

Oxidative Dehydrogenation of Coordinated 1,9-Bis(2-pyridyl)-2,5,8-triazanonane through Formation of a Cobalt Dioxxygen Complex Intermediate

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Received April 2, 1984

The oxidative rearrangement of the binuclear dioxxygen complex of (1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(II) ((PYDIEN)Co^{II}) has been investigated by spectroscopic methods, oxygen uptake, polarographic measurements, and product analysis. The reaction was found to undergo first-order conversion to mononuclear Co(II) chelates at 35 °C and 0.10 M ionic strength. Rate constants are reported as a function of p[H]. The coordinated polyamine of the dioxxygen complex undergoes oxidative dehydrogenation under anaerobic conditions to form an imine with the double bond conjugated to the pyridine ring. The cobalt(II) complex of the monoimine was found to undergo further oxygenation and dehydrogenation reactions resulting in the conversion of the ligand to the diimine. A probable reaction mechanism is suggested.

Introduction

Research on dioxxygen complexes has been concerned primarily with the equilibrium and kinetics of formation and their electronic and vibrational spectra, magnetic properties, and crystal structures.²⁻⁴ Relatively little work on chemical reactions involving dioxxygen complexes has been reported. The limited data thus far available on dioxxygen complex reactivity suggest that a characteristic reaction of cobalt dioxxygen complexes appears to be intramolecular redox rearrangement, producing an inert complex of the metal in its higher valence state, incapable of recombining with dioxxygen.^{3,5-8} With ligands resistant to oxidation, the cobalt complexes are converted to the corresponding cobalt(III) complexes with concomitant release of peroxide.⁷⁻⁹ In a few cases, the reaction involves dehydrogenation of the ligand coordinated to cobalt.¹⁰ Representative examples are given in Table I.¹¹⁻²³ Investigations by Curtis²⁴ and Busch et al.²⁵⁻²⁷ show that mac-

Table I. Metal Systems That Undergo Oxidative Dehydrogenation through Dioxxygen Complex Formation

metal ion	ligand	product	ref
Co(II)	glycylglycine	glyoxylglycine imine	11, 12, 13
Cu(II)	tetraglycine	diglycinamide, glyoxylglycine	14
Ni(II)	tetraglycine	triglycinamide, CH ₂ O, CO ₂	15
Os(II)	ethylenediamine	ethylenediimine (coordinated)	16
Ru(II)	ethylenediamine (+bipyridyl or o-phenanthroline)	ethylenediimine	17, 18
Fe(II)	ethylenediamine (+CN ⁻)	ethylenediimine	19
Ru(II)	2-(aminomethyl)- pyridine (+NH ₃)	2-pyridinecarbox- aldehyde imine	20
Co(II)	o-phenylenediamine	o-quinone diimine	21
Ru(II)	benzylamine (+NH ₃)	benzaldimine	22
Ru(II)	cyclohexylamine (+NH ₃)	cyclohexanone imine	23

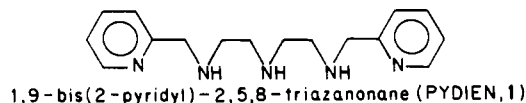
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rocyclic polyamine complexes of Ni²⁺, Cu²⁺, and Fe²⁺ react with dioxxygen to form products in which oxidative dehydrogenation of the coordinated ligand occurs. Analogous Co(III) complexes of polyamines have been observed to be resistant to dehydrogenation, thus indicating that an intermediate in the oxygenation process, or the dioxxygen complex itself, is somehow involved in the dehydrogenation of the ligand and reduction of the metal center. Nelson et al.²⁸ have suggested that a six-nitrogen, four-oxygen macrocycle forms a binuclear Cu(I) complex that reacts with molecular oxygen to form a (μ -peroxo)dicopper(II) intermediate that oxidatively dehydrogenates the macrocycle to initially produce two imine double bonds, the Cu(I) complex, and water. The mechanism suggested involves alternate aerobic and anaerobic steps with the formation of two imines in the first cycle followed by further oxidation to form four imine double bonds. Further oxidative dehydrogenation was found to be very slow, suggesting dehydrogenation of the ethylene bridging groups. Dehydrogenations of coordinated ligands reported to date involve amine complexes of Os(II),¹⁶ Ni(II),^{14,26,29-33} Ru(II),^{17,18,20,23,34-36} Cu-

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(II),^{15,28,30} Co(II),^{11-13,21,30} and Fe(II).^{19,24,25,37}

This paper presents a study of kinetics and mechanisms of oxidation of the coordinated ligand 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN, **1**) in the irreversible redox rearrangement



of (μ -peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)], a reaction that has been observed qualitatively but had not previously been subjected to detailed investigation.

Experimental Section

Reagents. Reagent grade cobaltous chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), cobaltous bromide ($\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$), sodium bromide (NaBr), sodium perchlorate ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$), potassium chloride (KCl), and potassium nitrate (KN_3) were obtained from Fisher Scientific Co. and were used without further purification. 2-Pyridinecarboxaldehyde and diethylenetriamine were purchased from Aldrich Chemical Co. and were distilled prior to use. Carbonate-free potassium hydroxide (2 M KOH) was obtained from J. T. Baker Chemical Co. and was used as obtained or diluted with CO_2 -free doubly glass-distilled water. High-purity oxygen, argon, and hydrogen gases were obtained from Airco Gas Products, Inc., and were used as received. All other chemicals and solvents used in this research were of reagent grade.

1,9-Bis(2-pyridyl)-2,5,8-triazanonane Trihydrochloride (PYDIEN-3HCl). This ligand was synthesized by a modification of the method of Harris et al.³⁸ 2-Pyridinecarboxaldehyde (0.20 mol) and diethylenetriamine (0.10 mol) were dissolved in 300 mL of absolute ethanol, and the mixture was heated to 50.0 °C for 20 min. The solution was then hydrogenated at room temperature over 10% platinum on activated carbon at slightly higher than 1 atm of hydrogen pressure. After the calculated volume of hydrogen was absorbed in the reaction, the catalyst was removed by filtration and the filtrate was saturated with hydrogen chloride until no additional colorless precipitate formed. The precipitate was filtered upon cooling, washed with absolute ethanol, and dried over potassium hydroxide pellets under vacuum. The trihydrochloride was recrystallized three times from ethanol and water; mp 213–216 dec. The pK_a values and molecular weight of the pure compound correspond to the previously reported values.

8-(2-Pyridyl)-1,4,7-triazaoctane Tetrahydrochloride. This ligand was prepared by modifying the procedure described by Harris et al.³⁸ 2-Pyridinecarboxaldehyde (5 mmol) and ethylenediamine (5 mmol) were dissolved in 100 mL of absolute ethanol, and the mixture was heated at 50.0 °C for 10 min. The resulting solution was hydrogenated and the ligand isolated and purified as described above for 1,9-bis(2-pyridyl)-2,5,8-triazanonane trihydrochloride; yield 80%; mp 206–208.

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{N}_4 \cdot 4\text{HCl}$: C, 35.29; H, 6.47; N, 16.20. Found: C, 35.20; H, 6.52; N, 16.20.

(μ -Peroxobis(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] Tetrabromide. A modified procedure similar to that of Timmons et al.³⁹ was employed. Sodium bromide (0.050 mol) and 50 mol of ethanolic 0.20 M 1,9-bis(2-pyridyl)-2,5,8-triazanonane (0.010 mol of free base) were added to 100 mL of absolute ethanol. The dissolved oxygen was removed by refluxing the solution under a stream of argon for 1 h. An ethanolic solution of cobaltous bromide (0.010 mol) was added to the cooled solution. A crystalline product formed only upon slow exposure of the solution to oxygen. The black crystalline product was filtered and washed with absolute alcohol.

Chloro(1,9-bis(2-pyridyl)-2,5,8-triazanonane-1,8-diene)cobalt(III) Perchlorate and Chloride Salts. 2-Pyridinecarboxaldehyde (0.025 mol), diethylenetriamine (0.013 mol), and 3.0 mL of triethyl orthoformate were dissolved in 30 mol of oxygen-free absolute alcohol. The solution was refluxed under argon for 30 min. An ethanolic solution of cobaltous chloride (0.013 mol) and 2.0 mL of triethyl orthoformate were added to the refluxing solution. After 12 h under argon, no precipitate was observed; however, a small amount of red-brown precipitate formed on exposure of the solution to oxygen. The precipitate of the chloride salt was filtered from the brown solution and washed with cool absolute ethanol. A water-ethanol solution containing sodium perchlorate (0.050 mol) was added dropwise to the filtrate, and a precipitate formed immediately. This complex was isolated and recrystallized from an etha-

not-water mixture by slow evaporation. The infrared spectrum showed an absorption band near 1600 cm^{-1} corresponding to the conjugated $\text{C}=\text{N}$ stretching vibration. The combined yield of the chloride and perchlorate salts was near 100%.

Instruments. Infrared absorption spectra were determined on potassium bromide pellets with a Pye Unicam Model 3-200 infrared spectrophotometer. UV-vis spectra and kinetics were measured with a Perkin-Elmer Model 553 Fast Scan UV-vis spectrophotometer.

Oxygenation and Redox Rearrangement of the Dioxygen Complex. Cobaltous chloride (0.010 mol) and 1,9-bis(2-pyridyl)-2,5,8-triazanonane trihydrochloride (0.010 mol) were dissolved in 50 mL of water at 35.0 °C with an ionic strength of 2.0 M adjusted with KCl. Carbonate-free potassium hydroxide (2.0 M) was added to maintain the p[H] at 11 (in this paper $-\log [\text{H}^+]$ is employed, with the designation p[H], rather than the less useful quantity $-\log a_{\text{H}^+}$, designated as pH), while CO_2 -free oxygen was bubbled through the reaction mixture. From this solution a red-brown precipitate formed. A similar experiment was performed on a solution having 2.0 M ionic strength with potassium nitrate as supporting electrolyte. A precipitate was obtained from this reaction also, and infrared spectra were taken of both solid oxidation products to determine the presence or absence of a $\text{C}=\text{N}$ stretching vibration resulting from oxidation of the ligand.

Thin-Layer Chromatography and Product Identification. Preparation of Reaction Mixtures. For thin-layer chromatographic separation and analysis two types of reaction mixtures were studied. The first type consisted of 1,9-bis(2-pyridyl)-2,5,8-triazanonane trihydrochloride (0.096 mmol) and anhydrous cobaltous chloride (0.011 mmol) dissolved in 1.0 mL of water at 35.0 °C, and the mixture was adjusted to 1.0 M ionic strength with potassium chloride and adjusted to p[H] 11.5 with 1.0 M carbonate-free potassium hydroxide under aerobic conditions. In order to minimize precipitation, an 8-fold excess of ligand was present in the solution.

In the second type of reaction mixture, (μ -peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] tetrabromide (0.010 mmol) was dissolved in 10 mL of water at 35.0 °C, and the mixture was adjusted to 1.0 M ionic strength with potassium chloride and adjusted to p[H] 11.0 with 1.0 M carbonate-free potassium hydroxide.

Reaction Mixture Workup. Isolation of the oxidation products involved removal of the metal from solutions described previously after 2–3 half-lives of decomposition of the dioxygen complex. The cobalt(III) was reduced in an air-tight glass apparatus to the divalent state in a solution adjusted below p[H] 1.0 under an argon atmosphere. The solution was poured over amalgamated zinc, and argon was bubbled through the solution for 30 min. The zinc amalgam was filtered off and the filtrate saturated with hydrogen sulfide. The p[H] was raised to between 8 and 9 by addition of potassium hydroxide, and a precipitate of CoS formed. The precipitate was separated off, and the colorless filtrate was either acidified and evaporated to dryness or extracted with methylene chloride and the methylene chloride layer dried with sodium sulfate.

Separations. Thin-layer chromatographic separations were obtained by the use of precoated silica gel 60 F_{254} on a plastic support with a layer thickness of 0.20 mm. The developing solutions for TLC were 9:1 and 8:2 v/v mixtures of chloroform and isopropylamine, respectively. A UV source, Mineralight UVS-11, or iodine vapor was used to develop and observe the separated zones.

Kinetics. a. Aerobic Reactions. Reaction rates were measured on solutions of the complex formed by the addition of CoCl_2 to a slightly acidic, dioxygen-saturated solution of the ligand, adjusted to 0.10 M ionic strength with KCl, with a 1:1 molar ratio of PYDIEN to cobalt. The solutions were adjusted to p[H] values between 5 and 11 by the addition of CO_2 -free 0.100 M KOH. A CO_2 -free dioxygen atmosphere was maintained under these conditions, and the reaction that occurred was followed spectrophotometrically. The concentrations of solutions for kinetic measurements ranged from 10^{-3} to 10^{-4} M.

b. Anaerobic Conditions. At p[H] 11.10, after dioxygen complex solution was obtained as described above, all excess dioxygen was removed with a flow of argon for a period of 30 min or more. A portion of the resulting solution was transferred to a 1.00-cm quartz cell for spectrophotometric analysis. The samples were maintained at constant temperature in the range 25.0–50.0 °C by the use of a jacketed reaction cell and a jacketed cell holder connected to a thermostated water bath.

The absorbance data were taken by observing the decrease in intensity of the strong ligand-to-metal charge-transfer band at 320 nm ($\pi^*_{\text{O}_2} \rightarrow d_{\pi}$).

Results

The oxygenation of aqueous solutions containing cobalt(II) and 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN, **1**) as a function of time is shown in Figure 1. The initial uptake of 0.50 mol of dioxygen/mol of cobalt(II) complex indicates the initial formation

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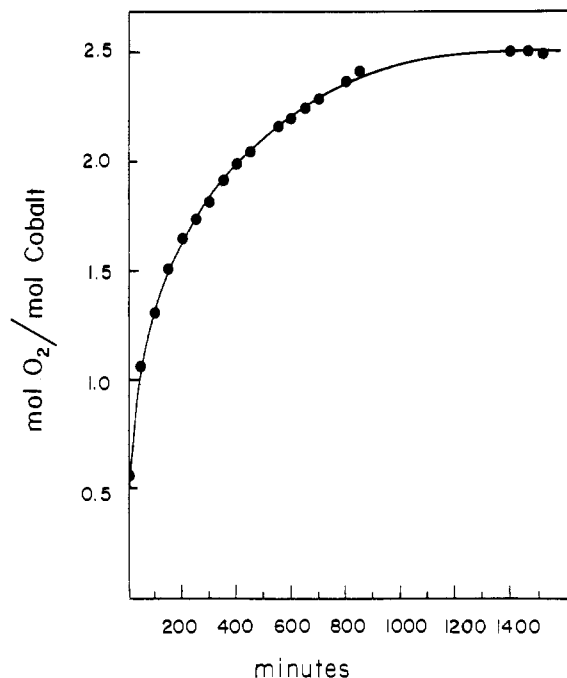


Figure 1. Dioxygen uptake at 35.0 °C under 1 atm of O₂ by a solution of PYDIEN-Co(II) at p[H] 11.0.

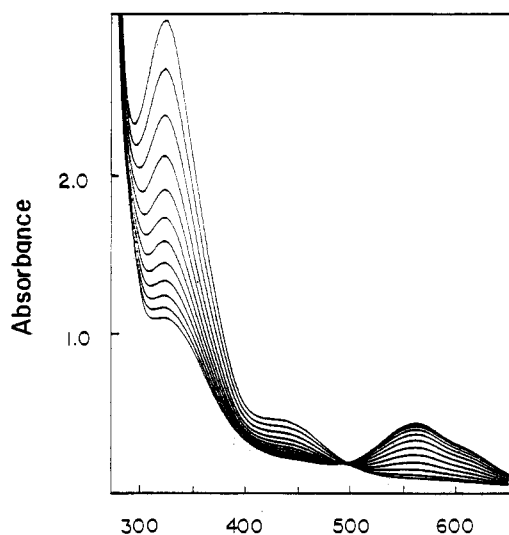


Figure 2. Variation of the absorbance with time of a solution of 0.83×10^{-3} M (μ -peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] at 35.0 °C, p[H] 11.1, $\mu = 0.10$ M (KCl), and time intervals of 4.0 min. Initial curve at zero time is shown at top left.

of the μ -peroxo-bridged dioxygen complex, but slower oxygen uptake is observed beyond the stoichiometric amount needed for the formation of the μ -peroxo cobalt(III) complex. Equilibrium studies of the μ -peroxo cobalt(III) complex with PYDIEN (1) as the ligand, with the aid of the program BEST,⁴⁰ indicate that it is fully formed at and above p[H] 2.4.

The absorbance spectra taken as a function of time of an oxygenated 1:1 Co:PYDIEN solution from which all excess dioxygen had been removed are illustrated in Figure 2. The strong absorbance band at 320 nm, which decreases in absorbance with time, is the ligand-to-metal charge-transfer band (LMCT $\pi^*_{O_2} \rightarrow d_x$) for the μ -peroxo-bridged cobalt(III) complex. A new absorbance band at 560 nm that increases with time does not correspond to cobalt(II) solutions with PYDIEN at identical hydrogen ion concentrations. The presence of an isobestic point in the absorbance spectrum indicates that the concentration of

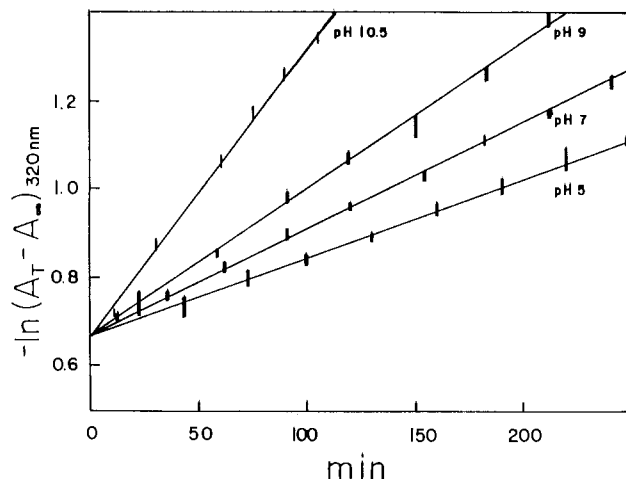


Figure 3. Pseudo-first-order plots for the disappearance of $[(Co(PYDIEN))_2O_2]^{4+}$ at 35.0 °C and 0.10 M ionic strength.

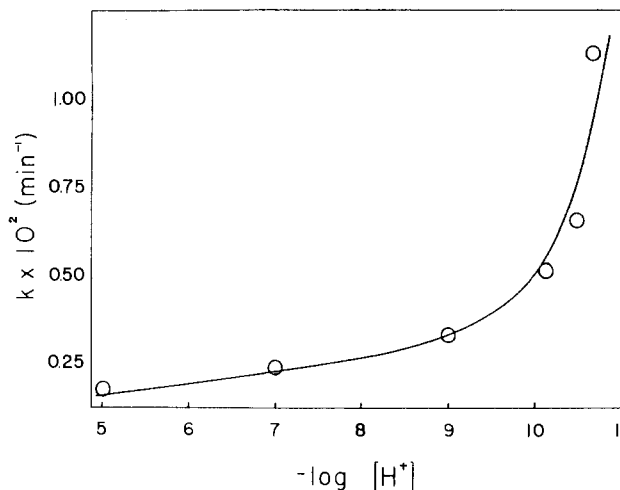


Figure 4. Variation in the rate constant for the disappearance of the LMCT ($\pi^*_{O_2} \rightarrow d_x$) as a function of p[H] for (μ -peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)].

the μ -peroxo-bridged cobalt(III) dioxygen complex is inversely related to the concentration of product formed and that no appreciable concentration of intermediate is present.

The product of the first redox rearrangement with an absorbance maximum at 560 nm completely disappears within the time of mixing on addition of excess dioxygen. Reoxygenation produces a complex with an adsorption spectrum that possesses a characteristic charge-transfer band different from that recorded for the original μ -peroxo-bridged cobalt(III) complex. A new ligand-to-metal charge-transfer band may exist at higher energy but cannot be identified because of the intense ligand absorptions at high frequency. The change in the absorbance spectrum at 320 nm provides an accurate measure of the rate of the initial step in the intramolecular oxidation process, regardless of the relative rates of subsequent reoxygenations. It was found that the spectral changes can be described by a pseudo-first-order rate equation, which after integration is expressed by

$$k_{\text{obsd}}t = -\ln(A_t - A_\infty) + C \quad (1)$$

where A_t and A_∞ are absorbances at 320 nm at any intermediate time and at infinite time, respectively. Values of k_{obsd} were determined by plotting $\ln(A_t - A_\infty)$ vs. time. Both the linearity of these plots (Figure 3) and the invariance of k_{obsd} with respect to changes in the initial concentration of the μ -peroxo-bridged cobalt(III) dioxygen complex support the proposed order of the reaction. Simple first-order dependence on hydrogen ion or hydroxide ion concentration was not observed in the range of p[H] from 5 to 9 in the system studied. The rate constants for the first step in the reaction demonstrate complex behavior with respect

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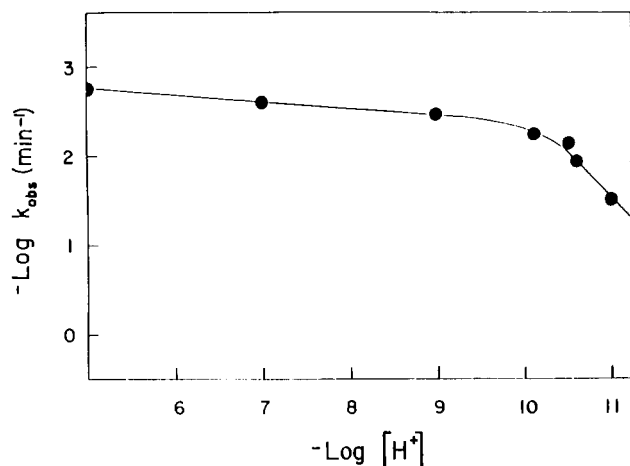


Figure 5. Plot of $-\log k_{\text{obs}}$ vs. $p[\text{H}]$ for the oxidative rearrangement of the μ -peroxo-bridged PYDIEN cobalt(III) dioxygen complex at 35.0 °C and $\mu = 0.10 \text{ M}$ (KCl).

to hydrogen ion concentration, with sharp increases in the rate constant above $p[\text{H}]$ 10, as can be seen in Figure 4. The dependence on hydroxide ion concentration may be expressed by eq 2. Thus higher order behavior is observed above $p[\text{H}]$ 10.

$$\text{rate} = k'[\mu\text{-peroxo}][\text{OH}^-]^n \quad (2)$$

With the assumption that the rate of reaction expressed by eq 2 is dependent on only the concentrations of the μ -peroxo-bridged cobalt(III) dioxygen complex and hydroxide ion, the plot of $-\log k_{\text{obs}}$ vs. the $p[\text{H}]$ should give the order n of the reaction with respect to hydroxide concentration. Both the linearity of this plot shown in Figure 5 and a slope of unity indicate first-order dependence in the hydroxide ion concentration above $p[\text{H}]$ 10.

Although an intermediate complex with an absorbance band at 560 nm cannot be detected in the presence of oxygen, the change in the absorbance spectrum at 320 nm in the absence of dioxygen provides an accurate measure of the rate of the initial step in the oxidative rearrangement. Under both aerobic and anaerobic conditions, the spectral changes can be described by the same pseudo-first-order rate equation. Thus at $p[\text{H}]$ 11.0 the calculated rate constants are $4.80 \times 10^{-4} \text{ s}^{-1}$ for the decrease at 320 nm in the absence of excess dioxygen, $7.0 \times 10^{-4} \text{ s}^{-1}$ for the increase at 560 nm in the absence of excess dioxygen, and $5.26 \times 10^{-4} \text{ s}^{-1}$ for the decrease at 320 nm in the presence of dioxygen. The close agreement of pseudo-first-order rate constants indicates that the initial reactions in the presence of and absence of dioxygen are exactly the same. If one excludes the measurement at 560 nm because of the lower accuracy in measuring this relatively weak band, the initial rate constant can be taken as $(5.0 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$. The rate constant did not vary with the changes in initial cobalt dioxygen complex concentration.

The oxidative rearrangement in the absence of dioxygen of the μ -peroxo-bridged cobalt(III) dioxygen complex was also monitored by polarographic techniques. Examination of the complex absorbing at 560 nm in a polarographic cell at 35.0 °C and $p[\text{H}]$ 11 gave no evidence for hydrogen peroxide or dioxygen, indicating that at such high $p[\text{H}]$ the formation of the dioxygen complex is sufficiently irreversible to degassing with argon that essentially all excess free dioxygen may be considered removed. A sampled dc polarogram for the potential of the absorbing species at 560 nm showed a negative current, indicating that the oxidatively rearranged cobalt compound is a cobalt(II) complex. Figure 6 shows the differential pulse polarograms at constant $p[\text{H}]$ for the initial cobalt(II) complex, the μ -peroxo-bridged cobalt(III) complex, the initial cobalt(II) oxidative-rearrangement product, and the oxidative-rearrangement product after reoxygenation. The μ -peroxo-bridged cobalt(III) dioxygen complex after the oxidative rearrangement has a negative shift of 30 mV for the observed reduction potential (Co(II)/Co(III)). Addition of dioxygen to the cobalt(II) product forms a new complex, resulting in a negative potential shift of 250 mV. A linear relationship for the decrease

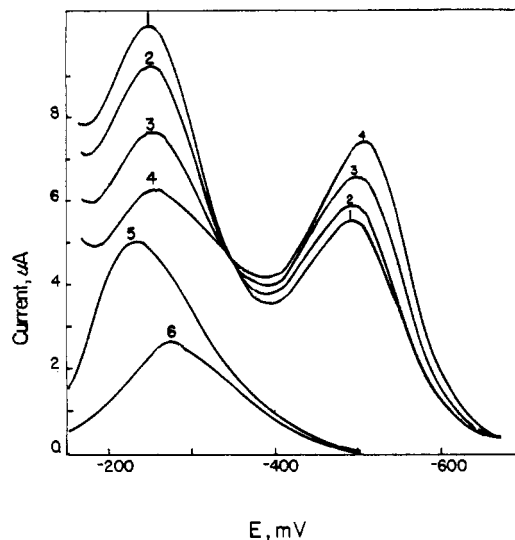


Figure 6. Differential-pulse polarograms of degassed solutions at $p[\text{H}]$ 11.0 after μ -peroxo complex formation: curve 1, one cycle of oxidative dehydrogenation; curve 2, addition of 0.100 mL of aerated H_2O ; curve 3, addition of 0.100 mL of aerated H_2O ; curve 4, addition of 0.100 mL of aerated H_2O ; curve 5, $[\text{Co}(\text{C}_{16}\text{H}_{23}\text{N}_3)\text{OH}_2]^{2+}$; curve 6, $[(\text{Co}(\text{C}_{16}\text{H}_{23}\text{N}_3)_2\text{O}_2)]^{4+}$. Potentials were measured vs. SSCE.

in concentration of the first oxidative-degradation product to the increase in concentration of the newly oxygenated complex is illustrated in Figure 6.

Solutions were also analyzed for hydrogen peroxide by standard iodide titrations and polarography, but hydrogen peroxide was not detected before or after 2 half-lives of the decomposition reaction. When hydrogen peroxide was added to the reaction mixture after the completion of the oxidative-rearrangement reactions, the appropriate H_2O_2 wave appeared at about -950 mV and remained detectable for over 10 h. With such a long persistence time, any hydrogen peroxide produced in the reaction would have been detected electrochemically or chemically.

The absence of dioxygen was also demonstrated through the absence of the corresponding reduction wave. Although Co-PYDIEN dioxygen complex formation is reversible, it is apparent that at $p[\text{H}]$ values far above that necessary for complete formation the concentration of oxygen at equilibrium is immeasurably low and purification of the oxygenated complex by degassing does not result in measurable dissociation over a short period of time. Further, the lack of an oxygen wave demonstrates the absence of hydrogen peroxide formation followed by disproportionation due to possible catalase activity of any cobalt complex that might have been formed. Thus the absence of dioxygen and peroxide in the reaction mixture indicates that the bridging peroxide is reduced to water. Dissociation of hydrogen peroxide followed by rapid reduction to water is not likely because the cobalt(II) complex that has been shown to be formed in the oxidative rearrangement would be easily oxidized to a cobalt(III) complex by hydrogen peroxide in the solution. Therefore, the first step in the oxidative rearrangement involves direct reduction of the coordinated dioxygen to water.

Product analysis on decomposition of the μ -peroxo-bridged cobalt(III) complex in an aqueous solution at $p[\text{H}]$ 11.0 indicates oxidative dehydrogenation of the coordinated ligands. The R_f values of the zones in the TLC separation are listed in Table II along with those of standard samples. The possibility that the oxidation of the ligand may take place without the coordinated metal ion was eliminated by analyzing the reaction products from an experiment with the same conditions as those employed in the ligand oxidation experiment, but in the absence of the metal ion. After 48 h, well beyond the time span of the oxidation reaction, no decomposition of the ligand could be detected by TLC analysis. If oxidative dehydrogenation occurs, imine formation would be expected and such groups would hydrolyze to produce the corresponding aldehyde and primary amine. Thus the identification

Table II. R_f Values Obtained from Thin-Layer Chromatographic Separation of Standard Compounds and Dehydrogenation Products of (μ -Peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)]

compd	R_f values	
	80:20 ^a	90:10
products separated from reaction mixture	0.73	0.67
	0.63	0.42
	0.52	0.20
	0.35	
	0.24	0.10
	0.10	0.01
	0.04	
1,9-bis(2-pyridyl)-2,5,8-triazanonane	0.23	0.10
8-(2-pyridyl)-1,4,7-triazaoctane	0.03	
2-pyridinecarboxaldehyde	0.73	0.68
diethylenetriamine		

^a Ratio of chloroform:isopropylamine, v/v.

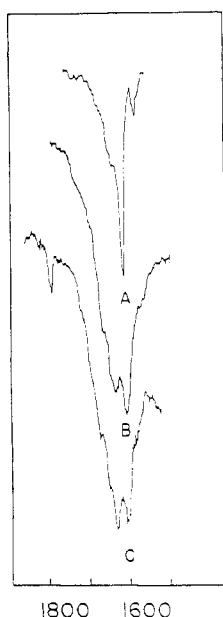
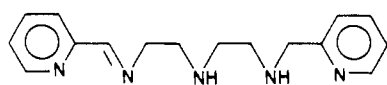


Figure 7. Infrared spectra (KBr pellets; cm^{-1}) of (A) (μ -peroxo)bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] tetrabromide, (B) chloro(1,9-bis(2-pyridyl)-2,5,8-triazanonane-1,8-diene)cobalt(III) nitrate, and (C) the cobalt(III) oxidative-dehydrogenation product.

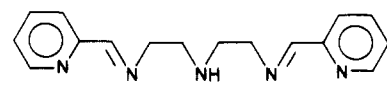
of 2-pyridinecarboxaldehyde and 8-(2-pyridyl)-1,4,7-triazaoctane in the product mixture supports oxidative dehydrogenation of the ligand PYDIEN in the dioxygen complex to form the monoimine **2**. The unidentified zones may well be the mono- and diimines



1,9-bis(2-pyridyl)-2,5,8-triazanon-1-ene (**2**)

that have not hydrolyzed; however, other oxidation products cannot be ruled out.

Attempts to isolate pure samples of the oxidized complexes from the reaction mixture have not been successful. However, IR spectra of the crude brown precipitate formed either in 2.0 M ionic strength nitrate or in potassium chloride solution at $\text{p[H]} = 11$ containing 0.010 M initial cobalt and ligand concentrations developed an absorption band with a frequency of 1630 cm^{-1} . Figure 7 compares the IR absorptions between 1500 and 1800 cm^{-1} of (A) the (μ -peroxo)dicovalent(III) complex, (B) the cobalt(III) complex of the oxidized ligand **3**, chloro(1,9-bis(2-pyridyl)-



1,9-bis(2-pyridyl)-2,5,8-triazanon-1,8-diene (**3**)

Table III. Infrared Frequencies (cm^{-1}) of Metal Imine Complexes

complex ^a	C=N	pyridine ring	ref
[Co(PY-DPT)I]·H ₂ O	1615	1595	41
[Co(PY-DPT)(NCS)]NCS·H ₂ O	1635	1591	41
[Co(PY-DPT)(NCSe)](NCSe)	1630	1595	41
[Co(PY-DPT)Br]Br·H ₂ O	1630	1605	41
[Co(PY-DPT)](PF ₆) ₂	1630	1595	41
[Co(PY-DPT)(NO ₃)]NO ₃ ·H ₂ O	1628	1600	41
[Co(PY-DPT)Cl]·H ₂ O	1625	1595	41
PY-DPT	1644	1587	41, 42
analogous Ni(II) complexes	1635–1648		42
analogous Mn(II) complexes	1645–1655		43
[Cu(Salam) ₂]-oxidized product	1625		44
oxidation product of dicopper	1630		45
30-member macrocyclic complex			

^a PY-DPT = 1,11-bis(2-pyridyl)-2,6,10-triazaundeca-1,10-diene; Salam = salicylideneamine.²⁸

2,5,8-triazanon-1,8-diene)cobalt(III) nitrate, which is the conjugated Schiff base complex derived from 1,9-bis(2-pyridyl)-2,5,8-triazanonane, and (C) the experimental oxidative rearrangement reaction product. The band at 1630 cm^{-1} is assigned to the imine stretching vibration of the redox-rearrangement product and is similar to other imine frequencies, as shown in Table III. The data in Figure 7 and Table III support the conclusion that PYDIEN undergoes oxidative dehydrogenation to the corresponding mono- and diimines.

Discussion

Given the oxidized cobalt(III)-reduced oxygen(-I) formalism for the μ -peroxo-bridged cobalt complex, the loss of the coordinated μ -peroxo group would not change the formal oxidation state of the cobalt and loss of the coordinated (reduced) dioxygen would therefore be an irreversible step. The resulting cobalt(III) complex would then be inert with respect to further reaction with dioxygen. The fate of the dioxygen may involve further reduction by the coordinated ligand or simple separation as hydrogen peroxide.

On the other hand, it is obvious from Figure 4, and sampled dc measurements, that after oxygenation of the initial cobalt(II) complex there is anaerobic intramolecular electron transfer to produce a new cobalt(II) complex, which then may be oxygenated to form a new complex with an observed potential at -510 mV vs. SSCE. This behavior indicates the formation of a Co(II) imine complex, which then undergoes reoxygenation. Although formation of imine groups reduces the basicity of the ligand, it is still sufficiently basic to promote dioxygen complex formation. The linear correlation of peak reduction potentials of dioxygen complexes vs. $\log K_{\text{O}_2}$ ⁴⁶ indicates that, with a potential of -510 mV vs. SSCE, the oxygenated cobalt complex with the (oxidized) imine ligands is reasonably stable. The increased conjugation of the ligand with consequent increased planarity as well as an increase in the tendency toward π bonding would be expected to contribute to the stability of the dioxygen complex.⁴ Since the evidence presented above indicates that hydrogen peroxide does not separate as an intermediate in the redox-degradation reaction, and since the complex formed in the first step definitely involves Co(II), the electron-transfer process must involve a concerted and probably sequential flow of four electrons to the coordinated dioxygen with simultaneous formation of two imine groups. Isolation of the monoimine **2**, of the ligand in the reaction mixture indicates that one imine group is formed on each of the coordinated ligands in the first oxidation cycle.

In principle, three secondary amino groups in PYDIEN may be oxidized to the corresponding Schiff bases. The more stable

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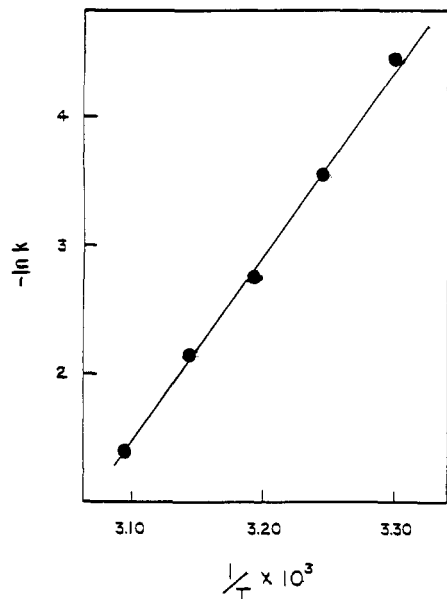


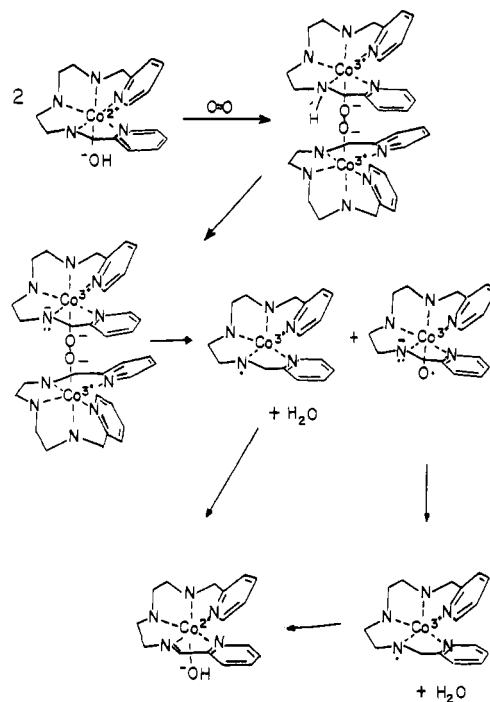
Figure 8. Plot of $\ln k$ vs. $1/T$ (T in K). From the slope, $E_a = 29.3$ kcal/mol.

Schiff bases are conjugated, and nonconjugated Schiff bases are more susceptible to hydrolysis in aqueous solution.⁴⁷ Furthermore, the IR frequency of the product isolated in the present investigation corresponds to frequencies of conjugated imine complexes of cobalt(II),⁴¹ nickel(II),⁴² manganese(II),⁴³ and copper(II)^{44,45} (see Table III). The data show that the product isolated does not have an imine group at the central secondary nitrogen, since its frequency would be considerably higher than that observed in Figure 7. This effect would shift the frequency of the central imine group to a value higher than that of a conjugated imine. The identification of 8-(2-pyridyl)-1,4,7-triazaoctane from TLC analysis provides additional evidence that a conjugated monoimine, **2**, is produced in the reaction mixture. It is also evident from the oxygen uptake experiments that the conjugated diimine **3** is the final dehydrogenation product.

From an Arrhenius plot of $-\ln k$ vs. T^{-1} (Figure 8) for the oxidative rearrangement reaction, an activation energy E_a was calculated. The linearity of the plot suggests that probably only one reaction is involved in the first stage of the reaction. In view of the destruction of the peroxy group in the oxidative-degradation reaction and the formation of two mononuclear cobalt(II) complexes, it is reasonable to expect that the value of ΔS be positive, corresponding to the increase of the number of particles in the activated complex. The second oxidative-rearrangement cycle would be expected to be similar to the first, in view of the fact that the dioxygen affinity is not greatly reduced by the formation of the imine double bond in the coordinated ligand.

Reaction Mechanism. The oxidative dehydrogenation of the coordinated amine ligand to an imine is necessarily a two-electron-transfer process, which may proceed by two successive one-electron transfers or by a two-electron transfer to form the imine group and H_2O . With polyamine ligands the overall reaction may involve the formation of the diimine by two successive two-electron transfers to coordinated oxygen (see Scheme I). The individual steps in this four-electron-transfer process usually require oxidation and reduction of the coordinated metal ion. As the conjugated system builds up in the oxidation process, the affinity of the ligand for cobalt(II) decreases, thus effecting a change in the activation of dioxygen and possibly offering an explanation for the slowing of the rate of dehydrogenation as the reaction proceeds. 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

Scheme I

Table IV. pK_a 's for Coordinated Amine Protons

complex ^a	pK_a (amine proton)	no. of pyridyl groups	ref
$[Os(en)_3]^{3+}$	5.8	0	16
$[Ru(bpy)_2(AMPY)]^{3+}$	2.4	5	47
$[Ru(NH_3)_5(py)]^{3+}$	9	1	48
$[Ru(NH_3)_6]^{3+}$	13.1-12.4	0	49
$[Co(AMPY)_2]^{2+}$	9.94	2	50
$[Co(AMPY)(H_1AMPY)]^+$	11.03	2	50
$[Co(DPA)(H_2O)]^{2+}$	8.5	2	50

^a en = ethylenediamine; bpy = 2,2'-bipyridine; AMPY = 2-(aminomethyl)pyridine; py = pyridine; DPA = bis(2-pyridylmethyl)amine.

process without the formation of higher energy free-radical intermediates. The energy barrier in the electron-transfer pathway is lowered by an increase in $p[H]$, a tendency that may be attributed in part to base-assisted deprotonation of the coordinated amine. In this connection, a number of recent reports have indicated that deprotonation is a necessary prior step in oxidative dehydrogenation.^{15,16,22,29-32,34-37} The pK_a 's of the amine complexes of osmium(IV)¹⁶ and ruthenium(III)^{31,48-50} have been reported, and a direct correlation has been made between the ease of deprotonation and the increased number of pyridyl groups in the coordinated ligands in the ruthenium(III) complexes. These results can be seen in Table IV along with proposed deprotonations in anaerobic cobalt(II) systems with 2-(aminomethyl)pyridine and bis(2-pyridylmethyl)amine.⁵¹

It has been pointed out that there is a marked increase in the rate of oxidative rearrangement as the value of $p[H]$ is raised to 10 and higher. This value of $\log [H^+]$ is close to the pK_a 's of the analogous anaerobic cobalt(II) systems in Table IV. With the μ -peroxy intermediate, an increase in hydroxide concentration to raise the $p[H]$ of the solution to near the pK_a of a coordinated amine will lower the activation energy for the oxidative dehydrogenation reaction, since a negative charge on the coordinated nitrogen would be expected to assist transfer of electrons to the dioxygen through the coordinated metal ion.

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The oxidative dehydrogenation of coordinated ligands is seen generally to produce only conjugated imines. Although different metal ions may involve different mechanisms for dehydrogenation, the buildup of conjugated systems can provide a low-energy pathway for an intramolecular oxidation. Future work in progress involves a study of the oxidative dehydrogenation of cobalt(II) complexes of 1,11-bis(2-pyridyl)-2,6,10-triazaundecane and 2-(aminomethyl)pyridine, with the use of fast-atom-bombardment

mass spectra as well as the techniques described above.

Acknowledgment. This research was supported by Grant A-259 from the Robert A. Welch Foundation.

Registry No. [(Co(PYDIEN))₂O₂]Br₄, 93983-48-3; chloro(1,9-bis(2-pyridyl)-2,5,8-triazanona-1,8-diene)cobalt(III) perchlorate, 93894-83-8; chloro(1,9-bis(2-pyridyl)-2,5,8-triazanona-1,8-diene)cobalt(III) chloride, 93894-84-9.

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Basic Methanolysis of (CF₃PCF₂)₂: New Bis(phosphino)difluoromethanes and (Difluoromethyl)phosphines. NMR Resolution of Double-Phosphine Diastereomers

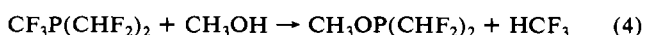
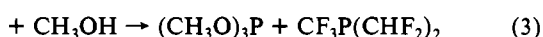
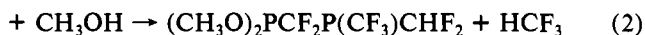
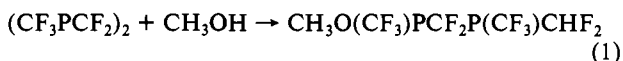
ANTON B. BURG

Received April 11, 1984

The methoxide-catalyzed methanolysis of (CF₃PCF₂)₂ converts first the highly strained cis isomer (and then the trans), opening the ring to form CH₃O(CF₃)PCF₂P(CF₃)CHF₂ (abbreviation: "MeOPCP"). The secondary attack occurs at the CH₃OPCF₃ group to form HCF₃ and (MeO)₂PCP. Further P-C bond cleavages occur at various points, forming (CH₃O)₃P, CH₃OP(CHF₂)₂, (CH₃O)₂PCHF₂, and CF₃P(CHF₂)₂, disproportionation of which leads to P(CHF₂)₃. The highly vulnerable CH₃OP(CF₃)CHF₂ is not observed. HCl replaces CH₃O by Cl on P, with P₄O₁₀ promoting the process by removing CH₃OH. Then either MeOPCP or ClPCP is converted, by base-catalyzed action of Zn(CH₃)₂, to MePCP, which forms a nonpolar BH₃ complex. Similarly, CH₃OP(CHF₂)₂ is chlorinated to ClP(CHF₂)₂, convertible by (CH₃)₂NH to (CH₃)₂NP(CHF₂)₂. The ¹H NMR spectra of the CHF₂ groups in MeOPCP, ClPCP, MePCP, and MePCP·BH₃ show the expected P-chiral diastereomers as interlaced but resolvable triplets of doublets. The ¹⁹F spectra of their CF₂ groups are separable and roughly interpretable as AB systems, except that F_A and F_B for P-CF₂-P are superposed in MePCP—but resolved in its BH₃ complex. These AB spectra, as well as those for most of the new RP(CHF₂)₂ compounds, are more complex at the fine-structure level, and not yet fully interpreted.

The base-catalyzed hydrolysis of P-CF₃ compounds, yielding P-OH compounds and HCF₃,¹ implies that a methoxide-catalyzed methanolysis of the P-CF₃ bond would give P-OCH₃ compounds and HCF₃. Similarly, any P-CF₂-P compound might be cleaved to form P-OCH₃ and HCF₂-P compounds. Thus an extensive methanolysis of either the cis or the trans isomer of (CF₃PCF₂)₂² could be expected to involve both reaction types, including ring cleavage to form open-chain P-CF₂-P compounds, convertible to interesting monophosphines. At each stage, one P-C bond could be more vulnerable than the others, according to rules worthy of discovery.

Indeed, a series of such methanolyses, using deficient portions of methanol, with removal of the volatile products at each stage and identification of these by NMR spectra, showed strong preference for four successive reactions:



all occurring in the presence of the catalyst NaOCH₃.

The rates of these reactions are not very different, for the methanol-deficient experiments showed some formation of the products of reactions 3 and 4 before reaction 1 was complete. The main rules of selective reactivity here seem to be as follows:

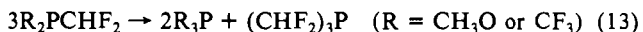
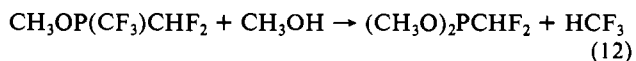
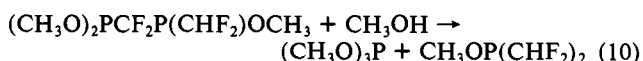
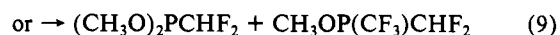
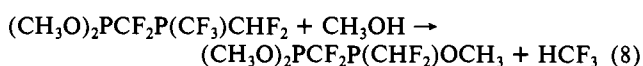
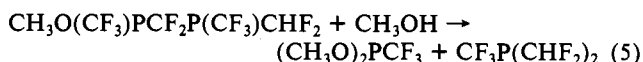
1. Cleavage of the strained ring occurs exclusively before P-CF₃ cleavage. Indeed, using a mixture of the isomers, one observes

complete elimination of the more strained cis form before much of the trans form has been consumed.

2. Attack at the methoxylated P atom is strongly favored.

3. Usually, P-CF₃ cleavage would be expected to occur before any P-CF₂X cleavage (cf. reaction 4; indeed, CH₂F₂ never was observed), but rule 1 governs reaction 1 and rule 2 governs reactions 2 and 3.

Although these rules seem very strong, some minor products indicate exceptions. All of the following possible processes would be expected to occur at least infinitesimally.



Indeed, it may be suggested that the phosphines from reactions 9, 11, and 12 are formed by no other processes.

Reaction 13, an unexpected catalyzed disproportionation, was indicated by the frequent appearance of the ¹⁹F and ³¹P NMR spectra of P(CHF₂)₃ in crude CF₃P(CHF₂)₂.

Parallel to reaction 3 is a process yielding a nonvolatile oil, often representing as much as half of the phosphorus material. This

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