and where it is uncomplicated by cis labilization, the trans effects and leaving group trends in d^6 carbonyl complexes of Cr, Mo, and W are remarkably similar to our results on FeN$_4$ systems. This suggests that unifying principles covering organometallic as well as classical complexes might be found if sought. At the present time, there is very little overlap in the types of ligands and solvents used in these two major areas of inorganic chemistry. Complexes of the type considered here may provide a bridge between the chemistry of classical Werner complexes and organometallic compounds.

Acknowledgment. Support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. FeN$_4$(py)$_2$, 24828-75-9; FeN$_4$(MeIm)$_2$, 57804-36-1; FeN$_4$(MeIm)CO, 61395-33-3; FeN$_4$(BzNC)$_2$, 59575-75-6; FeN$_4$(MeIm)(py), 100466-68-0; FeN$_4$(PBu$_3$)(py), 100485-19-6; FeN$_4$(P(OBu)$_3$)(py), 100485-20-9; FeN$_4$(BzNC)(py), 61395-34-4; FeN$_4$(TMIC)(py), 100485-21-0; FeN$_4$(py)CO, 54691-99-5; FeN$_4$(PBu$_3$)(MeIm), 100485-22-1; FeN$_4$(P(OBu)$_3$)(MeIm), 100485-23-2; FeN$_4$(BzNC)(MeIm), 59575-74-5; FeN$_4$(TMIC)(MeIm), 100485-24-3; FeN$_4$(PBu$_3$)$_2$, 100485-25-4; FeN$_4$(P(OBu)$_3$)(PBu$_3$), 100485-26-5; FeN$_4$(BzNC)(PBu$_3$), 100485-27-6; FeN$_4$(TMIC)(PBu$_3$), 100485-28-7; FeN$_4$(PBu$_3$)CO, 100485-29-8; FeN$_4$(P(OBu)$_3$)$_2$, 100485-30-1; FeN$_4$(BzNC)(P(OBu)$_3$), 100485-31-2; FeN$_4$(TMIC)(P(OBu)$_3$), 100485-32-3; FeN$_4$(P(OBu)$_3$)CO, 100485-33-4; FeN$_4$(BzNC)CO, 100485-34-5.

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Reactions of Dioxygen Complexes. Oxidative Dehydrogenation of 2-(Aminomethyl)pyridine through Cobalt Dioxygen Complex Formation

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Received October 14, 1985

The metal complex formation constants and the oxygenation constants of the cobalt(II) complexes of diethylenetriamine (DIEN) and 2-(aminomethyl)pyridine (AMP) have been determined by potentiometric measurements under N$_2$ and O$_2$. In the mixed-ligand systems three cobalt complexes are formed that are capable of combining with dioxygen: the 2:1 AMP complex, the 1:1:1 DIEN–AMP complex, and the 1:1 DIEN complex. The equilibrium constants for the mixed-ligand system have been employed to determine the conditions under which the concentration of the mixed-ligand complex has its maximum value and the conditions that favor the formation of the corresponding μ-peroxo cobalt complex. The kinetics of oxidative dehydrogenation of coordinated AMP through the formation and degradation of the mixed-ligand peroxo complex have been measured spectrophotometrically, and rate constants are reported. The reaction has been found to be second order, first order in the dioxygen complex and first order in the concentration of hydroxide ion. The reaction product in the two-electron oxidation of AMP is the corresponding imine, which under the reaction conditions employed is converted to pyridine-2-carboxaldehyde, determined quantitatively as the (2,4-dinitrophenyl)hydrazone. The proposed reaction mechanism involves deprotonation of the amino group, through the influence of the Co^{3+} center, as a preequilibrium step. This is followed by a concerted process involving homolytic fission of dioxygen, shift of an electron through the metal ion to the coordinated oxygen, and transfer of the α-proton to the coordinated oxygen atom. The two-electron oxidation of each AMP ligand is thus balanced by conversion of half of the dioxygen to water, with regeneration of cobalt(II). The proximity of the dioxygen to the α-CH$_2$ of the ligand is considered an important requirement for this concerted mechanism. The determination of large kinetic deuterium isotope effects (ca. 13–16) for the dehydrogenation rate constants seems to support the proposed mechanism.

Introduction

Polyamine complexes of cobalt(II) form binuclear dioxygen adducts having wide variations in thermodynamic stabilities and cobalt–dioxygen bond strengths.[1-4] With a large number of such complexes now available, it is of interest to examine their effectiveness as oxidants for hydroxylation and oxidative dehydrogenation of organic compounds. An important limiting factor in such studies is the tendency for all oxygen complexes to be converted to stable, inert complexes in which the coordinated ligand is oxidized, or the metal ion is oxidized to its higher valent form, and thus is no longer able to combine with dioxygen. Recently, bipyridyl was employed as a relatively refractory ligand for cobalt(II), resulting in the formation of a dioxygen complex, tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo)dicobalt(III), which is converted to inert dipyridylcobalt(III) complexes very slowly and is not appreciably decomposed during kinetic studies of its reactivity in the oxidation and oxygenation of 2,6-di-*tert*-butylphenol.[5] In a more recent kinetic study of the oxygenation and oxidative dehydrogenation of 2,6-di-*tert*-butylphenol by dioxygen complexes of a series of (polyamine)cobalt(II) complexes, it was found that quantitative determination of rate constants was not feasible for a number of relatively weak dioxygen complexes that undergo considerable decomposition during the course of the measurements.[6]

Because the rates of autoxidation reactions of μ-peroxo-bridged cobalt complexes are the limiting factors in catalytic oxidation and oxygenation studies, attention has recently been focused on the rates, reaction pathways, and mechanisms of these reactions.[7-10] With the coordinated polyamine ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN) and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT), oxidative dehydrogenation of the coordinated polyamine was found to occur during the autoxidation process.[7,10] With the pentadentate polyamines 2,6-bis(2-(3,6-diazahexyl))pyridine (EPYDEN), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (IMDIEN), and tetraethylenepentamine (TETREN), the autoxidation pathway was found to be entirely different in that, under the same reaction conditions, these coordinated ligands are not oxidized by coordinated dioxygen.[8-10] In the case of EPYDEN, which is a pyridyl-containing pentaamine, as are PYDIEN and PYDPT, the difference in reactivity seemed to be due to the conformation of the ligand in the dioxygen complex, which was not suitable for double-bond formation

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through oxidative dehydrogenation.[8,9]

A few other examples of oxidative dehydrogenation of coordinated amines through dioxygen complex formation may be found in the literature. It was found by Harris et al.[11,12] that binuclear cobalt dioxygen complexes with coordinated deprotonated dipeptides such as glycylglycine and analogous ligands undergo oxidative dehydrogenation at the N-terminal positions to form the corresponding (iminoacyl)amino acids. Autoxidation of a four-nitrogen cobalt(II) macrocyclic complex related to salcomine to give a cobalt(III) complex in which the ligand has two additional double bonds, reported by Black and Hartshorn,[13] certainly must occur through dioxygen complex formation. Also, the mechanism proposed by Burnett et al.[14] for the Cu(I)-catalyzed autoxidation of an $N_6O_4(30)$ macrocycle is considered to involve the formation of binuclear dioxygen complexes as intermediates, although in this case the binuclear (μ-peroxo)dicopper(II) complex is too unstable to be isolated and identified.

Because of the sensitivity of the autoxidation reaction to the composition and conformation of the coordinated ligands in the intermediate dioxygen complexes, the whole area of the relationship of dioxygen complex structure to ligand reactivity, and to the reactivity of coordinated dioxygen, deserves further detailed study. For the purposes of this investigation, it was decided to study the reactivity of coordinated dioxygen in dioxygen adducts formed from mixed-ligand polyamine complexes of cobalt—one of which is selected from a group believed to be highly susceptible to oxidative dehydrogenation via dioxygen complex formation (2-(aminomethyl)pyridine, AMP) and the other of which is believed to be resistant to autoxidation (diethylenetriamine, DIEN). Thus the possible formation of two double bonds through the attack on AMP by dioxygen in the complex $[(\mathrm{DIEN})(\mathrm{AMP})\mathrm{Co}^{\mathrm{III}}{-}^{-}\mathrm{O{-}O}^{-}{-}\mathrm{Co}^{\mathrm{III}}(\mathrm{AMP})(\mathrm{DIEN})]^{4+}$ should involve fairly clean and straightforward kinetics because of the simple stoichiometry of the net reaction: $2\mathrm{AMP} + \mathrm{O_2} \rightarrow 2\mathrm{IMP} + 2\mathrm{H_2O}$ (IMP is 2-(iminomethyl)pyridine). Prior to the kinetic studies, it is necessary to first identify the complex species present in solution, and to determine their concentrations as a function of pH and solute composition, through detailed equilibrium studies.

Experimental Section

Materials. Commercially available 2-(aminomethyl)pyridine was first distilled under reduced pressure, and the colorless oil was then converted to the corresponding dihydrochloride by treating the alcoholic solution of the free base with concentrated hydrochloric acid. Diethylenetriamine was also converted to the corresponding trihydrochloride. Both amines were obtained in pure form by two successive crystallizations of the hydrochlorides from water. Reagent grade cobaltous nitrate was obtained from Fisher Scientific Co. and was used without further purification. Carbonate-free potassium hydroxide was obtained from J. T. Baker Chemical Co. and was used after dilution with carbon dioxide free doubly distilled water. High-purity nitrogen, oxygen, and argon were obtained from Airco Gas Products Inc. and were used after passing the gases through Ascarite and pyrogallol scrubbers for nitrogen and argon and through Ascarite for oxygen in order to remove traces of impurities. Finally, these scrubbed gases were passed through 0.100 M standard KNO_3 solution to prevent evaporation of the experimental solution.

$NaBD_4$ (98 atom %D) was purchased from MSD Isotopes Co. 2-Cyanopyridine was obtained from Aldrich Chemical Co. Proton NMR spectra were recorded with a Varian EM-390 spectrometer with the sodium salt of Me_4Si as internal standard. The chemical shifts are given in ppm relative to Me_4Si.

Preparation of $C_5H_4NCD_2NH_2{\cdot}2HCl$. Completely α-deuterated 2-(aminomethyl)pyridine was synthesized by the reduction of 2-cyanopyridine with $NaBD_4$ by the use of a slight modification of the method of Yamada et al.[15] To 2.1 g of 2-cyanopyridine dissolved in 40 mL of absolute ethanol was added ca. 4.0 g of $NaBD_4$ stepwise, and the reaction mixture was refluxed for $5^1/_2$ h under an argon atmosphere. Initially the solution was colorless, but with the progress of the reaction a yellow color developed. It was then cooled to room temperature and filtered. Ethanol was stripped off by vacuum evaporation, and the residue was filtered to remove excess sodium borodeuteride. This process was repeated until most of the sodium borodeuteride had been filtered off. To the residue was added ca. 10 mL of water to form an aqueous solution having a pH of ca. 10.5–11.0. The free-amine base was extracted from the yellow solution with $CHCl_3$, leaving the colorless aqueous phase. After removal of all $CHCl_3$ from the extract, the remaining yellow oil was dissolved in absolute ethanol, and to this was added concentrated hydrochloric acid with constant stirring and cooling. The colorless solid that precipitated was filtered, washed with cold ethanol and finally with ether, and then air-dried; yield ca. 31%. ^{1}H NMR of $C_5H_4NCH_2NH_2{\cdot}2HCl$ (product obtained by $NaBH_4$ reduction of 2-cyanopyridine) (D_2O with 3 drops of KOD) (δ): 8.45 (1 H), 7.80 (1 H), 7.25, 7.50 (2 H), 3.85 (2 H). ^{1}H NMR of $C_5H_4NCD_2NH_2{\cdot}2HCl$ (product obtained by $NaBD_4$ reduction of 2-cyanopyridine) (D_2O with 3 drops of KOD) (δ): 8.60 (1 H), 7.90 (2 H), 7.55 (1 H).

Potentiometric Measurements. Potentiometric equilibrium measurements were carried out with a Corning Model 130 digital pH meter in a jacketed reaction vessel maintained at 25.00 ± 0.01 °C by the circulation of thermostated water. The potentiometric cell was fitted with glass and calomel electrodes that were calibrated with standard aqueous HCl and KOH solution to read $-\log [H^+]$ directly. In order to maintain the linearity of the EMF–hydrogen ion concentration calibration, the free H^+ and OH^- concentrations were limited to a small fraction of that of the supporting electrolyte by restricting the $-\log [H^+]$ measurements to the range 2–12. The titrant was delivered with a Metrohm piston buret. The ionic strength of the medium was maintained at 0.100 M by the addition of standard KNO_3 solution. The potentiometric measurements were carried out under an atmosphere of nitrogen and oxygen, respectively. For the potentiometric measurements at 25.00 °C the following solutions were measured:

Anaerobic solutions (under N_2): (1) $[\mathrm{AMP{\cdot}2HCl}] = 3.996 \times 10^{-3}$ M; (2) $[\mathrm{DIEN{\cdot}3HCl}] = [\mathrm{Co^{2+}}] = 4.085 \times 10^{-3}$ M; (3) $[\mathrm{AMP{\cdot}2HCl}] = 4.056 \times 10^{-3}$ M, $[\mathrm{Co^{2+}}] = 2.028 \times 10^{-3}$ M; (4) $[\mathrm{AMP{\cdot}2HCl}] = 5.493 \times 10^{-3}$ M, $[\mathrm{Co^{2+}}] = 1.830 \times 10^{-3}$ M; (5) $[\mathrm{DIEN{\cdot}3HCl}] = 3.937 \times 10^{-3}$ M; (6) $[\mathrm{DIEN{\cdot}3HCl}] = [\mathrm{AMP{\cdot}2HCl}] = [\mathrm{Co^{2+}}] = 2.338 \times 10^{-3}$ M.

Aerobic solutions (1.00 atm of O_2): (7) $[\mathrm{AMP{\cdot}2HCl}] = 4.056 \times 10^{-3}$ M, $[\mathrm{Co^{2+}}] = 2.028 \times 10^{-3}$ M; (8) $[\mathrm{DIEN{\cdot}3HCl}] = [\mathrm{AMP{\cdot}2HCl}] = [\mathrm{Co^{2+}}] = 2.338 \times 10^{-3}$ M.

The protonation constants of the ligands (solutions 1 and 5) were calculated with the aid of the program PKAS.[16] The stability constants of the binary and ternary metal chelates and the equilibrium constants for the formation of the oxygen adducts and the hydrolyzed oxygen adducts (solutions 2, 3, 4, 6, 7, and 8) were calculated with the aid of the computer program BEST.[17] The methods used for computation are the same as those described earlier.[18] Species distribution curves for both 1:2 Co^{2+}–AMP and 1:1:1 Co^{2+}–DIEN–AMP were generated with the aid of the Fortran computer program SPE written by R. J. Motekaitis, of this laboratory.

Spectrophotometric Measurements. The UV-vis absorption spectra of the complexes were recorded with a Perkin-Elmer Model 553 fast-scan UV/vis spectrophotometer equipped with a remote-control time-drive chart recorder and with matched quartz cells of path length 1.000 ± 0.001 cm. From time-dependent kinetic scan spectra a wavelength having the maximum difference in absorbance between the reactant and product was chosen for determination of rate constants. Kinetic data were obtained from aqueous solutions in a jacketed reaction vessel thermostated at 35.00 ± 0.01 °C. The kinetics of decomposition of the dioxygen complex were monitored by following the decrease in absorbance of the ligand-to-metal charge-transfer band ($O_2 \rightarrow d_{z^2}$). All the kinetic data presented are the means of three to five separate runs. Anaerobic conditions were employed to simplify the kinetic data obtained by avoiding continual reoxygenation during experimental runs.

Product Identification. In a separate experiment the dioxygen complex was digested at 35.0 °C for several half-lives in order to achieve complete decomposition under anaerobic conditions. The solutions thus obtained were then processed as usual to form the (2,4-dinitrophenyl)hydrazone derivative for the quantitative estimation of aldehyde formed from the reaction.

Analysis of Kinetic Data. Preliminary analysis of kinetic data revealed that the kinetics may be expressed in terms of two parallel pseudo-first-order reactions that can be represented as

$$\mathrm{A} \rightarrow \mathrm{C};\ \mathrm{B} \rightarrow \mathrm{C}$$

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Table I. Formation Constants of Complexes Formed in Aqueous Systems Containing Cobalt(II) 2-(Aminomethyl)pyridine and/or Diethylenetriamine in the Absence and in the Presence of Dioxygen (25.0 °C, μ = 0.100 M (KNO_3))

ligand(s)	quotient, Q	log Q^a	log Q^b	ref
DIEN (L′)	$[CoL'^{2+}]/[Co^{2+}][L']$	8.05	8.24	19
	$[CoL'_2{}^{2+}]/[Co^{2+}][L']^2$	13.93		
AMP (L)	$[CoL^{2+}]/[Co^{2+}][L]$	5.44	5.30	27
	$[CoL_2{}^{2+}]/[Co^{2+}][L]^2$	10.08		
DIEN (L′), AMP (L)	$[CoL'L^{2+}]/[Co^{2+}][L'][L]$	12.40		
DIEN (L′), O_2	$[Co_2L'_2(O_2)(OH)^{3+}][H^+]/[CoL'^{2+}]^2[O_2]$		1.1	28
AMP (L), O_2	$[Co_2L_4(O_2)(OH)^{3+}][H^+]/[CoL_2]^2[O_2]$	−1.77		
DIEN (L′), AMP (L), O_2	$[Co_2L_2L'_2(O_2)]/[CoL'L^{2+}][O_2]$	10.59		
EN (L″)	$[Co_2L''_4(O_2)(OH)^{3+}][H^+]/[CoL''_2{}^{2+}]^2[O_2]$		10.8	29, 30
DIPY (L‴)	$[Co_2L'''_4(O_2)^{4+}]/[CoL'''_2{}^{2+}]^2[O_2]$		4.2	31
	$[Co_2L'''_4(O_2)(OH)^{3+}][H^+]/[CoL'''_2{}^{2+}][O_2]$		2.6	32

[a] This work. [b] Other work (see references).

where C is the final reaction product. A and B are converted to C at different rates. Visual inspection of the absorption vs. time curves indicated that decomposition is rapid over an initial time period tentatively assigned to reaction A → C, while the final (slowly reacting) phase would involve the conversion B → C. Thus the initial and final phases would be analyzed separately by the integrated first-order expression

$$k_{obsd}t = -2.303 \log (A_t - A_\infty) + C \qquad (1)$$

where A_t and A_∞ are the absorbances of the LMCT band at any intermediate time and infinite time, respectively.

Results

From the potentiometric equilibrium curves (Figure 1) it appears that for a 1:2 molar ratio of Co^{2+}:(aminomethyl)pyridine dihydrochloride there are two inflections, at a = 2.0 and a = 4.0, indicating the liberation of two protons per coordinated ligand resulting in the formation of the 2:1 complex, **1** (Chart I). For the 1:1:1 Co^{2+}–AMP·2HCl–DIEN·3HCl system, Figure 1 shows a long buffer region terminated by a sharp inflection at a = 5.0. The equilibrium constant ([MLL′]/[M][L][L′]) for the formation of the 1:1:1 ternary complex, **2**, at 25.0 °C and ionic strength 0.1000 M (KNO_3) is $10^{12.40\pm0.05}$ M^{-1}. The equilibrium curve for the 1:2 Co^{2+}–AMP system under an oxygen atmosphere shows a long low-pH buffer region terminated by a sharp inflection at a = 4.5 whereas in the case of the 1:1:1 ternary system there is a long low-pH buffer region that terminates with a sharp inflection at a = 5.0. From this it is concluded that in the case of the ternary system the oxygenated species is a μ-peroxo complex, **3**, in which the metal ion, designated as formally Co(III), is fully coordinated by the peroxo ligand and the five basic nitrogens of the amines.

For the 1:2 Co^{2+}–(aminomethyl)pyridine system the potentiometric equilibrium curve indicates the base needed to form the oxygenated complex is 0.50 mol/mol of metal ion greater than that observed for the system under a nitrogen atmosphere, indicating the formation of a binuclear complex with μ-peroxo–μ-hydroxo bridging, **4**.

Since this study is mainly concerned with the dehydrogenation reactions of L (AMP), it is necessary to consider the distribution of the complexes of this ligand in the simple 2:1 AMP–Co^{2+} system under dioxygen and in the mixed-ligand system containing 1:1:1 molar ratios of AMP, DIEN, and Co^{2+}, also under dioxygen. The separate study of the 2:1 AMP–Co^{2+} dioxygen complex turned out to be necessary for the determination of equilibrium parameters because both the complex and its dioxygen adduct are not formed in sufficient concentrations in the mixed-ligand system to allow accurate calculation of equilibrium constants.

The stability constants and protonation constants, calculated from the potentiometric data by the method described in the Experimental Section, are presented in Table I, together with comparable values of related complexes obtained from the literature. In the two examples where comparison is possible, the stability constants of the cobalt(II) complexes determined in this study agree reasonably well with those previously reported.[19] The current values are considered more reliable because of improvements in instrumentation, in the method of calculation, and possibly in the purity of the ligand.

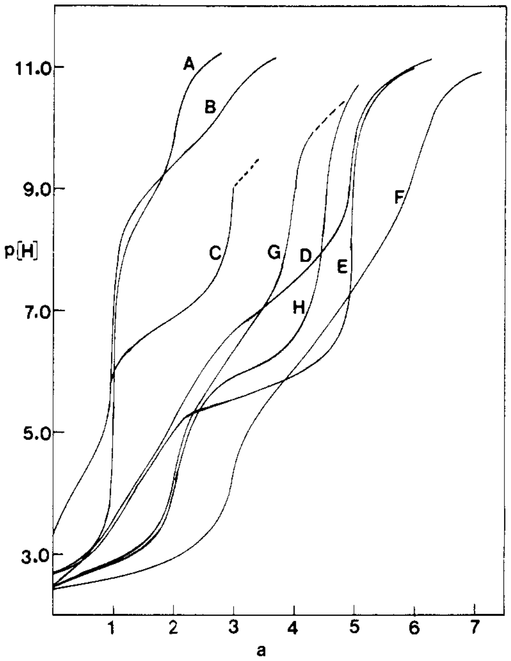

Figure 1. Potentiometric equilibrium curves for DIEN and AMP and for different mixtures of ligands with Co^{2+} under N_2 and O_2 (25.00 ± 0.05 °C, μ = 0.100 M (KNO_3)), a = no. of equiv of base added: A, AMP·2HCl alone; B, DIEN·3HCl alone; C, 1:1 DIEN·3HCl–Co^{2+} under N_2; D, 1:1:1 DIEN·3HCl–AMP·2HCl–Co^{2+} under N_2; E, 1:1:1 DIEN·3HCl–AMP·2HCl–Co^{2+} under O_2; F, 3:1 AMP·2HCl–Co^{2+} under N_2; G, 2:1 AMP·2HCl–Co^{2+} under N_2; H, 2:1 AMP·2HCl–Co^{2+} under O_2.

The oxygenation constants in Table I seem to follow the trends that are semiquantitatively predictable from the summation of the basicities (pK's) of the coordinated donor groups. The factors involved in such correlations are discussed in detail elsewhere.[3,4]

The distribution curves for the 2:1 AMP–Co^{2+} system under dioxygen (Figure 2) describe a relatively simple system in which the dibridged dioxygen complex is the major species above pH 7 and virtually the only species present above pH 8. On the other hand, in the mixed-ligand (1:1:1 AMP–DIEN–Co^{2+}) system a small amount of the dioxygen adducts of the single-ligand complexes $Co(AMP)_2{}^{2+}$ and $Co(DIEN)^{2+}$ are always present in the region of stability of the mixed-ligand dioxygen complex (Figure 3), which, however, is the predominant species above pH 7. It is seen that the concentration of the latter holds approximately steady from pH 7 to 10. Beyond that point there is a gradual drop-off in concentration because of the increasing stability of the dibridged dioxygen complex $Co_2L'_2(OH)O_2{}^{3+}$ (**5**) also present in solution. Its stability increases at high pH because of the presence of the hydroxo bridge. It is noted that the equilibria involving the dioxygen complexes present are reached rapidly and that the readjustment with changing conditions occurs readily. It is seen that the potentiometric data provide quantitative in-

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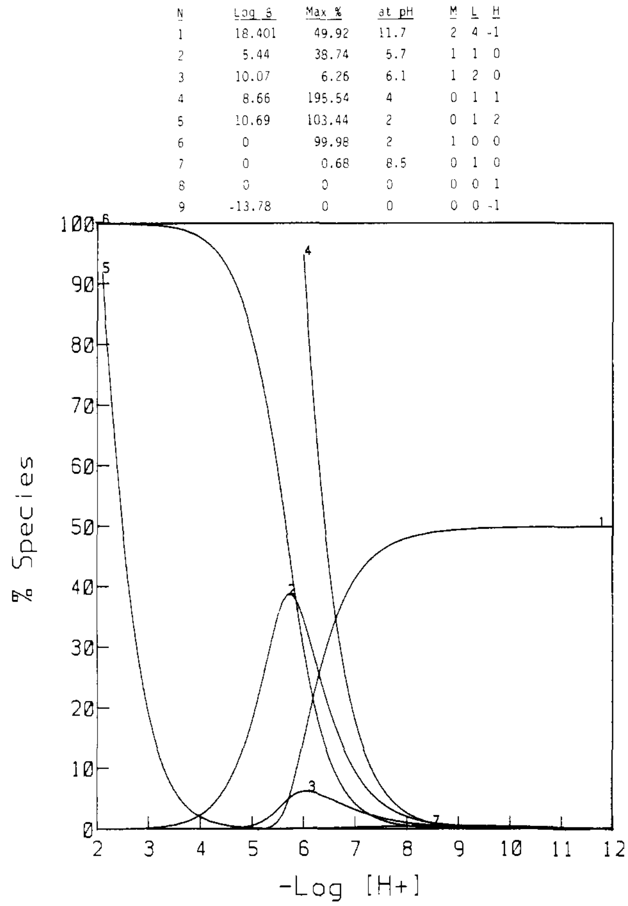


N	Log β	Max %	at pH	M	L	H
1	18.401	49.92	11.7	2	4	-1
2	5.44	38.74	5.7	1	1	0
3	10.07	6.26	6.1	1	2	0
4	8.66	195.54	4	0	1	1
5	10.69	103.44	2	0	1	2
6	0	99.98	2	1	0	0
7	0	0.68	8.5	0	1	0
8	0	0	0	0	0	1
9	-13.78	0	0	0	0	-1

Figure 2. Species distribution diagram for 1:2 Co(II)-2-(aminomethyl)pyridine (2.028×10^{-3} and 4.056×10^{-3} M, respectively) under O_2 (25.00 °C, μ = 0.100 M (KNO_3)).

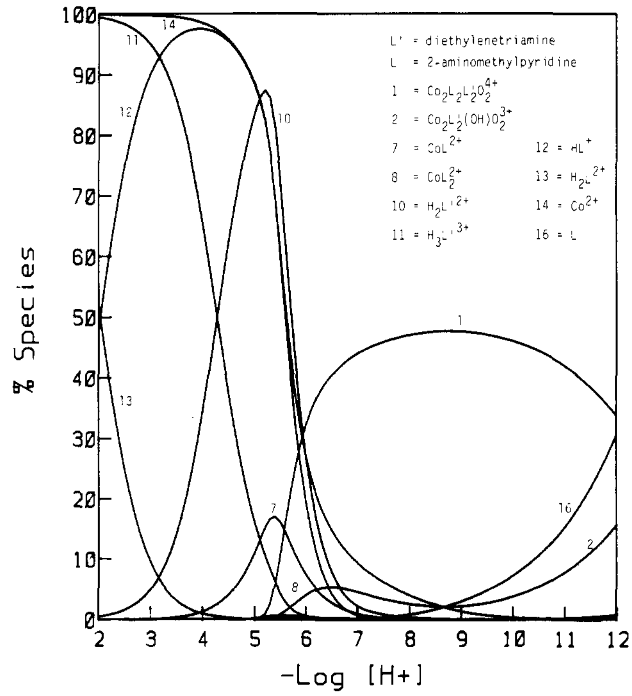


Figure 3. Species distribution diagram for 1:1:1 Co(II)-diethylenetriamine-2-(aminomethyl)pyridine (2.338×10^{-3} M) under O_2 (25.00 °C, μ = 0.100 M (KNO_3)).

formation on concentrations of dioxygen complexes under variable conditions of pH and ratios of reactants, thus providing the basic information needed for the interpretation of the kinetic data and the determination of specific reaction rates of these complexes.

Table II. Absorption Spectra of Co(II) Complexes and Their Dioxygen Adducts[a]

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$Co^{II}(AMP)_2(OH_2)_2^{2+}$	596	168
	364 (sh)	290
$([Co^{III}(AMP)_2]_2(O_2^{2-})(OH))^{3+}$	374	6208
$([Co^{III}(DIEN)(AMP)]_2(O_2^{2-}))^{4+}$	310 (pH 8.37)[b]	9972

[a] 35.0 °C, pH 9.97. [b] At higher pH the complex itself decomposes to give mixed species.

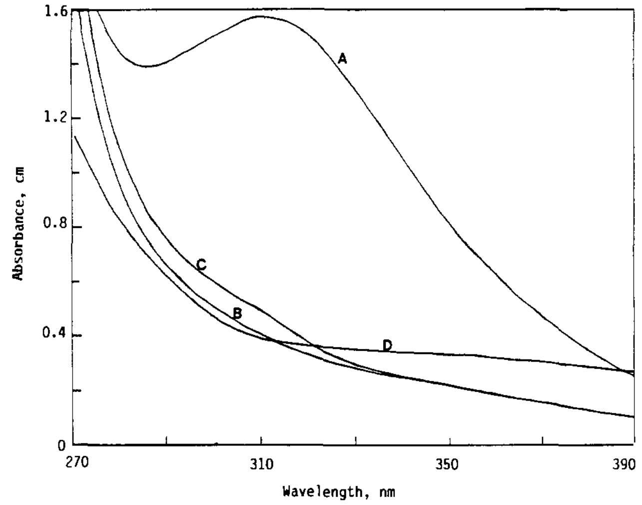


Figure 4. UV-vis spectra of the μ-peroxo complex formed from the 1:1:1 Co^{2+}-DIEN-AMP system: A, at pH 11.003 immediately after mixing; B, after complete decomposition of the dioxygen complex at pH 11.003 at 35.00 °C under anaerobic conditions; C, after reoxygenation of decomposition product. Curve D is the UV-vis spectrum of the 1:1:1:1 mixture of Co^{2+}-DIEN·3HCl-PY-2-carboxaldehyde-NH_4^+ at pH 10.996 after completion of reaction at 35.00 °C.

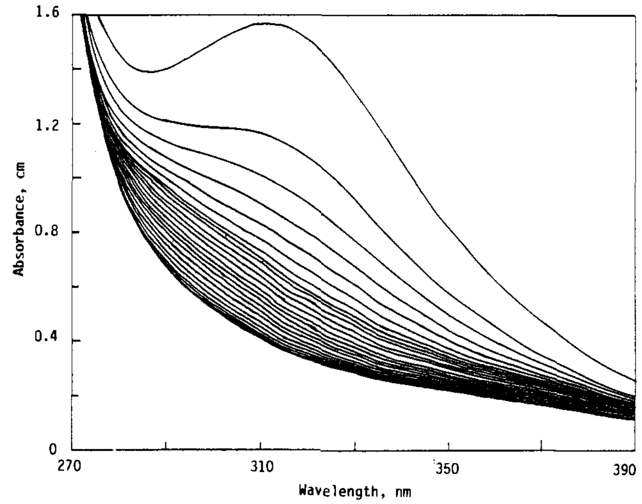


Figure 5. Kinetic spectral scans for the decomposition of the μ-peroxo complex of 1:1:1 Co^{2+}-DIEN-AMP at pH 11.003 (35.00 °C, μ = 0.100 M (KNO_3), [O_2 complex] = 1.595×10^{-4} M, Δt = 30 min).

Separate measurements on the single-ligand complexes present in this mixed-ligand system demonstrate that, at 35.0 °C, the corresponding single-ligand cobalt dioxygen complexes do not undergo appreciable degradation over the pH range of interest, even up to pH 12. Thus, the reactions observed under these conditions are due to the μ-peroxo mixed-ligand cobalt dioxygen complex.

Spectral Data and Product Characterization. The UV-visible spectral data of the diaquobis(2-(aminomethyl)pyridine)cobalt(II) chelate, $Co(AMP)_2(OH)_2^{2+}$, and its oxygen adduct, along with the oxygen adduct of the mixed-ligand complex, are reported in Table II. From a control run involving complete conversion (*t*

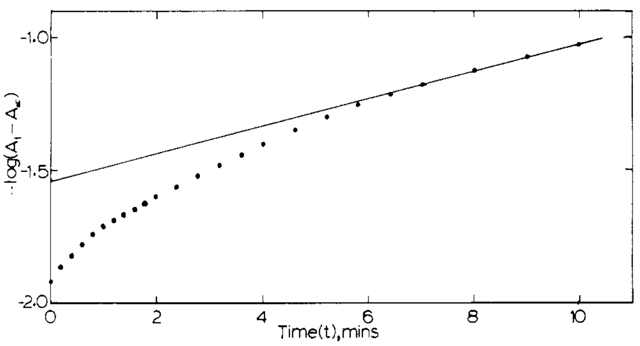


Figure 6. Plot of –log (A_t – A_∞) vs. time for evaluation of $k_{\text{obsd}}^{\text{slow}}$ (35.00 °C, μ = 0.100 M (KNO_3), pH 11.79).

= ∞) to reaction products it was found that the spectrum of the dioxygen adduct of the mixed-ligand complex is converted at pH 11.00 and 35.0 °C to that shown in Figure 4. From the scan spectra taken as a function of time (Figure 5) it is seen that at the initial stage of the reaction there is a rapid change in absorbance while the later stages are characterized by a much slower change, suggesting degradation reactions occurring at different rates. Curve A of Figure 4 represents the electronic absorption spectrum of the reactant, i.e. the dioxygen adduct of the mixed-ligand complex at pH 11.00 and 35.0 °C, and curve B is the final spectrum recorded after about 12 h. There is no change in absorptivity even on allowing the solution to stand overnight. On reoxygenation of this solution, which contains the products of complete decomposition of the dioxygen complex, there is a small increase in absorbance (curve C).

The absorbance curve C was considered to be due to the formation of the dioxygen adduct of the cobalt(II)–diethylenetriamine complex, since diethylenetriamine does not undergo dehydrogenation under the reaction conditions employed. In order to verify this, the electronic spectrum was measured on a solution containing equimolar concentrations of Co^{2+}, diethylenetriamine, pyridine-2-carboxaldehyde, and ammonia, at 2 times the concentration of the original dioxygen complex (curve A). The measurement was made under the same conditions (pH, temperature, and digestion period) as those employed for C and in the absence of dioxygen. The resulting spectrum (curve D) is nearly identical with that of the decomposition product C at the wavelength of interest.

Further information on the nature of reaction product was obtained by identification of pyridine-2-carboxaldehyde in the reaction mixture. The dioxygen complex was allowed to react through several half-lives at 35.0 °C and pH 11.70, and a measured aliquot was treated with an acidic solution of (2,4-dinitrophenyl)hydrazine. In three separate experiments the gravimetric determination of the (dinitrophenyl)hydrazone formed corresponding to the following equivalents of aldehyde: (1) 1.8, (2) 2.04, and (3) 1.97 with an average that is very close to the theoretical values of 2 equiv of aldehyde.

From these spectral and gravimetric experiments it is apparent that the ultimate product of the decomposition of the mixed-ligand cobalt dioxygen complex is pyridine-2-carboxaldehyde, ammonia, and the cobalt(II)–diethylenetriamine complex. The stoichiometry of the degradation reaction, illustrated by Scheme I, is based on the above information.

Kinetics. From the time-scan spectra (Figure 5) it was observed that the most suitable wavelength for following the decomposition of the cobalt dioxygen complex is 310 nm. The first-order plot of log (A_t – A_∞) vs. time was not linear throughout the total reaction time. There is a definite break between the initial time period and subsequent longer time interval, which suggests that the degradation reaction consists of at least two steps.

In a system such as

$$A \xrightarrow{k^f} C \qquad B \xrightarrow{k^s} C$$

(where $k^f \gg k^s$) the concentration of A rapidly becomes negligible so that the data near the end of the overall reaction time may be considered as a simple conversion of B → C. On that basis the rate constant for the slow step was computed from the slope of the linear portion of the plot of log (A_t – A_∞) vs. time. Figure 6 is a representative example of such a plot at pH 11.79. The same method was used for evaluating the rate constant for the slow steps at other pH values, and the results obtained are reported in Table III.

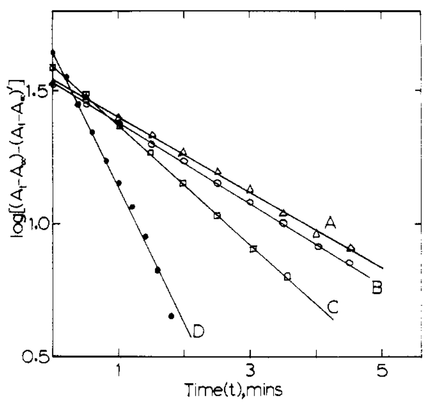


Figure 7. Plot of log [(A_t – A_∞) – (A_t – A_∞)′] vs. time (initial time period) for evaluation of $k_{\text{obsd}}^{\text{fast}}$ (35.00 °C, μ = 0.100 M (KNO_3)). pH: A, 11.05; B, 11.19; C, 11.41; D, 11.79.

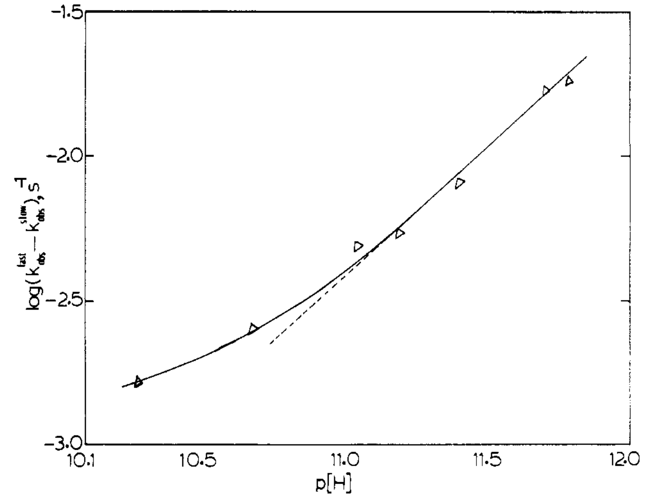


Figure 8. Dependence of pseudo-first-order rate constants on pH for the fast step (35.00 °C, μ = 0.100 M (KNO_3)).

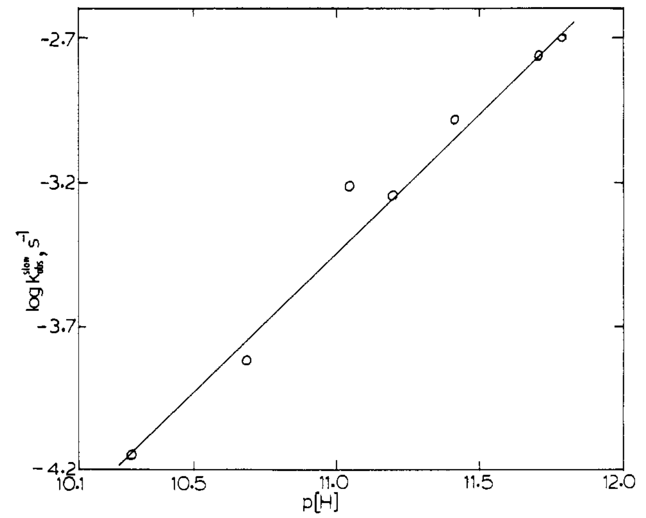
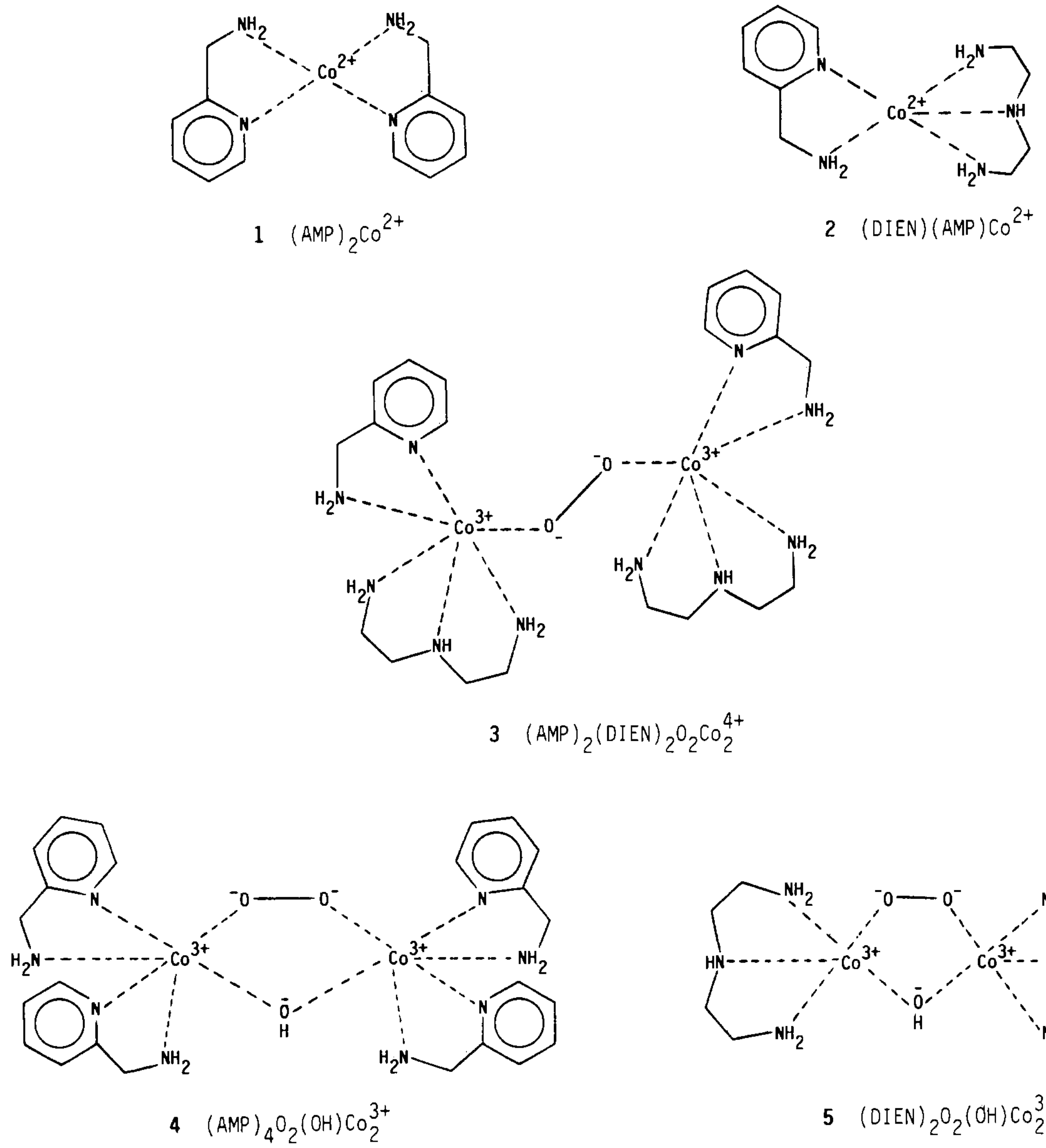


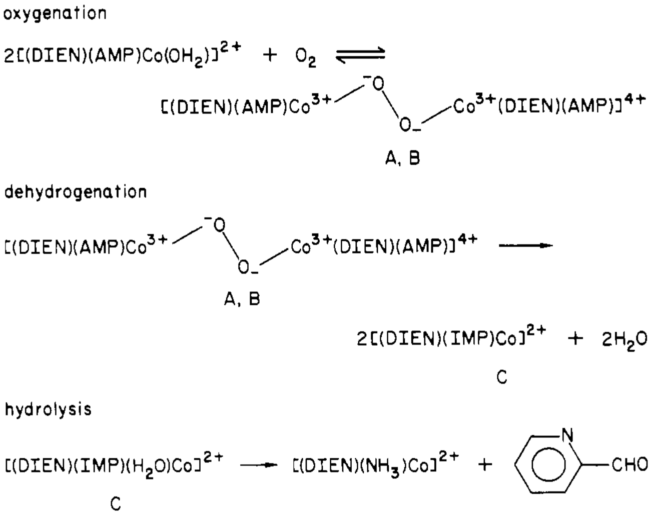
Figure 9. Dependence of pseudo-first-order rate constants on pH for the slow step (35.00 °C, μ = 0.100 M (KNO_3)).

The rate constant obtained from the linear part of Figure 6 provides a correction factor for the rate constant k_{obsd} taken from the initial part of the reaction, to give an adjusted value of k_f. A

Chart I



Scheme I. Reaction Stoichiometry of Dehydrogenation of AMP in the Co(II)-AMP-DIEN-Dioxygen System[a]



[a] The dioxygen complex consists of two reactive forms: A, which dehydrogenates rapidly, and B, which dehydrogenates slowly, to the imine C. It is assumed that the molar absorptivities of A and B are equivalent.

representative example for the graphical evaluation of k_{obsd} for the fast step at constant pH is shown in Figure 7. The plot of log k_{obsd} for both fast and slow steps are pH-dependent (Figures 8 and 9), and the linear portions of both plots of k_{obsd} vs. pH have a slope of unity, clearly indicating that both reaction steps have first-order dependence on hydroxide concentration, which becomes apparent at high pH. The rate constants obtained for the second-order reactions at high pH are listed in Table III. The rate behavior for the mixed-ligand complex is described by eq 2–6.

$$\frac{-d[A]}{dt} = k_1^f[A] + k_2^f[OH][A] \tag{2}$$

$$\frac{-d[B]}{dt} = k_1^s[B] + k_2^s[OH][B] \tag{3}$$

$$\frac{-d([A] + [B])}{dt} = k_{obsd}'([A] + [B]) = (k_1^f + k_1^s)([A] + [B]) + (k_2^f + k_2^s)[OH]([A] + [B]) \tag{4}$$

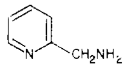
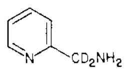
early stage

$$k_{obsd} = k_1^f + k_2^f[OH] + k_1^s + k_2^s[OH] \tag{5}$$

final stage

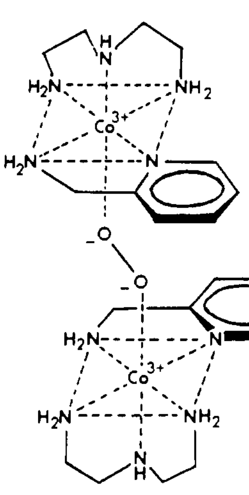
$$k_{obsd} = k_1^s + k_2^s[OH] \tag{6}$$

Table III. pH Dependence of the Pseudo-First-Order Rate Constants for Fast and Slow Steps (t = 35.0 °C, I = 0.100 M (KNO_3))

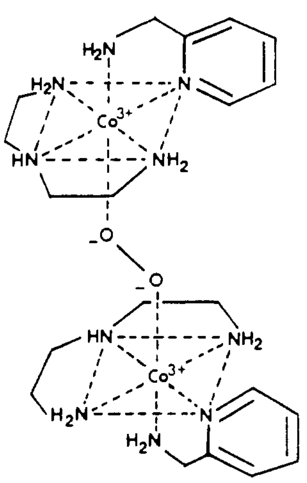
ligand	pH	$10^3[OH^-]$, M[a]	$10^3k_{obsd}^{f}$, s^{-1}	$k_1^{f,b}$ s^{-1}	$k_2^{f,b}$ M^{-1} s^{-1}	$10^4k_{obsd}^{s}$, s^{-1}	$k_1^{s,b}$ s^{-1}	$k_2^{s,b}$ M^{-1} s^{-1}
	10.28	0.697	1.7	9.7×10^{-4}	8.2×10^{-1}	0.71	0.9×10^{-4}	8.6×10^{-2}
	10.68	1.75	2.7			1.5		
	11.05	5.03	5.5			6.1		
	11.19	5.68	6.0			5.7		
	11.41	9.23	9.1			10.5		
	11.70	18.32	18.6			17.4		
	11.79	22.34	20.0			19.6		
	11.41	9.23	0.66	1.1×10^{-4} (9)	0.50×10^{-1} (16)	1.2	0.53×10^{-4} (2)	0.65×10^{-2} (13)
	11.61	14.86	1.0			1.5		
	11.79	22.34	1.5			2.0		

[a] Calculation of $[OH^-]$ based on pK_w = 13.44 at 35.0 °C and μ = 0.100 M (KNO_3). [b] Figures in parentheses denote isotope effects.

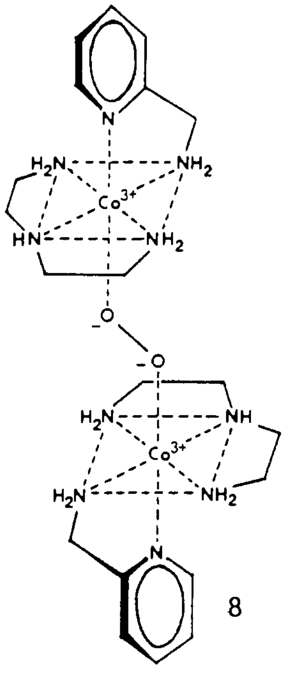
Chart II



6



7



8

In order to investigate the deuterium isotope effect, the kinetics of decomposition of the dioxygen complex formed from 1:1:1 Co^{2+}–DIEN–α-deuterated AMP were also measured under anaerobic conditions at three different pH values by the method described above. The values of rate constants obtained, and the corresponding deuterium isotope effects, are also presented in Table III.

Discussion

With two distinctly different rates of decomposition, the possible reaction pathways may be visualized as

$$\begin{tikzcd}
\text{(i)} & A \arrow[r, "k_1"] & C & \text{(ii)} & A \arrow[r, shift left] \arrow[dr, "k_1"'] & B \arrow[l, shift left] & \text{(iii)} & A \arrow[d, "k_1"'] & B \arrow[l, "k_2"'] \\
 & B \arrow[r, "k_2"] & C & & & C & & C &
\end{tikzcd}$$

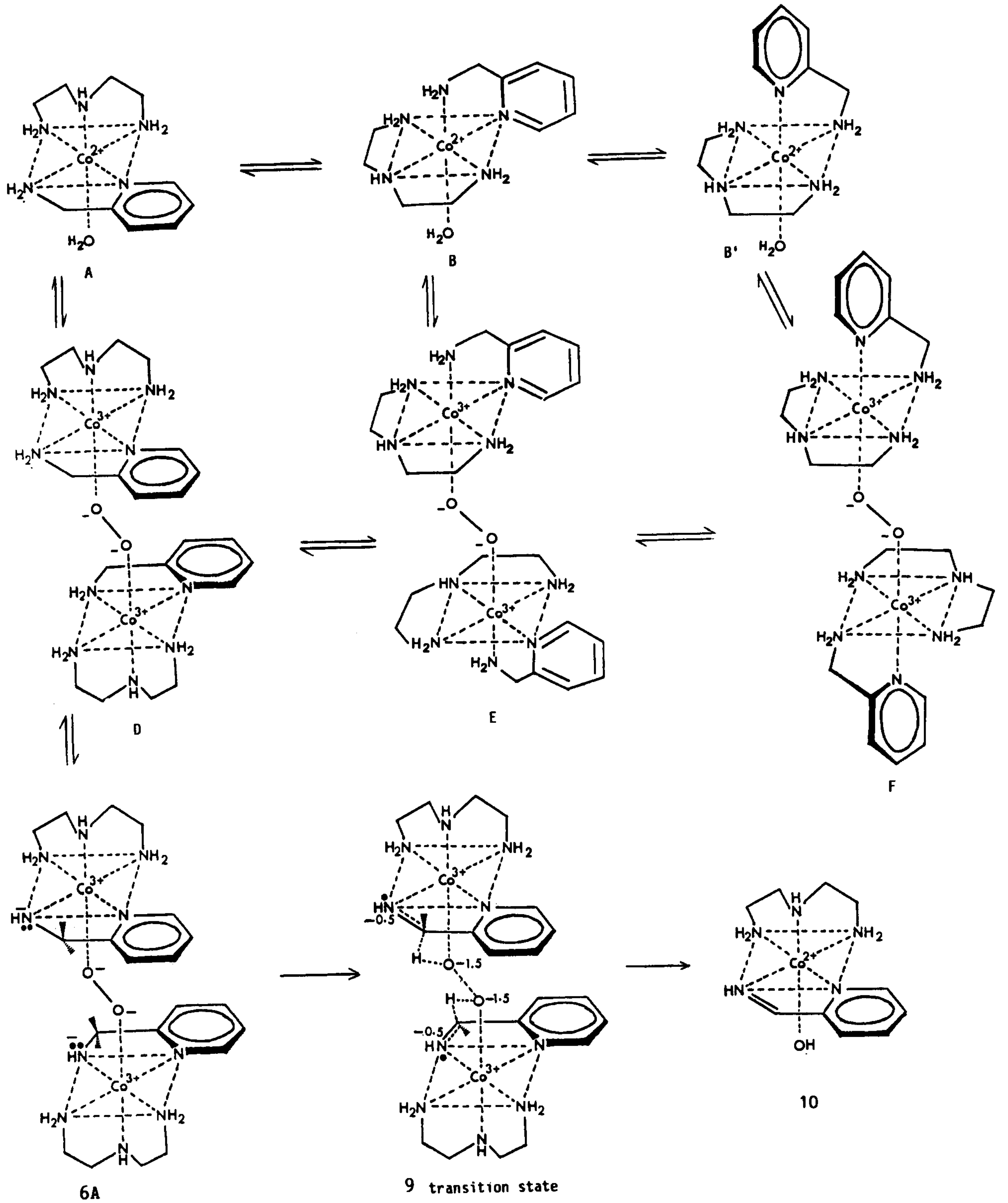
where A is the form that decomposes rapidly and B is the form that decomposes slowly.

A search for the probable origin of the fast and slow rates of oxidative dehydrogenation of AMP in the mixed-ligand complex **3** leads one to consider the possible conformations of the ligand AMP in the reaction mixture under conditions favoring **3** as the major species (Figure 4). Formulas **6**–**8** (Chart II) illustrate some of the possibilities with three different orientations of AMP relative to the peroxo bridge. Other dioxygen complex species with mixtures of the orientations shown are also possible. In structure **6** both the aliphatic amino group of AMP and the adjacent carbon atom are oriented close to the peroxo bridge. In structures **7** and **8** these groups are remote from the coordinated dioxygen.

Consideration of the factors that control oxidative dehydrogenation in dioxygen complexes that have been observed in this investigation and for those reported previously by Raleigh and Martell[7,10] indicates that **6** is the major reacting species present and that all other forms fail to meet the requirements in one way or another. On this basis it is suggested that species A in the reaction pathways suggested above has the conformation indicated by **6** and that the slowly reacting species B consists of one or more of the other possible conformations. Moreover, it appears that alternative pathway iii is the one that applies to this system, and the slow reaction is the conversion of one or more isomers to the reactive form A, and that in the second (slow) phase of the observed oxidative degradation reaction the fast reaction A → C is no longer rate-determining.

The oxidative dehydrogenation of coordinated (aminomethyl)pyridine to an imine ligand is a two-electron-transfer process. However, in a cobalt dioxygen complex successive one-electron transfers or a two-electron transfer may occur to form the imine group and H_2O. Thus, for two (aminomethyl)pyridine moieties coordinated in the dioxygen complex, a total of four electron transfers are required for the overall dehydrogenation process. Recalling the oxidative dehydrogenation reactions of PYDIEN and PYDPT,[7,10] it was observed that the simultaneous coordination of the oxygen and the ligand with the metal ion provides a low-energy pathway for the transfer of electrons in the oxidative dehydrogenation process. In the present situation the increase in rate constant with increase in pH clearly indicates that base-assisted deprotonation of the coordinated amine lowers the

Scheme II. Suggested Mechanism for Oxidative Dehydrogenation of 2-(Aminomethyl)pyridine through Formation of a Mixed-Ligand Binuclear Cobalt Dioxygen Complex



energy barrier for the electron-transfer process. Furthermore, it was found that at high pH the rates are dependent on the first power of the hydroxide ion concentration. From a comparison of the reported pK_a of the cobalt(II)–AMP complex with the lower limit of the pH dependence of the dehydrogenation reactions (Figures 8 and 9), it appears that deprotonation of coordinated amine is of prime importance in promoting the electron-transfer process.

As a result of deprotonation, the negative charges on the coordinated nitrogen would assist the transfer of electrons to the dioxygen through the coordinated metal ion as indicated in the proposed transition state, **9**. The oxidative dehydrogenation of coordinated 2-(aminomethyl)pyridine forms 2-(iminomethyl)pyridine, which is stabilized by conjugation to the pyridine ring. From product analysis it was found that the ultimate reaction product is an aldehyde, indicating that the imine intermediate undergoes subsequent base-catalyzed hydrolysis in aqueous solution to form the final products, aldehyde and ammonia.

To summarize, the following are the apparent controlling factors involved in the dehydrogenation of coordinated polyamine ligands in binuclear cobalt dioxygen complexes, which are deduced from the observations in this work and in that of Raleigh and Martell.[7–10]

1. All oxidative dehydrogenation reactions are base-catalyzed.
2. The imine group formed is conjugated with an aromatic ring (no dehydrogenation with aliphatic polyamines).
3. Conformation of polyamine ligands in a dioxygen complex must be compatible with the formation of a trigonal R—C=N—R′ group (R = aromatic).
4. When isomers are possible, only the configuration with the α-CH adjacent to coordinated dioxygen undergoes dehydrogenation.
5. There is a large deuterium isotope effect.

A tentative reaction mechanism for the oxidative degradation of coordinated AMP in the dioxygen complex at high pH is illustrated by Scheme II. It is seen that subsequent to the deprotonation reaction, reflecting base catalysis, homolytic O–O bond scission is suggested as occurring with concerted proton transfer to coordinated oxygen and with simultaneous electron transfer through the metal ion from the organic center undergoing dehydrogenation to the coordinated oxygen. All of these changes are expressed in transition state **9**.

It is obvious that this mechanism predicts the existence of a large kinetic deuterium isotope effect corresponding to the rate-determining transfer of a proton from the α-carbon of AMP to coordinated dioxygen. The reaction kinetics for the mixed-ligand dioxygen complex **3**, containing completely α-deuterated AMP, was carried out at three pH values in the high-pH range. The ratios $k_2^f(H)/k_2^f(D) = 16$ and $k_2^s(H)/k_2^s(D) = 13$ are considerably higher than expected. Also, the value of $k_1^f(H)/k_1^f(D) = 9$ is also compatible with the suggested proton-transfer mechanism. The much lower magnitude of $k_1^s(H)/k_1^s(D)$ is indicative of a different reaction mechanism for the slow step and is compatible with the suggested rate-limiting conversion of inactive coordination isomers to the active forms, **6** and **6A**, for this phase of the reactions. The large values of the measured isotope effects are not unreasonable in view of recent results in the field.[20-26] The large values of the observed isotope effects also open up the possibility that quantum-mechanical tunneling makes a contribution to proton transfer, thus further supporting the proposed mechanism.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. AMP, 3731-51-9; $C_5H_4NCD_2NH_2 \cdot 2HCl$, 100366-77-6; 2-cyanopyridine, 100-70-9.

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Oxidation of Cobalt(II) Pentaamine Complexes through the Formation of Dioxygen Complex Intermediates

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Received October 26, 1984

The oxidation of cobaltous complexes containing tetraethylenepentamine (TETREN), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (IMDIEN), 2,6-bis(3,6-diazahex-2-yl)pyridine (EPYDEN), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN), or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT) with molecular oxygen takes place through the formation of μ-peroxo-bridged cobalt(III) dioxygen complexes and ultimately results in either oxidative dehydrogenation of the coordinated ligand or simple "metal-centered" oxidation to form cobalt(III) complexes of the unchanged ligand and hydrogen peroxide. These reactions are shown to be first order with respect to the concentration of both the μ-peroxo-bridged cobalt(III) dioxygen complex and the hydroxide ion concentration. The cobalt(II) complexes of TETREN, IMDIEN, and EPYDEN undergo metal-centered oxidation, while the cobalt(II) complexes of PYDIEN and PYDPT undergo oxidative dehydrogenation of the coordinated amines to imines conjugated to the pyridine ring and coordinated to cobalt(II). The cobalt(II) complexes that have undergone oxidative dehydrogenation react with dioxygen to form new dioxygen complexes that undergo further oxidative dehydrogenation. It is proposed that the differences in reaction pathways and mechanisms of the oxidation reactions are dependent on the conformations of the aromatic and aliphatic amino groups in the coordination spheres of the μ-peroxo cobalt(III) dioxygen complexes having pyridyl-containing pentadentate polyamines as ligands.

Introduction

Recently attention has been focused on the mechanism of degradation reactions of μ-peroxo-bridged complexes of cobalt since the rates of such reactions are the limiting factors in catalytic oxidation and oxygenation studies involving cobalt dioxygen complexes as intermediates and determine the number of reversible oxygenations possible in the use of dioxygen complexes for oxygen separation processes. It has been proposed[2] that the degradation reaction involves remittal of oxygen as the result of the disproportionation of hydrogen peroxide[3] released from the oxygen complex and that the slow uptake of oxygen observed after initial rapid formation of the dioxygen complex is indicative of oxidation of the ligand. With the ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN, **1**) or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT, **2**) in the coordination sphere of the corresponding cobalt(II) dioxygen complexes, oxidative dehydrogenation of the coordinated ligand has been found to occur during the degradation

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(1) Abstracted in part from a dissertation by Carl J. Raleigh to the faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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