AN ABSTRACT OF THE THESIS OF

DONALD DEAN SCHMIDT for the DOCTOR OF PHILOSOPHY
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Title:  THE AUTOXIDATION OF DICHLOROBIS-

(TRIETHYLPHOSPHINE)COBALT(II)

Abstract approved: *Redacted for Privacy*

John T. Yoke III

The autoxidation of free trialkylphosphines in organic solution is known to result in the formation of a series of four organophosphoryl compounds, $R_nP(O)(OR)_{3-n}$, n = 0-3, by a free radical mechanism. The autoxidation of dichlorobis(triethylphosphine)cobalt(II), $CoCl_2 \cdot 2Et_3P$, in organic solvents was studied in order to establish the effect of coordination on the reactivity of the phosphine with oxygen.

A series of new complexes, $CoCl_2 \cdot 2Et_nP(O)(OEt)_{3-n}$, n = 0-3, was prepared as reference standards for the characterization of the product of the autoxidation reaction. A new method for the synthesis of triethylphosphine oxide, from triethylphosphine and mercury(II) oxide, was developed. In the drybox, stoichiometric amounts of the phosphoryl ligands were added to solutions of anhydrous cobalt(II) chloride in absolute ethanol to give a mole ratio of 2.00. The blue solid $CoCl_2 \cdot 2Et_3PO$ precipitated from ethanol solution on cooling.

The other three complexes were recovered as blue oils on evaporation of the solvent at room temperature. These complexes were found to be pseudo-tetrahedral in structure, according to the usual criteria of ligand field spectra and magnetic moments. These complexes were also characterized by chemical analysis, solubility behavior, and infrared spectra. The positions and relative intensities of the P=O and P-O-C bands in the infrared spectra were established as useful criteria for the identification of the autoxidation reaction product.

The ethyl phosphoryl complexes of cobalt(II) containing P-O-C ester groups were found to decompose above 140°. They gave off ethyl chloride (identified by vapor pressure and vapor density measurements) to form the complexes $Co[O_2PEt_n(OEt)_{2-n}]_2$, n = 0-2. These complexes were characterized by chemical analysis, solubility behavior, infrared spectra, and ligand field properties. From this information, they are believed to be coordination polymers with double-bridging $R_2PO_2^-$ groups connecting the tetrahedrally coordinated cobalt atoms.

It was found that solid $CoCl_2 \cdot 2Et_3P$ does not react with oxygen, contrary to an earlier report. The sole product of the autoxidation reaction in organic solvents was found to be $CoCl_2 \cdot 2Et_3PO$. The reaction of a known quantity of $CoCl_2 \cdot 2Et_3P$ in benzene with oxygen was conducted under conditions that insured completion of the reaction. The product was quantitatively recovered from solution. The gain in

weight corresponded to the reaction of 1.00 mole of $O_2$ with one mole of $CoCl_2 \cdot 2Et_3P$. Chemical analysis and the infrared spectrum of the reaction product clearly identified it as $CoCl_2 \cdot 2Et_3PO$. Autoxidation products recovered from reactions in o-dichlorobenzene and in t-butylbenzene were also identified as $CoCl_2 \cdot 2Et_3PO$ by their infrared spectra, chemical analyses, and their melting points.

Visible spectra of $CoCl_2 \cdot 2Et_3P$ solutions from partial autoxidations suggested the occurrence of the redistribution equilibrium

$$CoCl_2 \cdot 2Et_3P + CoCl_2 \cdot 2Et_3PO \rightleftharpoons 2CoCl_2 \cdot Et_3P \cdot Et_3PO$$
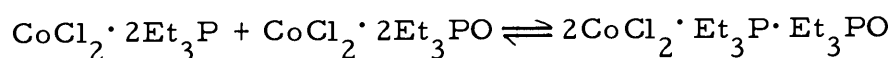
This was confirmed by the study of mixtures of solutions of the pure components. A very approximate value of the equilibrium constant was determined from spectrophotometric data in benzene and in t-butylbenzene. It was found to be of the order of magnitude of 10.

Absorption of oxygen by $CoCl_2 \cdot 2Et_3P$ solutions at constant oxygen pressure was measured as a function of time. These kinetic studies in t-butylbenzene solutions showed that the rate of the autoxidation reaction is first order in oxygen pressure and independent of added free radical initiator (AIBN) and inhibitor (hydroquinone). The reaction in the early stages was found to be first order in the concentration of $CoCl_2 \cdot 2Et_3P$. After approximately the first quarter-life, another unknown term in the rate law contributed to the absorption of oxygen. A mechanism was proposed for the reaction.

The Autoxidation of Dichlorobis(triethylphosphine)cobalt(II)

by

Donald Dean Schmidt

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*Redacted for Privacy*

Professor of Chemistry

*Redacted for Privacy*

Chairman of Department of Chemistry

*Redacted for Privacy*

Dean of Graduate School

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Typed by Gwendalyn Hansen for ___ Donald Dean Schmidt ___

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## (TRIETHYLPHOSPHINE)COBALT(II)

## I. INTRODUCTION

The purpose of this investigation was to study the reaction of

oxygen with a tertiary aliphatic phosphine coordinated to a transition

metal. Information was sought on the nature of the reaction products

and on the course of the reaction. The effect of coordination on the

reactivity of the phosphine could then be deduced from a comparison of

the results with the information available on the autoxidation of free

trialkylphosphines.

The coordination of a ligand can result in significant changes in

its chemical reactivity. The coordination number of the donor atom

increases as the lone pair becomes involved in the sigma portion of

the coordinate bond; additional back pi-bonding is also recognized as

important in phosphorus-transition metal coordination. These bonding

changes involve rehybridization of donor atom orbitals. The P-C-P

bond angles in trialkylphosphines are approximately 99°, correspond-

ing to an intermediate stage of hybridization; these would become more

nearly tetrahedral on coordination, with both steric and electronic

effects on the phosphine molecule. The electric polarization of a ligand

molecule may change the reactivity of other bonds present, such as

O-H or C-H. The metal may serve as a template to hold reactive

groups in position for sterically highly selective reactions with external

reagents or other ligands. Other examples of changes in ligand

reactivity on coordination include development of aromatic behavior

through electron delocalization in, e. g. , acetylacetonate and cyclo-

pentadienide ligands, and changes in internal multiple bond order in

olefin, carbon monoxide, and oxygen complexes.

The autoxidation of free tertiary aliphatic phosphines ($R_3P$)

occurs by a free radical mechanism, resulting in approximately 50%

of the phosphine oxide ($R_3PO$) and approximately 50% of the mixed

esters ($R_nP(O)(OR)_{3-n}$) (Buckler, 1962; Floyd and Boozer, 1963).

Little previous work has been done on the autoxidation of coordinated

trialkylphosphines. Jensen, Nielsen, and Pedersen (1963) reported

some interesting qualitative observations on the air oxidation of tri-

alkylphosphine complexes of nickel(II) and cobalt(II). Trimethyl-

phosphine complexes of nickel(II) and cobalt(II) (especially with bromide

and iodide) are reported to react with air to give trimethylphosphine

complexes of nickel(III) and cobalt(III); i. e. , the metal is oxidized in

preference to the ligand. It is said that the nickel(III) complexes then

undergo a decomposition to nickel(II) halide and trimethylphosphine

oxide. On the other hand, the triethylphosphine complexes of cobalt(II)

halides are said to be oxidized by air to give cobalt(II) complexes of

triethylphosphine oxide directly, without intermediate cobalt(III)

complexes being observed. Unfortunately, important experimental

details, such as conditions of the reactions, experimental evidence for

the formation of the phosphine oxides or of the oxidized metal species, and specific chemical formulas for the nickel(III) and cobalt(III) species, are not given. Many of their results seem questionable. From this qualitative report in the literature, though, it is apparent that coordination has a marked effect on phosphine autoxidation.

Dichlorobis(triethylphosphine)cobalt(II), $CoCl_2 \cdot 2PEt_3$, is a typical example of a pseudo-tetrahedral cobalt(II) complex, with spectral and magnetic properties well understood in terms of ligand field theory. Study of these properties may be expected to be useful experimentally in following the autoxidation reaction. The potential phosphine autoxidation products contain the P=O phosphoryl group. Compounds of this type are common as ligands in transition metal complexes. Infrared spectroscopic measurements are known to be especially useful in the study of such complexes. Additional preliminary considerations are that certain cobalt(II) complexes are known to be "carriers" of molecular oxygen, and that peroxy-bridged dinuclear complexes are known intermediates in the autoxidation of aqueous cobalt(II) amine complexes.

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## II. HISTORICAL

### A. Autoxidation of Free Trialkylphosphines

Buckler (1962) and Floyd and Boozer (1963) have studied the autoxidation of free tertiary aliphatic phosphines $R_3P$. By a careful study of the products of the reaction under different conditions, using, e.g., mixed phosphines and added alcohols, Buckler proposed the mechanism shown in Table 1. Floyd and Boozer supported Buckler's mechanism through an elementary kinetic study. Walling and Rabinowitz (1959) had earlier discussed the concept of the phosphoranyl intermediate.

Oxygen reacts with any free radicals in solution to form peroxy radicals (reaction 2). The phosphine then abstracts an oxygen atom from the peroxy radical to form the phosphine oxide and an alkoxy radical (reaction 3). The phosphine can react with alkoxy radicals to form an intermediate phosphoranyl radical, $RO\dot{P}R_3$. This can decompose in either of two ways (reactions 4a and 4b) to give a tertiary phosphine oxide or an alkyl dialkylphosphinite. The latter product can then react with peroxy radicals by oxygen-abstraction (reaction 5) or with alkoxy radicals to give another phosphoranyl radical which can decompose in two ways (reactions 6a and 6b). Additional reactions of the same type can then occur (reactions 7, 8, 9, 10). In this manner,

Table 1. Mechanism of Autoxidation of Free Trialkylphosphines

| Reaction # | Chemical reaction |
|---|---|

(1). Initiation (spontaneous
or initiator added): $\longrightarrow$ R$\cdot$ , RO$\cdot$ , RO$_2\cdot$

(2). $\qquad$ R$\cdot$ + O$_2 \longrightarrow$ RO$_2\cdot$

$R_3P$ Reactions:

(3). $R_3P$ + RO$_2\cdot \longrightarrow R_3\dot{P}OOR \longrightarrow R_3PO$ + RO$\cdot$

(4a). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\nearrow R_3PO$ + R$\cdot$

$R_3P$ + RO$\cdot \longrightarrow R_3\dot{P}OR$

(4b). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\searrow R_2POR$ + R$\cdot$

$R_2POR$ Reactions:

(5). $R_2POR$ + RO$_2\cdot \longrightarrow R_2(OR)\dot{P}OOR \longrightarrow R_2P(O)(OR)$ + RO$\cdot$

(6a). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\nearrow R_2P(O)(OR)$ + R$\cdot$

$R_2POR$ + RO$\cdot \longrightarrow (RO)_2\dot{P}R_2$

(6b). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\searrow RP(OR)_2$ + R$\cdot$

$RP(OR)_2$ Reactions:

(7). $RP(OR)_2$ + RO$_2\cdot \longrightarrow R(OR)_2\dot{P}OOR \longrightarrow RP(O)(OR)_2$ + RO$\cdot$

(8a). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\nearrow RP(O)(OR)_2$ + R$\cdot$

$RP(OR)_2$ + RO$\cdot \longrightarrow R\dot{P}(OR)_3$

(8b). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\searrow P(OR)_3$ + R$\cdot$

$P(OR)_3$ Reactions:

(9). $P(OR)_3$ + RO$_2\cdot \longrightarrow ROO\dot{P}(OR)_3 \longrightarrow (RO)_3P(O)$ + RO$\cdot$

(10). $P(OR)_3$ + RO$\cdot \longrightarrow RO\dot{P}(OR)_3 \longrightarrow (RO)_3P(O)$ + R$\cdot$

several products containing the P=O phosphoryl group are formed. The percentages of the different products differ slightly with different alkyl substituents on the phosphorus and in different solvents. A typical product distribution is as follows: 50% trialkylphosphine oxide $R_3PO$, 40% alkyl dialkylphosphinate $R_2P(O)(OR)$, 6% dialkyl alkyl-phosphonate $RP(O)(OR)_2$, and 3% trialkyl phosphate $(RO)_3P(O)$.

The amount of phosphine oxide formed was found to increase as the solvent became more polar. In hexane, the amount of phosphinate formed (ca. 50%) actually exceeded the amount of phosphine oxide formed (ca. 40%). In order to account for this product distribution, Buckler pointed out that reaction 4b must predominate over 4a, even though the phosphine oxide-formation is favored thermodynamically.

In every case, the reactive phosphorus species contained tervalent phosphorus. Once the phosphoryl group had been introduced (eliminating the lone pair and raising the coordination number to four) autoxidation ceased. This is relevant to the present work. In a metal complex, the lone pair of a phosphine ligand is involved in coordinate bonding and the coordination number of phosphorus is already four.

## B. Autoxidation of Coordinated Phosphines

There are some qualitative reports in the literature on the autoxidation of coordinated trialkylphosphines. In many cases, the information is incidental to other work and unclear, and experimental

details are completely lacking.

Jensen, Nielsen, and Pedersen (1963) report the following

reactions:

$$[NiX_2(Me_3P)_2]_{(s)} + O_2 \longrightarrow \{Ni(III) \text{ complex}\}$$
$$\downarrow$$
$$Ni(II) \text{ and trimethylphosphine oxide}$$

$$[NiX_2(R_3P)_2]_{(s)} + O_2 \longrightarrow \text{No reaction} \quad (R = Et, Pr, Bu)$$

$$[CoX_2(Me_3P)_2]_{(s)} + O_2 \longrightarrow \text{Co(III) complex}$$

$$[CoX_2(Et_3P)_2]_{(s)} + O_2 \longrightarrow \text{Co(II) complex of phosphine oxide}$$
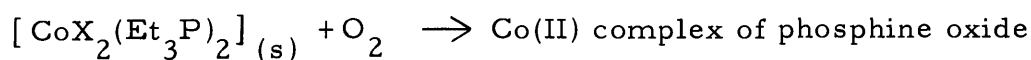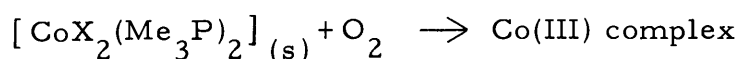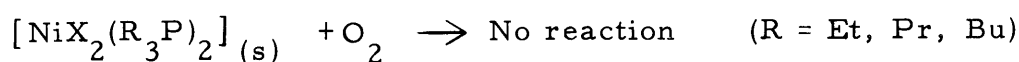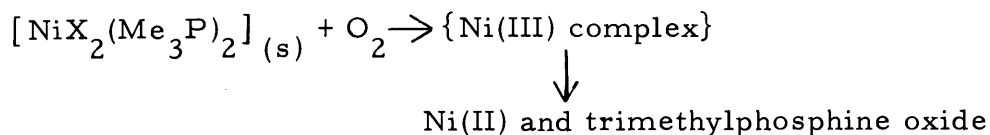
The most descriptive observations in their paper were with

regard to dichlorobis(triethylphosphine)cobalt(II), which is said to be

". . . easily oxidized on lying in the air. The deep blue $[CoCl_2(Et_3P)_2]$

attains a lighter blue color and becomes insoluble in pentane, being

transformed into a complex compound of the phosphine oxide." How-

ever, experimental evidence of any kind is missing and many of their

results seem questionable.

Chastain et al. (1968) report that solid $[NiBr_2(Me_3P)_3]$ is not

readily oxidized by air.

Turco and co-workers (Turco et al., 1963; Nicolini, Pecile, and

Turco, 1965) report that solid $[Co(SCN)_2(Et_3P)_2]$, stable at room tem-

perature for months in the absence of oxygen, decomposes in a few

seconds in contact with air.

The following reactions have been reported by Pignolet and

Horrocks (1969), in their proton nmr studies of diastereoisomeric

tertiary phosphine Ni(II) complexes:

$$[Ni(PRR'R'')_2X_2] + \tfrac{1}{2}O_2 \xrightarrow{CHCl_3} [Ni(OPRR'R'')(PRR'R'')X_2] \quad X = I$$
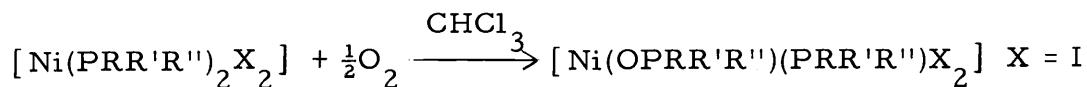
No reaction  X = Cl, Br

Also, infrared spectra of mixtures of nickel iodide, triphenylphosphine,

and molecular oxygen in chloroform and benzene showed the presence

of significant quantities of triphenylphosphine oxide. No observable

oxidation of triphenylphosphine occurred in the absence of nickel iodide

under otherwise identical experimental conditions.

Further examples below point out the many ways that oxygen

may react with transition metal-phosphine complexes:

$$[Co(\phi_2PCH_2CH_2P\phi_2)_2]X + O_2 \longrightarrow Co(II) + \phi_2P(O)CH_2CH_2P(O)\phi_2$$

X = $ClO_4^-$, $B\phi_4^-$  (Sacco, Rossi, and Nobile, 1966)

$$[Ir(\phi_2PCH_2CH_2P\phi_2)_2]X + O_2 \longrightarrow [O_2Ir(\phi_2PCH_2CH_2P\phi_2)_2]X$$

X = $ClO_4^-$, $B\phi_4^-$ reversible  (Sacco, Rossi, and Nobile, 1966)

X = $Cl^-$  irreversible  (Vaska and Catone, 1966)

$$[O_2IrCl(CO)(\phi_3P)_2] \xrightarrow[\text{slow}]{O_2,\ h\nu} \phi_3PO\ \text{complex} \qquad (\text{Vaska, 1963})$$

$$[M(\phi_3P)_4] \underset{\longleftarrow}{\overset{-2\phi_3P}{\rightleftharpoons}} [M(\phi_3P)_2] \xrightarrow{O_2} [O_2M(\phi_3P)_2]$$

recycle, 4 $\phi_3$P, catalytic ———— M + 2$\phi_3$PO
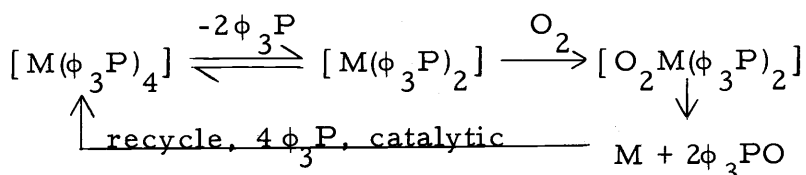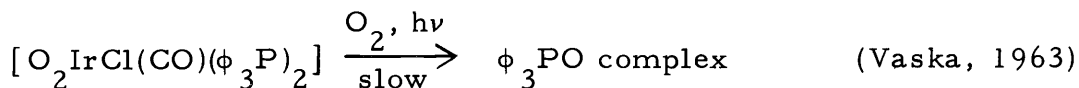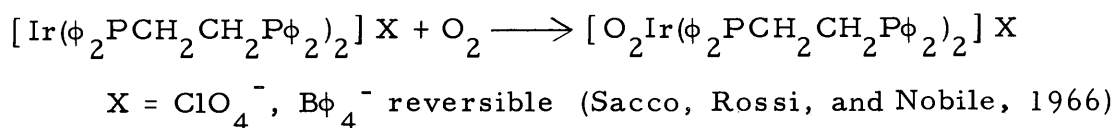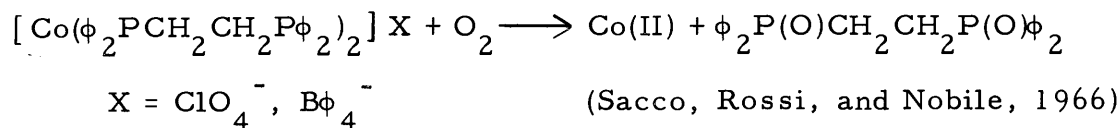
M = Ni, Pd, Pt  (Wilke, Schott, and Heimbach, 1967)

The above examples show that in addition to oxidation of the

phosphine or the metal, an oxygen complex of some stability may be

formed. Such binding of molecular oxygen to transition metal com-

plexes (often with phosphine ligands) is well known (Vaska, 1968;

Bayer and Schretzmann, 1967; Vogt, Faigenbaum, and Wiberley,

1963). Monomeric oxygen adducts of cobalt(II) prepared in solution and

isolated as crystalline solids are reported by Floriani and Calderazzo

(1969) and by Crumbliss and Basolo (1970). The oxygen may be bound

as a π-ligand (much like ethylene) or as a bridging ligand. In many

cases, an oxygen complex is considered to be a reactive intermediate

in the oxidation of auxiliary ligands or external reagents (Cook and

Jauhal, 1967; Birk, Halpern, and Pickard, 1968; Wilke, Schott, and

Heimbach, 1967).

## C. Phosphoryl Complexes of Transition Metals

Since compounds containing the phosphoryl (P=O) group are

potential products of phosphine autoxidation, their behavior as ligands

is of interest. A number of transition metal complexes with organo-

phosphoryl donors have been studied (Karayannis et al., 1970, 1969,

and references therein; Donoghue, Fernandez, and Peters, 1969;

Brodie et al., 1968). Most of the work has been done with various

phosphine oxide or phosphoramide donors. Trialkyl phosphates have

been studied extensively as extractants of various metal salts from

solution, but the resulting complexes have seldom been isolated and characterized. Very little work has been done with phosphinate or phosphonate complexes.

One of the interesting features of these complexes is the infrared stretching frequency of the phosphoryl group. In the free ligand, this increases with increasing electronegativity of the substituents on the phosphorus atom (Bell et al., 1954). The explanation for this trend lies in the nature of the phosphorus-oxygen double bond. The bond involves a dative $P^+ \rightarrow O^-$ $\sigma$-bond and some degree of back bonding by overlap of filled $p\pi$-orbitals of oxygen with the appropriate empty $d\pi$-orbitals of phosphorus. The observed increase in $\nu_{P=O}$ with increasing electronegativity of substituents on phosphorus is related to increasing partial positive charge on sigma-bonded phosphorus and a resulting increase in $p\pi$-$d\pi$ back bonding from oxygen to phosphorus. The result is an overall increase in bond strength.

Cotton, Barnes, and Bannister (1960) discuss the lowering of phosphoryl stretching frequencies upon complex formation. The decrease in $\nu_{P=O}$ on coordination of oxygen to a metal is related to the decrease in availability of oxygen electrons for back bonding to phosphorus, resulting in a net lowering of bond order.

# III. EXPERIMENTAL

## A. Materials

### 1. Preparation and Purification of Ligands

a. Triethylphosphine. Triethylphosphine was synthesized by a Grignard reaction with phosphorus trichloride, according to the method of Hibbert (1906), as modified by Mann and Wells (1938). The Grignard reagent was prepared from one g-atom (24 g) of magnesium turnings and one mole (74 ml) of ethyl bromide (MC&B, BX1225) in 500 ml of anhydrous ether (B&A, Code 1700). A crystal of iodine was added to initiate the formation of the Grignard reagent. Under a flow of pre-purified nitrogen, 0.30 mole (26 ml) of phosphorus trichloride (B&A, Code 2067) was added dropwise to the Grignard solution, cooled by a dry ice-acetone bath. Then the ether was distilled from the reaction flask under a stream of nitrogen and bubbled through aqueous $AgI_2^-$ solution. (The diiodoargenate(I) solution was prepared by adding 0.30 mole (70 g) of silver iodide to 600 ml of water, along with enough potassium iodide to dissolve the AgI.) The triethylphosphine was driven from the reaction flask by baking the flask for four to five hours at ca. 400° C under a stream of nitrogen, all gases being bubbled through the $AgI_2^-$ solution. The triethylphosphine and diiodoargenate ion reacted to form a triethylphosphine-silver iodide

adduct which precipitated as a white solid. (According to Wells (1962),

the "Et$_3$P· AgI" adduct is a tetrameric complex, tetrakis-$\mu_3$-

iodotetrakis(triethylphosphine)tetrasilver(I). ) The precipitate was

filtered, then dried and stored in vacuo over KOH. Yields up to 76%,

on the basis of the amount of PCl$_3$ added, were obtained.

An orange solid forms on the upper walls of the reaction flask

during the course of the Grignard reaction. A recent paper by

Spangenberg and Sisler (1969) indicates that this solid may have been

elemental phosphorus formed by the reaction of phosphorus trichloride

and triethylphosphine. Thus, in order to get a good yield of triethyl-

phosphine, an excess of phosphorus trichloride should be avoided,

keeping in mind that the conversion of magnesium turnings into ethyl-

magnesium bromide is less than quantitative.

Triethylphosphine was recovered from the silver iodide complex

by slowly heating the complex on the vacuum line. A system for

purifying the triethylphosphine by fractional condensation while

isolating it from the complex was developed. A flask containing up to

50 g of the complex was left open to the vacuum pump through a series

of four cold U-traps. The cold traps, from the flask toward the pump,

were at 0° (ice-water bath), -23° (carbon tetrachloride slush), -45°

(chlorobenzene slush), and -196° (liquid nitrogen bath), respectively.

After three to four hours, the 0° and -196° traps held very small

quantities of low and high volatility fractions. The -23° and -45°

traps contained nearly equal quantities of a tensiometrically homogeneous liquid. Experimental vapor pressures for different preparations were 12 torr at 22.5°, 13.5 torr at 24°, and 15 torr at 26°, all of which match well the vapor pressure curve (vp vs. T) for triethylphosphine drawn from data taken from Thompson and Linnett (1936), Hooge and Christen (1958), Kaesz and Stone (1959a), and Hatfield and Yoke (1962).

   b.   Triethylphosphine Oxide.   Triethylphosphine oxide was prepared by oxidation of triethylphosphine with mercury(II) oxide, using an adaptation of Zingaro's arsine oxide method (Merijanian and Zingaro, 1966). Triethylphosphine, 22 mmole (8 g), was condensed onto 22 mmole of mercury(II) oxide and 10 ml benzene in a 50 ml flask attached to a high vacuum line. The reaction mixture was stirred for two days at 50°, until all the solid was converted into mercury (appearing as a gray powder). The flask was cooled to room temperature and removed from the vacuum line, and the contents were filtered by gravity through paper in the open air. The benzene was then distilled from the clear filtrate in the vacuum line at room temperature. The whole solid product was melted and distilled in vacuo with mild application of heat. The yield of triethylphosphine oxide after purification was essentially quantiative.

   Four attempts to make triethylphosphine oxide from phosphorus oxychloride and ethylmagnesium bromide, following the method of

Pickard and Kenyon (1906), were unsuccessful. Recently, Miller (1969) reported that attempts to make trimethylphosphine oxide using methyl-magnesium bromide and phosphorus oxychloride were also unsuccessful. However, with methylmagnesium chloride, Miller obtained yields of ca. 50%, using the method of Burg and McKee (1951). In the latter method, the product was recovered by extraction into chloroform, rather than by the baking process used by Pickard and Kenyon for tri-propylphosphine oxide. Similar modifications in the Grignard synthesis of triethylphosphine oxide might well result in an acceptable yield.

c. Ethyl Diethylphosphinate. Ethyl diethylphosphinate was prepared as follows. Ethyldichlorophosphine, 0.2 mole, from the reaction of phosphorus trichloride and tetraethyl lead (Kharasch, Jensen, and Weinhouse, 1949), was added dropwise under nitrogen to a cold, stirred solution of 0.4 mole ethanol and 0.4 mole N,N-dimethylaniline in 200 ml light petroleum ether. The amine hydrochloride was removed by filtration under nitrogen in a dry box, the solvent was stripped from the filtrate, and the product, diethyl ethylphosphonite, was distilled at a reduced pressure. This was isomerized with ethyl iodide under nitrogen by the Arbuzov method (Kosolapoff, 1950, p. 121). The resulting ethyl diethylphosphinate was purified by distilla-tion at a reduced pressure, with a middle fraction taken; $n_D^{21}$ 1.4337; Razumov and Mukhacheva (1956) $n_D^{20}$ 1.4337.

d. Triethyl Phosphate and Diethyl Ethylphosphonate. Practical

Grade samples of triethyl phosphate (Eastman Kodak) and diethyl

ethylphosphonate (J. T. Baker) were distilled at reduced pressure

using a Nester-Faust Teflon spinning band column, and middle frac-

tions were taken; $(EtO)_3PO$: bp 93° (8 torr); $EtP(O)(OEt)_2$: bp 86°

(12 torr).

## 2. Solvents

a. <u>Ethanol</u>. A 60 ml quantity of Reagent Grade ethanol, 5 g

magnesium turnings, and a few drops of ethyl bromide were main-

tained at reflux in a one liter flask until nearly all the magnesium was

converted to the ethoxide. A large amount of ethanol was then added

and distilled from the magnesium ethoxide using dry apparatus. A

50 ml forerun was discarded.

b. <u>o-Dichlorobenzene</u>. o-Dichlorobenzene (MC&B, DX685) was

dried over silica gel and purified by vacuum distillation, with middle

fractions being collected (Floyd and Boozer, 1963). Typical boiling

points were 68° (14 torr) and 90° (40 torr). The recorded boiling

points agreed well with the Clausius-Clapeyron plot constructed from

the data in the Chemical Rubber Publishing Company Handbook (1968).

c. <u>t-Butylbenzene</u>. t-Butylbenzene (Aldrich Chemical Co.) was

distilled at atmospheric pressure; bp 168° (761 torr); Chemical Rub-

ber Publishing Co. Handbook (1968) 168.5° (760 torr). Foaming and

bumping of the t-butylbenzene made its distillation at reduced

pressures impractical.

   d. Other Solvents. Hexadecane, 99% Olefin Free (MC&B,

HX200) was used without further purification. Reagent Grade samples

of common organic solvents, such as benzene, acetone, chloroform,

and n-hexane, were distilled before use as solvents for spectral

studies or for studies of the autoxidation reaction. Benzene and

hexane were distilled from sodium wire.

## 3. Preparation of Complexes

   a. Dichlorobis(triethylphosphine)cobalt(II). Mixtures of

$CoCl_2 \cdot 6H_2O$ and triethylphosphine in 1:2 mole ratios in absolute

alcohol gave dichlorobis(triethylphosphine)cobalt(II) on cooling

(Jensen, 1936). Typically, 4 g of triethylphosphine was condensed

into a solution of 4 g of $CoCl_2 \cdot 6H_2O$ (MC&B, Reagent Grade, CX1800)

in 12 ml of ethanol. The contents were kept at ice temperature for a

few hours. The blue crystalline precipitate was filtered by suction in

a nitrogen-filled dry box, washed with a little chilled ethanol, and

stored in an evacuated desiccator over phosphorus(V) oxide; mp

(sealed tube, uncorr. ) 100-102° C; Jensen (1963) 101-102° C;

Nicolini, Pecile, and Turco (1965) 102° C. Anal. Calcd. for

$CoCl_2 \cdot 2(C_2H_5)_3P$:  Co, 16.09.. Found:  Co, 16.11.

   In earlier stages of the work, dichlorobis(triethylphosphine)-

cobalt(II) was prepared by direct combination of anhydrous cobalt(II)

chloride with an excess of triethylphosphine for approximately two weeks in an evacuated reaction tube. The excess phosphine was then pumped off. The formation of the complex by this method was slow, and the degree of reaction was indicated only by experimentally determined mole ratios, from initial and final tares. In a series of syntheses by this method, mole ratios $Et_3P:CoCl_2$ of 2.06, 1.95, 1.94, 2.00, 1.97, and 2.05 to 1.00 were found. Anal. Calcd. for $CoCl_2 \cdot 2(C_2H_5)_3P$: mole ratio 2.00; Co, 16.09; Cl, 19.36. Found: mole ratio 2.05; Co, 15.52; Cl, 18.86.

The anhydrous cobalt(II) chloride was prepared by dehydration of the hexahydrate at ca. 400° in a stream of hydrogen chloride. Anal. Calcd. for $CoCl_2$: Co, 45.39; Cl, 54.61. Found: Co, 45.06; Cl, 54.73.

In summary, phosphine complex prepared in alcohol solution gave better analyses and looked more crystalline than complex prepared by direct combination of the ligand with cobalt chloride.

Dichlorobis(triethylphosphine)cobalt(II) is soluble in benzene, acetone, and chloroform and is slightly soluble in paraffin hydrocarbons. Additional solubility behavior of the phosphine complex will be discussed later.

b. Ethyl Phosphoryl Complexes. In the dry box, stoichiometric amounts of the phosphoryl ligands were added to solutions of 2 g anhydrous cobalt(II) chloride in 20 ml absolute ethanol to give a mole

ratio of 2.00.  The blue solid dichlorobis(triethylphosphine oxide)-cobalt(II) precipitated on cooling; mp 76-77°.  The three complexes dichlorobis(ethyl diethylphosphinate)cobalt(II), dichlorobis(diethyl ethylphosphonate)cobalt(II), and dichlorobis(triethyl phosphate)cobalt(II) were recovered as blue oils on evaporation of the solvent $\underline{in}$ $\underline{vacuo}$ at room temperature.  Cobalt and chloride analyses for these new complexes are given in Table 2.  In addition, carbon and hydrogen analyses were performed on the phosphine oxide complex.  $\underline{Anal}$. Calcd. for $CoCl_2 \cdot 2(C_2H_5)_3PO$:  C, 36.20; H, 7.59.  Found:  C, 36.23; H, 7.61.

Table 2.  Cobalt and Chloride Analyses of Ethyl Phosphoryl Complexes

| Compound | Cobalt | | Chloride | |
|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found |
| $CoCl_2 \cdot 2(C_2H_5)_3PO$ | 14.80 | 14.74 | 17.81 | 17.76 |
| $CoCl_2 \cdot 2(C_2H_5)_2(C_2H_5O)PO$ | 13.70 | 13.57 | 16.48 | 16.35 |
| $CoCl_2 \cdot 2(C_2H_5)(C_2H_5O)_2PO$ | 12.75 | 12.88 | 15.34 | 15.32 |
| $CoCl_2 \cdot 2(C_2H_5O)_3PO$ | 11.93 | 11.67 | 14.35 | 13.97 |

The $CoCl_2 \cdot 2(C_2H_5)_n(C_2H_5O)_{3-n}PO$ complexes are all soluble in acetone and alcohol, somewhat soluble in ether and benzene, insoluble in paraffin hydrocarbons, and decomposed by water.  The thermal decomposition of the complexes containing P-O-C linkages is described in the Results and Discussion section.

4. Other Materials

a. Oxygen. Oxygen (NCG, Compressed Gas, U.S.P. Grade) was passed through Drierite for all reactions and kinetic runs.

b. AIBN. Azobisisobutyronitrile from K and K Laboratories was recrystallized from benzene; mp 102-104°; Floyd and Boozer (1963) mp 104-106°.

c. Benzoyl peroxide. Benzoyl peroxide (MC&B, BX470) was recrystallized by dissolving it in a minimum amount of chloroform and then adding twice the volume of methanol (Vogel, 1966).

d. Hydroquinone. Hydroquinone (MC&B, HX650) was used without further purification.

Unless otherwise stated, all other chemicals used in this study were of Reagent Grade or of the highest quality commercially available.

B. Analyses

1. Chloride

The chloride content was determined gravimetrically.

2. Cobalt

Cobalt content was determined by potentiometric titration with hexacyanoferrate(III) ion (bright Pt electrode vs. S. C. E. ). Accurately

weighed cobalt samples, from 0.20 to 0.25 g, were evaporated to dryness three times with concentrated nitric acid on a steam bath, then redissolved in water. A buffer, consisting of 75 ml of concentrated aqueous ammonia and 75 ml of concentrated (300 g/l) ammonium monohydrogen citrate, was added next to each sample, followed by a 25.00 ml aliquot of standard potassium hexacyanoferrate(III) solution. Crushed ice was added to lower the solution temperature to ca. 5° C. The excess of hexacyanoferrate(III) ion was then back-titrated with standard cobalt(II) chloride solution.

A 0.05 M cobalt(II) chloride solution was standardized by gravimetric chloride analysis, using 25.00 ml aliquots. A 0.05 M potassium hexacyanoferrate(III) solution was then standardized against the cobalt chloride solution by potentiometric titration, as above.

### 3. Carbon and Hydrogen

Carbon and hydrogen microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

### C. Instrumental Methods

### 1. Infrared Spectra

Infrared spectra, in the range 4000 to 625 $cm^{-1}$, were recorded on a Beckman Model IR-8 double-beam recording

spectrophotometer. Sodium chloride cells were used. Spectra were obtained using Nujol mulls, thin films, or. ca. 5% solutions in $CCl_4$ or $CHCl_3$ (in 0.1 mm matched cells, with solvent as reference). The wavelength scale was calibrated with the spectrum of a polystyrene film. A Beckman Model IR-7 double-beam recording spectrophotometer was used to record the infrared spectrum of triethylphosphine oxide.

## 2. Electronic Spectra

A Beckman Model DK-2 double-beam recording spectrophotometer was used to record solution spectra in the ultraviolet, visible, and near-infrared regions (50,000 to 4000 $cm^{-1}$). A pair of one cm near-infrared silica cells was used for solution studies. These cells were capped with ground-glass stoppers for spectra of air-sensitive solutions.

## 3. Magnetic Susceptibility Measurements

The effective magnetic moments of two of the cobalt complexes were obtained at room temperature using the Gouy method. Measurements were made at a field strength of about 5 kgauss, using an Alpha Model AL 7500 water-cooled magnet with 4-in. pole faces and a 1.5 in. air gap. The strength of the magnetic field was controlled by adjusting the current from an Alpha Model 7500 power supply. Gouy

tubes were calibrated with mercury(II) tetrathiocyanatocobaltate(II),

prepared by the method of Figgis and Nyholm (1958).

The gram susceptibility, $\chi_g$, of a complex was calculated from

the equation

$$\chi_g = \frac{\beta \cdot F'}{W}$$

where $\beta$ is the tube calibration constant, $F'$ is the weight gain (in

mg) of the paramagnetic sample in the magnetic field (corrected for

diamagnetic contribution from the Gouy tube), and $W$ is the weight of

the sample (in g). The molar susceptibility, $\chi_M$, was obtained by

multiplying the gram susceptibility by the molecular weight of the com-

plex. Pascal's constants (Figgis and Lewis, 1963) were used to cor-

rect the molar susceptibility for diamagnetic contributions from the

ligands. No correction for temperature independent paramagnetism

was made. Magnetic moments, $\mu_{eff}$, were calculated using the

equation

$$\mu_{eff} = 2.828\,(T \cdot \chi_M^{corr})^{\frac{1}{2}}$$

## 4. Conductivity Measurements

Conductivities of o-dichlorobenzene solutions were measured

with an Industrial Instruments Model RC16B2 conductivity bridge and

an Industrial Instruments conductivity cell. The cell constant of the

conductivity cell was determined by the manufacturers to be

$0.100 \text{ cm}^{-1}$.

The molar conductance, $\Lambda_M$ (ohm$^{-1}$ cm$^2$ mole$^{-1}$) is given by

$$\Lambda_M = (1000/M)(L)$$

where L (ohm$^{-1}$ cm$^{-1}$) is the measured conductance multiplied by the cell constant and M is the concentration of the solution in moles per liter.

## 5. Gas Chromatography

A temperature-programmed F and M Model 700 gas chromatograph was used to check the purity of the organophosphorus ligands and to analyze the product of the autoxidation reaction. A six foot stainless steel column packed with 10% SE-30 (methyl silicone gum rubber) on Chromosorb W gave incomplete separation of the organophosphoryl ligands but was useful for identification by comparison with authentic samples.

## D. Oxygen Uptake Measurements

## 1. Preliminary Methods

An experimental system and method similar to that described by Buckler (1962) was tried for the purpose of calculating the amount of oxygen consumed by dichlorobis(triethylphosphine)cobalt(II) solutions. A Beckman oxygen analyzer was used to measure the percentage

oxygen by volume in the gas stream exiting from the reaction vessel. The total volume of gas was measured with a wet test meter. Buckler's results were qualitatively reproduced with tributylphosphine solutions, but the autoxidation of dichlorobis(triethylphosphine)- cobalt(II) was too slow at both 26° and 59° to detect any significant decrease of the percent oxygen in the exit stream.

Warburg manometers, with vapor spaces of ca. 20 ml, are frequently used to measure the absorption of small quantities of gas in respiration and photosynthesis studies in aqueous systems (Umbreit, Burris, and Stauffer, 1957). Experiments with this type of apparatus were largely unsuccessful as a method of measuring oxygen uptake by the triethylphosphine complex in benzene. The small vapor space necessitated the use of small quantities of complex and made small changes in vapor pressure of the solvent significant.

The lower manifold of a vacuum line with adjacent mercury manometer was adapted for use as a manometric system. The vapor space of this system was approximately 400 ml. In addition, the solvent for the autoxidation was changed from benzene to o-dichloro- benzene, which is much less volatile. With these modifications, some quantitative measurements of oxygen uptake were measured as a func- tion of time. However, this system suffered from the disadvantage that neither the volume nor the pressure remained constant.

## 2. Kinetic Measurements

Kinetic measurements were made in a constant-pressure apparatus. A 3-way stopcock (leading to an oxygen source and to a vacuum pump), another stopcock with standard-taper joint for the reaction flask, a ball joint leading to a mercury manometer, and another ball joint leading to a 50 ml gas buret, were built onto a 20 cm manifold made of 12 mm o.d. glass tubing. The pressure of the system was kept constant during a kinetic run with a mercury leveling bulb attached to the gas buret. Before each volume reading, the pressure was adjusted to the pre-set value using a cathetometer to define the lower level of mercury in the manometer. Room temperature was held as constant as possible, usually within ± 1°.

A special reaction flask was constructed for the kinetic work. Four indentations were made in the walls of a 50 ml Erlenmeyer flask fitted with a standard-taper joint. Solutions were stirred magnetically; the indentations caused greater agitation of the solution for more efficient aeration. A jacket with hose connections was built around the flask for connection to a Haake Model "F" Constant Temperature circulator.

In a typical run, 40 ml of the dichlorobis(triethylphosphine)-cobalt(II) solution was pipetted into the reaction flask in a nitrogen-filled glove bag. The flask was fitted with a stopcock with joints,

and the vapor space was immediately evacuated with a vacuum pump.

The reaction flask was connected to the kinetic apparatus manifold.

The manifold was alternately filled with oxygen and evacuated four

times while the solution was brought to reaction temperature by the

circulating bath. The quiescent reaction solution was then exposed to

the oxygen atmosphere. As quickly as possible, the leveling bulb was

adjusted to give the desired pressure in the system, and the initial

volume reading was recorded. Then the magnetic stirrer was turned

on, thereby defining time $t = 0$ for the kinetic run. Calculations of

oxygen uptake were obtained from the ideal gas law, $\Delta n = (P/RT)(\Delta V)$,

using room temperature as the value of T.

Kinetic runs in t-butylbenzene solutions at different stirring

rates showed that the reaction rate was not limited by diffusion of

oxygen across the gas-liquid interface with the stirring rates that were

used. Unstirred solutions, however, did absorb oxygen more slowly

than stirred ones.

t-Butylbenzene solutions showed a large, rapid oxygen uptake in

the first two to three minutes that was not quantitatively reproducible

in either duplicate kinetic runs or blank runs with the solvent. The

magnitude of this initial absorption of oxygen by the solvent for each

kinetic run was then determined by plotting the kinetic data for the

first 5-7 minutes and extrapolating to the origin. The reason for this

irreproducibility is unknown, but may be related to an error in the

initial volume reading, from which all other readings are subtracted

for the calculation of the amount of oxygen consumed.

### 3. Exhaustive Autoxidation Method

A special one-piece glass apparatus was built for the purpose

of running autoxidation reactions under conditions that would insure

completion. A gas dispersion tube (coarse frit) extended toward the

bottom of a 500 ml flask with a West condenser attached to the neck.

The flask was set in a hot mineral oil bath and oxygen was bubbled

through the solutions and out a mineral oil trap for a long period of

time. Weight gains due to oxygen uptake by the solute were calculated

by carefully weighing the amount of complex put into the apparatus and

then quantitatively recovering the complex from the solvent after

exhaustive autoxidation.

## IV. RESULTS AND DISCUSSION

### A. Properties of the Cobalt Complexes

#### 1. Thermal Behavior of the Ester Complexes, $CoCl_2 \cdot 2Et_n(EtO)_{3-n}PO$

The removal of an excess of triethyl phosphate from cobalt(II)

chloride in a vacuum line reaction bulb at room temperature yielded

an oil with a negligible dissociation pressure, identical to the

$CoCl_2 \cdot 2(EtO)_3PO$ described earlier. However, when the same process

was carried out at an elevated temperature, a highly volatile sub-

stance was evolved (slowly at 140°, rapidly at 190°) and trapped in the

vacuum line. A dark blue-violet solid residue remained. The volatile

substance was identified as ethyl chloride by vapor density (mol wt

found 68; calcd. 64.5) and vapor pressure measurements in the range

0 to -53°, which gave excellent agreement with the literature data

(Chemical Rubber Publishing Company Handbook, 1968). The solid

residue gave only a slight turbidity with aqueous silver nitrate. It

was purified by dissolution in chloroform, removal of a trace of

insoluble material by filtration, and evaporation of the solvent from

the filtrate in vacuo. The product then gave a negative chloride test

and was found by analysis (Table 3) to be cobalt(II) diethylphosphate;

mp 181-182°. It is soluble in chloroform, very slightly soluble in

ethers, insoluble in acetone, carbon tetrachloride, paraffin and

aromatic hydrocarbons, and gives pink solutions in water and alcohols.

Table 3. Chemical Analyses of Thermal Decomposition Products.

| Compound | Cobalt | | Carbon | | Hydrogen | |
|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $Co[O_2P(OC_2H_5)_2]_2$ | 16.14 | 16.19 | 26.32 | 26.65 | 5.52 | 5.69 |
| $Co[O_2P(OC_2H_5)(C_2H_5)]_2$ | 17.69 | 18.11 | 28.85 | 27.42 | 6.05 | 5.91 |
| $Co[O_2P(C_2H_5)_2]_2$ | 19.57 | 19.35 | 31.91 | 31.72 | 6.69 | 6.72 |

When pure dichlorobis(diethyl ethylphosphonate)cobalt(II) or

dichlorobis(ethyl diethylphosphinate)cobalt(II) was heated at 190-200°

in a vacuum line bulb, ethyl chloride was evolved over several hours

and identified as above. With the former, the loss in weight cor-

responded to 2.13 ± 0.14 mole of ethyl chloride per mole of initial

complex, and analysis (Table 3) indicated imperfect purity of the

product. With the former, exactly 2.00 mole of ethyl chloride was

lost per mole of initial complex, and the analysis (Table 3) of the

product was satisfactory. Cobalt(II) ethyl ethylphosphonate is a dark

blue, very viscous tar, which solidifies on standing, and cobalt(II)

diethylphosphinate is a dark blue gummy solid. They are both soluble

in chloroform, and slowly give pink solutions in water.

Dealkylation of trialkylphosphates by thermal decomposition in

the presence of metal halides has been observed previously (Hayek

and Rhomberg, 1952; Gutmann and Fenkart, 1968; Zervas and Dilaris,

1955), but this is the first time that characterization of the alkyl

halide evolved has been reported.

A great deal of work has been done with dialkyl- and diarylphos-

phinate complexes, prepared in ways other than described above

(Coates and Golightly, 1962; Crescenzi, Giancotti, and Ripamonti,

1965; Block et al. , 1967, and references therein; Drinkard and

Kosolapoff, 1952). These complexes have been shown to be coordination

polymers, with double-bridged structures, as shown below.
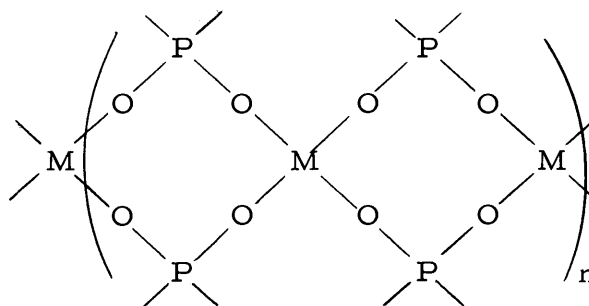


Coates and Golightly also pointed out that it is unlikely that

oxyacids can form four-membered rings with metals of tetrahedral

stereochemistry, as the steric strain, in the sense of deformation of

bond angles from their normal values, would be too great. Therefore,

it is unlikely that the $Co[O_2P(C_2H_5)_n(OC_2H_5)_{2-n}]_2$ complexes would

be monomeric, with chelating $O_2PRR'^-$ anionic ligands, as suggested

by Gutmann and Fenkart. The physical properties of these complexes

suggest double-bridged polymeric structures.

An interesting property of cobalt(II) diethylphosphate in chloro-

form was observed. A dark blue solution at room temperature turned

pink when cooled in a dry ice-acetone bath (-78°). The process was

completely reversible. Presumably, another type of association

occurs at the lower temperature, resulting in an octahedral environ-

ment around the cobalt atom.

## 2. Structure of the Cobalt Complexes

All the cobalt complexes prepared in this work are pseudo-

tetrahedral according to the criteria of Cotton and co-workers (Cotton,

Goodgame, and Goodgame, 1961). Such complexes are characterized

by magnetic moments in the range of about 4.3 to 5.0 Bohr Magnetons,

and by their ligand field spectra. Of the three $\underline{d}$-$\underline{d}$ transitions pre-

dicted, one assigned as $\nu_3 = {}^4A_2 \longrightarrow {}^4T_1(P)$ comes in the visible region

at the low energy end, and accounts for the characteristic "cobalt

blue" color of these materials. Even in rigorously tetrahedral micro-

symmetry (as of the $CoO_4$ chromophore) this transition commonly

shows some splitting due to spin-orbit coupling (Cotton $\underline{et}$ $\underline{al}$., 1961).

In mixed ligand complexes such as $CoX_2L_2$ of $C_{2v}$ symmetry, the

transition becomes ${}^4A_2 \longrightarrow {}^4A_2 + {}^4B_1 + {}^4B_2$, while in complexes

$CoX_2LL'$ of $C_s$ symmetry, it is ${}^4A'' \longrightarrow {}^4A' + 2{}^4A''$. Thus, the

"average ligand field" approximation may be applied to the center of

gravity of the transition envelope, and the absorption band may show

structure or be resolved into its three components.

The starting material for the autoxidation research,

$CoCl_2 \cdot 2Et_3P$, is a well-known example of such a pseudo-tetrahedral

complex, as indicated by its dipole moment of 8.7 Debye in benzene (Jensen, 1936) and its magnetism and electronic spectrum. Magnetic moments in the range 4.39 to 4.48 B.M. have been reported (Hatfield and Yoke, 1962; Nicolini, Pecile, and Turco, 1965); a value of 4.50 B.M. at 25° C was determined in this work. The electronic spectrum has been reported in benzene solution (Jensen et al., 1963) and by diffuse reflectance (Hatfield and Yoke, 1962).

In the present work, large solvent effects have been observed on the $^4A_2 \longrightarrow ^4T_1$(P) absorption band of this complex, both in terms of resolution of components and of details of peak positions, shapes, and intensities. The spectrum in benzene, shown in Figure 1, consists of a broad band with partially resolved maxima at 606 and 623 nm and a second rather narrow band at 730 nm. Spectra in acetone, chloroform, mesitylene, and t-butylbenzene are generally similar, but a significant difference is observed in o-dichlorobenzene as is shown in Figure 2. This is attributed to partial ionic dissociation in this solvent, with the formation of new complex solute species. The molar conductance of a 0.97 X $10^{-3}$ molar solution of $CoCl_2 \cdot 2Et_3P$ in o-dichlorobenzene was found to be 0.27 $ohm^{-1}cm^2mole^{-1}$; this may be compared to the value of 1.43 $ohm^{-1}cm^2mole^{-1}$ found for a typical 1:1 electrolyte, tetra-n-butylphosphonium chloride, in this solvent. In carbon tetrachloride, a $10^{-3}$ molar solution could not be prepared at room temperature; the solubility appeared to be somewhat less than half of this. The
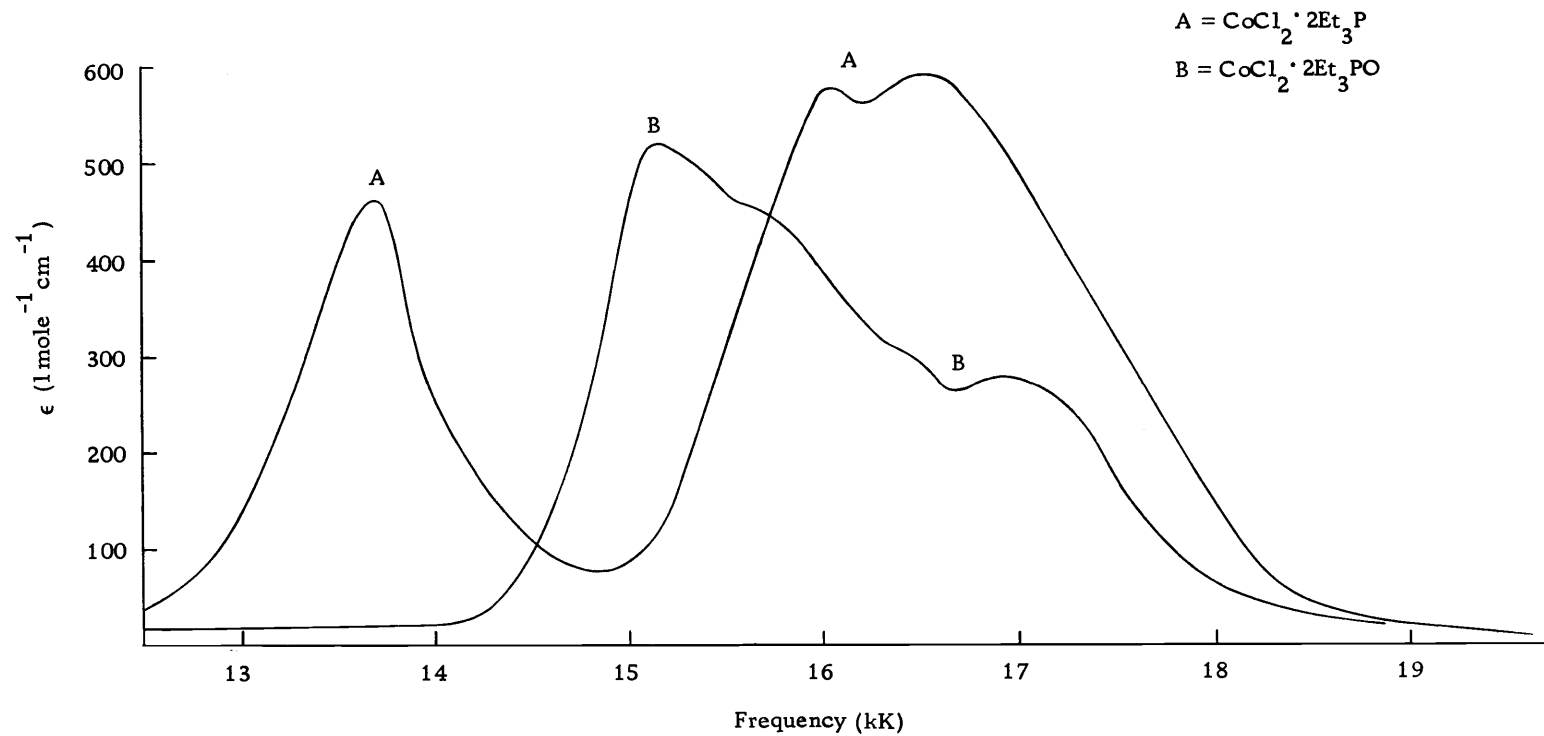
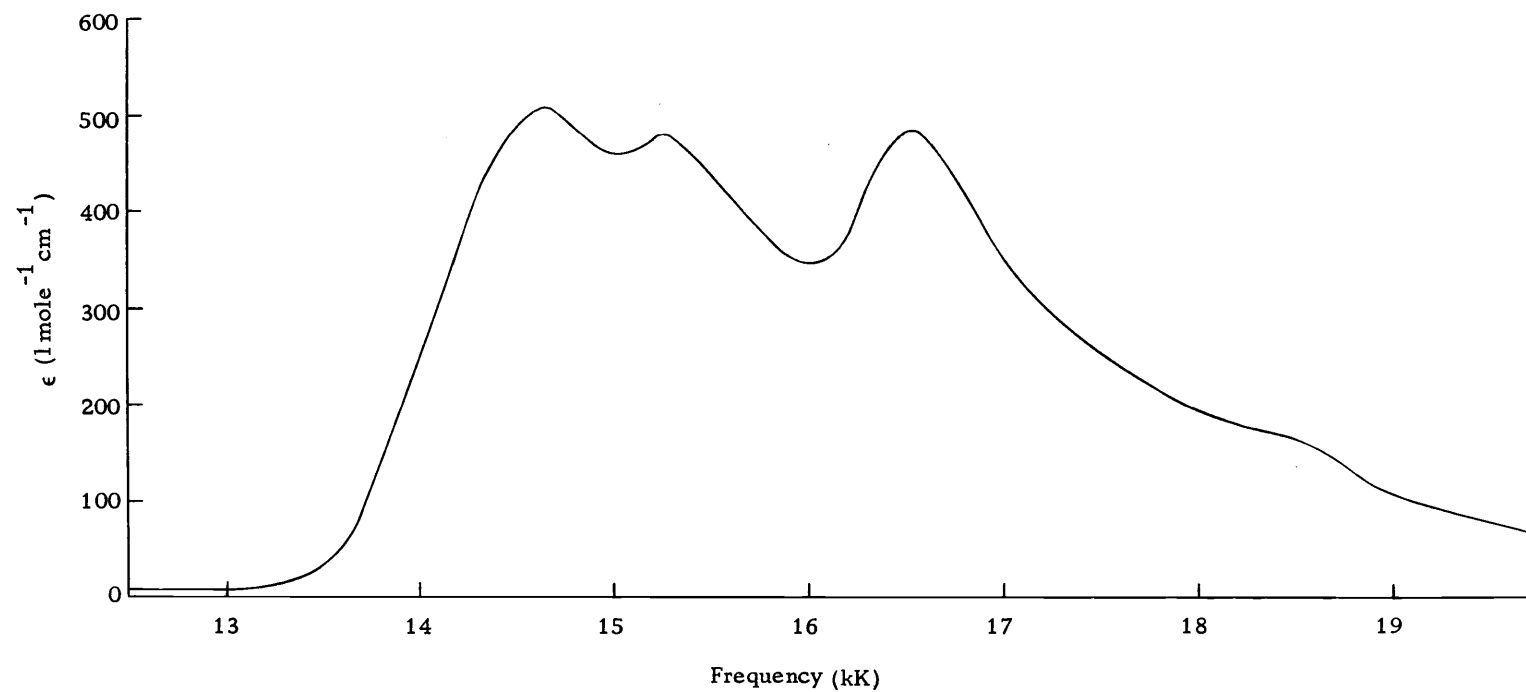Figure 1. Visible Spectra of $CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$ in Benzene

Figure 2.   Visible Spectrum of $CoCl_2 \cdot 2Et_3P$ in o-Dichlorobenzene at 50° C

spectrum of the deep violet saturated solution was characterized by an extremely intense symmetrical band at about 555 nm. The great spectral change is attributed to a rapid chemical change of an unknown nature. All of the spectra were taken using freshly prepared solutions protected from the air, to eliminate reaction with atmospheric oxygen. Details of the spectra of $CoCl_2 \cdot 2Et_3P$ in various solvents are given in Table 4.

Table 4. Solvent Effects on the Visible Spectrum of $CoCl_2 \cdot 2Et_3P$

| Solvent | Absorption Maxima (nm), (Extinction Coefficients) | | | | | |
|---|---|---|---|---|---|---|
| Benzene | 730 (460) s; | | | 623 (580), | 606 (590) | |
| Chloroform | 716 (450) s; | | | | 613 (650) | |
| Acetone | 715 (350) s; | | | 620 (430)sh, | 600 (470) | |
| n-Pentane | 730 br; | | 610 sh, | 590 sh, 580 br, | 570 sh | |
| t-Butylbenzene | 730 (380) s; | | | 622 (520), | 603 (530) | |
| o-Dichlorobenzene | 690 (430) ; | 654 (410), | 640 (410); | 608 (510) | | |
| o-Dichlorobenzene ($50^{\circ}$) | 683 (500) ; | 650 (480); | | 606 (480) | | |

s = sharp, br = broad, sh = shoulder

The visible spectra of all the ethyl phosphoryl complexes are listed in Table 5, and that of $CoCl_2 \cdot 2Et_3PO$ is displayed in Figure 1, for comparison with the spectrum of $CoCl_2 \cdot 2Et_3P$. The rule of average ligand environment is seen to apply to the $CoCl_2O_2$ chromophore better than to the $CoCl_2P_2$ chromophore; much less splitting of the $^4A_2 \longrightarrow {}^4T_1(P)$ transition into its components is apparent in the spectrum of the phosphine oxide complex. This is reasonable in terms

of the greater similarity of chloride to oxygen than to phosphorus in coordinate bond type and position in the spectrochemical series. The visible spectra of all the $CoCl_2 \cdot 2Et_n(EtO)_{3-n}PO$ complexes, n = 0-3, are nearly identical and hence worthless for distinguishing between them as possible autoxidation products. It is interesting that although significant substituent effects are noted on the phosphoryl infrared stretching frequencies in the $Et_n(EtO)_{3-n}PO$ series, the ligand field strengths of the different phosphoryl compounds are the same. The use of each of the three liquid members of the series as solvents for anhydrous cobalt(II) chloride did not give higher complexes; blue solutions were obtained with spectra identical to those in Table 5.

Table 5. Electronic Spectral Data for Cobalt(II) Compounds

| Compound | Wavelength, nm ($\epsilon$) | Solvent |
|---|---|---|
| $CoCl_2 \cdot 2Et_3PO$ | 662 (375); 640sh; 614sh; 596sh | $CHCl_3$ |
| $CoCl_2 \cdot 2Et_2(EtO)PO$ | 665 (350); 645sh; 614sh; 596sh | $C_6H_6$ |
| $CoCl_2 \cdot 2Et(EtO)_2PO$ | 665; 645sh; 614sh; 596sh | Neat |
| $CoCl_2 \cdot 2(EtO)_3PO$ | 668; 645sh; 614sh; 596sh | Neat |
| $Co[O_2P(OEt)_2]_2$ | 623 (280); 600sh; 580sh; 550sh | $CHCl_3$ |
| $Co[O_2P(OEt)Et]_2$ | 624 (290); 603sh; 581sh; 554sh | $CHCl_3$ |
| $Co[O_2PEt_2]_2$ | 631 (290); 604sh; 585sh; 547sh | $CHCl_3$ |

sh = shoulder

The spectra of the $Co[O_2PEt_n(OEt)_{2-n}]_2$ complexes, n = 0-2, are very similar to each other. Their transition comes at a somewhat higher energy, in accordance with the position of oxygen donors higher than chloride in the spectrochemical series, and the application of the average ligand field rule to the $CoO_4$ and $CoCl_2O_2$ chromophores.

The room temperature magnetic moments measured for $CoCl_2 \cdot 2Et_3PO$ (4.77 B.M.) and for $Co[O_2P(OEt)_2]_2$ (4.60 B.M.) are additional evidence for the assignment of pseudo-tetrahedral structures. The values are also in accord with the higher ligand field of the $CoO_4$ chromophore than of the $CoCl_2O_2$ grouping, since the amount by which the spin-only moment is exceeded varies inversely with ligand field strength (Cotton and Holm, 1959).

## 3. Infrared Spectra of the Complexes and Their Ligands

The infrared spectrum of $CoCl_2 \cdot 2Et_3P$ has been fully described by Jensen et al. (1963) and compared with the spectrum of free triethylphosphine as reported by Kaesz and Stone (1959b). Jensen et al. (1963) and Miller (1965) both make the observation that spectra of phosphines are not changed markedly when they are present as ligands in metal coordination compounds.

Infrared spectra of the four ethyl phosphoryl ligands $Et_nP(O)(OEt)_{3-n}$, n = 0-3, are shown adjacent to those of their

respective cobalt chloride complexes in Tables 5-8 and in Figures

3-6 (in the region 750-1500 $cm^{-1}$). The infrared spectra of

$Co[O_2PEt_n(OEt)_{2-n}]_2$, n = 0-2, are tabulated in Table 9, and the

spectra in the region 850-1500 $cm^{-1}$ are given in Figure 7.

Assignments for most of the absorption bands are designated in

the tables. These assignments were made by a careful comparison of

the spectra of the ligands and their cobalt(II) chloride complexes in

the progression from triethylphosphine to $(EtO)_nP(O)Et_{3-n}$, n = 0-3,

and by reference to similar correlation studies in the literature.

Particular attention was paid to the P=O and P-O-C bands. Their

presence or absence proved to be of critical significance in the com-

parison of these reference standards to the product of the autoxidation

reaction. McIvor, Grant, and Hubley (1956) observed that a weak

band occurs between 1107 and 1099 $cm^{-1}$, usually at 1105 $cm^{-1}$, in

all EtO-P compounds. Bellamy (1964), McIvor et al. (1956), and

Daasch and Smith (1951) describe a sharp, weak-medium intensity

peak at 1150-1170 $cm^{-1}$ which is characteristic of ethoxy phosphoryl

compounds. These two bands are observed in this series of compounds

when not obscured by stronger intensity peaks. Assignments for C-C

and C-H skeletal modes and for P-C stretches are made less con-

fidently than for the P=O and P-O-C vibrations; they are extensions of

the assignments that Kaesz and Stone (1959b) gave to $Et_3P$.

Assignments for $Co[O_2P(OEt)Et]_2$ in the region 1101-1050 $cm^{-1}$

Table 6. Infrared Spectra ($cm^{-1}$) of Triethylphosphine Oxide and Its $CoCl_2$ Complex

| $Et_3PO$ [a] | | $CoCl_2 \cdot 2Et_3PO$ | |
|---|---|---|---|
| (Soln. in $CCl_4$) | | (KBr disc) | |
| 2976, 2948m<br>2920, 2892m | } $CH_2$ stretch | 2976, 2940m<br>2907, 2874m | } $CH_2$ stretch |
| 1463m | $CH_3$ def., anti-sym. | 1451m | $CH_3$ def., anti-sym. |
| 1414m | $CH_2$ scissor | 1401m | $CH_2$ scissor |
| 1385w | $CH_3$ def., sym. | 1381w sh | $CH_3$ def., sym. |
| 1279w, 1268w sh<br>1250w | } $CH_2$ wag | 1282m br<br>1244vw | } $CH_2$ wag(?) |
| 1180vs | P=O stretch | 1124m sh [b]<br>1099s | ???<br>P=O stretch |
| 1040m<br>1024m<br>1010w | } $CH_3$ rock | 1044m<br>1028vw sh<br>1002w | } $CH_3$ rock |
| 997w<br>985w | } C-C stretch | 981w<br>783, 774s br<br>743, 725w | C-C stretch<br>P-C stretch(?)<br>$CH_2$ rock |

s = strong,  m = medium,  w = weak,  v = very,  sh = shoulder,  br = broad,  pk = peak

[a] The IR spectrum of $Et_3PO$ is also reported by Hooge and Christen (1958).

[b] The shoulder at 1124 $cm^{-1}$ may be due to a splitting of the phosphoryl frequency by complex formation, as discussed by Cousins and Hart (1967) and by Cotton et al. (1960).
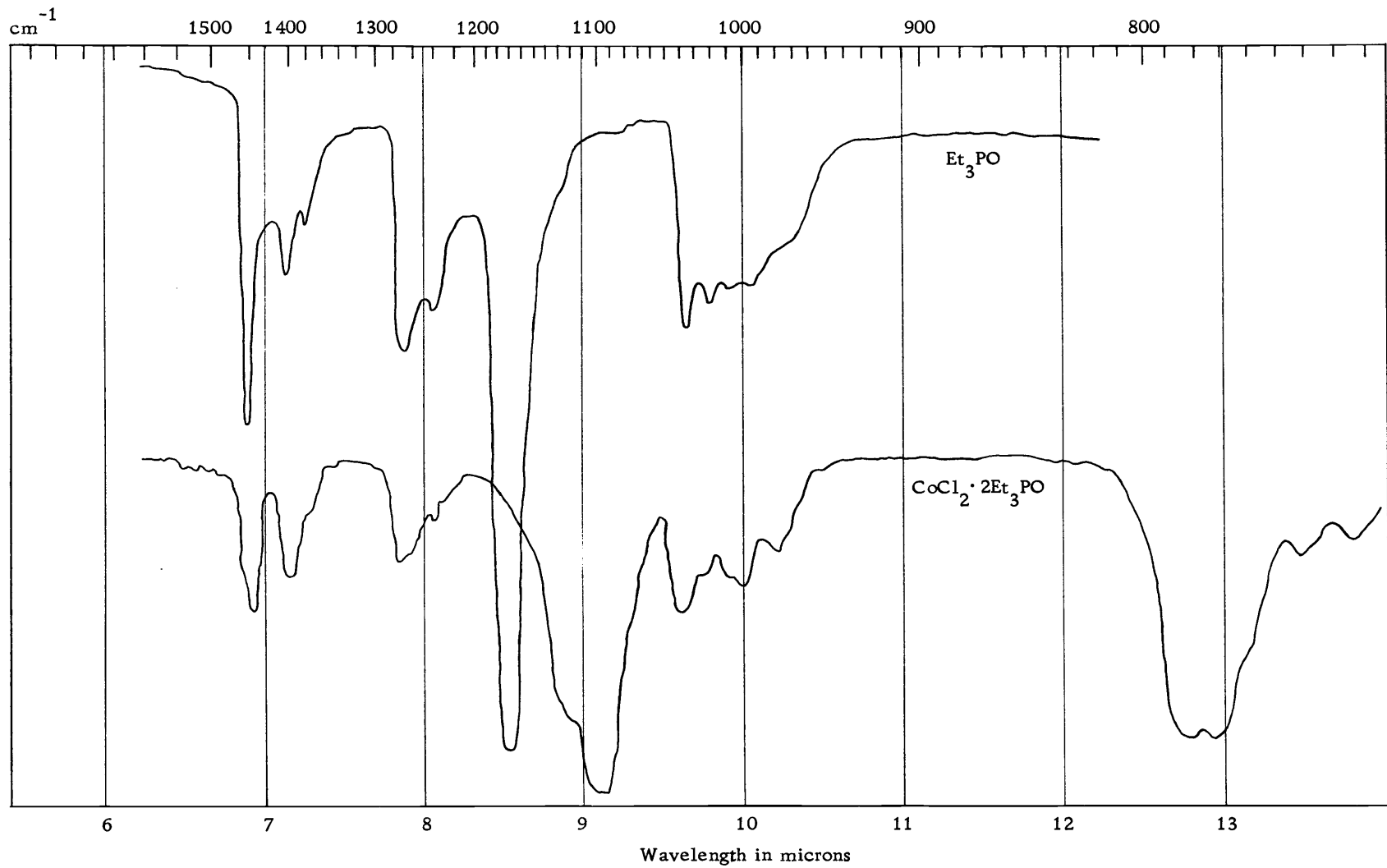
Figure 3. IR Spectra (ca. 750-1500 cm$^{-1}$) of Et$_3$PO and CoCl$_2 \cdot$ 2Et$_3$PO

Table 7.  Infrared Spectra (cm$^{-1}$) of Ethyl Diethylphosphinate and Its $CoCl_2$ Complex

| Et$_2$(EtO)PO | | CoCl$_2 \cdot$ 2Et$_2$(EtO)PO | |
|---|---|---|---|
| (Thin film) | | (Thin film) | |
| 3000-2890m | CH$_2$ stretch | 2994, 2959m<br>2924m<br>2900m | } CH$_2$ stretch |
| 1456 | CH$_3$ def., anti-sym. | 1458m | CH$_3$ def., anti-sym. |
| 1406m | CH$_2$ scissor(?) | | |
| 1391m | CH$_3$ def., sym. | 1397m | CH$_3$ def., sym. |
| 1271m | } CH$_2$ wag(?) | 1271m | } CH$_2$ wag(?) |
| 1245m | | 1236w | |
| 1201s | P=O stretch | 1136s br | P=O stretch |
| 1163w | P-O-Et | | |
| 1094w | P-O-Et | 1096w | P-O-Et |
| 1047s | P-O-C | 1042s sh | P-O-C |
| 1026s | P-O-C | 1021s | P-O-C |
| 949m | P-O-C | 954m | P-O-C |
| (800-760)m br | P-C(?) or sym. P-O-Et | 786m br | P-C(?) or sym. P-O-Et |
| | | 741vw | CH$_2$ rock |
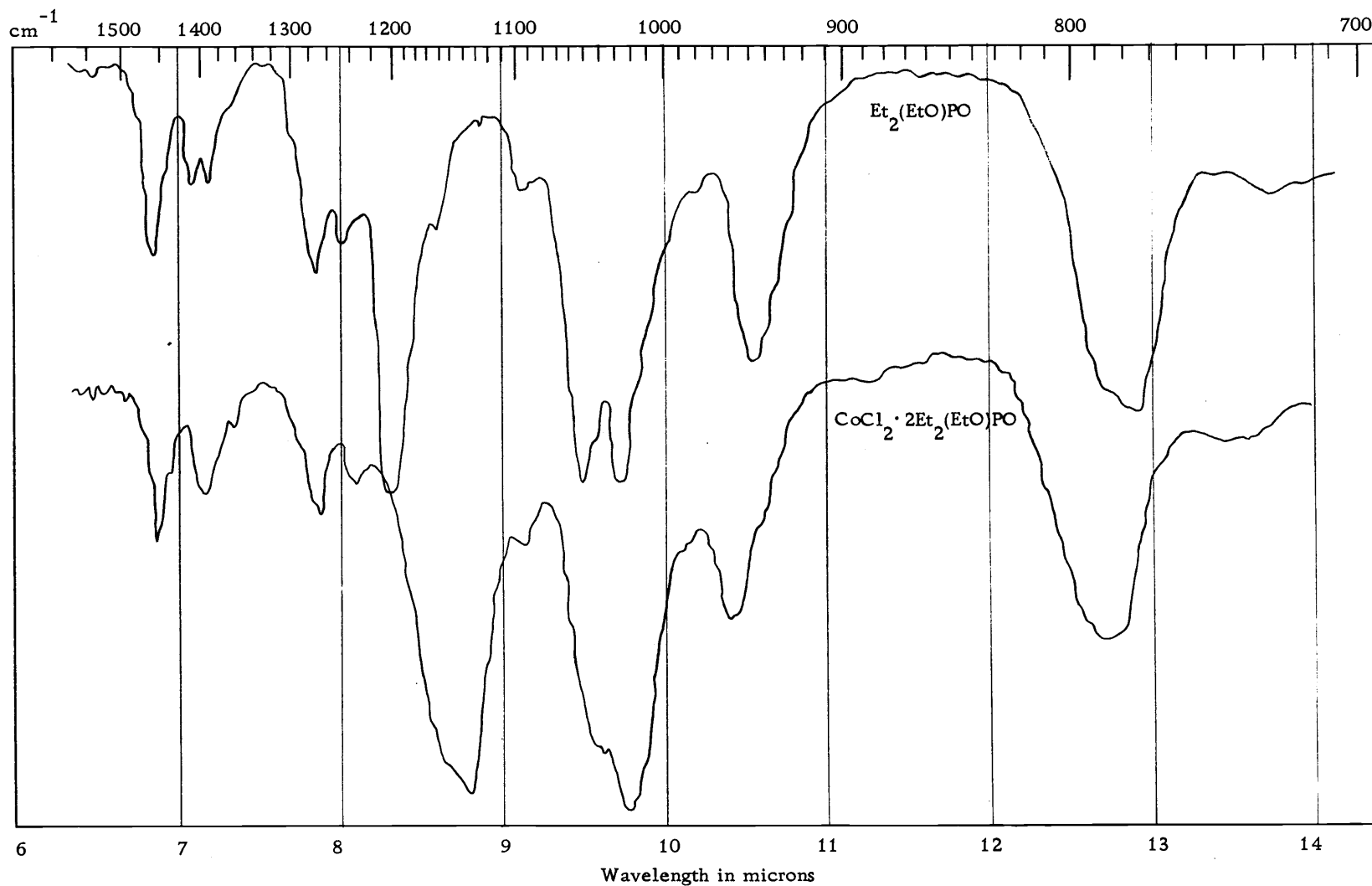
Figure 4. IR Spectra (<u>ca</u>. 750-1500 cm$^{-1}$) of Et$_2$(EtO)PO and CoCl$_2 \cdot$ 2Et$_2$(EtO)PO

Table 8. Infrared Spectra (cm$^{-1}$) of Diethyl Ethylphosphonate and Its CoCl$_2$ Complex

| Et(EtO)$_2$PO [a] | | CoCl$_2 \cdot$ 2Et(EtO)$_2$PO | |
|---|---|---|---|
| (Thin film) | | (Thin film) | |
| 2994, 2950m | | 2992, 2950m | |
| 2915m | } CH$_2$ stretch | 2924m | } CH$_2$ stretch |
| 2899m | | | |
| 1456m | CH$_3$ def., anti-sym. | 1473, 1465m | CH$_3$ def., anti-sym. |
| 1439m | CH$_2$ scissor | 1439m | CH$_2$ scissor |
| 1387m, 1366m | CH$_3$ def., sym. | 1389m, 1365w | CH$_3$ def., sym. |
| 1282 | CH$_2$ wag(?) | 1284m | } CH$_2$ wag |
| | | 1239m | |
| 1250, 1227s | P=O stretch | 1182s | P=O stretch |
| 1160m | P-O-Et | | |
| 1095m | P-O-Et | 1095m | P-O-Et |
| 1057, 1037vs | P-O-C | 1053s | P-O-C |
| 1021vs | P-O-C | 1013s | P-O-C |
| 1005vs | P-O-C | | |
| 954s | P-O-C | 965m | P-O-C |
| | | 920w | ??? |
| 792m vbr | P-C(?) or sym. P-O-Et | 794m br | P-C(?) or sym. P-O-Et |
| | | 706-692w | CH$_2$ rock |

[a] The IR spectrum of diethyl ethylphosphonate is also reported by Meyrick and Thompson (1950).

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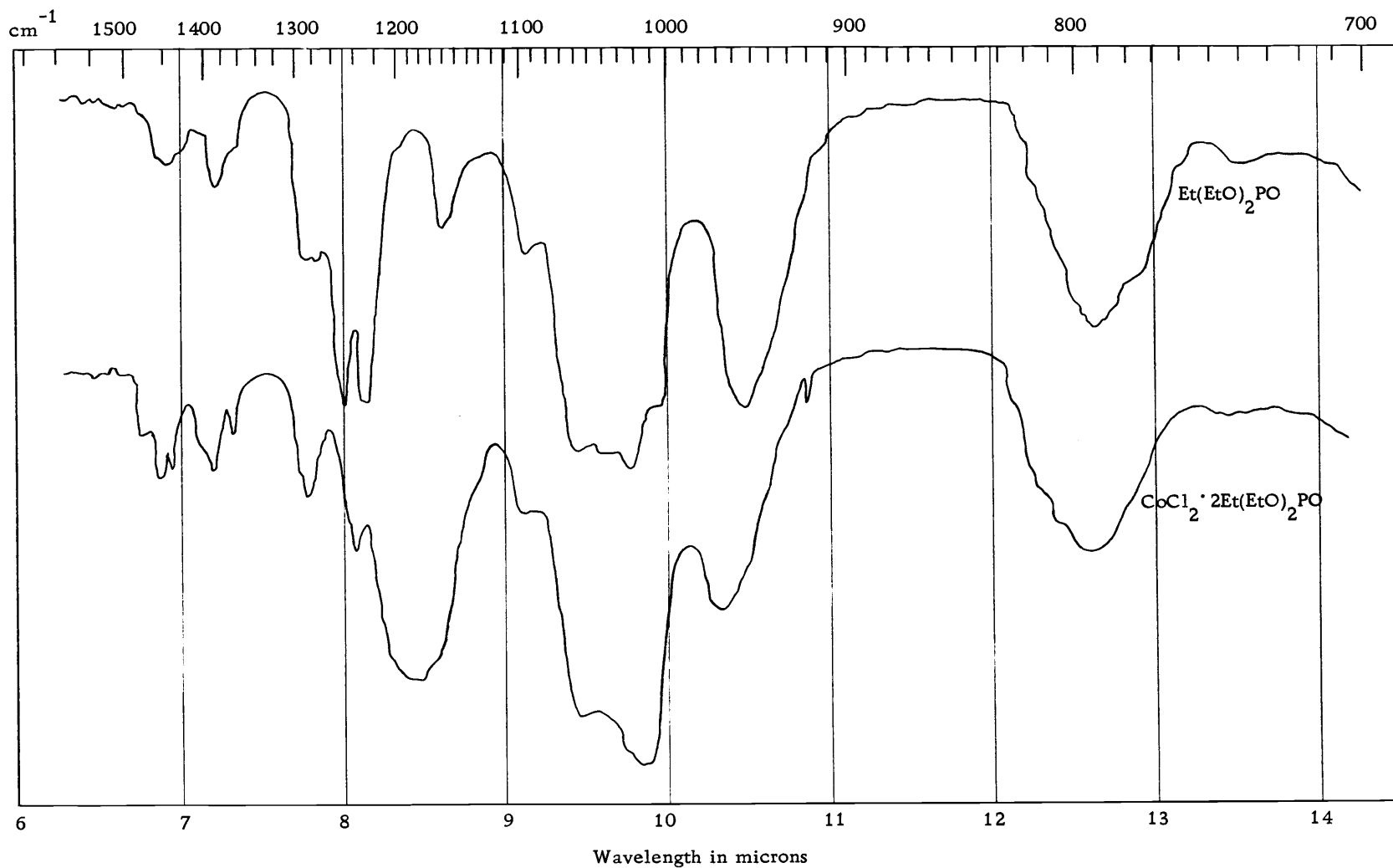
Figure 5. IR Spectra (ca. 750-1500 cm$^{-1}$) of Et(EtO)$_2$PO and CoCl$_2 \cdot$ 2Et(EtO)$_2$PO

Table 9. Infrared Spectra ($cm^{-1}$) of Triethyl Phosphate and Its Cobalt Chloride Complex

| $(EtO)_3PO$ [a] | | $CoCl_2 \cdot 2(EtO)_3PO$ | |
|---|---|---|---|
| (Thin film) | | (Thin film) | |
| 2994m <br> 2915m | } $CH_2$ stretch | 3003m <br> 2941m <br> 2882m | } $CH_2$ stretch |
| 1475m | $CH_3$ def., anti-sym. | 1475m | $CH_3$ def., anti-sym. |
| 1439m | $CH_2$ scissor | 1441m | $CH_2$ scissor |
| 1391m, 1368m | $CH_3$ def., sym. | 1391, 1368m | $CH_3$ def., sym. |
| | | 1290m | $CH_2$ wag(?) |
| 1271, 1263s | P=O stretch | 1227s | P=O stretch |
| 1163m | P-O-Et | 1163s | P-O-Et |
| 1093m sh | P-O-Et | 1099m | P-O-Et |
| 1029vs | P-O-C | 1031vs br | P-O-C |
| 963s | P-O-C | 982s | P-O-C |
| 810m br <br> 796m br | } sym. P-O-Et | 818m br <br> 800m br | } sym. P-O-Et |

[a] The existence of doublet phosphoryl absorptions is discussed by Bell et al. (1954) and by Thomas and Chittenden (1964). Gramstad (1964) reports 1279 and 1263 $cm^{-1}$ for the phosphoryl doublet of triethyl phosphate, and Bellamy and Beecher (1952) report 1280 and 1264 $cm^{-1}$.
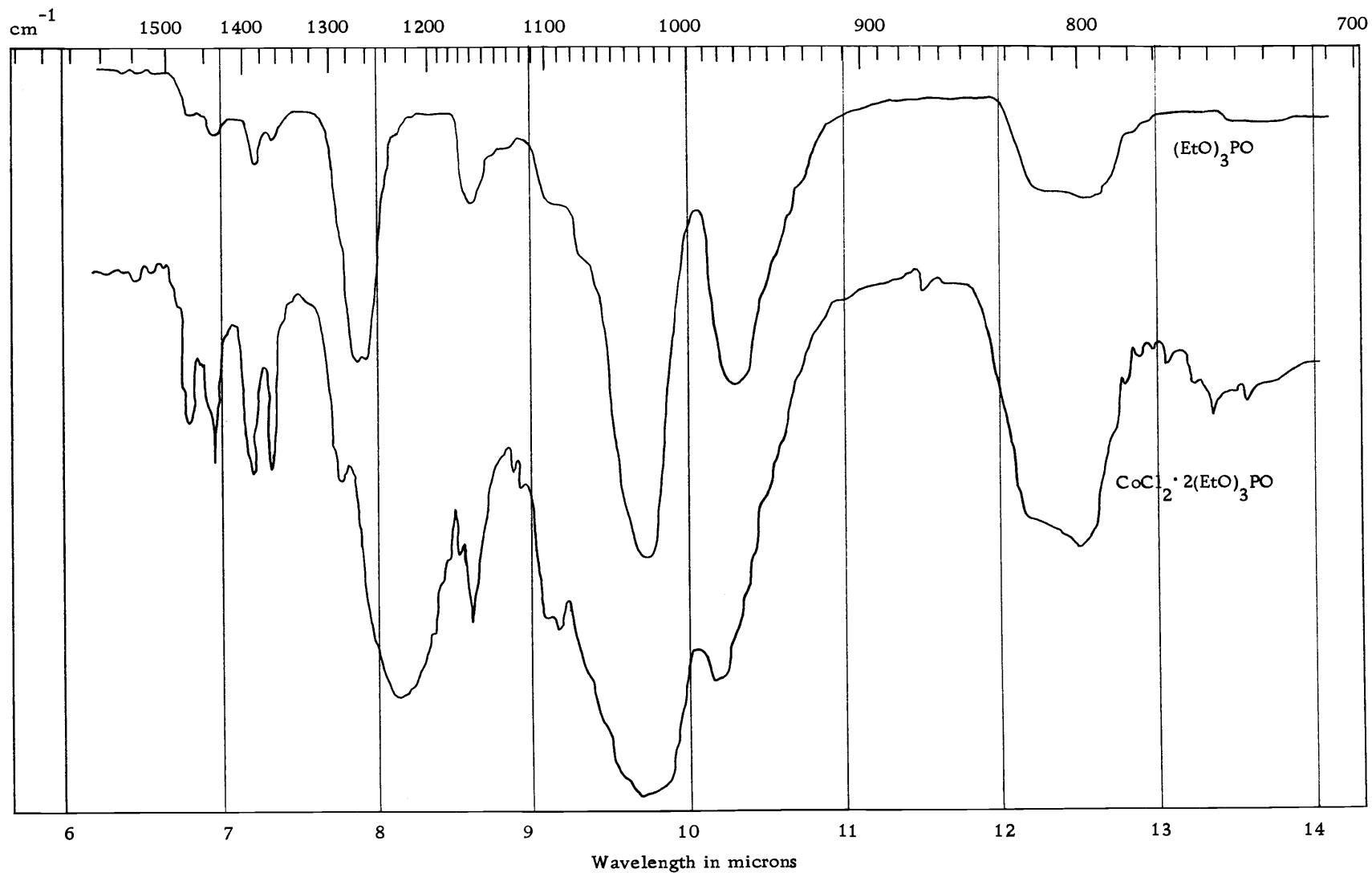
Figure 6. IR Spectra (ca. 750-1500 cm$^{-1}$) of (EtO)$_3$PO and CoCl$_2$·2(EtO)$_3$PO

Table 10.  Infrared Spectra $(\text{cm}^{-1})$ of the Thermal Decomposition Products in $CHCl_3$ Solution

| $Co(O_2PEt_2)_2$ | $Co(O_2P(OEt)Et)_2$ | $Co(O_2P(OEt)_2)_2$ | Assignments |
|---|---|---|---|
| 2994, 2959m | 2994, 2959m | 2294m | } $CH_2$ stretch |
| 2924, 2899m | | 2924m | |
| 1462m | 1456m | 1473w | $CH_3$ def., anti-sym. |
| 1408m | 1408m | 1439w | $CH_2$ scissor |
| 1379w | 1389m | 1392w, 1366w | $CH_3$ def., sym. |
| 1269m | 1280m | 1282w sh | |
| 1236w | 1236m | 1220m sh | } $CH_2$ wag(?) |
| 1208w | 1208m sh | | |
| 1119vs | 1148vs | 1178s | Anti-sym. $PO_2^-$ stretch |
| | | 1171 (bump on 1178 pk) | P-O-Et(?) |
| 1052vs | 1078vs | 1112s | Sym. $PO_2^-$ stretch |
| | 1101vs | 1087s | P-O-ET(?) |
| | 1050vs | 1075, 1058, 1048s br | P-O-C |
| 1004w | 1007m | | C-$CH_3$ rock |
| 992w | 979w | | |
| | 958s | 971s | P-O-C |

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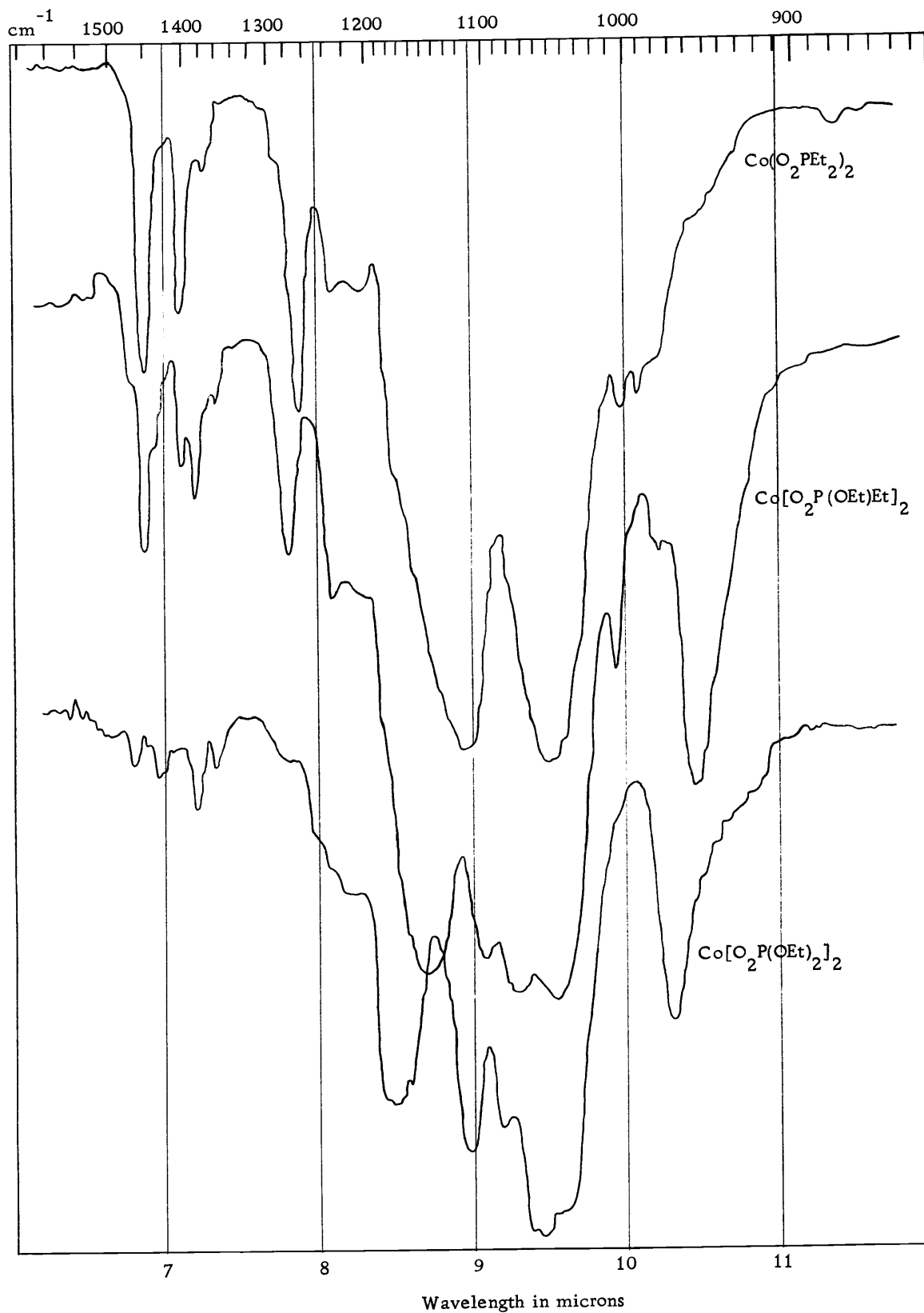


Figure 7. IR Spectra (ca. 850-1500 cm$^{-1}$) of the Thermal
Decomposition Products

are somewhat uncertain, and are made in comparison with the other

two anionic complexes. In $Co(O_2PEt_2)_2$, the very strong peaks at

1119 and 1052 $cm^{-1}$ are a doublet, as would be expected for asym-

metric and symmetric $PO_2$ stretching modes (Bellamy, 1964). The

$PO_2$ doublet for $Co[O_2P(OEt)_2]_2$ is assigned to the peaks at 1178 and

1112 $cm^{-1}$, even though the presence of the peak at 1171 $cm^{-1}$ appears

to make the former peak look broader than the latter. The separation

of the peaks in these doublets is about 67 $cm^{-1}$. The 1148 and 1078

$cm^{-1}$ peaks in $Co[O_2P(OEt)Et]_2$ have the same general shape and

percent transmittance minima and are 70 $cm^{-1}$ apart. In this empiri-

cal manner they are assigned as members of the $PO_2$ doublet.

Some characteristic infrared frequencies of all the phosphoryl

compounds are summarized in Table 11 as a more convenient

reference for the following discussion.

The presence or absence of P-O-C groups is readily apparent

from the intensities of peaks in the 940-1060 $cm^{-1}$ region. Triethyl-

phosphine oxide, dichlorobis(triethylphosphine oxide)cobalt(II), and

cobalt(II) diethylphosphinate show only weak absorptions in this region,

attributed to $C-CH_3$ modes in triethylphosphine (Kaesz and Stone,

1959b). In marked contrast, all the compounds containing P-O-C ester

groups exhibit a sharp strong band in the 949-982 $cm^{-1}$ region, as

well as one or two broad, very strong bands in the 1013-1058 $cm^{-1}$

region. In addition, the weak P-O-Et absorption described by

Table 11. Infrared Spectral Data $(cm^{-1})$ for the Ethyl Phosphoryl Compounds

| | 940 - 1060 Region | P-O-Et | P=O | $\Delta\nu_{P=O}$ |
|---|---|---|---|---|
| $Et_3PO$ | - ; 997w; 1010w; 1024w; 1040w | - | 1180s | |
| $CoCl_2 \cdot 2Et_3PO$ | - ; 981w; 1002w; 1028w; 1044w | - | 1099s | 81 |
| $Et_2(EtO)PO$ | 949s; 1026s, br; 1047s, br | 1094w | 1202s | |
| $CoCl_2 \cdot 2Et_2(EtO)PO$ | 954s; 1021s, br; 1042s, br | 1096w | 1136s | 66 |
| $Et(EtO)_2PO$ | 945s; 1013s, br; 1057s, br | 1095w | 1227, 1250s(d) | |
| $CoCl_2 \cdot 2Et(EtO)_2PO$ | 965s; 1013s, br; 1053s, br | 1095w | 1176s | 63 |
| $(EtO)_3PO$ | 963s 1029s, br | 1093w | 1263, 1271s(d) | |
| $CoCl_2 \cdot 2(EtO)_3PO$ | 982s; 1031s, br | 1099w | 1227s | 40 |
| $Co[O_2P(OEt)_2]_2$ | 971s; 1058s, br | 1087 | 1112, 1178s(d) | |
| $Co[O_2P(OEt)Et]_2$ | 958s; 1050s, br | 1101 | 1078, 1148s(d) | |
| $Co(O_2PEt_2)_2$ | - ; 992w; 1004w | - | 1052, 1119s(d) | |

s = strong,    w = weak,    br = broad,    d = doublet

McIvor et al. (1956) is seen at about $1095 \text{ cm}^{-1}$.

As was discussed in the Historical Section, the P=O absorption

decreases as the number of ethoxy substituents on the phosphorus

increases, due to an increase of back $\pi$-bonding from oxygen to

phosphorus (Bell et al., 1954). Also, the P=O frequency decreases

upon the complexing of the organophosphoryl ligand to cobalt chloride,

due to the donation of a pair of oxygen electrons to the cobalt. This

lowers the availability of these electrons for back bonding to the

phosphorus, resulting in a net lowering of the bond order (Cotton

et al., 1960). As shown in the final column of Table 11, the magnitude

of this frequency shift on coordination itself shows a steady decrease

in the progression from the phosphine oxide to the phosphate. This

trend reflects the competition between the two effects above. That

is, in the complexes the phosphorus and cobalt atoms are competing

for the electron density on the oxygen atom. The greater the inductive

effect on the phosphorus atom from ethoxy groups, the more favorably

the phosphorus atom will be able to compete with the cobalt atom for

the oxygen electron density and to retain the $\pi$-bond character of the

phosphorus-oxygen bond. This competition is helpful for analytical

purposes as it, in effect, spreads out the position of the phosphoryl

frequency in the complexes. For example, the free phosphine oxide

and phosphinate phosphoryl frequencies are $1202 - 1180 = 22 \text{ cm}^{-1}$

apart, whereas the corresponding frequencies for the complexes are

$1136 - 1099 = 36 \text{ cm}^{-1}$ apart.

## B. Studies of the Autoxidation of $CoCl_2 \cdot 2Et_3P$

### 1. No Solvent

In contradiction to the report of Jensen et al. (1936), solid $CoCl_2 \cdot 2Et_3P$ was found to be stable in dry air. In contact with an atmosphere of dry $O_2$ for a day, the complex did not change in appearance and did not gain any weight. The pressure of the closed system remained constant. The solubility of the complex in pentane was identical both before and after exposure to oxygen, also contrary to the report of Jensen. The solubility was slight and the very light blue solution turned blue-violet upon contact with the air. The complex is slightly hygroscopic, picking up water very slowly over long periods of time. However, no weight gain due to absorption of water was observed after ten minutes of exposure to open air. Presumably, Jensen's observations were due to atmospheric moisture.

### 2. Reaction in Solution. Stoichiometry of the Reaction

It was found that autoxidation of $CoCl_2 \cdot 2Et_3P$ does take place in solution in various organic solvents. The reaction was slow at room temperature. Qualitative indications of the reaction were the consumption of oxygen, a color change from dark to light blue, and

changes in the infrared spectrum of the complex.

A 2.8512 g quantity of $CoCl_2 \cdot 2Et_3P$ was quantitatively trans-ferred into the exhaustive autoxidation apparatus (described in the Experimental Section) and was dissolved in approximately 150 ml of benzene. A steady stream of dry oxygen was bubbled through the solution at 70° for two weeks. The blue solid complex recovered after removal of the solvent weighed 3.1001 g. The weight gain cor-responded to 1.00 mole $O_2$ per mole of original $CoCl_2 \cdot 2Et_3P$. The visible and infrared spectra of the reaction product were identical to those of authentic $CoCl_2 \cdot 2Et_3PO$. Anal. Calcd. for $CoCl_2 \cdot 2(C_2H_5)_3PO$: Co, 14.80; Cl, 17.81. Found for reaction product: Co, 14.86; Cl, 17.80.

The same type of reaction was conducted in o-dichlorobenzene at 130° for one week. Nearly all the solvent was then removed at reduced pressure. At this stage the reaction product was a blue paste. It was recrystallized from ethanol, giving a blue crystalline solid. Evaporation of the ethanol filtrate also gave a blue powder. The infrared spectra of both these samples were identical to that of $CoCl_2 \cdot 2Et_3PO$. Their analyses also proved that $CoCl_2 \cdot 2Et_3PO$ was the sole product of the quantitative autoxidation. Anal. Calcd. for $CoCl_2 \cdot 2Et_3PO$: Co, 14.80; Cl, 17.81. Found for the recrystallized sample of reaction product: Co, 14.75; Cl, 17.81. Found for the sample recovered by evaporation of the filtrate: Co, 14.33; Cl,

17.59. Traces of o-dichlorobenzene were believed to be present in the latter sample.

A similar exhaustive autoxidation study was not conducted in t-butylbenzene. However, the product of the reaction in this solvent was also shown to be $CoCl_2 \cdot 2Et_3PO$ by the following evidence. Both $CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$ solutions in t-butylbenzene gave visible spectra nearly identical to their spectra in benzene solutions. Likewise, solutions of mixtures of the two complexes and solutions of $CoCl_2 \cdot 2Et_3P$ that had undergone partial autoxidation gave similar visible spectra in both solvents (vide infra). $CoCl_2 \cdot 2Et_3PO$ is not soluble in t-butylbenzene to the extent of $10^{-2}$ M. In the reaction of oxygen with $10^{-2}$ M solutions of $CoCl_2 \cdot 2Et_3P$ in t-butylbenzene, a blue precipitate formed after the reaction had proceeded nearly half way. Blue precipitates collected from several different autoxidation reactions ranged from light blue powders to dark blue crystals, depending upon the conditions of the reaction. Their melting points were identical to or one or two degrees lower than the melting point of authentic $CoCl_2 \cdot 2Et_3PO$. The infrared and visible spectra of these precipitates were identical also to those of the phosphine oxide complex.

In early stages of this work, evidence for the formation of $CoCl_2 \cdot 2Et_3PO$ was obtained by displacement of triethylphosphine oxide chemically (using pyridine) from reaction product samples from incomplete autoxidations. An excess of pyridine was placed over such

a reaction product sample for a week. Then the volatile materials

were removed on the vacuum line into a series of cold traps. A

small amount of white solid collected in a trap at 0°. It was character-

ized as triethylphosphine oxide by its melting point of 51.5°; mp

$Et_3PO$ (Hein and Hecker, 1960) 50-51°.

In summary, the stoichiometry of the autoxidation reaction has

been well established to be as follows:

$$CoCl_2 \cdot 2Et_3P + O_2 \xrightarrow[\text{solvents}]{\text{organic}} CoCl_2 \cdot 2Et_3PO$$
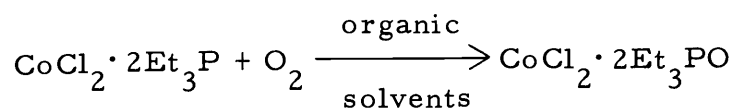
## 3. Solution Equilibrium Between $CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$

The visible spectra were recorded of benzene solutions of $CoCl_2 \cdot$

$2Et_3P$ after the autoxidation reaction had been allowed to proceed part

way. These spectra consisted of three major peaks, the positions of

which did not correspond to any of the peaks in the visible spectra of

the starting material, $CoCl_2 \cdot 2Et_3P$, or of the reaction product,

$CoCl_2 \cdot 2Et_3PO$. This apparently anomalous result was explained by

the finding that mixtures of benzene solutions of authentic samples

of these two chemicals did not obey Beer's Law and possessed identical

three-peak spectra. The spectrum of an equimolar solution is shown

in Figure 8. The relative intensities and the wavelengths of the peaks

shift with relative concentration in passing from the spectrum of one

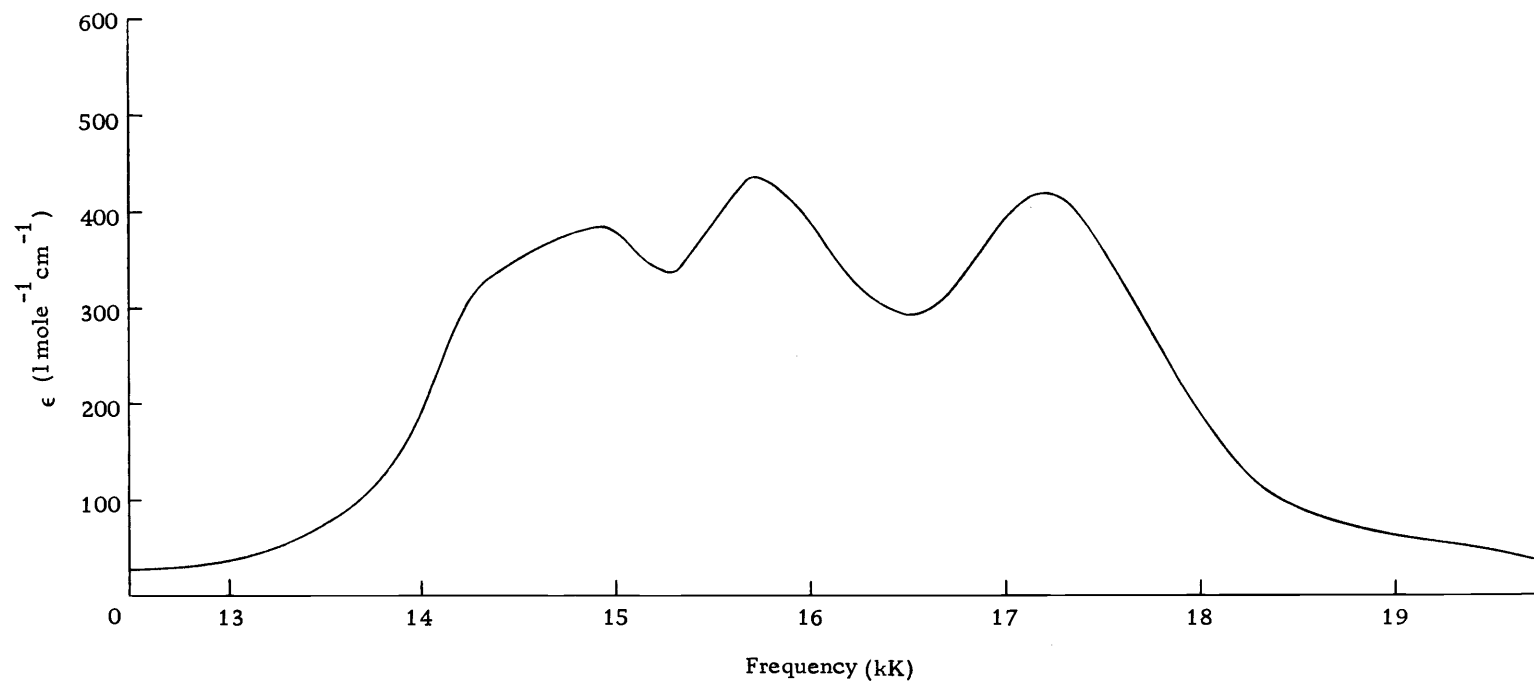component to the other, as is shown by the data of Table 12.

Figure 8. Visible Spectrum of an Equimolar Mixture of $CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$ in Benzene

Table 12.  Electronic Spectra in $C_6H_6$ of $CoCl_2 \cdot 2Et_3P$ (A) and $CoCl_2 \cdot 2Et_3PO$ (B) Mixtures

| % A in A + B | Wavelength in nm (Relative Intensity) |
|---|---|
| 100 | 730(0.78);                                    623sh(0.98), 606(1.00) |
| 83 | 728(0.58); 708+695(0.52); 627(1.00); 592(0.94) |
| 67 | 686(0.79); 632(1.00); 582(0.98) |
| 50 | 669(0.86); 636(1.00); 582(0.95) |
| 33 | 667(0.98); 637(1.00); 580(0.86) |
| 17 | 665(1.00); 639(0.91); 587(0.61) |
| 0 | 662(1.00), 640sh(0.87), 614sh(0.60), 596(0.54) |

Maximum differences from simple additivity were found at 700 nm and at 669 nm, and measurements at these wavelengths were used to establish the stoichiometry of the interaction by Job's Method of Continuous Variations (Rossotti and Rossotti, 1961). The data are shown in Figure 9, which is a plot of $\Delta\alpha$, the difference between the absorbance observed and that calculated on the basis of additivity, versus the molar ratio of $CoCl_2 \cdot 2Et_3PO$ to the sum of $CoCl_2 \cdot 2Et_3P$ plus $CoCl_2 \cdot 2Et_3PO$, this sum being held constant. The maximum absorbance difference at a ratio of 0.5 indicates that the two components interact chemically on a 1:1 basis, as in the reorganization equilibrium,
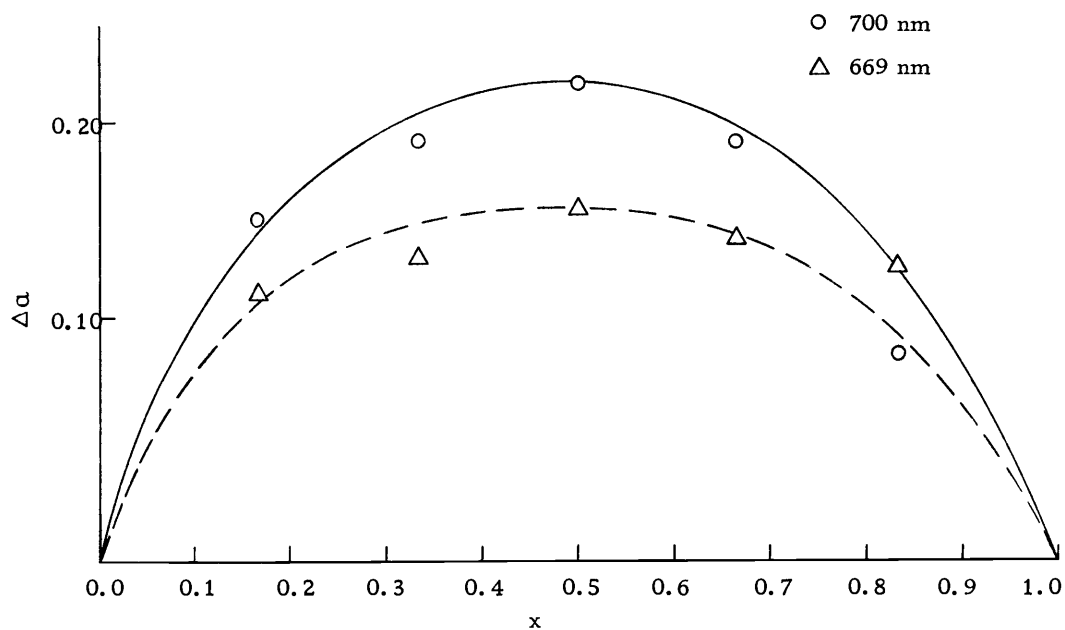
$$CoCl_2 \cdot 2Et_3P + CoCl_2 \cdot 2Et_3PO \rightleftharpoons 2CoCl_2 \cdot Et_3P \cdot Et_3PO$$

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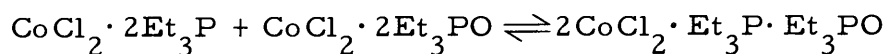


Figure 9. $CoCl_2 \cdot 2Et_3P$ (A) + $CoCl_2 \cdot 2Et_3PO$ (B) in Benzene at 24°. $x = [B]/[A] + [B]$. $[A] + [B] = 1.00 \times 10^{-13}$ M.
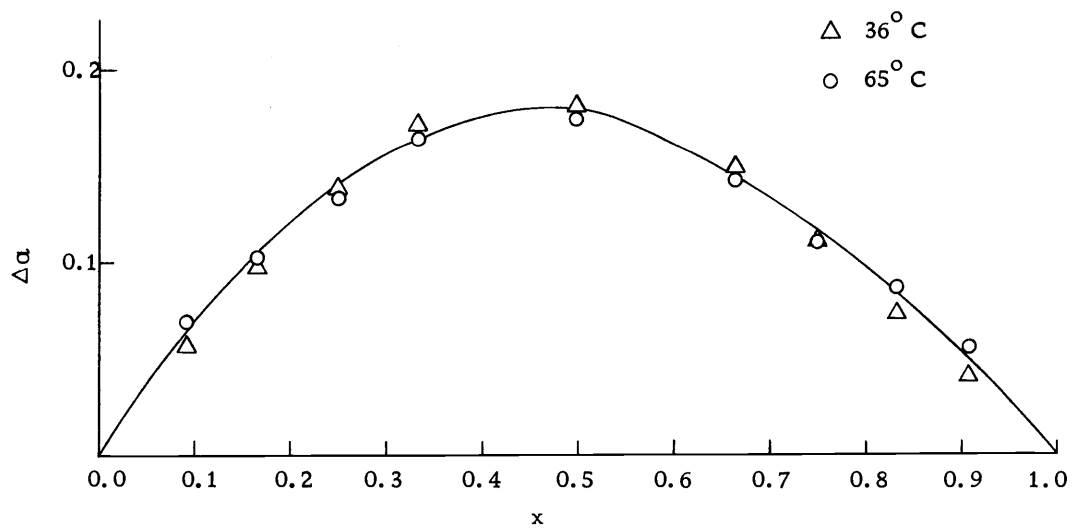


Figure 10. $CoCl_2 \cdot 2Et_3P$ (A) + $CoCl_2 \cdot 2Et_3PO$ (B) in t-Butylbenzene at 700 nm. $x = [B]/[A] + [B]$. $[A] + [B] = 1.00 \times 10^{-3}$ M.

Although the two complexes on the left would be only very slightly dissociated in separate solutions, such complexes are known to be kinetically labile (Pignolet and Horrocks, 1968). Such redistribution reactions are frequently encountered; in the formation of the mixed ligand complexes, bond energy changes approach zero and a favorable entropy change arises statistically. The mixed ligand product, $CoCl_2 \cdot Et_3P \cdot Et_3PO$, has three different kinds of donor atom and is of microsymmetry $C_s$. As indicated previously, splitting of the tetrahedral ligand field transition into three components occurs here, corresponding to the three peaks resolved in the spectrum.

Similar Job's Method studies conducted in t-butylbenzene as solvent revealed the same sort of redistribution equilibrium. A plot of the data for this system is shown in Figure 10.

Estimates of the equilibrium constant for the redistribution reaction in t-butylbenzene were made in two ways from the spectrophotometric data. Using Schaeppi and Treadwell's method (Rossotti and Rossotti, 1961; Schaeppi and Treadwell, 1948), the constant was calculated by drawing tangents to the Job's plot curve at solute mole fraction = 0 and 1. The $\Delta \alpha$ value at the intersection of the tangents at a mole ratio of 0.5 would represent the absorbance that $CoCl_2 \cdot Et_3P \cdot Et_3PO$ (C) would have if it were completely formed from $CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$. The observed $\Delta \alpha$ at this point was thereby related to the concentration of C actually present in solution.

In a more rigorous treatment, Schwarzenbach's method (Rossotti and Rossotti, 1961) was modified somewhat for use with a curve-fitting, or non-linear least squares, computer program (DeGroot, 1969). Unfortunately, the experimental data available were not well-suited for an accurate evaluation of the equilibrium constant. The limited solubility of the phosphine oxide complex in t-butylbenzene required the use of dilute solutions. While the three complex cobalt(II) species have significantly different spectral maxima, the spectra overlap continuously over the region of interest. For these two reasons, the measured values of $\Delta \alpha$ are quite small and subject to considerable experimental error. The spectrophotometer was not well suited for highly precise wavelength and absorbance measurements.

The results of the quantitative estimation of the equilibrium constant in benzene at room temperature and in t-butylbenzene at 36° and 65° were quite disappointing. The values ranged from 4 to 30 with very large standard deviations. It can only be said that the equilibrium constant has an order of magnitude value of 10. Kinetic observations, as described below, also substantiate the existence of this redistribution equilibrium and the estimated magnitude of the equilibrium constant.

Job's Method calculations in o-dichlorobenzene resulted in such small differences between the recorded and calculated absorbances that no conclusion could be drawn about the existence of a redistribution

equilibrium in this solvent. As noted earlier (Figure 2, Table 4), the

visible spectrum of $CoCl_2 \cdot 2Et_3P$ in o-dichlorobenzene is significantly

different from its spectrum in other common organic solvents. Con-

ductivity measurements in o-dichlorobenzene (Table 13) suggest that

$CoCl_2 \cdot 2Et_3P$ and $CoCl_2 \cdot 2Et_3PO$ are significantly ionized in this sol-

vent. Thus, the solution chemistry of these two complexes would be

expected to be somewhat different from that in the less polar solvents

benzene and t-butylbenzene.

Table 13. Conductivity Studies in o-Dichlorobenzene at Room Tem-
perature

| Solution | Concentration (moles/l) | Conductance (ohm$^{-1}$) | Molar Conductance (ohm$^{-1}$cm$^2$/mole) |
|---|---|---|---|
| Pure solvent | --- | $0.4 \times 10^{-6}$ | --- |
| n-Bu$_4$P$^+$Cl$^-$ | $0.969 \times 10^{-3}$ | $13.9 \times 10^{-6}$ | 1.43 |
| $CoCl_2 \cdot 2Et_3P$ | $0.994 \times 10^{-3}$ | $2.7 \times 10^{-6}$ | 0.27 |
| $CoCl_2 \cdot 2Et_3PO$ | $0.997 \times 10^{-3}$ | $4.8 \times 10^{-6}$ | 0.48 |

## 4. Kinetic Studies of the Autoxidation Reaction

The rate of autoxidation of $CoCl_2 \cdot 2Et_3P$ in t-butylbenzene was

determined by measuring the absorption of oxygen gas at constant

pressure as a function of time. At the temperatures and pressures

used, the solubility of oxygen in t-butylbenzene was found to be

appreciable, but it was not determined quantitatively. In blank runs,

it was shown that t-butylbenzene did not react measurably with oxygen under the conditions used. It was also shown that the speed of stirring did not affect the reaction rate, i. e. , that diffusion of oxygen across the gas-liquid interface was a fast step and that the reaction can be treated as homogeneous.

Some conclusions about the order of the reaction, in terms of the concentration of $CoCl_2 \cdot 2Et_3P$ and the pressure of oxygen, can be drawn from the data shown in Figure 11. While the data are not highly accurate, the apparent order of the reaction could be determined from the initial rates. The initial rates (slopes of the approximately linear portions of the curves for the first few minutes) show that: (1) at constant oxygen pressure, the rate is directly proportional to the con-centration of $CoCl_2 \cdot 2Et_3P$ (three values); (2) at constant cobalt com-plex concentration, the rate is directly proportional to the oxygen pres-sure (two values) and hence (assuming Henry's Law) to the concentra-tion of oxygen in solution. Thus, the rate law based on initial rate data and applying to early stages of the reaction is second order

$$\text{Rate} = k[O_2][CoCl_2 \cdot 2Et_3P]$$

or, at constant oxygen pressure, pseudo-first order

$$\text{Rate} = k'[CoCl_2 \cdot 2Et_3P] \ ,$$

where $k' = k[O_2]$.

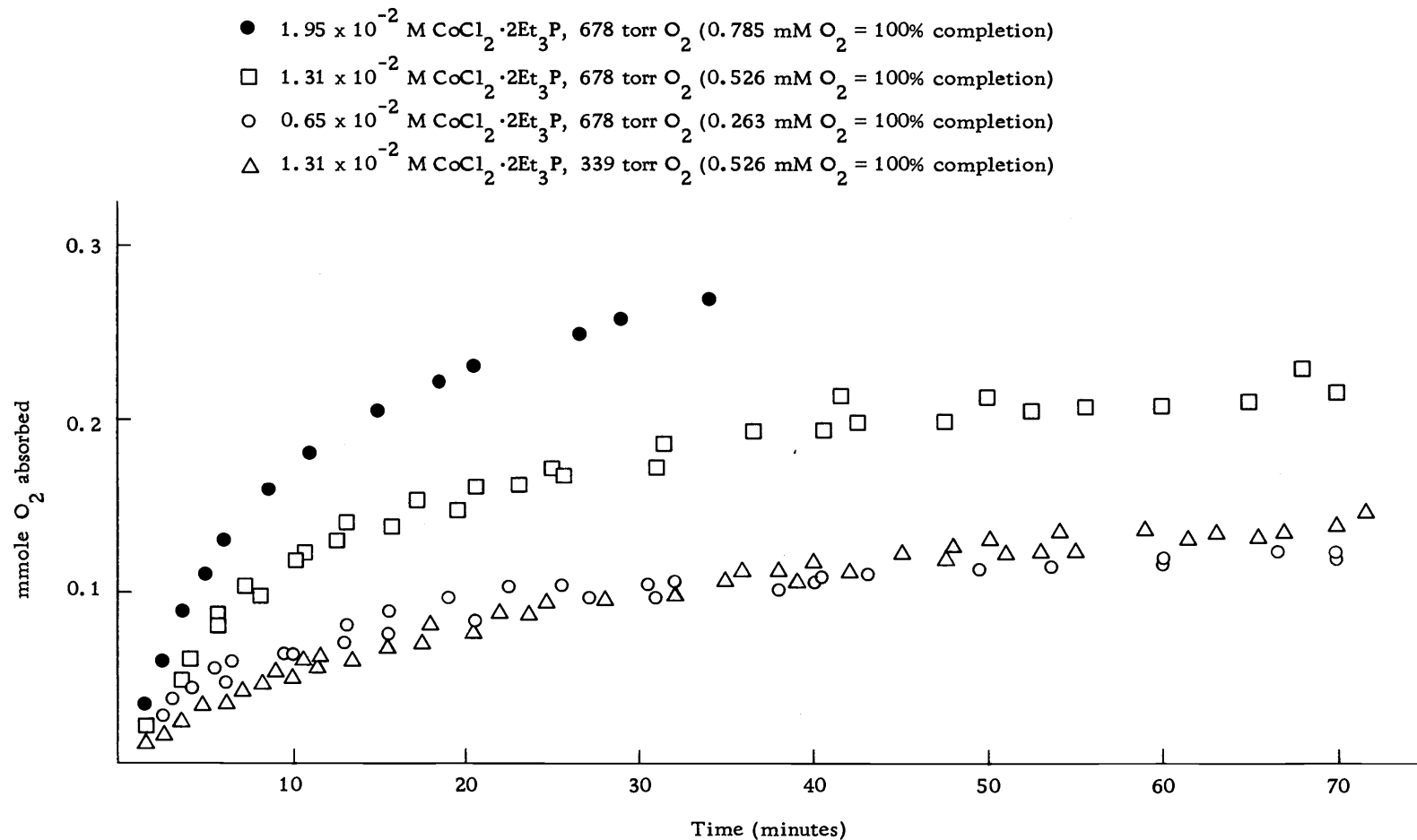The applicability of this rate law to later stages of the reaction

●    $1.95 \times 10^{-2}$ M $CoCl_2 \cdot 2Et_3P$, 678 torr $O_2$ (0.785 mM $O_2$ = 100% completion)

□    $1.31 \times 10^{-2}$ M $CoCl_2 \cdot 2Et_3P$, 678 torr $O_2$ (0.526 mM $O_2$ = 100% completion)

○    $0.65 \times 10^{-2}$ M $CoCl_2 \cdot 2Et_3P$, 678 torr $O_2$ (0.263 mM $O_2$ = 100% completion)

△    $1.31 \times 10^{-2}$ M $CoCl_2 \cdot 2Et_3P$, 339 torr $O_2$ (0.526 mM $O_2$ = 100% completion)

Figure 11. Oxygen Uptake vs. Time of 40 ml Aliquots of t-Butylbenzene Solutions of $CoCl_2 \cdot 2Et_3P$ at 36°

remained to be determined. Pseudo-first order plots were con-

structed from the kinetic data, to test the equation

$$\ln \frac{[CoCl_2(Et_3P)_2]}{[CoCl_2(Et_3P)_2]_o} = -k't \ .$$

The logarithmic function was expressed in terms of the experimental

data (oxygen absorption) using the stoichiometric equation

$$CoCl_2 \cdot 2Et_3P + O_2 \longrightarrow CoCl_2 \cdot 2Et_3PO$$
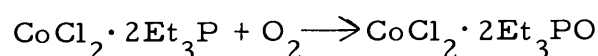
and neglecting the reorganization equilibrium. Then

$$\frac{[CoCl_2(Et_3P)_2]}{[CoCl_2(Et_3P)_2]_o} = \frac{[(\text{mmoles } CoCl_2(Et_3P)_2)_o - \text{mmoles } O_2 \text{ absorbed}]/\text{Vol.}}{(\text{mmoles } CoCl_2(Et_3P)_2)_o/\text{Vol.}}$$

$$= [1 - \frac{\text{mmoles } O_2 \text{ absorbed}}{(\text{mmoles } CoCl_2(Et_3P)_2)_o}]$$

A plot of the (base 10) logarithm of this function versus time would

give a straight line of slope -2.303k' and intercept zero, if first order

kinetics were obeyed and to the extent that additional consumption of the

starting material by reaction with the product could be neglected. Such

a plot is shown in Figure 12 (pseudo-first order, oxygen pressure being

constant) for data from the experiments with three different cobalt com-

plex concentrations. The direct dependence of this pseudo-first order

constant on oxygen pressure is demonstrated in Figure 13 using data

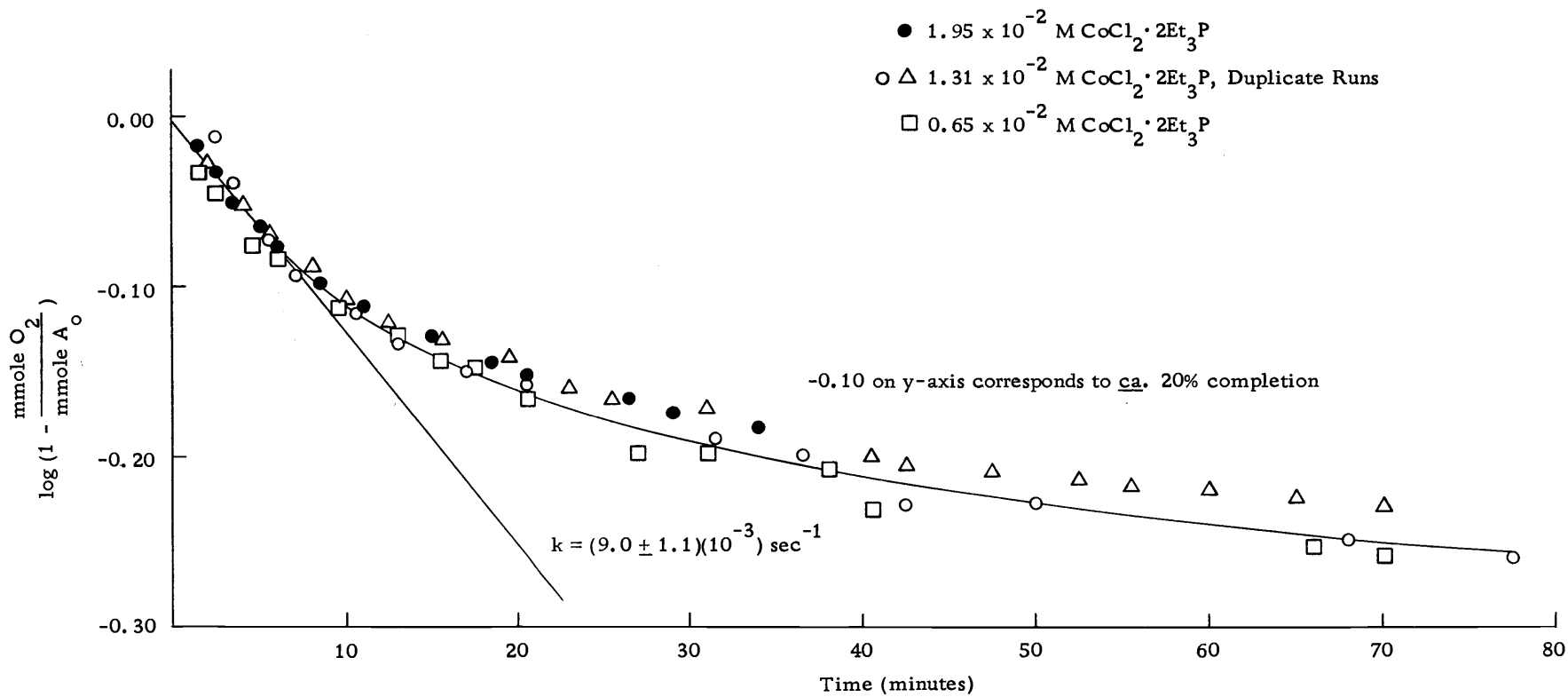from the experiments with two oxygen pressures at constant cobalt

Figure 12. Pseudo-First Order Plots of Oxygen Uptake Data of 40 ml Aliquots of t-Butylbenzene Solutions of $CoCl_2 \cdot 2Et_3P$ at 36°, 678 torr $O_2$, and Different Concentrations of the Complex

$\triangle$ 678 torr $O_2$
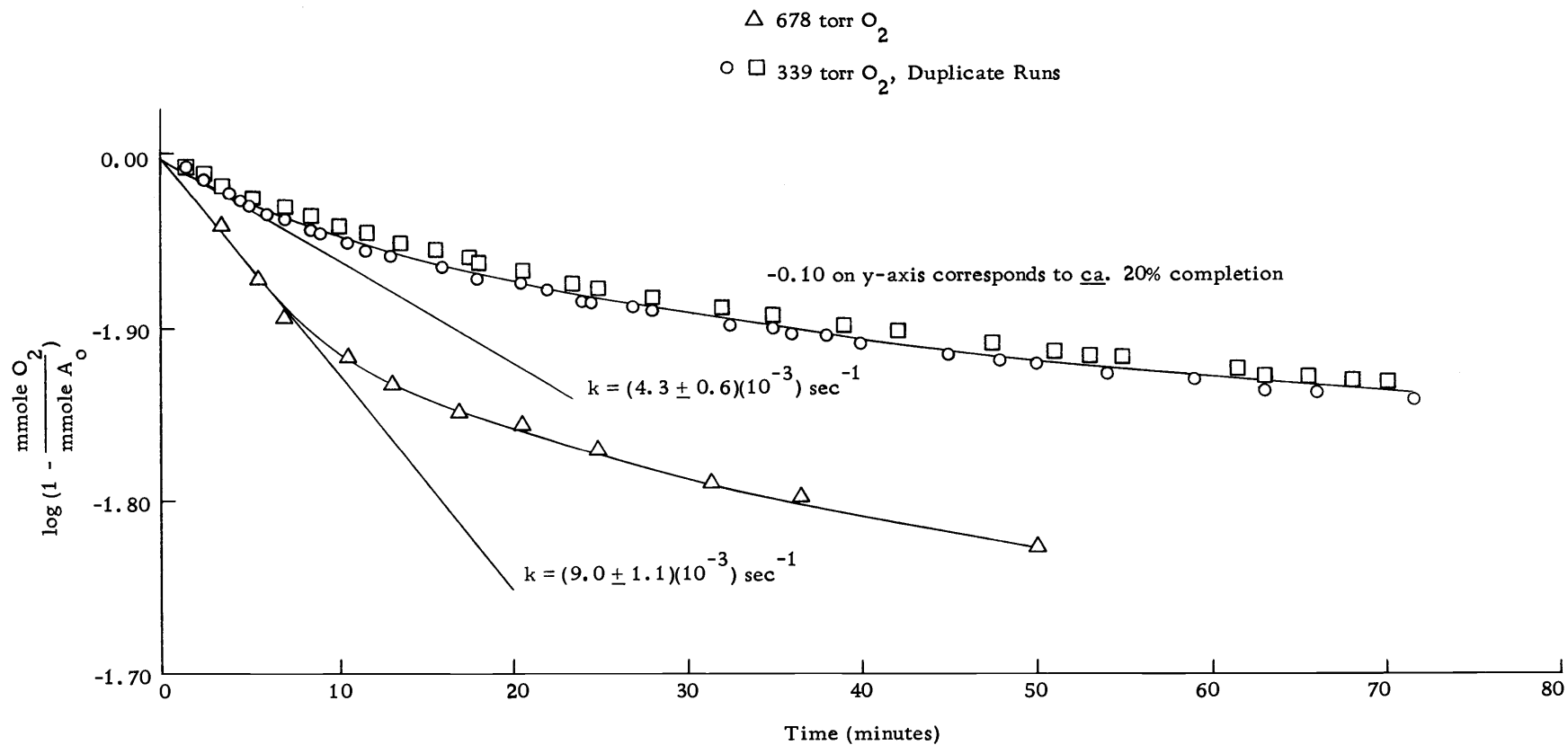
$\bigcirc$ $\square$ 339 torr $O_2$, Duplicate Runs

0.00

-0.10 on y-axis corresponds to ca. 20% completion

-1.90

$k = (4.3 \pm 0.6)(10^{-3})$ sec$^{-1}$

$\log \left(1 - \dfrac{\text{mmole } O_2}{\text{mmole } A_o}\right)$

-1.80

$k = (9.0 \pm 1.1)(10^{-3})$ sec$^{-1}$

-1.70

0    10    20    30    40    50    60    70    80

Time (minutes)

Figure 13.  Pseudo-First Order Plots of Oxygen Uptake Data of 40 ml Aliquots of $1.31 \times 10^{-2}$ M Solutions in t-Butylbenzene at 36° and at Different $O_2$ Pressures

complex concentration. In both figures, the experimental lines curve

upward, presumably due to the neglected redistribution equilibrium.

"Best" values of pseudo-first order rate constants k' were calculated

from data at early stages of the reaction. Data from all the kinetic

runs at the same oxygen pressure but different concentrations of

$CoCl_2 \cdot 2Et_3P$ fell on the same curve.

The effect of the redistribution equilibrium on the kinetic data

was then checked. The redistribution reaction between $CoCl_2 \cdot 2Et_3P$

and the autoxidation reaction product, forming the mixed species

$CoCl_2 \cdot Et_3P \cdot Et_3PO$, removes additional starting material and causes

its concentration to decrease faster than is accounted for on the basis

of oxygen consumption alone.

As a specific example of this correction in the calculation of

equilibrium concentrations of $CoCl_2 \cdot 2Et_3P$, data were chosen from

one of the experiments shown in Figure 12 (circles). Three reasonable

values for the redistribution equilibrium constant were used: K = 10,

20, and 40. The results for K = 10 are shown in Table 14. Figure 14 is

a pseudo-first order plot of the equilibrium corrected data for the three

different values of K. It is seen that the corrections for the redistribu-

tion equilibrium in the calculation of $[CoCl_2 \cdot 2Et_3P]$ are not sufficient

to produce a straight line in the pseudo-first order plot. The upward

curvature of the experimental line after approximately the first

quarter-life of the reaction (ca. 13 minutes for the data of Figure 12)

Table 14. Calculated Concentrations of Cobalt Complexes in Solution During a Kinetic Run, Assuming $K = 10$ for the Redistribution Equilibrium Constant. $[CoCl_2 \cdot 2Et_3P]_o = 0.526$ mmole/40.5 ml $= 13.0 \times 10^{-3}$ M.

| time (minutes) | mmole $O_2$ absorbed | $[CoCl_2 \cdot 2Et_3P]$ uncorrected | $[CoCl_2 \cdot 2Et_3P]$ at equilibrium | $[CoCl_2 \cdot Et_3P \cdot Et_3PO]$ at equilibrium | $[CoCl_2 \cdot 2Et_3PO]$ at equilibrium |
|---|---|---|---|---|---|
| 3.5 | 0.047 | $11.81 \times 10^{-3}$ M | $10.68 \times 10^{-3}$ M | $2.26 \times 10^{-3}$ M | $0.05 \times 10^{-3}$ M |
| 5.5 | 0.080 | 10.99 | 9.14 | 3.70 | 0.15 |
| 7.0 | 0.102 | 10.44 | 8.15 | 4.58 | 0.26 |
| 10.5 | 0.123 | 9.91 | 7.23 | 5.36 | 0.40 |
| 13.0 | 0.139 | 9.51 | 6.56 | 5.90 | 0.53 |
| 17.0 | 0.152 | 9.19 | 6.05 | 6.28 | 0.66 |
| 20.5 | 0.160 | 8.99 | 5.73 | 6.52 | 0.74 |
| 25.0 | 0.171 | 8.71 | 5.30 | 6.82 | 0.87 |
| 31.5 | 0.186 | 8.34 | 4.76 | 7.16 | 1.07 |
| 36.5 | 0.193 | 8.16 | 4.51 | 7.30 | 1.18 |
| 50.0 | 0.214 | 7.64 | 3.82 | 7.64 | 1.53 |
| 68.0 | 0.230 | 7.24 | 3.33 | 7.82 | 1.84 |
| 77.5 | 0.237[a] | 7.06 | 3.12 | 7.88 | 1.99 |

[a]Corresponds to 45% completion.
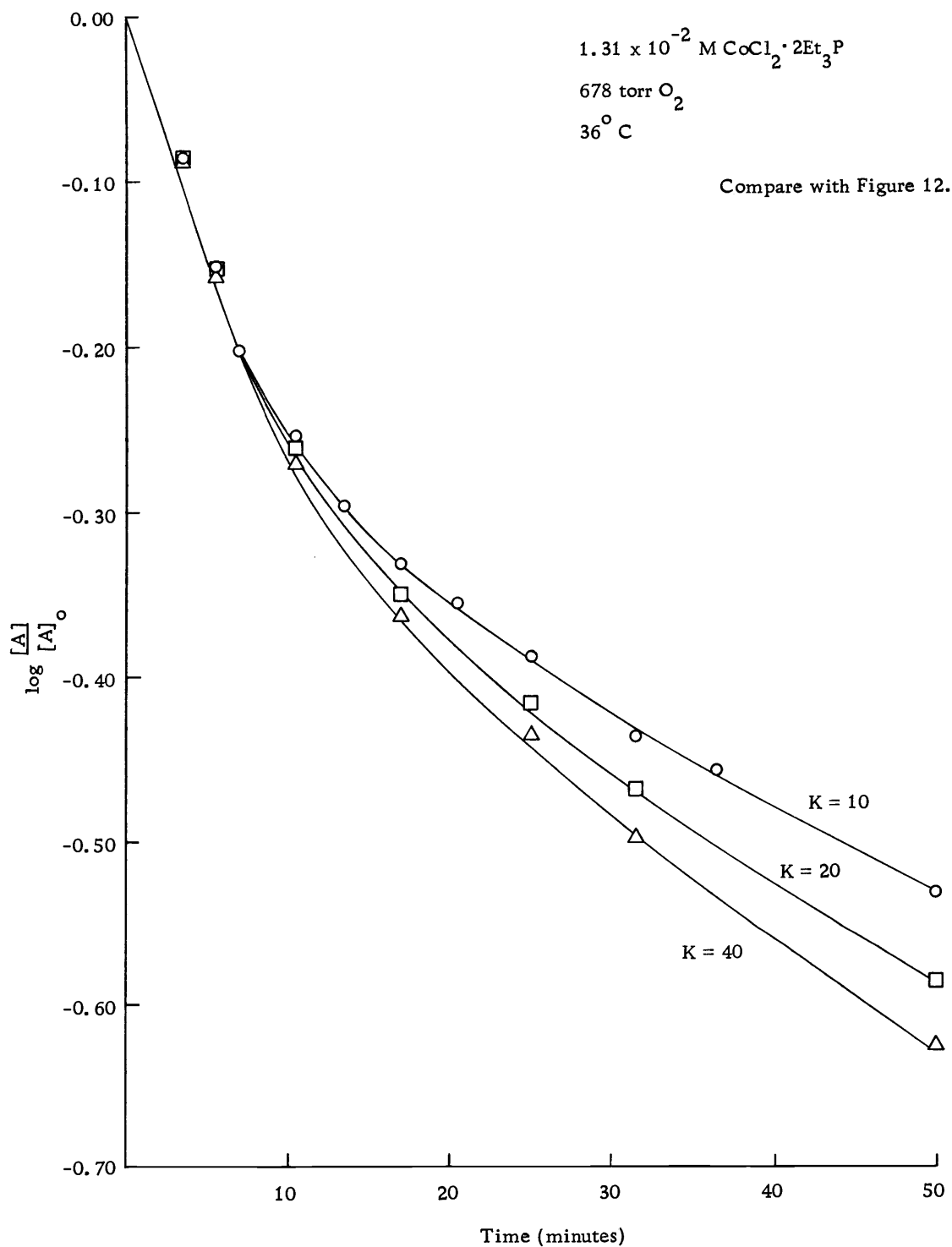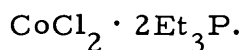
Figure 14.  Pseudo-First Order Plots, with [ CoCl₂· 2Et₃P]
Calculated Using Estimated Values of the Redistribu-
tion Equilibrium Constant.

suggests, therefore, a contribution from other unknown terms in the

total rate law besides the initial first order dependence in

$CoCl_2 \cdot 2Et_3P$.

From Figures 11 and 15, it is seen that the rate decreases con-

siderably after the first 15-20 minutes. The concentration of

$CoCl_2 \cdot Et_3P \cdot Et_3PO$ increases during the reaction up to 50% com-

pletion, whereas the concentration of $CoCl_2 \cdot 2Et_3P$ steadily decreases

(Table 14). Thus, if $CoCl_2 \cdot Et_3P \cdot Et_3PO$ is reacting with oxygen, it

reacts at a much slower rate than $CoCl_2 \cdot 2Et_3P$ does.

Figure 15 shows the results of a series of kinetic runs at 65°

testing the effect of added free radical initiator and inhibitor on the

rate of the reaction. AIBN, a common free radical initiator with an

approximate half-life of 12 hours at 65° (Walling, 1957), did not speed

up the reaction; hydroquinone, a common free radical inhibitor, did

not slow down the reaction. Thus, it appears that the autoxidation of

the coordinated triethylphosphine does not proceed by a free radical

mechanism such as is found for free trialkylphosphines.

Pseudo-first order plots of duplicate kinetic runs at 65° are

shown in Figure 16. A calculated pseudo-first order rate constant

is shown. The reaction is seen to proceed approximately twice as fast

at 65° as at 36°. The activation energy can not be estimated from

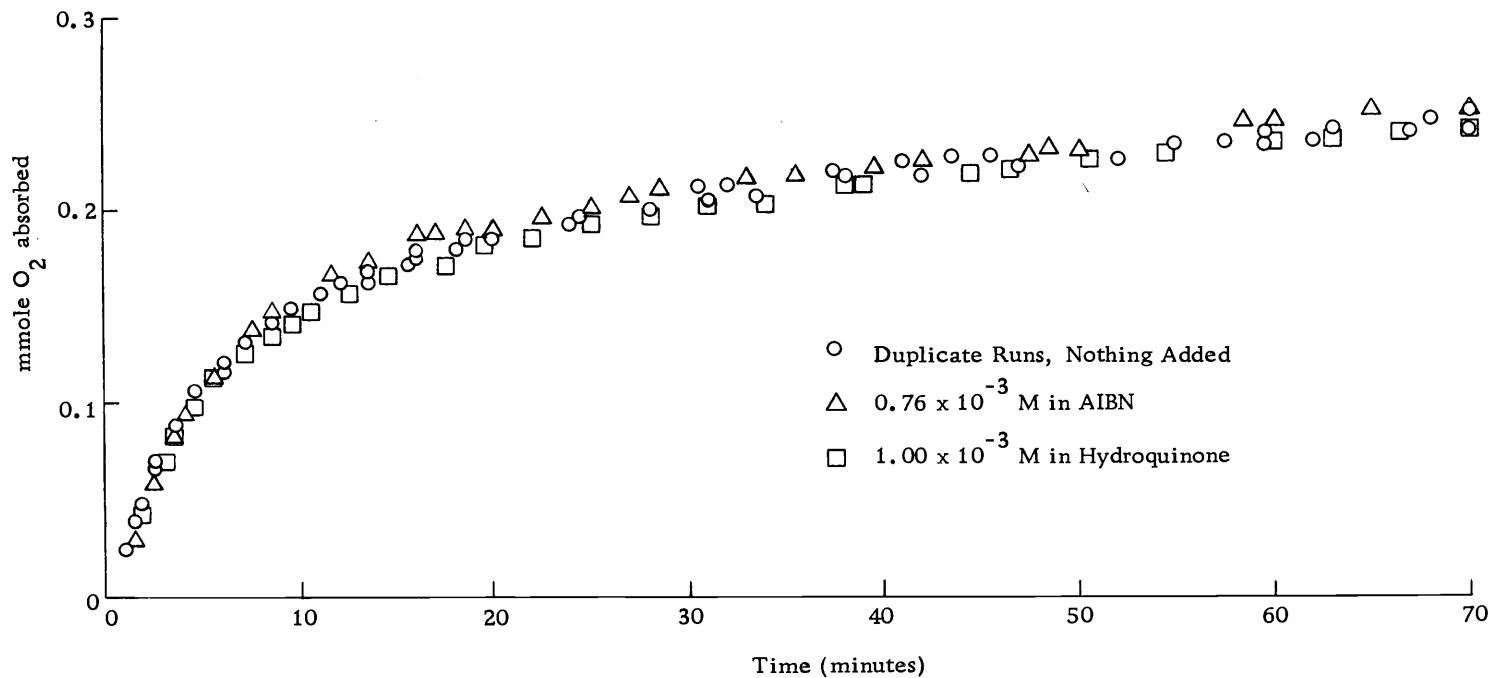these limited data because the temperature variation in the solubility

Figure 15. Oxygen Uptake vs. Time of 40 ml Aliquots of $1.31 \times 10^{-2}$ M Solutions of $CoCl_2 \cdot 2Et_3P$ in t-Butylbenzene at 65° and 679 torr $O_2$, Testing the Effect of Added Free Radical Initiator and Inhibitor.
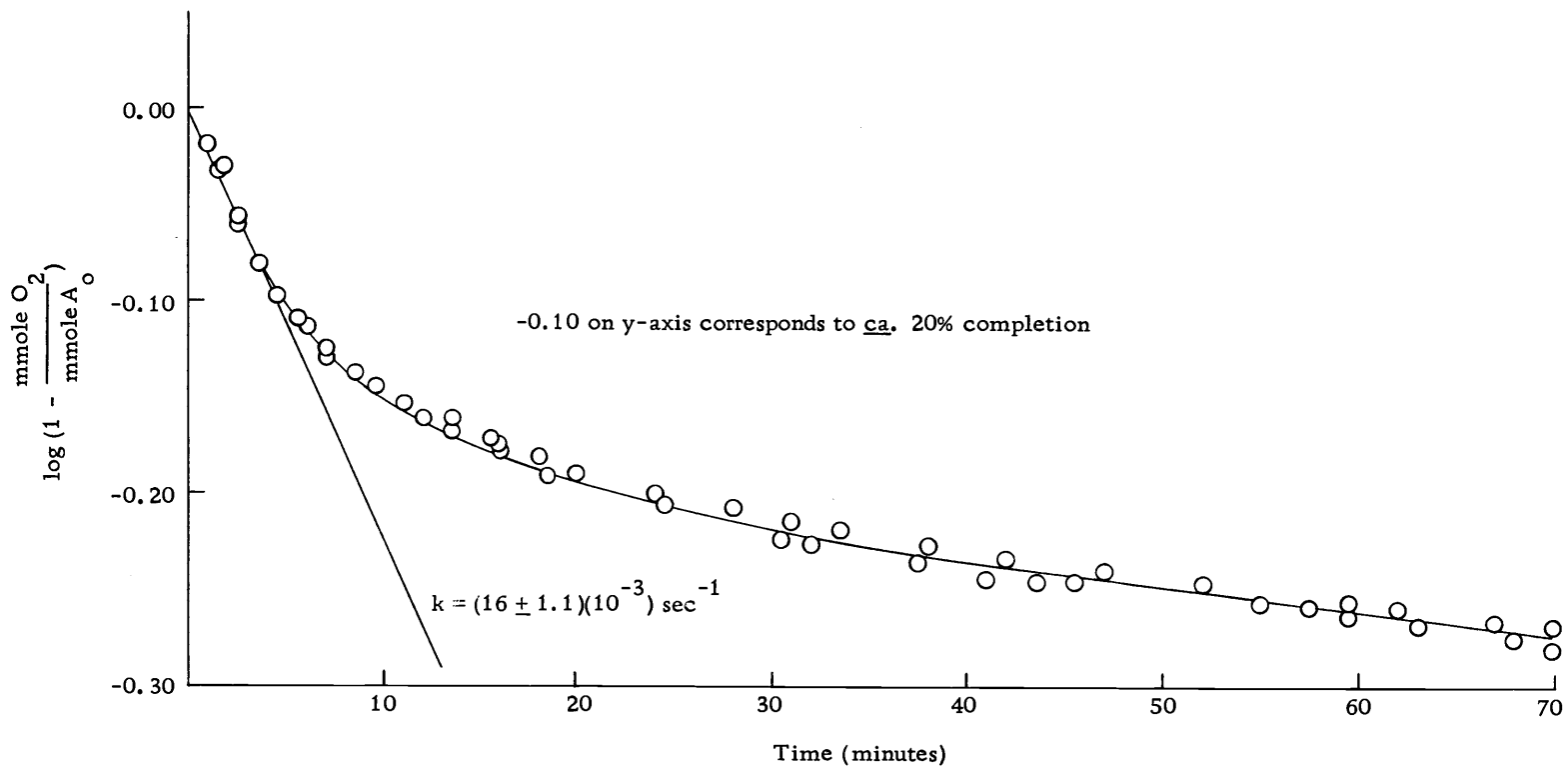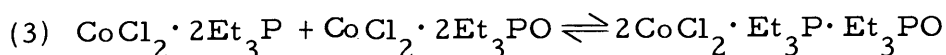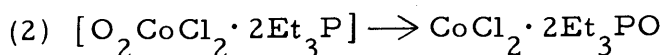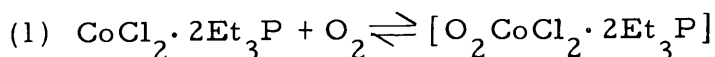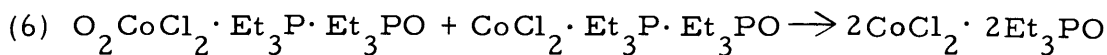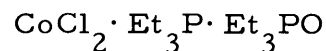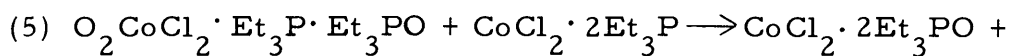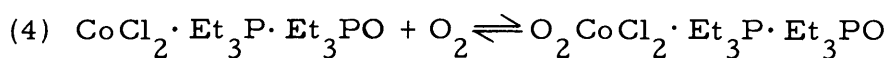
Figure 16. Pseudo-First Order Plots of Duplicate Kinetic Runs of 40 ml Aliquots of $1.31 \times 10^{-2}$ M $CoCl_2 \cdot 2Et_3P$ in t-Butylbenzene at 65° and 679 torr $O_2$

of oxygen in t-butylbenzene is unknown.

The following general mechanistic considerations may be proposed to account for all the experimental information. The key step is postulated to be the formation of an adduct of the cobalt(II) complex with molecular oxygen. In the subsequent reaction of such an adduct, the breaking of the O-O bond presumably would be nearly simultaneous with the formation of two P-O bonds. At initial stages of the reaction, these bond making and breaking steps would take place during an intramolecular rearrangement of the postulated species $O_2CoCl_2 \cdot 2Et_3P$, giving $CoCl_2 \cdot 2Et_3PO$ as product. Apparently the mixed complex, $CoCl_2 \cdot Et_3P \cdot Et_3PO$, which accumulates at intermediate stages of the reaction by equilibrium between starting material and product, may also form an oxygen adduct. Reaction of this with a cobalt complex containing either one or two phosphine ligands would maintain the nearly simultaneous bond breaking and making steps. Such reactions might proceed by formation of binuclear Co-O-O-Co intermediates, well known in related systems. This would also account for the observed slowing down of the reaction in its intermediate stages. These proposed steps may be summarized as follows:

(1)  $CoCl_2 \cdot 2Et_3P + O_2 \rightleftharpoons [O_2CoCl_2 \cdot 2Et_3P]$

(2)  $[O_2CoCl_2 \cdot 2Et_3P] \longrightarrow CoCl_2 \cdot 2Et_3PO$

(3)  $CoCl_2 \cdot 2Et_3P + CoCl_2 \cdot 2Et_3PO \rightleftharpoons 2CoCl_2 \cdot Et_3P \cdot Et_3PO$

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Final.

solutions with visible spectra typical of the cobalt(II) complexes of the ethyl phosphoryl ligands.

$CoCl_2 \cdot 2Et_3P$ is only very slightly soluble in hexadecane, giving a light blue solution with a visible spectrum very similar to that described for pentane solutions in Table 4. When such a solution was stored in vacuo for several days, there was no change in the appearance of the solution. However, when stored under an atmosphere of dry oxygen, the light blue solution turned violet in a few hours. After a few days, the visible spectrum of the dark violet solution was recorded. The spectrum was dominated by a broad peak centered at 550 nm, with a maximum absorbance over twice that of the original blue solution. The peak at ca. 730 nm, however, had diminished in intensity only slightly.

The nature of the chemical species responsible for this very intense absorption band is unknown. The conditions under which the violet solutions formed appeared to be conditions in which free radicals could be present, suggesting possibly the formation of a complex of the type $RO_2^{\delta-} Co^{(2+\delta)+}$. The existence of such a species is highly speculative; Ingold (1968) proposed such a species as a possible explanation for the inhibition of autoxidation of organic substances. The fact that $CoCl_2 \cdot 2Et_3P$ dissolved in $CCl_4$ also gave dark violet solutions with an extremely intense band centered at 555 nm lends support to this theory; $CCl_4$ commonly gives $CCl_3 \cdot$ radicals. The

possibility that the same adduct of oxygen with $CoCl_2 \cdot 2Et_3P$

postulated as an autoxidation intermediate is the species absorbing

at 550-570 nm was considered. It was ruled out on the basis that the

violet color did not disappear when the solutions were kept under an

atmosphere of oxygen for long periods of time.

## V.  CONCLUSIONS

A simple method for the synthesis of triethylphosphine oxide has been developed.  Cobalt(II) chloride forms complexes with the ethyl phosphoryl ligands $Et_nP(O)(OEt)_{3-n}$, n = 0-3, of the general formula $CoCl_2 \cdot 2L$.  These complexes are all pseudo-tetrahedral in structure, according to the usual criteria of ligand field spectra and magnetic moments.  The visible spectra of the four complexes are nearly identical.  These compounds were also characterized by chemical analysis, solubility behavior, and infrared spectra.  The compounds containing P-O-C groups, n = 0-2, undergo a thermal decomposition when heated to 140° or higher.  They give off ethyl chloride and form the complexes $Co[O_2PEt_n(OEt)_{2-n}]_2$, n = 0-2.  These latter complexes were also characterized by their ligand field spectra, infrared spectra, chemical analyses, solubility behavior, and in one case (n = 0) by the magnetic moment.  They are believed to be coordination polymers with double-bridging $R_2PO_2^-$ groups connecting the tetrahedrally coordinated Co atoms.

Solid $CoCl_2 \cdot 2Et_3P$ does not react with oxygen.  It does react with oxygen in organic solvents but at a much slower rate than reported for the autoxidation of free trialkylphosphines.  The sole product of the autoxidation reaction in organic solution is $CoCl_2 \cdot 2Et_3PO$, as established by mass balance, chemical analysis,

and infrared spectrum of the product. A dissociative mechanism is ruled out since autoxidation of free triethylphosphine gives a mixture of ethyl phosphoryl compounds, $Et_nP(O)(OEt)_{3-n}$.

The autoxidation reaction was studied chiefly in benzene, o-dichlorobenzene, and t-butylbenzene. The visible spectrum of $CoCl_2 \cdot 2Et_3P$ is sensitive to solvent effects. The spectrum in o-dichlorobenzene is significantly different from that in the other two solvents. Because of the similarity of the visible spectra of all the phosphoryl cobalt chloride complexes, the final product could not be characterized uniquely by the ligand field spectrum. However, spectral changes in the visible region during the reaction gave additional information. The spectra of solutions from partial autoxidations indicated the occurrence of the reorganization equilibrium

$$CoCl_2 \cdot 2Et_3P + CoCl_2 \cdot 2Et_3PO \rightleftharpoons 2CoCl_2 \cdot Et_3P \cdot Et_3PO.$$
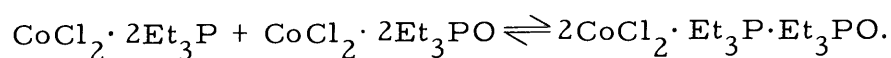
This equilibrium was clearly indicated in benzene and t-butylbenzene but not in o-dichlorobenzene.

Kinetic studies in t-butylbenzene showed that the rate of the autoxidation reaction is first order in the oxygen pressure and independent of added free radical initiator or inhibitor. The order of the reaction in the concentration of the phosphine-containing cobalt complexes is somewhat in doubt. The reaction in the early stages (up to one quarter-life) has been shown to be first order in the concentration

of $CoCl_2 \cdot 2Et_3P$. After approximately one quarter-life, other unknown terms in the rate law apparently contribute to the absorption of oxygen. A mechanism was proposed to account for the experimental information.

The effect of the coordination of triethylphosphine to cobalt chloride on the reaction of the phosphine with oxygen is seen to be very great. Both the rate and the products are affected. The complete nature of the reaction is altered, as it is no longer a free radical reaction. The new reaction mechanism leads to the formation of only one ethyl phosphoryl compound, coordinated triethylphosphine oxide.

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