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Kinetics of isotopic exchange between chloride and trichloro (ethylene) platinate (II)

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KINETICS OF ISOTOPIC EXCHANGE BETWEEN CHLORIDE
AND TRICHLORO(ETHYLENE) PLATINATE(II)

by

Stanley Jerome Lokken

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

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1962

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I. INTRODUCTION

A. Development of Platinum Chemistry

In many of the early studies of the chemistry of platinum the objective was to synthesize new compounds. However, the observations of the synthetic inorganic chemists soon led to speculation about the structure of the compounds they obtained and to interest in directive effects in syntheses. For example, it soon became apparent that there were two different compounds with the simplest formula $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Analyses of both for the elements indicated the same formula, but many of the other physical and chemical properties were different.

Werner (1) suggested a possible explanation for isomerism in platinum(II) complexes. He said that if the four bonds of the platinum were directed to the corners of a square, instead of a tetrahedron, two stereoisomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ would be expected. These were designated cis and trans forms. Although this square planer structure is now accepted as correct, other explanations for isomerism in platinum(II) complexes have been proposed.

Reihlen and Nestle (2) stated that their molecular weight determinations indicated trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ was the dimeric form of the cis compound. Drew et al. (3) claimed for a time that there was a third isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$,

and they stated that the three isomers were structural and not stereoisomers. Later work refuted these arguments against the square planer structure of platinum(II) compounds, and led Rosenblatt and Schleede (4) to conclude again that the two isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ are stereoisomers. At about the same time Cox and coworkers (5-7) made structural investigations of several platinum(II) complexes with x-rays. Their results gave further proof of the square planer configurations of these complexes.

As new platinum compounds were synthesized, it also became apparent that there was some sort of directive effect. The reaction of NH_3 with $\text{K}_2[\text{PtCl}_4]$ yielded cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$; the reaction of HCl with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ gave trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Werner (1) had mentioned in 1893 that reactivity of a group in a coordination compound was influenced by the nature of the group in the trans position. However, Chernyaev (8) was the first to use the term "trans-effect". In 1927 he suggested that the varying mobility of groups connected with a central atom could be explained by the trans-effect. He decided trans-effect was inversely proportional to metallic character. Thus, electronegative groups would have a higher trans-influence than neutral substituents, and the reactions to give the cis- and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ could be explained.

In 1943 Grinberg (9) stated that the weakening of the bond trans to a group of strong trans-effect was due to the mobility of electrons in this group and consequent ease of shift of these electrons toward the platinum atom. The belief that the effect is due to polarizability is then a special form of this theory. The idea that direction of a substituent into the position trans to a given group is due to the weakening of the bond to the substituent formerly in the trans position was so firmly established at this time that Quagliano and Schubert (10) defined trans-effect in this way in their review article.

Later, it was suggested by Syrkin (11) that d-orbitals are involved and that "dp" bond hybridization is important in platinum(II) complexes. This results in two hybrid covalent bonds at right angles to each other. Then the most covalently bound group enhances the covalent character of bonds occupying a position cis to it; the group in the trans position is labilized. This concept of $d\pi-d\pi$ bonding was extended by Chatt (12). Also Craig et al. (13) and Jaffe (14) suggested bonds involving d-orbitals are important.

A more complete hypothesis to explain the trans-effect was given by Chatt et al. (15) in 1955. They suggested that there is dative π -bond formation from a d_{xz} -orbital of the platinum towards a ligand of high trans-effect. This results in electron withdrawal which increases the electron affinity

of the metal and perhaps increases the strength of all σ -bonding to other ligands. The electrons are withdrawn mainly from the antinodes remote from the strong trans director, thus decreasing the tendency of the ligand in the trans position to form a dative π -bond. The bond to this ligand trans to the strong trans director will be weakened only if a dative π -bond is an essential component. If not, strengthening of the σ -bond could increase the bond strength. Then trans-effect cannot be defined in terms of bond weakening. Therefore, they defined trans-effect as the tendency of a group to direct an incoming substituent group into the position trans to itself.

Since the bond to the ligand trans to the strong trans director may be strengthened, a dissociative substitution mechanism is ruled out. Then the operation of the trans-effect is probably by a bimolecular mechanism. Increase of double bonding by a strong trans director increases electron affinity of the metal and hence ease of nucleophilic attack. In addition, since the electron withdrawal occurs at the antinodes of the d_{xz} -orbital remote from the strong trans director, the attack takes place there displacing this ligand. Orgel (16) has given a similar interpretation based on a trigonal bipyramid pentacoordinate transition state.

Powell (17) pointed out that infra red spectra indicate the bond from Pt to an NH_3 which is trans to ethylene or

diethyl sulfide is weakened, so the NH_3 is more likely to dissociate than when another group is trans to it. So bond weakening appears to have at least a contributing role in the trans-effect. Also, the results of work by Dunning and Martin (18) on mixed tetra-(chlorobromo)-platinate(II) failed to indicate that the higher stability of the bromide ligand results primarily from increased π -bonding.

As Powell (17) points out the following observed order of increasing trans-effect is predicted quite well: $\text{H}_2\text{O} < \text{OH}^- < \text{NH}_3 < \text{R}\cdot\text{NH}_2 < \text{pyridine} < \text{Cl}^- < \text{Br}^- < \text{CNS}^- \sim \text{I}^- \sim \text{NO}_2^- \sim \text{SO}_3\text{H} \sim \text{PR}_3 \sim \text{R}_2\text{S} \sim \text{SC}(\text{NH}_2)_2 < \text{NO} \sim \text{CO} \sim \text{C}_2\text{H}_4 \sim \text{CN}^-$.

As early as 1893 Werner and Miolati (19) had shown that the conductivity of some solutions of platinum(II) complexes increased from the initial value as they aged. King (20) and Jensen (21) explained the increase in conductivity of various chloroammine complexes of platinum(II) by an aquation process in which chloride ligands were replaced by water. Since then aquation or acid hydrolysis in platinum(II) complexes has been reported by many other investigators (22-25). The reversible aquation process can provide an important path for isotopic exchange, and it may be the only path in some systems. According to Taube (26) the ability of the water molecule to form complexes is so high that in solutions it is hard for direct ligand exchange to compete.

In contrast Rich and Taube (27) found that exchange in platinum(IV) complexes did not proceed through an aquation type of process, but occurred by an oxidation reduction chain mechanism in which platinum(III) was said to play a role.

In one of the earliest isotopic exchange studies, Grinberg and Filinov (28) studied the $[\text{PtBr}_4]^- - \text{Br}^-$ system. Since that time isotopic exchange in several other platinum(II) complexes has been studied. Grinberg and Nikol'skaya (29) investigated $[\text{PtX}_4]^- - \text{X}^-$ systems where X represents one of several ligands. Grantham et al. (22) studied the $\text{K}_2[\text{PtCl}_4] - \text{Cl}^-$ system; Elleman et al. (30) studied the $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3] - \text{Cl}^-$ system; and Reishus and Martin (25) investigated the cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] - \text{Cl}^-$ system.

In general, platinum(II) complexes have half-times for exchange of ligands which are convenient to measure. Taube (26) used the term inert to describe complexes in which an exchange reaction could be observed to be taking place after the reactants had been dissolved and mixed. Labile complexes were those in which exchange equilibrium had already been reached in the one or two minutes necessary to dissolve the chemicals.

Banerjea et al. (24) studied the substitution reactions of a variety of nucleophilic reagents with several platinum(II) complexes. They discovered that the reactions could be divided into two categories. In the first category the

reaction is first order in the complex and zero order in the reactant. The reactions take place at approximately the same rate, and the reactants in this category have a low trans-effect. In the second category the reaction is first order in both complex and reactant. The reaction rates are faster than those in the first category, and the reactants are usually high in the trans-effect series. The authors suggested a "dissociation" mechanism.

Later, Basolo and Pearson (31, pp. 186-189) gave a revised form in their book. They suggested that in solution besides the four strongly bound ligands in the plane of the platinum there are two solvent molecules weakly bound, one above and one below the plane. Then they suggested that in the first category the reaction goes through a square pyramid intermediate. The slow rate determining step was said to be dissociation of the ligand that is replaced, to leave a pentacoordinated intermediate. The reactant then rapidly enters to give the product.

For reactions in the second category there usually is either a ligand in the original complex capable of π -bonding, or the reactant is capable of π -bonding. First, one of the weakly bound solvent molecules is replaced by the reactant, and then a trigonal bipyramid intermediate is formed in the slow rate determining step. Either the second solvent molecule or the ligand being replaced can be lost in

forming this intermediate. This mechanism extended that proposed earlier by Orgel (16) to consider the possibility that the entering ligand may form π -bonds to stabilize the intermediate. In the mechanisms for both categories the solvent obviously plays an important role.

B. Zeise's Salt, $K[Pt(C_2H_4)Cl_3]$

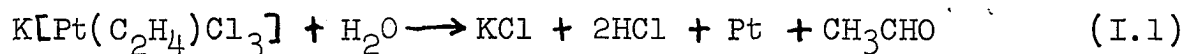
The subject of this thesis is the isotopic exchange between chloride and trichloro(ethylene)platinate(II) ion.

The first published report which indicated the existence of $K[Pt(C_2H_4)Cl_3]$ was in a note by Zeise (32) in 1827 about work in his laboratory on platinum compounds. Three years later his work was published in Latin (33), and the following year a condensed form appeared in German (34). When Zeise boiled $PtCl_4$ with ethanol an acidic solution resulted. He added KCl and obtained golden yellow crystals. After these crystals were dried, his analytical results indicated the composition of the anhydrous substance was $K[Pt(C_2H_4)Cl_3]$.

Ethylene is not the only olefin which forms a complex compound with platinum(II). Various investigators have reported other olefinic complexes. Billmann and Hoff (35) described complexes with allyl alcohol and with vinylacetic acid. Derivatives of acids with a double bond between the α and β carbon atoms could not be obtained. Compounds with the double bond farther from the carboxyl group gave

platinum(II) complexes. Pfeiffer and Hoyer (36) made several olefinic complexes of platinum(II). Hel'man (37, 38) made propylene, butylene, styrene, and butadiene complexes of platinum(II). In each case a high trans-effect was observed. Each double bond in butadiene reacted but with different platinum atoms, so a five membered ring with platinum was not obtained.

The manner in which ethylene is linked to platinum has been the subject of considerable speculation. Anderson (39) found that when $K[Pt(C_2H_4)Cl_3]$ was heated at $90^\circ C$ in water 60% of the ethylene was recovered as such. He also heated $K[Pt(C_2H_4)Cl_3]$ to $100^\circ C$ in water in a nitrogen stream and discovered acetaldehyde was one of the decomposition products, which indicated the reaction was:



This he considered to be evidence of an unsymmetrical linkage of ethylene to platinum.

Chernyaev and Hel'man (40) found that ethylene had a very strong trans directing influence in contrast to earlier ideas (8) that all neutral substituents should be weak trans directors. Later Hel'man (41) made a somewhat vague suggestion that platinum acts first as an electron donor to activated ethylene and then becomes an acceptor; the result would be formation of a four electron covalent bond. Pfeiffer and Offermann (42) offered evidence that the

addition center is the ethylene linkage.

Electrometric oxidative titrations of various platinum complex compounds were considered by Hel'man and Ryabchikov (43) to establish the quadrivalency of platinum in $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$. The initial potential value was in the range characteristic of platinum(IV) compounds, and no potential jump indicative of oxidation occurred. Hel'man and Gorushkina (44) found ethylene in $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ was replaced by NH_3 , pyridine, NO_2^- , or CN^- to yield compounds with bivalent platinum, but they found the action of CH_3MgI on $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ gave $[(\text{CH}_3)_3\text{PtI}]$ in which platinum is quadrivalent. They concluded that platinum in Zeise's salt is quadrivalent.

In 1951 Chatt (45) proposed a substituted ethylidene structure for olefinic complexes of platinum. Then Zeise's salt would be $\text{K}[\text{CH}_3\text{CH} = \text{PtCl}_3]$. The platinum would still be in the platinum(II) planar dsp^2 hybridized state, attached by four σ -bonds to surrounding groups. But in addition there would be π -bonding through a d-orbital to one carbon atom, so the platinum would supply four electrons as it does in the platinum(IV) state.

The preparation of $[\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2]$ by Chatt and Wilkins (46) rendered invalid structures, like Hel'man's (41), which would require the supply of four electrons by platinum for each olefinic group attached.

Later, the infrared spectra of olefinic coordination compounds, including $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, were studied by Chatt and Duncanson (47). They concluded that the olefins retained their double bonds in the complexes and were symmetrically attached to platinum. They found the lowering of the C=C stretching frequency to be about twice that observed for Ag(I) complexes. From these facts, and all other information in the literature, they concluded that a σ -type bond is formed by overlap of a $5d6s6p^2$ -hybrid orbital of the platinum atom with a bonding π -orbital of the olefin. In addition, a π -type bond is formed by overlap of a hybridized $5d6p$ -orbital of the metal with the antibonding π -molecular orbital of the olefin. They found no more than one third double bond character in the C_2H_4 to platinum bond. The evidence that the platinum in $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ is quadrivalent (44) is consistent with bivalency since $\text{Na}_2[\text{PtCl}_4]$ also reacts with CH_3MgI to form $[(\text{CH}_3)_3\text{PtI}]$.

The crystal structure of Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$, was investigated by Wunderlich and Mellor (48). Their x-ray studies indicated that the platinum and the three chlorine atoms were coplanar. Two of the Pt-Cl bonds were found to be of normal length (2.32\AA), but the third, trans to the ethylene, was found to be abnormally long (2.42\AA). The carbon to carbon axis forms a right angle with the plane of the PtCl_3 group. They gave the carbon to carbon

distance as $1.5\overset{\circ}{\text{A}}$ and the C-Pt distance as $2.2\overset{\circ}{\text{A}}$.

Powell and Sheppard (49) made a fairly complete assignment of the fundamental vibration frequencies of the bonded ethylene molecule in a number of complexes of platinum and palladium. They agreed that the double bond was retained in ethylene. At the same time Babushkin et al. (50) made a different assignment of certain bands. They decided that the bands at $1490\text{-}1510\text{ cm}^{-1}$ were due to the scissors deformation vibration of CH_2 units, instead of the valence vibration of a carbon to carbon double bond. From this they concluded there was a three membered ring of carbon, platinum, and carbon with all three bonds single bonds.

Later Powell and Sheppard (51) resolved the ambiguity in favor of the existence of the carbon to carbon double bond. They demonstrated that the band at 1500 cm^{-1} persists in the infrared spectrum of $\text{K}[\text{Pt}(\text{cis-CH}_3\text{-CH=CH-CH}_3)\text{Cl}_3]$, where the C=CH_2 group is not present. In general, they found that the coordinated hydrocarbon groups have electronic properties much closer to those of the parent olefins, than to structures of the ring types.

About 110 years after Zeise first made $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, Hel'man (52) found a new method of synthesis. In this method ethylene was passed through an aqueous solution of $\text{K}_2[\text{PtCl}_4]$ for 15 days. Chatt and Duncanson (47) used a modification of this method; an aqueous solution of $\text{K}_2[\text{PtCl}_4]$ and HCl was

shaken under an atmosphere of ethylene.

Leden and Chatt (53) found that the aquation equilibrium

$$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^- + \text{H}_2\text{O} \rightleftharpoons \text{trans-}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] + \text{Cl}^- \quad (\text{I.2})$$

was reached in less than two minutes. So the trans chloride is labile, unlike ligands in other platinum(II) complexes. They found the value of the equilibrium constant for the reaction in equation (I.2) was $(3.0 \pm 0.5) \times 10^{-3}$.

II. EXPERIMENTAL

A. Chemicals

1. Platinum

Platinum was obtained in the form of $K_2[PtCl_6]$ from the Fisher Scientific Company; and in the form of $H_2[PtCl_6] \cdot nH_2O$ from the Mallinckrodt Chemical Works, the Braun Chemical Company, and the General Chemical Division of Allied Chemical Corporation.

Platinum as purchased may contain a significant amount of iridium. Therefore, before preparation of compounds for use in exchange studies the platinum obtained was purified by fractional crystallization of $K_2[PtBr_6]$. This method was suggested by Jowanovitz et al. (54) as the best means of purification of platinum from iridium.

In a basic aqueous medium the iridium free $K_2[PtBr_6]$ was reduced with a small excess of hydrazine to platinum metal. Platinum metal was recovered in the same manner from all waste solutions and solids containing platinum. Washing with hot HNO_3 and hot HCl , with intervening water washes, was used to remove less noble metals and leave pure platinum metal.

2. Potassium hexachloroplatinate(IV)

$K_2[PtCl_6]$ was prepared by dissolution of platinum metal in hot aqua regia, dilution with water, and addition of an

excess of aqueous KCl. The bright yellow precipitate of $K_2[PtCl_6]$ was then filtered, washed with alcohol and ether, and dried.

3. Potassium tetrachloroplatinate(II)

$K_2[PtCl_4]$ was prepared from $K_2[PtCl_6]$ by reduction with a stoichiometric amount of potassium oxalate in aqueous medium. A small amount of platinum black was used as a catalyst. These materials were refluxed until only a trace of solid $K_2[PtCl_6]$ was visible, and then the hot solution was filtered to remove platinum black and unreacted $K_2[PtCl_6]$. Dark red crystals of $K_2[PtCl_4]$ were obtained when the filtrate was cooled. The oxalate reduction method for preparation of $K_2[PtCl_4]$ was first used by Vezes (55).

4. Ethylene

Ethylene was obtained as the compressed gas from the Matheson Co., Inc.

5. Potassium trichloro(ethylene)platinate(II)

$K[Pt(C_2H_4)Cl_3]$ was prepared by the method of Chatt and Duncanson (47). In 75 milliliters of 3% HCl, 15 grams of $K_2[PtCl_4]$ was shaken continuously for a period of 10 to 15 days. The solution changed color from dark brownish red to golden yellow. After the solution was filtered and cooled in ice water, crystals of $K[Pt(C_2H_4)Cl_3] \cdot H_2O$ were obtained.

These crystals were recrystallized three times from 3% HCl and dried in a desiccator over CaSO_4 (Drierite) desiccant. After drying for a week, analyses agreed with the formula $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$.

When the supernates from the recrystallizations were allowed to evaporate slowly, open to the laboratory atmosphere, large crystals of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$ formed separately from crystals of KCl, unreacted $\text{K}_2[\text{PtCl}_4]$, and unreacted $\text{K}_2[\text{PtCl}_6]$. These crystals of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3] \cdot \text{H}_2\text{O}$ were picked out, dissolved, dirt removed by filtration, recrystallized, and dried to yield more pure $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$.

6. Chlorine-36

Chlorine-36 was obtained from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. The isotope was obtained in the form of approximately 2N HCl. Chlorine-36 emits a 0.71 Mev beta, and it has a half-life of about 3.5×10^5 years (56).

7. Sodium tetraphenylboron

Sodium tetraphenylboron was obtained as the reagent grade chemical from the Fisher Scientific Company.

8. Water

Distilled water was redistilled from alkaline permanganate solution before use in experiments.

9. Tetraphenylarsonium acetate

Tetraphenylarsonium acetate solutions were prepared for use as a precipitating agent by passing $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$ solutions through a Dowex 1 anion exchange resin in the acetate cycle. Completeness of replacement of the chloride ion by the acetate ion was shown by failure of silver ion to give a precipitate when added to a portion of the effluent. The tetraphenylarsonium chloride was obtained as reagent grade from the Fielding Chemical Company.

10. Additional reagents

Many other common laboratory reagents were used. These were usually reagent grade, and were obtained from such sources as the Mallinckrodt Chemical Works and the J. T. Baker Chemical Company.

B. Equipment

1. Constant temperature baths

Each constant temperature bath consisted of a tank of water in which there were intermittent heaters and a circulation pump manufactured by E. H. Sargent and Company. The heaters balanced the cooling effect of tap water run through a cooling coil, and they were controlled by a thermostat manufactured by the Precision Scientific Company which allowed temperature control within 0.1°C of the desired

temperature. At 15°C the water cooling coil was replaced by a refrigeration coil attached to a unit manufactured by the Blue M. Electric Company.

2. Geiger-Muller counter and scaler

Sample activities were measured with a TGC-1 Geiger-Muller counter manufactured by Tracerlab Inc. The tube, which had a dead time of approximately 300 microseconds, was housed in a lead shield in order to minimize the background counting rate. Pulses from the counter tube were recorded by a Berkeley Decimal Scaler, Model 100. All samples were positioned on the top shelf 7 millimeters vertically below the counting tube window.

3. Filtering apparatus

The filtering apparatus consisted of a sintered glass disk 28 millimeters in diameter sealed into the top of a funnel, and a glass chimney with an inside diameter of 28 millimeters. Hooks on the sides of the funnel and chimney made it possible for them to be held together, by rubber bands, with a weighed filter paper held between. The slurry to be filtered was poured in the top of the chimney and a partial vacuum was applied to the end of the funnel. Uniform deposits of $[\text{O}_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ were obtained on the filter paper. These were washed with water, with due care so that the uniformity of the deposit would not be disturbed, before

they were dried and counted. If stirred up after once deposited, the precipitate would redeposit unevenly in large aggregates.

4. Additional equipment

A "Time It" timer manufactured by the Precision Scientific Company was used to accurately measure counting times and the times exchange samples were taken.

Samples were weighed to the nearest tenth of a milligram on an Ainsworth & Sons Chain-Weight balance.

Analytical determinations of platinum by electrolysis were made with a Sargent-Slomin Electrolytic Analyzer.

For pH measurements a Beckman Model G pH meter was used.

A Cary Recording Spectrophotometer, Model 12, manufactured by the Applied Physics Corporation, was used to obtain ultraviolet spectra from 220 $m\mu$ to 400 $m\mu$. No temperature control was possible with this instrument.

Individual radioactive samples were covered and held in place on cardboard squares by one thickness of Scotch Electrical Tape #5, manufactured by Minnesota Mining and Manufacturing Company. This transparent tape has a thickness of 8.15 mg. per cm.².

C. Procedures

1. Analysis of $K[Pt(C_2H_4)Cl_3]$

A sample of each preparation of $K[Pt(C_2H_4)Cl_3]$ was analyzed for platinum, chlorine, and potassium before portions of that preparation were used in exchange experiments. A weighed sample was dissolved, acidified with a few drops of H_2SO_4 , and platinum was electroplated onto a weighed platinum gauze cathode. The increase in weight of the cathode gave the amount of platinum in the sample. Then the chloride in the solution was determined gravimetrically by adding $AgNO_3$ to yield $AgCl$.

The gravimetric method given by Gloss (57) was used to determine potassium. Another weighed sample was dissolved and potassium precipitated as $K[B(OH)_4]$ by the addition of $Na[B(OH)_4]$ solution. (Inconsistent results were obtained when analyses were made on the same solutions used for platinum and chloride analyses, after the removal of excess silver ion by addition of a slight excess of chloride ion.) Typical analyses were:

<u>Element</u>	<u>Calculated %</u>	<u>Observed %</u>			
Pt	52.95	52.95	52.88	52.75	53.02
Cl	28.82	29.45	28.82	27.78	29.00
K	10.60	10.90	10.24	10.77	11.46

2. Analysis of $[\Phi_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$

A weighed sample of $[\Phi_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ was dissolved in a milliliter of N,N-dimethylformamide, and the solution was diluted with water. Then the $[\Phi_4\text{As}]^+$ ion was determined gravimetrically by precipitating the insoluble $[\Phi_4\text{As}]\text{ClO}_4$ by the addition of KClO_4 . Platinum and chloride could then be determined by the methods previously given.

3. Exchange experiments

The correct amounts of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, KCl , and K_2SO_4 were weighed and placed in a volumetric reaction flask, which was wrapped with black opaque tape. Then the correct amounts of standardized H_2SO_4 solution and water were added to dissolve the chemicals. The flask was placed in a constant temperature bath for a sufficient period of time, so that the contents would be certain to be in a state of equilibrium before the Cl^{36} was added. The K_2SO_4 and H_2SO_4 were used to maintain the ionic strength at 0.318 moles per liter and the hydrogen ion concentration at 0.143 moles per liter.

Upon completion of the equilibration process, 5 to 20 lambda of Cl^{36} solution were introduced. The time of introduction of the tracer solution was the zero time, t_0 , of the exchange experiment. The amount of tracer solution used was so small that the concentration change upon its introduction was insignificant.

Measured aliquots of the exchange solution were removed at known intervals of time after the zero time. From each aliquot $[\text{P}_4\text{As}] [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ was precipitated by the addition of approximately a four-fold excess of tetraphenylarsonium acetate. The slurry was immediately transferred to the filtering apparatus described previously, and the precipitate was collected on a weighed filter paper. The paper and sample were washed twice with water and then allowed to dry until the next day. The weight of the filter papers was a function of the humidity; therefore, the change in weight of a set of papers without precipitates was used to make a humidity correction in the weights of the papers with precipitates. The original weight of the paper was subtracted from the corrected weight of sample plus paper to give the sample weight.

After weighing, each sample and filter paper was placed on a cardboard square and covered with Scotch Electrical Tape #5. The cardboard square was taped to a metal holder and counted on the top shelf of the Geiger counter. A dead time correction, based on an experimentally measured 300 micro-second tube deadtime, was used to correct for loss of counts at high counting rates. Then the background counting rate was subtracted to give the counting rate of the sample. Since the weights of samples for any given experiment fell in

a narrow range, no corrections were made for sample precipitate thickness.

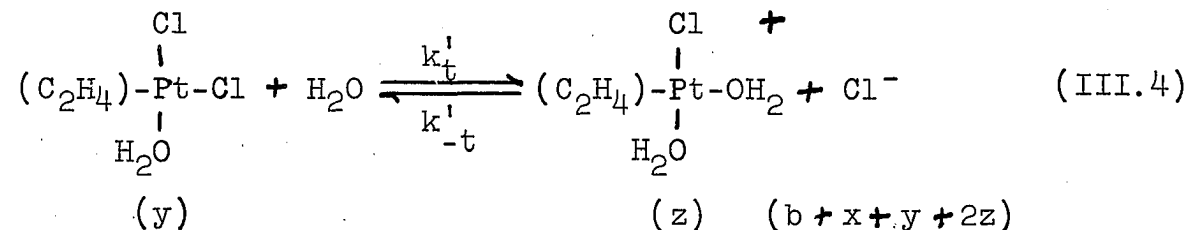
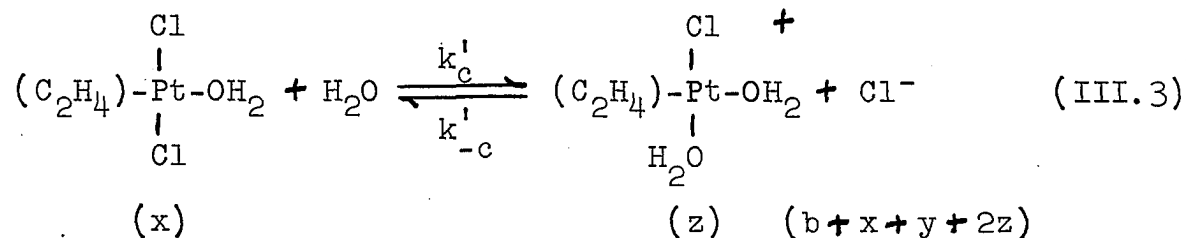
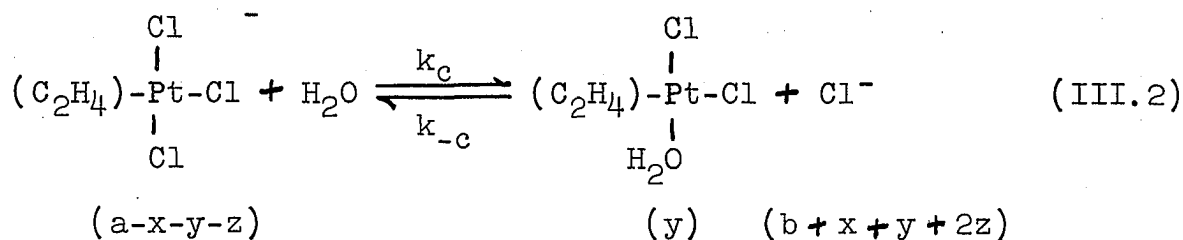
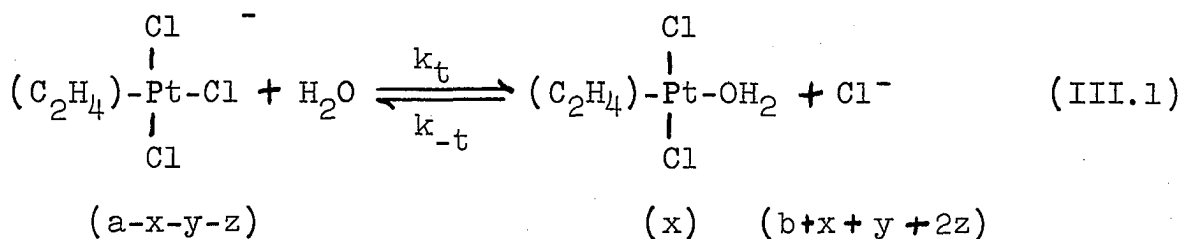
From the counting rate of each sample and its weight it was possible to determine the specific activity, S , of that sample. Then these experimental values of specific activity could be used to evaluate the exchange.

Most aliquots were taken before the exchange of Cl^{36} with the complex had reached equilibrium. However, four or six samples were taken at a much later time, when the tracer was known to be at least 99% equilibrated between ionic chloride and the ligands of the complex. These samples were known as infinity samples with specific activity designated by S_{∞} . Since it was the ratio of S to S_{∞} that was of importance, the counting geometry did not have to be known, but only had to be kept constant for all samples.

III. PRELIMINARY CALCULATIONS

A. Definitions of Symbols and Units

For convenience, the symbols which will be used several times in the following pages are defined in this section. First, the reactions to be considered are listed in equations (III.1) to (III.4). The rate constants anticipated from the stoichiometry of these reversible reactions are indicated.



Next, symbols for the amounts of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ and KCl used in preparation of an exchange solution are defined.

a = initial $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ concentration (moles l.^{-1})

b = initial KCl concentration (moles l.^{-1})

Some other symbols are defined for a solution in which equilibrium has been established in the reactions listed in equations (III.1) to (III.4).

x = trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ concentration at equilibrium (moles l.^{-1})

y = cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ concentration at equilibrium (moles l.^{-1})

z = cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]^+$ concentration at equilibrium (moles l.^{-1})

Thus, when equilibrium has been established in an exchange solution, the concentrations of the important species which are present are those indicated by the symbols given below the species in equations (III.1) to (III.4). The respective equilibrium constants can then be defined.

$$K_t = k_t/k_{-t} = (x)(b + x + y + 2z)/(a - x - y - z)$$

$$K_c = k_c/k_{-c} = (y)(b + x + y + 2z)/(a - x - y - z)$$

$$K'_c = k'_c/k'_{-c} = (z)(b + x + y + 2z)/(x)$$

$$K'_t = k'_t/k'_{-t} = (z)(b + x + y + 2z)/(y)$$

The following set of symbols will also be used:

R = reaction rate (moles $\text{l.}^{-1} \text{ sec.}^{-1}$, unless another unit is specified)

- t = time (sec., unless another unit is specified)
- μ = ionic strength
- I = activity of Cl^{36} added (cts. sec.⁻¹ l.⁻¹)
- u = activity in the cis positions of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ and trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ (cts. sec.⁻¹ l.⁻¹)
- S = specific activity in $[\text{O}_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ precipitate (cts. sec.⁻¹ (moles Cl)⁻¹)
- S_∞ = S for a sample taken after Cl^{36} is in exchange equilibrium with the complex
- F = S/ S_∞
- S_u = specific activity in the positions cis to ethylene in $[\text{O}_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ precipitate (cts. sec.⁻¹ (moles Cl)⁻¹)
- S_s = specific activity of ionic chloride, which includes Cl that is found trans to ethylene in $[\text{O}_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ since equilibrium is established rapidly in the reaction of equation (III.1) (cts. sec.⁻¹ (moles Cl)⁻¹)

B. Ionization Concentration Quotient for HSO_4^-

In order to make solutions of ionic strength 0.318 containing sulfuric acid, it was necessary to know the second ionization concentration quotient of sulfuric acid. Although there are many articles with information on the second thermodynamic equilibrium constant for sulfuric acid, they usually give information on the concentration quotient only

for solutions with ionic strength below 0.1.

Bray and Liebhafsky (58) studied the reaction of bromate ion with bromide ion in the presence of various concentrations of sulfuric acid. They determined values of the second ionization concentration quotient of sulfuric acid at different ionic strengths up to 0.5. From their data the value of the quotient at ionic strength 0.318 is 0.059.

Another method uses a Debye-Huckel type of approximation. In a review article Young and Blatz (59) give data obtained from this method. From their data the value of the quotient at ionic strength 0.318 was calculated to be 0.052.

Rao (60) has used Raman spectra to determine the equilibrium concentration quotient in concentrated sulfuric acid solutions. There is a gap over a large concentration range between data obtained from Raman spectra and the data at lower concentrations obtained using either of the methods mentioned previously. Young and Blatz (59) showed graphs in which the data from Raman spectra were joined to the data at lower concentrations to give curves covering the entire concentration range. The data of either method at lower concentrations fits equally well. Thus the Raman spectra data cannot be used to choose one of the values at ionic strength 0.318 over the other.

In the absence of better information the concentration quotient at ionic strength 0.318 was taken as an average

value of 0.055.

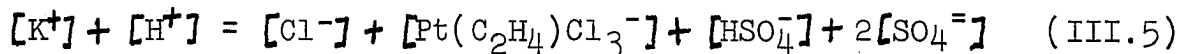
C. Preparation of Exchange Experiment Solutions

In this section the equations are developed that were used to calculate the amounts of H_2SO_4 and K_2SO_4 needed to prepare the desired volume of an exchange experiment solution. In the majority of exchange experiments H_2SO_4 and K_2SO_4 were added to the chosen amounts of KCl and $K[Pt(C_2H_4)Cl_3]$ in order to adjust the ionic strength to 0.318 and the hydrogen ion concentration to 0.143. The following symbols were used:

M_a = moles H_2SO_4 added per liter of exchange solution

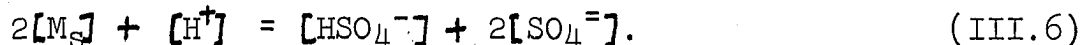
M_s = moles K_2SO_4 added per liter of exchange solution

In each solution there must be a balance of charge.



Part of the $[K^+]$ is balanced by $[Pt(C_2H_4)Cl_3^-]$ and by $[Cl^-]$.

After subtraction of these quantities, the balance of charge equation becomes



From these equations an expression was obtained for $[H^+]$ in terms of $[M_a]$ and $[M_s]$.

$$\begin{aligned}
 [\text{H}^+] = & [\text{M}_a] \left[1 + \frac{[\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]}{[\text{H}^+] + [\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]} \right] \\
 & - [\text{M}_s] \left[1 - \frac{[\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]}{[\text{H}^+] + [\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]} \right] \quad (\text{III.8})
 \end{aligned}$$

Similar substitutions in the ionic strength equation yield another useful equation.

$$\begin{aligned}
 2\mu = & [\text{H}^+] + [\text{K}^+] + [\text{Cl}^-] + [[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-] + [\text{HSO}_4^-] \\
 & + 4[\text{SO}_4^{=}] \quad (\text{III.9})
 \end{aligned}$$

$$\begin{aligned}
 2\mu - 2[\text{Cl}^-] - 2[[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-] - [\text{H}^+] = & \\
 & [\text{M}_a] \left[1 + \frac{3([\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-])}{[\text{H}^+] + [\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]} \right] \\
 & + 3[\text{M}_s] \left[1 + \frac{[\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]}{[\text{H}^+] + [\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-]} \right] \quad (\text{III.10})
 \end{aligned}$$

These two equations, (III.8) and (III.10), can be solved for the quantities $[\text{M}_a]$ and $[\text{M}_s]$ for any desired $[\text{H}^+]$ and μ .

$$\text{When } \mu = 0.318, [\text{H}^+] [\text{SO}_4^{=}] / [\text{HSO}_4^-] = 0.055 \quad (\text{III.11})$$

Therefore, under the usual experimental conditions, with

$$\mu = 0.318 \text{ and } [\text{H}^+] = 0.143, \text{ equations (III.8) and (III.10)}$$

simplified to the following equations.

$$0.143 = 1.2777[\text{M}_a] - 0.7222[\text{M}_s] \quad (\text{III.12})$$

$$\begin{aligned}
 0.493 - 2[\text{Cl}^-] - 2[[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-] = & 1.8333[\text{M}_a] \\
 & + 3.8333[\text{M}_s] \quad (\text{III.13})
 \end{aligned}$$

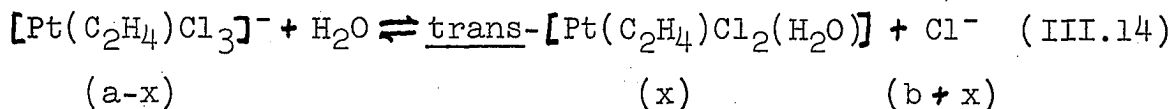
After initial amounts of KCl and $K[Pt(C_2H_4)Cl_3]$ were chosen for an exchange experiment, the two simultaneous equations, (III.12) and (III.13), were solved to determine the proper amounts of H_2SO_4 and K_2SO_4 .

D. Concentration of Trans- $[Pt(C_2H_4)Cl_2(H_2O)]$

It was found by Leden and Chatt (53) that when $K[Pt(C_2H_4)Cl_3]$ is dissolved, the reaction which yields trans- $[Pt(C_2H_4)Cl_2(H_2O)]$ reaches equilibrium in less than two minutes. They gave the equilibrium constant for this reaction as $K_t = (3.0 \pm 0.5) \times 10^{-3}$. Their studies were made at ionic strength 0.2 instead of 0.318. However, this difference is not unduly large, especially for a reaction in which an ion with a minus one charge is transformed into a neutral complex. The value of K_t is not known very accurately, but it did not appear that an improvement in their method was feasible.

From this value of K_t it is possible to calculate the concentration of trans- $[Pt(C_2H_4)Cl_2(H_2O)]$, or (x), in the solution. In order to do this it must be assumed that the amounts of cis- $[Pt(C_2H_4)Cl_2(H_2O)]$ and cis- $[Pt(C_2H_4)Cl(H_2O)_2]^+$ are much less than the amount of trans- $[Pt(C_2H_4)Cl_2(H_2O)]$ in solution. The limits of the equilibrium constants given later in Table 1 indicate that this assumption is valid. Then the concentrations indicated under equation (III.1)

simplify to those indicated under equation (III.14), and it is possible to solve for (x) as shown.



$$K_t = (x)(b+x)/(a-x) \quad \text{(III.15)}$$

$$x = \frac{-(K_t + b) \pm \sqrt{(K_t + b)^2 + 4K_t a}}{2} \quad \text{(III.16)}$$

E. Treatment of Isotopic Exchange

The experimental quantities obtained from an exchange experiment were the values of specific activity, S, as a function of time. From these experimental quantities the half-time of exchange was determined by plotting $(1-S/S_0)$, or $(1-F)$, on a log scale versus time on a linear scale. Now it was possible to calculate the value this quantity should have at the zero time of the exchange experiment. Comparison of the theoretical $(1-F_0)$ value with the actual experimental value gave an indication of the accuracy of the experimental data.

The amounts of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ and of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]^+$ which do not react with chloride ion rapidly enough to enter the $[\Phi_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ precipitate are negligible as far as this calculation is concerned. Due to the rapidity with which the Cl^{36} was introduced into the trans position, initially the Cl^{36} was distributed in $(a+b)$

moles Cl/l. At equilibrium Cl^{36} was distributed in $(3a+b)$ moles Cl/l. Therefore, the value of $(1-F_0)$ could be calculated in the following manner:

$$S_{\infty} = \frac{I}{3a+b}, \quad (\text{III.17})$$

and
$$S_0 = \frac{I}{3(a+b)} \quad (\text{III.18})$$

since initially all chlorine in cis positions is inactive.

$$\frac{S_0}{S_{\infty}} = \frac{3a+b}{3(a+b)} = F_0 \quad (\text{III.19})$$

$$(1-F_0) = \frac{2b}{3(a+b)} \quad (\text{III.20})$$

F. Reaction Rate

Here a quantitative expression is developed for the rate of reaction of chloride in solution with the chloride ligands in the cis positions in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$. By the time the first sample could be taken, equilibrium had already been reached in the aquation reaction given by equation (III.1). Therefore, increase in measured activity was due to introduction of Cl^{36} into the cis positions.

When $[\Phi_4\text{As}]^+$ ion was added to an exchange solution, $[\Phi_4\text{As}][\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ precipitated quantitatively. This occurred because as soon as $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ ion was precipitated, the trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ reacted with chloride to give this ion and also precipitated. Cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ and cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]^+$ would not react as rapidly with

the chloride to give $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$, but the quantity $(y+z)$ in solution is small, and it can be considered negligible as far as this derivation is concerned.

$$\text{Then} \quad S_u = \frac{u}{2a}, \quad (\text{III.21})$$

$$\text{and} \quad S_s = \frac{I-u}{b+a}. \quad (\text{III.22})$$

The net rate of formation of (u) is given by the rate of its formation minus the rate of its removal. So

$$\frac{du}{dt} = R(S_s - S_u) \quad (\text{III.23})$$

Upon substitution of the respective values into this equation and rearrangement, the following differential equation is obtained:

$$\frac{du}{dt} + \frac{R(b+3a)u}{2a(b+a)} = \frac{IR}{b+a} \quad (\text{III.24})$$

This first order linear differential equation can be solved by the ordinary method of using an integrating factor. Upon integration with time from zero to t the equation is

$$u = \frac{2aI}{b+3a} \left[1 - e^{-R(b+3a)t/2a(b+a)} \right]. \quad (\text{III.25})$$

$$\text{Now } S = \frac{u + aS_s}{3a} = \frac{I}{3(b+a)} + \frac{ub}{3a(b+a)} \quad (\text{III.26})$$

Then substitution of (III.25) into (III.26) gives the next equation:

$$S = \frac{I}{3(b+a)} + \frac{2abI}{3a(b+a)(b+3a)} \left[1 - e^{-R(b+3a)t/2a(b+a)} \right] \quad (\text{III.27})$$

Now consider what happens when $t = \infty$. Then

$$S_{\infty} = \frac{I}{3(b+a)} + \frac{2bI}{3(b+a)(b+3a)} = \frac{I}{(b+3a)}. \quad (\text{III.28})$$

$$\text{So } S = S_{\infty} - \frac{2bI}{3(b+a)(b+3a)} \left[e^{-R(b+3a)t/2a(b+a)} \right], \quad (\text{III.29})$$

$$\text{or } S = S_{\infty} - \frac{2bS_{\infty}}{3(b+a)} \left[e^{-R(b+3a)t/2a(b+a)} \right]. \quad (\text{III.30})$$

The quantity S/S_{∞} is defined by F . Then

$$\frac{S_{\infty} - S}{S_{\infty}} = (1-F) = \frac{2b}{3(b+a)} \left[e^{-R(b+3a)t/2a(b+a)} \right] \quad (\text{III.31})$$

Here it is seen again that at $t = 0$, $(1-F_0) = 2b/3(b+a)$.

$$\text{Now } -\ln(1-F) + \ln \frac{2b}{3(b+a)} = \frac{R(b+3a)t}{2a(b+a)} \quad (\text{III.32})$$

So, from the slope of a plot of $(1-F)$ on a log scale versus time on a linear scale, $t_{\frac{1}{2}}$ can be obtained. Thus, R can be determined from experimental data using equation (III.33)

$$R_{\text{exp.}} = \frac{(\ln 2) 2a(b+a)}{t_{\frac{1}{2}}(b+3a)} \quad (\text{III.33})$$

IV. RESULTS

A. Cis-[Pt(C₂H₄)Cl₂(H₂O)]

Since it seemed probable that cis-[Pt(C₂H₄)Cl₂(H₂O)] would exist in aged solutions of K[Pt(C₂H₄)Cl₃], as well as the trans isomer, some investigations were made to see if its existence could be detected.

Since both trans- and cis-[Pt(C₂H₄)Cl₂(H₂O)] would be expected to act as weak acids, titrations with base were expected to yield information about the rate of cis aquation and the amount of cis-[Pt(C₂H₄)Cl₂(H₂O)] in solution. An equivalent of K[Pt(C₂H₄)Cl₃] in solution would require an equivalent of base to titrate trans-[Pt(C₂H₄)Cl₂(H₂O)], since it would form as rapidly as neutralized by base. More base would be required for any aquation in the cis positions.

However, the instability of an aqueous solution of K[Pt(C₂H₄)Cl₃] in the absence of an added acid made it impossible to obtain quantitative information on rates by titrations. Although solutions of K[Pt(C₂H₄)Cl₃] in 3% HCl were observed to be stable for more than six months, a solution of K[Pt(C₂H₄)Cl₃] in water alone would show signs of decomposition within 24 hours.

When a solution of K[Pt(C₂H₄)Cl₃] in water was aged for three days it became black due to a suspension of finely divided platinum, and a titration curve showed two inflection

points. The first inflection indicated HCl was a decomposition product, in agreement with equation (I.1); the second indicated a weak acid was present. Now when a solution was aged for no more than six hours no evidence of decomposition was apparent. However, at the end of a titration requiring 25 minutes the solution was gray yellow. There was one inflection point, about 12% past the equivalence point; however, since the solution was gray yellow, this may not be an indication of the existence of cis-[Pt(C₂H₄)Cl₂(H₂O)]; but rather it may be evidence that HCl was being rapidly formed during the titration. Solutions were kept in the dark while aging.

When a solution was aged for only five minutes before a 25 minute titration the inflection point was 7 to 10% past the equivalence point. If the titration period was shortened the equivalence point and the inflection point moved closer together. In the case in which base equivalent to the amount of platinum present was added in less than one minute, the pH was the same as the pH of 8.6 of the inflection points in previous titrations. So, if points on a titration curve could have been obtained rapidly enough, the equivalence and the inflection points would have coincided. Also, the more rapid the titration the less the solution was changed in color at the finish. However, after completion of these titrations the solutions quickly became gray yellow,

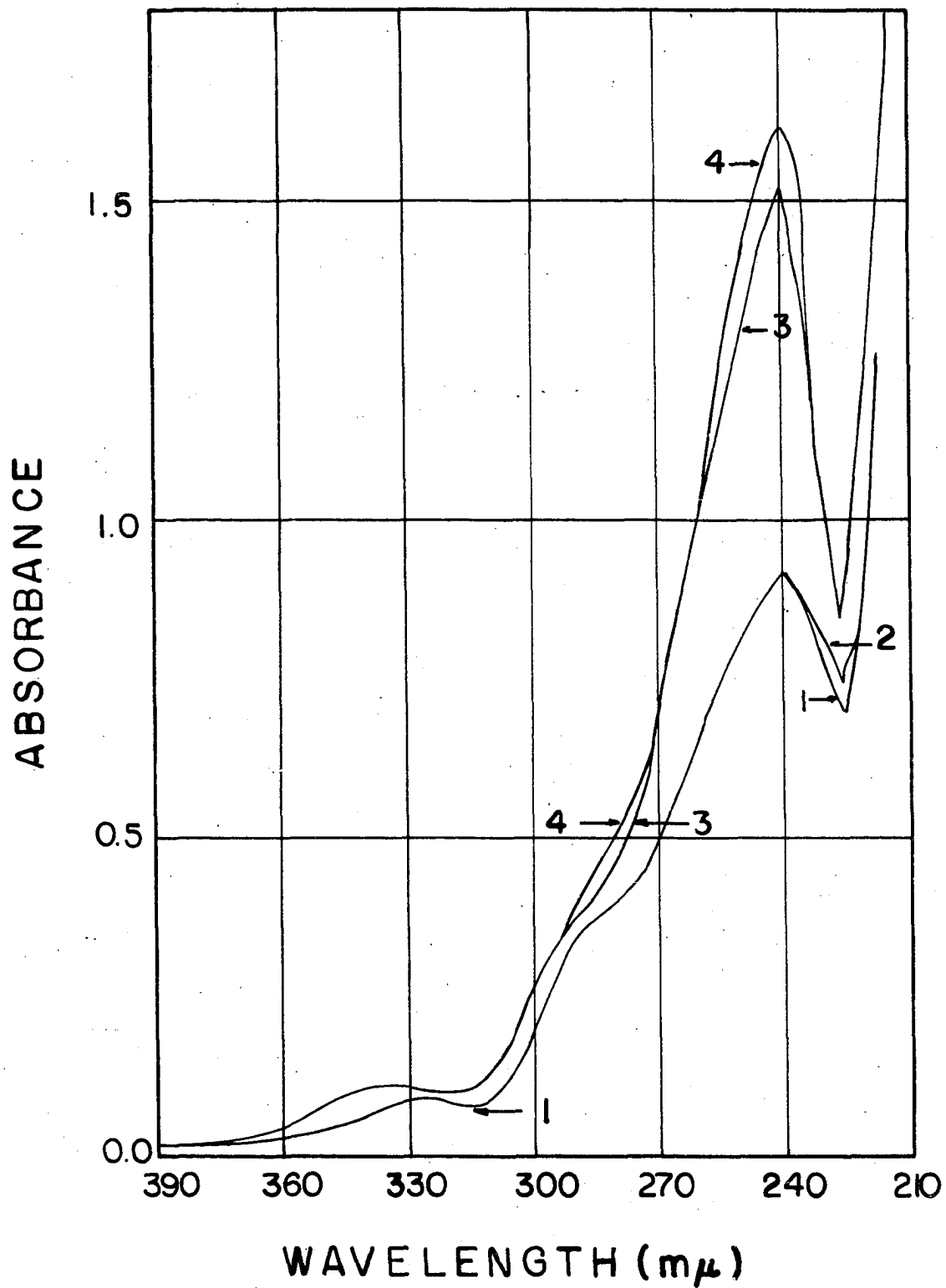
indicative of rapid decomposition.

Another method, which was used in an attempt to obtain some information about cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$, was the observation of spectral changes in solutions of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ in the region from 200 to 400 millimicrons with the Cary Spectrophotometer. K_2SO_4 and H_2SO_4 were used to adjust the ionic strength to 0.318 and the hydrogen ion concentration to 0.143. Equilibrium should have been established in the process of introduction of H_2O into the position trans to the ethylene before the first spectrum could be recorded. So, it was considered that any changes which might occur in the spectrum with time would be due to aquation in the positions cis to the ethylene. With no additional chloride added to a solution 0.001 molar in $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, it was calculated that initially 21% of the platinum complex should be in the form of the $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ ion and 79% in the form of trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$.

The main features of the spectral changes are shown in Fig. 1. Longer cells and a higher concentration of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ made it possible to observe details at the higher wavelengths which are not noticeable in Fig. 1. In solutions of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, with no additional chloride added, peaks were observed at 240 millimicrons and at 328 millimicrons. A shoulder from 275 to 285 millimicrons and an inflection at 250 millimicrons indicated there were two

Fig. 1. Spectral changes in 0.0005 molar $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ solution. Temp. = 25°C . 1 cm. cells used.

$\mu = 0.318$ initially. 1, 5 min. after dissolving complex; 2, 4 hours to 4 weeks after dissolving; 3, 2 min. after adding KCl to solution to make .134 molar in KCl; 4, 4 hours to 17 days after adding the KCl.



additional peaks. Upon aging up to four hours valleys at 226 and 316 millimicrons became less deep. Upon further aging, up to four weeks, no further spectral change was observed. These changes were all quite small in magnitude.

Now when enough KCl was added to change the percentage of the non-aquated ion from 20% to 98%, the immediate result was considerably greater absorbance over the entire range from 210 to 400 millimicrons. The peak at 328 shifted to 335 millimicrons. Upon aging, the valley at 317 millimicrons became slightly deeper, and the peak at 240 became higher. Once again the changes were small in magnitude.

However, all the spectral changes required about an hour to undergo half of the total change in magnitude of the absorbance. Since these changes are caused by aquation in the cis positions, it can be seen from equations (III.1) to (III.4) that the rate of change in the solution can be expressed by the following equation:

$$\frac{d(y+z)}{dt} = k_c(a-x-y-z) + k'_c(x) - k_{-c}(y)(b+x+y+2z) - k'_{-c}(z)(b+x+y+2z) \quad (\text{IV.1})$$

It is possible to solve for (y) and (z) in terms of (y+z).

$$z = \frac{(y+z)K'_t}{K'_t + (b+x+y+2z)} \quad (\text{IV.2})$$

$$y = \frac{(y+z)(b+x+y+2z)}{(b+x+y+2z) + K'_t} \quad (\text{IV.3})$$

After substitution of these values in (IV.1) and rearrangement the following equation was obtained:

$$\frac{d(y+z)}{dt} = - \left[\frac{k_{-c}(b+x+y+2z)^2 + k'_{-c}K'_t(b+x+y+2z)}{(b+x+y+2z) + K'_t} + k_c \right] (y+z) + k_c(a-x) + k'_c(x) \quad (\text{IV.4})$$

$$\frac{d(y+z)}{dt} = k_c(a-x) + k'_c(x) - \frac{0.693}{t_{\frac{1}{2}}} (y+z) \quad (\text{IV.5})$$

At equilibrium $d(y+z)/dt$ equals zero. Then

$$(y+z) = \frac{[k_c(a-x) + k'_c(x)] t_{\frac{1}{2}}}{0.693} \quad (\text{IV.6})$$

The concentrations of trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ and of chloride are not actually invariant quantities, but the concentration changes probably are of less importance than the uncertainties in the values of the rate constants. Even less certain is the value of $t_{\frac{1}{2}}$. Therefore, the approximation that these concentrations are constant is consistent with the accuracy of the data.

The values of k_c and k'_c were taken from Table 8 at 25°C. Now, $K_t = 3 \times 10^{-3}$, and the total amount of platinum in the various complexes was 0.001 moles per liter. With this information values of the equilibrium constants; K_c , K'_c , and K'_t ; and the rate constants; k_{-c} and k'_{-c} ; could be determined for any ratio of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$: cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]^+$ from 0 to ∞ . The calculations were made for the case of the appearance of the species aquated in the

cis positions after $K[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ was dissolved.

However, it was not possible to determine which ratio of $\text{cis}-[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] : \text{cis}-[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]^+$ was correct, since no independent method of determining one of the constants was feasible. Only the limits of the constants could be determined for the extreme cases in which it was assumed that all of the quantity $(y+z)$ was (y) or all was (z) . These limits are shown in Table 1.

Table 1. Limits of constants

Constant	Value if $(y+z) = (y)$	Value if $(y+z) = (z)$
K_c	4.5×10^{-4}	0
K'_c	0	1.4×10^{-4}
K'_t	0	∞
k_{-c}	6.5×10^{-3} (sec. ⁻¹ M. ⁻¹)	∞
k'_{-c}	∞	0.20 (sec. ⁻¹ M. ⁻¹)

Although nothing could be learned about the value of K'_t , the reaction given in equation (III.4) probably attains equilibrium as rapidly as the reaction in (III.1).

In addition, a third method was used to attempt to determine the amount of aquation in the cis positions of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$. An anion exchange column was used to try and

separate cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ from $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$.

In the first experiment a 0.01 molar $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ solution was aged for 8 days. By this time equilibrium should have been established in all the aquation reactions. Then KCl was added to make the solution 0.4 molar in KCl in order to replace all H_2O trans to ethylene in the complexes with Cl. The solution was immediately put through the anion exchange column. Within ten minutes from the time the KCl was added to the solution the elution was complete, including a column wash. It was considered that the reaction of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ with chloride ion, unlike that of the trans isomer, might be slow enough that essentially all of this neutral species would pass through. In order to determine the amount of platinum that came through the column, the platinum was electroplated onto a platinum gauze cathode. Of the 97.6 milligrams of platinum originally in solution in the complexes, 1.0 milligram was plated on the cathode.

In another experiment with identical $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ and the same K_2SO_4 and H_2SO_4 concentrations as in the previous experiment only enough KCl was added to make the solution 0.01 molar in KCl before passage through the anion column. In this case a higher platinum content in the eluant was expected, because the lower concentration of chloride would reduce its rate of reaction with cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$. Also, the rate of elution was faster. However, no platinum

could be plated from the eluant, so there was less than 0.1 milligram present.

In each experiment before the elution the anion exchange column was equilibrated with a solution containing the same concentrations of all substances except $K[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$. If these experiments represent the limits of errors in the process of plating and weighing the cathode, 0.5 milligrams can be assumed to be the amount of platinum that would be obtained on the average. Then the concentration of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ could be calculated. In order to find the chloride concentration in solution before addition of the KCl it was assumed that K_t was much greater than K_c . Calculated on this basis it was found that $K_c = 2.1 \times 10^{-5}$. However, from the range of values of the rate constants for the reverse reaction given in Table 1 it can be seen that this method is too slow. Therefore, an attempt to obtain more accurate results was not made.

B. Exchange Experiments

The procedure used in these experiments has already been described in chapter II. In chapter III it was shown that in each exchange experiment the half-time of exchange could be found from a plot of $(1-F)$ on a log scale versus time on a linear scale. Plots of two experiments are given in Fig. 2 and 3 which represent extremes in the ratio of KCl to

Fig. 2. High chloride exchange experiment. $\mu = 0.318$.
Initial $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ concentration = 0.01
molar. Initial KCl concentration = 0.134
molar. Temp. = 15°C . $t_{\frac{1}{2}} = 8.6$ days or 206.4
hours. Actual $(1-F_0) = 0.620$. Theoretical
 $(1-F_0) = 0.620$.

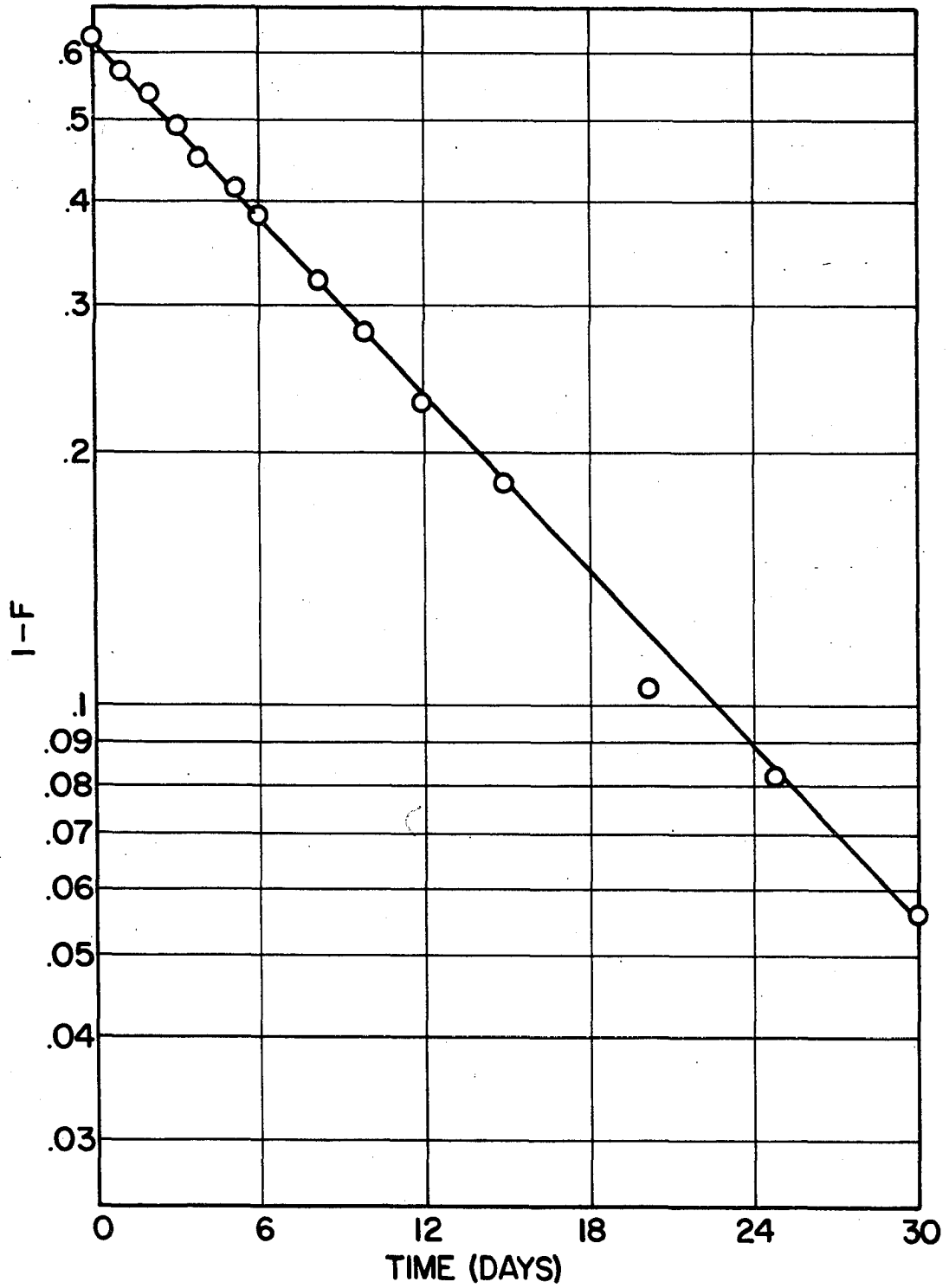
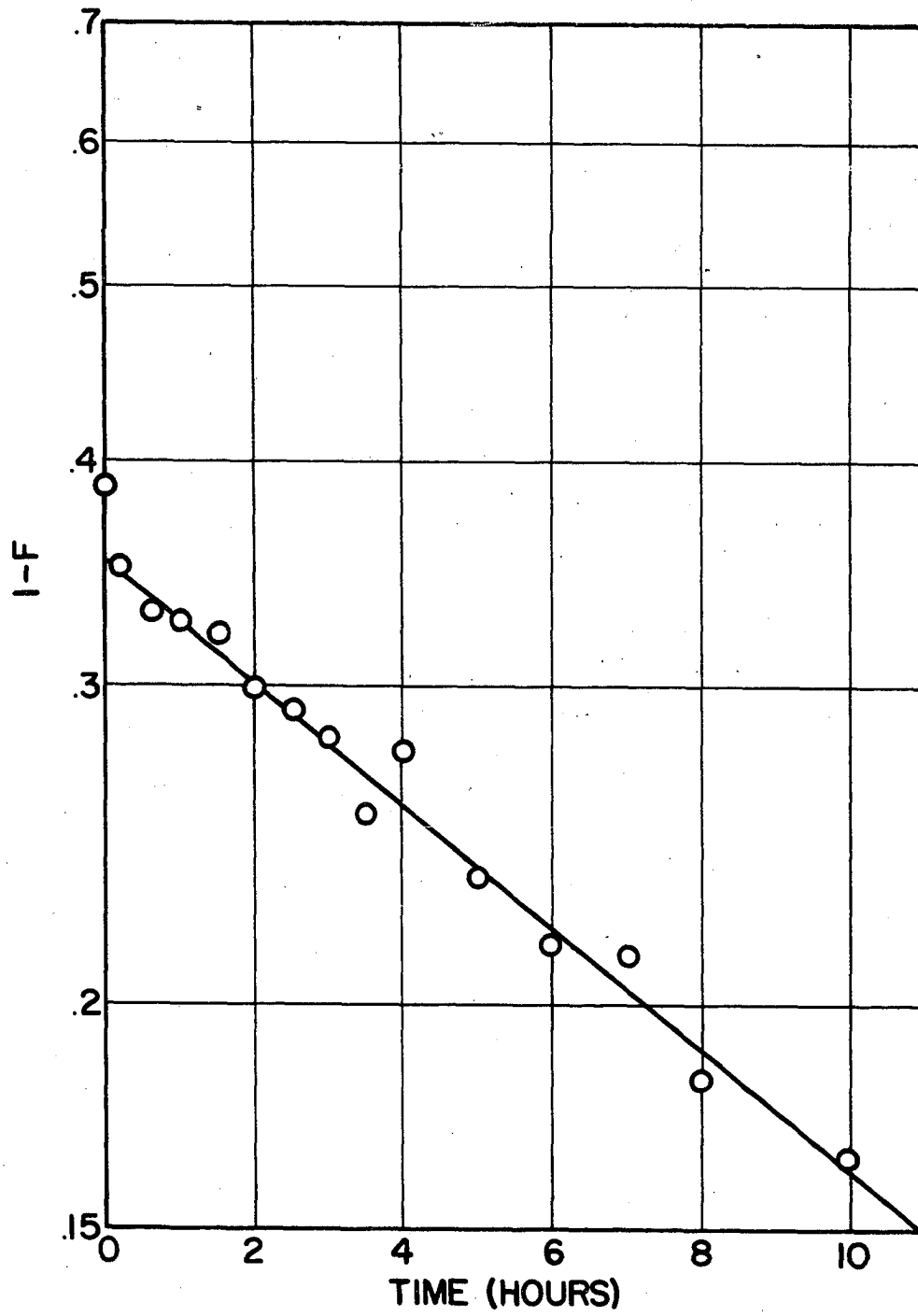


Fig. 3. Low chloride exchange experiment: $\mu = 0.318$.
Initial $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ concentration = 0.01
molar. Initial KCl concentration = 0.01
molar. Temp. = 25°C . $t_{\frac{1}{2}} = 8.9$ hours.
Theoretical $(1-F_0) = 0.333$. Actual $(1-F_0) =$
0.350.



$\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$. Fig. 2 shows the plot for an experiment with a high ratio. Fig. 3 shows the plot for the case of a low ratio. For ratios less than one the scatter of the points was too great to allow accurate determination of exchange half-times.

The data obtained in experiments performed at 25°C . are given in Table 2. The data obtained from experiments at 15°C . and 35°C . are given in Tables 3 and 4 respectively. Definitions of the symbols and methods of calculating the quantities given in the Tables were shown in chapter III.

In all the experiments listed in Tables 2 to 4 the ionic strength was 0.318 and the hydrogen ion concentration was 0.143. The theoretical value of $(1-F)$ at the zero time of the exchange was calculated for each experiment by the method given in the chapter on preliminary calculations, and it was compared with the actual value. In only one of the experiments listed in Tables 2 to 4 was there a greater disparity between the actual experimental value and the theoretical value of $(1-F_0)$ than in the experiment shown in Fig. 3. However, a duplicate of this experiment yielded exactly the same half-time and the correct initial value of $(1-F)$. This good agreement of theoretical and experimental $(1-F_0)$ values was an indication that the experimental procedure was reliable.

In the first experiments which were done, the temperature was 25°C .; the initial amount of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, or

Table 2. Exchange experiments at 25°C.

a^a	b^b	$t_{\frac{1}{2}}^c$	$R_{\text{exp.}}(10^4)^d$	$(x)(10^4)^e$	$(a-x)(10^3)^f$
0.01	0.134	61.2	1.98	2.19	9.78
0.01	0.100	54.7	2.14	2.90	9.71
0.01	0.050	36.0	2.89	5.60	9.44
0.01	0.010	8.95	7.74	20.0	8.00
0.01	0.025	19.0	4.64	10.3	8.97
0.006	0.010	13.0	3.66	12.6	4.74
0.02	0.025	10.2	14.4	20.0	18.0
0.006	0.025	29.0	2.06	6.29	5.37
0.01	0.010	8.90	7.79	20.0	8.00
0.02	0.100	36.4	5.71	5.79	19.4
0.02	0.050	19.0	9.28	11.1	18.9
0.006	0.006	8.95	4.65	16.8	4.32
0.03	0.030	7.40	28.1	25.3	27.5
0.03	0.030	7.30	28.4	25.3	27.5
0.03	0.075	17.9	14.8	11.4	28.9

a_a = initial amount of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ (moles l.^{-1}).

b_b = initial amount of KCl (moles l.^{-1}).

$t_{\frac{1}{2}}^c$ = half-time of exchange (hr.).

$dR_{\text{exp.}}$ = rate from equation (III.33) (moles $\text{l.}^{-1} \text{ hr.}^{-1}$).

e_x = trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ concentration (moles l.^{-1}).

$f(a-x)$ = $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ concentration (moles l.^{-1}).

Table 3. Exchange experiments at 15°C.^a

a	b	$t_{\frac{1}{2}}$	$R_{\text{exp.}}(10^4)$	$(x)(10^4)$	$(a-x)(10^3)$
0.01	0.010	27.9	2.48	20.0	8.00
0.01	0.050	110.4	0.942	5.60	9.44
0.01	0.025	60.0	1.47	10.3	8.97
0.01	0.134	206.4	0.589	2.19	9.78
0.03	0.030	24.0	8.65	25.3	27.5
0.006	0.010	44.5	1.05	12.6	4.74
0.02	0.050	63.0	2.80	11.1	18.9

^aColumn headings the same as Table 2.

Table 4. Exchange experiments at 35°C.^a

a	b	$t_{\frac{1}{2}}$	$R_{\text{exp.}}(10^4)$	$(x)(10^4)$	$(a-x)(10^3)$
0.01	0.010	2.70	25.6	20.0	8.00
0.01	0.134	19.2	6.34	2.19	9.78
0.01	0.050	10.2	10.2	5.60	9.44
0.01	0.025	5.70	15.5	10.3	8.97
0.01	0.010	2.70	25.6	20.0	8.00
0.006	0.025	9.00	6.65	6.29	5.37
0.02	0.100	11.5	18.1	5.79	19.4
0.03	0.075	6.00	44.1	11.7	28.8

^aColumn headings the same as Table 2.

(a), was 0.01 molar; and the initial amount of KCl, or (b), was varied from experiment to experiment. Since other platinum(II) complexes had been shown to undergo exchange by acid hydrolysis mechanisms (22, 25), an attempt was made to fit the data from these experiments to the following form of rate law:

$$R = k_c(a-x) + k'_c(x) \quad (\text{IV.7})$$

$$\text{or } R = k_c(a) + (k'_c - k_c)(x) \quad (\text{IV.8})$$

These first experiments did indeed seem to be in agreement with the rate law of equation (IV.8). Fig. 4 shows that a straight line was obtained in a plot of R versus (x) for (a) = 0.01. Then, since the intercept at (x) = 0 is equal to $k_c(a)$ and the slope of the line equals $(k'_c - k_c)$, the dashed lines indicate where the experimental points would have fallen for (a) = 0.02 and 0.006 respectively, if the rate law of (IV.8) were valid. The solid lines show where these experimental points actually fell when these experiments were performed.

So, a different rate law was needed to explain the experimental results. One law considered was the following:

$$R = k_c(a-x) + k_2(a-x)(x) \quad (\text{IV.9})$$

If this were the correct rate law, a plot of $R/(a-x)$ versus (x) would be a straight line. Fig. 5 shows that this is not the case. Also in Fig. 5 it can be seen that experiments at the same initial concentration of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, or (a),

Fig. 4. R versus (x) for some exchange experiments from Table 2. (x) = trans-[Pt(C₂H₄)Cl₂(H₂O)] concentration. R = reaction rate (moles l.⁻¹ hr.⁻¹). Solid circles, (a) = 0.02; open circles, (a) = 0.01; squares, (a) = 0.006. Dashed lines calculated for (a) = 0.02 and 0.006 on basis of equation (IV.8), using constants found for (a) = 0.01.

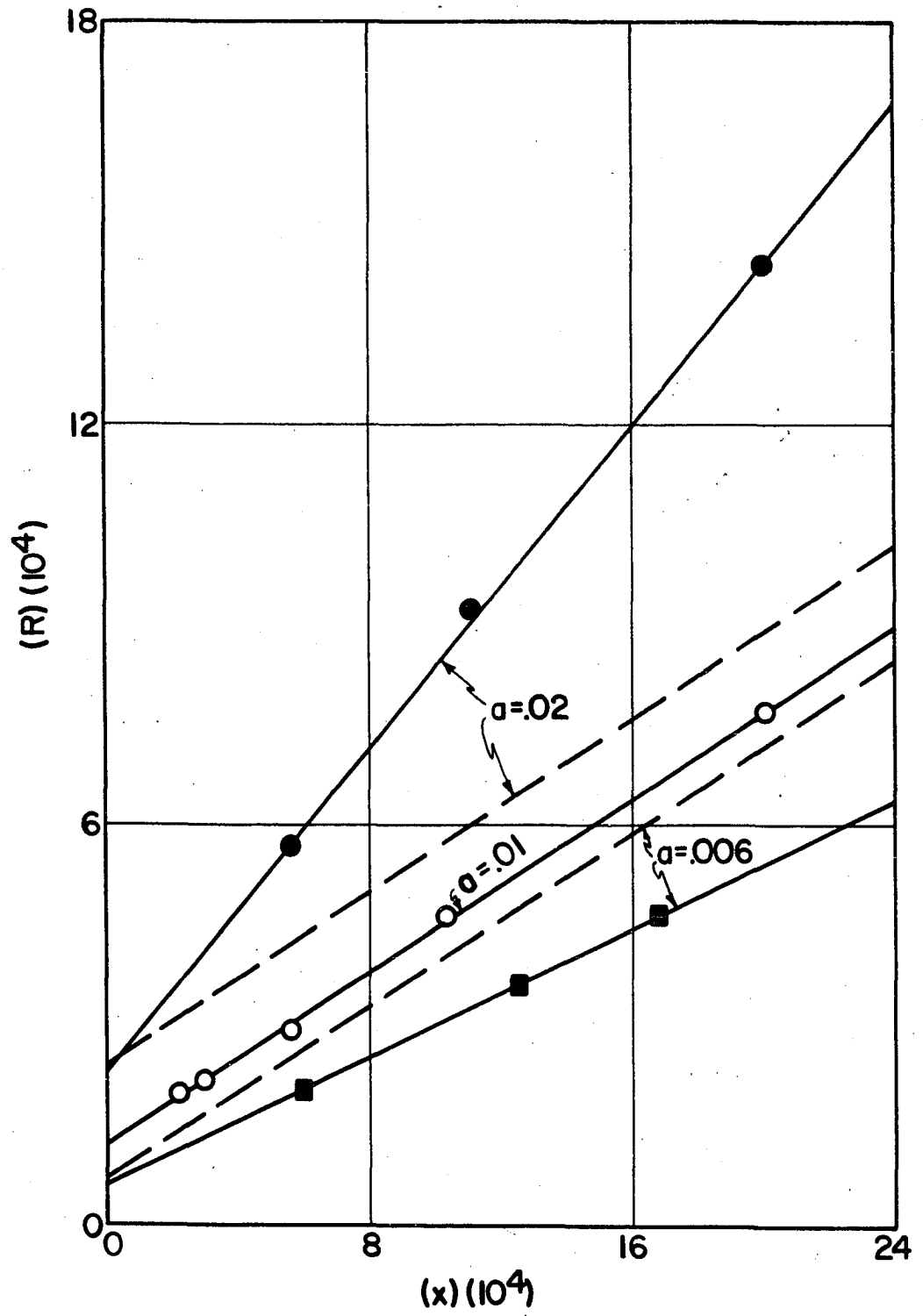
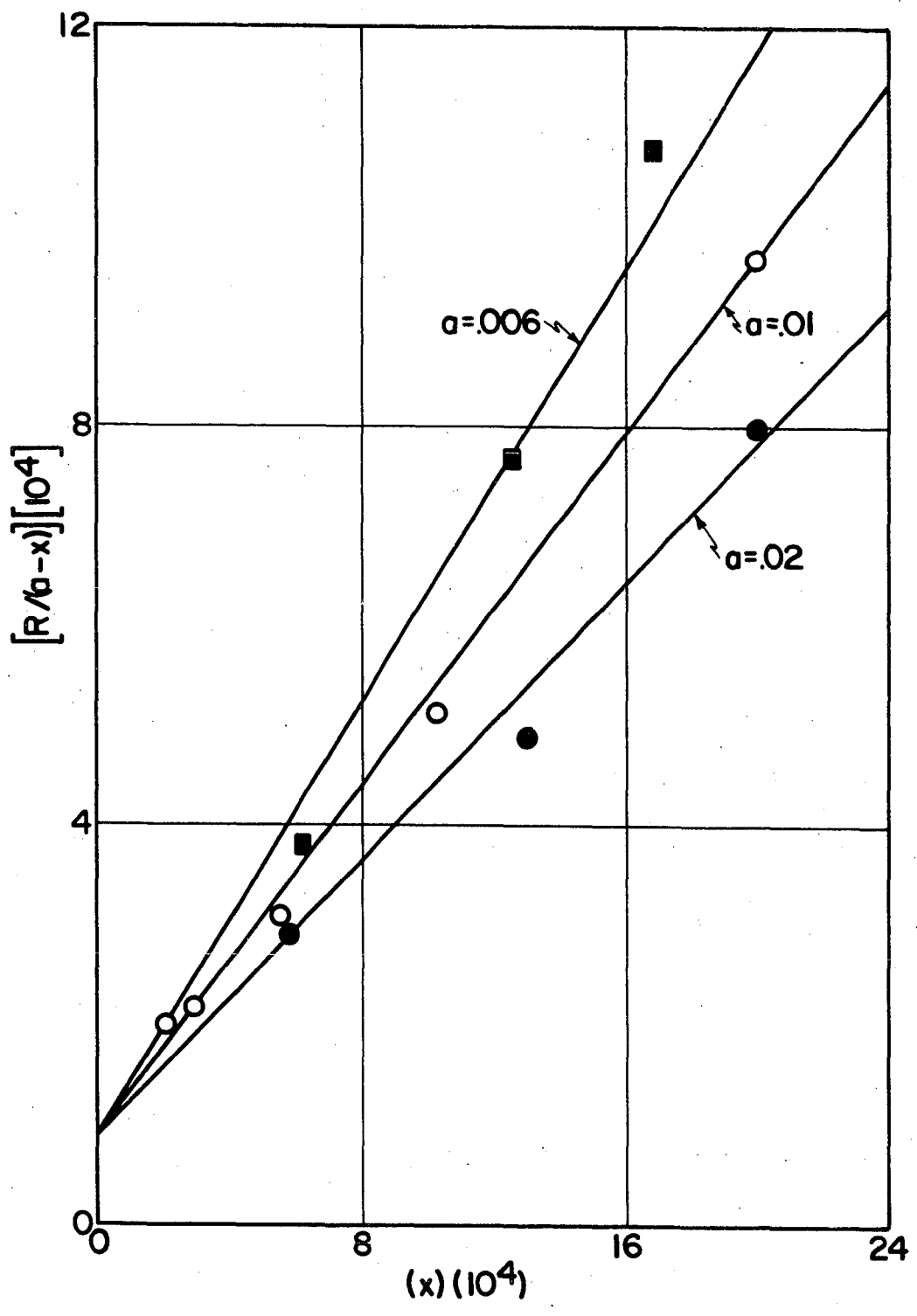


Fig. 5. $R/(a-x)$ versus (x) for some exchange experiments from Table 1. $(x) = \text{trans-}$
 $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ concentration. $R =$ reaction
rate (moles $\text{l.}^{-1} \text{ hr.}^{-1}$). Solid circles,
 $(a) = 0.02$; open circles, $(a) = 0.01$; squares,
 $(a) = 0.006$.



fall close to a straight line. Those at a different concentration fall near a different line. The lines diverge as the trans-[Pt(C₂H₄)Cl₂(H₂O)] concentration, or (x), becomes large. In addition, three curves, each with curvature in the same direction, would fit the points better than straight lines.

These facts indicated addition of a term in (x) to (IV.9) would be helpful. Such a term would have the greatest corrective effect where the divergence is greatest since then (x) is largest. Then the rate law would be

$$R = k_c(a-x) + k_2(a-x)(x) + k_c'(x) \quad (\text{IV.10})$$

This rate law with three constants fits better than any other rate law with three or less constants.

Tables 5, 6, and 7 compare the experimental values of R with those calculated from equation (IV.10) at 25°C., 15°C., and 35°C., respectively. The values of the rate constants at each temperature are tabulated in Table 8 along with the activation enthalpies and entropies.

At each temperature the constants in equation (IV.10) were varied until the set was found that gave a minimum for the sum of the absolute values of the differences between R_{exp.} and R_{cal.}. Then, these constants were converted to the units shown in Table 8 in order to correspond with accepted units for rate constants.

Table 5. Experimental and calculated reaction rates at 25°C.

a	b	$R_{\text{exp.}}(10^4)^{\text{a}}$ (moles l. ⁻¹ hr. ⁻¹)	$R_{\text{cal.}}(10^4)^{\text{b}}$	Difference of $R_{\text{exp.}}$ from $R_{\text{cal.}}$
0.01	0.134	1.98	1.91	4.0%
0.01	0.100	2.14	2.18	-1.9%
0.01	0.050	2.89	3.20	-9.6%
0.01	0.010	7.74	7.80	-0.7%
0.01	0.025	4.64	4.84	-4.2%
0.006	0.010	3.66	3.61	1.4%
0.02	0.025	14.4	15.1	-4.5%
0.006	0.025	2.06	2.24	-7.8%
0.01	0.010	7.79	7.80	-0.1%
0.02	0.100	5.71	6.10	-6.4%
0.02	0.050	9.28	9.59	-3.2%
0.006	0.006	4.65	4.40	5.7%
0.03	0.030	28.1	27.0	4.2%
0.03	0.030	28.4	27.0	5.3%
0.03	0.075	14.8	14.3	3.2%

^a $R_{\text{exp.}}$ = experimental reaction rate from Table 2.

^b $R_{\text{cal.}}$ = reaction rate calculated from equation (IV.10).

Table 6. Experimental and calculated reaction rates at 15°C.

a	b	$R_{\text{exp.}}(10^4)$ (moles l. ⁻¹ hr. ⁻¹)	$R_{\text{cal.}}(10^4)$	Difference of $R_{\text{exp.}}$ from $R_{\text{cal.}}$
0.01	0.010	2.48	2.37	4.6%
0.01	0.050	0.942	0.962	-2.1%
0.01	0.025	1.47	1.47	-0.1%
0.01	0.134	0.589	0.566	4.0%
0.03	0.030	8.65	8.55	1.2%
0.006	0.010	1.05	1.07	-1.9%
0.02	0.050	2.80	2.98	-6.0%

Table 7. Experimental and calculated reaction rates at 35°C.

a	b	$R_{\text{exp.}}(10^4)$ (moles l. ⁻¹ hr. ⁻¹)	$R_{\text{cal.}}(10^4)$	Difference of $R_{\text{exp.}}$ from $R_{\text{cal.}}$
0.01	0.010	25.6	24.3	5.4%
0.01	0.134	6.34	6.13	3.4%
0.01	0.050	10.2	10.1	1.3%
0.01	0.025	15.5	15.2	2.0%
0.01	0.010	25.6	24.3	5.4%
0.006	0.025	6.65	7.09	-6.2%
0.02	0.100	18.1	19.1	-5.6%
0.03	0.075	44.1	45.3	-2.6%

Table 8. Constants in $R = k_c(a-x) + k_2(a-x)(x) + k'_c(x)$

	k_c (sec. ⁻¹)	k_2 (sec. ⁻¹ M. ⁻¹)	k'_c (sec. ⁻¹)
15°C.	8.3×10^{-7}	2.83×10^{-3}	6.9×10^{-6}
25°C.	2.9×10^{-6}	8.61×10^{-3}	2.8×10^{-5}
35°C.	9.7×10^{-6}	2.58×10^{-2}	9.2×10^{-5}
ΔH^\ddagger (kcal./mole)	21.0	19.2	22.2
ΔS^\ddagger (e. u.)	-13	-2.3	-4.5

In the rate law, equation (IV.10), the first and third terms are zero order in chloride, and are first order in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ and trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ respectively. This suggests that both these complex species can have chlorine introduced into the positions cis to the ethylene by an acid hydrolysis mechanism. Any additional mechanism first order in one of these complexes and zero order in chloride would be indistinguishable from the acid hydrolysis mechanism, since there was no feasible method of measuring the hydrolysis rate constants directly. However, the rate constants, k_c and k'_c , given are at least upper limits of the acid hydrolysis rate constants.

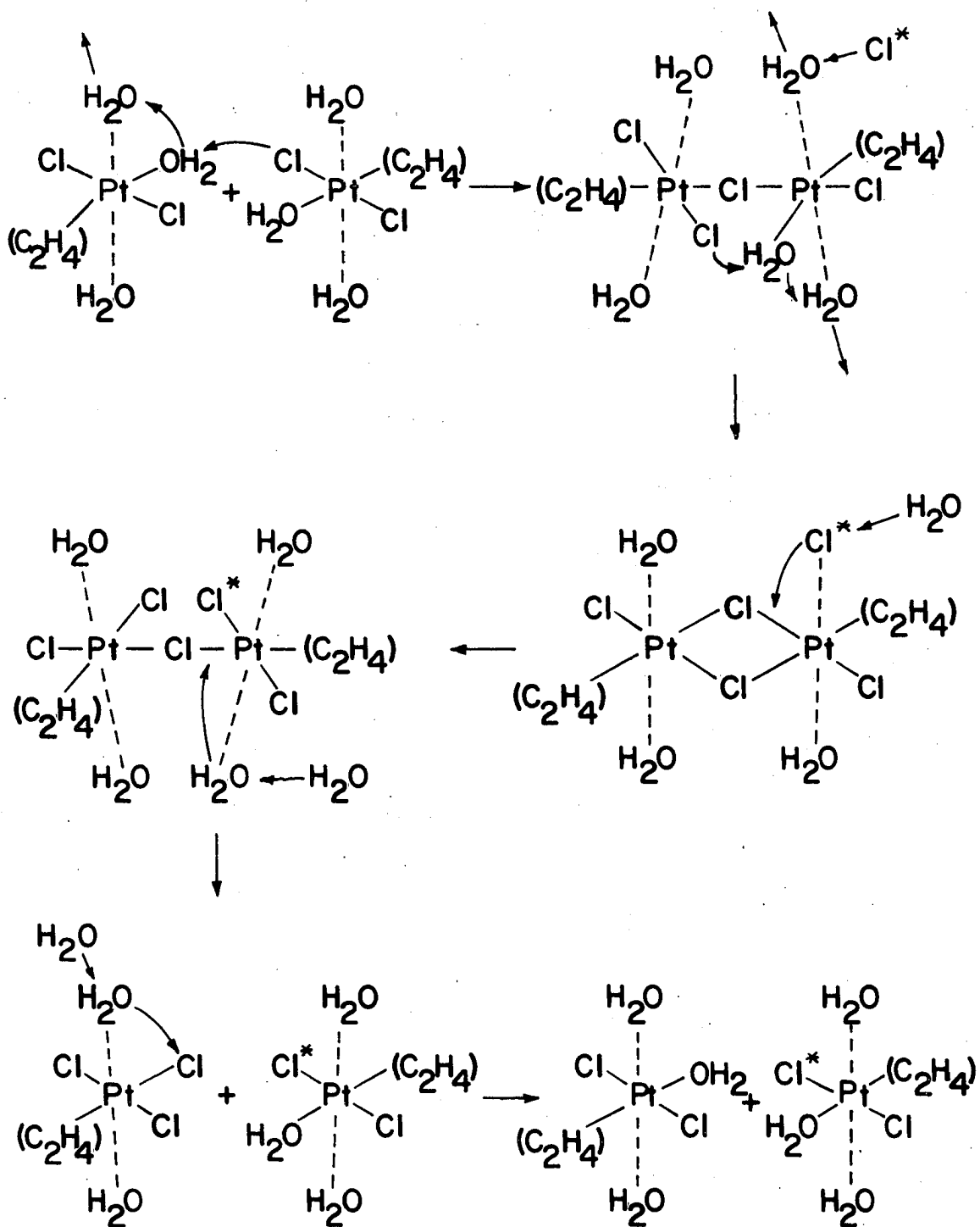
Now, in 26 out of the 30 experiments listed in Tables 5, 6, and 7 the second term in equation (IV.10) is larger

than either of the other two terms. In the other four experiments the first term was the largest. These were the four experiments in which the highest KCl concentrations were used; therefore, the trans-[Pt(C₂H₄)Cl₂(H₂O)] concentrations were low. In Fig. 6 a mechanism is given which may be the explanation of the second term in equation (IV.10). The product $(x)(a-x)$ is proportional to $(a-x)^2/(b+x)$ and to $(x)^2(b+x)$. Thus, mechanisms involving different species are possible explanations of this second term.

Other platinum(II) complexes that have been studied (22, 25, 30) were found to undergo exchange by acid hydrolysis processes, so the first and third terms in the rate law were not unexpected, but in these other systems there was no term similar to the second term in equation (IV.10). Thus, in future work in platinum(II) kinetics a search might be made for other systems that would show the same isotopic exchange kinetics as the trichloro(ethylene)platinate(II)-chloride system. Of course, other olefinic complexes of platinum(II) are known (35, 36, 37, 38), but it might be more interesting to study one of the recently synthesized acetylenic complexes of platinum(II) (61).

Since the value of K_t was not known with much precision, the effect of different values of K_t on the form of the rate law was investigated. Calculations based on $K_t = 2 \times 10^{-3}$ or 4×10^{-3} gave no indication that another type of rate law would

Fig. 6. Bimolecular mechanism of exchange between chloride and trichloro(ethylene)platinate(II) ion.



fit if the value of K_t were different.

A few experiments besides those listed in the Tables were performed to study the effect of other variables on the exchange. When Cl^{36} was added immediately instead of aging the solution first, the same half-time was obtained as in corresponding aged solution experiments.

The hydrogen ion concentration was 0.143 molar in all the experiments listed in the Tables. In experiments in which the hydrogen ion concentration was 0.01 or 0.243 molar the same exchange half-times were found as in the corresponding listed experiments. In the one experiment in which no H_2SO_4 was used to increase the hydrogen ion concentration, the solution decomposed during the eight day aging period.

The exchange solutions were kept in flasks covered with opaque black tape in order that light would not be able to influence the exchange. In order to study the effect of light some solutions were started aging in untaped flasks. During this period laboratory lights were left on continuously, and a 100 watt light was kept burning near the constant temperature bath in which the solutions were aging. In each case the complex decomposed during the eight day aging period. When the KCl concentration was lowest the decomposition was fastest. The decomposition occurred despite the fact the hydrogen ion concentration was 0.143 molar in each case, and $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ had been observed to be stable in 3%

HCl for more than six months stored in a bottle exposed to laboratory lights. Apparently the presence of an anion other than chloride leads to instability. Solutions kept in taped flasks never showed signs of decomposition, even when kept as long as six months.

In another experiment the solution was aged in a taped flask, but the tape was removed when the Cl^{36} was added and the exchange started. The complex decomposed before infinity samples could be taken. However, an S_{∞} value was assumed that gave the correct initial value of $(1-F)$. This made it possible to estimate an exchange half-time 25% shorter than in a corresponding experiment in which all other conditions were the same, but the flask was kept taped.

Solid $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ must be stored in a desiccator in humid weather. A quantity that was stored in the laboratory atmosphere in a weighing bottle with a ground glass stopper picked up moisture from the air and slowly turned black. This is further evidence of the unstable nature of this compound.

V. SUMMARY

Evidence was found for the existence of cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ and cis- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}(\text{H}_2\text{O})_2]$ in aged solutions of $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$. The equilibrium constants for aquation in the cis positions could not be uniquely determined, but their limits could be determined for the extreme cases of the sum of the concentrations of the two species set equal to the concentration of one of them. All evidence indicated that trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ was present in much larger amounts than any other aquo species.

The kinetics of the isotopic exchange between chloride and trichloro(ethylene)platinate(II) was unexpectedly complicated. In the rate law there were three terms. Two terms were zero order in chloride and first order in trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$ and $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ respectively. These terms could be explained by reversible acid hydrolysis processes.

The other term in the rate law was the product of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ and trans- $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$. This was explained by a bimolecular mechanism with a transition state that involved a dimer with Cl bridging between the two platinum atoms.

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