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Exchange Reactions of Cyclopentadienyl Cobalt Compounds[1]

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Exchange reactions have been studied between bis-(cyclopentadienyl)-cobalt compounds in anhydrous acetone solution. No exchange occurs between $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ and Co^{++}. Exchange between $Co^{II}(\pi\text{-}C_5H_5)_2$ and $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ is instantaneous. Minute traces of oxygen cause oxidation of the former to a derivative with two molecules of $Co(C_5H_5)_2$ per oxygen atom which undergoes slow exchange with $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$, probably by an ionization mechanism. A trichloromethyl derivative formed by reaction between $Co^{II}(C_5H_5)_2$ and CCl_4 does not exchange Co with $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ or Cl^- with LiCl.

Although a large number of π-bonded organometallic compounds have been prepared and investigated since the discovery of bis-(cyclopentadienyl)-iron (ferrocene),[3] relatively few studies of isotopic exchange have been conducted on these materials.[4,5] It was of interest, therefore, to investigate in some detail the exchange reactions of a family of π-bonded cyclopentadienyl compounds. Since the bis-cyclopentadienyl derivatives of cobalt exist in two oxidation states, $Co^{II}(\pi\text{-}C_5H_5)_2$ and $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$, it was felt that a study of their exchange reactions might yield some interesting information about their nature. Exchange between these two species was studied, and the effect of traces of oxygen on the nature of the exchange reaction was investigated in some detail. The exchange between the cobalticinium[6] and Co^{++} ions also was studied. During the course of the work a trichloromethyl derivative of cobaltocene was prepared. It was described previously[7] and has been characterized by Green, Pratt, and Wilkinson[8] as $Co(\pi\text{-}C_5H_5)(1\text{-}CCl_3\cdot C_5H_5)$. Processes involving exchange of cobalt between this compound and the cobalticinium ion and exchange of chloride between it and the free chloride ion were investigated.

Experimental

Materials. —The sodium tetraphenylborate employed in this study was Baker Analytical Grade. The *n*-decane was Phillips Petroleum Company Pure Grade, used without further purification.

Acetone was purified by adding in succession 30 ml. of 1.1 *M* $AgNO_3$ and 30 ml. of 1 *M* NaOH to 1 l. of Mallinckrodt Analytical Grade acetone. The mixture was agitated for 15 min. and filtered. The acetone was dried over $CaSO_4$ and distilled over fresh $CaSO_4$, only the middle one-third portion being retained for experimental use. It was deaerated by bubbling dry, oxygen-free helium through boiling acetone for 30 min.

Labeled LiCl was prepared by adding 0.3 g. of LiCl to a dilute HCl solution containing approximately 0.5 μcuries of Cl^{36} (Oak Ridge National Laboratory). The water was evaporated and the LiCl was dried at 120° for 24 hr.

Labeled $Co(ClO_4)_2$ was prepared by adding a 0.1 *M* HCl solution containing 500 μcuries of Co^{60} (Oak Ridge National Labratory) to 50 g. of $CoCl_2\cdot 6H_2O$ in 50 ml. of water. Cobalt(II) hydroxide was precipitated under a helium atmosphere with 0.03 *M* NaOH, separated by centrifugation, and dissolved by the dropwise addition of 0.03 *M* $HClO_4$. The precipitation and dissolution were repeated until a negative test for chloride was obtained with $AgNO_3$.

$Co(\pi\text{-}C_2H_5)_2$ was prepared by literature methods.[4]

$Co(\pi\text{-}C_5H_5)_2ClO_4$ was prepared by agitating a benzene solution of cobaltocene, $Co(\pi\text{-}C_5H_5)_2$, and an aqueous 0.01 *M* $HClO_4$ solution in air for 15 min. The aqueous phase was washed several times with benzene, heated with activated charcoal, filtered, and concentrated by evaporation. The yellow crystals of $Co(\pi\text{-}C_5H_5)_2ClO_4$ which were formed on cooling the solution to 0° were recrystallized several times from water.

The composition of the crystals was determined by a procedure developed on the basis of the observation by Fischer and Jira[9] that precipitation of $[Co(C_5H_5)_2][B$

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[2] Correspondence should be addressed to this author.

[3] G. Wilkinson and F. A. Cotton, *Prog. Inorg. Chem.*, **1**, 1–124 (1959).

[4] G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

[5] N. Sutin and R. W. Dodson, *ibid.*, **6**, 91 (1958).

[6] The trivial name "cobaltocene" is quite widely used for the compound $Co(\pi\text{-}C_5H_5)_2$ in analogy with "ferrocene." The name "cobalticinium" also has been used for the ion of trivalent cobalt, $[Co(\pi\text{-}C_5H_5)_2]^+$ and is so used in this paper. See, for example, E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 71 (1959).

[7] S. Katz, J. F. Weiher, and A. F. Voigt, *J. Am. Chem. Soc.*, **80**, 6459 (1958).

[8] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

[9] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8B**, 1 (1953).

$(C_6H_5)_4]$ could be used as a quantitative method for the determination of the $[Co(\pi\text{-}C_5H_5)_2]^+$ cation. The weighed crystals were dissolved in 80 ml. of water and to this was added 0.5 ml. of concentrated HCl and 20 ml. of 0.6% sodium tetraphenylborate solution. After digesting for 1 hr. the solution was allowed to stand at room temperature for several hours and then chilled in an ice bath. The precipitate was filtered in weighed sintered glass crucibles and washed three times with 10 ml. of a chilled saturated solution of the precipitate. The crucibles were dried at 110° for 2 hr., desiccated, and weighed. The washing and weighing procedure was repeated until two successive weights agreed to ±0.2 mg. This procedure was found to be accurate to ±0.5%.

In the case of the perchlorate crystals the composition was found to be 65.9% $Co(C_5H_5)_2$; calculated for $Co(C_5H_5)_2ClO_4$: $Co(C_5H_5)_2$, 65.5%.

Labeled $Co(\pi\text{-}C_5H_5)_2ClO_4$ was prepared by the preceding method using cobaltocene which was synthesized from Co^{60}-labeled $CoCl_2$.

$Co(\pi\text{-}C_5H_5)(CCl_3\cdot C_5H_5)$ was prepared by the method described in an earlier paper.[7] When cobaltocene is added to carbon tetrachloride, it reacts to precipitate $Co(C_5H_5)_2Cl$, leaving the trichloromethyl compound in solution. It can be isolated by vacuum distillation and purified by sublimation and fractional crystallization from hexane.

Exchange Experiments and Results

General Exchange Procedure.—For each exchange experiment two solutions with a total volume of 100 ml., each containing one of the components of the exchange, were placed in separate chambers of a partitioned flask. The flask and its contents were allowed to achieve thermal equilibrium by standing for 2 hr. in a water bath, thermostatically controlled to ±0.1°. The solutions then were mixed. Ten-ml. aliquots of the reacting solution were removed periodically and quenched by ejecting the sample into a separation medium. In the studies involving $Co(C_5H_5)_2$ with acetone as the solvent, both the solvent and atmosphere were maintained free of water and air. Samples were removed with a hypodermic syringe and needle through a mercury-covered serum stopper which was attached to the flask.

After separation of the components, each was converted to a common chemical form, mounted, dried, weighed, and counted. Cobalt-60 was determined by counting either its beta or gamma radiation; Cl^{36} was determined by beta counting.

Gamma radiation was counted with a 5-cm. cylindrical NaI (Tl activated) scintillation crystal fitted with a photomultiplier and cathode follower and feeding into a Nuclear-Chicago Model 1810 single channel pulse height analyzer and Model 186 scaler. The beta radiation was counted with a mica window Geiger-Mueller tube and Nuclear-Chicago Model 165 scaler. The beta counting was corrected for self-absorption and backscattering with an experimental curve, and in all cases reference standards were prepared in an identical manner.

Co^{++}–$[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ Exchange.—The exchange between cobaltous and cobalticinium ions in perchlorate solutions was conducted at 25° in aqueous solution, pH 1.99, in the presence of air and the absence of light. The concentrations of $Co(ClO_4)_2$ and $Co(C_5H_5)_2ClO_4$ were $1.73 \times 10^{-3}\ M$ and $3.66 \times 10^{-3}\ M$, respectively. Initially, only the $Co(ClO_4)_2$ contained Co^{60}.

The components were separated by adding a 10-ml. aliquot of the exchange solution to 7 g. of NaSCN, converting the Co^{++} to $Na_2Co(SCN)_4$. This compound was extracted into 10 ml. of 1:3 *n*-amyl alcohol–diethyl ether and the phases were separated and washed. The cobaltous ion was reëxtracted into 6 *N* NH_4OH and precipitated as the sulfide with $(NH_4)_2S$. This precipitate was dissolved in 5 ml. of 3:2 concentrated HNO_3–H_2SO_4 and heated to fumes of SO_3 to convert it to the sulfate. The residual solution was diluted with 5 ml. of water and 7 ml. of concentrated NH_4OH and 2 g. of $(NH_4)_2SO_4$ was added. Cobalt was plated onto a weighed platinum planchet using a current of 0.3 amp. for 1 hr. The planchet was washed with ethanol, dried, weighed, and counted.

The cobalticinium ion, which remained in the original aqueous phase as the perchlorate, was precipitated with 7 ml. of 0.6% sodium tetraphenylborate solution and converted to Co^{++} by perchloric acid oxidation. The procedure for preparing the counting sample was identical to the above, starting with the sulfide precipitation.

The specific activity of the initial $CoClO_4$ was 5610 ± 40 counts/min. × mg. Co. Four samples of the exchange solution taken over a 30-day period averaged 5420 ± 80 counts/min. × mg., which would correspond to a fraction exchanged of 0.05 ± 0.02. However, the average specific activity found in five aliquots of the $Co(C_5H_5)_2ClO_4$ fraction over this period was only 2.5 ± 1.0 counts/min. × mg. Co, which corresponds to a fraction exchanged of $(1.4 \pm 0.6) \times 10^{-3}$. Hence, it was concluded that this exchange does not occur or occurs only extremely slowly under these conditions.

$Co(\pi\text{-}C_5H_5)_2ClO_4$–$Co(C_5H_5)(CCl_3 \cdot C_5H_5)$ Exchange.—The exchange experiments between cobalticinium perchlorate and the trichloromethyl compound were carried out in acetone solution at 0° in the presence of light and air. The concentrations of the two reactants were 2×10^{-3} *M* with the cobalticinium ion labeled. The reactants were separated by introducing a 10-ml. aliquot of the exchanging solution into a flask containing 10 ml. each of water and petroleum ether at 0°. The perchlorate was extracted into the aqueous phase and discarded. The trichloromethyl compound passed into the organic phase which was washed once with water. Ten ml. each of water and acetone were added, the mixture was refluxed, converting the cobalt compound to cobalticinium chloride, and the organic solvents were evaporated.

Radiochemical analysis was made by counting the cobalt as the tetraphenylborate. The cobalticinium chloride solution was evaporated to 1 ml. and 2 ml. of 0.3 *M* HCl was added. A 0.6% solution of $Na[B(C_6H_5)_4]$ was added dropwise until precipitation ceased; the solution was filtered onto paper disks for counting. Precautions were necessary to avoid losses during filtration; the precipitation was made from a hot solution and the filtration rate was low.

The radiochemical analysis was made on the originally inactive trichloromethyl compound. The initial specific activity of the perchlorate was 3220 counts/min. × mg. Co. In six samples taken over a 24-hr. period the specific activity of the trichloromethyl compound averaged 4.1 ± 3.7 counts/min. × mg. Co. This corresponds to $(2.1 \pm 1.9) \times 10^{-3}$ fraction exchanged or essentially zero within the experimental error. Experiments were not carried out past 24 hr. because of the decomposition of the trichloromethyl compound.

$LiCl$–$Co(C_5H_5)(CCl_3 \cdot C_5H_5)$ Exchange.—The exchange of chloride between the trichloromethyl compound and labeled chloride ion was studied in acetone at 0° in the presence of light and air with the concentration of $Co(C_5H_5)(CCl_3 \cdot C_5H_5)$ at 6.5×10^{-3} *M* and the LiCl at 3×10^{-2} *M*. The components were separated by transferring a 10-ml. aliquot of the acetone solution to a flask containing 10 ml. each of water and petroleum ether and extracting the chloride into the aqueous phase.

Since no procedure was available for a radiochemical analysis of the trichloromethyl compound, the organic phase was discarded. After washing the aqueous phase with petroleum ether, the chloride was precipitated with silver nitrate, filtered, washed, dried, weighed, and counted. Weights of all counting and reference samples were essentially the same, so no correction was applied for self-absorption.

The specific activity of three samples of the original chloride averaged 66.2 ± 1.3 counts/min. × mg. AgCl. The average counting rate of six samples after exchange times up to 20 hr. was 66.1 ± 0.7 counts/min. × mg. The average fraction exchange calculated from these data was 0.004 ± 0.06, or zero exchange well within the experimental error.

$Co^{II}(\pi\text{-}C_5H_5)_2$–$[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ Exchange.—The electron exchange between the two bis-(cyclopentadienyl)-cobalt species was carried out in acetone at 0° in the absence of air and light. For the short times an apparatus designed for rapid removal of samples was used.[10] The concentration of $Co(\pi\text{-}C_5H_5)_2$ was varied from 10^{-3} to 10^{-2} *M*; the $Co(\pi\text{-}C_5H_5)_2ClO_4$, which initially contained the Co^{60}, was at 2×10^{-3} *M* in all cases.

The exchange was quenched by adding a 10-ml. aliquot of the reacting solution to 90 ml. of petroleum ether at 0°. The resulting precipitate of $Co(C_5H_5)_2ClO_4$ was filtered, dissolved in 2 ml. of 0.3 *M* HCl, and the tetraphenylborate was precipitated and prepared for counting as in the exchange studies with the trichloromethyl compound. The $Co(C_5H_5)_2$ remained in the petroleum ether, was oxidized to $Co(C_5H_5)_2Cl$, and extracted by shaking with 10 ml. of 0.3 *M* HCl. This was evaporated to small volume, and the same procedure was followed for preparing a counting sample.

These experiments indicated what appeared to be a large amount of zero-time or separation-induced exchange. The fraction exchanged at zero-time, obtained by extrapolating the curves of fraction exchanged *vs.* time, showed a rough increase from 0.55 to 0.99 as the concentration of the cobaltocene was increased from 10^{-3} to 10^{-2} *M*. The remainder of the exchange took place with a rather low rate, a half-time of the order of 200 min.

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[10] S. Katz, "Exchange and Chemical Reactions of Cyclopentadienyl Cobalt Compounds," Ph.D. Thesis, Iowa State College, 1958; *Dissertation Abstr.*, **19**, 2242 (1959); also available as AEC Report ISC-1096.

Since cobaltocene is highly sensitive to oxygen[11,12] it was suspected that this phenomenon might be due to its oxidation by traces of oxygen remaining in the system in spite of precautions. This indeed was found to be the case as demonstrated by the following experiments.

In order to eliminate separation-induced processes as a cause of the high zero-time exchange, two other separation processes were tried. These procedures, the partition of the two species between toluene and water, and the precipitation of cobaltocene by quenching the solution in water, gave the same results as the method described above, the precipitation of the perchlorate in petroleum ether. Hence, it was concluded that the zero-time exchange was not induced by the separation process.

As the concentration of cobaltocene was increased from 10^{-3} to 10^{-2} M the fraction of the exchange occurring initially increased from 0.55 to 0.99. At the higher concentrations a small amount of oxygen would react with a smaller fraction of the total cobaltocene, leaving more of it unchanged to undergo the rapid electron-exchange process.

Small amounts of oxygen were admitted to the system prior to the initiation of the exchange. In these experiments the zero-time exchange was eliminated and half-times of the order of 100–150 min. were observed.

It was concluded that the large zero-time exchange was the actual electron transfer between the two similar species $Co^{II}(\pi C_5H_5)_2$ and $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ occurring too rapidly for measurement of the rate by these techniques. Also, the slow process which followed was an exchange reaction between the cobalticinium ion and an oxygen derivative of cobaltocene. The amount of cobaltocene in excess over the oxygen in the system exchanged instantaneously; that which reacted with oxygen exchanged much more slowly.

The Oxygen Derivative of Bis-(cyclopentadienyl)-cobalt (II).—Attempts were made to prepare, isolate, and characterize the oxygen derivative which appeared in these experiments, but they were in the main unsuccessful. Gas titration experiments were conducted with acetone solutions of cobaltocene at 0°, giving a definite end-point at 4.1 ± 0.2 moles of $Co(C_5H_5)_2$ per mole of O_2, or the ratio $[Co(C_5H_5)_2]/0.5$ O. The color of the solution changed from an initial red-brown to cherry-red. However, it was not possible to isolate a compound by cooling to $-76°$ or by adding non-polar solvents, such as petroleum ether. The material was decomposed during vacuum distillation of the acetone. Addition of water yielded basic solutions (pH$\sim$10) containing high yields of the cobalticinium ion; addition of acids made this conversion quantitative. A test for peroxide involving the addition of acidic solutions of KI and $(NH_4)_2MoO_4$ to solutions of the derivative was negative; no iodine or $[Co(C_5H_5)_2]I_3$ was formed.

Further study of the oxygen uptake in acetone solutions of cobaltocene at 0° indicated that with a 2–3-fold excess of oxygen the reaction stops at a ratio of $Co(C_5H_5)_2/O$ of 2/1 and does not go beyond this in at least 10 hr. However, at 25° it continues on to close to a 1/1 ratio, the cherry-red color of the 2/1 product changing to a brown color.

Studies in a number of other solvents were undertaken in attempts to isolate a compound or at least to learn more about the reaction. Experiments in N,N-dimethylformamide, quinoline, and di-*n*-butylphthalate were largely non-productive. A more extensive study of the kinetics of the reaction in mesitylene did not yield the 2/1 product but at 0° a 1/1 product was obtained which then oxidized further. At 25° in mesitylene the oxidation continued without breaks in the rate-of-uptake curves until the $Co(C_5H_5)_2/O$ ratio was about 1/3. The products of these experiments were not identifiable.

Although isolation of the 2/1 material was not achieved, it was possible to study its exchange behavior with cobalticinium and in that way to learn more about its nature and to infer something about its structure. For the sake of brevity in discussing its exchange reactions we refer to this compound as "oxygenated cobaltocene" and use the formula $[Co(C_5H_5)_2]_2O$ without at this time implying that this actually represents the molecular formula.

$Co(C_5H_5)_2ClO_4$–Oxygenated Cobaltocene Exchange.—The study of the exchange between cobalticinium perchlorate and the oxygenated cobaltocene was carried out in acetone at various concentrations and temperatures with the Co^{60} initially present in the perchlorate. The oxygenated cobaltocene was prepared one hour prior to the beginning of the exchange experiment by introducing a definite amount of oxygen, a 2–3-fold excess over the 1/4 mole ratio, into the

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[11] G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, **76**, 1970 (1959).

[12] E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8B**, 327 (1953).

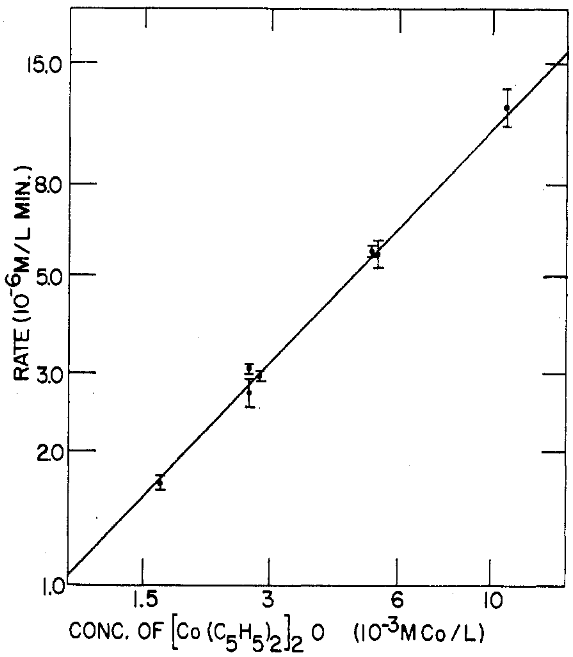

Fig. 1.—Effect of concentration of oxygenated cobaltocene on its exchange with $Co(C_5H_5)_2ClO_4$.

reaction flask, which contained acetone solutions of cobaltocene in one chamber and the perchlorate in the other. The cobaltocene was found to be completely converted to the oxygen derivative within less than 30 min. at 0°, and the solutions did not show any decomposition for periods of up to 10 hr.

The separation procedure for this study was identical to that used in the experiments with cobaltocene and the cobalticinium ion. The exchange was quenched by transferring an aliquot into petroleum ether, and the precipitated perchlorate was filtered and converted to the tetraphenylborate for counting. Between five and ten samples were withdrawn during the course of a run.

The half-times of exchange ($t_{1/2}$) were determined from the data by calculating the least squares straight lines of plots of log $(1 - F)$ *vs.* time. The fraction exchanged, F, is defined as

$$F = (S - S_0)/(S_\infty - S_0)$$

in which S, S_0, and S_∞ are the specific activities of a component at times t, zero, and infinity, respectively. To determine S_∞ an unquenched sample of the mixture was shaken with 0.3 M HCl, thereby converting all of the cobalt to the same form, cobalticinium chloride, for the measurement of its specific activity.

The points of the least squares lines were weighted in proportion to $(1 - F)^2$, since the $(1 - F)$ values were considered to have approximately the same standard deviation. The rates of exchange (R) were calculated from the first order exchange law[13,14] according to the expression

$$R = ab/(a + b) \times 0.693/t_{1/2}$$

in which a and b are the concentration of the components in moles of cobalt per liter.

A series of experiments was run to determine the dependence of the exchange rate on the concentration of the oxygenated cobaltocene. In these experiments the concentration of the cobalticinium perchlorate was kept at 2.8×10^{-3} mole/l., while that of the oxygen derivative was varied from 1.65×10^{-3} to 1.08×10^{-2} mole of Co/l. The half-times of exchange ranged from 419 to 128 min. under these conditions, corresponding to a variation in rate from 1.69×10^{-6} to 12.0×10^{-6} moles/l. min. A log-log plot of the rate *vs.* the concentration of the oxygenated cobaltocene (Fig. 1) has a slope of unity, demonstrating that the exchange is first order with respect to this species. The rate data thus can be expressed by an equation of the form $R = k[[Co(C_5H_5)_2]_2O]$, in which $k = (1.07 \pm 0.05) \times 10^{-3}$ min.$^{-1}$.

Experiments with varying concentrations of cobalticinium perchlorate gave the results shown in Table I. The constancy of the values shows that the exchange rate is independent of the concentration of this species.

Experiments were performed to determine the effect of diluting the solvent, acetone, with a non-polar solvent, *n*-decane. The conditions for the experiments were 0° and constant concentrations of $[Co(C_5H_5)_2]_2O = 0.587 \times 10^{-3}$ mole Co/l. and $Co(C_5H_5)_2ClO_4 = 2.17 \times 10^{-3}$ M. As is readily seen from Table II, the rate of exchange is depressed by the addition of *n*-decane.

Table I

Dependence of Exchange Rate on the Concentration of $Co(C_5H_5)_2ClO_4$ at 0°

Concentrations			
$Co(C_5H_5)_2ClO_4$ mole/l. $\times 10^3$	$[Co(C_5H_5)_2]_2O$ mole Co/l. $\times 10^3$	$t_{1/2}$, min.	R, mole/l. min. $\times 10^6$
1.76	2.82	122 ± 6	6.2 ± 0.3
1.76	2.72	119 ± 10	6.2 ± 0.5
2.64	2.48	131 ± 7	6.8 ± 0.4
3.52	2.57	162 ± 9	6.3 ± 0.4
8.30	2.51	212 ± 1	6.30 ± 0.04

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(13) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(14) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

TABLE II

DEPENDENCE OF RATE OF EXCHANGE ON SOLVENT COMPOSITION

Vol. % acetone	$t_{1/2}$, min.	R, mole/l. min. × 10^6
51	229 ± 9	4.8 ± 0.2
70	190 ± 7	5.9 ± 0.3
95	125 ± 7	8.6 ± 0.1
100	119 ± 3	9.1 ± 0.2
100	119 ± 2	9.3 ± 0.2

Experiments were conducted on the effect of ionic strength on the rate of exchange between the oxygenated cobaltocene and cobalticinium perchlorate. Since increasing the concentration of the perchlorate increases the ionic strength, it was of interest to see if the independence of the rate on the concentration of this species would be maintained under conditions of constant ionic strength. Sodium perchlorate was added to keep the ionic strength constant at 1.9 × 10^{-2} M; the concentration of cobalticinium perchlorate was varied from 8 × 10^{-4} to 3.2 × 10^{-3} M while that of the oxygen derivative was kept constant at 2.4 × 10^{-3} M. The results indicated a slight negative dependence on the concentration of cobalticinium perchlorate under these conditions. Since at constant ionic strength a decrease in the concentration of $Co(C_5H_5)_2ClO_4$ corresponds to an increase in the $NaClO_4$ concentration, this points to a strong effect of $NaClO_4$ on the rate of exchange.

Further experiments were carried out with large changes in the concentration of sodium perchlorate, *i.e.*, from 0.0055 to 0.13 M. The apparent effect was indeed pronounced. A dependence on the formal sodium perchlorate concentration of somewhat greater than first order was observed, actually $R \propto (NaClO_4)^{1.2}$.

The temperature dependence of the rate was determined between 0 and 20° at constant composition with the concentration of the oxygen derivative = 5.36 × 10^{-3} mole Co/l. and that of $Co(C_5H_5)_2ClO_4$ = 2.78 × 10^{-3} mole/l. An activation energy of 18 ± 0.2 kcal./mole was determined from the slope of a plot of log R *vs.* 1/T (Fig. 2).

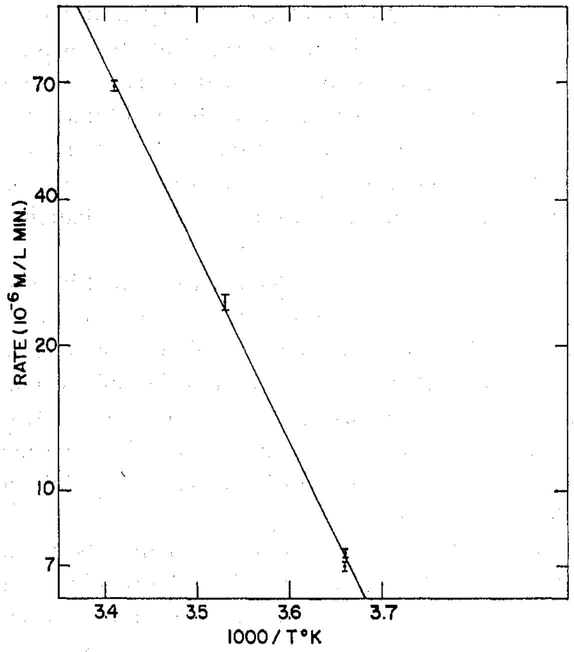

Fig. 2.—Temperature dependence of exchange between $Co(C_5H_5)_2ClO_4$ and oxygenated cobaltocene.

Discussion

The lack of exchange between cobalt and cobalticinium ions demonstrates the strong and inert π-bonding of the cyclopentadienyl groups to the metal in the latter. It is expected in analogy with the lack of exchange reported for the ferrous ion–ferricinium system.

The failure to observe exchange between $Co(C_5H_5)(CCl_3 \cdot C_5H_5)$ and $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ is consistent with the non-equivalent structures assigned to the components.[7,15] In these suggested structures the former has a single π-bonded cyclopentadienyl ring and a trichloromethyl cyclopentadiene ring which is bonded to the cobalt in some fashion, probably involving the two double bonds. The $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$, of course, contains two π-bonded cyclopentadienyl rings. Although the trichloromethyl group can be removed by hydrolysis with acid to form the $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ ion, exchange between the trichloromethyl compound and the ion does not occur in acetone solution. It also has been observed that the hydride analogous to the trichloromethyl compound, $Co(\pi\text{-}C_5H_5)(C_5H_6)$, does not exchange with lithium aluminum deuteride.[8] Thus there appears to be a non-labile bond connecting the carbon of the cyclopentadiene ring to the added group, whether this is the CCl_3 group or the hydrogen atom.

The lack of exchange between chloride and the trichloromethyl compound which was observed in these experiments indicates that the C–Cl bond in this compound is also non-labile.

As was mentioned earlier, the initial rapid ex-

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(15) G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6148 (1952).

change observed between $Co(\pi\text{-}C_5H_5)_2$ and $[Co^{III}(\pi\text{-}C_5H_5)_2]^+$ is attributed to rapid electron transfer between the two π-bonded species. These results are in agreement with those obtained for the analogous $Fe^{II}(\pi\text{-}C_5H_5)_2$ and $[Fe^{III}(\pi\text{-}C_5H_5)_2]^+$ exchange[5] and are taken as further evidence of the similarity in structure of the two exchanging species.

The properties of the derivative formed by the action of oxygen on cobaltocene in acetone at 0° were such that it was not possible to isolate it or study it carefully. The simplest formula which agrees with the observed stoichiometry is $[Co(C_5H_5)_2]_2O$, but any solvation of this molecule by the acetone would not have been detectable in the experiments.

The salient features of the exchange between this oxygen derivative and the cobalticinium ion are: first order dependence on the oxygen derivative, zero order depencence on the ion, a decreasing rate as the solvent is diluted with *n*-decane, and an increasing rate with addition of sodium perchlorate or water.

In the study of the effect of sodium perchlorate on the rate, the results indicated a pronounced effect of both sodium ions and sodium perchlorate ion pairs on the rate of exchange. In further investigations the dissociation constants of sodium and cobalticinium perchlorates in acetone were determined conductimetrically. These results were combined with the exchange data to give a rate equation of the type

$$R = [[Co(C_5H_5)_2]_2O](k_1 + k_2[Na^+] + k_3([NaClO_4]))$$

which fit the ionic strength data over the whole range.

The possibility exists, however, that a trace of water may have entered the system with the sodium perchlorate in these studies and that the increase in rate is due to water rather than to sodium perchlorate and sodium ions. For either case it appears to be related to a change in the atmosphere of the solution.

The observed dependences on the concentrations of the exchanging species and these effects of changing the solvent atmosphere suggest an ionization as the rate determining step

$$[Co(C_5H_5)_2]_2O \rightleftharpoons [Co(C_5H_5)_2]^+ + [Co(C_5H_5)_2O]^-$$

The $[Co(C_5H_5)_2]^+$ released in this ionization would be indistinguishable from the labeled cobalticinium ion introduced as the perchlorate, thus leading to exchange by isotopic dilution. The behavior of the oxygen derivative toward water and acids yielding $[Co(C_5H_5)_2]^+$ could be explained by the above reaction, since water would be expected to shift the equilibrium to the right. The increase in pH observed with the addition of water could be due to the hydrolysis of the anion from the above reaction

$$[Co(C_5H_5)_2O]^- + H_2O \rightleftharpoons Co(C_5H_5)_2{}^+ + 2OH^-$$

Addition of acid then would shift this reaction and the preceding one quantitatively to the right. The activation energy observed for the exchange also is consistent with the assumption that an ionization process is the rate determining step.

Any other statements about the oxygen derivative would be in the nature of conjecture. It is not claimed that a compound of this formula has been prepared, but the formation of a substance of this nature is in agreement with the stoichiometry of the oxidation, the behavior of the solutions with water and acid, and the kinetics data for the exchange. The lack of stability would seem to rule out any type of bonding between the rings, but a rather ionic Co–O–Co linkage between the two cyclopentadienyl cobalt entities would be consistent with the observations. Solvation with acetone or even incorporation of acetone into the structure is not ruled out.