mn^{2+}		M = Zn^{2+}	
$10^3 [H^+]$, M	$10^3 k_{obs}$, s^{-1}	$10^4 [Cd^{2+}]$, M	$10^4 k_{obs}$, s^{-1}	$10^4 [Mn^{2+}]$, M	$10^4 k_{obs}$, s^{-1}	$10^4 [Zn^{2+}]$, M	$10^4 k_{obs}$, s^{-1}
1.00 (pH 3)	0.826[c]	0	8.26	0	8.26	0	8.26
1.95	1.25[d]	1.05	8.05	1.94	7.45	0.99	3.76
3.90	2.27	2.21	7.98	3.87	7.40	1.97	3.15
5.86	3.45	4.41	7.76	7.75	7.36	3.97	3.02
7.81	4.64	8.82	7.50	13.8	7.30	7.89	2.41
11.7	6.42	17.6	7.11			10.9	2.68
13.7	7.24					13.8	2.45
15.6	7.83					15.8	1.80
						19.7	1.86

[a] T = 25.0°C, I = 0.1 M (KNO_3), $[Co(trpy)(H_2O)_3]_0^{2+} = 2.2 \times 10^{-4}$ M.
[b] All experiments (except acid catalyzed runs) performed at pH = 3.
[c] Average standard deviation of six runs is ±0.016
[d] Average of two runs for this and all other acid/metal concentrations.

SCHEME I



on hydrogen ion concentration, viz.,

$$k_{obs} \cong \frac{k_a + k_1k_b[H^+]}{1 + k_b[H^+]} \qquad (3)$$

where

$$k_a = k_1k_3k_5/k_2k_4 + k_2k_5 + k_3k_5$$

and

$$k_b = k_6k_8k_{10}/k_2(k_7k_9 + k_7k_{10} + k_8k_{10})$$

At low $[H^+]$, when $k_b[H^+] < 1$, $k_{obs} \cong k_a + k_1k_b[H^+]$. A plot of k_{obs} *vs.* $[H^+]$ is linear in this region with an intercept $\sim 1.8 \times 10^{-4}$ s^{-1} (k_a) and a slope ~ 0.56 (k_1k_b). This shows that the value of k_a is always smaller than $k_1k_b[H^+]$. Thus, $k_{obs} = k_1k_b[H^+]/(1 + k_b[H^+])$ and a plot of k_{obs}^{-1} *vs.* $[H^+]^{-1}$ over the latter $[H^+]$ range is possible. This plot yields a slope = 1.52 ($1/k_1k_b$) and intercept = 30.2 ($1/k_1$). From these, values of $k_1 = 0.331$ s^{-1} and $k_b = 19.9$ $M^{-1}s^{-1}$ are obtained.

These values of k_1 and k_b can now be compared with similar values found for the bis-terpyridine system. The values of k_1 are 0.0331 s^{-1} *vs.* 125 s^{-1} while k_b values are 19.9 $M^{-1}s^{-1}$ *vs.* 0.2 $M^{-1}s^{-1}$ (for mono *vs.* bis systems). The wide differences between these values can be attributed to steric constraints in the bis system. Although the terpyridine chelate opens more readily in the bis system, it is more difficult to protonate due to the presence of the second bound ligand. We are currently studying the dissociation process in mixed-ligand systems to gain a better understanding of the factors involved.

Metal Ion Reactions

Several divalent transition metal ions were tested to study the effect of such species on the disproportionation reaction. The results reported here are those for which reaction (2) occurs to a reasonable extent. These were for Cd^{2+}, Mn^{2+} and Zn^{2+}. The results for these ions are also shown in Table I. All three ions retard the disproportionation reaction with regard to both rate and extent of reaction. This indicates that the formation of metal(II) terpyridine species is competing with the formation of $Co(trpy)_2^{2+}$.

Similar results were noted in the presence of iron(II), nickel(II) and copper(II). In these systems no $Co(trpy)_2^{2+}$ was observed. Instead, the overall reaction proceeded to yield the $M(trpy)_2^{2+}$ species (M = Fe, Ni or Cu). For the Cu^{2+} and Ni^{2+} systems, no measurable spectral changes were observed under the conditions employed ($[Co(trpy)(H_2O)_3^{2+}] = 2.0 \times 10^{-4}$ M, $[M^{2+}] \cong 2.0 \times 10^{-5} - 2.0 \times 10^{-3}$ M). In the Fe^{2+} case, we were able to follow the appearance of $Fe(trpy)_2^{2+}$ at 550 nm ($\epsilon = 11{,}300$ $M^{-1}cm^{-1}$). These runs were performed at $[H^+] = 0.0174 - 0.0191$ M (to prevent hydrolysis). A similar decrease (of k_{obs} with increasing Fe^{2+} concentration in the range 2.2 to 11.1×10^{-5} M Fe^{2+}) is observed as in the other metal ions reported above. This is shown in Figure 2. At higher Fe^{2+} concentrations the observed rate constant increases again; for $Fe^{2+} = 1.75 \times 10^{-3}$ M, $k_{obs} = (3.9 \pm 0.1) \times 10^{-3}$ sec^{-1}. This may be due to a different mechanism becoming operative at these higher concentrations.

The variation of k_{obs} with metal ion concentration for the four metal ions studied can be treated according to the mechanism outlined in Scheme II. Steady-state conditions are again assumed for all intermediate species. The initial product of the reaction in the presence of added metal ions is the monoterpyridinemetal(II) complex which

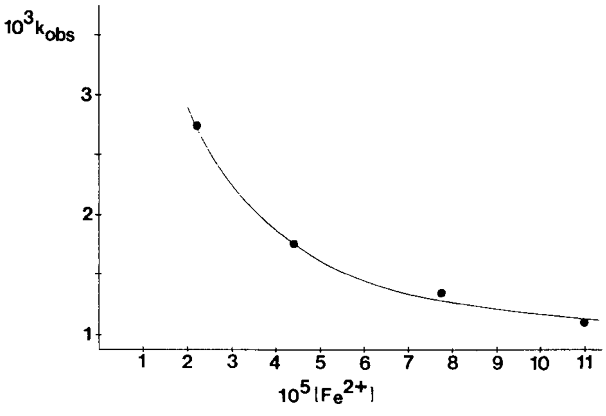
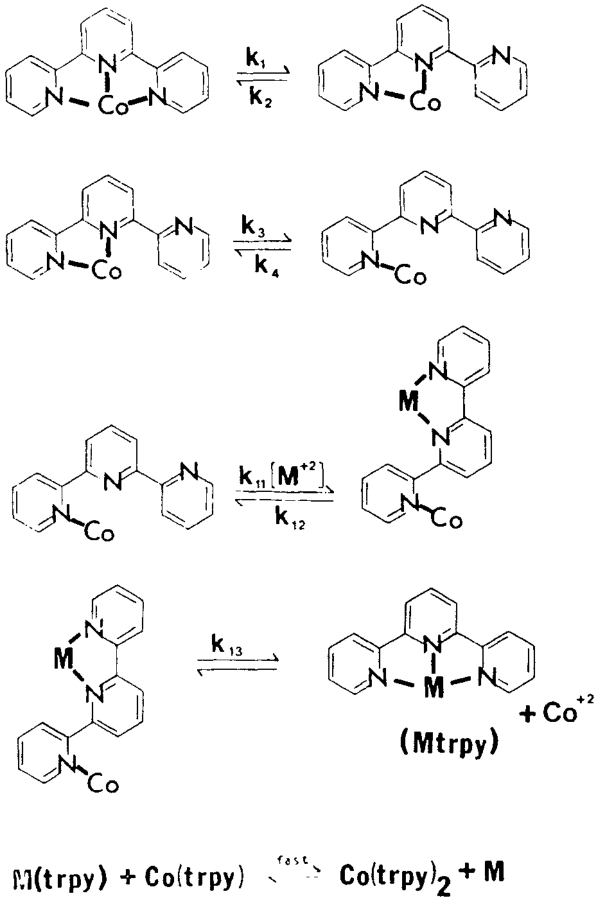


FIGURE 2 Dependence of the observed first-order rate constant on the concentration of added Fe^{2+}.

SCHEME II



subsequently reacts with monoterpyridinecobalt(II) to produce the bisterpyridinecobalt(II) species.

Solution of the rate law for Scheme II yields the following relation between k_{obs} and the concentration of added metal ion:

$$k_{obs} = \frac{k_a + k_1[M^{2+}]}{k_c + k_d[M^{2+}]} \qquad (4)$$

where

$$k_c = \frac{k_2 k_4}{k_3 k_{11}}\left(\frac{k_{12}}{k_{13}} + 1\right)$$

and

$$k_d = \frac{k_2}{k_3} + 1$$

Using values of 1.8 x 10^{-4} s^{-1} and 3.31 x 10^{-2} s^{-1} for k_a and k_1 (as determined above) it is apparent that except for the Fe^{2+} runs, the expression for k_{obs} (Eq. 4) cannot be further simplified. In these cases both k_a and k_1 [M^{2+}] contribute significantly to the rate expression. For the runs performed in the presence of Fe^{2+}, k_1 [Fe^{2+}] $<<$ k_a and Eq. 4 can be rewritten as

$$k_{obs} = \frac{k_a}{k_c + k_d[Fe^{2+}]} \qquad (5)$$

For these runs a plot of k_{obs}^{-1} *vs.* [Fe^{2+}] is linear and yields values of 2.33 x 10^{-2} for k_c and 3.80 x 10^2 for k_d. Attempts to determine the individual rate constants were not successful. Studies with other monoterpyridine metal complexes[3] may be more successful and shed more light on the details of the mechanism. Studies with [M(trpy)]$^{2+}$, M = Fe, Mn and Ni, are contemplated.[7]

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7. Partially supported by a Grant-in-Aid of Research from Sigma Xi, The Scientific Research Society.