1958

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Recommended Citation

Katz, Seymour, "Exchange and chemical reactions of cyclopentadienyl cobalt compounds " (1958). *Retrospective Theses and Dissertations*. 1667.
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EXCHANGE AND CHEMICAL REACTIONS OF CYCLOPENTADIENYL COBALT COMPOUNDS

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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Iowa State College
Ames, Iowa
1958

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I. INTRODUCTION

The purpose of this work is to study the chemistry and properties of cyclopentadienyl-cobalt compounds. Interest in this field was aroused by the intensive work that had been done in preparing and characterizing the remarkable π bonded transition metal-cyclopentadienyl compounds.

The fact that the cobalt(II) and cobalt(III) derivatives were stable, and that radioactive cobalt-60 was available, made radiochemical studies of these species attractive. The measurement of the lability of the cobalt to ring bonding, and the electron exchange between the two bis(π-cyclopentadienyl) cobalt species was performed using this technique. The strong reducing properties of bis(π-cyclopentadienyl)cobalt(II), $(C_5H_5)_2Co$, arising from its unpaired electron, were investigated through the reaction between oxygen and $(C_5H_5)_2Co$ in organic solvents. An effort was made to measure the kinetics and isolate intermediates of this reaction.

A new class of cyclopentadienyl-cobalt compounds was obtained from the reaction between $(C_5H_5)_2Co$ and halogenated hydrocarbons. Physical and chemical measurements were carried out on $(C_5H_5)_2(CCl_3)Co$, which was obtained from the reaction of $(C_5H_5)_2Co$ and carbon tetrachloride, to elucidate the structure, bonding and the mechanism of formation of this compound and its analogues.

II. REVIEW OF LITERATURE

Due to the instability and scarcity of organometallic compounds of Groups IIIA-VIII (1), the discovery of the unusually stable bis(π-cyclopentadienyl)iron(II) (2, 3) initiated an intensive effort to determine the physical and chemical properties of this compound. From X-ray (4, 5), infra red and magnetic data (6), it was found that the iron atom was symmetrically placed between parallel cyclopentadienyl rings. This has appropriately been described by Wilkinson as a "sandwich" structure. The nature of the metal-ring bonding is the subject of considerable controversy, however, all proposed models require the availability of d orbitals. This condition is satisfied by the transition metals, all of which have been shown capable of forming such cyclopentadienyl derivatives.

The metal-cyclopentadienyl compounds that have been characterized thus far can be divided into three general classes according to the type of metal-carbon bonding. Ionic cyclopentadienyl compounds such as $(C_5H_5)K$ (7) and $(C_5H_5)MgBr$ (8) have long been known. It has been recently pointed out that the electropositive elements in general may be expected to form salts of the $(C_5H_5)^-$ ion, and ionic derivatives of scandium, yttrium and several of the rare earth elements of the formula $(C_5H_5)_3M$ have been described (9, 10). The ionic $(C_5H_5)_2Mn$ (11) has also been prepared. These compounds are characterized by their high melting points, their reactivity with ferrous chloride to form $(C_5H_5)_2Fe$, and the production of cyclopentadiene and metal hydroxides with water. The magnetic susceptibilities also indicate ionic bonding.

Elements such as copper, mercury (12), silicon (13) and lead (14) have no readily available d orbitals and form cyclopentadienyl compounds which are not of the "sandwich" type. The metal-ring linkage is of the type usually found in organometallic compounds, with the metal atom bonded to a particular carbon atom in the ring. This is referred to as σ bonding. The reaction of these compounds with maleic anhydride to form Diels-Alder adducts demonstrates that the rings have retained their diene character.

The third class of metal cyclopentadienyl compounds are those formed with Group IVA-VIII metals and whose bonding is typified by $(C_5H_5)_2Fe$. The central metal atom does not form localized metal-carbon bonds but is considered to be bonded to the entire cyclopentadienyl ring. These delocalized bonds are thought to be formed between the metal and the ring electron cloud and are called π bonds. Because of its great stability, $(C_5H_5)_2Fe$ has been used most frequently in physical and chemical studies. It has been shown that its properties are those of the entire class and can be extended to the numerous analogues.

Bis(π-cyclopentadienyl)iron(II) and its analogues behave as typical covalent compounds. They are soluble in common organic solvents, may be steam distilled, and sublime at relatively low temperatures (50-100°C). The similarity in physical properties is strikingly illustrated by the melting points which are all at or within a few degrees of 173°C for metals of Period IV. It has been shown by Fischer and his collaborators (15-17) that the bis-π-cyclopentadienyl derivatives of magnesium, vanadium, chromium, iron, cobalt and nickel crystalize in the monoclinic system, space group $P2_1/c$, and have very similar unit cell dimensions. Thus the same geometrical arrangement must apply to all.

Great similarity is also shown from the infra-red spectra of these compounds (18-20). The infra-red and Raman spectra of $(C_5H_5)_2Fe$, $(C_5H_5)_2Ni$ and $(C_5H_5)_2Ru$ have been analyzed in detail by Lippincott and Nelson (21, 22). By including in their study the completely deuterated derivative $(C_5D_5)_2Fe$, they were able to assign all the absorptions with the exception of a group of medium-strong bands around $1700cm^{-1}$.

The most striking feature of the spectra is their simplicity, which arises from the high symmetry of the molecules. There are only five strong bands; a C-H stretching frequency at $3075cm^{-1}$ which is in the region for aromatic C-H bonds; C-H bending frequencies at 811 and $1002cm^{-1}$; and bands at 1108 and $1411cm^{-1}$ which are attributed to antisymmetrical ring breathing and C-C stretching vibrations respectively.

The thermodynamic stability of the bis(π-cyclopentadienyl)-metal compounds has been assessed for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ by measurement of the heats of combustion (18, 23). From these values the standard heats of formation are deduced to be +33.8 and +62.8 kcal $mole^{-1}$ respectively. From the vibrational spectra of the gaseous molecules (21) and the heats of sublimation (24), values of +40.7 and +62.8 were obtained. By using these data to estimate their heats of formation and correcting for the energy required to promote the electrons into their valence states, values were calculated for the metal-ring bonding energies. These are -273 and -151 kcal $mole^{-1}$ for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ (25) respectively. The large difference in energy is reflected in the longer metal-ring distance in $(C_5H_5)_2Ni$ and the greater reactivity of this compound.

The thermodynamic stability of the compounds of other metals has not been determined, but it is reasonable to assume on the basis of theory and X-ray data that $(C_5H_5)_2Co$ will be of intermediate stability between $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$. The oxidation potentials of a number of bis(π-cyclopentadienyl)-metal compounds have been determined (18, 20, 26-28). Most of them are similar to the potentials for the free ions and related complexes.

Several methods have been developed for the preparation of these compounds (2, 20, 29, 30), the most useful being:

1. $MX_n + 2(C_5H_5)MgX \longrightarrow (C_5H_5)_2MX_{n-2} + 2MgX_2$
2. $MX_n + 2(C_5H_5)Na \longrightarrow (C_5H_5)_2MX_{n-2} + 2NaX$

$$3.\quad M(SCN)_2 + 2(C_5H_5)Na \xrightarrow[NH_3]{Liq.} (C_5H_5)_2M + 2Na(SCN)$$

in which M equals transition metal ions and X equals halogens. The direct reaction of cyclopentadiene with iron has been reported (3); the low yield which result from the high temperatures (375°C) which are required preclude its use for the less stable derivatives. The gas phase reaction of a metal carbonyl and cyclopentadiene has been employed successfully in the preparation of $(C_5H_5)_2Cr$ (31). However, the yields for other metals were extremely low.

Although unsuccessful in this respect, the carbonyl method produced a new class of cyclopentadienyl compounds in which only one ring was π bonded to a transition metal atom. Compounds such as $[C_5H_5W(CO)_3]_2$ (31), $C_5H_5Co(CO)_2$ and $[C_5H_5Fe(CO)_2]_2$ were prepared by Wilkinson and were regarded as intermediate in character between bis-π-cyclopentadienyl derivatives and metal carbonyls. Fischer and his associates prepared similar derivatives of other metals (32-34) by the reaction of bis(π-cyclopentadienyl)-metal compounds with carbon monoxide (100-250 atm and 7100°C). Other methods for preparing these compounds have been reported (35, 36). It is of interest that hydrides such as $C_5H_5Cr(CO)_3H$ were prepared (34), analagous to the simple metal carbonyl hydrides $Co(CO)_4H$. Cyclopentadienyl-metal-nitrosyls (37, 38) and carbonyl-nitrosyls (34, 39) have also been reported.

Jaffé and Doak (40, 41) have discussed the instability of simple σ bonded alkyls and aryls of the transition metals in terms of molecular orbital theory. The ionic resonance energy contributions are small because of the small difference in electronegativity between carbon and the metals. Calculated overlap integrals for suitable metal orbitals and the sp^3 hybrid atomic orbitals of carbon are small for transition metals using sd^n orbitals compared to Group B metals which can use sp^n hybrids.

Summers and Uloth (42) have demonstrated that aryllithium compounds replace the halogens in $[(C_5H_5)_2Ti]Cl_2$ to form the neutral diaryl derivatives in which, presumable, the aryl groups are σ bonded to the metal. Fischer (43, 44) and Piper (45-47) have since reported the preparation of several compounds in which aryls and alkyls were σ bonded to the metal of π-cyclopentadienyl-metal-carbonyl compounds. The stability of these σ bonded groups has been qualitatively explained (47). In order to form a stable σ metal-carbon bond strongly directed orbitals are necessary. These may be obtained by adding considerable p character to the normal sd^n orbitals; a condition that is fulfilled in the "sandwich" compounds.

To complete the description of the various types of organometallic compounds which are related to $(C_5H_5)_2Fe$, mention must be made of the metal-idenyl systems and Fischer's amazing metal-benzene compounds. Indene, which can be thought of as cyclopentadiene with a benzene ring fused to it, forms a less stable series of derivatives similar to the cyclopentadienyl-metal compounds (48-51). Due to the decreased stability of the indenyl system, it is not surprising that derivatives of fluorene have not been prepared.

The prediction of Longuet-Higgins (52) that benzene could form "sandwich" compounds was realized when Fischer and Hafner (53, 54) prepared di(π-benzene)chromium(0). The compound was formed by the following reaction using aluminum chloride as a catalyst:

$$C_6H_6 + CrCl_3 + Al \longrightarrow Cr(C_6H_6)_2 + AlCl_3.$$

The chromium and molybdenum (54) compounds are quite stable and crystalize in the cubic system (55). The physical and chemical properties of this system have been studied and found to be analagous to the cyclopentadienyl-metal systems. Recently, Zeiss and Tsutsui (56) completed a study of the "polyphenyl" chromium compounds first described by Hein in 1919 (57-59). These for many years have been considered anomalies in the organometallic chemistry of the transition metals because of their great stability. They have shown that these compounds are not phenyl in nature but that they are the di(π-biphenyl) and (π-benzene)(π-diphenyl) analogues of di (π-benzene)chromium(0).

The view held by the American school is that the rings in π bonded "sandwich" compounds undergo typical aromatic substitution reactions. This has been contested by the German researchers. In an early paper (60), Woodward <u>et al.</u> demonstrated that $(C_5H_5)_2Fe$ undergoes Friedel-Crafts acylations. They showed that the rings lost their diene character; they no longer reacted with maleic anhydride to form Diels-Adler adducts. The fact that $(C_5H_5)_2Fe$ could not be hydrogenated, whereas benzene could, led them to suggest that in this sense $(C_5H_5)_2Fe$ was more aromatic than benzene. The metallation (61, 62) and sulfonation (63) of $(C_5H_5)_2Fe$, the single aromatic like C-H stretching frequency from infra-red data, and the identical C-C bond distance for these compounds and benzene, have been taken as further proof of the aromatic nature of the rings.

The opposite view has been expounded by Fischer (64, 65). The fact that $(C_5H_5)_2Fe$ cannot be hydrogenated and that the indenyl analogue is reduced to bis(π-tetrahydroindenyl)iron(II) is taken as evidence that the π ring electrons are tied up by the metal and are not readily available for aromatic substitution. Further support for this claim is that $[(C_5H_5)_2Co]^+$ cannot be ozonated, nitrated or sulfonated and that di(π-benzene)chromium(0) will not undergo metallation reactions or the Chichibabin reaction. The fact that Friedel-Crafts acylations have been successfully performed on non-aromatic cyclic systems leads Fischer to conclude that the acylations reported by Woodward <u>et al.</u> (60) were of this type. In rebuttal, Cotton and Wilkinson (66) argue that the reason for the lack of halogenation, nitration and sulfonation is that compounds such as $(C_5H_5)_2Fe$ and $(C_5H_5)_2Co$ are oxidized to the unipositive ions making electrophylic substitutions virtually impossible. The arguments regarding the aromatic nature of the rings are closely related to the disagreement between the two schools about bonding in these compounds.

One of the first proposals for the structure of bis(π-cyclopentadienyl)iron (6) suggested that the iron atom attained an inert gas configuration (krypton) by the donation of five electrons from each ring to the valency shells of the metal. Others (4) suggested that the iron atom formed three electron pair bonds with each ring, the six metal bonds being directed to corners of an octahedron (d^2sp^3 hybridization). Jaffé (67), using a molecular orbital approach, suggested that 16 electrons are involved in the bonding.

A new molecular orbital model, proposed by Dunitz and Orgel (68) and later amplified by themselves (25) and by Moffitt (69), has gained wide acceptance from American and British researchers in the field. According to this theory a single delocalized covalent bond links the metal to each ring. If the five linearly independent 3d orbitals of a metal of Period IV are considered, they may be distinguished by the components of angular momentum which they have about a given axis ($m_l = 0, \pm 1, \pm 2$). The Dunitz-Orgel-Moffitt theory shows that only the pair having $m_l = \pm 1$ has the same transformational properties and also approximately the same energy as one of the available orbitals in each of the cyclopentadienyl rings; this is the condition for strong bonding. One of these orbitals of the metal will combine with the appropriate orbital of each ring to give a strongly bonding (and anti-bonding) molecular orbital. Each ring is considered as a whole so that the metal-ring bond is delocalized; the metal is not bonded to any single carbon atom.

Another requirement (69) is that the 4s and the 3d ($m_1 = 0$) orbitals, both of which have the same transformational properties, hybridize to form a bonding and anti-bonding orbital. This is brought about by the coulombic repulsion due to the rings in regions where the metal 4s and 3d ($m_1 = 0$) orbitals have high density. Of the pair of hybrids produced only the bonding orbital is occupied in $(C_5H_5)_2Fe$. The energy of the anti-bonding orbital is high, approximately equal to the 4p orbitals in the metal. Compounds such as $(C_5H_5)_2Co$ have an electron in this orbital accounting for the strong reducing properties of the compound. The 4s-3d hybridization is necessary in order to explain the magnetic properties of the "sandwich" compounds.

The independence of the two rings suggests that they are "free" to rotate with respect to one another. This has been substantiated by electron diffraction (70) and nuclear magnetic resonance data (71) on $(C_5H_5)_2Fe$ and dipole moment measurements on bis(π-acetylcyclopentadienyl)iron(II) (72). Purely chemical evidence for the "free" rotation is demonstrated by the fact that no rotational isomers have been isolated. Another important implication of this theory is that the rings retain a high degree of π character because only one electron from each ring is utilized in the bonding. The attainment by a metal of an inert gas configuration is of little consequence. The preparation of $[(C_5H_5)_2Ti]^{++}$ in which the titanium cannot attain the krypton structure is taken as confirmatory evidence for this view.

Fischer (4, 64, 73-76) and his collaborators have consistently maintained that the attainment of the inert gas structure, and bonding similar to d^2sp^3 bonding are the important factors in the stability of the π bonded compounds. Ruch (77) has calculated overlap integrals for these compounds and claims that the theory discussed previously has neglected certain important interactions. Only preliminary reports of these views have been published (73, 76).

The implications of Fischer's model are that the rings are not aromatic because the requirement for d^2sp^3 bonding removes much of the π electron density. Also, the p orbitals of the metals should be filled, which was not the case in the previous treatment. Evidence to support the view of filled p orbitals is given by Yamada et al. who have measured the dichroism of $(C_5H_5)_2Fe$ (78) and more particularly from the study of X-ray absorption edges (64) of various compounds. If one considers that the cyclopentadienyl ion donates six electrons to the metal ion, as Fischer does, the metal in cyclopentadienyl-metal carbonyls attains an inert gas configuration (the previous method gives 14 electrons). The attainment of inert gas structures by metals in metal carbonyls has long been recognized (79). Ruch has claimed, but to date has not provided data, that the inability of the theory to correctly predict the magnetic properties of $(C_5H_5)_2Ni$ and "free" rotation of the rings has been overcome, (76).

Linnett (80), using the method of equivalent orbitals and data on overlap integrals calculated by Dunitz and Orgel (25), concludes that the views of Fischer and Moffitt are not as different as is sometimes supposed. The calculations performed by Linnett involved the transformation of the familiar molecular orbitals, used by Dunitz and Moffitt, into a new (equivalent) set, which provided an alternate description of the electronic wave function. From this treatment the system is described as having three electron pair bonds to each ring, the electrons favoring positions closer to the ring than to the transition metal. The rings are free to rotate. Three orbitals, which to a first approximation are non-bonding lie in the plane between the rings. It is claimed that the new wave function represents the system more accurately because equivalent orbitals, as a rule, do not have large absolute values in the same spacial regions.

Linnett concurs with Fischer in the belief that the 18 electron rule is important, but not indespensible, to the stability of these systems. Compounds having fewer than 18 valency electrons will have vacancies in the three non-bonding orbitals; for $[(C_5H_5)_2Ti]^{++}$ these would be entirely empty.

The work presented in this thesis deals only with cyclopentadienyl-cobalt compounds. A brief review of the work done in this field to date will now be described.

Bis(π-cyclopentadienyl)cobalt(II) is a typical π bonded system (18, 81). It melts at 173°C, is soluble in organic solvents yielding red-brown solutions, and is insoluble in water. Crystal structure determination (81) has shown that it crystalizes in the monoclinic system with Co-C = 2.00Å and C-C = 1.41Å. It has one electron more than $(C_5H_5)_2Fe$ and is therefore paramagnetic and a strong reducing agent. Bis(π-cyclopentadienyl)cobalt(II) is oxidized by oxygen and dilute acids to form the bis(π-cyclopentadienyl)-cobalt(III)ion, $[(C_5H_5)_2Co]^+$, $E^o_{ox} = -1.16$ vs. saturated calomel electrode (27).

This ion (82, 83) is isoelectronic with $(C_5H_5)_2Fe$ and is analagously diamagnetic and very stable. The ion cannot be destroyed by boiling in aqua-regia, concentrated sulfuric acid or nitric acid, but is destroyed by fuming perchloric acid. Salts of $[(C_5H_5)_2Co]^+$ are ionic and very soluble in water giving yellow solutions. It has been impossible to crystalize the common salts from aqueous solutions, however, salts containing large anions have been crystalized (picrate, dinitrophenolate and triiodide and in this research the perchlorate was crystalized). The ion behaves like a large unipositive Group IA ion, it can be precipitated by chloroplatinic acid, silicotungstic acid (83) and sodium tetraphenylborate (82). The ionization constant of $[(C_5H_5)_2Co]OH$ has been measured and found to be 8.2×10^{-3}. The crystal structure of $[(C_5H_5)_2Co]ClO_4$ is at present being determined (84). It crystalizes in the tetragonal system, a = b 18.34Å and c = 13.61Å, having the I4/mcm space group.

Piper et al. (38) and Fischer and Jira (85) have prepared $C_5H_5Co(CO)_2$. The former has shown that the carbon monoxide groups can be replaced by PCl_3 and $P(SCN)_3$ and that the ring is π bonded to the metal. Bis(π-indenyl)cobalt(III) ion was prepared (26, 49) and behaves similarly to the $[(C_5H_5)_2Co]^+$ ion. The oxidation potential of the indenyl compound was determined polarographically and found to be -0.61 vols vs. standard calomel electrode (26) which indicates that the cobalt(II) indenyl compound is more stable to oxidation than the corresponding cyclopentadienyl compound.

Complete surveys of the work done on the π-cyclopentadienyl compounds can be found in review articles written by Pauson (86) and by Fischer (87).

III. APPARATUS, MATERIALS AND ANALYSES

A. Apparatus

1. Dry boxes

A vacuum dry box built at the Ames Lab was used to prepare solutions in the electron exchange study. The box was evacuated twice to 100 μ Hg and filled with argon (99.99%) after each evacuation.

All other work requiring a dry box was preformed in a steel Blickman dry box. This box consisted of two chambers, a main working chamber equipped with neoprene gloves and a window, and a smaller chamber from which air could be removed rapidly. The two sections were separated by a gas tight door.

Articles to be taken into the dry box were placed in the small chamber and helium (99.99%) was passed through the chamber at a rapid rate for one hour to remove the air. The articles were then passed into the main box in which a dry helium atmosphere was always maintained.

2. Counting equipment

Radiochemical analyses were made using a Tracerlab type TG-2/1B84 Geiger-Mueller counting tube and a Nuclear Instrument and Chemical Corporation model 164 scaling unit. The counting tube had a mica end window of 1.8 mg/cm^2 thickness and all of the counting data were taken using the same lead housing, plastic counting mount and aluminum sample holder.

3. Exchange apparatus

The problem of measuring the electron exchange kinetics between $(C_5H_5)_2Co$ and $(C_5H_5)_2CoClO_4$ was complicated by the fact that the half times for the reaction were fast and that $(C_5H_5)_2Co$ was unstable in air.

A system was built which divided a reacting solution into six samples, which could be quenched individually at the operator's discretion. The apparatus was capable of quenching one sample every 30 seconds with an accuracy of ± 1 second. This made it suitable for measuring half times greater than one minute. It was also designed so that it could be filled with an inert atmosphere.

To fulfill the requirement of obtaining speedy sampling and quenching in a closed system, it was necessary to build a complicated piece of equipment. A full discussion of its construction and operation is given in the appendix.

The cobalt exchange reaction between $[(C_5H_5)_2Co]ClO_4$ and the cobaltous ion was carried out in a 500 milliliter erlenmeyer flask fitted with a 24/40 standard taper. The flask was made opaque to light by spraying it several times with black "Krylon" acrylic spray.

An apparatus (Figure 1) was designed to measure exchange rates with half times greater than 30 minutes and was particularly well adapted for studying reactions from which air and water had to be carefully excluded. This apparatus consists

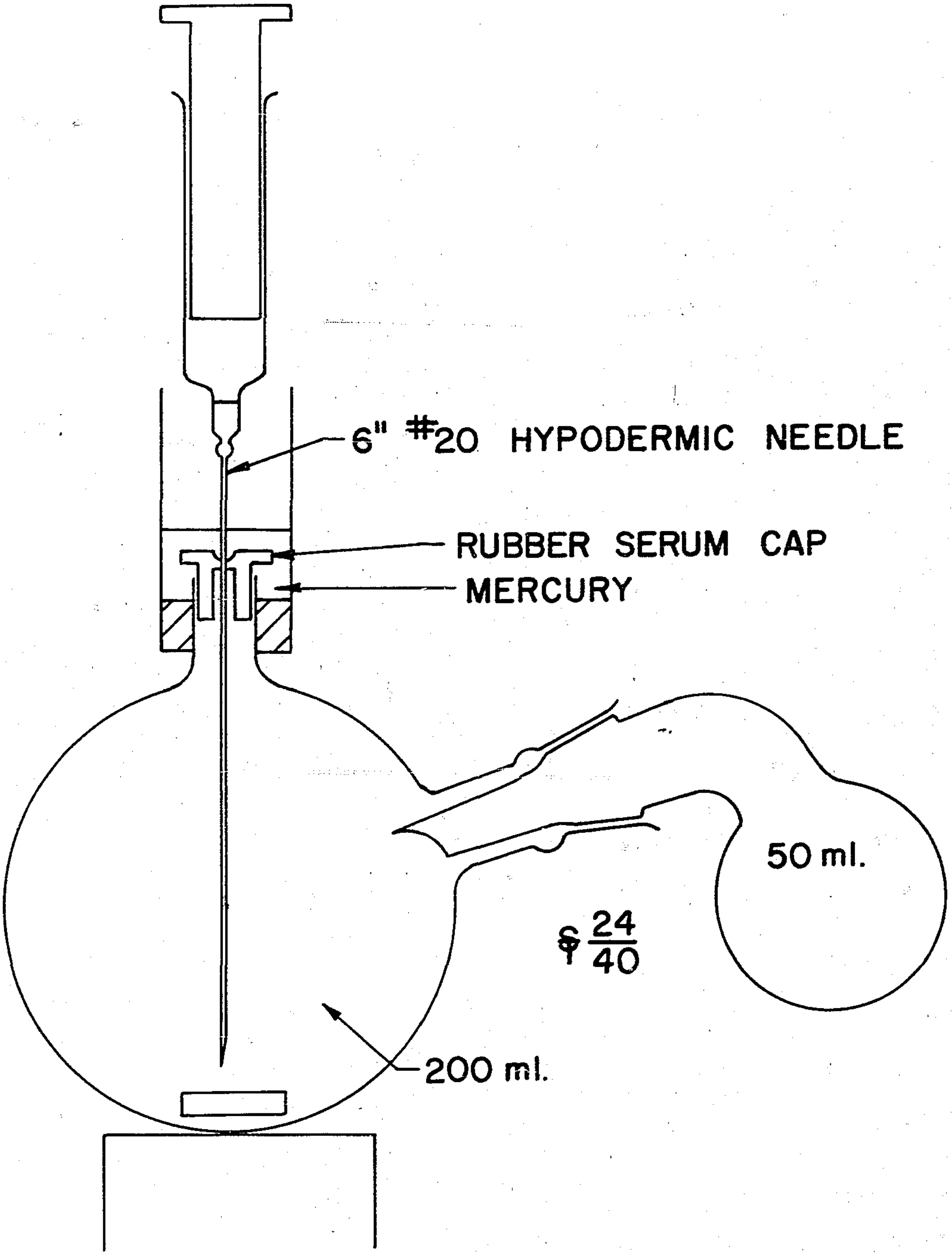

Figure 1. Exchange apparatus for the study of slow reactions

of a 200 ml round bottom flask, a 50 ml bulb with a "drip tip" and a rubber serum cap covered with mercury. The hypodermic needle and syringe in Figure 1 demonstrates the procedure for removing samples from the flask.

One of the two reacting solutions and a "teflon" covered magnetic stirring bar were placed in the 200 ml flask. The other reacting solution was placed in the 50 ml bulb. If the reaction required an inert atmosphere, this operation was performed in a dry box. The apparatus was placed in a constant temperature bath and the solution in the 200 ml flask was stirred with a magnetic stirrer. After two hours the 50 ml bulb was rotated 180 degrees about the 24/40 standard taper and the solution it contained emptied into the main vessel. This time was taken as the start of the reaction. At appropriate times, samples of solution were removed for analysis.

The method of removing samples consisted of piercing the rubber cap with a six inch #20 hypodermic needle and withdrawing the desired amount of solution into a syringe. The needle was removed from the flask and the mercury on top of the cap covered the hole produced so that no air or water could enter the system.

If the pressure in the flask was too low it was difficult to withdraw the samples, and there was a tendency for mercury to leak into the flask when the cap was being punctured by the needle. If the pressure was maintained close to atmospheric pressure the serum cap could be punctured 20 to 30 times before mercury leaked in. In order to maintain atmospheric pressure in the vessel, the syringe was filled with an amount of gas equal or greater than the volume of sample to be removed. This gas was injected into the apparatus and the sample was then removed.

In oxygen sensitive reactions, the quenching solution was placed in quenching flasks similar to the ones shown in the appendix. For these reactions, the flasks were fitted with serum caps so that the syringe could be emptied in the absence of air.

When reactions were carried out at 0°C, a polyethylene jacket was placed around the syringe and it was filled with water and ice. When it was necessary to run experiments in the dark, the apparatus was wrapped in a double thickness of aluminum foil.

4. Gas reaction apparatus

All reactions involving the study of oxygen or hydrogen were carried out in the apparatus shown in Figures 2 and 3.

The entire system was filled with a gas to a desired pressure. The stopcock S_3 was closed, trapping a volume of gas in the bulb. The level of the liquid was the same in both arms of the differential manometer. As gas was consumed in the reaction, the pressure on the right side of the system decreased and the differential manometer was no longer balanced. Mercury was introduced into the gas buret until the

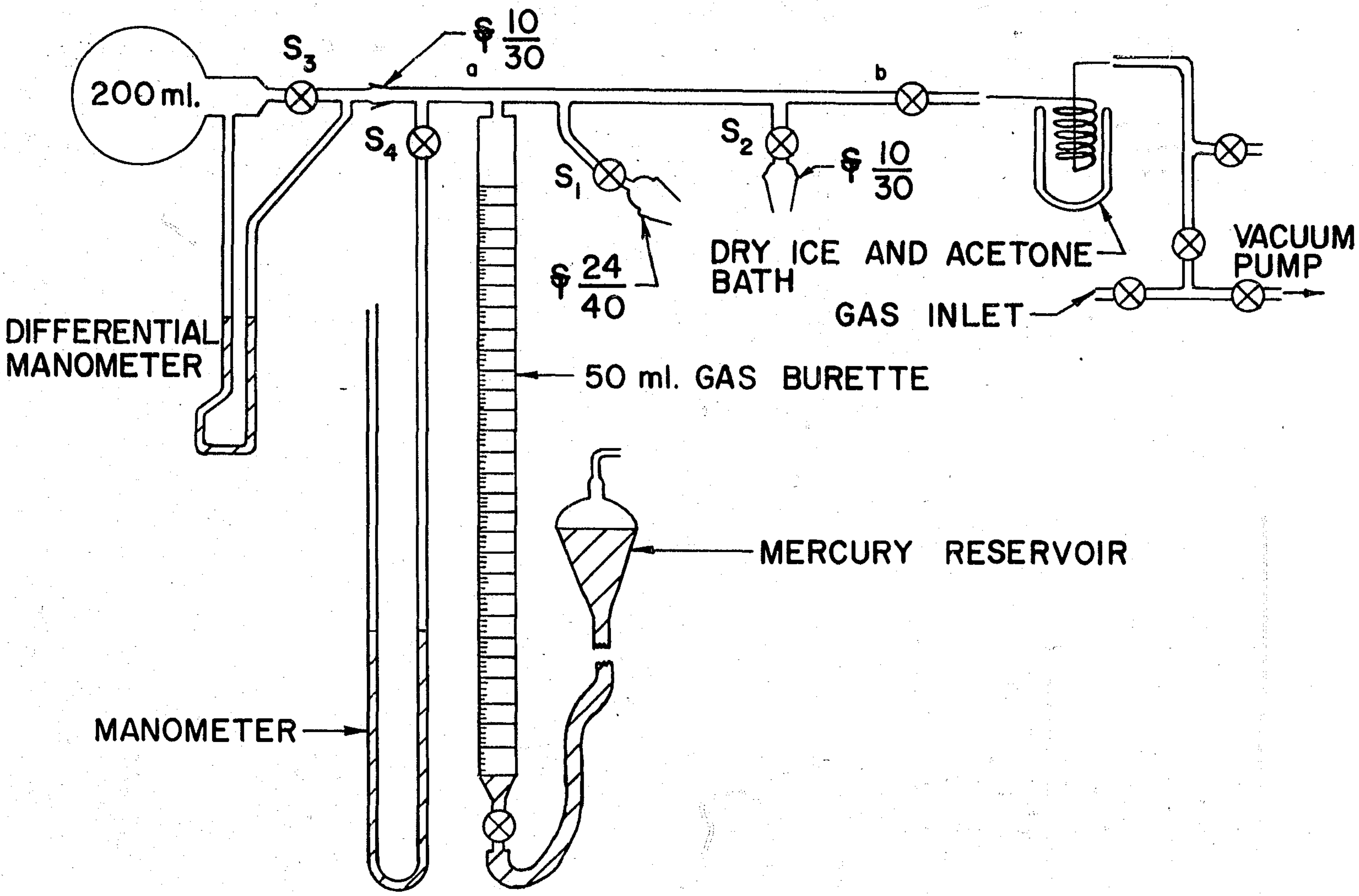

Figure 2. Apparatus for the study and reactions with gases

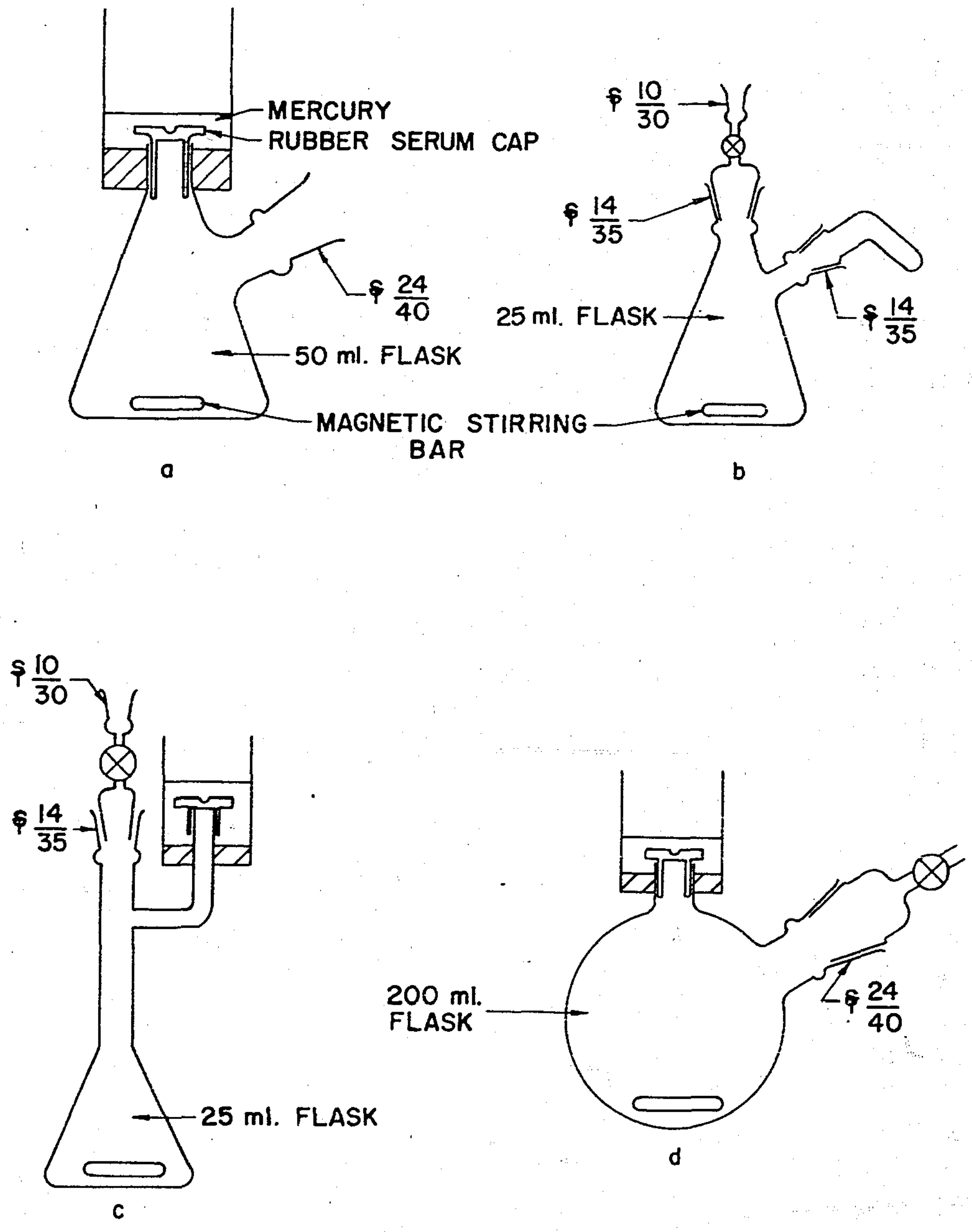

Figure 3. Apparatus for the study of reactions with gases

manometer was balanced. The volume of mercury added to the gas buret corresponded to the volume of gas consumed.

The differential manometer acted as a reference pressure system. When the liquid levels in the arms were the same, the pressure in the system was known. Knowing the temperature, pressure and the change in volume, the number of moles of gas consumed was calculated from the ideal gas law.

The utility of the system, as thus far presented, is that for a given change in the number of moles of gas, the volume change measured is independent of temperature. In many experiments the reaction vessel was maintained at a temperature other than that of the differential manometer and the gas buret. In this case the volume change was no longer independent of temperature and a one degree change in room temperature caused a 1-5% error in a determination. Another source of error was the level of the constant temperature bath surrounding the sample flask. Small changes in the level of the bath caused noticeable pressure changes. For these reasons, reactions operating at temperatures other than room temperature were run for no longer than one hour. For this length of time the error incurred due to these limitations was negligible.

The liquid most often employed in the differential manometer was di-<u>n</u>-butyl phthalate. Because of its low density (d = 1.05), changes in volumes as small as 0.005 ml were detectable, however the gas buret could only be read with an accuracy of ± 0.02 milliliters. Mercury was used in the differential manometer only when volatile solvents were employed. This was necessary because solvent vapors tended to dissolve in the di-n-butyl phthalate causing erratic readings.

Two general types of studies were made using this apparatus; kinetic studies involving oxygen and titration of compounds with gases.

In the kinetic studies the rates of uptake of oxygen with respect to time were measured. The reaction vessels that were used are shown in Figure 3a and 3c. Type C was used for oxygen sensitive reactions and was loaded in a dry box.

Only solids were placed in the reaction vessels. The entire system was evacuated and the stopcock (S_1 or S_2) between the reaction vessel and the gas measuring system was closed. The system was filled with gas to the desired pressure and solvent was injected through the serum cap of the reaction vessel using techniques described previously. Oxygen free solvents were stored in the vessel shown in Figure 3d. After temperature equilibration and dissolution of the solid, either stopcock S_1 or S_2 was opened. The remainder of the procedure is described at the beginning of this section.

When S_1 or S_2 was opened to permit gas into the reaction vessel, the pressure in the system fluctuated for about 10 seconds. In this time some reaction took place, so that it was difficult to observe the beginning of a reaction. For this reason this method was not used for quantitative measurements. With this procedure it was necessary in each case to determine the amount of gas that dissolved in the solvent. To accomplish this, blanks were run. When the exclusion of light was necessary, the reaction vessel and the glass tubing from a to b in Figure 2 were wrapped in a double thickness of aluminum foil.

Reaction vessel B (Figure 3b) was used for quantitative measurements. In this case the solvent was placed in the flask and the solid in the small arm. The solution was equilibrated with the reacting gas so that no blank was necessary. The solid was then dropped into the solvent. It was possible to run titrations in this manner because the solid reacted much more slowly with the gas than did its solutions.

5. Infra-red spectrometer

Two infra-red spectrometers were used in this study; a Perkin-Elmer Infracord and a Baird Atomic, Inc. Model B. Both machines were double beam instruments using sodium chloride optics.

B. Reagents and Solvents

1. Reagents

All reagents used in this work were prepared from reagent grade chemicals unless otherwise specified.

2. Skelly B

Skelly B is the commercial name for a petroleum fraction, boiling range 60 to 80°C, consisting of saturated hydrocarbons. It is marketed by the Skelly Oil Company.

Skelly B was shaken with successive portions of concentrated sulfuric acid until the acid phase was only lightly colored, washed once with acidic potassium permanganate, twice with water and finally with a 10% sodium carbonate solution. It was distilled and stored over calcium sulfate.

3. Acetone

To one liter of acetone (Baker and Adamson reagent grade) were added 4.5 grams of silver nitrate in 30 ml of water, and 30 ml of 1N sodium hydroxide, the mixture was shaken for ten minutes and then filtered. The acetone was left over calcium sulfate over night after which it was filtered and distilled saving only the middle one-third portion. The acetone was stored over calcium sulfate in amber bottles.

Deoxygenated acetone was needed for some of the exchange work. The acetone was distilled into a flask which had a side arm and a bubbling tube built into it. The acetone was boiled for thirty minutes while dry, oxygen free helium was passed through, it was frozen in liquid nitrogen and the helium was pumped out of the flask. The flask was sealed *in vacuo* and was stored in a dark place.

4. Mesitylene

Mesitylene is 1, 3, 5 trimethylbenzene. Eastman white label mesitylene was dried over calcium hydride and then distilled through a spinning band column of 30 theoretical plates at 14mm Hg at 55°C.

Deoxygenated mesitylene was prepared in the apparatus shown in Figure 3d. Mesitylene was distilled into the flask through the stopcock, and was frozen in dry ice and acetone. The flask was evacuated, removed from the cooling bath and allowed to warm to room temperature after which it was again frozen and evacuated. This was repeated two more times and then an atmosphere of helium was placed over the mesitylene.

5. Tetrahydrofuran

Eastman white label tetrahydrofuran was refluxed over lithium aluminum hydride for eight hours. It was refluxed over sodium for another eight hours, and then distilled at 64°C. Tetrahydrofuran was always used within four hours after distillation.

C. Preparation of Compounds

1. Labeled cobaltous perchlorate

Cobalt-60 was obtained from the Oak Ridge National Laboratory as cobaltous chloride in a 0.1N hydrochloric acid solution. The half life of cobalt-60 is 5.24 years. Its radiation is essentially a beta ray ($E_{max} = 0.309$ mev) and two gamma rays in cascade with energies of 1.173 and 1.323 mev (88).

Approximately 100 μcuries of cobalt-60 was added to 0.240 grams of cobaltous chloride in 20 ml of water and cobaltous hydroxide was precipitated by adding 0.3N sodium hydroxide. Nitrogen was bubbled through the water to prevent oxidation of the cobalt. The cobaltous hydroxide was centrifuged, the supernatant liquid was discarded, and the precipitate was dissolved by the dropwise addition of 0.3N perchloric acid. This procedure was repeated until the solution gave a negative chloride test with silver nitrate.

2. Bis(π-cyclopentadienyl)cobalt(II)

Bis(π-cyclopentadienyl)cobalt(II) was prepared using Wilkinson's method (11); reacting cyclopentadienyl sodium with anhydrous cobaltous chloride. Dicyclopentadiene (Eastman Organic Chemicals Technical Grade) was cracked by heating and the cyclopentadiene monomer was distilled at 42°C. This cyclopentadiene (1.65g) was added to 5.8g of sodium sand in tetrahydrofuran in an ice bath. The mixture was stirred vigorously and kept free of air by bubbling helium through it. Anhydrous cobaltous chloride prepared by heating the hexahydrate in a vacuum at 200°C for 24 hours was added to the solution. The mixture was stirred for two hours and the tetrahydrofuran was removed by vacuum distillation. The residue was heated to 70°C in a high vacuum (10^{-6}mm Hg) and bis(π-cyclopentadienyl)cobalt(II) sublimed as large black crystals.

3. Bis(π-cyclopentadienyl)cobalt(III) perchlorate

Two methods were used for preparing $[(C_5H_5)_2Co]ClO_4$, one used by Wilkinson (83) to obtain solutions of this compound and another developed here. In the Wilkinson method $(C_5H_5)_2Co$

was treated in ether solutions with picric acid, oxidizing the cobalt and precipitating orange bis(π-cyclopentadienyl)cobalt-(III) picrate. This was recrystalized twice from aqueous picric acid solutions and dissolved in water. The solution was passed through a Dowex-I anion exchange column in the perchlorate form yielding yellow solutions of bis(π-cyclopentadienyl)cobalt(III) perchlorate.

Though not previously reported it was found that evaporation of these solutions gave stable yellow crystals of anhydrous $[(C_5H_5)_2Co]ClO_4$. The composition was established by the quantitative precipitation of $[(C_5H_5)_2Co][(C_6H_5)_4B]$ by adding sodium tetraphenylborate to solutions of the yellow crystals. The theoretical amount of $[(C_5H_5)_2Co]^+$ in $[(C_5H_5)_2Co]ClO_4$ is 65.54%, the amount found was 65.96%.

After it was found that the perchlorate salt could be crystalized it was no longer necessary to use the picrate and ion exchange transfer of anions. Simple air oxidation of $(C_5H_5)_2Co$ in benzene in contact with a large quantity of dilute aqueous perchloric acid (0.01N) produced an aqueous solution of the perchlorate. This solution was washed twice with benzene and purified by heating it with activated charcoal. After filtration, the solution was evaporated to a small volume and cooled to 0°C to crystalize the perchlorate which was recrystalized five times from water.

4. <u>Labeled bis(π-cyclopentadienyl)cobalt(III) perchlorate</u>

Bis(π- cyclopentadienyl)cobalt(III) perchlorate was labeled with cobalt-60 obtained from the Oak Ridge National Laboratory. The cobalt-60 was introduced into this compound by adding 500 μ curies of tracer to 50 grams of cobaltous chloride hexahydrate in 50 ml of water. The water was evaporated and the method previously used for preparing $[(C_5H_5)_2Co]ClO_4$ was followed.

5. Cyclopentadienyl-trichloromethyl-cobalt compound $[(C_5H_5)_2(CCl_3)Co]$

Four grams of $(C_5H_5)_2Co$ in an evacuated flask was dissolved in 5 ml of deoxygenated carbon tetrachloride and the solution was stirred for one hour. During this time a yellow-green precipitate of $[(C_5H_5)_2Co]Cl$ precipitated. After the reaction was completed, air was allowed to enter the flask and the solution was filtered, the $(C_5H_5)_2(CCl_3)Co$ remained in solution. The carbon tetrachloride, after two water extractions, was removed by vacuum distillation. The red-brown residue was heated to 40°C in a high vacuum (10^{-6} mm Hg) and $(C_5H_5)_2(CCl_3)Co$ sublimed as deep red crystals.

Because of the great solubility of $(C_5H_5)_2(CCl_3)Co$ in all common organic solvents, recrystalization was impractical. The $(C_5H_5)_2(CCl_3)Co$ was precipitated several times from hexane or acetone solutions by quickly cooling them in hexane slush baths (-95°C) or dry ice and acetone baths (-77°C). Infra-red spectra of $(C_5H_5)_2(CCl_3)Co$ taken after sublimation and after each precipitation from hexane and acetone were identical.

6. Labeled lithium chloride

Chlorine-36 obtained from the Oak Ridge National Laboratory as a dilute solution of hydrochloric acid was used to label the lithium chloride. Chlorine-36 has a half life of 2.5×10^5 years, emits one beta particle ($E_{max} = 0.714$ mev) and no γ rays (88). Approximately 0.5 μ curies of chlorine-36 and 0.30 g of lithium chloride was dried at 120°C for 24 hours.

D. Analyses

1. Quantitative analysis of the bis(π-cyclopentadienyl)-cobalt(III) ion

Fischer and Jira (82) mentioned that precipitation of $[(C_5H_5)_2Co][(C_6H_5)_4B]$ could be used as a quantitative method for the determination of the bis(π-cyclopentadienyl)-cobalt(III) cation. A gravimetric method, accurate to ± 0.5%, was developed here based on Fischer's suggestion.

An aqueous solution containing approximately 0.2 millimole of $[(C_5H_5)_2Co]^+$ is diluted to 80 ml and to it is added 0.5 ml concentrated hydrochloric acid and 20 ml of 0.6% sodium tetraphenylboron solution. After digesting it for one hour, the solution is allowed to stand at room temperature for several hours and then chilled in an ice bath. The precipitate is filtered in weighed sintered glass crucibles and washed three times with 10 ml portions of a cold wash solution of $[(C_5H_5)_2Co][(C_6H_5)_4B]$ is used. The crucible is dried at 110°C for two hours, desiccated and weighed. The washings and weighings are continued until two successive weights agree to ± 0.2 mg.

2. Infra-red analyses

Infra-red spectra were frequently used in this study for qualitative and structural analysis. All the work was done using sodium chloride optics in the wave length region 2.0-16.0μ. Spectra of solutions were often used but the solvents absorbed strongly in regions of interest blanking any solute bands that might have been present. In order to get a complete spectrum, it was necessary to combine the spectra obtained from the use of several solvents.

If the compound was insoluble in the solvents commonly used for infra-red analysis (carbon tetrachloride, chloroform, bromoform, carbon disulfide), the spectra were determined from a "Nujol" mull. "Nujol" is the commercial name for a pure grade of mineral oil. A finely powdered sample was ground with a few drops of "Nujol" so that a suspension resulted. This suspension was placed on a sodium chloride plate and analyzed.

In the examination of solid compounds the technique was used of preparing KBr pellets from an intimate mixture of 200 mg potassium bromide and 2-10 mg of the compound. Alternately, a film was deposited on a sodium chloride plate by evaporating a solution.

Figure 4 shows the spectra of $[(C_5H_5)_2Co]ClO_4$ and $[(C_5H_5)_2Co][(C_6H_5)_4B]$ which were used as standards when analyzing for the bis(π-cyclopentadienyl)cobalt(III) cation.

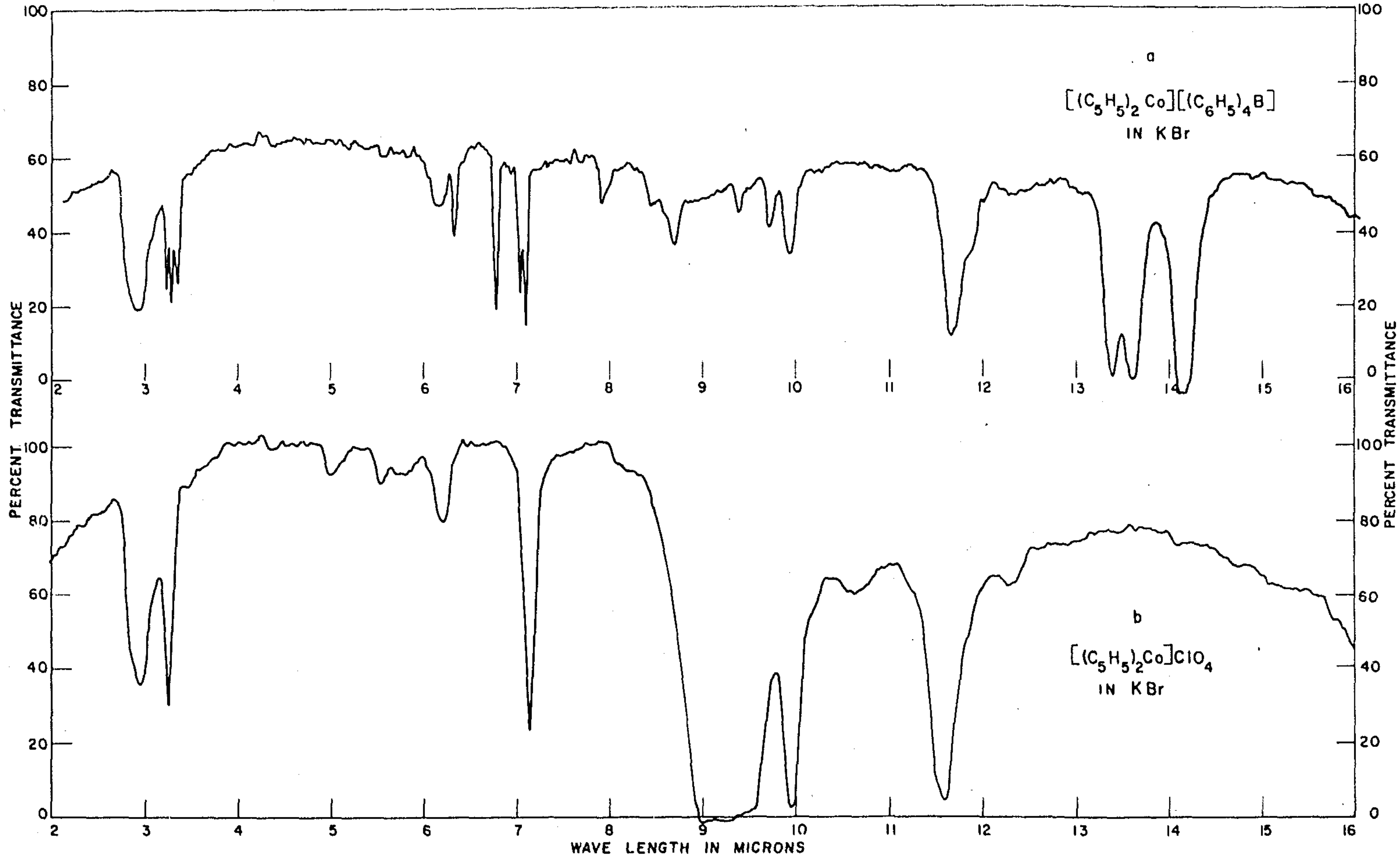

Figure 4. Infra-red spectra of $[(C_5H_5)_2Co][(C_6H_5)_4B]$ and $[(C_5H_5)_2Co]ClO_4$ in KBr

The spectra in Figure 4 were determined in "KBr pellets". The absorption at 2.9 μ was due to water impurities in the potassium bromide. The significance of the bands will not be discussed here; for qualitative analysis, it was only necessary to check the bands of a spectrum against these standards.

Structural and functional group analysis involves checking a spectrum for a band or a group of bands. To illustrate this, a comparison between Figures 4a and 4b shows that all the bands attributable to the $[(C_5H_5)_2Co]^+$ ion are to be found in both spectra. A discussion of other absorptions which are important to this study will be presented later.

3. Cobalt exchange

The procedure described here is the one that was used to prepare samples for radiochemical analysis in the exchange between the cobaltous ion and $[(C_5H_5)_2Co]ClO_4$. A 10 ml aliquot of the reacting solution was added to 7 g of sodium thiocyanate. The $Na_2Co(SCN)_4$ produced was extracted into 10 ml of a 1:3 mixture of n-amyl alcohol and diethyl ether and the phases were separated and washed. The cobaltous ion was re-extracted into a 6N ammonium hydroxide solution and cobaltous sulfide was precipitated by adding ammonium sulfide. After centrifugation, the precipitate was dissolved in 3 ml concentrated nitric acid, 2 ml of concentrated sulfuric acid was added and the solution was heated to copious fumes of sulfur trioxide. The solution was cooled and 5 ml of water, 7 ml concentrated ammonium hydroxide and 2 g ammonium sulfate were added. Cobalt was plated onto a weighed platinum planchet using a current of 0.3 amp for 1 hour.

To the aqueous phase containing the $[(C_5H_5)_2Co]^+$ ion was added 7 ml of 0.6% sodium tetraphenylboron and the resulting precipitate was destroyed by a perchloric acid oxidation. The cobaltous perchlorate solution obtained was, by the method given above, precipitated as the sulfide, converted to the sulfate and plated. The samples were washed with 95% ethanol, air dried, weighed on a microbalance and counted.

Three samples were taken to determine the specific activity (counting rate per unit weight) of the unexchanged cobaltous ion. One milliliter of the cobaltous perchlorate stock solution was added to 1.5 ml concentrated ammonium hydroxide and 1.3 g ammonium sulfate. The cobalt was plated at 0.5 amperes and 6.5 volts for 50 minutes and then at 0.5 amperes and 6.5 volts for 10 minutes. The samples were plated on platinum planchets that were previously weighed on a microbalance, these were washed with 95% ethanol, air dried, weighed on a microbalance and counted.

4. Radiochemical analysis for $[(C_5H_5)_2Co]^+$ ion

In both the electron exchange and the $[(C_5H_5)_2Co]ClO_4$ *vs.* $(C_5H_5)_2(CCl_3)Co$ exchange experiments the samples were weighed and counted as $[(C_5H_5)_2Co][(C_6H_5)_4B]$. Solutions containing about 6 mg of a bis(π-cyclopentadienyl)cobalt(III) salt were evaporated to one milliliter and 2 ml of 0.3N hydrochloric acid was added. A 0.6% solution of sodium tetraphenylborate was added dropwise, with shaking, until precipitation ceased. The solution was then filtered.

The $[(C_5H_5)_2Co][(C_6H_5)_4B]$ precipitate had a tendency to peptize. To precipitate 10 mg of the tetraphenylborate; the solution volume could not exceed 5 ml; the acid concentration had to be kept above 0.05N; and the solution had to be hot. Even if these precautions were taken, the precipitate had to be filtered slowly or it would run through the filter paper (Schleicher and Schuell red ribbon).

To insure good counting data, the reactants in an exchange reaction were counted in the same chemical form and on identical backings. In this case the form chosen was $[(C_5H_5)_2Co][(C_6H_5)_4B]$ and the backing was of aluminum. The filter chimneys were of almost identical diameter (1.73 ± 0.01cm) so that the geometry of the samples could be kept constant. A cobalt-60 standard was counted with every determination so that data taken at different times could be compared. Self absorption and self scattering corrections were made, as explained below.

The samples of $[(C_5H_5)_2Co][(C_6H_5)_4B]$ analyzed had a wide range of weights. In order to accurately compare samples, their specific activities had to be corrected for the absorption and scattering of beta particles due to varying sample thicknesses. A series of samples having the same specific activity but different weights was counted and the "apparent" specific activity was plotted as a function of weight (Figure 5). Using this curve, the "apparent" specific activity of a sample was corrected to the hypothetical value it would have had if its weight had been zero. Samples having weights below 6 mg were not used because these corrections could not be made with any confidence.

5. Electron exchange reactions

The $[(C_5H_5)_2Co]ClO_4$ was analyzed as described in the preceding section. The organic solution of $(C_5H_5)_2Co$ was analyzed by shaking it with a small amount of 0.3N hydrochloric acid which oxidized the sample to $[(C_5H_5)_2Co]Cl$. This extracted into the aqueous phase and was analyzed radiochemically

6. Chloride exchange reaction

In the exchange reaction between $(C_5H_5)_2(CCl_3)Co$ and lithium chloride the following procedure was used to radiochemically analyze for chloride. The aqueous solution containing lithium chloride was diluted to 80 ml and 1 ml of concentrated ammonium hydroxide was added. To precipitate silver chloride, a 10% silver nitrate solution was added till a trace of silver oxide was detected. Three drops of 2N nitric acid was added to dissolve the silver oxide and the sample was then filtered, washed first with water and then with acetone. The samples were heated at 110°C for 30 minutes then

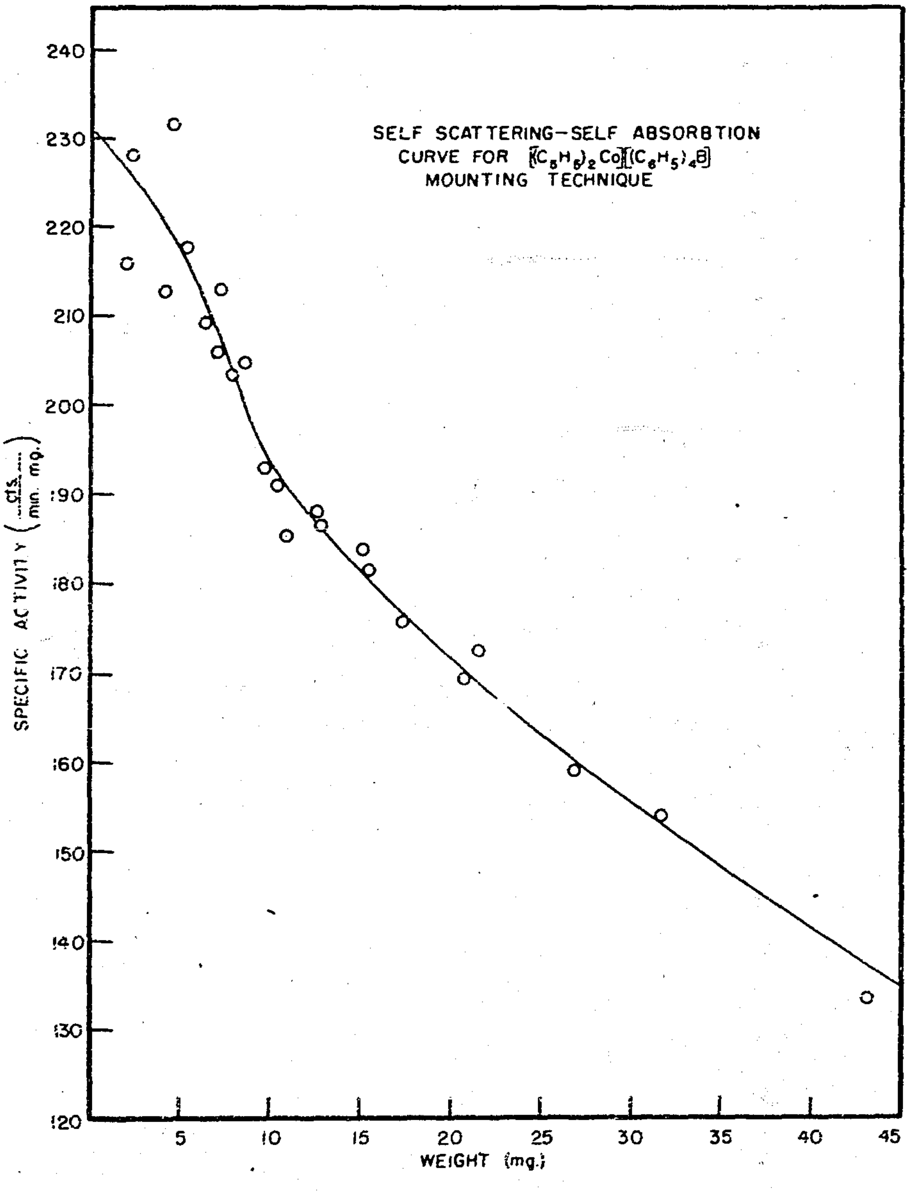

Figure 5. Self scattering-self absorption curve for counting samples containing radioactive $(C_5H_5)_2Co^+$

desiccated, weighed and counted. The weights of the samples were very close to constant, therefore no corrections were made for self scattering and self absorption.

IV. EXPERIMENTAL PROCEDURES AND RESULTS

A. Exchange of Cobalt Ions

The study of the exchange of cobalt between cobaltous perchlorate and $[(C_5H_5)_2Co]ClO_4$:

$$Co^*(ClO_4)_2 + [(C_5H_5)_2Co]ClO_4 \rightleftharpoons Co(ClO_4)_2 + [(C_5H_5)_2Co^*]ClO_4$$

was carried out in an aqueous solution at 25 ± 0.1°C. The cobaltous perchlorate was labeled with cobalt-60 so that any exchange of cobalt between the two species would result in the net transfer of tracer to $[(C_5H_5)_2Co]ClO_4$. The progress of the reaction was monitored by observing the change in specific activity of the reactants with time.

To a 250 ml aliquot of stock $[(C_5H_5)_2Co]ClO_4$ solution in a 500 ml opaque erlenmeyer flask was added 35 ml of the labeled cobaltous perchlorate solution. This operation took about four minutes and the time after two minutes was considered the zero time for the reaction. Replicate 10 ml aliquots of the exchanging solution were removed periodically for separation and analysis. The addition of the reactants and the removal of samples were performed in the light produced by two ruby red darkroom bulbs.

The separation of the reactants was accomplished by adding a 10 ml aliquot to seven grams of sodium thiocyanate and extracting the resulting $Na_2Co(SCN)_4$ into 10 ml of 1:3 solution of n-amyl alcohol and ether. The samples were then analyzed radiochemically.

To avoid inaccuracies in the counting data, both reactants were counted in the same chemical form with identical backings. The radiochemical data was not corrected for self absorption and self scattering due to sample thickness because such a refinement was unnecessary to interpret the data. This correction should have been small since the samples were thin (0.2-0.6 mg/cm^2). Accurate comparisons could be made in the series of samples for each reactant because the weight of cobalt plated for each reactant was fairly constant. The cobaltous perchlorate and the $[(C_5H_5)_2Co]ClO_4$ sample weights were 0.76-0.84 and 1.4-1.8 mg respectively. The initial specific activity of cobaltous perchlorate was determined from three analyses of the cobaltous perchlorate stock solution. Values of 5547, 5638 and 5633 cts/min mg were obtained and the average value, 5606 ± 39 cts/min mg, was used in the calculations. The specific activities of all samples were corrected for the decay of cobalt-60 so that they could be compared to the above value.

To determine the concentration of the reactants in the exchange mixture, three analyses were performed on both the $[(C_5H_5)_2Co]ClO_4$ stock solution and the cobaltous perchlorate solution; the exchange solution was found to be 0.00173M in cobalt and 0.00366M in $[(C_5H_5)_2Co]^+$. The pH of the solution as determined with a Beckman pH meter was 1.99. The data obtained from this experiment is summarized in Table 1.

Table 1. $Co(ClO_4)_2$ *vs.* $[(C_5H_5)_2Co]ClO_4$ exchange data

	Specific activity (cts/min mg Co)		Fraction exchange $x10^2$	
Time	$Co(ClO_4)_2$	$[(C_5H_5)_2Co]ClO_4$	$Co(ClO_4)_2$ fraction	$[(C_5H_5)_2Co]ClO_4$ fraction
1 hour		2.9 ± 1.0		0.16 ± .05
8 hours	5485 ± 140	3.0 ± 1.1	3.2 ± 3.7	0.17 ± .06
26 hours	5495 ± 50	3.3 ± 1.0	2.9 ± 2.0	0.18 ± .06
7 days	5365 ± 94	2.4 ± 1.7	6.3 ± 2.5	0.13 ± .11
28 days	5340 ± 50		7.0 ± 1.4	
30 days		0.7 ± 0.9		0.04 ± .05

The fraction of exchange (F) is the standard form for reporting exchange data. McKay (89) has shown that for a simple homogeneous exchange reaction it can be represented as:

$$F = 1 - \exp(-Kt) = \frac{S - S_0}{S_\infty - S_0}, \qquad (1)$$

where K is a function of the concentrations and the rate constant for the exchange, S, S_∞ and S_0 represent the specific activity of the cobalt in the two species at times

(t) t = t, t = ∞ , and t = o respectively. Assigning the subscript A to the cobaltous perchlorate and B to $[(C_5H_5)_2Co]ClO_4$ and also noting that $S_{B_o} = 0$ because B was initially inactive, we may rewrite the above equation:

$$F = \frac{S_A - S_{A_o}}{S_{A\infty} - S_{A_o}} = \frac{S_B}{S_{B\infty}}.$$

Knowing the concentrations of the reactants (C_A and C_B) and S_{A_o}, $S_{A\infty}$ can be calculated from the following equation:

$$S_{A\infty} = \left(\frac{C_A}{C_B + C_A}\right)S_{A_o}.$$

Because the specific activity refers to the same chemical form,

$$S_{A\infty} = S_{B\infty}.$$

The calculation of the fraction exchange for cobaltous perchlorate involves the difference of two large numbers. Thus the best indication of the amount of cobalt transferred between the species can be obtained from a comparison of the $[(C_5H_5)_2Co]ClO_4$ data. These values (Table 1) indicate that over a period of 30 days essentially no cobalt exchanges. Incomplete separation of the cobaltous perchlorate most probably accounts for the specific activities of the $[(C_5H_5)_2Co]ClO_4$. A dry run of the procedure indicated that about 25 cts/min of cobalt activity remain with the $[(C_5H_5)_2Co]^+$ after separation. The values of the fraction exchange for each reactant do not change appreciably with time, indicating that they are due to systematic errors.

B. Electron Exchange

The fact that $(C_5H_5)_2Co$ and $[(C_5H_5)_2Co]^+$ are stable and that cobalt-60 activity is readily available, made the measurement of the electron exchange between these two species a feasible experiment. Bis(π-cyclopentadienyl)cobalt(II) and (III) differ only in that the former has one more electron. Though no net chemical reaction takes place, the transfer of electrons between the two forms can be considered as a simple oxidation-reduction reaction:

$$(C_5H_5)_2Co + [(C_5H_5)_2Co^*]^+ \rightleftharpoons [(C_5H_5)_2Co]^+ + (C_5H_5)_2Co^*.$$

The labeling of one of the species with a tracer (cobalt-60) makes possible the determination of the electron exchange rate; since it can be measured by the changes in the specific activity of the two reactants as a function of time. Although only electrons are involved in the reaction, it can be thought of as a case of isotope exchange because the transfer of cobalt atoms would give the same results. The first-order homogeneous isotopic exchange law can therefore be used. The fraction of exchange (F) can be written (89)

$$F = 1 - \exp\left(-\frac{(A) + (B)}{(A)(B)}Rt\right) = \frac{S_B - S_{B_0}}{S_{B_\infty} - S_{B_0}} = \frac{S_A}{S_{A_0}} \qquad (2)$$

in which R is the constant rate of exchange of electrons between $(C_5H_5)_2Co$(A) and $[(C_5H_5)_2Co]^+$(B).

Taking the natural logarithm of equation 2 and rearranging terms one obtains

$$Rt = -\frac{(A)(B)}{(A) + (B)} \ln(1 - F). \tag{3}$$

The semi-logarithmic plot of (1-F) against time results in a straight line intercepting the ordinate at (1-F) = 1. In practice it is often found that the extrapolated value of F is greater than zero. This is called zero-time exchange. For the remainder of the derivation this possibility is excluded. A good discussion of zero-time exchange can be obtained from references (90) and (91).

A useful term is the half-time of exchange ($t_{\frac{1}{2}}$) which is defined as the time necessary for the fraction of exchange to reach a value of one half. Substituting 0.5 for F and $t_{\frac{1}{2}}$ for t in equation 3 gives:

$$R = \frac{(A)(B)}{(A) + (B)} \cdot \frac{0.693}{t_{\frac{1}{2}}} . \tag{4}$$

R is not a rate constant but is dependent on the concentration of A and B. In the simplest case, of a bimolecular second order exchange,

$$R = k(A)(B) \tag{5}$$

in which k is the rate constant for the exchange reaction.

This reduces equation 4 to

$$t_{\frac{1}{2}} = \frac{0.693}{k[(A) + (B)]} \qquad (6)$$

To determine a rate constant it is necessary to determine $t_{\frac{1}{2}}$ from the semi-logarithmic plot and using equation 6 obtain k. If the mechanism is complicated, R is for a number of varied conditions that are evaluated (using equation 5) and the general procedures of chemical kinetics are applied.

All the electron exchange reactions were run in the dark at 0°C. Because of the insolubility of $(C_5H_5)_2Co$ in water, and of $[(C_5H_5)_2Co]ClO_4$ in non-polar solvents, a solvent of intermediate character, acetone, was used. The original labeling with cobalt-60 was in the cobalt(III) compound.

The apparatus described in the appendix was employed when reaction times of 0-10 minutes were to be studied (runs 1-3). For longer times, the apparatus shown in Figure 2 was used (runs 4-18). In both cases the methods of preparing solutions and of analysis were the same.

Because of the sensitivity of $(C_5H_5)_2Co$ to oxygen, all solutions were prepared in the vacuum dry box. The small size of the box made accurate pipeting difficult and it was impossible to use large pipets. To cut down on the number of operations, a special set of short pipets was made so that unusual volumes could be aliquoted in one pipeting. The pipets were calibrated with acetone.

An accurately weighed amount of $[(C_5H_5)_2Co]ClO_4$ and a crudely weighed amount of $(C_5H_5)_2Co$ were separately dissolved in known amounts of acetone. Aliquots of the solutions were placed into separated chambers of reaction vessels and acetone was added so that the total volume was 87.4 ml. The reaction vessels were then completely assembled and removed from the dry box. An accurate account of the procedure followed during the run can be found in the sections describing exchange apparatus. In all the experiments the concentration of $[(C_5H_5)_2Co]ClO_4$ was held constant (0.00203 molar); the concentration of $(C_5H_5)_2Co$ was varied from 0.00109 to 0.00995 molar.

The method of quenching the reactions was the same in all the runs; a 10 ml sample of the reacting solutions was introduced to 90 ml of Skelly B at 0°C, and the ionic $[(C_5H_5)_2Co]ClO_4$ precipitated and was filtered. The $(C_5H_5)_2Co$ remained dissolved in the acetone-Skelly B mixture. The samples were then analyzed radiochemically.

The concentrations of $(C_5H_5)_2Co$ solutions were only approximately known, their exact values were determined by the method of isotopic dilution. A 10 ml sample of the reacting solution was removed and added to 10 ml of 0.1N hydrochloric acid. The radioactive $[(C_5H_5)_2Co]^+$ was diluted by the amount of $(C_5H_5)_2Co$ that was oxidized. The quotient of the specific activity of this sample (S_{B_∞}) over the value (S_{B_o})

for undiluted $[(C_5H_5)_2Co]^+$ was used to determine the concentration ratio of the reactants, $\frac{(A)}{(B)}$, as follows:

$$\frac{S_{B_o}}{S_B} = \frac{(A)}{(B)} + 1.$$

Since the concentration of $[(C_5H_5)_2Co]^+$ was accurately known, using the ratio determined above, the concentration of $(C_5H_5)_2Co$ was calculated. Five determinations of the specific activity of initial $[(C_5H_5)_2Co]ClO_4$ were made, the values obtained as cts/min mg $[(C_5H_5)_2Co][(C_6H_5)_4B]$ were 411, 412, 419, 425 and 428; the average value of 419 cts/min mg (S_{B_o}) was used in the calculations. A summary of the results of these experiments is given in Table 2.

Table 2. Zero time exchange and half times for electron exchange experiments

Run	Molarity $(C_5H_5)_2Co \times 10^3$	Zero time exchange $\times 10^2$	$t_{\frac{1}{2}}$ (min)
12	9.95	99	a
13	3.86	97	a
3	3.00	93	b
4	2.29	93	a
6	2.27	80	185

[a] Half times could not be measured due to very high zero time exchange.

[b] Half times could not be determined because the duration of the experiments was less than 15 minutes.

Table 2. (Continued)

Run	Molarity $(C_5H_5)_2Co \times 10^3$	Zero time exchange $\times 10^2$	$t_{\frac{1}{2}}$ (min)
7	2.27	78	165
11	1.99	81	150
2	1.91	80	b
9	1.79	77	190
8	1.21	65	265
10	1.09	55	265

The values in columns 3 and 4 were determined from semilogarithmic plots of (1-F) vs. time. To determine if the zero time exchange was "separation induced", other quenching solutions were tested. They were: water, from which $(C_5H_5)_2Co$ precipitated; water and toluene, and water and Skelly B which separated the reactants by partition. These solutions did not reduce the values for zero time exchange, indicating that the values were not "separation induced". The zero time is a function of the $(C_5H_5)_2Co$ concentration; as the concentration increases so does the zero time exchange.

C. Reactions between Bis(π-Cyclopentadienyl)Cobalt(II) and Oxygen

Bis(π-cyclopentadienyl)cobalt(II) is known to react with oxygen (18, 81), but no effort has been made to determine the mechanism or characterize the products of the reaction. To elucidate the nature of the $(C_5H_5)_2Co$-oxygen reaction, two acetone solutions of $(C_5H_5)_2Co$ were titrated with oxygen using the apparatus shown in Figures 2 and 3b. The experiments were run at 0°C without the exclusion of light. The results are shown in Table 3.

Table 3. Oxygen uptake by acetone solutions of $(C_5H_5)_2Co$

Conc $(C_5H_5)_2Co$ (m moles)	O_2 pickup (m moles)	$\frac{\text{m moles } (C_5H_5)_2Co}{\text{m moles } O_2}$
0.445	0.1097	4.06
0.977	0.234	4.17

The color of the solutions changed from the initial red-brown to cherry-red, but no product could be isolated by cooling the acetone solutions in a dry ice-acetone bath or by adding Skelly B. On the addition of water to one of the solutions it turned yellow, had a pH ~ 10, and gave a positive test for $[(C_5H_5)_2Co]^+$ _viz._ the precipitation of $[(C_5H_5)_2Co][(C_6H_5)_4B]$. The addition of an aqueous acid solution of potassium iodide and ammonium molybdate (used as a catalyst) to a sample of the acetone solution did not result in any iodine being liberated, thus eliminating the possibility of the formation of a peroxide compound. On standing in air, a small amount of precipitate formed in the acetone solutions. Based on this evidence, it seems likely that the product of the oxidation is bis(π-cyclopentadienyl)cobalt(III) oxide.

$$4(C_5H_5)_2Co + O_2 \longrightarrow 2[(C_5H_5)_2Co]_2O$$

Three experiments were performed to determine the nature of the exchange of $[(C_5H_5)_2Co]^+$ between the new product and $[(C_5H_5)_2Co]ClO_4$; these were conducted at 0°C in the absence of light. The $[(C_5H_5)_2Co]ClO_4$ concentration was 0.00203 molar and the oxide concentrations were 0.00345 and 0.00189 molar. The preparation of the solutions was the same as in the electron exchange experiments and the reaction was run in the apparatus shown in Figure 1. In run 14, after achieving thermal equilibrium, the apparatus was opened to air and the solutions were agitated; the $(C_5H_5)_2Co$ thereby was converted to the oxide. The solutions were allowed to stand for 10 minutes and the reaction was started. In runs 15 and 16, air was allowed to enter two hours before the reaction was started. Samples were removed over a three hour period and were analyzed radiochemically. The electron exchange quenching procedure was used because the oxide was soluble in the acetone-Skelly B mixture. The results of these experiments are shown in Table 4. The data indicates that the rate of exchange of $[(C_5H_5)_2Co]^+$ between the two species is slow, and in contrast to the electron exchange data there is no appreciable zero time exchange.

Table 4. Zero time exchange and half times for the $[(C_5H_5)_2Co]_2O$ vs. $[(C_5H_5)_2Co]ClO_4$ exchange

Run	Conc $[(C_5H_5)_2Co]_2O$ (molarity) x 10^3	Zero time exchange $x10^2$	$t_{\frac{1}{2}}$
15	3.45	2	93
16	3.45	0	95
14	1.89	0	145

Acetone, because of its high vapor pressure (229.2 mm Hg at 25°C (92)), was not suitable for the study of the $(C_5H_5)_2Co$-oxygen reaction over long periods of time; since it was very difficult to equilibrate the system (Figures 2 and 3) with solvent vapor. The lack of equilibrium was reflected in a slow increase in pressure on the right side of the system (Figure 2). Since stopcock S_3 was closed, a corresponding increase in pressure in the bulb did not occur, thus resulting in the continual imbalance of the differential manometer arms even though no reaction was occuring. To eliminate the error produced by equilibration, low vapor pressure solvents were employed. The same equilibration difficulties were encountered with these solvents, but due to the low value of the vapor pressure, the pressure increase on the right side of the system was small making the error insignificant.

Preliminary investigations of the reaction of $(C_5H_5)_2Co$

and oxygen were made in N, N-dimethylformamide, quinoline and di-n-butyl phthalate. An extensive study of the kinetics and products of this reaction made using mesitylene as the solvent; this was chosen both for its low vapor pressure (Table 5) and its relative inertness.

The kinetic experiments were carried out in absence of light and at temperatures ranging from -22.6 to 25.0°C. The oxygen pressure and the $(C_5H_5)_2Co$ concentrations were varied between 0.5-1.0 atmospheres and 0.044-0.110 molal respectively. The sample volumes were 10 ml.

Table 5. The vapor pressure of mesitylene at various temperatures (92)

Temperature (°C)	Vapor pressure (mm Hg)
25	2.7
0	0.45
-22	0.062

To determine the dependence of the kinetics on the oxygen concentration (pressure) three experiments (Figures 6 and 7) were run at 25°C in which the rate of reaction of oxygen was followed over a period of 2000 minutes (33 hours). The concentration of $(C_5H_5)_2Co$ was held relatively constant 0.0454-0.0461 molal and the oxygen pressure varied between 369-663 mm Hg. The curves are complex; however, over the

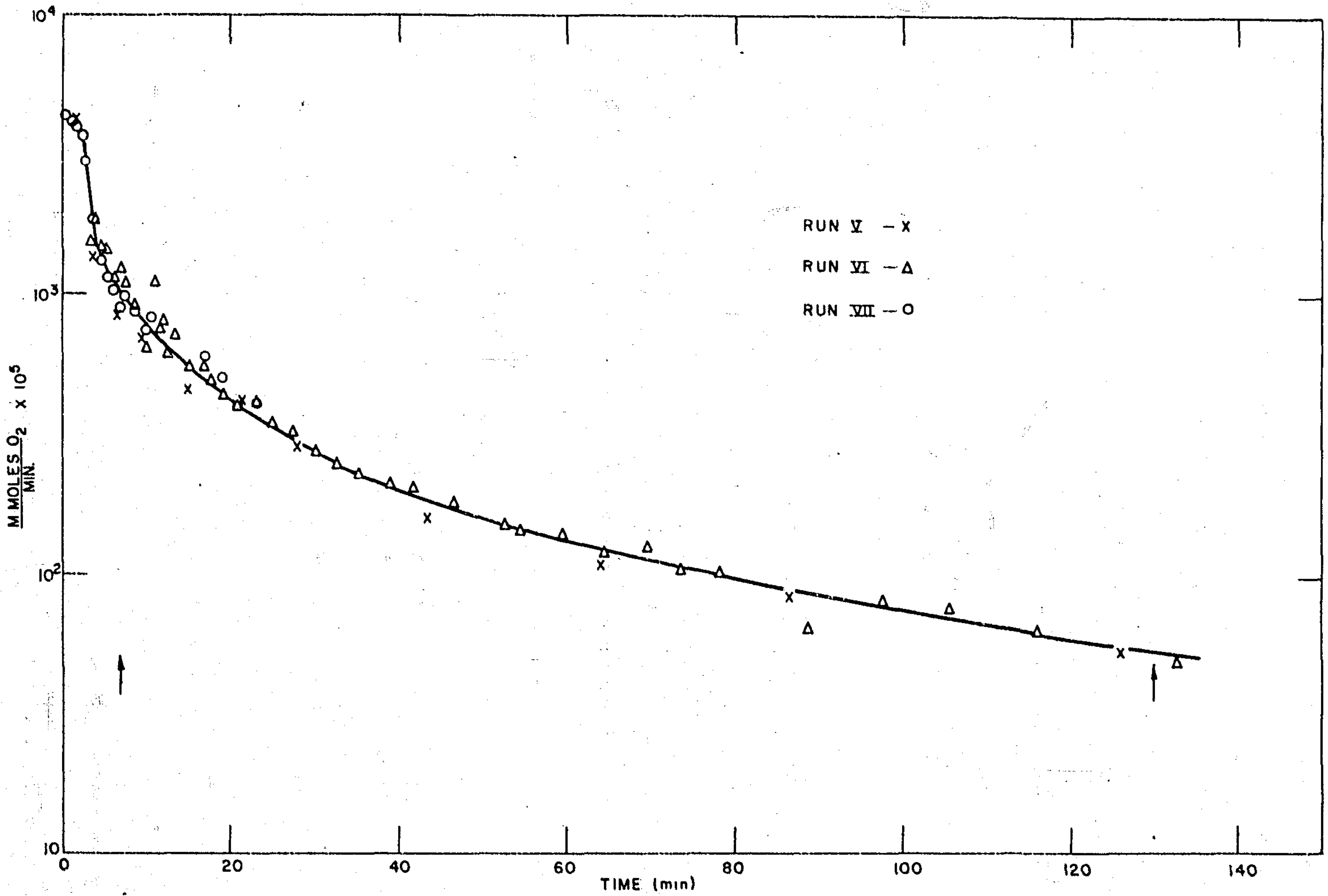

Figure 6. The rate of uptake of oxygen as a function of time for the reaction of $(C_5H_5)_2Co$ with oxygen

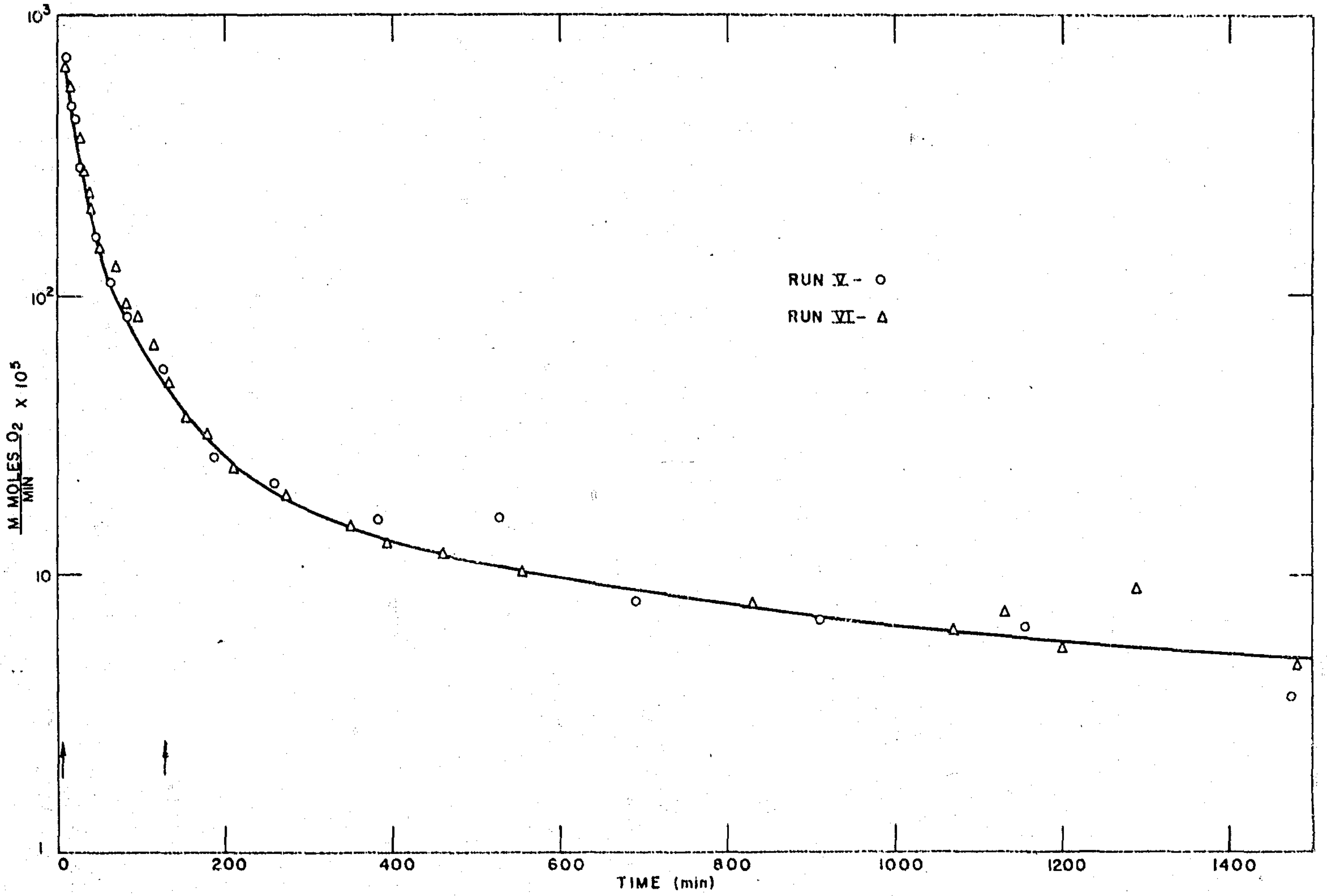

Figure 7. The rate of uptake of oxygen as a function of time for the reaction of $(C_5H_5)_2Co$ with oxygen

period and concentrations measured, the rate of reaction is not a function of the oxygen concentration (zero order in oxygen). The arrows marked on the figures indicate the times when 0.5 and 1.0 moles of oxygen had reacted per mole of $(C_5H_5)_2Co$. After 1700 minutes 1.5 moles of oxygen were picked up. One reaction was followed for 4745 minutes at which time it had consumed 1.6 moles of oxygen per mole of $(C_5H_5)_2Co$.

To determine the $(C_5H_5)_2Co$ dependence of the kinetics, the data from the preceding runs were compared with a run at 25°C in which the concentration of the $(C_5H_5)_2Co$ was 0.1097 molal and the oxygen pressure was 732 mm Hg. Because of the zero order dependence of oxygen, the pressure differences between the experiments is of no consequence. The solid line in Figures 8 and 9 represents the data of Figures 6 and 7. The concentration of $(C_5H_5)_2Co$ in runs V-VII is 0.42 times the concentration in run II. If the kinetic order for $(C_5H_5)_2Co$ is unity,

$$R = k\left[(C_5H_5)_2Co\right],$$

in which R is the rate of uptake of oxygen and k a constant. At any time the rate of oxygen uptake in runs V-VII should be 0.42 times the value for run II. Thus in plotting the data in Figures 8 and 9, the values for run II were multiplied by 0.42. If a first order relationship exists, the two sets of data will superimpose. Except for the region 70-200 minutes the two curves fulfill the condition for a

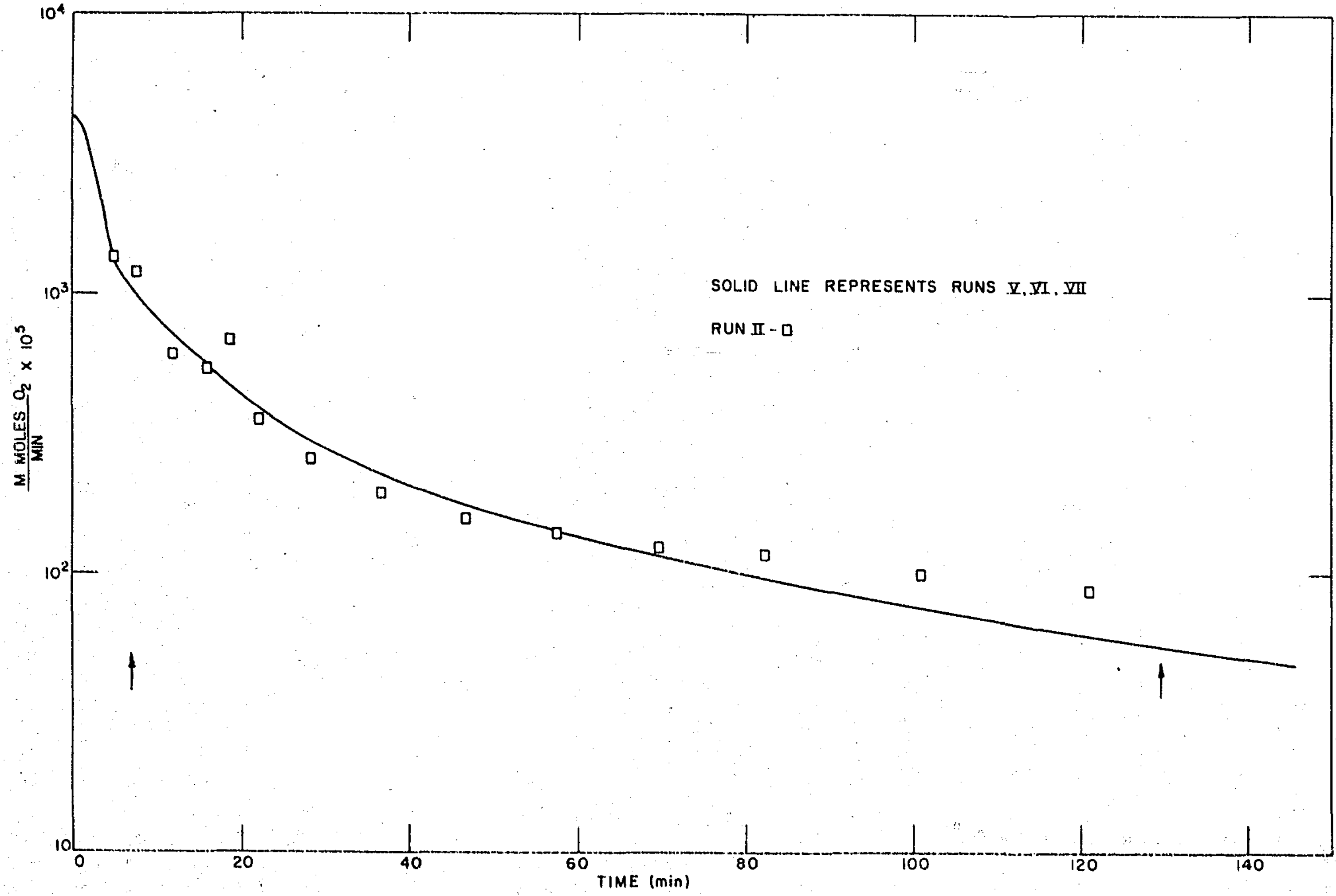

Figure 8. The rate of uptake of oxygen as a function of time for the reaction of $(C_5H_5)_2Co$ with oxygen

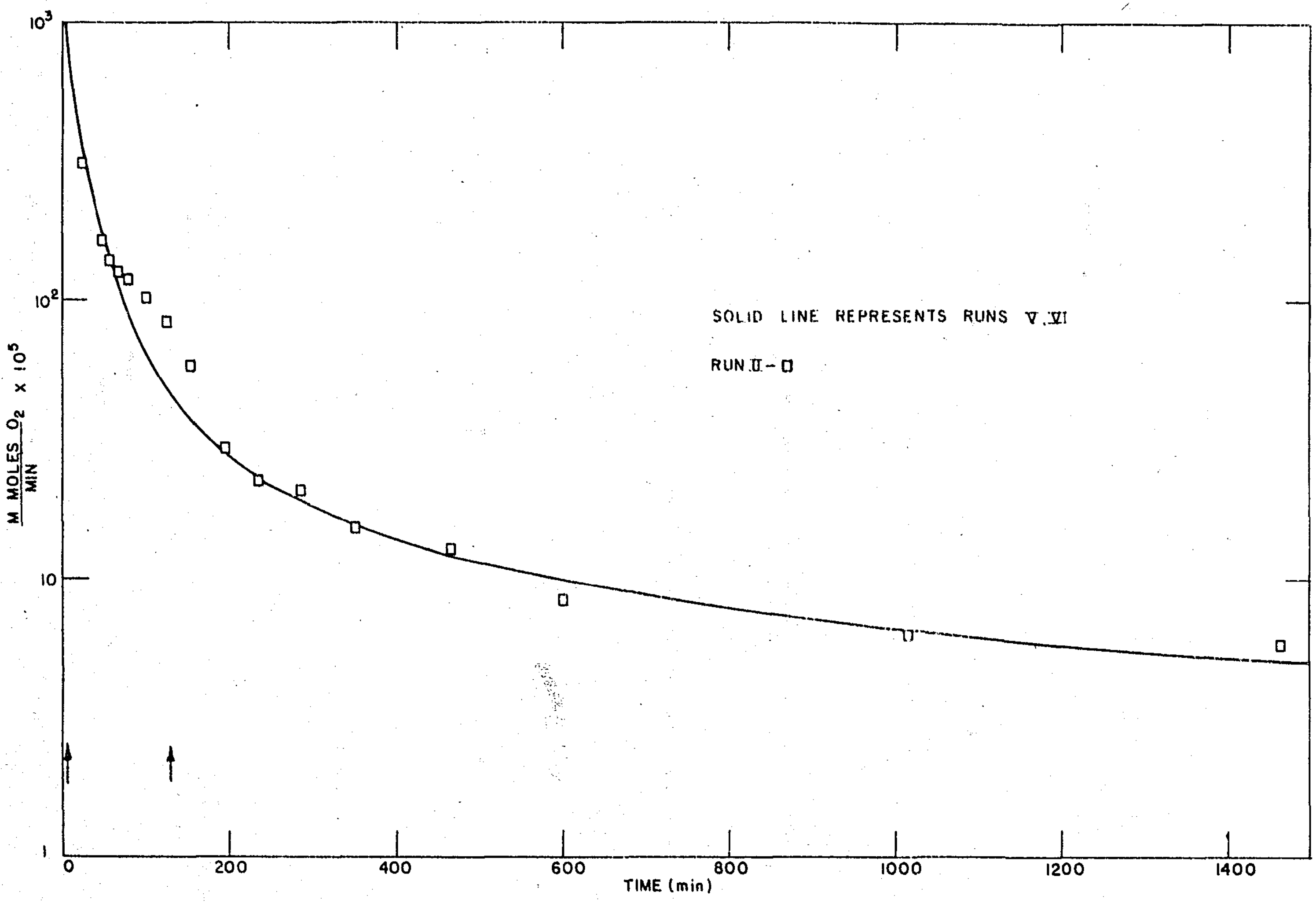

Figure 9. The rate of uptake of oxygen as a function of time for the reaction of $(C_5H_5)_2Co$ with oxygen

first order dependence.

The rapid drop of the rate during the first ten minutes of reaction (Figures 6 and 8) suggested that this might represent the initial reaction between $(C_5H_5)_2Co$ and oxygen. To better distinguish the rates in this region, the reaction was studied at temperatures between -22.6 and 4°C. Temperatures of 0°C, 1-4°C and -22.6°C were obtained from an ice bath, circulating cold water and a carbon tetrachloride slush bath respectively. A total of seven runs was performed in the 0-4°C range, the results are similar and therefore only one set is shown. Several features of the reactions (Figure 10) are that the rates between 0-4 minutes were dependent on the stirring rate; the volume of oxygen consumed in this interval corresponded to 0.43-0.46 moles of oxygen per mole of $(C_5H_5)_2Co$; the volume of oxygen removed between 4-10 minutes was equivalent to the solubility of oxygen in the solvent; and there was an induction period (see dotted lines in Figure 10) between the first and second reaction.

To obtain a better value for the moles of oxygen consumed per mole of $(C_5H_5)_2Co$ three titration experiments were performed at 0-2°C, using the reaction vessel shown in Figure 3b. The results of these experiments are shown in Table 6, and Figure 11.

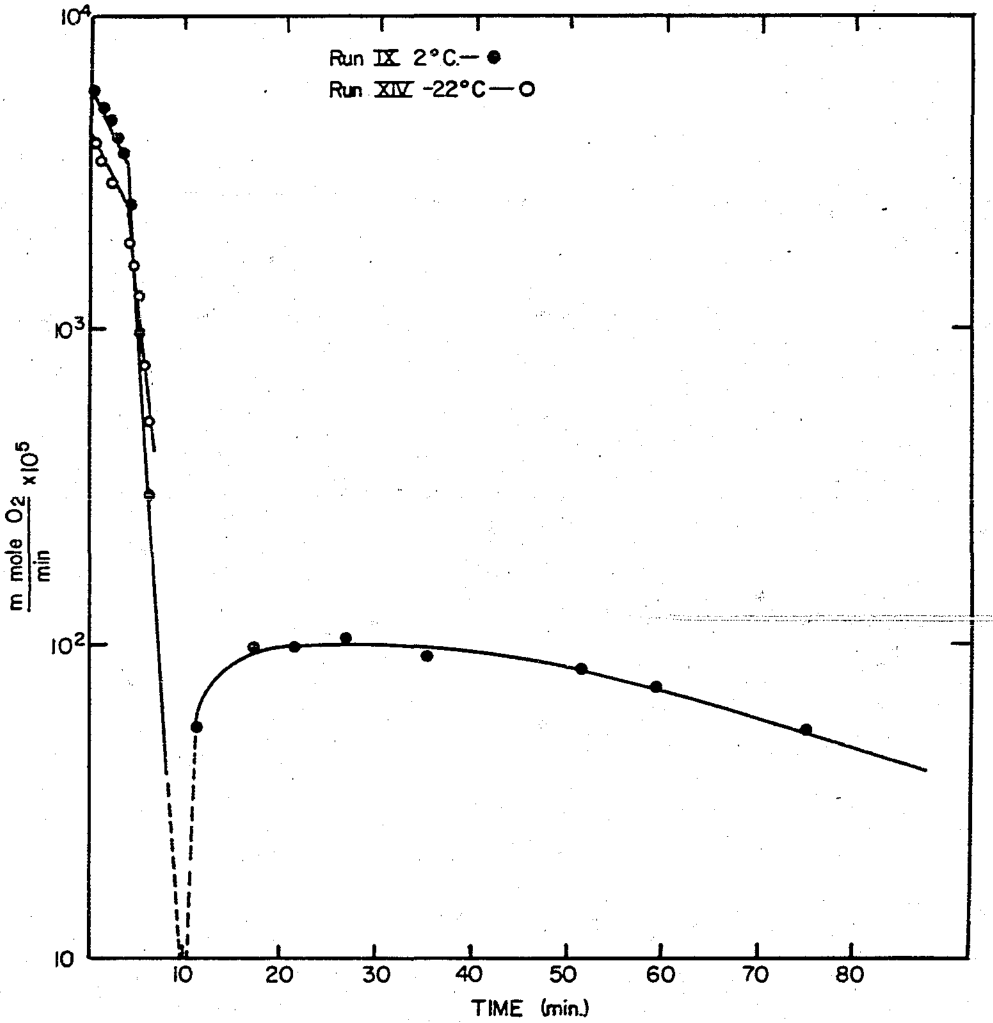

Figure 10. The rate of uptake of oxygen as a function of time for the reaction of $(C_5H_5)_2Co$ with oxygen

Table 6. Uptake of oxygen by $(C_5H_5)_2Co$ in mesitylene solutions

Run	Conc $(C_5H_5)_2Co$ (m moles)	O_2 pickup (m moles)	$\frac{\text{m moles } (C_5H_5)_2Co}{\text{m moles } O_2}$
1-T	15.26	7.20	0.472
2-T	18.10	8.27	0.480
3-T	12.78	6.07	0.476
		expected value	0.500

The initial rise in the curve (Figure 11) represents the dissolution of the sample; the discontinuity in the curve was taken as the end point. Extraction of the titrated solutions with water resulted in a basic (pH∼ 9) aqueous phase from which $[(C_5H_5)_2Co][(C_6H_5)_4\bar{B}]$ was precipitated. The identification of this compound was made by infra-red analysis. The aqueous solutions gave a negative test for the cobaltous ion <u>i.e.</u>, after the addition of sodium thiocyanate, ether and <u>n</u>-amyl alcohol to the aqueous phase from the extraction no blue color $(Na_2Co(SCN)_4)$ was observed in the organic layer.

It was suspected that the first product of the $(C_5H_5)_2Co$-oxygen reaction was bis(π-cyclopentadienyl)cobalt(III) peroxide. However, aqueous extracts of these solutions did not liberate iodine on the addition of acidic solutions of potassium iodide and ammonium molybdate and would not react with hydrogen using palladium-charcoal as a catalyst. In the

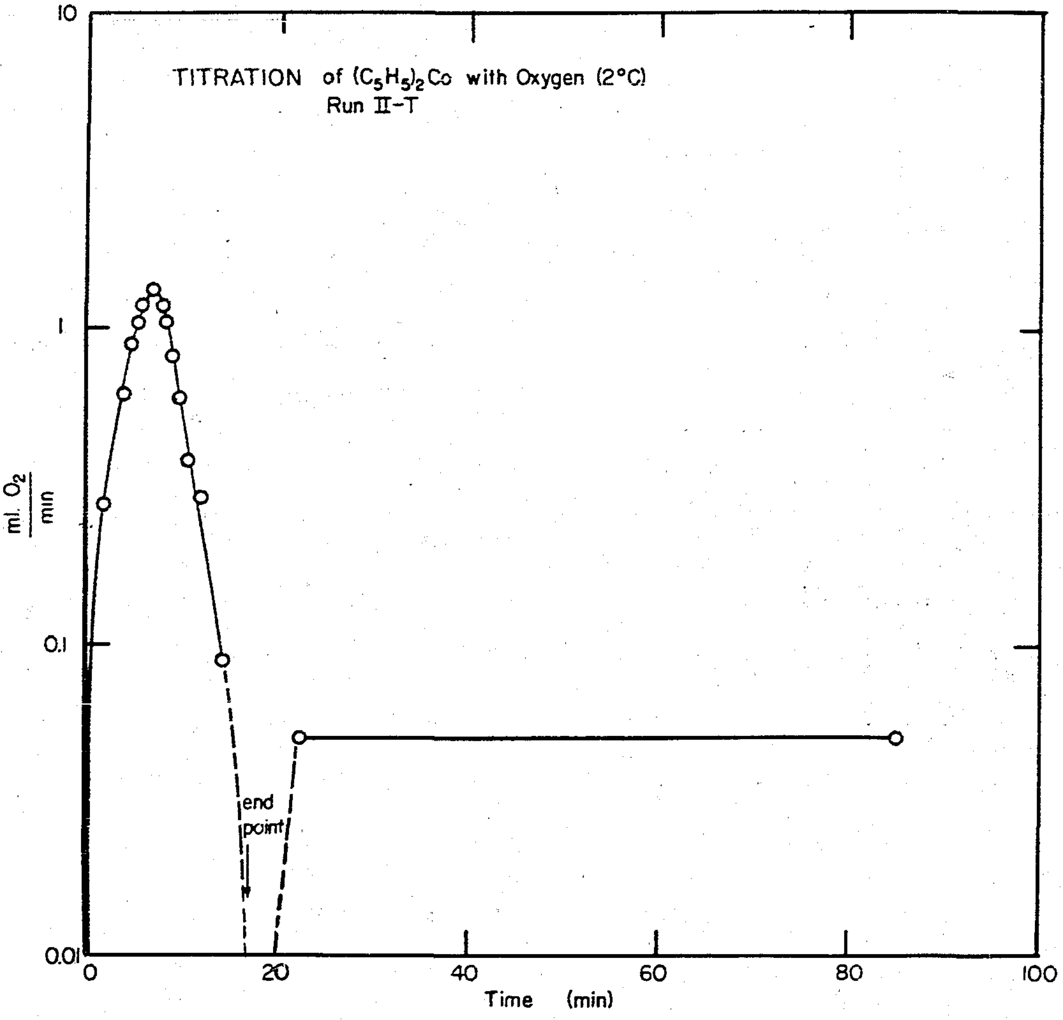

Figure 11. The rate of uptake of oxygen as a function of time for the titration of $(C_5H_5)_2Co$ with oxygen

three attempts that were made to liberate iodine from the aqueous phase, the $[(C_5H_5)_2Co]^+$ was first removed as the tetraphenylborate so as to prevent the formation of the insoluble bis(π-cyclopentadienyl)cobalt(III) triiodide which would obscure the iodine color. Three hydrogenation experiments were performed on the products obtained after the titrations. To accomplish this, the entire system was pumped out to remove all the oxygen and palladium-charcoal catalyst was added as a suspension using syringe techniques. The system was filled with hydrogen to one atmosphere pressure, the stopcock S_3 in Figure 2 was closed and the solution was stirred; no hydrogen reacted.

A compilation of the kinetic and chemical data obtained for the reaction of $(C_5H_5)_2Co$ with oxygen is given below.

1. The initial reaction between $(C_5H_5)_2Co$ and oxygen is very rapid and under the conditions measured was diffusion controlled.

2. A yellow precipitate was observed at $0^\circ C$ during the first reaction. It was stable in the dark for 1 hour but started to decompose immediately on warming to room temperature (*in vacuo*).

3. The molar ratio oxygen uptake to $(C_5H_5)_2Co$ is 0.5.

4. Analysis of these solutions indicates the presence of $[(C_5H_5)_2Co]^+$ and no cobaltous ions.

5. Extraction of these solutions with water yields basic solutions (pH$\sim$9).

6. The compound does not cause the liberation of iodine from potassium iodide and cannot be hydrogenated with the usual catalysts.

7. At 0°C an induction period occurs between the first and second reactions.

8. The reaction at 25°C is first order with respect to $(C_5H_5)_2Co$ and zero order with respect to oxygen from 10-1500 minutes (from 0.5-1.5 moles oxygen/mole $(C_5H_5)_2Co$).

9. A red-brown precipitate begins to appear in the solutions (at 25°C) after the first reaction is completed.

10. Analysis of the mixture after the uptake of 1 mole of oxygen/mole $(C_5H_5)_2Co$ indicates only trace amounts of $[(C_5H_5)_2Co]^+$, large amounts of the cobaltous ion and a red-brown insoluble compound that does not contain cobalt.

11. The red-brown precipitate is soluble in hot nitric acid giving yellow solutions from which no precipitate is obtained on the addition of sodium tetraphenylborate. The precipitate is insoluble in water, cold acids, benzene and acetone but is soluble in N, N dimethylformamide. Infra-red analysis shows general absorption over the entire spectrum with a large broad band at 6.2μ. The material must be polymeric in nature.

D. Reactions between Bis(π-Cyclopentadienyl)Cobalt(II) and Halogenated Hydrocarbons

Wilkinson et al. (11) has reported that bis(π-cyclopentadienyl)cobalt(II) reacts with ethyl bromide to form bis(π-cyclopentadienyl)cobalt(III) bromide. It has been found here that with carbon tetrachloride a new covalent cyclopentadienyl cobalt compound is formed as well as the bis(π-cyclopentadienyl)cobalt(III) chloride. A study of the structure, bonding and the mechanism of formation of this compound will be presented here.

On the addition of $(C_5H_5)_2Co$ to carbon tetrachloride in an inert atmosphere, with or without the presence of light, $[(C_5H_5)_2Co]Cl$ precipitates and a cyclopentadienyl cobalt compound remains in solution. Removal of the solvent by vacuum distillation leaves a residue which after sublimation and reprecipitation from hexane has the composition $(C_5H_5)_2(CCl_3)Co$ (Table 7). The compound is red, melts between 79.5-80.5°C, is very soluble in the common organic solvents and appears stable below 40°C. In concentrated solutions at room temperature some decomposition occurs after a few hours.

The molecular weight of $(C_5H_5)_2(CCl_3)Co$ was determined to be 315 (theoretical 307.5) by the freezing point lowering method (Beckmann method). A good description of the apparatus and method of procedure is given in reference (93). A theoretical discussion of freezing point depression is given in reference (94). Cyclohexane (Phillip's 66, research grade) was used as the solvent and a Beckmann thermometer which could be read to ± 0.001°C was used to measure temperatures. The freezing point of the pure solvent was determined five times, the values obtained agreeing to 0.004°C. Four determinations of the freezing point depression agreed to 0.4%.

Table 7. Analysis of $(C_5H_5)_2(CCl)_3Co$[1]

Element	Theoretical (%)	Found (%)
C	42.96	42.94
H	3.28	3.46
Co	19.17	19.34
Cl	34.59	33.04
Total	100.00	98.78

---

[1] The carbon and hydrogen analyses were performed by the Midwest Microlab Inc., Indianapolis, Indiana. The cobalt and chlorine analyses were performed by M. Togami of this laboratory, Ames, Iowa.

To determine the number of unpaired electrons in $(C_5H_5)_2(CCl_3)Co$, the magnetic susceptibility was measured. To 0.26505 g of $(C_5H_5)_2(CCl_3)Co$ was added 15 ml of cyclohexane (Phillip's 66 research grade). The densities of the pure solvent and the solution was determined with a pycnometer. The solvent and solution were given to J. P. LaPlate who determined the magnetic susceptibility using a Gouy balance.

The compound was found to be diamagnetic, χ^{298}_{mole} = -20×10^{-6} cgsu. Substracting the diamagnetism due to the rings and the CCl_3 group ($\chi^{298}_{\text{mole}} = -147 \times 10^{-6}$ cgsu) (95) the susceptibility of the cobalt was found to be χ^{298}_{mole} = $+127 \times 10^{-6}$ cgsu which is equivalent to 0.551 Bohr magnetons (magnetic dipole moment) or 0.14 free electrons. The value is so small that for practical purposes the cobalt can be considered diamagnetic. The paramagnetism may be due to the decomposition of the sample; if cobaltous ions were produced, decomposition on the order of 5% would account for the value. This seems quite probable since, as noted before, $(C_5H_5)_2(CCl_3)$-Co decomposes slowly in organic solvents. A complete description of the theory and calculations involved in magnetic susceptibility measurements can be found in reference 95.

Infra-red spectra of $(C_5H_5)_2(CCl_3)$Co in various media (carbon tetrachloride, chloroform and "Nujol"), using 0.5 mm cells, are shown in Figures 12 and 13. The background due to the imbalance of the cells is shown as a heavy line above each spectrum in Figure 12. In Figure 13, the bands at 3.35, 6.80 and 7.24 μ are "Nujol" absorptions.

The ultra-violet spectra of 3.32×10^{-5}, 6.65×10^{-5} and 3.32×10^{-4}M solutions in cyclohexane were measured in the region 2250-4000Å using a Cary recording spectrophotometer. Peaks at 2725Å and 3300Å obey Beer's Law over the concentration

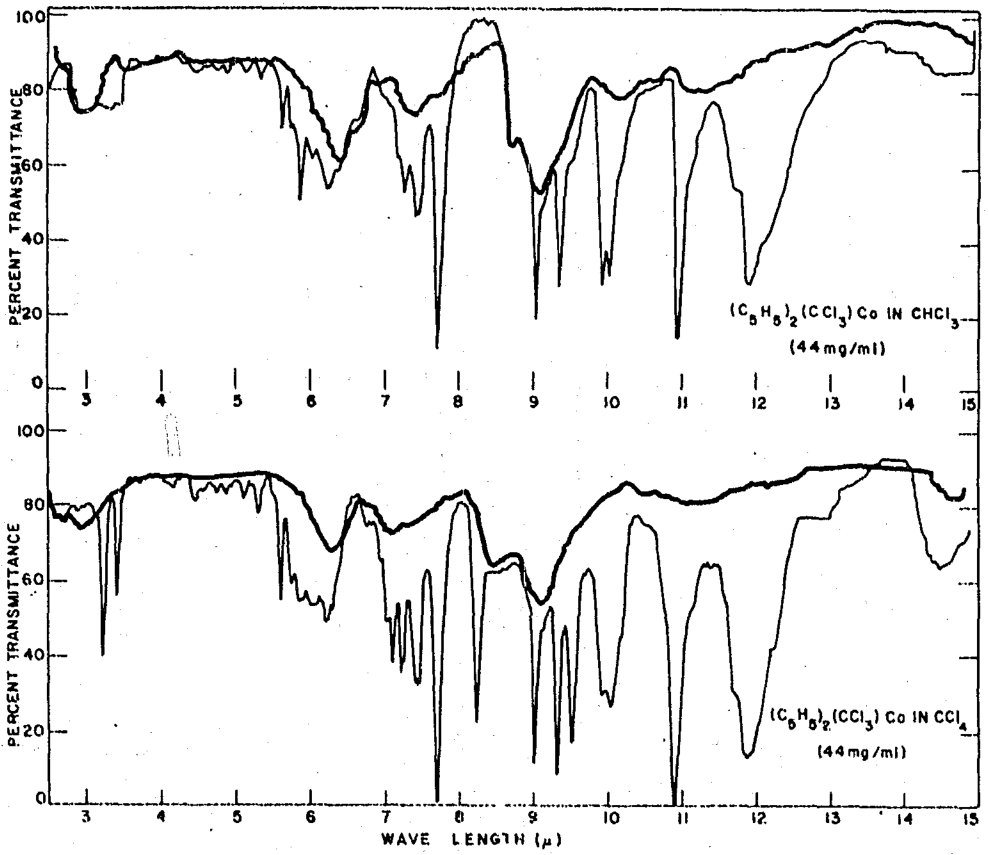

Figure 12. Infra-red spectra of $(C_5H_5)_2(CCl_3)Co$ in chloroform and carbon tetrachloride solutions

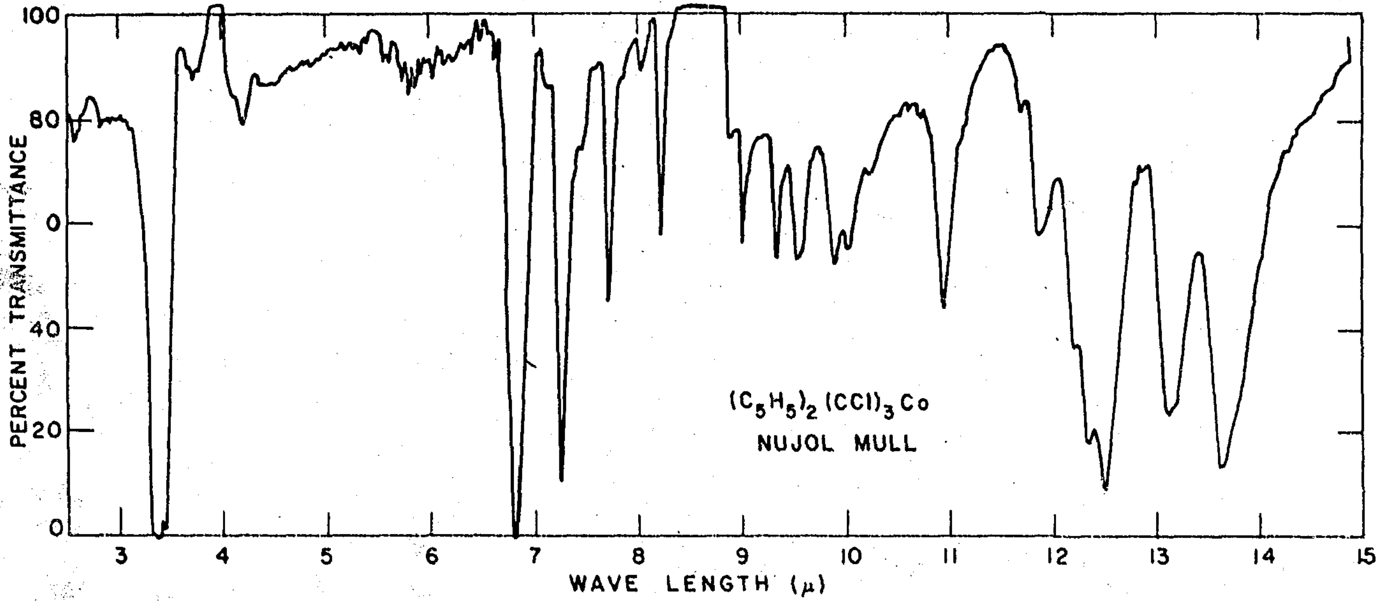

Figure 13. Infra-red spectrum of $(C_5H_5)_2(CCl_3)Co$ in "Nujol"

measured. The solid line in Figure 14 represents the molar extinction coefficient of $(C_5H_5)_2(CCl_3)Co$ as a function of wave length; the dotted line is the ultra-violet spectrum of $[(C_5H_5)_2Co]ClO_4$ in water as measured by Wilkinson (83).

To determine if a simple stochiometric relationship exists for the reaction, two weighed samples of $(C_5H_5)_2Co$ were added to carbon tetrachloride and the products were analyzed for chloride and $[(C_5H_5)_2Co]^+$. The amount of $(C_5H_5)_2(CCl_3)Co$ formed was determined by vacuum distilling the solvent (after removal of the $[(C_5H_5)_2Co]^+$ and chloride by water extractions) and weighing the residue. All three products were found to be present in equimolar amounts (Table 8), which indicates the reaction proceeds in the following manner:

$$2(C_5H_5)_2Co + CCl_4 \longrightarrow [(C_5H_5)_2Co]^+Cl^- + (C_5H_5)_2(CCl_3)Co \, .$$

Based on this equation the yields of $(C_5H_5)_2(CCl_3)Co$ were about 90%.

Table 8. Molar ratios of the products of $(C_5H_5)_2Co$-CCl_4 reaction

Sample	Wt$(C_5H_5)_2Co$ (grams)	$(C_5H_5)_2Co^+/Cl^-$	$\frac{(C_5H_5)_2Co\,Cl}{(C_5H_5)_2(CCl_3)Co}$
1	2.003	1.05	1.2
2	4.70	0.90	1.0

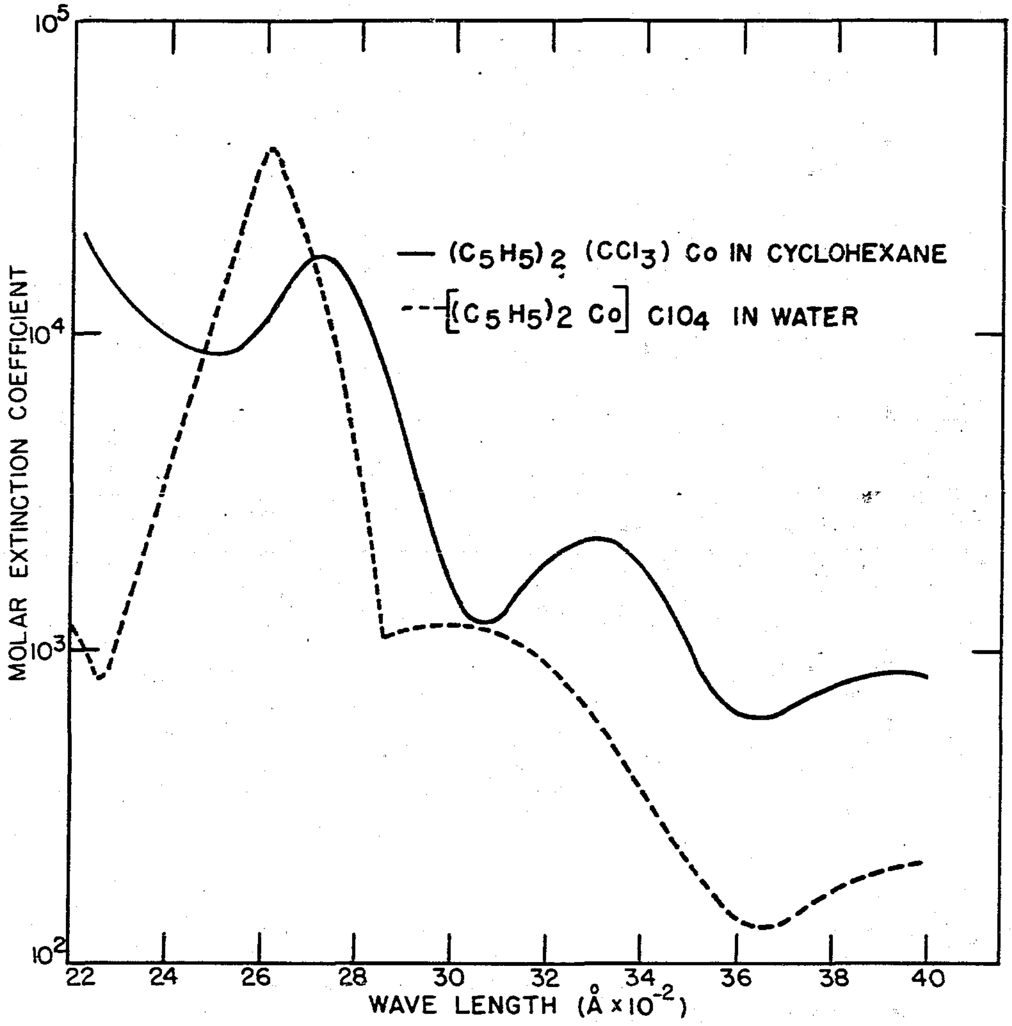

Figure 14. Ultra-violet spectra of $(C_5H_5)_2(CCl_3)Co$ and $(C_5H_5)_2Co\ ClO_4$

Several reactions were performed to determine the stability of $(C_5H_5)_2(CCl_3)Co$ towards various chemical agents. Twenty milligrams of the dry compound were placed in the reaction vessel shown in Figure 3a. A "teflon" covered magnetic stirring bar continuously pulverized the sample and the oxygen pickup was followed for 36 hours. The experiment was repeated with the sample dissolved in 10 ml of di-n-butyl phthalate. In both experiments no oxygen was consumed.

The compound is quite active toward other agents. It is decomposed by glacial acetic acid, concentrated mineral acids and by bases. The compound also decomposes rapidly when sodium thiocyanate or silver nitrate is added to its ethanolic solutions, forming $Na_2Co(SCN)_4$ and silver chloride respectively. A blue precipitate which gives a positive test for cobalt forms immediately on bubbling chlorine through an n-hexane solution of $(C_5H_5)_2(CCl_3)Co$. The addition of maleic anhydride to warm benzene solutions of the compound results in the rapid formation of a black tar.

The addition of an active form of ferrous chloride (11) in tetrahydrofuran to $(C_5H_5)_2(CCl_3)Co$ caused immediate decomposition. After adding water and Skelly B to the sample and evaporating the organic phase, a small amount of a yellow compound was found. A blue color developed when 6N nitric acid was added, this being a qualitative test for bis(π-cyclopentadienyl)iron(II) (6). The aqueous phase contained a small amount of $[(C_5H_5)_2Co]^+$ ($\sim$10% based on the original amount of $(C_5H_5)_2(CCl_3)Co)$. It was interesting to note that a high conversion ($\sim$65%) of $(C_5H_5)_2(CCl_3)Co$ to $[(C_5H_5)_2Co]^+$ was obtained when a sample was refluxed in 95% ethanol for one hour. The analyses indicated that $[(C_5H_5)_2Co]^+$ and chloride were present in equimolar amounts.

In an effort to learn more about the bonding and structure of the compound two tracer experiments were performed, the exchange of $[(C_5H_5)_2Co]^+$ between $[(C_5H_5)_2Co]ClO_4$ and $(C_5H_5)_2(CCl_3)Co$ and the chlorine exchange between LiCl and the new compound.

The exchange of $[(C_5H_5)_2Co]^+$ between $[(C_5H_5)_2Co]ClO_4$ and $(C_5H_5)_2(CCl_3)Co$ was measured in an acetone solution at 0°C. The apparatus shown in Figure 1 was used; light and air were not excluded. The concentrations of $(C_5H_5)_2(CCl_3)Co$ and labeled $[(C_5H_5)_2Co]ClO_4$ were 2.10×10^{-3} and 2.01×10^{-3} molal respectively. Six samples were removed over a period of 24 hours. Longer times were not run because $(C_5H_5)_2(CCl_3)$-Co begins to decompose under these conditions after 24 hours.

To separate the reactants, a 10 ml aliquot of the reacting solution was introduced to a flask containing 10 ml each of water and Skelly B at 0°C, the $[(C_5H_5)_2Co]ClO_4$ was extracted into the aqueous phase while the $(C_5H_5)_2(CCl_3)Co$ remained in the Skelly B phase. The organic phase was washed with water and 10 ml each of water and acetone were added. The organic solvents were removed by evaporation, leaving an aqueous solution of $[(C_5H_5)_2Co]Cl$ which was analyzed. Because very little exchange took place, only the $(C_5H_5)_2(CCl_3)Co$ fraction was analyzed (see page 43). The initial $[(C_5H_5)_2Co]ClO_4$ specific activity was 376 cts/min mg $[(C_5H_5)_2Co][(C_6H_5)_4B]$. The results are shown in Table 9.

Table 9. $[(C_5H_5)_2Co]^+$ exchange between $[(C_5H_5)_2Co]ClO_4$ and $(C_5H_5)_2(CCl_3)Co$

Sample	Time (min)	$(C_5H_5)_2(CCl_3)Co$ fraction	
		Specific activity (cts/min mg)	Fract. ex. x10^2
1	2.5	0.89	0.40
2	13.5	0.57	0.25
3	71.6	0.99	0.44
4	184.7	0.42	0.19
5	626.1	0	0.00
6	1422.2	0	0.00

The chlorine exchange between $(C_5H_5)_2(CCl_3)Co$ and labeled lithium chloride was carried out in an acetone solution at 0°C. The apparatus shown in Figure 2 was used without the exclusion of light and air. The concentrations of $(C_5H_5)_2(CCl_3)Co$ and lithium chloride were 6.50×10^{-3} and 3.13×10^{-2} molal respectively. Six 10 ml aliquots were removed over a period of 24 hours and the reactants were separated by the same method discussed above. The lithium chloride extracted into the aqueous phase. The $(C_5H_5)_2(CCl_3)$-Co was not analyzed because a good analytical method could not be found. The specific activity of three samples of the initial lithium chloride was measured. The values obtained were 64.8, 67.4 and 66.5 cts/min mg, the average value 66.2 was used in the calculations. The data indicate (Table 10) that, within the experimental error of 1-2%, no chlorine exchange took place between the species over a period of 24 hours.

Table 10. Chlorine exchange between LiCl and $(C_5H_5)_2(CCl_3)Co$

Sample	Time (min)	Specific activity (cts/min mg)	Fract. ex. x10^2
1	1.9	65.3	2.2
2	12.0	65.6	1.5
3	42.0	66.1	0.24
4	134.4	66.1	0.24
5	372.9	67.3	0.00
6	1180.3	66.2	0.00

Bis(-cyclopentadienyl)cobalt(II) was found to react with several halogenated hydrocarbons, chloroform, bromoform, ethylene dibromide and triphenylmethyl chloride. A study of the $(C_5H_5)_2Co-CHCl_3$ reaction indicated that two products are formed, $(C_5H_5)_2(CCl_3)Co$ (identified by its melting point and infra-red spectrum) and a small amount of $[(C_5H_5)_2Co]Cl$. No gas evolution was ever observed during the reaction. In one run the $CHCl_3$ solution was extracted with water and the solution was analyzed for $[(C_5H_5)_2Co]^+$ and chloride. The $[(C_5H_5)_2Co]^+$ found represented a conversion of 10% of the initial $(C_5H_5)_2Co$, the $[(C_5H_5)_2Co]^+:Cl^-$ ratio was 1:3.

V. DISCUSSION

A. Cobalt Exchange

The lack of exchange of cobalt between cobaltous perchlorate and bis(π-cyclopentadienyl)cobalt(III) perchlorate over a period of 30 days reflects the stability and covalent nature of the cobalt-ring bonding. Likely paths leading to cobalt exchange are represented by the following equilibria:

$$[(C_5H_5)_2Co]^{+} \rightleftharpoons [(C_5H_5)Co]^{++} + (C_5H_5)^{-} \qquad (7)$$

$$[(C_5H_5)Co]^{++} + Co^{60++} \rightleftharpoons [(C_5H_5)Co^{60}]^{++} + Co^{++} \qquad (8)$$

$$[(C_5H_5)Co]^{++} \rightleftharpoons Co^{+++} + (C_5H_5)^{-} \qquad (9)$$

$$Co^{+++} + Co^{60++} \rightleftharpoons Co^{++} + Co^{60+++} \qquad (10)$$

The electron exchange in equation 10 has been reported (96) to be very fast, so that the lack of exchange must be ascribed to strong covalent bonding between the metal and rings. A similar conclusion was drawn for the isoelectronic bis(π-cyclopentadienyl)iron(II) system (11) when no exchange was observed between ferrous chloride and $(C_5H_5)_2Fe$ over a period of one year.

Since most of the π-bonded "sandwich compounds" have comparable metal-ring stability, little exchange would be expected to take place between these metals and their cyclopentadienyl derivatives. It would be interesting however, to study the $(C_5H_5)_2Cr$-chromium exchange, for although the magnetic susceptibility indicates that $(C_5H_5)Cr$ (31) is a π-bonded system, its conductivity in liquid ammonia (a saturated solution at -33°C has a specific conductivity of 4.0×15^4 ohm^{-1})(11) and the rapid reaction with ferrous chloride to form bis(π-cyclopentadienyl)iron(II) indicate that the metal ring bonding may have considerable ionic character.

B. Electron Exchange

The slow exchange of $[(C_5H_5)_2Co]^+$ observed between $[(C_5H_5)_2Co]ClO_4$ and $[(C_5H_5)_2Co]_2O$ (Table 4) indicated that the oxide might account for the anomalous nature of the zero time exchange (Table 2) in the electron exchange experiments. If trace amounts of oxygen were picked up in the dry box or from incompletely deoxygenated acetone a portion of the $(C_5H_5)_2Co$ would be oxidized forming a third exchanging species. If the following reactions are assumed,

$$2(C_5H_5)_2Co + \tfrac{1}{2}O_2 \longrightarrow [(C_5H_5)_2Co]_2O \qquad (11)$$

$$(C_5H_5)_2Co + [(C_5H_5)_2Co^*]^+ \rightleftharpoons [(C_5H_5)_2Co]^+ + (C_5H_5)_2Co^* \quad \text{(very fast)} \qquad (12)$$

$$[(C_5H_5)_2Co^*]^+ + [(C_5H_5)_2Co]_2O \overset{k_1}{\rightleftharpoons} [(C_5H_5)_2Co]^+ + [(C_5H_5)_2Co^*][(C_5H_5)_2Co]O \quad \text{(slow)} \qquad (13)$$

$$(C_5H_5)_2Co^* + [(C_5H_5)_2Co]_2O \overset{k_2}{\rightleftharpoons} (C_5H_5)_2Co + [(C_5H_5)_2Co^*][(C_5H_5)_2Co]O \quad \text{(slow)} \qquad (14)$$

the electron exchange results can be qualitatively explained. Small amounts of oxygen react with the $(C_5H_5)_2Co$ to form $[(C_5H_5)_2Co]_2O$ (equation 11) before the reactants are mixed. If the electron exchange represented by equation 12 is very fast and the last two reactions are comparatively slow then, upon mixing the reactants a zero time exchange would be observed, corresponding to the amount of $(C_5H_5)_2Co$ that remains unoxidized. Equations 13 and 14 would be responsible for the measured half times. When two nonequivalent species exchange with a third, one expects the plot of ln(1-F) vs. time to be a curve which is the sum of two straight lines, each representing the exchange of one of the former species with the third. This would be the case for equation 13 and 14. However, the added condition that the first two species exchange very rapidly (equation 12) reduces the complex curve to a straight line in which the rate of exchange (in this case the rate of exchange of $[(C_5H_5)_2Co]^+$) is the sum of the two individual exchange rates.

It was of interest to determine the amount of $(C_5H_5)_2Co$ that must be assumed to be oxidized in each of the electron exchange experiments to account for the data. Assuming that the above mechanism is correct, an expression can be derived from which one can calculate the amount of $(C_5H_5)_2Co$ oxidized. The derivation is based on equations 1-6.

Let X = m moles of $(C_5H_5)_2Co$ initially added to the reaction vessel.

x = m moles of $(C_5H_5)_2Co$ that are oxidized to the oxide.

Y = m moles of $[(C_5H_5)_2Co]ClO_4$ involved in the exchange.

S_{B_o} = specific activity of the cobalt in unreacted $[(C_5H_5)_2Co]ClO_4$.

S_∞ = the specific activity of cobalt in all three reactants after they have exchanged for an infinite amount of time.

If we assume that the electron exchange between $(C_5H_5)_2Co$ and and $[(C_5H_5)_2Co]ClO_4$ is infinitely fast, then at $t = 0$ the initial specific activity of $[(C_5H_5)_2Co]^+$, (S_{B_o}), is reduced to S_{B_t}. S_{B_t} is the infinite time specific activity for the electron exchange between Y m moles of $[(C_5H_5)_2Co]^+$ and $(X-x)$ m moles of $(C_5H_5)_2Co$. Using equation 6 the concentration ratio of the reactants can be expressed as

$$\frac{S_{B_o}}{S_{B_t}} = \frac{X - x}{Y} + 1, \tag{15}$$

similarly,

$$\frac{S_{B_o}}{S_\infty} = \frac{X}{Y} + 1. \qquad (16)$$

Eliminating X and solving for x

$$x = YS_{B_o} \left(\frac{1}{S_\infty} - \frac{1}{S_{B_t}}\right). \qquad (17)$$

The value of S_{B_t} is not experimentally known but can be deduced from the extrapolated value $(1-F_o)$ where F_o is the zero time exchange, obtained from a semi-logarithmic plot of (1-F) vs. time. Rearranging equation 2 gives

$$(1-F_o) = 1 - \frac{S_{B_t} - S_{B_o}}{S_\infty - S_{B_o}}. \qquad (18)$$

Solving for S_{B_t} and substituting into equation 17 yields

$$x = YS_{B_o} \left(\frac{1}{S_\infty} - \frac{1}{[(1-F_o) - 1][S_{B_o} - S_\infty] + S_{B_o}}\right). \qquad (19)$$

All the values but x are known (see experimental section). The calculated values are shown in Table 11.

Table 11. Amounts of $(C_5H_5)_2Co$ oxidized in electron exchange experiments

Run	m moles$(C_5H_5)_2Co$ oxygenated
12	0.046
13	0.020
3	0.049
4	0.023

Table 11. (Continued)

Run	m moles $(C_5H_5)_2Co$ oxygenated
6	0.056
7	0.060
11	0.053
2	0.064
9	0.053
8	0.050
10	0.055

The relative constancy of the values in column 2 lends support to the proposed reactions, for it is logical to assume that approximately the same amount of oxygen would contaminate each sample since the same dry box and acetone were used for all the experiments.

The relationship between the half times measured in the electron exchange and $[(C_5H_5)_2Co]ClO_4$ vs. $[(C_5H_5)_2Co]_2O$ experiments can be more clearly shown by calculating the rate constants k_1 and k_2 (equations 13 and 14). To accomplish this, it is necessary to derive the homogeneous exchange law which applies to equations 12-14.

Let R_β = rate of exchange of species in equation 13,

R_γ = rate of exchange of species in equation 14,

t = time,

(A), (B), (C) = concentration of cobalt (gram-atoms/liter) in $[(C_5H_5)_2Co]_2O$, $[(C_5H_5)_2Co]ClO_4$ and $(C_5H_5)_2Co$ respectively,

(A'), (B'), (C') = concentration of cobalt-60 (grams-atoms/liter) in $[(C_5H_5)_2Co]_2O$, $[(C_5H_5)_2Co]ClO_4$ and $(C_5H_5)_2Co$ respectively,

F = fraction exchange of $[(C_5H_5)_2Co]_2O$.

Assume that the reaction represented by equation 12 takes place immediately (t=0) so that the activity originally in (B) is now diluted. The values for the concentration of cobalt-60 in (B) and (C) at the start of the reactions represented in equations 13 and 14 are (B_o') and (C_o'). The fraction exchange (F) may be defined as

$$F = \frac{(A')}{(B_o') + (C_o')} \cdot \frac{(A) + (B) + (C)}{(A)} . \qquad (20)$$

The specific activity of the three reactants may be written as

$$S_A = \frac{(A')}{(A)}, \; S_B = \frac{(B')}{(B)}, \; S_C = \frac{(C')}{(C)} . \qquad (21)$$

The rate of increase (d(A')/dt) in the concentration of cobalt-60 in $[(C_5H_5)_2Co]_2O$ is given by

$$\frac{d(A')}{dt} = R_\beta S_B(1-S_A) - R_\beta S_A(1-S_B) + R_\gamma S_C(1-S_A) - R_\gamma S_A (1-S_C). \qquad (22)$$

The rate of appearance of $[(C_5H_5)_2Co^{60}]^+$ in (A) from (B) is

$R_\beta S_B(1-S_A)$ because R_β is the rate of exchange of $[(C_5H_5)_2Co]^+$ between (A) and (B), S_B is the fraction of (B) that is radioactive, and $(1-S_A)$ is the fraction of (A) that is not radioactive. Only collisions resulting in the exchange of a radioactive group for an inactive one lead to a change in (A'). Similar reasoning leads to the conclusion that $R_\beta S_A(1-S_B)$ is the rate of disappearance of $[(C_5H_5)_2Co^{60}]^+$ from (A). The values $R_\gamma S_C(1-S_A)$ and $R_\gamma S_A(1-S_C)$ are analagous to the above terms but apply to equation 14.

Because the electron exchange is so fast

$$S_B = S_C. \tag{23}$$

Substituting this in equation 22 gives

$$\frac{d(A')}{dt} = (R_\beta+R_\gamma)\ (S_B-S_A). \tag{24}$$

Replacing S_B and S_A by equation 21

$$\frac{d(A')}{dt} = (R_\beta+R_\gamma)\ \frac{(A)(B') - (B)(A')}{(A)(B)}\ . \tag{25}$$

A conservation equation can be written

$$(A') + (B') + (C') = (A'_\infty) + (B'_\infty) + (C'_\infty). \tag{26}$$

Also from equation 12 and from the fact that at $t = \infty$ the specific activities of the three reactants are equal the following equations can be written

$$(C') = \frac{(B')(C)}{(B)}$$

$$(B'_\infty) = \frac{(B)(A'_\infty)}{(A)}$$

$$(C'_\infty) = \frac{(C)(A'_\infty)}{(A)}$$

Substituting these values into equation 26

$$(A') + (B') + \frac{(C)}{(B)}(B') = (A'_\infty) + \frac{(B)}{(A)}(A'_\infty) + \frac{(C)}{(A)}(A'_\infty).$$

Rearranging terms and solving for (B') gives

$$(B') = \frac{(B)}{(B) + (C)}\left[\left(1 + \frac{(B)}{(A)} + \frac{(C)}{(A)}\right)(A'_\infty) - (A')\right]$$

Substituting this value into equation 25

$$\frac{d(A')}{dt} = \frac{(R_\beta + R_\gamma)}{(A)(B)}\left[\frac{(B)}{(B) + (C)}\Big[\big((A) + (B) + (C)\big)(A'_\infty) - (A)(A')\Big] - (B)(A')\right]$$

and rearranging terms

$$\frac{d(A')}{dt} = \frac{(R_\beta + R_\gamma)}{(A)(B)}\left[\frac{(B)[(A) + (B) + (C)]}{(B) + (C)}\right]\Big[(A'_\infty) - (A')\Big]. \tag{27}$$

Let f be the coefficient of $[(A'_\infty) - (A')]$. Rearranging equation 27 yields

$$\frac{d(A')}{(A'_\infty) - (A')} = f\,dt.$$

Integrating this

$$-\ln\big[(A'_\infty) - (A')\big] = ft + \text{constant}. \tag{28}$$

The constant of integration may be evaluated at t = 0 when

$(A') = 0$,

constant $= -\ln (A'_\infty)$

Substituting this into equation 28 gives

$$-\ln \left[\frac{(A'_\infty) - (A')}{(A'_\infty)}\right] = ft. \tag{29}$$

The left side of this expression may be written

$$-\ln \left[1 - \frac{(A')}{(A'_\infty)}\right] = -\ln(1-F). \tag{30}$$

Substituting equation 30 into equation 29, expressing f as defined and rearranging terms yields

$$-\frac{(A)[(B) + (C)]}{(A) + (B) + (C)} \ln(1-F) = (R_\beta+R_\gamma)t. \tag{31}$$

It is now apparent that, as in the case of simple homogeneous exchange, a plot of ln(1-F) <u>vs.</u> time will give a straight line. If we substitute 0.5 for F and $t_{\frac{1}{2}}$ for t, equation 31 gives

$$(R_\beta+R_\gamma) = \frac{(A)[(B) + (C)]}{(A) + (B) + (C)} \cdot \frac{0.693}{t_{\frac{1}{2}}} . \tag{32}$$

Let us assume that the reactions shown in equations 13 and 14 proceed by way of a bimolecular mechanism so that R_β and R_γ may be written

$$R_\beta = k_1(A)(B)$$

$$R_\gamma = k_2(A)(C). \tag{33}$$

Adding the two equations and assuming

$$k_1 = k_2, \tag{34}$$

equation 33 gives

$$(R_\beta + R_\gamma) = k_1(A)\left[(B) + (C)\right].$$

Substituting this equation into equation 32, one obtains

$$t_{\frac{1}{2}} = \frac{0.693}{k_1\left[(A) + (B) + (C)\right]}\,. \tag{35}$$

The value for k_1 has the units liter/gram-atom sec, to convert this to more familiar units ($k_1' =$ liter/mole sec) k_1 is multiplied by two. This arises from the fact that oxide has two gram-atoms of $[(C_5H_5)_2Co]^+$ per mole. Using equation 35 and the concentrations calculated for $[(C_5H_5)_2Co]_2O$ and $(C_5H_5)_2Co$, the values for k_1' were calculated (Table 12). With the exception of the value for run 11 the k_1' values for both the electron exchange (runs 1-13) and the $[(C_5H_5)_2Co]_2O$ vs. $[(C_5H_5)_2Co]ClO_4$ exchange (runs 14-16) experiments are in close agreement and indicate that the half times observed in the electron exchange experiments are due to exchange reactions involving $[(C_5H_5)_2Co]_2O$ (equations 13 and 14).

Many rate equations involving half integral and integral orders from 0-4 were also tested in equation 32. Only the rate expressions represented in equation 33 gave a consistent value for the rate constant. This is not surprising, for in the simplest cases of the transfer of ligands one would expect the reaction to proceed via a bimolecular mechanism. A logical explanation for the rate constants k_1 and k_2 being equal is that the electron exchange between $(C_5H_5)_2Co$ and $[(C_5H_5)_2Co]_2O$ (equation 14) is very fast and the rate determining step involves the transfer of the groups which should be similar for equations 13 and 14.

Table 12. Rate constants for exchange reactions

Run	Gram-atoms/liter x10^3		$t_{\frac{1}{2}}$ (min)	k_1'
	$(C_5H_5)_2Co$	$[(C_5H_5)_2Co]_2O$		(lit/mole sec)
		Electron exchange experiments		
6	1.48	0.79	185	0.028
7	1.66	0.61	165	0.032
11	1.38	0.61	150	0.038
9	1.18	0.61	190	0.032
8	0.64	0.57	265	0.027
10	0.36	0.73	265	0.028
		$[(C_5H_5)_2Co]ClO_4$ vs. $[(C_5H_5)_2Co]_2O$ experiments		
15		6.90	93	0.028
16		6.90	95	0.027
14		3.78	145	0.028

On theoretical grounds, it seems very likely that the single electron exchange between $(C_5H_5)_2Co$ and $[(C_5H_5)_2Co]^+$

would be rapid. The Franck-Condon principle states that electronic transitions are very rapid compared to the motion of nuclei and the most probable transitions are those that involve the least alteration of atomic structure. The structure and metal-ring bond distances of the two cobalt compounds should be almost identical so that the electron exchange between them should be rapid. Ruch (76) has pointed out that in all the theories on the bonding of the π bonded "sandwich compounds", the lowest energy anti-bonding orbital has its greatest density at the periphery of the molecule. In $(C_5H_5)_2Co$ this orbital is occupied by an unpaired electron, the one which presumably exchanges. The high probability of finding an electron "outside" the molecule should certainly enhance the exchange. Since one of the reactants in uncharged, there should be very little coulombic repulsion to hinder the close approach of the species. Again this would enhance the probability of electron transfer.

Throughout the discussion of the electron exchange experiments it has been assumed that the bis(π-cyclopentadienyl)cobalt-oxygen species was the oxide. This was deduced from two titration experiments (Table 2), but it is felt that this may not be sufficient proof. It would be of interest to determine the species more accurately and also to study the exchange with $[(C_5H_5)_2Co]^+$ and $(C_5H_5)_2Co$ under more carefully controlled conditions. It should be mentioned that the exact nature of the oxidized compound is unimportant to the arguments for fast electron exchange.

C. Bis(π-Cyclopentadienyl)Cobalt(II)-Oxygen Reaction

The reactions between $(C_5H_5)_2Co$ and oxygen in mesitylene can only be qualitatively described. From reactions at 0° and -22.6°C it appears that the first reaction involves one half a mole of oxygen per mole of $(C_5H_5)_2Co$, three reactions may be written which satisfy this condition, when RH

$$2(C_5H_5)_2Co + O_2 \longrightarrow [(C_5H_5)_2Co]_2O_2 \qquad (36)$$

$$2(C_5H_5)_2Co + O_2 + 2RH \longrightarrow 2[(C_5H_5)_2Co]OR + H_2 \qquad (37)$$

$$2(C_5H_5)_2Co + O_2 + 2RH \longrightarrow 2[(C_5H_5)_2Co]OH + RR \qquad (38)$$

represents the solvent. The inability of the compound to liberate iodine with potassium iodide and the failure to react with hydrogen makes the formation of a peroxide (equation 36) seem unlikely. The formation of alcoholates appears equally improbable because with such a reaction (equation 37) there should be no net change in the gaseous volume of the system. The formation of a hydroxide (equation 38) fits the observed data best; the $(C_5H_5)_2Co$-oxygen molar ratio is 0.5, the product would be expected to give basic solutions on extraction into water, and not to react with potassium iodide or with hydrogen as is observed.

On this basis, it seems most likely that the first product of the reaction of $(C_5H_5)_2Co$ and oxygen in mesitylene is bis(π-cyclopentadienyl)cobalt(III)hydroxide.

The reason for the difference in the oxygen uptake for the first reaction in mesitylene and in acetone is not apparent. The presence of water in the acetone might account for the difference through the following reaction:

$$4(C_5H_5)_2Co + O_2 + 2H_2O \longrightarrow 4[(C_5H_5)_2Co]OH.$$

Reactions beyond 0.5 moles of oxygen at $0^\circ C$ and 1.0 moles at $25^\circ C$ are probably heterogeneous, and zero order oxygen kinetics (97) are to be expected since the rate of reaction should be diffusion controlled. If the range of particle sizes remain constant with changes in $(C_5H_5)_2Co$ concentration then the kinetics should also be first order in $(C_5H_5)_2Co$.

The data at $25^\circ C$ indicate that the $[(C_5H_5)_2Co]^+$ ion decomposes in the time interval during which the second $\frac{1}{2}$ mole of oxygen reacts per mole of $(C_5H_5)_2Co$. A strong positive test for $[(C_5H_5)_2Co]^+$ and a negative cobalt test are obtained after 0.5 moles of oxygen have been added, on the other hand a test for cobalt was observed with the virtual disappearance of $[(C_5H_5)_2Co]^+$ after one mole of oxygen has reacted. From visual observations it appears that this reaction is homogeneous at $25^\circ C$. The kinetics may be qualitatively explained by the slow thermal decomposition of $[(C_5H_5)_2Co]OH$

followed by the rapid reaction of oxygen with the decomposition products. The instability of $[(C_5H_5)_2Co]OH$ has been observed here. The compound was prepared by passing a solution of $[(C_5H_5)_2Co]ClO_4$ through Dowex I anion exchange column in the hydroxide form followed by the vacuum distillation of the solvent. A bright yellow solid which closely resembled in appearance the first product, remained which decomposed <u>in vacuo</u> in a few minutes.

D. New Cyclopentadienyl Cobalt Compounds

The discovery that bis(π-cyclopentadienyl)cobalt(II) reacts with carbon tetrachloride to form the compound $(C_5H_5)_2(CCl_3)Co$, raised the interesting question as to how the cyclopentadienyl rings and the trichloromethyl groups are bonded to the central cobalt atom. Chemical and infra-red data as well as steric considerations lead to the suggestion that at least one of the cyclopentadienyl rings and the trichloromethyl group are σ bonded to the metal. The attainment of such a structure involves the rearrangement of stable π bonds to the less stable σ bonds. A similar rearrangement has been proposed by Fischer and Wirtzmuller (98) to account for the magnetic susceptibility of $(C_5H_5)_2Re(CO)_2H$ which was prepared by the reaction of carbon monoxide (250 atm, 90°C) with the π bonded $(C_5H_5)_2ReH$. It is assumed that one of the (C_5H_5) groups in $(C_5H_5)_2Re(CO)_2H$

is bonded to the metal. In an effort to clearly demonstrate the possibility of such rearrangements a detailed study was made on the bis-cyclopentadienyl-trichloromethyl-cobalt(III) compound $[(C_5H_5)_2(CCl_3)Co]$.

As mentioned previously, σ bonded alkyl and aryl derivatives of transition metal cyclopentadienyl-carbonyl and nitrosyl compounds have been prepared. The formation of these compounds has been accomplished either by the direct addition of groups (47) as

$$\pi\text{-}(C_5H_5)Fe(CO)_2Na + C_2H_5I \longrightarrow \pi\text{-}(C_5H_5)Fe(CO)_2C_2H_5 + NaI$$

or by the replacement of halogen or hydrogen (47)

$$\pi\text{-}C_5H_5Cr(NO)_2I + CH_3MgI \longrightarrow \pi\text{-}(C_5H_5)Cr(NO)_2CH_3 + MgI_2$$

$$\pi\text{-}C_5H_5Mo(CO)_3H + CH_2N_2 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3CH_3 + N_2.$$

Wilkinson and co-workers have made a considerable effort to determine the chemical and physical properties of these compounds (47) and have been able to ascribe certain characteristics to the σ-bonded alkyl or aryl group. Particular attention has been paid to the σ bonded cyclopentadienyl group (σ-$(C_5H_5)Si(CH_3)_3$ (13), π-$(C_5H_5)_2$ σ-$(C_5H_5)Mn_2(NO)_3$ (56), σ-$(C_5H_5)CuP(C_2H_5)_3$ (12), σ-$(C_5H_5)_2Hg$ (12), π-(C_5H_5) σ-$(C_5H_5)Cr(NO)_2$ (56), π-(C_5H_5) σ-$(C_5H_5)Fe(CO)_2$ (47)).

The characteristics of the σ-(C_5H_5) group are as follows.

All the compounds react with maleic anhydride although only in the cases of the mercury and silicon compound have the adducts been characterized. The compounds react slowly with ferrous chloride in tetrahydrofuran to form low yields of bis(π-cyclopentadienyl)iron(II).

In contrast to the simple spectra of the π-cyclopentadienyl compounds, the infra-red spectra of the σ-cyclopentadienyl compounds are quite complex. The region characteristic of C-H stretching vibrations contain a band at 3.25 μ of medium intensity and one or two other weaker bands. Cyclopentadiene itself absorbs at 3.25 and 3.40 μ; a π-cyclopentadienyl ring on the other hand has but one band in this region at 3.25 μ (see Figure 4b). In addition, the spectra of the σ-(C_5H_5) compounds have weak absorption bands at 6.10-6.25 μ which may be due to a C = C stretching mode, and at least one very strong band at 13.5-13.90 μ. With the exception of the wave lengths mentioned above the spectra of different σ bonded compounds bear little resemblence to one another.

The ultra-violet absorption spectra of the σ-(C_5H_5) compounds have intense absorption in the region where a diene system might be expected to absorb (ϵ = 10,000 at 2400Å, see Figure 14). However, this is characteristic of all the π-cyclopentadienyl-metal systems which contain σ bonded alkyls and aryls. The nuclear magnetic resonance spectra (47) of the mixed π and σ cyclopentadienyl compounds show two peaks whereas the purely π bonded compounds show only one. The second band in the mixed compound has been attributed to the σ-cyclopentadienyl ring.

In the light of these characteristics the bonding in $(C_5H_5)_2(CCl_3)Co$ can be discussed. The five most conceivable structures for this compound are shown in Figure 15. The π-bonded and σ-bonded rings are drawn as rectangles and petagons respectively. The compound shown in Figure 15a has one less hydrogen than the assumed formula; however, it cannot be neglected on this basis since the hydrogen analysis (Table 7) was not good enough to distinguish between nine or ten hydrogens.

The structure (Figure 15d) in which both rings are bonded to the cobalt is rejected because no pure σ bonded organometallic compounds of Group VIII, with the exception of platinum, have ever been prepared. Also the molecular orbital treatment of Jaffé and Doak (40) has shown that such compounds should be exceedingly unstable. The compound represented by Figure 15a is also unacceptable since it would be paramagnetic. The trichloromethyl group has replaced one of the hydrogens of $(C_5H_5)_2Co$ and the odd electron will still be present. If the electron is removed a cation will result. The non-ionic nature of $(C_5H_5)_2(CCl_3)Co$ as demonstrated by its melting point, vapor pressure and solubility in organic solvents eliminates this possibility. The infra-red spectrum for the ring substituted structure (Figure 15a) should have

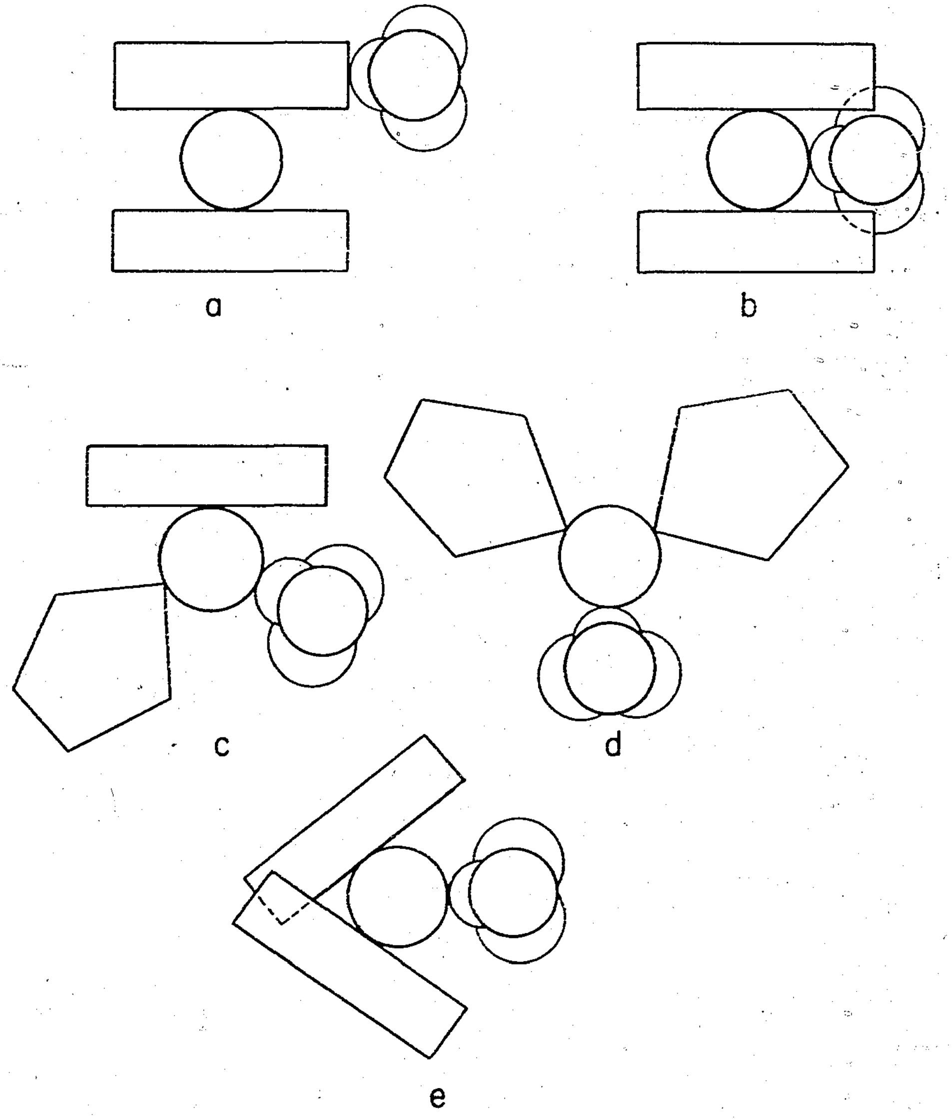

Figure 15. Possible structures for $(C_5H_5)_2(CCl_3)Co$

but one C-H stretching frequency since it still is a π-bonded compound. However as seen in Figure 12b there are two C-H stretching bands at 3.25 and 3.40 μ. The formation of $[(C_5H_5)_2Co]^+$ on refluxing an ethanolic solution of $(C_5H_5)_2(CCl_2)Co$ clearly shows that the trichloromethyl group is not on the ring.

Of all the structures, the (π-cyclopentadienyl) (σ-cyclopentadienyl)trichloromethylcobalt(III) compound (Figure 15c) fits the data best. Since one ring is σ bonded it would be expected that the properties of this combination would be similar to the (π-cyclopentadienyl)(σ-cyclopentadienyl) metal compounds described by Wilkinson; this is found to be the case. The reaction of $(C_5H_5)_2(CCl_3)Co$ with maleic anhydride and ferrous chloride have been observed. The infra-red spectrum has two C-H stretching absorptions at 3.25 and 3.40 μ as well as bands in the 6.10-6.25 μ and 13.15-13.90 μ regions <u>viz</u> 6.25 and 13.65 μ. The 13.65 μ band is, however, in the general region for C-Cl_3 vibrations (99). The infra-red spectrum of the compound formed between $(C_5H_5)_2Co$ and dibromomethane, presumably π-(C_5H_5) σ-$(C_5H_5)(CH_2Br)Co$, (100) is almost identical to that of $(C_5H_5)_2(CCl_3)Co$ including a band at 13.45 μ. Since C-Br vibrations do not occur in this region, it is felt that the 13.65 μ band in $(C_5H_5)_2(CCl_3)Co$ can be attributed to a σ-cyclopentadienyl ring.

The results of the tracer experiments are in line with this structure. The lack of chloride exchange between the trichloromethyl compound and lithium chloride eliminates the possibility of ionic chloride and the lack of exchange of bis(π-cyclopentadienyl)cobalt(III) ions is consistent with the proposed difference in structure between $[(C_5H_5)_2Co]^+$ and the trichloromethyl compound.

The high molar extinction coefficient at 2400Å is similar to that of the σ bonded compounds. However, this can be ascribed to the trichloromethyl group and does not necessarily indicate a σ-cyclopentadienyl ring. The compound is diamagnetic as is to be expected since the isoelectronic, isomorphic system $[\pi\text{-}(C_5H_5)Fe(CO)_2]^+$ has been shown to be diamagnetic (38). If this is the correct configuration then the formation of $[(C_5H_5)_2Co]^+$ in boiling ethanol solutions of $(C_5H_5)_2(CCl_3)Co$ involved a second rearrangement i.e., from σ to π bonding. Such a rearrangement has been observed by Herwig and Zeiss (101) in the formation of (π-biphenyl)(π-benzene)chromium(0) from tris(σ-phenyl)chromium(III).

Steric considerations make it doubtful that Figures 15b and e can represent the system since in the former the trichloromethyl group is too large to fit between the rings and in the latter, part of both rings must occupy the same region of space. The compound as represented by Figure 15b also has the disadvantage that two electrons must go into anti-bonding orbitals which would certainly be reflected by a highly labile

$Co-CCl_3$ bond. It is also difficult to explain why such a compound would decompose to give the cobalt ion instead of $[(C_5H_5)_2Co]^+$ when relatively weak agents such as sodium thiocyanate and silver nitrate are added. It is difficult to discuss the properties represented by Figure 15e since no stable compounds having such a structure have been isolated. The compound $(C_5H_5)_3UCl$ has been prepared (102) in which the rings are assumed to be π bonded. The compound is so unstable that no good physical measurements have been made.

A strained configuration intermediate between the extreme forms represented by Figures 15b and e may explain the observed data. Again, since no similar compounds have been isolated the properties assumed are merely conjecture. It is reasonable to assume that in such a structure there will be considerable steric interference between the three groups and as a result the rings will be bent out of their normally planar configuration. This would amount to adding diene character to the rings, which would explain the reactivity with maleic anhydride and the observed infra-red spectrum. Also, it would not be necessary to postulate π to σ and σ to π rearrangements. The ultra-violet spectrum (Figure 14) appears similar to that of $[(C_5H_5)_2Co]ClO_4$ except at the low wave length end which should be attributed to the $Co-CCl_3$ σ bond. It is questionable if such a system would be stable. The loss of much π character in the ring-metal bonding and the distortion of strongly directional π bonds should certainly lead to a quite unstable compound. It would also be expected that the reduced stability of the system would shift the ultra-violet spectrum of the trichloromethyl compound relative to $[(C_5H_5)_2Co]^+$ to lower wave lengths rather than to higher.

Nuclear magnetic resonance measurements of $(C_5H_5)_2(CCl_3)Co$ should distinguish between the strained and σ bonded structure since both rings of the strained system are equivalent and should show only one n.m.r. peak. An X-ray crystalographic study of the structure of $(C_5H_5)_2(CCl_3)Co$ has been undertaken by Mr. D. Williams of the Iowa State College Chemistry Department; however, no results have been obtained as yet.

The mechanism of formation of $(C_5H_5)_2(CCl_3)Co$ is interesting. Bis(π-cyclopentadienyl)cobalt(II) usually acts as a strong reducing agent. However, in this reaction the mechanism appears to be free radical in nature. The observed data can be explained by the following mechanism:

$$(C_5H_5)_2Co + CCl_4 \longrightarrow (C_5H_5)_2(CCl_3)Co + Cl\cdot$$

$$(C_5H_5)_2Co + CCl_4 \longrightarrow [(C_5H_5)_2Co]Cl + CCl_3\cdot$$

$$(C_5H_5)_2Co + \cdot CCl_3 \longrightarrow (C_5H_5)_2(CCl_3)Co$$

$$(C_5H_5)_2Co + \cdot Cl \longrightarrow [(C_5H_5)_2Co]Cl$$

Positive confirmation of the free radical mechanism was obtained by the formation of $(C_5H_5)_2(CCl_3)Co$ from the reaction of $(C_5H_5)_2Co$ and chloroform. If the reaction involves an ionic mechanism the formation of $(C_5H_5)(CHCl_2)Co$ and $[(C_5H_5)_2Co]Cl$ would be expected. It has long been known that chloroform preferentially forms the trichloromethyl and hydrogen radicals in free radical reactions (103-105).

VI. SUMMARY

Exchange studies on the system bis(π-cyclopentadienyl)-cobalt(III) perchlorate-cobaltous perchlorate showed no exchange in times up to 30 days. This lack of exchange of cobalt indicates the great stability and covalent nature of the cobalt-ring bonding.

The electron exchange between bis(π-cyclopentadienyl)-cobalt(II) and bis(π-cyclopentadienyl)cobalt(III) perchlorate in acetone solutions was studied at 0°C in the virtual absence of air. An apparently large zero time exchange followed by a slow exchange reaction was observed. A study of the effect of $(C_5H_5)_2Co$ concentration on the zero time exchange and the half time of the slow reaction led to the conclusion that the electron exchange was very rapid ($t_{\frac{1}{2}} < 5$ secs). The high zero time exchange is attributed to this reaction and the slow exchange to the following two equilibria:

$$[(C_5H_5)_2Co^{60}]^+ + [(C_5H_5)_2Co]_2O \xrightleftharpoons{k_1} [(C_5H_5)_2Co]^+ + [(C_5H_5)_2Co^{60}][(C_5H_5)_2Co]O$$

$$(C_5H_5)_2Co^{60} + [(C_5H_5)_2Co]_2O \xrightleftharpoons{k_2} (C_5H_5)_2Co + [(C_5H_5)_2Co^{60}][(C_5H_5)_2Co]O.$$

The presence of $[(C_5H_5)_2Co]_2O$ in the reaction solutions is assumed to be due to the oxidation of $(C_5H_5)_2Co$ by oxygen impurities. It appears that $k_1 = k_2$ (0.029 liter/mole sec) and that the overall kinetics for both reactions is second order, i.e., first order in each of the reactants.

A qualitative understanding was obtained of the complex reaction between $(C_5H_5)_2Co$ and oxygen in mesitylene solutions. The uptake of oxygen was studied over a range 0-1.5 moles of oxygen per mole of $(C_5H_5)_2Co$. The initial reaction was observed to be very fast and chemical evidence indicates that the first product formed was $[(C_5H_5)_2Co]OH$. At 0°C this reaction takes place during the uptake of 0.-0.5 moles of oxygen per mole of $(C_5H_5)_2Co$.

The second reaction appears to accompany the decomposition of $[(C_5H_5)_2Co]OH$ which is complete after the uptake ratio (moles O_2/mole $(C_5H_5)_2Co$) is unity. The products of this reaction have not been identified, however a positive qualitative test for the cobaltous ion was obtained and a red-brown solid was isolated which appears to be an organic polymer. The kinetics for this reaction is first order in $[(C_5H_5)_2Co]OH$ and zero order in oxygen. The reaction seems to be homogeneous, but this point is still in question. The oxygen reaction beyond an uptake ratio of 1.0 also is first order in the cobalt compound and zero order in oxygen. This reaction is most probably heterogeneous.

From the reaction of $(C_5H_5)_2Co$ with carbon tetrachloride a new type of cyclopentadienyl cobalt compound was isolated which had the formula $(C_5H_5)_2(CCl_3)Co$. It has been named (π-cyclopentadienyl)(σ-cyclopentadienyl)trichloromethyl-cobalt(III) since the infra-red and chemical data lead us to the conclusion that the formation of the compound involves an interesting rearrangement in the bonding, from very stable π to less stable σ. The conversion of this compound in ethanol solutions to $[(C_5H_5)_2Co]^+$ indicates that a reverse rearrangement of σ to π bonding also occurs. The production of $(C_5H_5)_2(CCl_3)Co$ from the reaction of $(C_5H_5)_2Co$ and chloroform demonstrated that the mechanism of its formation involves free radical reactions.

VII. LITERATURE CITED

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VIII. APPENDIX

The apparatus used for measuring fairly rapid reaction rates, when reactants are sensitive to air, is shown in Figure 16.

The apparatus consisted of four main sections.

I. Gas regulating system
  - a) Helium gas
  - b) Tube of copper turnings at 600°C to remove any oxygen present in the helium
  - c) Water trap (T_2) immersed in dry ice and acetone
  - d) Mercury reservoirs (R_1 and R_2)
  - e) Manometer (M)
  - f) Gas trap (T_1) immersed in liquid nitrogen
  - g) Vacuum pump

II. Reaction flask
  - a) Chambers for storing the two reaction solutions (A and B)
  - b) Teflon covered stirring bar (D)
  - c) Magnetic stirrer (E) in a water tight brass jacket
  - d) Sealed glass tip (F)

III. Sampling chamber
  - a) Glass hammer attached to a stopcock
  - b) Sampling tubes (1-7). Tubes 1-6 have volumes of about 10 ml below the line a-b. Tube 7 had a volume of 25 ml below b.

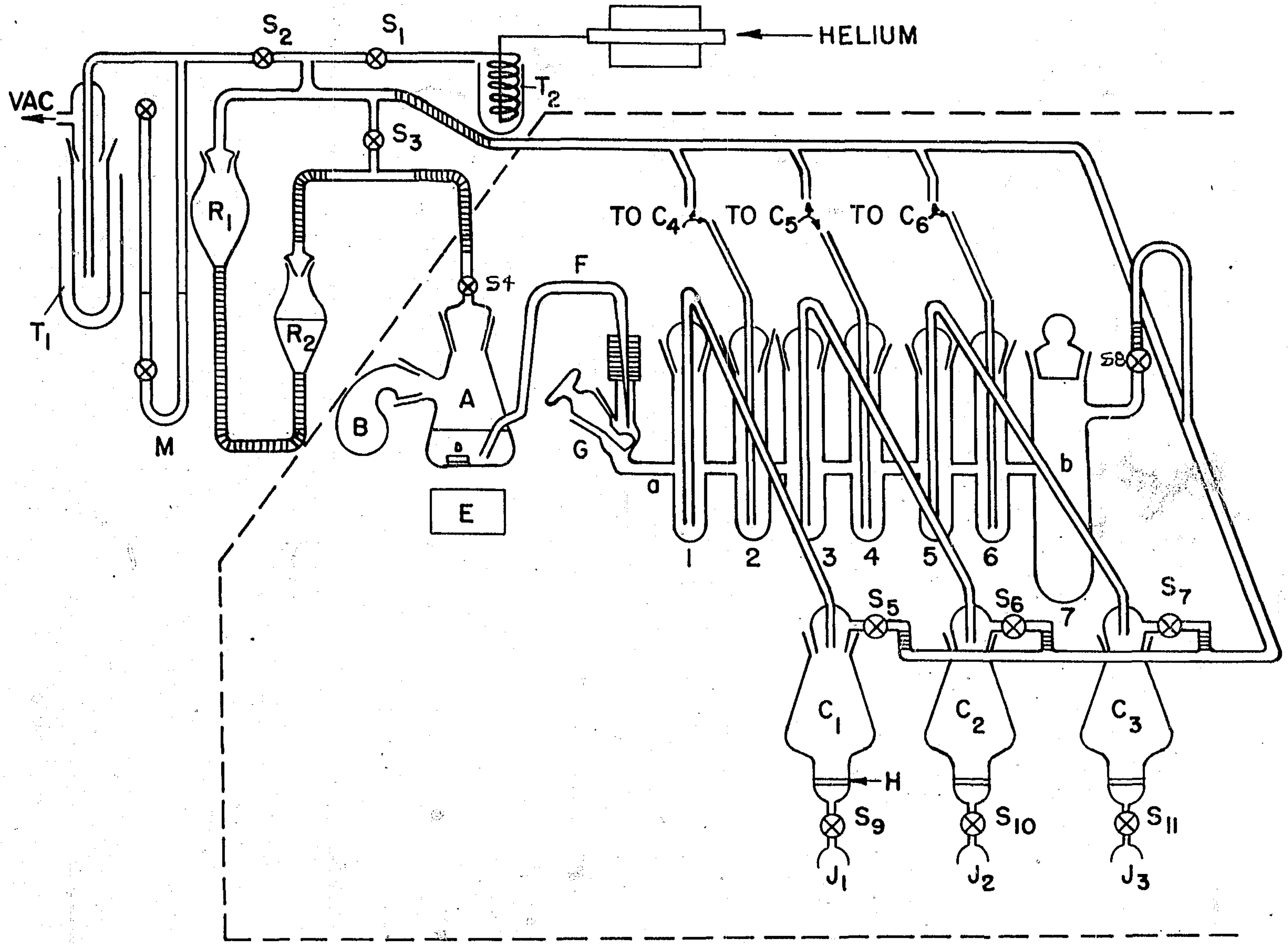

Figure 16. Exchange apparatus for the study of fast reactions

IV. Quenching system

a) Flasks (C_1-C_6) contained quenching solutions.

b) Sintered glass disc (H) of Pyrex medium porocity used to filter precipitated reactant.

c) Stopcocks S_9-S_{14} were greased with "Nonaq" because organic liquids had to be drawn through them.

In a dry box the two reacting solutions were placed separately into A and B. The reaction vessel was connected into the system at S_4 and F_1. Stopcocks S_1, S_4 and J_1 to J_6 were closed and the entire system was evacuated. After one hour of pumping, S_2 was closed.

A solvent bulb, Figure 17, which held one liter of quenching solution was placed so that ball joints J_1 and J_a were in contact, stopcock S_r was opened, the space between S_9 and S_a was evacuated and S_b was then closed. Stopcocks S_9 and S_a were opened and the solution was allowed to enter flask C_1. The volume of the flask was 150 ml. When the level of liquid reached a predetermined point, S_9 and S_a were closed and the solvent bulb was removed. This procedure was repeated on flasks C_2-C_6. If during the filling procedure the pressure in the solvent bulb became too low to force the quenching solution out, a small amount of helium was admitted through S_c. Stopcock S_1 was opened, helium was allowed to fill the system to atmospheric pressure and S_1 was then closed.

The portion of the apparatus enclosed by a dotted line in Figure 16 was immersed in a constant temperature bath and

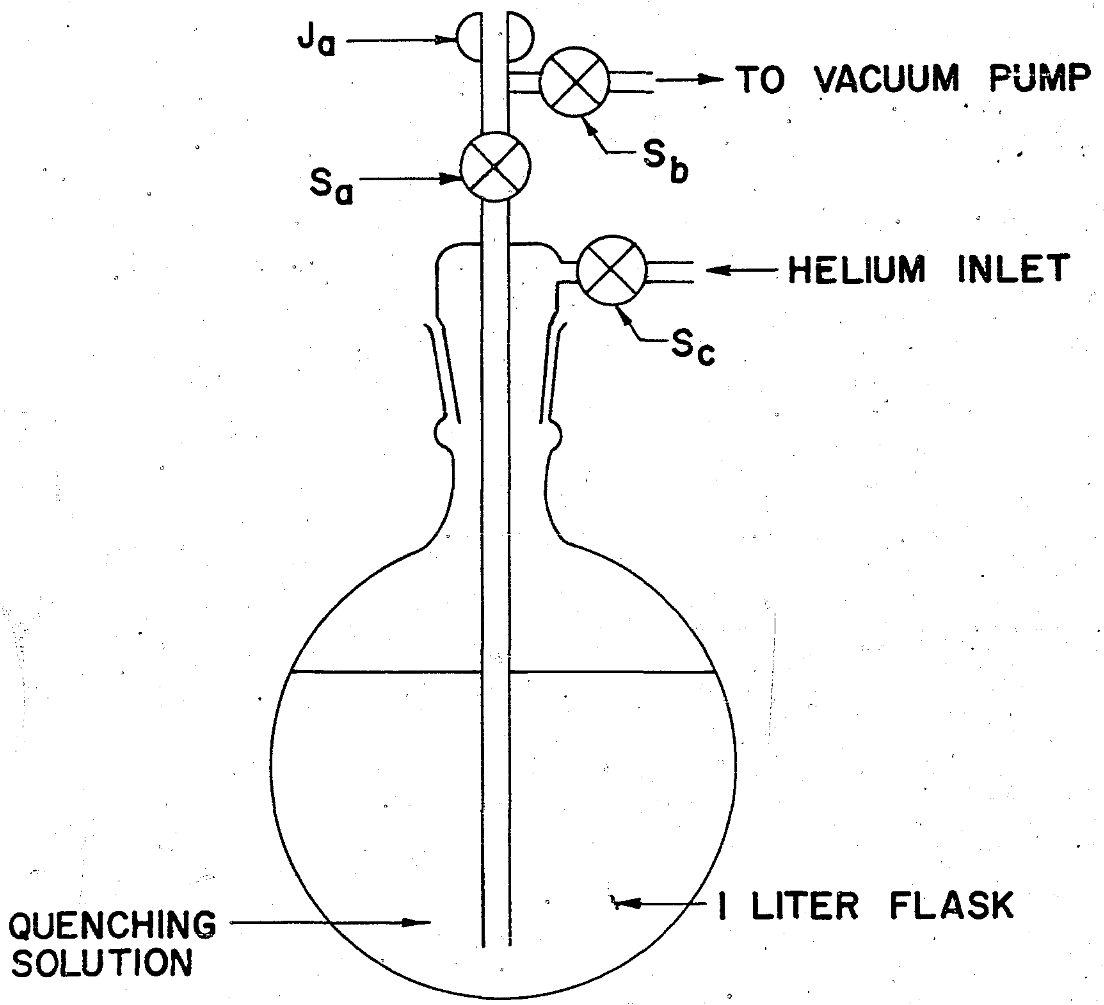

Figure 17. Flask for filling quenching flasks of the exchange apparatus

allowed to equilibrate for three hours. After equilibration all of the open stopcocks were closed with the exception of S_4 and S_8. Mercury reservoir, R_2, was lowered so that there was an increase of pressure in A and B and the magnetic stirrer was turned on.

Arm B of the reaction vessel was turned to allow the solution contained in it to flow into A. This time was considered zero time for the reaction. After stirring for ten seconds, G was rotated and the hammer broke the tip of F. The excess pressure in A caused the solution to flow quickly through F and into the sampling chamber at a. The sample tubes 1-6 were filled (to the mark along a-b) and the overflow was collected in tube 7. Stopcock S_3 was opened, R_2 was raised and stopcock S_8 was closed.

To quench the first sample stopcock S_5 was opened, S_3 was closed and R was quickly lowered. This operation increased the pressure in the sample chamber causing sample tube #1 to empty its contents into flask C. The time of entry of sample #1 into C_1 was noted and the difference in time t_1-t_o was considered the reaction time for sample #1. The time necessary for all operations from t_o to t_1 is about 45 seconds. S_5 was closed, S_3 was opened and R_2 was then raised to its original position. S_6 was opened and S_3 was closed. The system was now in position to empty sample #2. This procedure was repeated until all six samples were quenched. The time necessary to perform all operations between samples was less than 30 seconds.

The immersed portion of the apparatus was removed from the constant temperature bath. The liquids in the quenching flasks were removed into separate suction flasks. The precipitated compound was thereby filtered on to the sintered glass discs (H). The suction flasks were fitted with ball joints so that they could make contact with the ball joints at the bottom of the quenching flasks. The precipitated compound was washed off the sintered glass discs, and the separated samples were ready for analysis.

In order to operate this apparatus quickly, it was necessary to have two operators. One person manipulated the various stopcocks, the other took charge of starting the reaction, injecting the samples by moving R_2 and recording the times of quenching for the samples.

The apparatus was too large to be wrapped with opaque materials. In order to run experiments in the absence of light, the entire room had to be darkened. This was easily achieved since the room in which the apparatus was located had no windows. Two 8 candle power Nalco ruby red dark room lamps were used for lighting.

IX. ACKNOWLEDGMENTS

The author wishes to express his gratitude to the many people who have aided in this research, especially to Dr. A. F. Voigt for his guidance of the research, to J. F. Weiher for his invaluable aid and ideas and to Mickey and Laurie for their encouragement and for just being here.