1961

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Recommended Citation

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WEIHER, James Frederick, 1933-
EXCHANGE REACTIONS IN CYCLOPENTADIENYL-
COBALT COMPOUNDS.

Iowa State University of Science and Technology
Ph.D., 1961
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

EXCHANGE REACTIONS IN CYCLOPENTADIENYLCOBALT COMPOUNDS

by

James Frederick Weiher

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:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

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Iowa State University
Of Science and Technology
Ames, Iowa

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I. INTRODUCTION

A. Review of the Literature

In the last decade a large number of stable organometallic compounds of the transition metals have been prepared in which the π-electrons of an organic ligand are utilized in the bonding. The metal, in such cases, is bonded not to individual carbon atoms as in σ-bonded organometallic compounds like tetramethylsilane but rather to a unit of several carbon atoms by means of electrons in delocalized molecular orbitals.

The first such compound to be discovered was di-π-cyclopentadienyliron(II), commonly known as "ferrocene" (31, 34). On the basis of X-ray diffraction, infrared absorption, and magnetic susceptibility investigations, it was quickly decided that the molecule was centrosymmetric with the metal atom located between the two parallel cyclopentadienyl rings (6, 22, 50). Analagous compounds using as the central metal, nickel (19, 49), rhodium, iridium (5), cobalt (44), ruthenium (43), and chromium (14), to mention just a few, were soon synthesized.

That compounds of this type were not limited to cyclopentadienyl rings was demonstrated early by the preparation and characterization of di-π-indenylnickel, di-π-indenylcobalt (23), and di-π-benzenechromium (16). It was also shown that asymmetric compounds with only one ring could be formed, e.g., π-cyclopentadienylmolybdenum dicarbonyl nitrosyl (12, 40), π-cyclopentadienyliron dicarbonyl chloride (39), di(π-cyclopentadienyltungsten tricarbonyl) (45), π-cyclopentadienylrhodium cycloocta-1, 5-diene (2), and π-cyclopentadienyltitanium trichloride (25). Compounds with one cyclopentadienyl ring σ-bonded to the metal atom were also found possible, e.g., π-cyclopentadienyl (σ-cyclopentadienyl)iron dicarbonyl, and π-cyclopentadienyl (σ-cyclopentadienyl)chromium dinitrosyl (40).

More recently it has been shown that a multitude of organic systems with π-electrons available for bonding can form organometallic compounds similar to those already mentioned. For a complete up to date listing and discussion of cyclopentadienyl and arene metal complexes, reference should be made to extensive reviews by Fischer (8, 11, 13), Pauson (36, 37, 38), and others (41, 46).

The work presented in this thesis deals only with cyclopentadienylcobalt compounds. A brief review of the preceding work in this area follows.

Di-π-cyclopentadienylcobalt(II) is a typical case of a transition metal bonded to two organic rings with π-bonds (20, 49). It sublimes at 80°C. in vacuo to form violet crystals which are soluble and stable in oxygen-free organic solvents, insoluble in water, and easily oxidized by air and dilute acids to the di-π-cyclopentadienylcobalt(III) cation. Di-π-cyclopentadienylcobalt(II) is paramagnetic, having one unpaired electron (20). Since di-π-cyclopentadienyliron(II) is considered to have all its low energy orbitals filled, the extra electron in the cobalt compound would lie in a higher level, and consequently would explain the ease of oxidation.

Di-π-cyclopentadienylcobalt(III) picrate (44), bromide, and tetraphenylborate (7) have been shown to be diamagnetic as is to be expected of the oxidized form of di-π-cyclopentadienylcobalt. The di-π-cyclopentadienylcobalt(III) cation gives a well defined cathodic wave at a dropping mercury electrode with a half wave potential at -1.16v. relative to the standard calomel electrode, but can not be reduced to di-π-cyclopentadienylcobalt(II) by electrolysis (35). The cation behaves much like the large unipositive ions of Group IA. Its common salts are very soluble in aqueous solutions although the picrate, dinitrophenolate, triiodide (44), and perchlorate (29) are slightly soluble. The di-π-cyclopentadienylcobalt(III) ion can be precipitated from aqueous solutions with chloroplatinic acid, silicotungstic acid (44) and sodium tetraphenylboron (18). It cannot be destroyed by boiling in nitric acid, concentrated sulfuric acid, or aqua-regia, but can be destroyed by boiling concentrated perchloric acid or molten potassium pyrosulfate (18, 44).

Although the reduction of the ion to di-π-cyclopentadienylcobalt(II) with lithium aluminum hydride is reported (1), attempted reduction with sodium borohydride produces π-cyclopentadienylcobalt cyclopentadiene by the addition of hydride to one of the rings (26). In this case only one of the rings retains its symmetry. The other ring, a cyclopentadiene molecule, is linked to the cobalt by dative π-bonds from the two conjugated double bonds.

A related trichloromethyl derivative is formed by the reaction of carbon tetrachloride with di-π-cyclopentadienylcobalt(II) (30). It is red, melts between 79.5-80.5°C., is very soluble in common organic solvents with slow decomposition and appears stable in a dry atmosphere below 40°C. Although slow decomposition occurs in solution, this derivative is more stable than the cyclopentadienylcobalt cyclopentadiene complex (29). It is however rapidly decomposed by glacial acetic acid, concentrated mineral acids, and bases. Ethanolic solutions are decomposed by the addition of sodium thiocyanate or silver nitrate. In ethanol-water solution the trichloromethyl derivative is converted to the di-π-cyclopentadienylcobalt(III) ion by boiling. The structural similarity of the logical parent compound, π-cyclopentadienylcobalt cyclopentadiene, and the trichloromethyl derivative is clearly indicated by the analysis of the infrared and nuclear magnetic resonance spectra (26).

By the reaction of either di-π-cyclopentadienylcobalt with carbon monoxide under pressure or dicobalt octacarbonyl with cyclopentadiene, a compound with only one ring, π-cyclopentadienylcobalt dicarbonyl, is formed (21, 39). It is diamagnetic, unstable in air, and soluble in organic solvents.

A mysterious cyclopentadienylcobalt compound has been reported (9) to contain five cyclopentadienyl rings and two cobalt atoms per molecule. This material is diamagnetic in the crystalline form, but paramagnetic with one unpaired electron in benzene solution.

By reacting di(cobalt tetracarbonyl)mercury with tetracyclone at 100°C. Weiss and Hübel have prepared an anion in which a cobalt atom is sandwiched between two substituted cyclopentadienone rings (42). A related compound, π-(C_5H_5), π-$(C_5H_5O^-)$Co, has been prepared by the reaction of π-cyclopentadienylcobalt dicarbonyl with 2 butyne (33). The bonding in these compounds has been considered as a resonance hybrid of the usual highly delocalized symmetric bonding of the di-π-cyclopentadienylmetal compounds and the more localized dative π-bonding of the diene complexes.

Di-π-cyclopentadienylcobalt(II) in organic solvents free of water reacts with oxygen to form a cherry-red oxygen compound (29). If the oxygenation is stopped at or before 4 moles of cyclopentadienylcobalt per mole of oxygen, the oxygen compound can be converted to the di-π-cyclopentadienylcobalt(III) cation by the addition of water or dilute acid.

B. Purpose of the Investigation

In work carried out in this laboratory, it was found that labeled di-π-cyclopentadienylcobalt(III) perchlorate did not exchange with the trichloromethyl derivative of di-π-cyclopentadienylcobalt(II), but did exchange with the oxygen compound formed from di-π-cyclopentadienylcobalt(II).

The oxygen compound was formed by introducing oxygen into water-free organic solutions of di-π-cyclopentadienylcobalt(II). In many solvents the oxygenation proceeded uniformly to the final destruction of the sandwich compound, but in acetone the oxygenation could be stopped at four moles of cobalt per mole of oxygen. This material, of the stoichiometry $(C_5H_5)_4Co_2O$, appeared to have greater stability in acetone than in other solvents in that only in acetone could the reaction be stopped at this stoichiometry. Attempts to obtain the material in the solid state for analysis and spectral investigations led to the complete decomposition of the compound. It could, however, be converted to the di-π-cyclopentadienylcobalt(III) cation by the addition of water or dilute acid to the acetone solutions.

This investigation was undertaken as an effort to elucidate the structure and chemical reactivity of the oxygen compound. It was thought that the kinetics of the exchange reaction between di-π-cyclopentadienylcobalt(III) perchlorate and the oxygen compound might aid in determining the nature of the oxygen compound. A preliminary investigation of this exchange reaction led Katz (29) to postulate a bimolecular reaction involving the collision of the oxygen compound with the di-π-cyclopentadienylcobalt(III) cation. Although this is not an unreasonable suggestion, it was felt that the experimental basis for it was rather meager. It was therefore decided to examine the kinetics of the exchange reaction in greater detail in order to clarify the situation and determine with greater certainty the kinetics and possible mechanism of the exchange reaction.

II. APPARATUS AND MATERIALS

A standard dry box, manufactured by S. Blickman, Inc., was outfitted for use with an helium atmosphere. Two tapered slotted metal tubes of 1 inch diameter were mounted near the top of the main compartment to approximate a uniform displacement of the compartment atmosphere by the entering helium. Two similar tubes were mounted at the bottom of the compartment to allow uniform removal of the displaced gas. The entry port, designed to work on the principle of the air lock, was likewise outfitted to allow rapid and efficient flushing. A system of 3/8 inch copper tubing was arranged on the outside of the dry box to permit the flushing of the main compartment alone, the entry port alone, or the main compartment and the entry port in series. The flushing system was connected to two helium tanks through standard reducing valves. The exit gas was passed through a rotameter and mineral oil trap to the external atmosphere.

United States Bureau of Mines helium of minimum purity 99.99 percent was used to flush the dry box and to maintain the inert atmosphere. In the early experiments the tank helium was passed through a Dry Ice trap to remove traces of water and a hot copper tube (24) to remove traces of oxygen. It was later found that straight tank helium of 99.99 percent purity was sufficiently pure for the experiments under consideration and the purification train was removed.

For each entry into the dry box, the entry port was flushed with about 400 liters of helium, or about eight times the volume of the port, to reduce the oxygen content in the port to less than 0.01 percent (4).

Small tubes, pipets, and similar difficult to flush apparatus were brought into the dry box in evacuated containers. The flushing of flasks with narrow necks and similar pieces of equipment was facilitated by an auxiliary tube in the entry port which was connected in parallel with the usual flushing system.

The exchange experiments were carried out in the apparatus shown in Figure 1. The main body of the apparatus was a 300 ml. round bottom flask with a 24/40 standard taper joint and a 16 mm. tube about 45° from the taper. An auxiliary reservoir was a 50 ml. bulb with a sleeve type 24/40 standard taper and "drip tip". A serum cap fitted snugly into the 16 mm. tube of the main body of the apparatus was covered with mercury to seal the system from the atmosphere during the extraction of samples.

A hypodermic syringe fitted with a 5 inch hypodermic needle was used for the removal of samples. In Figure 2 the syringe can be seen with its water jacket. The water jacket was a polyethylene bottle with the bottom removed and a serum stopper fitted to the neck.

The quenching apparatus is shown in Figure 3. The sintered glass disc in the apparatus to the left permitted the filtration of the quenched exchange solution in an inert atmosphere. It was later found that the same results could be obtained if the apparatus on the right was used to quench the exchange. With this apparatus, after quenching the exchange, the stopper was removed and the solution filtered rapidly in the open atmosphere with an ordinary sintered glass funnel of medium porosity and suction filtering flask.

Radiochemical analyses were made using a Nuclear-Chicago Model 1810 Single Channel Pulse Height Analyzer and a Nuclear-Chicago Model

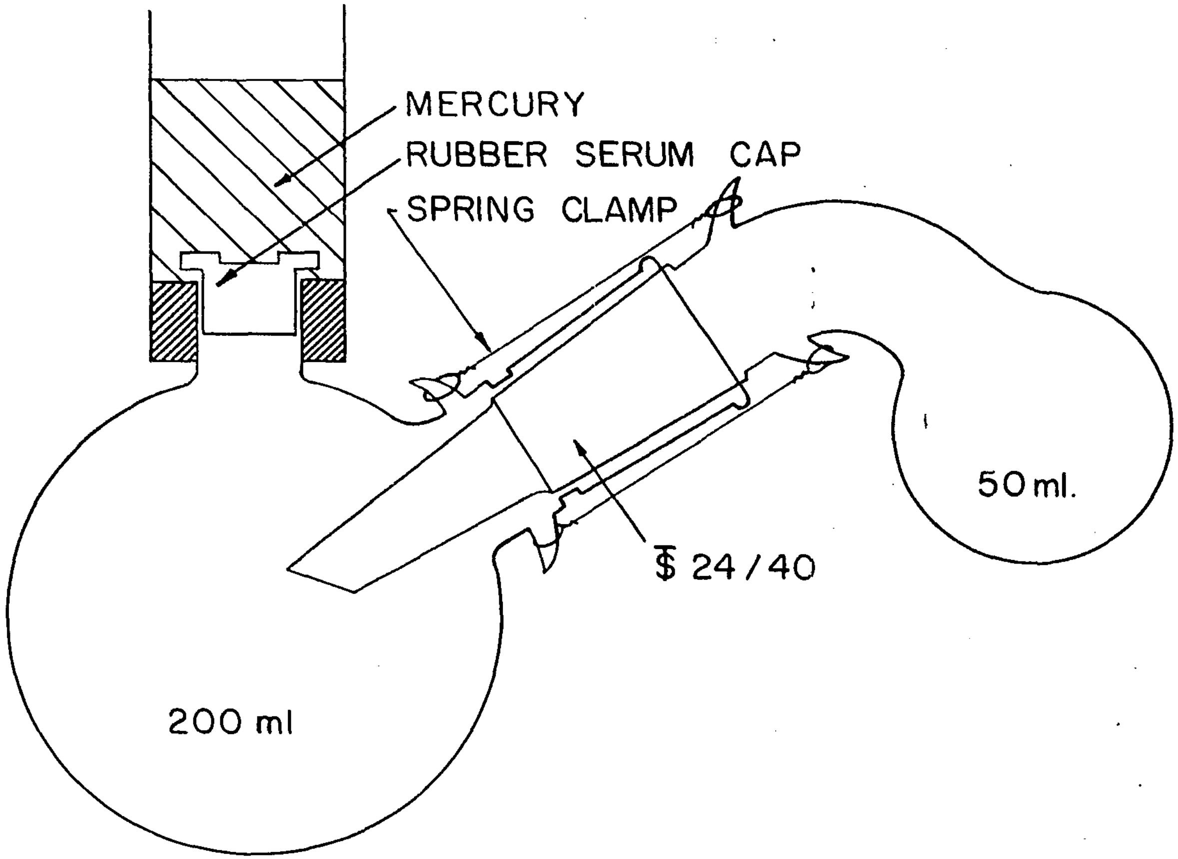


Figure 1. Exchange reaction apparatus

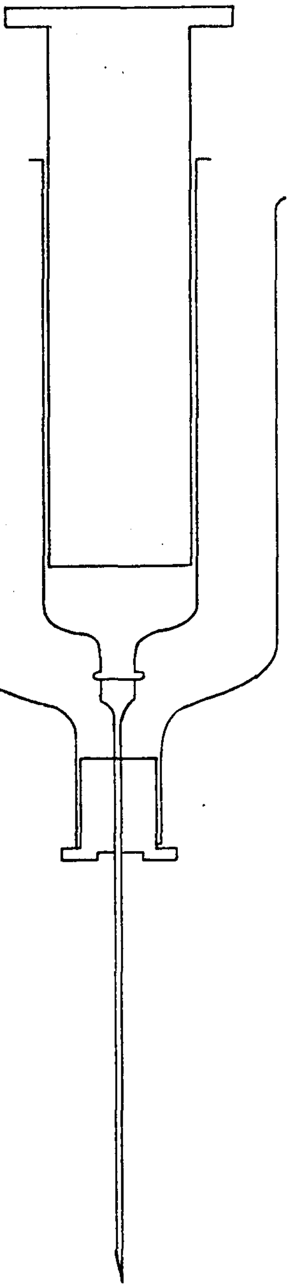


Figure 2. Hypodermic assembly

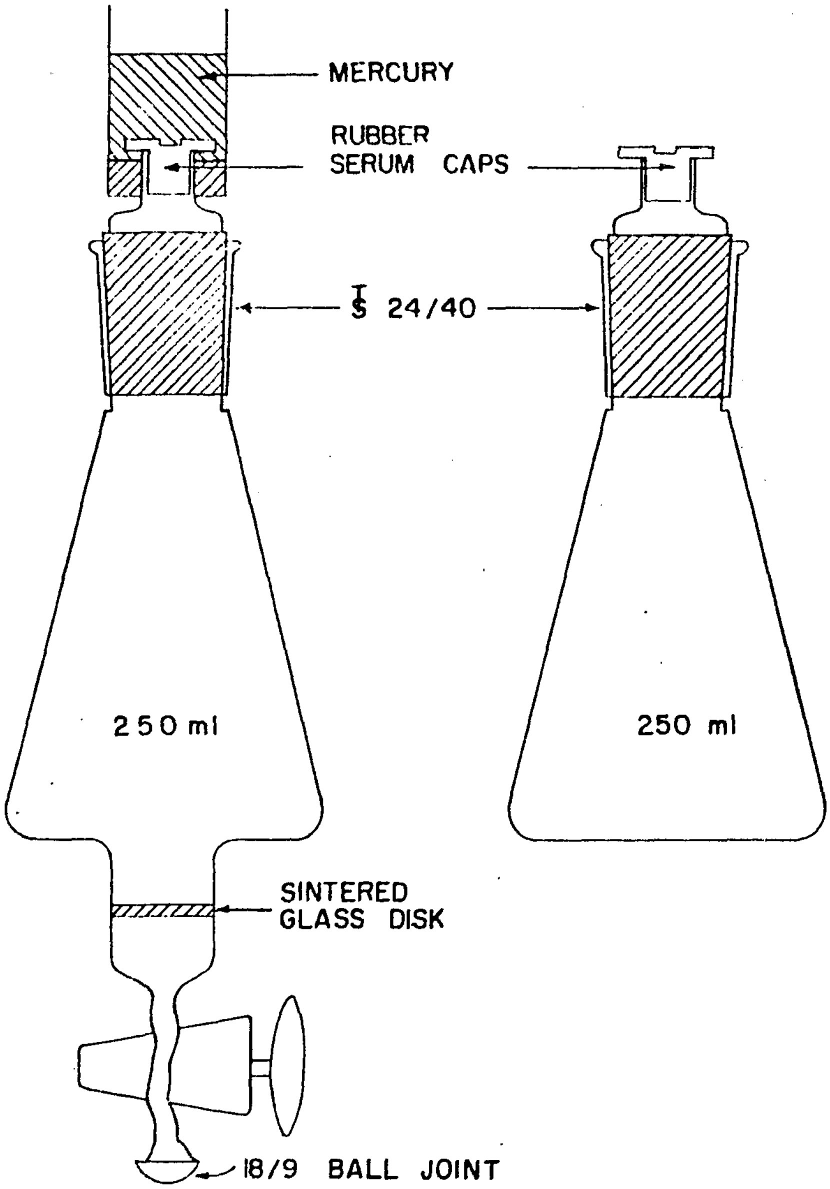


Figure 3. Quenching apparatus

186 Decade Scaler. The 1.33 and 1.17 Mev gamma radiation of cobalt-60 was detected with a 2 inch cylindrical sodium iodide (thallium activated) scintillator fitted with photomultiplier and cathode follower. As a measure of the activity of the samples integral counting above 400 Kev was chosen for the best compromise among high counting rate, low background rate, and reproducibility.

For the determination of the degree of oxygenation of di-π-cyclopentadienylcobalt(II) in acetone the apparatus in Figure 4 was employed. The manometer served to measure the total pressure in the system; the differential manometer to measure the change in pressure; the buret and bulb which contained mercury to change the volume of the system; the cold trap to remove water from the gas initially introduced; reaction flask to contain the solvent; and break tip assembly to break the glass ampule containing the sample to be oxygenated.

The conductivity measurements were made with a General Radio Co. type 716C capacitance bridge in conjunction with the model 1432M decade resistor box, the 1231 B amplifier and null detector and the 1231P5 narrow band bypass filter. A Hewlett Packard model 200CD wide range oscillator was used for a signal source.

Mallinckrodt Analytical Reagent acetone was purified by contacting for 15 minutes with silver oxide which was precipitated in the solvent by adding appropriate amounts of aqueous silver nitrate and sodium hydroxide. The acetone mixture was filtered, dried with calcium sulfate, distilled over fresh calcium sulfate, deoxygenated by bubbling oxygen-free helium through the solution, and stored in the drybox.

Skelly-B, a petroleum fraction marketed by the Skelly Oil Company,

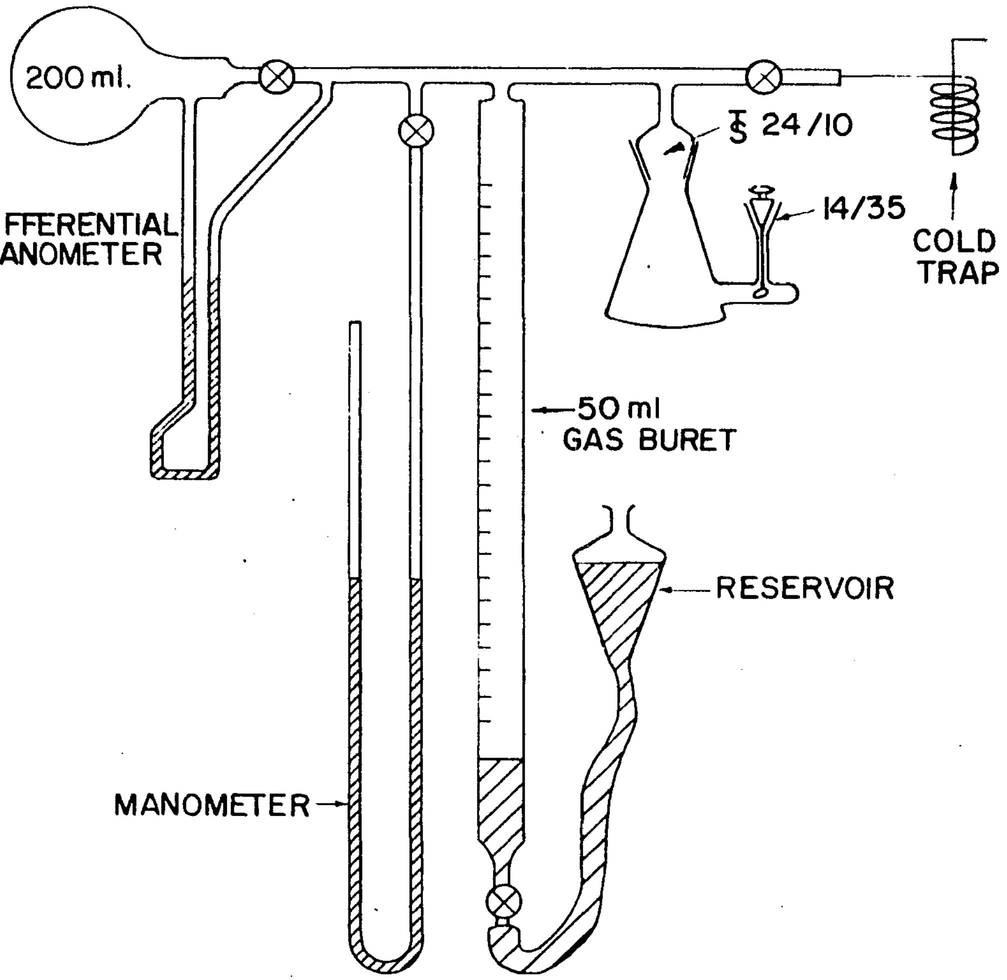


Figure 4. Gas reaction apparatus

is a mixture of saturated hydrocarbons with a boiling point range 60-80°C. The commercial product was purified by contacting twice with concentrated sulfuric acid, or until the sulfuric acid remained only light straw colored, washing with aqueous sodium carbonate, contacting with dilute aqueous potassium permanganate, washing twice with water, and drying with calcium sulfate. The purified Skelly-B was distilled and stored over calcium sulfate.

Phillips 66 Pure Grade n-decane was dried over sodium wire, distilled, and stored in the dry box.

G. Frederick Smith Reagent Grade anhydrous sodium perchlorate was dried at 150°C. under reduced pressure, c. 10 microns, for 24 hours before use.

Eastman White Label tetrahydrofuran was refluxed over lithium aluminum hydride for eight hours, refluxed over sodium for eight hours, and distilled at 64°C. The tetrahydrofuran was always used within four hours after distillation.

Di-π-cyclopentadienylcobalt(II) was prepared by Wilkinson's method (47) by reacting cyclopentadienylsodium with anhydrous cobaltous chloride. Eastman Organic Chemicals Technical Grade di-cyclopentadiene was cracked to the monomer by heating and distilled at 42°C. The cyclopentadiene was allowed to react with sodium sand in tetrahydrofuran solution at 0°C. in an atmosphere of dry oxygen-free helium. The anhydrous cobaltous chloride was prepared by heating the hexahydrate for 24 hours at 200°C *in vacuo*. The cyclopentadienylsodium was allowed to react with the anhydrous cobaltous chloride for two hours with vigorous stirring. The tetrahydrofuran solvent was removed by vacuum distillation and di-π-cyclopentadienylcobalt(II) sublimed from the residue at 70°C. and 10^{-6}mm. Hg.

Di-π-cyclopentadienylcobalt(III) perchlorate was prepared by the oxidation of di-π-cyclopentadienylcobalt(II). A ten-fold excess of .01 M. perchloric acid was shaken in air with a benzene solution of di-π-cyclopentadienylcobalt(II) to form an aqueous solution of di-π-cyclopentadienylcobalt(III) perchlorate. The aqueous perchlorate solution was washed with benzene, heated with activated charcoal, filtered, and concentrated by evaporation of solvent. The di-π-cyclopentadienylcobalt(III) perchlorate was crystallized from the solution at 0°C. and recrystallized from water six times.

Labeled di-π-cyclopentadienylcobalt(III) perchlorate was prepared using 500 microcuries of cobalt-60 from the Oak Ridge National Laboratory. Di-π-cyclopentadienylcobalt(III) perchlorate was prepared in the previously described manner using labeled cobaltous chloride. The labeled cobaltous chloride was prepared by adding the cobalt-60 in dilute hydrochloric acid solution to 50 grams of cobaltous chloride hexahydrate in 25 ml. of water, and slow evaporation to dryness.

III. EXPERIMENTAL PROCEDURES

A. Formation of Oxygen Compound

The degree of oxygenation of di-π-cyclopentadienylcobalt(II) in acetone was redetermined with the gas reaction apparatus shown in Figure 4. In the dry box samples of freshly sublimed di-π-cyclopentadienylcobalt(II) were weighed, transferred into glass ampules with break tips, and dissolved in acetone. The ampules were isolated with a stopcock, removed from the dry box, immersed in liquid nitrogen, sealed *in vacuo*, and introduced with about 200 ml. of acetone into the reaction flask. The system was pumped down to the vapor pressure of acetone, filled with dry oxygen and allowed to come to equilibrium as determined by the differential manometer. After attainment of equilibrium the oxygenation was initiated by breaking the ampule with the break tip assembly, and the stopcock of the differential manometer was closed. The volume of the system was changed with the buret and bulb to maintain constant pressure as determined by the differential manometer. This change in level of mercury in the buret was taken as the volume of oxygen taken up by the sample.

With this arrangement the di-π-cyclopentadienylcobalt(II) was released from the ampule slowly so that small amounts of the compound were always in the presence of a large excess of oxygen. Under these conditions the oxygenation at 25°C. continues beyond the ratio of 1 mole of oxygen per 4 moles of cobalt to within about 15% of 1 mole of oxygen per 2 moles of cobalt. This oxygen product is brown in acetone and can be converted to the di-π-cyclopentadienylcobalt(III) cation by addition of 1 mole of hydrogen ion per 2 moles of cobalt and dilution with water.

The oxygenation of di-π-cyclopentadienylcobalt(II) to one mole of oxygen per four moles of cobalt takes place at 0°C. when the cobalt compound is in the presence of only a small amount of oxygen. Under these conditions the cherry-red product of approximate stoichiometry, $(C_5H_5)_4Co_2O$, is formed. This reacts further with oxygen to produce the brown product only at higher temperatures and larger excesses of oxygen. As reported by Katz (29) the cherry-red product can be converted to the di-π-cyclopentadienylcobalt(III) cation by the addition of water and acid.

In the exchange experiments the cherry-red product, $(C_5H_5)_4Co_2O$, was produced by the addition of a two to three fold excess of oxygen. The oxygen was introduced into the apparatus with a hypodermic syringe and needle about one hour before the exchange was initiated. After about one half hour at 0°C the maximum red color was attained. In the exchange experiments, no decomposition of the red oxygen compound or conversion to the brown product was observed over periods of up to 10 hours.

B. Exchange Experiments

Prior to each series of exchange experiments stock solutions of labeled di-π-cyclopentadienylcobalt(III) perchlorate and di-π-cyclopentadienylcobalt(II) in acetone were prepared. These solutions were made up to the desired concentration at 25 ± 1°C. in the following manner. Labeled di-π-cyclopentadienylcobalt(III) perchlorate was weighed to the nearest 0.1 mg. after drying at 70°C. overnight, introduced into the dry box, and dissolved in acetone in a volumetric flask. Di-π-cyclopentadienylcobalt(II) was weighed to the nearest 0.1 g. in the dry box and dissolved in acetone to an approximately known concentration. The exact concentration of di-π-cyclopentadienylcobalt(II) was determined by isotopic dilution in the infinite time samples from the exchange experiments.

In the dry box the appropriate volume of di-π-cyclopentadienylcobalt(II) solution was pipeted into the reservoir of the exchange apparatus, the appropriate volumes of the other constituents were pipeted into the main body of the apparatus, a teflon covered magnetic stirring bar was added, and the apparatus was assembled using silicone lubricant on the standard taper and no lubricant on the serum cap. The apparatus was removed from the dry box and the serum cap was sealed from the atmosphere with mercury. Oxygen was introduced to oxygenate the di-π-cyclopentadienylcobalt(II) and the apparatus was placed in a constant temperature bath.

After about one hour the exchange was initiated by turning the reservoir one half turn to allow the isolated solution to flow into the main body of the apparatus. This mixing was taken as the zero time of the exchange. Six to ten samples of 10 to 15 ml. each were taken over a period of two to three times the half time of exchange. The syringe with which the samples were removed from the exchange apparatus was kept at the reaction temperature by water in the water jacket of the syringe assembly. The hypodermic syringe and needle were flushed with dry helium prior to extracting the samples to avoid introducing water vapor into the reaction flask and also to avoid reducing the pressure in the flask to the point where removal of the samples was difficult.

Immediately after removal the sample was ejected into the quenching flask containing c. 120 to 150 ml. of Skelly-B at the reaction temperature. Upon contact with the Skelly-B the di-π-cyclopentadienylcobalt(III) perchlorate precipitated leaving the oxygen compound in solution.

After quenching the exchange, the Skelly-B, containing the oxygen compound, was filtered through a sintered glass disk and agitated with 10 ml. of aqueous 0.1M. hydrochloric acid. The oxygen compound in contact with the acid was converted to the cationic species and was extracted into the aqueous phase within 15 minutes. The latter was concentrated to about 1 ml. on a hot plate to remove acetone and to raise the concentration for later precipitation.

The exchange apparatus was removed from the constant temperature bath after the last sample had been extracted, opened, and the remaining solution split into three portions to serve as infinite time samples. To each of these portions 10 ml. of 0.1M. hydrochloric acid was added to convert the oxygen compound to the di-π-cyclopentadienylcobalt(III) cation. The resulting samples, containing both components of the exchange as the di-π-cyclopentadienylcobalt(III) cations were further treated in the same manner as the other samples.

After concentration all samples were filtered through a sintered glass filter to remove foreign matter introduced during the concentration step, warmed on a hot plate, and precipitated by adding 0.6 percent aqueous sodium tetraphenylboron dropwise with stirring. The precipitated samples were filtered onto 7/8 inch filter papers, previously brought to constant weight, using the standard radiochemical procedure of glass chimney and sintered glass disc. The filter papers carrying the samples were dried at 70°C. for 1 hour, dessicated for 1 hour, weighed, mounted on aluminum planchets with mylar tape, and counted to within one percent standard deviation.

Four standards made from the labeled di-π-cyclopentadienylcobalt(III) perchlorate were used to check the operation of the counting equipment and to determine the initial specific activity of the di-π-cyclopentadienylcobalt(III) perchlorate.

C. Conductivity Measurements

The conductivities of acetone solutions of di-π-cyclopentadienylcobalt perchlorate and sodium perchlorate were measured in order to determine the degree of association of their ions under the conditions of the exchange experiments. The measurements were made at 0°C. on 10^{-3}M. solutions which were prepared 25°C. During the measurements the temperature was held constant by placing the conductivity cell in a dewar filled with ice and water.

Bright platinum electrodes were chosen in order to eliminate the possibility of decomposition of the acetone in contact with platinum black. Errors due to polarization were eliminated by extrapolating the resistances measured at 5, 10, 50 and 100 Kc. to infinite frequency on a linear resistance versus reciprocal root frequency plot.

The specific conductivity of the acetone used for these experiments was less than 10^{-6} mho cm^{-1} and since the conductivities of the solutions measured were all larger by at least two orders of magnitude, the contribution of the solvent to the total conductivity was ignored. To be certain that the conductivity measured corresponded to the concentration of the sample, the cell was rinsed three times with the sample before filling and after the measurement emptied, refilled, and remeasured.

IV. CALCULATIONS AND RESULTS

A. Rates of Exchange

The general equation for an isotopic exchange reaction may be written

$$AX + BX^* \rightleftarrows AX^* + BX \qquad (1)$$

where X^* represents the radioactive isotope from the initially labeled component BX. McKay (32) has demonstrated that such an exchange can be formulated as a first order process,

$$-Rt = \frac{ab}{a+b} \ln(1-F) \qquad (2)$$

where: $F = (S-S_o)/(S_\infty - S_o)$; R is the rate of exchange; t is the time;

S, S_o, S_∞ are the specific activity, zero time specific activity and infinite time specific activity, respectively;

a, b are the component concentrations.

Harris (28) has further shown that this law is followed regardless of the exchange mechanism, the number of chemically equivalent exchangeable groups and any differences in isotopic exchange rates, as long as the concentrations are expressed in equivalents per liter.

The half time for each exchange experiment was determined by the least squares straight line for the log (1-F) versus time plot assuming no error in the time.

Worthing and Geffner (52) list the formulae for fitting a straight line of the form

$$y = mx + b \qquad (3)$$

by a weighted least squares method assuming no error in x as

$$m = \frac{\Sigma wx\,\Sigma wy \;-\; \Sigma w\,\Sigma wxy}{D} \tag{4}$$

$$b = \frac{\Sigma wx\,\Sigma wxy \;-\; \Sigma wx^2\,\Sigma wy}{D} \tag{5}$$

$$D = (\Sigma wx)^2 \;-\; \Sigma w\,\Sigma wx^2 \tag{6}$$

where x and y are the experimentally observed quantities and the subscripts for the summations have been omitted. Using the same method and notation a line required to pass through the origin

$$y = mx \tag{7}$$

is determined by

$$m = \frac{\Sigma wxy}{\Sigma wx^2} \quad . \tag{8}$$

From the law of propogations of errors, which for m is given by:

$$\sigma_m{}^2 = \sigma_{y_i}{}^2\,\Sigma\left(\frac{\partial m}{\partial y_i}\right)^2 \quad , \tag{9}$$

it may be shown that for a line of the form of equation 3,

$$\sigma_m{}^2 = \sigma_{y_i}{}^2\;\frac{(\Sigma w)^2\,\Sigma(wx)^2 + \Sigma w^2(\Sigma wx)^2 - 2\Sigma w^2x\Sigma w\Sigma wx}{D^2} \tag{10}$$

and similarly

$$\sigma_b{}^2 = \sigma_{y_i}{}^2\;\frac{(\Sigma wx^2)^2\Sigma w^2 + (\Sigma w^2x^2)^2 - 2\Sigma w^2x\Sigma wx^2\Sigma wx}{D^2} \tag{11}$$

where by definition

$$\sigma_{y_i}{}^2 = \frac{n\Sigma w(y-mx-b)^2}{(n-2)\Sigma w} \quad . \tag{12}$$

For a line of the form of equation 7 the formulae for the standard deviation can be simplified to read

$$\sigma_m^{\ 2} = \sigma_{y_i}^{\ 2} \frac{\Sigma(wx)^2}{(\Sigma wx^2)^2} \tag{13}$$

where

$$\sigma_{y_i}^{\ 2} = \frac{n}{(n-1)\Sigma w} [\ \Sigma wy^2 - \frac{(\Sigma wxy)^2}{\Sigma wx^2}\ ] \quad . \tag{14}$$

With the exception of three exchange experiments, viz. 60, 64, 65, the log (1-F) versus time plots obviously passed through the origin and were fitted with a line of the form of equation 7. The plots for experiments 60, 64, 65 were such that it was not obvious that the zero time exchange was zero and these plots were fitted with a general straight line, equation 3.

The values of (1-F) for any one experiment were considered to have approximately the same standard deviation and consequently the log (1-F) values were weighted in porportion to the reciprocal dispersion. Thus since

$$\sigma_{\log x}^{\ 2} = \frac{(\log e)^2 \sigma_x^{\ 2}}{(\log x)^2} \quad , \tag{15}$$

the weighting factors were taken proportional to $(1-F)^2$.

Since on a plot of

$$\log (1-F) = mt + b \ , \tag{16}$$

the value of log (1-F) at time zero is given by b, the half times of exchange were calculated according to the value of t when $(1-F) = \frac{1}{2}(1-F)_o$. Thus:

$$t_{\frac{1}{2}} = -\frac{.3010}{m} \tag{17}$$

$$\sigma_{t_{\frac{1}{2}}} = \left| \frac{\sigma_m}{m} \right| t_{\frac{1}{2}} \tag{18}$$

The rates of exchange were calculated from the experimental half times of exchange, $t_{\frac{1}{2}}$, according to the first order rate law, equation 2, as follows:

$$R = \frac{.693\,ab}{t_{\frac{1}{2}}(a+b)} \tag{19}$$

$$\sigma_R^{\,2} = \frac{1}{(a+b)^2}\left(\left[\frac{\sigma_a}{X}\right]^2 + [X\sigma_b]^2\right) + \left(\sigma_{t_{\frac{1}{2}}}/t_{\frac{1}{2}}\right)^2 \tag{20}$$

where X = a/b and a, b, represent the total concentrations of the exchanging components in terms of moles of cobalt per liter. For simplification in the calculation of the standard deviation of the rates of exchange, the relative standard deviation of the concentrations were taken as a constant 1 percent. Thus $\sigma_a/(a+b)$ was given the constant value of 0.5×10^{-2}.

The rates of exchange calculated as above and the conditions of the experiments are listed in Table 1. Those experiments which were not completed because of breakage of apparatus, accidental mixing of solutions before the apparatus was cooled to the reaction temperature or before the di-π-cyclopentadienylcobalt(II) was oxygenated, or entrance of water into the apparatus are not included in this table.

In Figure 5 and Figure 6 some of the log (1-F) versus time plots with straight lines fitted by least squares are shown as representative examples of the data obtained from the exchange experiments.

B. Concentrations

In non-aqueous solvents the association of strong electrolytes into ion pairs can be described by the Ostwald dilution function

$$K = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} \tag{21}$$

Table 1. Rates of exchange (at 0°C. and 100% acetone except where otherwise noted)

Series	Expt.	$t_{\frac{1}{2}}$ (min.)	Concentrations[a] $(C_5H_5)_2CoClO_4$	Concentrations[a] $(C_5H_5)_4Co_2O$	Other conditions	Rate[a] (10^{-6}M./min.)
1	25	212.2± 1.2	8.30	2.51		6.30± .04
	26	162.4± 8.9	3.52	2.57		6.33± .35
	27	121.9± 6.3	1.76	2.82		6.16± .32
	28	118.7±10.0	1.76	2.72		6.24± .53
	29	130.9± 7.4	2.64	2.48		6.77± .39
2	30	311.6± 3.3	2.85	2.68		3.07± .04
	32	353.2±20.3	2.85	2.68		2.71± .16
	33	332.3± 3.4	2.85	2.83		2.96± .04
	36	419.3±11.9	2.70	1.65		1.69± .05
	37	217.0± 4.4	2.70	5.22		5.68± .13
	39	227.5±16.2	2.78	5.37		5.58± .40
	40	128.0± 9.5	2.78	10.8		12.0 ±1.1

---

[a] Concentrations with respect to cobalt with ca. 1% standard deviation

Table 1. (Continued)

Series	Expt.	$t_{\frac{1}{2}}$ (min.)	Concentrations[a]		Other conditions	Rate[a] (10^{-6}M./min.)
			$(C_5H_5)_2CoClO_4$	$(C_5H_5)_4Co_2O$		
3	41	224.6 ± 1.2	2.78	5.40		5.66± .30
	42	387.3 ± 5.4	10.8	5.70		6.68± .12
	43	347.4 ± 1.8	8.11	5.51		6.55± .35
4	44	18.4 ± .3	2.78	5.36	20°C	68.9 ± 1.2
	45	170.3 ± 1.8	2.78	5.38		7.46± .11
	46	14.5 ± .5	2.78	5.42	78.0[b]	87.9 ± 3.2
	47	51.1 ± .5	2.78	5.36	10°C.	24.8 ± .35
	48	183.5 ± 1.7	2.78	5.24		6.86± .09
5	52	6.33± .6	2.78	5.71	130[b]	205. ±21.
	53	9.94± .04	2.78	5.77	75.2[b]	131. ± 1.5
	54	16.5 ± .1	2.78	5.82	47.0[b]	79.0 ± 1.0
	55	62.2 ± 1.5	2.78	5.80	9.39[b]	20.9 ± .55

---

[b] Concentration of sodium perchlorate added in mmol./liter

Table 1. (Continued)

Series	Expt.	$t_{\frac{1}{2}}$ (min.)	Concentrations[a]		Other conditions	Rate[a] (10^{-6}M./min.)
			$(C_5H_5)_2CoClO_4$	$(C_5H_5)_4Co_2O$		
6	56	25.0± .4	1.11	5.61	9.98[b]	25.7 ± .77
	57	59.4±3.0	2.78	5.48	8.32[b]	21.5 ±1.1
	58	121.1±1.3	5.56	5.32	5.55[b]	15.6 ± .17
	59	247.9±1.0	11.1	5.45		10.2 ± .11
7	60	125.0±1.3	2.17	5.33	94.9[c]	8.56± .14
	63	119.3±2.7	2.17	5.69	100.0[c]	9.13± .24
	64	189.8±6.6	2.17	6.16	69.7[c]	5.86± .30
	65	119.3±2.0	2.17	6.13	100.0[c]	9.30± .20
	66	229.1±8.7	2.17	6.05	50.5[c]	4.83± .20
8	67	31.7± .6	2.18	2.42	36.8[b]	25.2 ± .50
	68	48.6±2.5	4.13	2.51	34.7[b]	22.8 ±1.2
	69	53.9±1.1	6.53	2.26	32.4[b]	21.6 ± .61
	70	65.0±1.6	8.67	2.52	30.3[b]	20.8 ± .64

[c] Concentration of acetone in solvent in volume-%

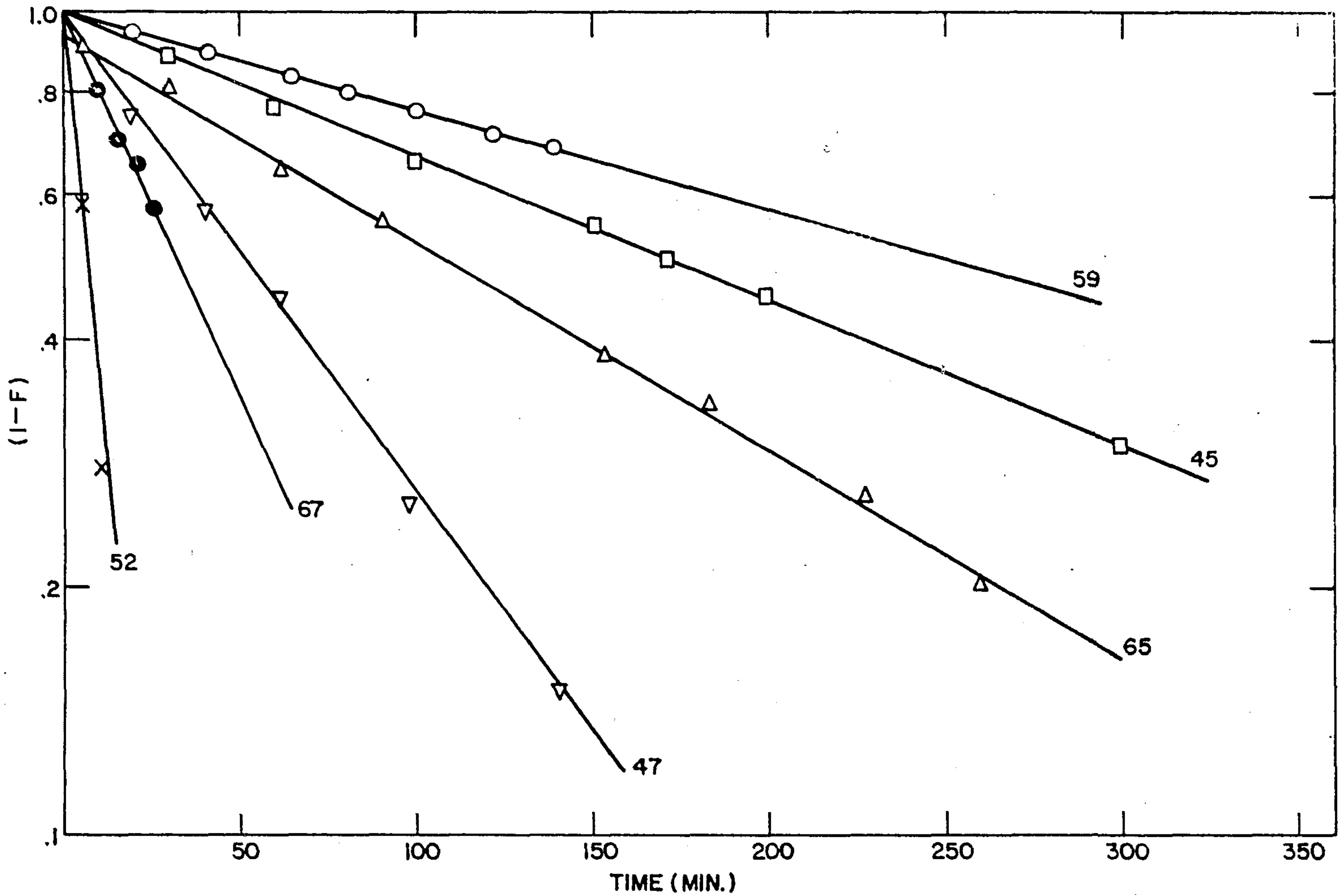


Figure 5. Examples of exchange experiment data

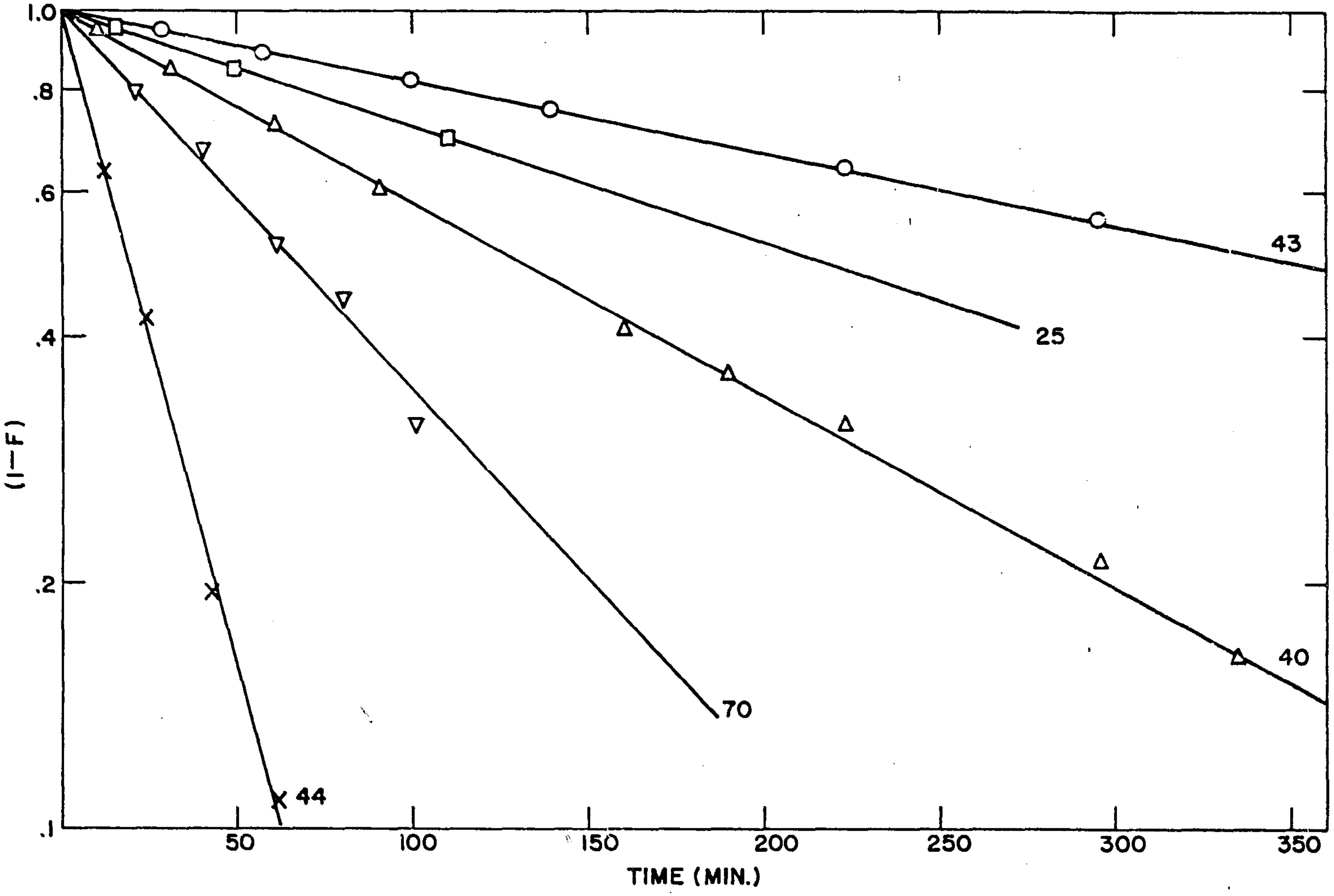


Figure 6. Examples of exchange experiment data

where K is the dissociation constant;

Λ, Λ_o are the equivalent conductivity and equivalent conductivity at infinite dilution respectively;

C is the concentration.

Although this expression is not exact, it serves as a first approximation for solutions of ion concentration about 10^{-3}M.

Harned and Owen (27, pp. 186-190) discuss various methods of improving this value of the dissociation constant by taking into account the activities of the ions and long range interionic forces. It was decided that neither the precision of the data nor the use to which it would be put justified such an improvement by successive approximation.

Since in non-aqueous solvents Λ_o can not be determined independently, both Λ_o and K must be determined from the same data. This is accomplished most conveniently by rearranging equation (21) to read

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda}{K\Lambda_o^2} \quad , \tag{22}$$

and determining $1/\Lambda_o$ and $1/K\Lambda_o^2$ as intercept and slope of the linear plot of $1/\Lambda$ versus $C\Lambda$. In Tables 2 and 3 the specific conductivities of the di-π-cyclopentadienylcobalt(III) perchlorate and sodium perchlorate solutions are given.

In Figure 7 the required functions for the di-π-cyclopentadienylcobalt(III) perchlorate and sodium perchlorate solutions are plotted. The parameters for the straight line fitted by least squares with points equally weighted are found in Table 4.

From the parameters of these lines the dissociation constants of di-π-cyclopentadienylcobalt(III) perchlorate, K_1, and of sodium

Table 2. Equivalent conductivity of di-π-cyclopentadienylcobalt(III) perchlorate in acetone at 0°C.

Concentration[a] (mmol./liter)	Λ (ml./ohm cm. equiv.)	$\frac{10^3}{\Lambda}$	$c\Lambda$ $(10^{-3}\text{ohm}^{-1}\text{cm.}^{-1})$
0.988±.020	1269. ±25.	0.788±.016	1.27±.04
2.34 ±.047	1185. ±24.	0.844±.017	2.77±.05
4.23 ±.085	1064. ±21.	0.940±.019	4.50±.13
5.46 ±.11	1015. ±20.	0.985±.020	5.54±.16
7.76 ±.16	917.5±18.4	1.090±.022	7.12±.20
10.86 ±.22	862.1±17.2	1.160±.023	9.36±.26
12.01 ±.24	844.3±16.9	1.184±.024	10.14±.29

[a] Solutions prepared at 25.0°C.

Table 3. Equivalent conductivity of sodium perchlorate in acetone at 0°C.

Concentration[a] (mmol./liter)	Λ (ml./ohm cm. equiv.)	$\frac{10^3}{\Lambda}$	$c\Lambda$ $(10^{-3}\text{ohm}^{-1}\text{cm.}^{-1})$
1.12±.022	1358. ±27.	0.736±.015	1.52±.04
2.36±.047	1255. ±25.	0.797±.016	2.96±.08
3.59±.072	1164. ±23.	0.859±.017	4.18±.12
5.96±.12	1094. ±22.	0.914±.018	6.52±.18
8.17±.16	1030. ±21.	0.971±.019	8.42±.24
10.37±.21	1029. ±21.	0.972±.019	10.66±.30
11.96±.24	975.8±20.	1.025±.020	11.67±.33
17.30±.35	895.4±18.	1.117±.022	15.49±.44

[a] Solutions prepared at 25.0°C.

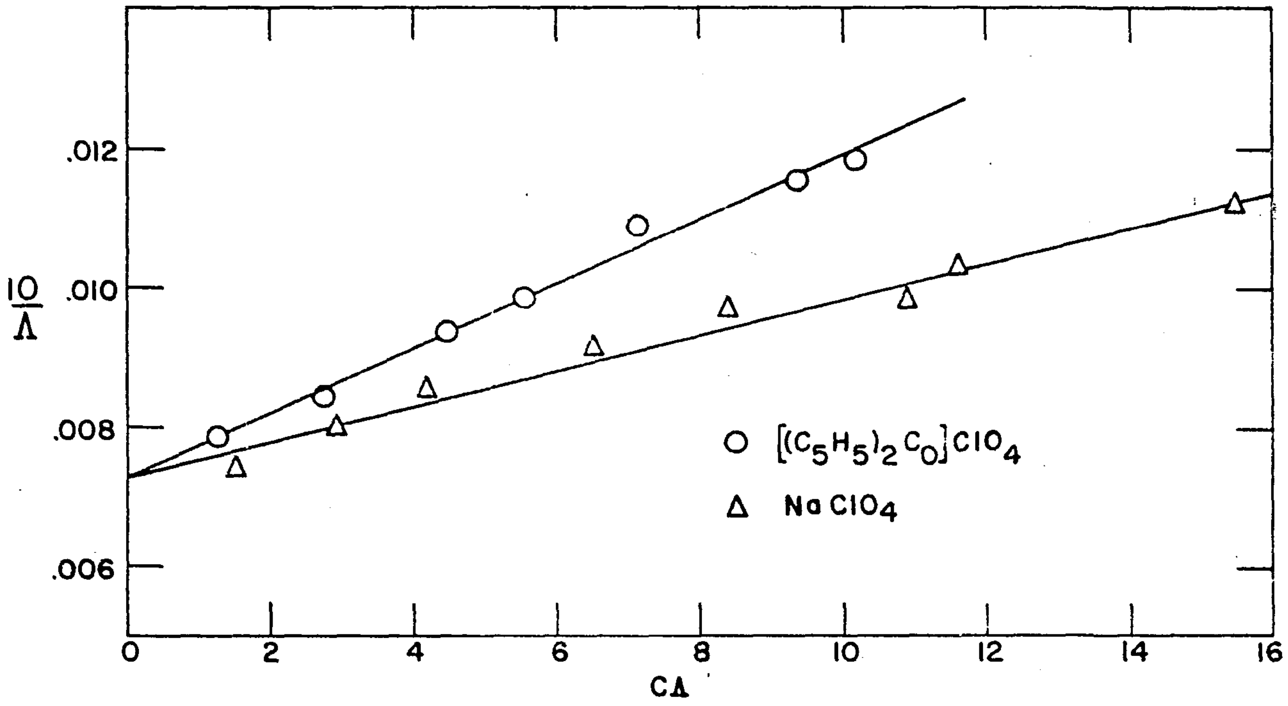


Figure 7. Conductivities of $NaClO_4$ and $(C_5H_5)_2CoClO_4$ in acetone

Table 4. Parameters of the equation for equivalent conductivities

Compound	Slope (ohm^{2}cm.^{2} equiv. ml.$^{-1}$)	Intercept (ohm cm. equiv. ml.$^{-1}$)
$(C_5H_5)_2CoClO_4$	$(4.64\pm .53)\times 10^{-2}$	$(7.29\pm .05)\times 10^{-4}$
$NaClO_4$	$(2.55\pm .59)\times 10^{-2}$	$(7.28\pm .06)\times 10^{-4}$

perchlorate, K_2, in acetone at 0°C. were found to be:

$$K_1 = (1.15\pm .15)\ 10^{-2}M. \tag{23}$$

$$K_2 = (2.08\pm .48)\ 10^{-2}M. \tag{24}$$

The concentrations of dissociated di-π-cyclopentadienylcobalt(III) cation and perchlorate anion were calculated using these dissociation constants and are listed in Table 5.

Table 5. Concentrations of dissociated ionic species

Experiment	Concentrations (10^{-3}M.)	
	$[(C_5H_5)_2Co^+]$	$[ClO_4^-]$
25	5.58	5.58
26	2.82	2.82
27,28	1.55	1.55
29	2.22	2.22
30,32,33	2.72	2.72
36,37	2.26	2.26

Table 5. (Continued)

Experiment	Concentrations (10^{-3}M.) $[(C_5H_5)_2Co^+]$	 $[ClO_4]$
39,40,41,45,46,48	2.32	2.32
42	6.78	6.78
43	5.48	5.48
52	.585	43.0
53	.751	31.0
54	.920	23.2
55	1.61	8.30
56	.657	7.90
57	1.66	7.73
58	3.37	7.46
59	6.92	6.92
63	1.86	1.86
67	.801	19.7
68	1.60	19.5
69	2.44	19.3
70	3.25	19.1

C. Concentration Effects

The effect of the oxygen compound on the exchange reaction was studied by varying the concentration from 10^{-2} to 10^{-3} equiv./liter holding other variables constant. The data for these experiments are presented in Table 6. The log rate versus log concentration plot, Figure 8, has a slope of unity indicating that the exchange between the oxygen compound and the di-π-cyclopentadienylcobalt(III) cation is first order with respect to the concentration of the oxygen compound.

Table 6. Rate of exchange as a function of the concentration of the oxygen compound

Experiment	Concentration[a, b] (10^{-3}M.)	Rate (10^{-6}M./min.)
30	2.68	3.07± .033
32	2.68	2.71± .16
33	2.83	2.96± .031
36	1.65	1.69± .048
37	5.22	5.68± .11
39	5.37	5.58± .40
40	10.8	11.97±1.14
41	5.40	5.66± .30

[a] Relative error about one percent

[b] $[(C_5H_5)_2CoClO_4] = (2.46\pm.06)\ 10^{-3}$M.

The effect of di-π-cyclopentadienylcobalt(III) perchlorate on the exchange reaction was studied by observing the rate of exchange of various concentrations of that component with a constant concentration

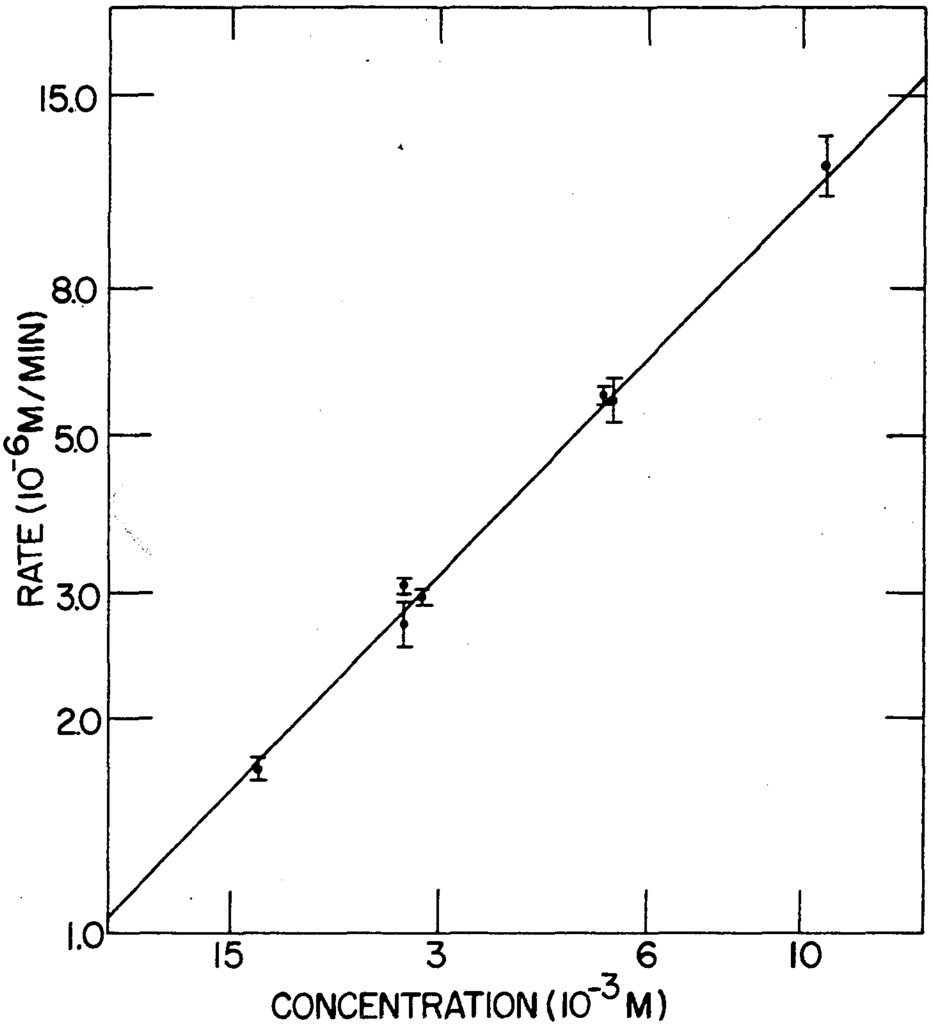


Figure 8. Effect of oxygen compound on exchange reaction

of the oxygen compound. The results are given in Table 7.

Table 7. Rate of exchange as a function of di-π-cyclopentadienylcobalt perchlorate concentration

Experiment	Concentration[a, b] $(C_5H_5)_2CoClO_4$ (10^{-3}M.)	Rate (10^{-6}M./min.)
25	8.30	6.30±.04
26	3.52	6.34±.35
27	1.76	6.16±.32
28	1.76	6.24±.53
29	2.64	6.77±.39

[a] Relative error about 1 percent

[b] $[(C_5H_5)_4Co_2O] = (2.62\pm.13) \times 10^{-3}$M.

The plot log rate versus concentration, Figure 9, shows a slope very close to or equal to zero. Thus di-π-cyclopentadienylcobalt(III) perchlorate has little or no net effect on the rate of exchange, at least as long as the concentrations of the di-π-cyclopentadienylcobalt(III) cation and the perchlorate anion are equal.

In order to determine if the approximately zero order result from Figure 9 was due to the cancellation of an ionic strength effect with a di-π-cyclopentadienylcobalt(III) cation effect, a series of experiments was carried out at constant ionic strength. Sodium perchlorate was added so that the dissociated perchlorate concentration, which in this

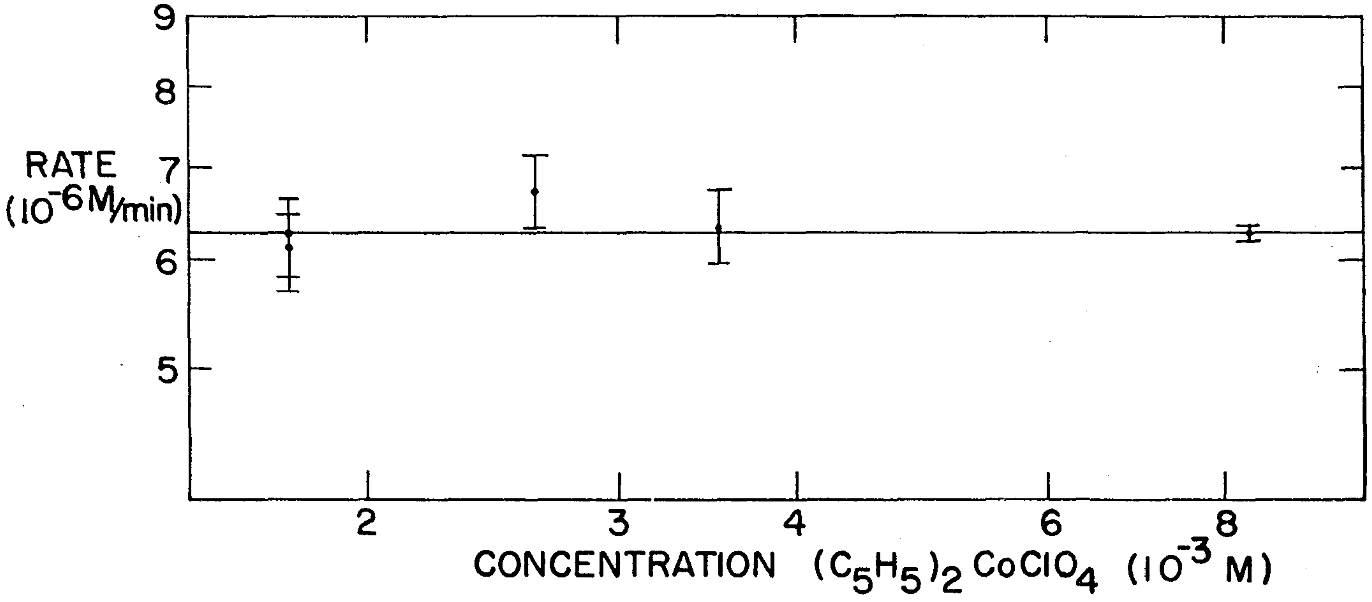


Figure 9. Effect of di-π-cyclopentadienyl(III) perchlorate on exchange reaction

case is equal to the ionic strength, would be constant. The results are presented in Table 8.

Table 8. Rate of exchange as a function of di-π-cyclopentadienylcobalt cation concentration

Experiment	Concentration[a, b] $[(C_5H_5)_2Co^+]$ (10^{-3}M.)	Rate (10^{-6}M./min.)
67	0.801	25.2± .50
68	1.60	22.8±1.2
69	2.44	21.6± .61
70	3.25	20.8± .64

[a] $[ClO_4^-]$ = (19.4±.2) x 10^{-3}M. = ionic strength

[b] $[(C_5H_5)_4Co_2O]$ = (2.43±.10) x 10^{-3}M.

The data in Table 8 are shown graphically in Figure 10. This plot with slope equal to -.14 indicates the possibility of the di-π-cyclopentadienylcobalt(III) cation having a small depressing effect on the rate of exchange.

The effect of ionic strength on the exchange reaction was studied by adding various amounts of sodium perchlorate. Although the di-π-cyclopentadienylcobalt(III) cation concentration thereby varied the effect of the latter was known and the rates of exchange were adjusted correspondingly according to

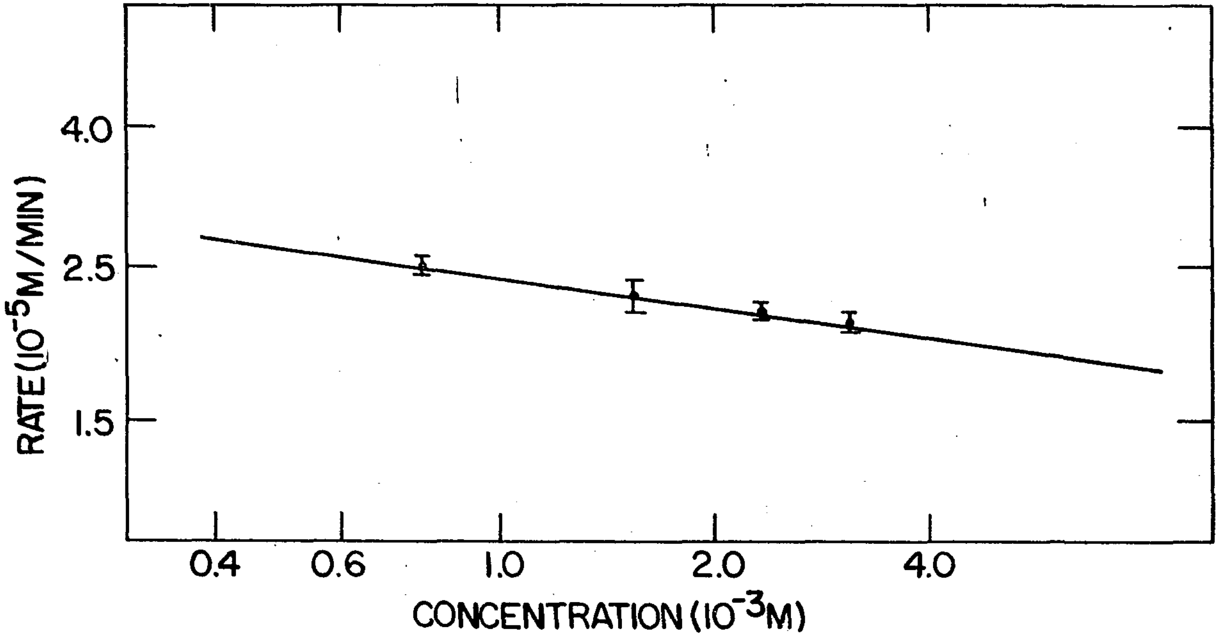


Figure 10. Effect of di-π-cyclopentadienylcobalt(III) cation at constant ionic strength on exchange reaction

$$R = [(C_5H_5)_2Co]^{-.14} \quad . \tag{25}$$

The rates of exchange observed in these experiments are listed in Table 9.

Table 9. Rate of exchange as a function of ionic strength

Experiment	Concentrations[a] $(10^{-3}M.)$		Rate	Corr. rate[b]
	$[(C_5H_5)_2Co^+]$	μ	$(10^{-6}M./min.)$	$(10^{-6}M./min.)$
52	.585	42.3	205. ±20.	190. ±20.
53	.751	31.0	131. ± 1.5	126. ± 2.0
54	.920	23.2	79.0± 1.0	78.0± 1.4
55	1.61	8.33	20.9± .55	22.4± .69
56	.657	7.90	25.7± .77	24.2± 1.0
57	1.66	7.73	21.5± 1.1	23.0± 1.8
58	3.37	7.46	15.6± .17	18.6± .29
59	6.92	6.92	10.2± .11	13.4± .21

[a] $[(C_5H_5)_4Co_2O] = (5.64 \pm .19)10^{-3}M.$

[b] Calculated to $[(C_5H_5)_2Co^+] = (1.00 \times 10^{-3})M.$ according to $R \alpha [(C_5H_5)_2Co^+]^{-.14}$

The data in Table 9 show a definite strong curvature when either rate or corrected rate are plotted versus ionic strength or versus the square root of ionic strength. A plot of log rate versus log ionic strength, Figure 11, however, gives a straight line. This unexpected form for the relation between ionic strength and the rate of exchange strongly

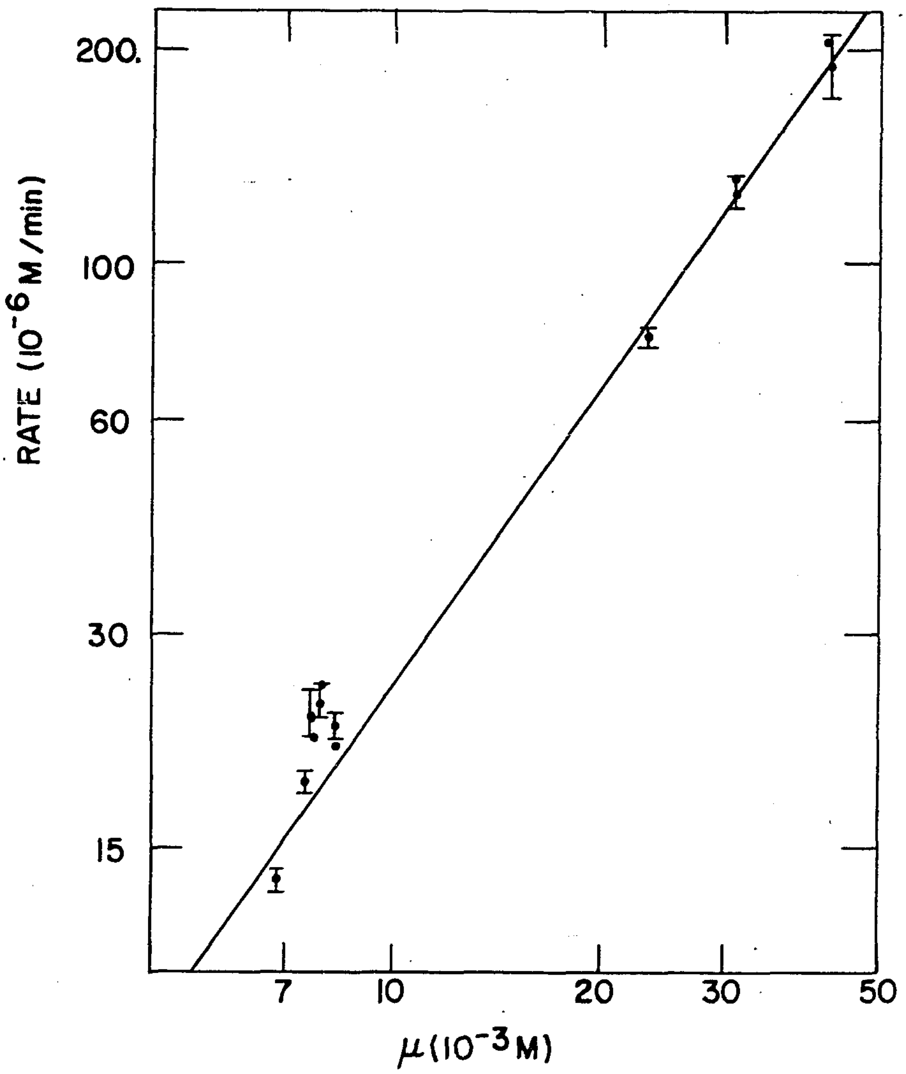


Figure 11. Effect of ionic strength on exchange reaction

suggests a quite direct action of the ions in the exchange process.

D. Solvent and Temperature Effects

The rates of exchange of di-π-cyclopentadienylcobalt(III) with the oxygen compound in mixtures of n-decane and acetone are presented in Table 10.

Table 10. Rate of exchange in acetone-decane mixtures

Experiment	Acetone Concentration (vol.-%)	(M.)	Rate[a] (10^{-6}M./min.)
60	94.9	12.9	8.56±.14
63	100.0	13.6	9.13±.24
64	69.7	9.05	5.86±.34
65	100.0	13.6	9.30±.20
66	50.5	6.87	4.83±.20

[a] $[(C_5H_5)_2CoClO_4] = 2.17 \times 10^{-3}$M.; $[(C_5H_5)_4Co_2O] = 5.87 \times 10^{-3}$M.

These data, plotted in Figure 12, show a strong depression of the rate with increasing dilution of acetone with n-decane. This depression indicates the formation of an ionic species, the stability of which is increased by solvation with acetone.

In order to determine the activation energy of the exchange reaction, experiments were carried out at several temperatures. The results of these experiments are listed in Table 11. The slope of the lnR versus 1/T plot, Figure 13, as determined by least squares with

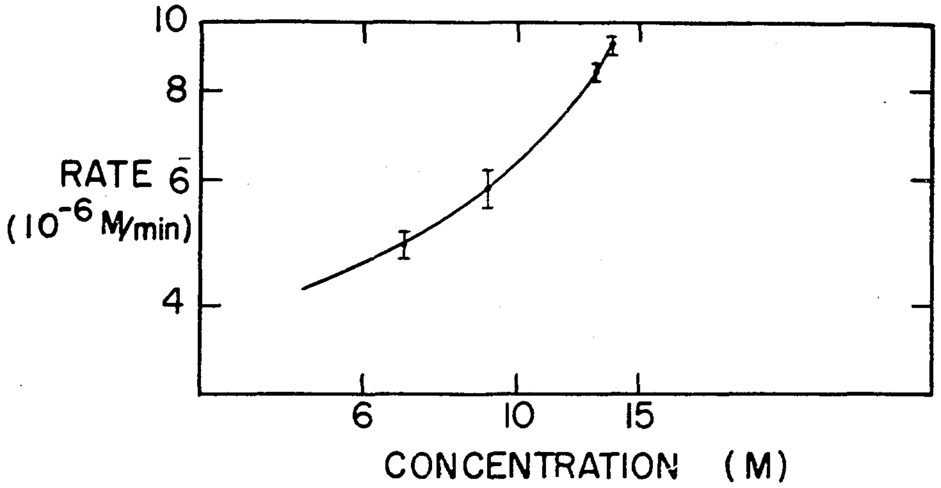


Figure 12. Effect of dilution of solvent with n-decane on exchange reaction

Table 11. Temperature dependence

Experiment	Temperature (°C.)	Rate[a] (10^{-6}M./min.)
44	20.0 ±.1	68.9 ±1.2
45	0.00±.1	7.46± .11
47	10.0 ±.1	24.8 ± .35
48	0.00±.1	7.00± .10[b]

[a] $[(C_5H_5)_2CoClO_4]$ = 2.78x10^{-3}M.±1%; $[(C_5H_5)_4Co_2O]$ = 5.36x 10^{-3}M.±1%

[b] Rate calculated to that at $[(C_5H_5)_4Co_2O]$ = 5.36 from 5.24 assuming rate proportional to $[(C_5H_5)_4Co_2O]$

equally weighted points is (-9.07±.01)10^3 °K^{-1}. This corresponds to an activation energy of 18.0±.2 Kcal./mol. °K.

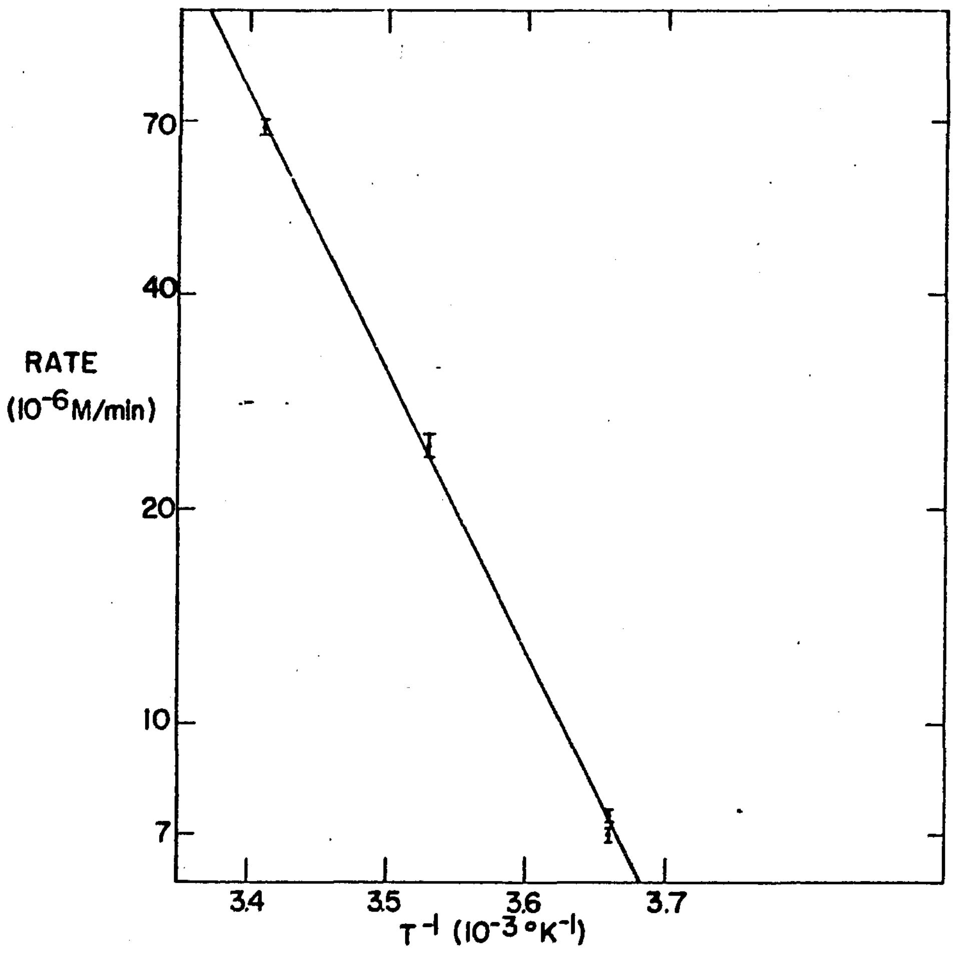


Figure 13. Effect of temperature on exchange reaction

V. DISCUSSION

A. Interpretation of Results

In the exchange reaction between di-π-cyclopentadienylcobalt(III) perchlorate and the oxygen compound formed from di-π-cyclopentadienylcobalt(II) a first order dependence on the concentration of the oxygen compound is clearly evident, cf. Figure 8. The effect of the other component in the exchange is, however, not immediately obvious.

At a constant concentration of the oxygen compound a zero or nearly zero order dependence of di-π-cyclopentadienylcobalt(III) perchlorate is indicated by Figure 9. This means that either the rate of exchange is independent of the concentration of the di-π-cyclopentadienylcobalt(III) cation and ionic strength, or that the rate is dependent on both in opposing directions such that the net effect is zero.

Exchange experiments at constant ionic strength and varying di-π-cyclopentadienylcobalt(III) ion concentration, cf. Figure 10, indicate, however, only a small negative effect on the rate by the di-π-cyclopentadienylcobalt(III) cation. The effect of ionic strength for di-π-cyclopentadienylcobalt(III) perchlorate must then be small.

If the ionic strength is varied by adding sodium perchlorate in amounts 10 to 100-fold greater than the di-π-cyclopentadienylcobalt(III) perchlorate present, a very strong ionic strength effect is observed, cf. Figure 11. This is taken to mean that the ionic strength effect for sodium perchlorate is large, but the ionic strength effect for di-π-cyclopentadienylcobalt(III) perchlorate is very small.

Furthermore, the sodium perchlorate ionic strength effect is not of the form expected for ions which effect the rate merely by changing the electronic environment of the reacting species. The ionic strength effect is also larger than usually observed, cf. doubling the rate by increasing the ionic strength by less than two-fold. This unusual effect of sodium perchlorate was taken to indicate a direct action of sodium perchlorate in the exchange reaction.

The results of the experiments with added sodium perchlorate are listed in Table 12 and additional plots of the data shown in Figures 14 and 15. These plots show that the total amount of sodium perchlorate added affects the rate of exchange in a manner expected for a directly involved species. It appears also that the effect of sodium ions and sodium perchlorate ion pairs is about the same.

Thus the small decrease in rate of exchange in Figure 10 is due not to a depressing effect of di-π-cyclopentadienylcobalt(III) ion concentration, but rather to the decreasing amounts of sodium perchlorate added.

The above analysis indicates a rate law of the form,

$$R = [(C_5H_5)_4Co_2O]\ (k_1 + k_2[Na^+] + k_3[Na^+ClO_4^-])\ . \qquad (25)$$

The relative effect of sodium ions and sodium perchlorate ion pairs can be determined by rearranging equation 25 to read:

$$\frac{\frac{R}{[(C_5H_5)_4Co_2O]} - k_1}{[Na^+]} = k_2 + k_3\frac{[Na^+ClO_4^-]}{[Na^+]}\ . \qquad (27)$$

The first term in equation 27, k_1, is due to the rate of exchange in the absence of any added sodium perchlorate and can be evaluated from those experiments in which the exchange between the oxygen compound and di-π-cyclopentadienylcobalt(III) perchlorate in pure acetone was

Table 12. Rate of exchange as a function of total sodium perchlorate added

Experiment	Rate (10^{-6}M./min.)	Concentrations added (10^{-3}M.) $(C_5H_5)_4Co_2O$	$(C_5H_5)_2CoClO_4$	$NaClO_4$
39	5.59	5.37	2.78	0.00
41	5.66	5.40	2.78	0.00
42	6.68	5.70	10.8	0.00
43	6.55	5.51	8.11	0.00
45	7.46	5.38	2.78	0.00
48	6.86	5.24	2.78	0.00
52	205.	5.71	2.78	130.
53	131.	5.77	2.78	75.2
54	79.0	5.82	2.78	47.0
55	20.9	5.80	2.78	9.39
56	25.7	5.61	1.11	9.98
57	21.5	5.48	2.78	8.32
58	15.6	5.32	5.56	5.55
59	10.2	5.45	11.1	0.00
63	9.13	5.69	2.17	0.00
67	25.2	2.42	2.18	36.8
68	22.8	2.51	4.13	34.7
69	21.6	2.26	6.53	32.4
70	20.8	2.52	8.67	30.3

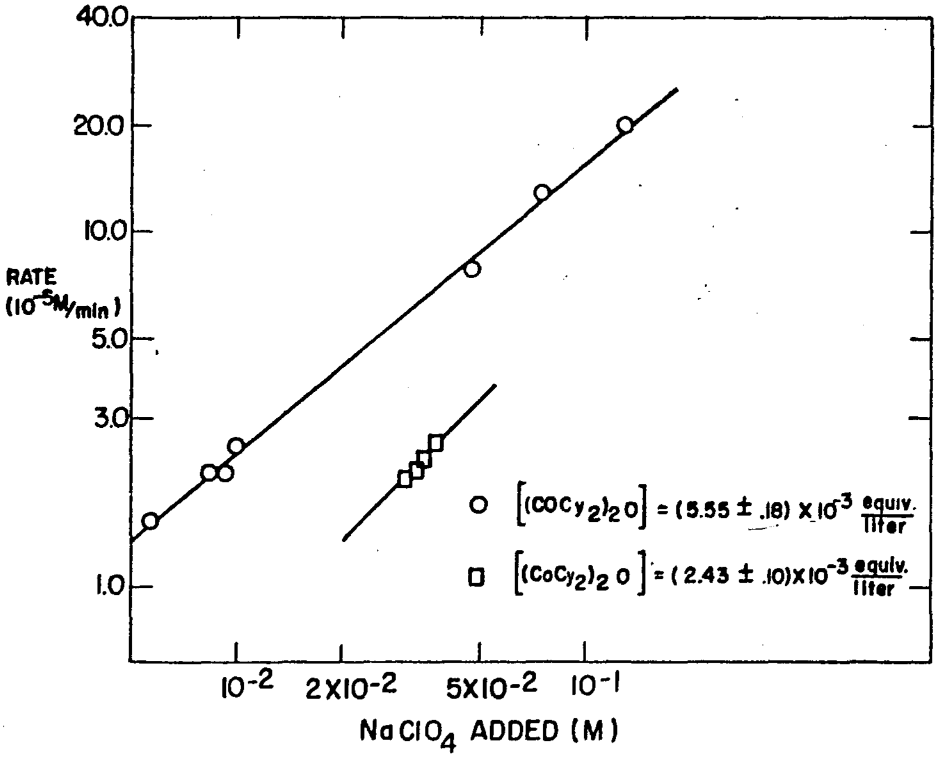


Figure 14. Plot of log rate versus log sodium perchlorate added

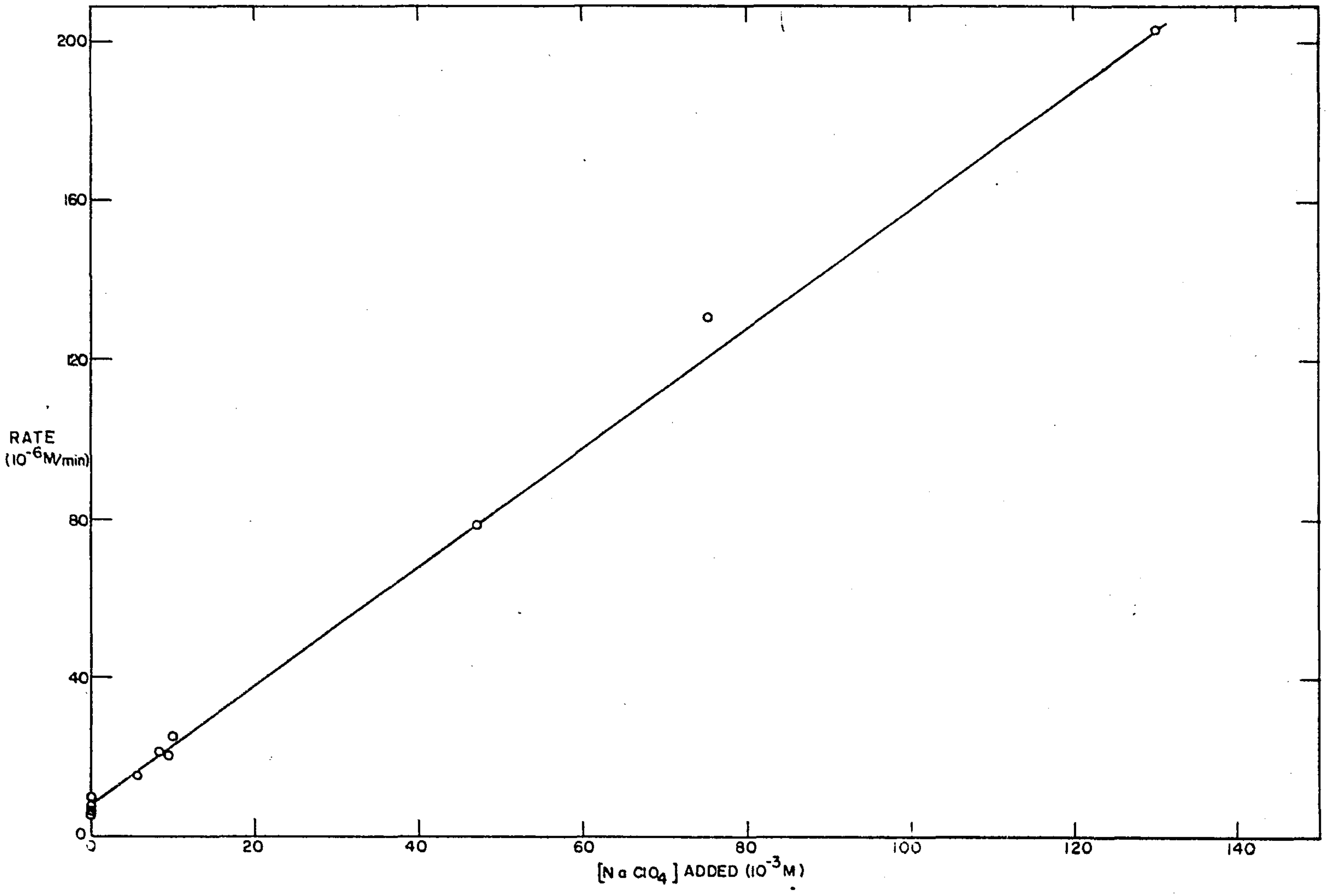


Figure 15. Plot of rate versus sodium perchlorate added

followed at 0°C. These data are given in Table 13. As can be seen the

Table 13. Rate constants for exchange in pure acetone at 0°C in the absence of sodium perchlorate

Series	Experiment	$[(C_5H_5)_4Co_2O]$	Rate	k_1
1	25	2.51	6.30	2.52
	26	2.57	6.33	2.46
	27	2.82	6.15	2.18
	28	2.72	6.24	2.29
	29	2.48	6.77	2.73
2	30	2.68	3.07	1.14
	32	2.68	2.71	1.01
	33	2.83	2.96	1.05
	36	1.65	1.69	1.02
	37	5.22	5.68	1.09
	39	5.37	5.58	1.04
	40	10.8	12.0	1.11
3	41	5.40	5.66	1.05
	42	5.70	6.68	1.17
	43	5.51	6.55	1.19
4	45	5.38	7.46	1.39
	48	5.24	6.86	1.31

value of k_1 is relatively constant in the experiments in series two and three, but that a different value is found for those experiments in series one and four. This difference is probably due to either impure acetone or the presence of foreign ions in these experiments.

The average value for series two and three was taken as the most probable value for k_1. Using this value, $k_1 = (1.09 \pm .06) \times 10^{-3}/\text{min.}$, the appropriate functions for equation 27 are listed in Table 14 and plotted in Figure 16. The least squares straight line of this plot has a slope of 0.234±.039 and intercept of 0.306±.041. This indicates that in equation 27, $k_2 = (0.31 \pm .04)\text{M.}^{-1}\text{min.}^{-1}$ and $k_3 = 0.23 \pm .04\ \text{M.}^{-1}\text{min.}^{-1}$.

B. Mechanism of the Exchange

As seen from Figure 12, the rate of exchange decreases with increasing dilution of solvent with n-decane. This dilution of acetone with n-decane not only decreases the concentration of acetone but also decreases the dielectric constant. A rate determining step involving the separation of an activated complex or solvated molecule into ions is consistent with this observation, since both ionization as well as solvation would be expected to decrease with acetone concentration and dielectric constant.

The basic exchange reaction of the oxygen compound with di-π-cyclopentadienylcobalt(III) is thus viewed as follows:

$$(C_5H_5)_4Co_2O + \text{solvent} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} (C_5H_5)_4Co_2O_{(\text{solvated})} \qquad (28)$$

$$(C_5H_5)_4Co_2O_{(\text{solvated})} \overset{\text{slow}}{\rightleftharpoons} [(C_5H_5)_2Co^{+}]_{(\text{solvated})}(C_5H_5)_2CoO^{-}_{(\text{solvated})} \qquad (29)$$

The accelerating effect of sodium perchlorate can be viewed as the contribution of an alternate path, in which solvation is probably also a contributing factor:

Table 14. Rate as a function of sodium ion and sodium perchlorate ion pair concentrations

Experiment	$\frac{R}{[(C_5H_5)_4Co_2O]}$ $(10^{-3}/min.)$	$[Na^+]$ $(10^{-3}M.)$	Y^a $(M.^{-1}min.^{-1})$	$\frac{[Na^+ClO_4^-]}{[Na^+]}$
52	35.9	42.4	.821	2.07
53	22.7	30.2	.715	1.49
54	13.6	22.2	.563	1.11
55	3.60	6.69	.294	.403
56	4.58	7.24	.482	.379
57	3.92	6.07	.466	.370
58	2.93	4.09	.450	.357
67	10.4	18.9	.493	.943
68	9.08	17.9	.446	.935
69	9.56	16.8	.504	.926
70	8.25	15.8	.453	.917

$$^{a}Y = \frac{\frac{R}{[(C_5H_5)_4Co_2O]} - k_1}{[Na^+]}$$

$$(C_5H_5)_4Co_2O + Na^+ \xrightleftharpoons{\text{fast}} (C_5H_5)_4Co_2O\cdots\cdot Na^+ \qquad (30)$$

followed by

$$(C_5H_5)_4Co_2O\cdots\cdot Na^+ \xrightleftharpoons{\text{slow}} (C_5H_5)_2Co^+ + (C_5H_5)_2CoO^-Na^+$$

or possibly the contribution of a displacement reaction with sodium:

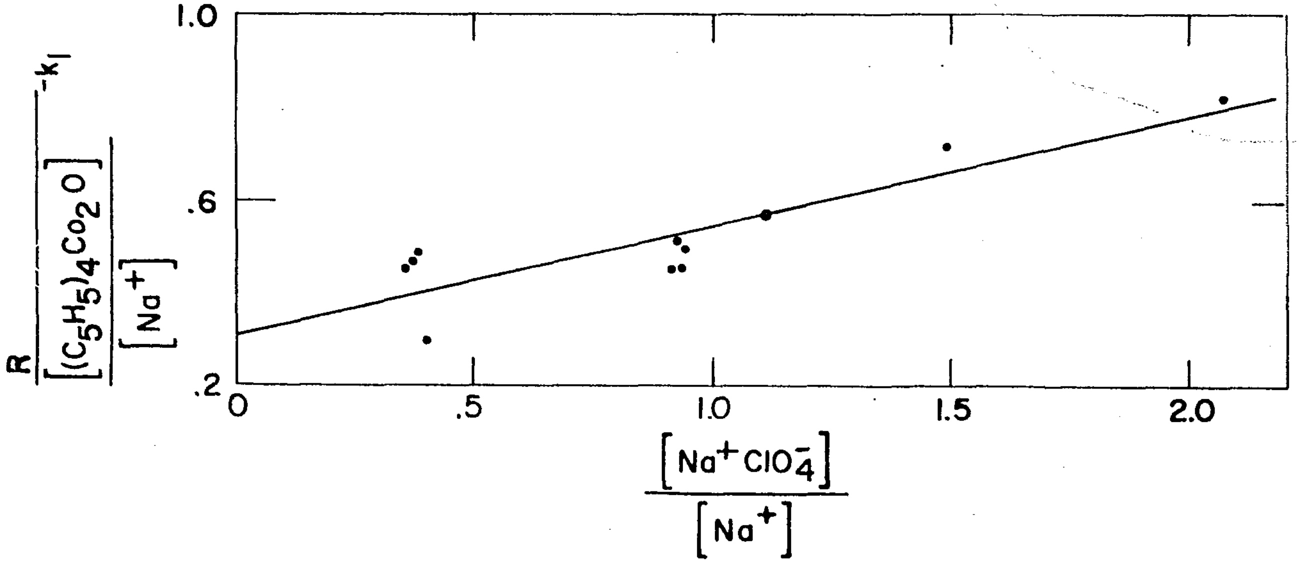


Figure 16. Rate of exchange as a function of sodium ion and sodium perchlorate ion pair concentrations

$$(C_5H_5)_4Co_2O + Na^+ \xrightleftharpoons{\text{slow}} (C_5H_5)_2Co^+ + (C_5H_5)_2CoO^- \, Na^+ \quad (31)$$

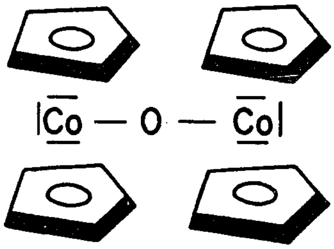
The strong contribution by sodium ions or sodium perchlorate ion pairs and the small effect of di-π-cyclopentadienylcobalt(III) perchlorate is explained by the relative sizes of the species. The sodium ion with smaller size and larger charge density would be expected to interact much more strongly.

C. Bonding and Exchange

Di-π-cyclopentadienylcobalt(II) with one unpaired electron readily reacts with carbon tetrachloride and oxygen to form a trichloromethyl compound and an oxygen compound respectively. The trichloromethyl derivative has been isolated and characterized as a π-cyclopentadienylcobalt trichloromethylcyclopentadiene complex. Attempts to remove the solvent from the oxygen compound have lead to its destruction. For this reason the determination of the structure by isolation and x-ray, infrared, or nuclear magnetic resonance analysis is eliminated.

Whereas labeled di-π-cyclopentadienylcobalt(III) does not exchange with the trichloromethylcompound, it does exchange with the oxygen compound. The latter proceeds by the ionization of the oxygen compound into two ions one of which is either indistinguishable from or rapidly exchanges with the labeled di-π-cyclopentadienylcobalt(III) ion.

Possible structures for the oxygen compound are schematically presented in Figure 17. Structure I involves cobalt-oxygen bonding whereas structure II involves carbon-oxygen bonding. In structure I all four rings retain the full symmetry of the π-bonded metal-ring systems, but in structure II two of the rings are bonded to the metal



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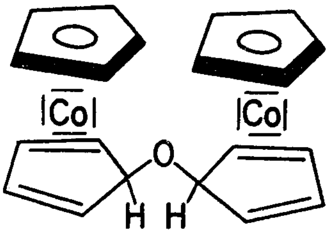

II

Figure 17. Possible structures of oxygen compound

by only dative π-bonds of the type found in the trichloromethyl compound.

Although the ionization of structure II seems highly unlikely, if it did occur, it would lead to a cation of structure different from the labeled di-π-cyclopentadienylcobalt(III). This would necessitate a structural rearrangement to the much more stable di-π-cyclopentadienylcobalt(III) structure and the reverse rearrangement in order to explain the exchange. The reverse rearrangement seems improbable. It is even more improbable that the cation from structure II exchanges with the di-π-cyclopentadienylcobalt(III) cation, without any rearrangement, as this would involve two double electron transfers.

It is much simpler and more reasonable to assume that the oxygen compound is of the structure I, and the ionization leads to a cation indistinguishable from the labeled di-π-cyclopentadienylcobalt(III) cation. Therefore, it is felt that in this case the great difference in exchangeability of the trichloromethyl compound and the oxygen compound is due to the different structures.

VI. SUMMARY

Di-π-cyclopentadienylcobalt(II) has been found to react with oxygen in water-free acetone solution to form an oxygen compound of stoichiometry, $(C_5H_5)_4Co_2O$. Using di-π-cyclopentadienylcobalt(III) perchlorate labeled with cobalt-60, the exchange reaction of this species with the oxygen compound was studied.

The rate of exchange of the labeled di-π-cyclopentadienylcobalt(III) cation with the oxygen compound in c. 10^{-3}M. solutions at 0°C was found to be approximately zero order with respect to the former and first order with respect to the latter. The concentration of the dissociated ions of di-π-cyclopentadienylcobalt(III) perchlorate did not strongly affect the rate of exchange, i.e. less than 10 percent increase in rate by increasing the concentration by a factor of four.

The addition of sodium perchlorate in amounts from 10^{-3}M. to 10^{-1}M. was found to strongly accelerate the rate of exchange, approximately doubling the rate by doubling the concentration. The effect of dissociated sodium ions and sodium perchlorate ion pairs was found to be equal within experimental error. Dilution of the solvent with n-decane depressed the rate of exchange, and in the region 0-20°C. the activation energy for the exchange reaction in pure acetone was found to be 18.0±0.2 Kcal./mol. °K.

Consistent with the observed rates of exchange is the following expression:

$$R = [(C_5H_5)_4Co_2O] \ (k_1 + k_2[Na^+] + k_3[Na^+ClO_4^-]) \ ,$$

where $k_1 = (1.09 \pm .06) \times 10^{-3}$/min.

$k_2 = (0.31 \pm .04)$ M.$^{-1}$min.$^{-1}$

$k_3 = (0.23 \pm .04)$ M.$^{-1}$min.$^{-1}$

The proposed mechanism of the exchange process is the dissociation of the oxygen compound into two ions one of which is either indistinguishable from or rapidly exchanges with the di-π-cyclopentadienylcobalt(III) cation. The strong acceleration of the rate of exchange by sodium ions and sodium perchlorate ion pairs is suggested to be due to a strong interaction with the oxygen compound, either by a displacement reaction, or an association similar to solvation which aids in the ionization. The lack of acceleration by the di-π-cyclopentadienylcobalt(III) cation is viewed as due to the relatively large size and low charge density of this ion as compared to the sodium ion.

Further investigations with added large ions, e.g. tetrabutylammonium, and small ions, e.g. lithium, would determine if the proposed suggestion for the acceleration of the exchange by small ions, such as sodium , is correct.

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VIII. ACKNOWLEDGMENTS

The author wishes to thank the many people who have aided in this research, especially Dr. Adolf F. Voigt for his counsel and encouragement during the course of the investigation.