prisms from a benzene/hexane mixture. The infrared spectrum of the complex $PtCl(t\text{-}Bu_2PCMe_2CH_2)(CO)$ showed a band of 2055 cm^{-1} due to a terminal carbonyl group. Analytical and spectral data of the complex are given in the tables.

(d) With Dimethyl Sulfide. To a solution of dimeric complex **1** in benzene was added an excess of dimethyl sulfide, and the reaction mixture was stirred at room temperature for $\simeq$3 h. The solvent was removed, and the proton NMR spectrum of the resulting product was recorded in $CDCl_3$. This showed the presence of 1 molar equiv of Me_2S complexed to platinum, confirmed by the appearance of ^{195}Pt satellites [J(Pt–H) = 22 Hz] for the methyl signals. During the attempted crystallization of the complex from benzene/hexane, dimethyl sulfide was found to be displaced and the starting material **2** crystallized out.

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Registry No. **1**, 63230-78-4; **2a**, 74523-69-6; **2b**, 74523-70-9; **5** (L = PEt_3), 74482-66-9; **5** (L = P-*i*-Pr_3), 74482-67-0; **5** (L = P-c-Hx_3), 74482-68-1; **5** (L = P-*t*-Bu_2Me), 74482-69-2; **5** (L = PPh_2Me), 74482-70-5; **5** (L = PPh_3), 74482-71-6; **5** (L = PPh_2-*t*-Bu), 74482-72-7; **5** (L = $AsPh_3$), 74482-73-8; **5** (L = CO), 74482-74-9; **5** (L = py), 74482-75-0; **5** (L = Me_2S), 74482-76-1; *cis*-PtCl(P-C)($P(OPh)_3$), 74482-77-2; *trans*-PtCl(P-C)($P(OPh)_3$), 74523-71-0; *cis*-PtCl(P-C)($SbPh_3$), 74482-78-3; *trans*-PtCl(P-C)($SbPh_3$), 74559-66-3; *trans*-$PtCl_2(NCPh)_2$, 51921-56-3; $[(Bu_3P)HgCl_2]_2$, 41665-95-6; *t*-Bu_3PHCl, 63197-35-3.

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Evidence for Cobalt(II) Catalysis and for an Intermediate Dioxygen Adduct in the Autoxidation of Cobalt(II) Chloride Complexes of Ethyl Phosphinite, Phosphonite, and Phosphite Esters[1]

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With use of the ligands L = $Et_nP(OEt)_{3-n}$, n = 0–2, the equilibrium constants and thermodynamic functions have been determined for the high-spin low-spin equilibria $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$ in benzene. In the autoxidation both of $CoCl_2L_2$ complexes and of $CoCl_2L_3 \rightleftharpoons CoCl_2L_2 + L$ equilibrium systems, all the L is converted to its phosphoryl derivative LO with no change in the value of n. In their initial stages the reactions are first order in cobalt complex; first-order dependence on oxygen was demonstrated in representative cases. The autoxidation rate constants for the high-spin $CoCl_2L_2$ complexes and the low-spin $CoCl_2L_3$ complexes are not very different; autoxidation of $CoCl_2(Et_3P)_2$ is 1 order of magnitude slower. For the n = 1 system, the 1:1 dioxygen adduct intermediate was prepared at a low temperature, and the stoichiometry and kinetics of its irreversible rearrangement were determined. In the proposed autoxidation mechanism, formation of the dioxygen adduct is the rate-determining step. Ligand redistribution equilibria make kinetics complex in the latter stages of the autoxidation. A catalytic cycle has been demonstrated in the autoxidation of triethyl phosphite under mild conditions.

Introduction

Tertiary aliphatic phosphines and phosphorus esters, $R_nP(OR)_{3-n}$, n = 0–3, react with dioxygen by a radical chain mechanism to give phosphoryl oxidation products.[2] With free radical or photoinitiation, tertiary phosphites (n = 0) are oxidized quantitatively to phosphates $P(O)(OR)_3$, but all the others give a mixture of oxidation products. For example, a phosphinite ester R_2POR gives some $RP(OR)_2$ and $P(OR)_3$ intermediates and $R_2P(O)OR$, $RP(O)(OR)_2$, and $P(O)(OR)_3$ final products.[3] This is because the mechanism[2] involves formation of intermediate phosphoranyl radicals, e.g., eq 1,

$$RO\cdot + R_2POR \rightarrow R_2\dot{P}(OR)_2 \tag{1}$$

which can decompose either by C–O bond rupture (eq 2a) to give a final phosphoryl product or by C–P bond rupture (eq 2b) to give a new trivalent phosphorus intermediate subject to further oxidation.

$$R_2\dot{P}(OR)_2 \rightarrow R_2P(O)OR + R\cdot \tag{2a}$$

$$\rightarrow RP(OR)_2 + R\cdot \tag{2b}$$

In contrast, it has been shown[4] that triethylphosphine in its cobalt(II) chloride complex $CoCl_2(Et_3P)_2$, in organic solvents, is oxidized quantitatively to the phosphine oxide complex $CoCl_2(Et_3PO)_2$ by a nonradical pathway. The proposed mechanism involves formation and decomposition of an intermediate cobalt(II)–dioxygen adduct, eq 3.

$$CoCl_2(Et_3P)_2 + O_2 \rightarrow O_2CoCl_2(Et_3P)_2 \rightarrow CoCl_2(Et_3PO)_2 \tag{3}$$

Triethylphosphine has the largest steric requirement of the four $Et_nP(OEt)_{3-n}$ ligands.[5] Its only cobalt(II) chloride complex is $CoCl_2(Et_3P)_2$, as has been shown by studies of the solid–vapor equilibrium system[6] and of solutions of the components in organic solvents.[7] It alone fails to participate in the high-spin (quartet state) low-spin (doublet state) equilibrium reactions, eq 4, the equilibrium constants for which

$$CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3 \tag{4}$$

have been reported[8] in *tert*-butylbenzene solution with the ligands L = $Et_nP(OEt)_{3-n}$, n = 0–2. All three types of species in the equilibrium mixture are susceptible to autoxidation. It is of interest to see what effect the differences in cobalt paramagnetism and coordination number will have on the rates and products of the reaction with dioxygen and to see if cobalt(II) chloride can bring about oxidation of large amounts of substrate in a catalytic cycle, as well as of stoichiometric amounts in the complexes. The postulated role of a cobalt–dioxygen adduct is also to be investigated. In all cases except n = 0, there is the possibility that autoxidation of free phosphorus ligand can be distinguished from autoxidation of coordinated ligand by detection of mixed phosphoryl products,

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some with changed values of *n*.[3]

Experimental Section

Materials. Diethyl ethylphosphonite $EtP(OEt)_2$ and ethyl diethylphosphinite Et_2POEt were prepared under nitrogen by the reactions of absolute ethanol with ethyldichlorophosphine and diethylchlorophosphine, respectively, in the presence of *N*,*N*-diethylaniline to take up the liberated hydrogen chloride. Commercially available triethyl phosphite was refluxed over sodium, which reacts with any diethyl hydrogen phosphonate impurity present. The three $Et_nP(OEt)_{3-n}$ esters were carefully fractionated: for $n = 0$, bp 152 °C (760 torr); for $n = 1$, bp 48 °C (17 torr), 137 °C (760 torr); for $n = 2$, bp 84 °C (150 torr), 132 °C (760 torr). Dichlorobis(triethylphosphine)cobalt(II) was prepared as described previously.[4] Solvents and other reagents were purified by standard methods. All transfers and preparations of solutions were conducted under Pre-Purified grade nitrogen in a Forma welded steel drybox with an evacuable lock; the box atmosphere was continuously circulated through a tower containing heated BTS catalyst[9] and through tubes packed with 4A, 5A, and 13A molecular sieves. Standard high-vacuum-line and Schlenk techniques were also used.[9]

Equilibrium Constants. The thermodynamic functions for the high-spin–low-spin equilibrium systems of eq 4 were determined in benzene solution by the precise application of the Evans NMR method in exactly the manner described previously.[8] The solutions were 0.01 M cobalt(II) chloride in benzene containing 5.00 vol % cyclohexane as the NMR reference. The ligand:cobalt(II) chloride mole ratios encompassed the ranges 3.100–3.400 with triethyl phosphite, 2.800–3.400 with diethyl ethylphosphonite, and 3.000–3.400 with ethyl diethylphosphinite. Densities of the solvent and solutions used in the NMR studies were measured dilatometrically as a function of temperature.[10] The NMR frequency shifts, $\Delta\nu$, of the various solutions were measured from 10 to 45 °C at 5° intervals.

Autoxidation Studies. Benzene solutions containing the desired substrate mixture and *o*-dichlorobenzene as the internal standard for GC analysis were placed in pear-shaped flasks immersed in a constant temperature (±0.5 °C) bath. Stopcocks could be turned in a gas manifold to admit nitrogen, oxygen, or dry air through a gas inlet tube terminating in a frit for the dispersion of fine bubbles. The gas exited through an efficient reflux condenser system and a bubbler; tests showed that variations in the rate of bubbling over a wide range had no effect on the kinetics, proving that the solutions remained effectively saturated during the reactions. Samples removed at various times were quenched with an excess of ethylenediamine. All volatile materials were quantitatively pumped off in the high-vacuum line and recovered for GC analysis. The first injection, on a UC W98 column at 100 °C, resulted in excellent separation of the solvent, all $Et_nP(OEt)_{3-n}$ compounds, and the internal standard. The second injection, on a Reoplex 400 column at 170 °C, resulted in excellent separation of the internal standard and all $Et_nP(O)(OEt)_{3-n}$ components.

Dioxygen Adduct Studies. In work at low temperatures, it was necessary to use *tert*-butylbenzene (mp −58 °C) as the solvent instead of benzene. Oxygen gas was bubbled for 1–2 h through an inlet tube into a green *tert*-butylbenzene solution of dichlorotris(diethyl ethylphosphonite)cobalt(II) in a multinecked flask at −46 °C (chlorobenzene slush bath) attached to a high-vacuum line. Physically dissolved oxygen was then completely removed by a series of −196 °C freeze, pump, −23 °C thaw cycles. For the EPR measurements, the cold solution was transferred by syringe techniques through a double-pointed steel needle to a quartz tube at −46 °C. The tube was then immersed in liquid nitrogen to give a *tert*-butylbenzene glass. The Varian E4 spectrometer was calibrated by using DPPH. For decomposition stoichiometry studies of the oxygenated and then degassed reaction mixture, the green solution was allowed to warm to room temperature, during which it turned blue irreversibly. In a typical experiment, the initial solution was 0.0894 M in $CoCl_2(EtP(OEt)_2)_3$, while analysis of the final reaction mixture showed 0.180 M $EtP(O)(OEt)_2$ and 0.0890 M $EtP(OEt)_2$. For the kinetic study of adduct decomposition, a solution was prepared similarly at −46 °C in a special glass apparatus which, after degassing, could be shut off, removed from the vacuum line, and rotated so that the cold solution would flow into a 1-cm quartz cuvette attached to the side. The entire apparatus would fit into the sample chamber of a Bausch and Lomb Spectronic 600 spectrophotometer. The temperature was regulated by circulation of methanol through a copper coil immersed in an appropriate cold bath and through the sample compartment; it was measured by using a mercury thermometer immersed in pure solvent in the reference cuvette. The kinetics of the green to blue transformation were followed in the range −9 to +11 °C by measuring the increase in absorbance at 550 nm. To avoid the zero time error caused by the need for thermal equilibration, we only used points on the smoothly increasing portion of the absorbance vs. time curve in the function (5), where A_1 represents an effective A_0 after the mixture

$$\ln\,[(A_\infty - A_1)/(A_\infty - A_t)] = k(t - t_1) \qquad (5)$$

has warmed to the specified temperature.

Results and Discussion

Equilibrium Constants. As has been shown,[8] the Evans equation can be written on a molar basis for the calculation of corrected molar magnetic susceptibilities; see eq 6, where

$$\chi_M^{\text{cor}} = \frac{3(\Delta\nu)(10^3)}{2\pi\nu M} + \chi_0(\text{MW}) + \frac{\chi_0(d_0 - d_s)(10^3)}{M} + \text{DC} \qquad (6)$$

$\Delta\nu$ is the difference in proton resonance frequencies (in an NMR spectrometer of frequency ν) of the cyclohexane (inert reference) in the presence and absence of paramagnetic solute, M is the molarity (adjusted for changes in solution density with temperature), MW is the molecular weight of the paramagnetic solute, d_0 is the density of the solvent, and d_s is the density of the solution. The χ_M^{cor}, MW, and DC values are known individually for each high-spin complex A and low-spin complex B. Weighted average values are to be used for the equilibrium mixtures of solute mole fractions N_A and N_B ($=1 - N_A$). Trial values of N_A are first obtained from the approximation (7). These are used to calculate trial values of

$$N_A \approx (\Delta\nu_{\text{obsd}} - \Delta\nu_B)/(\Delta\nu_A - \Delta\nu_B) \qquad (7)$$

$\overline{\text{MW}}$ and $\overline{\text{DC}}$ which in turn permit calculation of trial values of χ_M^{cor} by using eq 6. These lead to recalculated values of N_A according to eq 8 with reiteration until all values become constant.

$$N_A = \frac{\chi_M^{\text{cor}}(\text{obsd}) - \chi_M^{\text{cor}}(\text{B})}{\chi_M^{\text{cor}}(\text{A}) - \chi_M^{\text{cor}}(\text{B})} \qquad (8)$$

As described previously,[8] at each temperature for a series of samples whose phosphorus ester:cobalt(II) chloride mole ratios (MR) are known from preparation of the solutions, the final N_A values may be entered into the function (9) which

$$\text{MR} + N_A - 3 = (1/K_{\text{eq}})[(1 - N_A)/(N_A M)] \qquad (9)$$

is of the form $y = mx$. In a linear least-squares fit, the closeness of the correlation coefficient to unity and of the intercept to zero serve as tests of the method. On only 1 out of 24 occasions was one subset of data rejected because for it the intercept did not include zero within three standard deviations. In every case, the correlation coefficients exceeded 0.94. Next, a linear least-squares fit was obtained from the function (10) to give best values of the slope $-\Delta H°/R$ and the

$$\ln K_{\text{eq}} = -\Delta G°/RT = -\Delta H°/RT + \Delta S°/R \qquad (10)$$

intercept $\Delta S°/R$. These last values, incorporating all data points, were finally used in eq 10 to give smoothed values of the equilibrium constants at any temperature.

The equilibrium constants and thermodynamic functions in benzene solution are compared in Table I with the results previously obtained[8] for *tert*-butylbenzene solutions. The 25 °C equilibrium constants in that solvent are about 3 times larger than in benzene. In every case, the equilibrium constants decrease with increasing temperature as the reactions

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(9) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; pp 3 ff, 145 ff, 177.

(10) Hwang, W. S. Dissertation, Oregon State University, 1979, p 74.

Table I. Thermodynamic Functions[a] for $CoCl_2L_2 + L \rightleftharpoons CoCl_2L_3$

	in benzene[b]				in *tert*-butylbenzene[c]			
ligand	$\Delta H°$[d]	$\Delta S°$[e]	$\Delta G°_{298}$[d]	$K_{eq,298}$	$\Delta H°$[d]	$\Delta S°$[e]	$\Delta G°_{298}$[d]	$K_{eq,298}$
Et_2POEt	-12.0 ± 0.3	-29.1 ± 0.8	-3.3	2.5×10^2	-13.9 ± 0.2	-33.2 ± 0.7	-4.0	8.5×10^2
$EtP(OEt)_2$	-10.6 ± 0.2	-20.6 ± 0.8	-4.5	1.8×10^3	-8.6 ± 0.1	-11.9 ± 0.3	-5.0	4.8×10^3
$P(OEt)_3$	-6.2 ± 0.7	-11.6 ± 2.2	-2.7	9.9×10	-5.9 ± 0.3	-8.5 ± 0.9	-3.3	2.8×10^2

[a] Errors shown are based on one standard deviation of the slope and intercept in the linear regression. [b] This work. [c] Reference 6. [d] kcal/mol. [e] cal/(mol deg).

Table II. Pseudo-First-Order and Second-Order Rate Constants for Autoxidation at Mole Ratio $L:CoCl_2 = 2.00$ in Benzene at 25 °C and 1.00 of Atm O_2 (100% of Co in Form $CoCl_2L_2$)

L	10^3k, s^{-1}	k_2, $M^{-1}\ s^{-1}$
Et_3P	0.35	0.038
Et_2POEt	5.1	0.56
$EtP(OEt)_2$	3.3	0.36
$P(OEt)_3$	6.2	0.68

Table III. Initial Distribution of Oxidizable Species and Pseudo-First-Order and Second-Order Rate Constants for Autoxidation at Mole Ratio $L:CoCl_2 = 3.00$ in Benzene at 25 °C and 1.00 Atm of O_2

L	$[CoCl_2L_3]_0$, M	$[CoCl_2L_2]_0$, M (=$[L]_0$, M)	10^3k, s^{-1}	k_2, M^{-1} s^{-1}
Et_2POEt	0.101 (83.4% of Co)	0.0201 (16.6% of Co)	9.8	1.1
$EtP(OEt)_2$	0.0483 (90.4% of Co)	0.00515 (9.6% of Co)	12	1.3
$P(OEt)_3$	0.0562 (70.2% of Co)	0.0238 (29.8% of Co)	5.3	0.58

are exothermic with formation of an additional bond. The entropy change is negative corresponding to the formation of a more ordered system in the reaction. The decrease in spin multiplicity makes a contribution of −2.2 eu to $\Delta S°$. The solvent effect is irregular; for the triethyl phosphite and diethyl ethylphosphonite systems both $\Delta H°$ and $\Delta S°$ are more negative in benzene than in *tert*-butylbenzene, while the converse is true for the ethyl diethylphosphinite system.

The effect of the electronegativity of the ethyl and ethoxy substituent groups should make ethyl diethylphosphinite the best σ donor and poorest π acceptor of the three ligands. Since for it $\Delta H°$ is the most negagive, suggesting that the new bond being formed is strongest, it appears that the σ bonding is the more important. The much more negative $\Delta S°$ value in the above reaction for ethyl diethylphosphinite is indicative of steric crowding on going from the four-coordinate to the five-coordinate complex. The dominant effect of steric hindrance is, of course, emphasized by the nonexistence of the five-coordinate complex when $n = 3$, i.e., for triethylphosphine. Of the $Et_nP(OEt)_{3-n}$ series, triethylphosphine has the largest steric requirement, as measured by the phosphorus cone angle.[5]

Autoxidation at $L:CoCl_2$ Mole Ratio 2.00. Each of the complexes $CoCl_2L_2$, $L = Et_nP(OEt)_{3-n}$, $n = 0-3$, in benzene solution at 25 °C was found to react with oxygen (1 atm) with the quantitative stoichiometry (11) and with no change in the

$$CoCl_2L_2 + O_2 \rightarrow CoCl_2(OL)_2 \qquad (11)$$

value of n. Samples were withdrawn at various times for kinetic studies. On the assumption that the rate law (12)

$$\text{rate} = k[CoCl_2L_2]P_{O_2} \qquad (12)$$

applies to all the complexes, pseudo-first-order behavior should be observed at constant oxygen pressure. First-order plots of $\ln([L]_0/[L]_t)$ vs. time, giving the pseudo-first-order rate constants as the slopes, were indeed linear up to about 60%, 50%, 60%, and 35% of completion for $n = 0$, 1, 2, and 3, respectively. The deviation in the latter stages of the reaction is attributed to a redistribution reaction of starting material with product, which will be discussed below.

The reaction stoichiometry and first-order rate dependence on substrate found for autoxidation of $CoCl_2L_2$, where $L = Et_nP(OEt)_{3-n}$, $n = 0-2$, is in agreement with that previously reported (and now reconfirmed) for the $n = 3$ system. First-order dependence on oxygen pressure was demonstrated[4] for the $n = 3$ case and is assumed to apply to all the systems.

The pseudo-first-order rate constants for 1 atm of oxygen are given in Table II. The value at 25 °C for the $n = 3$ case, $3.5 \times 10^{-4}\ s^{-1}$, compares reasonably with the value at 36 °C, $5.4 \times 10^{-4}\ s^{-1}$, which can be calculated from the data of Schmidt[11] for 1 atm of oxygen. Schmidt used a completely different experimental method to follow the kinetics, measuring the rate of decrease of gas volume at constant pressure. The solubility of oxygen[12] under 1 atm in benzene at 25 °C is 0.009 11 M. Second-order rate constants for the function (13),

$$-d[CoCl_2L_2]/dt = k_2[CoCl_2L_2][O_2] \qquad (13)$$

which can be calculated by dividing the pseudo-first-order constants by 0.009 11 M, are also given in Table II. The rate constants given in Table II show a curious trend; the values for $n = 0-2$ vary by less than a factor of 2, while the value for $n = 3$ is 1 order of magnitude less than the others. This suggests the existence of steric hindrance, before or during the rate-determining step, which is of major importance only for the triethylphosphine system. This is similar to the special steric factor which accounts for the nonexistence of $CoCl_2L_3$ with this ligand.

Autoxidation at $L:CoCl_2$ Mole Ratio 3.00. Unlike the case at mole ratio 2.00, where all the substrate is present in a single form $CoCl_2L_2$, at mole ratio 3.00 the $CoCl_2L_3$ complexes, $L = Et_nP(OEt)_{3-n}$, $n = 0-2$, partially dissociate into $CoCl_2L_2$ and uncoordinated L according to eq 4. The initial distribution of species for any particular solution can be calculated by using the known equilibrium constants. Typical data are shown in Table III.

Because a mixture of oxidizable species is present, various possibilities arise at a $L:CoCl_2$ mole ratio of 3.00 for the stoichiometry and products of the autoxidation reaction. The actual results obtained correspond to the simple stoichiometry in eq 14. In both the ethyl diethylphosphinite and the diethyl

$$CoCl_2L_3 + {}^3\!/_2O_2 \rightarrow CoCl_2(OL)_2 + LO \qquad (14)$$

ethylphosphonite systems, where mixed phosphoryl products, some with changed values of n, are obtained from the free-radical autoxidation of the uncoordinated ligands,[3] only a single phosphoryl compound with n unchanged is observed in both the $CoCl_2(OL)_2$ and the uncoordinated LO products. This demonstrates that autoxidation of the uncoordinated ligand present in the solutions at mole ratio 3.00 is unable to compete in rate with the autoxidation of coordinated ligand. Again, pseudo-first-order kinetics were assumed at constant oxygen

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(11) Schmidt, D. D. Dissertation, Oregon State University, 1971, pp 65–66.

(12) Horiuti, J. *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn.*) **1931**, *17*, 125. Cited by: Seidell, A. "Solubilities of Inorganic and Metal-Organic Comopunds", 3rd ed.; Van Nostrand: New York, 1940; p 1358.

pressure (1 atm). Plots of ln $([L]_0/[L]_t)$ vs. time were linear up to about 70%, 90%, and 80% of completion of reaction for $n = 0$, 1, and 2, respectively. To confirm the assumed first-order dependence on oxygen, we carried out an autoxidation experiment using dry air ($P_{O_2} = 0.209$ atm) in the $n = 0$ system. It also showed pseudo-first-order dependence on cobalt, with a rate constant of 1.4×10^{-3} s^{-1} consistent with the value 1.1×10^{-3} s^{-1} predicted as 20.9% of the pseudo-first-order constant at 1 atm of oxygen. Thus, the rate law is as in eq 15.

$$-d[CoCl_2L_3]/dt = k'[CoCl_2L_3]P_{O_2} \qquad (15)$$

The pseudo-first-order constants for 1 atm of oxygen are given in Table III. These may be converted to second-order constants by dividing by the molar solubility of oxygen. The ratios of the rate constants for $CoCl_2L_3$ autoxidation at 1 atm of oxygen pressure in Table III to the corresponding rate constants for $CoCl_2L_2$ autoxidation in Table II range from a low of 0.85 to a high of 3.6. This indicates that predissociation of the $CoCl_2L_3$ complexes to give $CoCl_2L_2$ species is *not* required for reaction with dioxygen; the $CoCl_2L_2$ complexes are only minor solute species at mole ratio 3.00. The result that all the rate constants for both high-spin bis(phosphorus ester) and low-spin tris(phosphorus ester) complexes are so similar is surprising. A greater effect of the cobalt paramagnetic spin state and coordinate geometry on the rates of reaction with dioxygen might have been expected.[13]

Cobalt(II)–Dioxygen Adduct Intermediate. Green *tert*-butylbenzene solutions prepared from 1.00 part of cobalt(II) chloride and 3.00 parts of diethyl ethylphosphonite (i.e., of formal composition $CoCl_2L_3$) were saturated with oxygen gas at 1 atm at −46 °C. Physically dissolved oxygen was then completely removed. If such solutions were allowed to warm to room temperature, they turned blue irreversibly. In one experiment, when the solvent and free organophosphorus material were pumped off, the latter was found to be entirely $EtP(OEt)_2$ while the nonvolatile residue was found to be the phosphoryl complex $CoCl_2(EtP(O)(OEt)_2)_2$. In another case, the coordinated phosphorus ester was displaced from the cobalt and all organophosphorus material was pumped off quantitatively. Analysis then showed that 2.01 parts of $EtP(O)(OEt)_2$ and 0.996 part of $EtP(OEt)_2$ were present. These quantitative results constitute clear evidence for reactions 16 and 17.

$$CoCl_2L_3 + O_2 \xrightarrow{-46\ °C} O_2CoCl_2L_3 \text{ (or } O_2CoCl_2L_2 + L) \qquad (16)$$

$$O_2CoCl_2L_3 \xrightarrow{\text{room temp}} CoCl_2(OL)_2 + L \qquad (17)$$

A solution was prepared as described above but not allowed to warm above −46 °C. Its −196 °C EPR spectrum consisted only of a 200 G wide resonance centered at $g = 2.08$, with no resolution of hyperfine components. This may be due to the physical nature of the frozen *tert*-butylbenzene; resolvability of such spectra is sensitive to the quality of the glass.[14] An attempt to detect the weak ν_{O-O} absorption expected[15] at about 1120 cm^{-1} could not be made as this is a region of strong P–O–Et absorption.[16]

Irreversible Rearrangement of the Dioxygen Adduct. The kinetics of the green to blue transformation corresponding to eq 17 were followed spectrophotometrically in the range −9 to +11 °C. Least-squares rate constant slopes of the first-order function of eq 5 were obtained with linear correlation coefficients greater than 0.999 and are given in Table IV. Next, from the Arrhenius function (eq 18) one may calculate the

Table IV. First-Order Rate Constants for Thermal Decomposition of $O_2CoCl_2L_3$, L = $EtP(OEt)_2$

temp, K	10^3k, s^{-1}	temp, K	10^3k, s^{-1}
264	0.36	280	3.4
271	0.91	284	5.7
276	2.0		

$$\ln k = \ln A - E_a/RT \qquad (18)$$

values $A = 5.72 \times 10^{13}$ s^{-1} and $E_a = 21$ kcal/mol. Extrapolation to 25 °C gives $k = 3.2 \times 10^{-2}$ s^{-1} and $t_{1/2} = 22$ s. With use of the transition-state theory, corresponding values of $\Delta H^{\ddagger} = 20.2$ kcal/mol and $\Delta S^{\ddagger} = 2.4$ cal/(mol deg) were obtained.

Mechanistic Considerations. The low-spin $CoCl_2L_3$ complexes are the major solute species at mole ratio 3. In their autoxidation, the first and rate-determining step is thought to be formation of an intermediate cobalt(II)–dioxygen adduct. From the information at hand, it cannot be specified if this involves formation of a six-coordinate $O_2CoCl_2L_3$ species (eq 19a) or if there is displacement of one phosphorus ligand to give $O_2CoCl_2L_2$ (eq 19b). The tris complexes before oxygenation were thought[8] to have approximately square-pyramidal structures with phosphorus donor atoms in an axial and in two trans basal positions. That there are major steric effects operative in these systems is made obvious by the irregular variation with n of the equilibrium constants (Table I) for eq 4 and by the nonexistence of $CoCl_2L_3$ when $n = 3$. Because of these steric factors, eq 19b seems preferable to eq 19a and will be used in the discussion below.

$$CoCl_2L_3 + O_2 \rightarrow O_2CoCl_2L_3 \qquad (19a)$$

$$\rightarrow O_2CoCl_2L_2 + L \qquad (19b)$$

The high-spin $CoCl_2L_2$ complexes are the sole solute species at mole ratio 2. Here also, formation of a dioxygen adduct intermediate is thought to be the rate-determining step (eq 20); this was postulated a decade ago for autoxidation of dichlorobis(triethylphosphine)cobalt(II).[4] It is well-known that such adducts, with doublet spin states,[17] can be formed starting with cobalt(II) complexes in either doublet[18] or quartet[19] spin states.

$$CoCl_2L_2 + O_2 \rightarrow O_2CoCl_2L_2 \qquad (20)$$

As evidence that formation of the dioxygen adduct is the rate-determining step, a comparison may be made of the overall reaction rate constant for $CoCl_2L_3$ with $n = 1$ at 25 °C and 1 atm of oxygen (1.2×10^{-2} s^{-1}) and the rate constant of irreversible rearrangement of the dioxygen adduct of $CoCl_2(EtP(OEt)_2)_3$ extrapolated to 25 °C (3.2×10^{-2} s^{-1}). Since the second step is somewhat faster than the total reaction, the first step is rate determining at least in this case.

As for the mechanism of the second step, it may be noted that the two oxygen atoms which are structurally nonequivalent in 1:1 cobalt(II)–dioxygen adducts in the solid state[20] appear equivalent in solution according to EPR studies of ^{17}O-substituted adducts[21] due to rapid equilibrium 21. A

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(16) Studer, H. V. M.S. Thesis, Oregon State University, 1972, pp 26–28.

(17) A report of a high-spin cobalt(II)–dioxygen adduct (Willis, C. J. *J. Chem. Soc., Chem. Commun.* **1974**, 117) is now thought to be in error (F. Basolo, personal communication).

(18) For example: Crumbliss, A. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 55.

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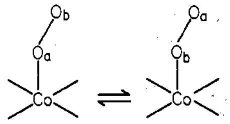
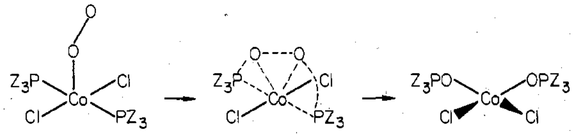


(21)

possible transition state for this exchange is the symmetrical side-on structure, which in turn would lead to an attractive candidate for the transition state for dioxygen adduct decomposition (eq 22).



(22)

At mole ratio 2, the formation according to eq 20 of the intermediate adduct and its decomposition constitute the reaction mechanism[22] during the initial stages of the reaction and correspond to the rate law of eq 12. However, the latter stage kinetics deviate from this simple behavior. This is attributed to the known[4,25] redistribution reaction (eq 23) in

$$CoCl_2L_2 + CoCl_2(OL)_2 \rightleftharpoons 2CoCl_2L(OL) \qquad (23)$$

which starting material and product react to give a mixed complex with only one oxidizable ligand. The net reaction stoichiometry according to eq 11 is quantitative; i.e., all oxidizable ligand eventually becomes oxidized. Schmidt and Yoke[4] emphasized the importance of the formation of two P=O bonds to compensate energetically for the rupture of the O–O bond and therefore postulated an alternative autoxidation path for $CoCl_2L(OL)$ built up in the latter stages of the reaction (eq 24–26).

$$CoCl_2L(OL) + O_2 \rightarrow O_2CoCl_2L(OL) \qquad (24)$$

$$O_2CoCl_2L(OL) + CoCl_2L(OL) \rightarrow (LO)LCl_2CoOOCoCl_2L(OL) \qquad (25)$$

$$(LO)LCl_2CoOOCoCl_2L(OL) \rightarrow 2CoCl_2(OL)_2 \qquad (26)$$

The critical feature at mole ratio 3 is that all the ligand L is oxidized to phosphoryl product LO according to eq 14 with no change in the value of n. It is known[3] that uncoordinated ethyl diethylphosphinite and diethyl ethylphosphonite undergo autoxidation to give mixed products, i.e., with changes in the value of n. It is known that only bis complexes $CoCl_2(OL)_2$[26] and $CoCl_2L(OL)$[4] are formed by the phosphoryl esters. Therefore, the third phosphorus ligand, released either in the formation of the dioxygen adduct by eq 19b or in its decomposition, must become recoordinated to cobalt and oxidized there much faster than it is autoxidized in the free condition. The mixed ligand complex formed in eq 27 is the same one

$$CoCl_2(OL)_2 + L \rightleftharpoons CoCl_2L(OL) + LO \qquad (27)$$

formed in the redistribution equilibrium of eq 23 and can undergo autoxidation by the mechanism of eq 24–26.

Autoxidation at High Mole Ratios. Catalysis. The type of displacement of phosphoryl ligand from cobalt by unoxidized ligand indicated in the equilibrium of eq 27 would be carried on still further at high L:$CoCl_2$ mole ratios (eq 28). Equations

$$CoCl_2L(OL) + L \rightleftharpoons CoCl_2L_2 + LO \qquad (28)$$

27, 28, and 11 constitute a catalytic cycle for autoxidation. For demonstration of this catalytic cycle, triethyl phosphite was chosen because, of all the ligands in the group, it alone does not react with oxygen in the absence of added initiator.[4] Autoxidation was carried out at 25 °C and 1 atm oxygen pressure by using solutions with constant triethyl phosphite concentration and $CoCl_2$:L mole ratios of 1:53, 1:103, and 1:153. The cobalt(II) concentrations in the three solutions were thus in the ratio 1.00:0.51:0.35. The experimental results showed that all the triethyl phosphite was readily oxidized to the phosphate and with graphically evaluated initial rates in the ratio 1.00:0.59:0.36. Trace amounts of cobalt(II) chloride thus catalyze autoxidation of macro amounts of the phosphite with initial rates directly proportional to the cobalt concentration. Such catalysis may be of practical importance since it gives a rapid reaction with a quantitative yield at atmospheric pressure and room temperature. This contrasts, for example, to the 90–95% yields obtained by using aluminum oxide at 120 °C.[27]

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Registry No. $CoCl_2(Et_2POEt)_2$, 58673-04-4; $CoCl_2(EtP(OEt)_2)_2$, 58673-02-2; $CoCl_2(P(OEt)_3)_2$, 58673-01-1; $CoCl_2(Et_3P)_2$, 14784-62-4; $CoCl_2(Et_2POEt)_3$, 58673-05-5; $CoCl_2(EtP(OEt)_2)_3$, 58673-03-3; $CoCl_2(P(OEt)_3)_3$, 22016-97-3; $O_2CoCl_2(EtP(OEt)_2)_2$, 74542-88-4.

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(22) A mechanism has been proposed[23] for phosphine autoxidation catalysis involving dioxygen adducts of platinum(0), in which the actual oxidizing agents are platinum(II) and hydroperoxide ions. If the autoxidation mechanism in the present systems were analogous, the oxidizing agents would be cobalt(III) and superoxide ions, but the former is known to give stable phosphine complexes[24] and the latter would be expected to initiate radical chain autoxidation[2] leading to mixed products with changes in the value of n. These are not observed.

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