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CHLORODICHLOROBIS(ETHYLENE) DIPLATINUM (II).

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REACTIONS OF TRANS-DI-μ-  
CHLORODICHLOROBIS(ETHYLENE)DIPLATINUM(II)

by

Douglas Glenn McMane

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Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

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## INTRODUCTION

The first platinum-olefin complex was discovered, and its chemical formula determined, long before Werner's classic work elucidated the structure of coordination complexes. It was more than one hundred years after they were first synthesized that the presently accepted bonding scheme for these compounds was proposed. This proposal led directly to a useful and widely applicable explanation for the trans effect in square planar complexes.

Although square planar coordination complexes, such as the platinum-olefin complexes, are formed by relatively few of the transition metal ions, they have been very extensively studied. This study has led to a sophisticated and powerful reaction mechanism theory for square planar complexes.

There was a great advance in the understanding of square planar complex bonding and kinetics between 1952 and 1955. The  $\pi$ -bonding explanation for the trans effect was proposed, and a very general rate law for ligand substitution in square planar complexes was reported for the first time. The presently accepted explanation of the nature of the metal-olefin bond in platinum-olefin complexes was also proposed at this time.

All the more recent work in the field took inspiration from three or four crucial papers published during these years.

The bonding theory and the rate law enabled the correlation of observed results, and the prediction of new results. The ability to do this led to greatly increased interest in the study of the reactions and kinetics of the square-planar complexes. These successful studies have significantly contributed to the revival of interest in the general field of inorganic chemistry which took place in the years immediately after 1955 and continues into the present.

### Early Work

#### Metal-olefin complexes

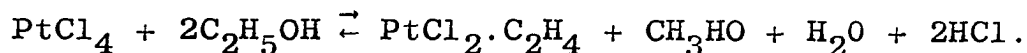
The first metal-olefin compound was prepared by Zeise (1) in 1827 by boiling platinum(IV) chloride with ethanol. In 1830 Berzelius (2) synthesized the same compound by refluxing ethanol with sodium tetrachloroplatinate(II). By this method an acid solution was obtained from which precipitated yellow crystals upon evaporation with potassium chloride. Zeise analysed his compound and obtained the composition  $\text{KCl} \cdot \text{PtCl}_2 \cdot \text{C}_2\text{H}_4$ . Liebig (3) disputed this analysis, obtaining the composition  $2\text{KCl} \cdot 2\text{PtCl}_2 \cdot \text{C}_4\text{H}_{10}$  for the same compound.

Thus began more than a century of controversy over this and other metal-olefin complexes. Zeise's analysis proved to be correct, and potassium trichloro(ethylene)platinate(II) is still commonly called Zeise's salt.

With the chemical composition determined, attention turned to the question of the presence of ethylene in the compound. Was it really present as such, and if so how was

it bonded to the metal?

Birnbaum (4) knew that ethylene could be obtained as one of the thermal decomposition products of Zeise's salt and attempted a direct synthesis by reacting ethylene with a tetrachloroplatinate(II) compound dissolved in dilute hydrochloric acid. This synthesis was successful, and hence ethylene was presumed to be present in the compound. He suggested that since an aldehyde was produced during the refluxing of platinum(IV) chloride with an alcohol Zeise's synthesis probably followed the reaction



Much later, Anderson (5) separated a compound with composition  $\text{PtCl}_2 \cdot \text{C}_2\text{H}_4$  from a brown, tarry mixture produced when sodium tetrachloroplatinate(II) was evaporated from an alcohol solution under vacuum. This compound was called ethylene platinous chloride. Kharasch and Ashford (6) synthesized this compound by reacting tetrachloroplatinate(II) ions with ethylene in anhydrous solvents such as benzene.

Though platinum seemed best able to form these metal-olefin complexes, other metals did form them to a limited degree. Palladium-olefin complexes, in particular, were found to be quite similar to platinum-olefin complexes. An excellent review was made by Keller (7) of this subject up to 1941.

Ethylene platinous chloride and its palladium analogue were found to be dimeric in benzene solution (6). This was

considered reasonable, since it maintained a coordination number of four for the metal. This compound is now characterized as  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ , and in modern nomenclature its name is trans-di- $\mu$ -chlorodichlorobis(ethylene)diplatinum(II).

There was much discussion, now of primarily historical interest, on the nature of the olefin-metal bond, and on whether the bridging groups in the dimer were chlorine atoms or olefin molecules.

Pfeiffer and Hoyer (8) thought that the double bond was still functioning in the complex because many unsaturated organic compounds, e.g., unsaturated alcohols, acids, and aldehydes, form analogous complexes, but no saturated organic compound was known that would coordinate in a similar metal complex. The exact nature of the bond to the metal was unknown. Hel'man (9) made one of the best, though rather vague, early guesses when she proposed that platinum functions first as a donor, and then as an acceptor, of electrons. She suggested that this results in the formation of a four electron bond between the olefin and the metal.

#### The trans effect and synthesis of square planar complexes

In 1844 and 1845 Reiset (10) and Peyrone (11) reported the preparation of two isomers of the compound now called dichlorodiammineplatinum(II). Werner (12), in the course of his extensive investigation of coordination complexes, proposed that these were geometric isomers of a square planar type complex. He also suggested a trans elimination process

to account for some of the early experimental observations.

This concept, which proposed that ligands in the square plane are more easily replaced if they are in a trans position to some particular ligands showing a strong trans directing influence, was useful in the systematic synthesis of many square planar complexes. Much of this work was done by Russian chemists. Chernyaev (13) was one of the first to clearly state the principle, and did much of this type of synthesis work.

From observations made while synthesizing platinum(II) complexes, and from kinetic studies of the rate of ligand substitution of these complexes, many ligands can be listed in order of decreasing ability to labilize the ligands trans to themselves in square planar complexes. Such a list has been given by Basolo and Pearson (14, p. 385) as  $\text{CN}^-$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{NO} > \text{SC}(\text{NH}_2)_2$ ,  $\text{PR}_3$ ,  $\text{SR}_2 > \text{NO}_2^- > \text{I}^-$ ,  $\text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3$ , pyridine,  $\text{RNH}_2 > \text{OH}^- > \text{H}_2\text{O}$ .

Russian chemists were responsible not only for making use of the trans effect in synthetic work but also for proposing an early theory to explain the effect. As developed by Grinberg (15) from ideas of Nekrasov (16) this theory predicted that ligands which could be easily polarized would be strong trans directors. The platinum carries a positive charge, and this would induce a dipole in the trans directing ligand such that negative charge would accumulate on the side of the trans director toward the platinum. This would in turn induce



dipoles in the platinum and in the leaving ligands trans to the trans director such that negative charge in the leaving ligand would accumulate on the side away from platinum. If the bond to the leaving ligand were formed by electron donation from ligand to platinum, this would have the effect of weakening the bond. The bond weakening would then lead to a faster rate of substitution for this ligand.

The polarization theory has been largely superseded by theories making use of molecular orbital bonding concepts, as will be described in the next section.

#### Recent Work

#### Kinetics and mechanism of ligand substitution reactions of square planar complexes

A rate law has been found which adequately characterizes the kinetics of ligand substitution reactions of many square planar complexes.

$$R = (k_1 + k_2 [Y]) [C] \quad \text{Eq. 1}$$

where  $[Y]$  is concentration of entering ligand and  $[C]$  is concentration of complex.

This rate law was first proposed in an important paper by Rich and Taube (17). They investigated the exchange kinetics of chloride ion with the tetrachloroaurate(III) ion, found that the system followed the rate law of Eq. 1, and postulated the basic mechanistic course of the reaction.

Their suggestion was that the exchange through the path characterized by  $k_2$  occurred upon the formation of a trigonal

bipyramidal intermediate, with the entering and leaving groups occupying the apical positions. They also proposed that hydrolysis by an SN2 mechanism was the rate determining step for the path characterized by  $k_1$ . They postulated that this path might be related to the availability of axial positions above and below the platinum atom in its square plane for bonding to solvent molecules.

The next important contributions to the understanding of the mechanism of ligand substitution in square planar complexes were made independently and nearly simultaneously by Chatt et al. (18) and by Orgel (19).

These workers attempted to explain the mechanism of the trans effect, discussed in the preceding section, through the use of  $\pi$ -bonding and molecular orbital theories. The formation of a dative  $\pi$ -bond with a ligand, as shown in Fig. 1, would utilize the  $d_{xz}$  orbital of the platinum atom and its electrons to form a  $d\pi$ - $p\pi$ -bond with a vacant p orbital on the ligand. This would withdraw electrons from the two  $d_{xz}$  antinodes in the position trans to the ligand, and permit easier nucleophilic attack down the Z axis toward the platinum and through the XZ plane to the position occupied by the trans leaving group. In Fig. 1 the trans directing group is L, C and C' are the unaffected cis groups, Y is the entering group, and X is the leaving group.

This mechanism postulated that a trigonal bipyramidal transition state was indeed formed, but that it was the trans

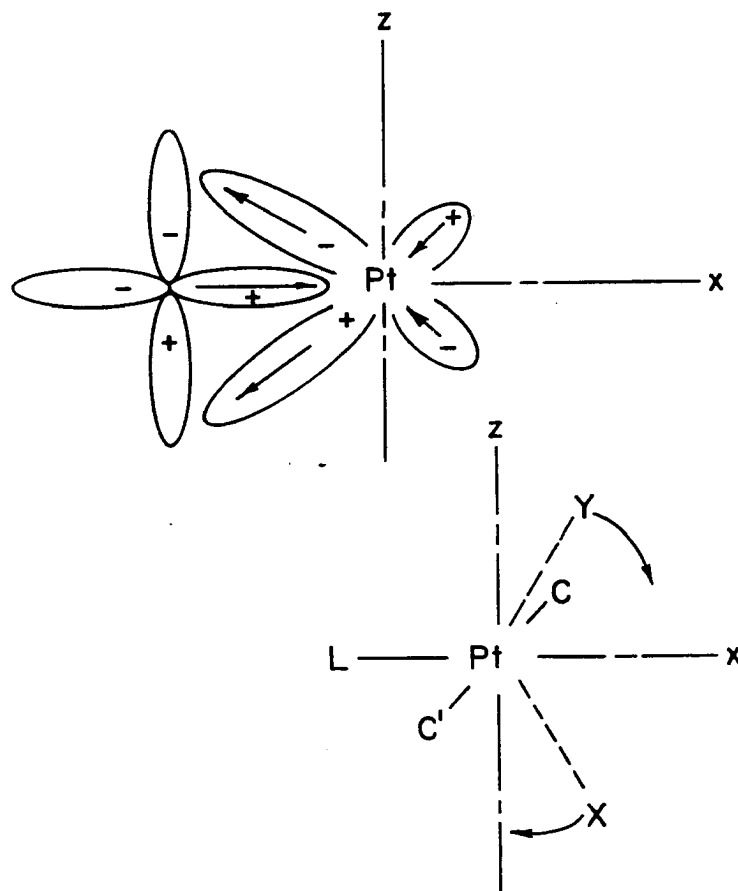


Fig. 1. Electron drift in bond to  $\pi$ -bonding trans director and site of attack of entering ligand

directing ligand, the entering, and the leaving groups that formed the trigonal equatorial plane.

Orgel mentioned that this particular  $d\pi-p\pi$ -orbital mixing should always be present in the transition state, and that the presence of a good trans director, i.e., a ligand that could easily accept the platinum  $\pi$ -electrons, would lower the activation energy of the transition state. Chatt made a special point of mentioning that, contrary to the then current assumption, the Pt\_\_X bond in Fig. 1 would not necessarily be weakened by the presence of a good trans directing ligand. He suggested that the  $\sigma$ -bond formed by the ligand X donating electrons to the platinum would not be affected by the trans director, and the Pt\_\_X bond would be weakened by the trans director only if X were itself a trans director in the sense of being able to form dative  $d\pi-p\pi$ -bonds. In this case there would be competition for platinum electrons between the two trans directing groups, and the bonds to both would be weakened.

It has become apparent that a  $\pi$ -bonding explanation alone is not enough to account for the trans directing influence of all ligands. Some good trans directors, such as  $H^-$ , have no low energy orbitals available to accept electrons for the formation of the  $\pi$ -bond. It was found by Chatt et al. (20) that  $\pi$ -bonding was not very important in Pt\_\_Cl bonds, yet the length of the Pt\_\_Cl bond trans to ethylene in  $Pt(C_2H_4)Cl_3^-$  is 0.1 Å longer than the Pt\_\_Cl bonds cis to

ethylene. From these observations it was clear that both  $\sigma$ - and  $\pi$ -bonding effects were contributing to the trans effect. Langford and Gray (21) have recently proposed a combined  $\sigma$ - and  $\pi$ -bonding molecular orbital explanation of the trans effect.

They proposed that if the orbitals of a ligand have large overlap with the  $6p_{\sigma}$  orbital on platinum a strong  $\sigma$ -bond will be formed between the ligand and platinum. The bond to the ligand trans to this strong  $\sigma$ -bond will be weakened as the strongly bonded trans director moves toward the platinum and the less strongly bonded leaving group moves away. This provides a larger share of the p orbital to the bond with the greatest overlap. Since in the transition state the entering and leaving group share a  $p_z$  orbital and the  $p_x$  orbital is available primarily to the trans director, the energy difference between ground and transition state would be smaller for the case where a good  $\sigma$ -bonding trans director was present. They calculated the overlap between the ligand orbitals involved in  $\sigma$ -bonding and the  $6p_{\sigma}$  orbital on platinum and found that  $H^-$ ,  $PR_3$ , and  $CH_3^-$  do have unusually large overlap for  $\sigma$ -bonding to platinum. On the basis of these calculations it also seemed likely that the trans effect of  $SCN^-$  and  $I^-$  are primarily due to  $\sigma$ -bonding effects.

When the overlap of empty  $\pi$ -bonding ligand orbitals with  $5p_{\pi}$  orbitals on platinum was calculated, it was found that  $CO$ ,  $CN^-$ , and  $C_2H_4$  had large  $\pi$ -bonding overlap. The trans effect

of these ligands was attributed primarily to  $\pi$ -bonding effects, much as explained by Chatt et al. (18).

Banerjea et al. (22) reported kinetic studies showing that ligands which were good trans directors were also good entering ligands for square planar complexes, and replaced other ligands primarily by the path characterized by the second order  $k_2$  term in Eq. 1. This they explained by suggesting that in the trigonal plane of the activated species there are free d electrons available for dative  $\pi$ -bonding to a ligand which has empty  $\pi^*$ -orbitals. These electrons are in  $d_{xz}$  and  $d_{x^2-y^2}$  orbitals and form a partial bond with the entering group to stabilize the transition state. Since it is just the same availability of empty ligand  $\pi^*$ -orbitals which gives the ligand its trans directing property, the entering ligand would be expected to accept these platinum electrons and stabilize the transition state. Poor trans directors, which could not form these partial bonds to stabilize the transition state, were not found to be good entering groups. For these reagents the  $k_2$  path in the rate law was not so important, and in many cases was not observed.

A slightly different mechanism for ligand substitution has been suggested (22) in which the bond from platinum to the leaving group dissociated as solvent molecules in the axial positions moved in toward the platinum. Once this bond dissociated, the site in the square plane was postulated to be available for bonding to a solvent molecule, followed by rapid

replacement of the solvent by the entering reagent. This mechanism would give the path characterized by  $k_1$  in the rate law of Eq. 1. The entering reagent might alternatively directly replace the dissociated leaving group, to give the exchange path characterized by  $k_2$ .

This differed from the first mechanism, in which the attacking group would bond to the axial site and then move in the XZ plane down to its ultimate site in the square plane as the leaving group moved down into the other axial position

Martin and coworkers (23-27) investigated chloride exchange and aquation rates in tetrachloroplatinate(II) and the series of chloroammine complexes of platinum(II). Their work substantiated the rate law of Rich and Taube, and they also found that the value of  $k_1$  was essentially independent of the charge on the substrate complex. This demonstrated that the path characterized by  $k_1$  was leading to ligand substitution through an aquation of the complex as the slow step. If a simple dissociation were leading to exchange, charge separation would be an important factor and there would be a marked dependence on substrate charge for the value of  $k_1$ . They also showed that the aquation rate was consistent with the exchange rate given by the  $k_1$  path.

Elleman et al. (25) suggested that a square bipyramidal transition state, with dissociation of the bond to the leaving group, required, by the principle of microscopic reversibility, another path by which the entering group would directly

attack the leaving group site in the square plane while the leaving group was still bonded. They preferred the trigonal bipyramidal transition state proposed by Chatt and Orgel to account for the trans effect.

This trigonal bipyramidal transition state was confirmed by Gray and Olcott (28). They studied the substitution reactions of  $\text{Pt}(\text{dien})\text{X}^+$ , where dien was diethylenetriamine and X was  $\text{Cl}^-$  or  $\text{NO}_2^-$ . They argued that if a square pyramidal transition state and dissociative mechanism led to the aquation of  $\text{Pt}(\text{dien})\text{X}^+$ , then the transition state reacted only with solvent, and never with the entering reagent. For if the transition state, with the bond to the leaving group dissociated, could be attacked by the entering reagent, the first order exchange rate would be faster than the rate of aquation. This would contradict Martin and coworker's findings in the series of chloroamines.

Gray and Olcott then demonstrated that the reaction of the  $\text{Pt}(\text{dien})\text{H}_2\text{O}^+$  species with  $\text{X}^-$  also followed the rate law indicated in Eq. 1, with one term first order in complex only, and one term second order in  $[\text{complex}][\text{X}]$ . The value of the first order constant  $k_1$  was the same for  $\text{X} = \text{Cl}^-$  and  $\text{X} = \text{NO}_2^-$ . This indicated that the water to platinum bond could dissociate, to be followed by rapid addition of X. The transition state would be just the same as for the  $\text{Pt}(\text{dien})\text{X}^+$  square pyramidal transition state. But they had argued that if this transition state existed for  $\text{Pt}(\text{dien})\text{X}^+$  it could not



react with X without giving faster exchange than was observed.

By this elegant argument it was shown that the existence of a square pyramidal dissociation transition state for  $\text{Pt}(\text{dien})\text{X}^+$  was impossible because it demonstrably did exist for the  $\text{Pt}(\text{dien})\text{H}_2\text{O}^+$  species.

It has been found (29) that blocking the axial positions by steric hindrance decreases the rate of ligand substitution. When this was done, the kinetics resembled those of ligand exchange of octahedral complexes. Ligands are exchanged in octahedral complexes by a dissociative process, and it is reasonable that with the axial positions effectively blocked square planar complexes would exchange by the same mechanism.

The trigonal bipyramidal transition state is now generally accepted as the mechanism leading to ligand substitution in square planar complexes whose axial positions are not blocked by steric hindrance.

Pearson et al. (30) studied the effect of the solvent medium on the first order path for relatively poor entering reagents. Chloride replacement for trans-dichlorodipyridine-platinum(II) was studied in many different solvents. They found that the solvents could be divided into two groups. In poor solvents for ions the chloride ion had a high reactivity, and a second order path in  $[\text{complex}] [\text{Cl}^-]$  fit the rate data. Further, in solvents that were known to interact strongly with the axial positions of the platinum(II) ion, the second order path was not important regardless of the solvating ability of

the solvent.

It was found that in solvents where second order dependence was not important, the exchange rates paralleled the  $\pi$ -bonding ability of the solvents rather than the solvating power, or dielectric constants, of the solvents.

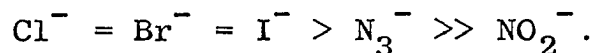
Drago et al. (31) have reported a study suggesting that in some cases the solvating power of the solvent, rather than its coordinating ability, determines the importance of the solvent path characterized by the  $k_1$  term. Both properties apparently make some contribution, so that though the coordinating ability of the solvent is the major factor to be considered, the solvating properties of the solvent cannot be ignored.

Belluco and coworkers (32-41) have reported the results of a series of studies on the kinetics of the ligand substitution in platinum(II) complexes, including the effects of solvent changes.

They have shown that ligands with empty  $\pi^*$ -orbitals available, such as  $\text{HNO}_2$ , are excellent entering reagents (32), in agreement with Banerjee et al (22). They also found that anions, such as  $\text{NO}_2^-$ , are not as good entering reagents. If the  $\pi$ -bonding theory were correct, this result would be expected since the anion would not be able to accept electrons as readily to form the dative  $\pi$ -bond to platinum.

They showed that changing from protic to dipolar aprotic solvents does not change the order of reactivity of entering ligands, and that there is little solvent effect on the relative

ease of displacement of different leaving ligands. Also, there did not seem to be a direct relationship between the order of reactivity of entering groups and the order of ease of displacement of leaving groups. While the entering group reactivity paralleled the trans director ability, the ease of replacement was in the order



Since the entropies of activation are in general negative for ligand substitution reactions of platinum(II) complexes, and since studies of the solvent effect on these reactions indicated that solvation effects were not able to account for the negative entropies of activation, Belluco et al. (37) have concluded that in the transition state bond making is more important than bond breaking. They believed that for  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  leaving groups the bond breaking step is fast compared to the bond making step. But for leaving ligands which can accept electrons from platinum to form the dative  $\pi$ -bond, the bonding between platinum and the leaving group further facilitates the bond making step, exactly as is done by a trans director. They have postulated that with these ligands as leaving groups the bond making step becomes faster than the bond breaking step. This is especially likely to happen if there is a strong trans director in the position trans to the leaving group. In these cases, they suggested, the ease with which the bond from platinum to the leaving group can dissociate influences the rate of ligand substitution.

Their general conclusion was that the mechanism involves two transition states and a transient intermediate. The rate determining step is usually the formation of the five coordinate intermediate. The negative entropy of activation is primarily due to a net increase in bonding in the transition state. There is some solvation effect on the rate of ligand substitution but in general, and especially in dipolar aprotic solvents, it is less important than the ability of the solvent to coordinate to platinum.

Bonding, structure, and reactions of the trichloro(ethylene)-platinate(II) ion

The nature of the platinum-olefin bond was brilliantly deduced in a short series of papers by Chatt and coworkers (42-44). Chatt (42) recognized that the nature of the bonding in these complexes must be such as to require an extension or modification of the lone pair coordination bond theory then current.

Before his work it was not known whether one olefin molecule was attached to one platinum atom, and some workers (6) had suggested that platinum-olefin-platinum bridges were responsible for the bonding. Chatt confirmed by a molecular weight determination that ethylene platinous chloride was dimeric in boiling benzene. But he was also able to show from molecular weight measurements in boiling and freezing benzene that  $C_6H_4Me.NH_2.C_2H_4.PtCl_2$  existed as a monomer in solution.

It was obvious from this that an olefin bridge between two platinum atoms was not an essential feature of the bonding, and Chatt considered ways in which one olefin molecule could be bonded to a single platinum atom.

He demonstrated that ethylene did not interact with trimethylboron and concluded that since this species should accept electrons as readily as a platinum atom, more than the usual lone pair acceptor bond to the central metal atom was involved.

He made the observation that in general only elements at the end of a transition series were able to form metal-olefin complexes. This gave credence to Hel'man's suggestion (9) that filled metal d orbitals contributed to the bonding.

In 1952 Chatt and Wilkins (43) reported the preparation of  $\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2$  by passing ethylene into an acetone or methyl ethyl ketone solution of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  at  $-70$  degrees C. In doing this they discredited at least part of Hel'man's bonding scheme, as she had proposed that not more than one olefin molecule could be coordinated to a platinum atom.

Chatt and Duncanson (44) then proposed the generally accepted bonding scheme for  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ . They determined from infrared spectra and dipole moment studies that the double bond was still present in the coordinated ethylene, and that the olefin-platinum bond probably had about one-third double bond character. They postulated that electrons from the ethylene double bond were donated to an empty  $5d6sp^2$

orbital on the platinum to form a  $\sigma$ -type bond. Back donation of electrons from a filled 5d6p orbital on platinum to an occupied  $\pi$ -antibonding orbital on ethylene formed a  $\pi$ -bond that accounted for the partial double bond character.

Their proposed bonding scheme and structure for Zeise's anion, trichloro(ethylene)platinate(II), can be seen in Fig. 2. It is most interesting to note the similarity between Fig. 1 and Fig. 2. Chatt published his  $\pi$ -bonding explanation for the trans effect a year after this paper appeared, but most of the essential thinking had been done here. He even shows the antinodes on the  $d_{xz}$  orbital trans to ethylene to be smaller than those directed toward the ethylene. Only the concept of axial attack of the entering group on the square plane was needed to explain the ability of ethylene to labilize the position trans to itself.

In 1959 Babushkin et al. (45) published an infrared spectrum analysis of trichloro(ethylene)platinate(II) which indicated that the carbon-carbon bond had essentially single, rather than double, bond properties. For some time after Chatt's work was published they argued that he had made the wrong assignment of an infrared band and that this bonding proposal was wrong. Recent analysis of the infrared spectrum by Grogan and Nakamoto (46) and Pradilla-Sorzano and Fackler (47) indicate that Chatt was essentially correct in his assignment, but Grogan and Nakamoto warn that carbon-carbon stretching vibration couples with an in-plane  $\text{CH}_2$  scissoring

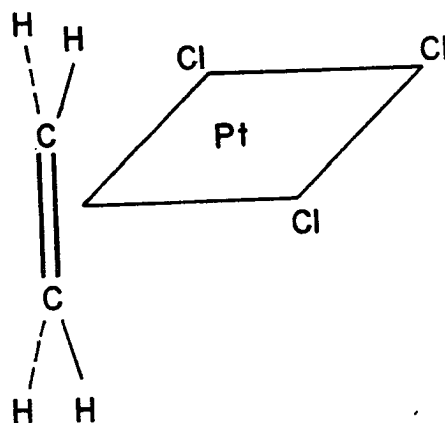
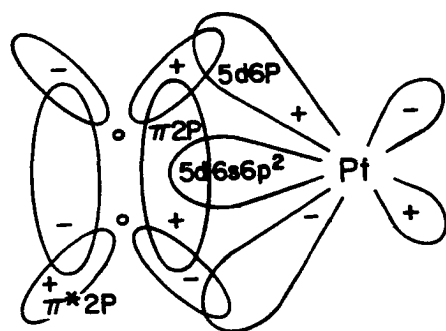


Fig. 2. Bonding and structure in Zeise's anion,  
 $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$

vibration, and cannot be used as an unambiguous indicator of the amount of double bond character.

Bokki and Kukina (48) and Wunderlich and Mellor (49) have done crystal x-ray analyses of potassium trichloro(ethylene)-platinate(II) monohydrate. These analyses both agree that the carbon-carbon bond is perpendicular to the square plane and that both carbon atoms are equidistant from the plane. Wunderlich and Mellor (50), in an addition to their first analysis, gave the carbon-carbon distance as 1.5 Å, the platinum-cis chloride distance as 2.32 Å, and the platinum-trans chloride distance as 2.42 Å. The platinum-chloride distances were well determined, and showed that there was bond weakening to the chloride trans to ethylene. The carbon-carbon distance was uncertain. The results tended to confirm Chatt's bonding and structure proposals.

No x-ray crystal structure of the  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  dimer has been found in the literature but Dempsey and Baenziger (51) have reported the structure of the palladium analogue. They indicated that the plane of ethylene was perpendicular to a line joining palladium and the double bond center. The palladium-chloride-palladium bond angle was nearly ninety degrees, but the palladium-chloride bond trans to ethylene and in the bridge was 2.43 Å long, 0.1 Å longer than the palladium-chloride bridge bond trans to chloride.

In 1958 Dyatkina (52) had published a



molecular orbital treatment of platinum-ethylene compounds that included double bond character in the platinum-olefin linkage as an essential feature.

The nature of the carbon-carbon bond in these compounds has also been investigated by nuclear magnetic resonance techniques. Powell and Sheppard (53) found from the chemical shifts of the carbon-hydrogen bonds in ethylene that the coordinated ethylene has an electronic structure much closer to free ethylene than would be expected for a structure with a carbon-carbon single bond and a triangular bonding coordination with the platinum.

The ethylene in the complex was found by Cramer (54) to exchange rapidly. He studied the ethylene exchange by nuclear magnetic resonance techniques, and found that the rate of exchange was greater than  $70 \text{ sec}^{-1}$  at temperatures as low as  $-75$  degrees C.

Chloride exchange studies of trichloro(ethylene)platinate-(II) have been carried out by Grinberg and Kuz'mina (55) and Lokken and Martin (56).

Grinberg found that the chloride trans to ethylene exchanged too rapidly to be distinguished from the free chloride in solution, and the chlorides cis to ethylene were stabilized. He measured the activation energy of the cis chloride exchange as 12 Kcal/mole. He concluded that exchange was by a dissociation mechanism with the probable intermediate formation of aquated ions.

In the much more thorough study by Lokken and Martin the exchange rate for the cis chlorides was found to be best described by the expression

$$R = k_c [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + k_2 [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + k_c' [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]. \quad \text{Eq. 2}$$

The values of the rate constants and entropies and enthalpies of activation are given in Table 1.

Table 1. Constants in  $R^a = k_c [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + k_2 [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] + k_c' [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]$

	$k_c$ ( $\text{sec}^{-1}$ )	$k_2$ ( $\text{sec}^{-1} \text{M}^{-1}$ )	$k_c'$ ( $\text{sec}^{-1}$ )
15°C	$8.3 \times 10^{-7}$	$2.83 \times 10^{-3}$	$6.9 \times 10^{-6}$
25°C	$2.9 \times 10^{-6}$	$8.61 \times 10^{-3}$	$2.8 \times 10^{-5}$
35°C	$9.7 \times 10^{-6}$	$2.58 \times 10^{-2}$	$9.2 \times 10^{-5}$
$\Delta H^\ddagger$ (kcal/mole)	21.0	19.2	22.2
$\Delta S^\ddagger$ (cal/mole degree)	-13	-2.3	-4.5

<sup>a</sup>Rate of cis chloride exchange at 0.318 M ionic strength.

The value of  $k_c$  was smaller than expected, agreeing with the results of Grinberg and Kuz'mina (55), and indicating a stabilization of the cis positions. The absence of a chloride dependent path was not surprising, at least for the trichloro species, as it is negatively charged. The dichloroaquo species was always present in comparatively small amounts, so that a rather small chloride dependent term involving it might not

have been observable.

The path second order in complex was surprising; it dominated in experiments with a relatively high concentration of the trichloroaquo species.

A mechanism was proposed in which the dimer species  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ , known to exist in benzene solution and as a solid, was postulated as a transient intermediate in the aqueous solution. A bridging chloride was postulated to be labilized, relative to a cis chloride in  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$ , by the presence of an ethylene group trans to it. This trans ethylene group would facilitate attack, and it might then be expected that a chloride in the bridge would exchange faster than a cis chloride in  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$ . When the dimer was cleaved by solvent attack the platinum-chloride bond trans to ethylene was postulated to break, leaving the exchanged bridging chloride in the cis position of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$ .

Grinberg and Shagisultanova (57) mentioned they had found some indication that at high complex concentrations bromide exchange in tetrabromoplatinate(II) proceeded by a path higher than first order in complex.

This was confirmed by Teggin et al. (58). Table 2 gives the rate constants and entropy and enthalpy of activation reported for the rate law

$$R = k_1 ([\text{PtBr}_4^{2-}] + [\text{PtBr}_3(\text{H}_2\text{O})^-]) \\ k_3 [\text{PtBr}_4^{2-}] [\text{PtBr}_3(\text{H}_2\text{O})^-]. \quad \text{Eq. 3}$$

Table 2. Constants in  $R^a = k_1([PtBr_4^{2-}] + [PtBr_3(H_2O)^-]) + k_3[PtBr_4^{2-}][PtBr_3(H_2O)^-]$

Temperature	$k_1$ ( $sec^{-1}$ )	$k_3$ ( $sec^{-1} M^{-1}$ )
15°C	$7 \times 10^{-5}$	$1.3 \times 10^{-1}$
25°C	$2.2 \times 10^{-4}$	$2.2 \times 10^{-1}$
40°C	$1.15 \times 10^{-3}$	$4.0 \times 10^{-1}$
$\Delta H^\ddagger$ (Kcal/mole)	19	8
$\Delta S^\ddagger$ (cal/mole degree)	-10	-36

<sup>a</sup>Rate of bromide exchange at 0.318 M ionic strength.

Although the planar doubly bridged dimer species  $Pt_2Br_6^{2-}$  is known to exist as a solid (59), absorption spectra data indicated that its rate of formation and cleavage in water was too slow to account for the second order in complex exchange term observed.

A single bromine bridge between the tetrabromo and tribromoaquo species was postulated to form as a transient intermediate, with one bromide being lost to solution in the bridge formation. This could lead to the observed second order exchange path observed for bromide exchange.

Teggins and Martin (60) have reported that the bromide exchange of  $Pt(dien)Br^+$  is catalyzed by the presence of  $PtBr_4^{2-}$ . The rate constant for the term  $k_a[Pt(dien)Br^+][PtBr_4^{2-}]$  was  $0.20 \text{ sec}^{-1} M^{-1}$  at 25 degrees C.

The enthalpy of activation was 15 Kcal/mole and the entropy of activation was -16 cal/degree mole. The exchange of bromide in the  $\text{PtBr}_4^{2-}$  was catalyzed by the presence of the bromodiethylenetetrammine complex at about the same rate.

$\text{Pt}(\text{dien})\text{Br}^+$  can form only a single bromide bridge, and the authors postulated that exchange occurs by the reverse of a process in which a bromide is lost in the formation of such a bridge. They believed it most likely that the approximate equality of the second order in complex rate constants for both species involved is coincidental.

In this thesis a report will be made on reactions, especially isotopic chloride exchange, of trans-di- $\mu$ -chlorodichlorobis(ethylene) diplatinum(II). It was thought likely that since the doubly bridged dimer is crystallized from ethanol it would exist primarily as the dimer species in ethanol solution. Hence, a comparison of the cis chloride exchange rate in ethanol with the rate for the trichloro(ethylene)platinate(II) species in water might be expected to further elucidate the nature of the mechanism leading to the second order in complex rate path.

## EXPERIMENTAL

## Chemicals

Platinum

Platinum was obtained as wire from the J. Bishop Chemical Company. It was dissolved in boiling aqua regia and the solution made alkaline with sodium hydroxide. Platinum black was obtained by reduction with hydrazine from the hot alkaline solution. Less reactive metals were removed by washing the platinum black with hot nitric acid, rinsing with water, and washing with hot hydrochloric acid. The platinum black was again dissolved in aqua regia, and the platinum purified from iridium, as suggested by Jowanovitz et al. (61). The iridium was removed by three successive crystallizations of the platinum from solution as potassium hexabromoplatinate(IV). This was necessary because iridium impurities are known to affect reactions of platinum complexes (62, 63).

The purified hexabromoplatinate(IV) was converted to the hexachloro form by boiling several times to near dryness with excess hydrochloric acid.

After use in experiments the platinum was reclaimed by reducing hot alkaline solutions of the waste compounds with hydrazine. The platinum black was then washed as above with nitric and hydrochloric acid.

Potassium hexachloroplatinate(IV)

After the platinum was purified, dissolved in aqua regia, and taken to the hexachloro form by boiling to near dryness several times with hydrochloric acid, the potassium salt was precipitated by the addition of potassium chloride.

Potassium tetrachloroplatinate(II)

Potassium oxalate and a small amount of platinum black were refluxed with an equimolar amount of potassium hexachloroplatinate(IV) for about an hour to prepare potassium tetrachloroplatinate(II). This oxalate reduction method was first suggested by Vezes (64). The solution was filtered while hot and then allowed to evaporate almost to dryness. Small amounts of water were used to extract the salt away from the potassium chloride impurity, but no attempt was made to completely purify this compound.

Potassium trichloro(ethylene)platinate(II)

This compound was synthesized by the method of Chatt and Searle (65). An aqueous solution of the moderately pure potassium tetrachloroplatinate(II) containing 10 % by volume concentrated hydrochloric acid was put in a tightly stoppered glass flask. The flask was connected to a tank of ethylene and a manometer was put in the line between the flask and tank to allow control of the pressure. The flask was mechanically shaken for six or seven days under about ten pounds pressure of ethylene. At the end of this time the solution had changed from red to a greenish-yellow color, and

there was a little platinum black on the bottom of the flask, indicating that some decomposition had occurred. When this solution was filtered, the filtrate was clear and light yellow. As it evaporated at room temperature it became golden yellow with no indication of further decomposition. The concentrated solution was evaporated to dryness in a vacuum desiccator containing concentrated sulfuric acid to absorb the water and a dish of potassium hydroxide pellets to absorb the hydrochloric acid. Some white crystals of potassium chloride were formed during this evaporation, and a little unreacted potassium tetrachloroplatinate(II) was observed. The compound was purified by recrystallization from water. The ultraviolet absorption spectrum of the product was compared with a spectrum of purified and analyzed compound obtained by Lokken and Martin (56). The spectrum compared with theirs in all respects. In particular, the valleys, which are very sensitive to impurities, were as deep as those they obtained.

Trans-di- $\mu$ -chlorodichlorobis(ethylene)diplatinum(II)

This compound was also synthesized by the method of Chatt and Searle (65). Potassium trichloro(ethylene)platinate(II) was dissolved in 95 % ethanol with about 5 % by volume of concentrated hydrochloric acid added. The potassium chloride that precipitated was filtered off, and the filtrate was slowly evaporated to dryness under vacuum. The yellow color of the original solution gradually became deeper, and finally



the solution became orange and viscous. At this point the temperature was raised to 60 degrees C and the evaporation continued to dryness. This product was purified by refluxing with boiling toluene for about two minutes with a small amount of activated charcoal added. The refluxed solution was quickly filtered through a rapid flow heavy duty filter paper in a heated glass funnel. The filtrate was cooled in an ice bath and the product collected. The color of the product varied from orange to light brown. It was stored in a desiccator in the dark. Typical analyses gave 1.99 moles of platinum and 3.90 moles of chloride per nominal mole of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ . The platinum was analyzed as weight of residue after heating in a 300 degree C oven. The chloride was analyzed as silver(I) chloride after boiling the compound in a concentrated ammonia solution and precipitating with silver nitrate.

#### Ethanol

Ethanol, both 95 % and absolute, was from stock drums supplied by the Commercial Solvents Corporation. At the beginning of the research an attempt was made to prepare dry ethanol from the 95 % ethanol by a modification of the method of Vogel (66, p. 166). The 95 % ethanol was refluxed, first over calcium oxide, and then over anhydrous calcium sulfate. After the ethanol was distilled away from the calcium sulfate its water content was determined by the method of Vogel (66, p. 20). This method makes use of the critical

solution temperature of a three phase mixture of ethanol, water and bicyclohexyl. The dried ethanol typically contained 0.2 or 0.3 % by weight water, and was satisfactory for use. The ethanol was stored in a glass stoppered bottle. Even after storing for several months it did not gain more than an additional 0.1 % by weight water.

This ethanol was used as solvent in preliminary experiments, but the method of preparation was time consuming. It was decided to investigate the properties of absolute ethanol as supplied by Commercial Solvents Corporation. There was some concern that benzene impurities would interfere with the determination of the ultraviolet spectra of compounds, but it was found that there was no interference. While the absorption was about 0.05 absorption units higher than in the 95 % ethanol and dried ethanol below 3300 Å, the characteristic sharp peaks of benzene were not observed. The water content of the absolute ethanol was about 0.1 % by weight, better than had ever been obtained with the drying procedure. It was believed that if there were trace organic impurities in the absolute ethanol they were less likely to cause difficulties than the undetectable traces of basic ionic impurities that might be carried over in the distillation of the dried ethanol. The absolute ethanol was therefore used as solvent in the major portion of the experimental work.

Chlorine 36

Chlorine 36, a pure beta emitter with a half-life of  $3.0 \times 10^5$  years, was obtained as 2.04 N hydrochloric acid, with a specific activity of  $0.037 \pm 10$  % mc/ml, from the Oak Ridge National Laboratory.

Tetraphenylarsonium acetate

This chloride free precipitating agent for the trichloro-(ethylene)platinate(II) ion was required to make the chemical separation necessary for the study of the exchange kinetics. It was prepared by passing tetraphenylarsonium chloride through an anion exchange resin in the acetate form.

Tetraphenylarsonium chloride

This compound was obtained from the Aldrich Chemical Company.

Ethylene

A tank of C. P. ethylene was supplied by the Matheson Company, Inc.

Bicyclohexyl

The bicyclohexyl used in the determination of the water content of the ethanol was obtained in purified form from the Eastman Organic Chemicals Division of the Eastman Kodak Company.

Anhydrous calcium sulfate

Calcium sulfate was obtained in the anhydrous form as Drierite, from the W. A. Hammond Company.

Tris(hydroxymethyl)aminomethane

A primary standard grade of this reagent, used for standardizing stock solutions of hydrochloric acid in ethanol, was obtained from the Fisher Scientific Company.

Benzil

Benzil was used as the standard for molecular weight determinations in ethanol solution, and was obtained from the Matheson Scientific Company. Benzil is a common name for the ketone  $C_6H_5COCOC_6H_5$ .

Exchange resin

The resin used for conversion of tetraphenylarsonium chloride to the acetate salt was Amberlite I R A 400, a strong base anion exchange resin.

Water

Distilled water, which was used only as a solvent for the determination of equilibrium quotients, and not as a solvent for exchange kinetic studies, was used as supplied to the building. It had been condensed from steam and ionic impurities had been removed by ion exchange.

Miscellaneous chemicals

Various other common reagents and solvents were used, and were supplied in reagent grade by such companies as J. T. Baker, Matheson Scientific, and Allied Chemical Company.

EquipmentCounting devices

A model 196 scalar manufactured by Nuclear Chicago was

used for counting the  $\text{Cl}^{36}$  beta emitter. The scalar was equipped with a timer also supplied by Nuclear Chicago. The Geiger-Mueller counting tube was a Nuclear Chicago type D-34, with a window thickness of  $1.4 \text{ mg/cm}^2$ .

#### Spectrophotometer

The ultraviolet absorption spectrophotometer, used in the determination of equilibrium quotients, and for identification of species in solution was a Cary Model 14 with hydrogen lamp. This is a recording spectrophotometer with a range from 0.0 to 2.0 absorption units on a linear scale. The precision is 0.005 absorption units when readings are taken from the chart paper.

Silica or Vycor cells were used for optimum transmission in the ultraviolet range. Path lengths available were 0.1, 1.0, 2.0, 5.0 and 10.0 cm. All but the 0.1 cm cells were closed by ground glass stoppers.

Temperature control in the cell compartment was provided by circulating water from an external bath through the walls of the cell compartment. The temperature of the external bath was regulated so that the temperature in the cell compartment, as determined by a thermometer extending through a hole in the cover and into a small beaker of water in the cell compartment, was at the desired point.

#### Vapor phase osmometer

This instrument, used in the determination of molecular weights in ethanol solutions, was manufactured by the

Hewlett-Packard Company, Model 301 A. It was equipped with a non-aqueous solvent thermistor assembly to be used at  $25.0 \pm 0.2$  degrees C.

#### Balances

Three balances were used, the choice for a particular application depending on a compromise between convenience and precision. The most precise was a semi-micro analytical balance for weighings to 0.01 mg, the next a chain type analytical balance for weighings to 0.1 mg, and the least precise was a single pan automatic type balance for weighings to about 0.2 mg. All were manufactured by Wm. Ainsworth and Sons, Inc.

#### Water Baths

Temperature control was maintained with E. H. Sargent and Company water baths equipped with a NSI-12 Sargent circulating and heating unit and control unit. The controlling heater was turned on and off by a Philadelphia Micro-Set mercury in glass thermoregulator. Temperature control in the baths was maintained to  $\pm 0.1$  degree C.

#### Thermometers

E. H. Sargent and Company 0.1 degree C mercury in glass thermometers were available that had been company calibrated against a National Bureau of Standards certified thermometric system. These were used to standardize working thermometers.

## Procedures

Spectrophotometric determination of equilibrium constants

Careful control of the platinum concentration was required for precision in the determination of the equilibrium constants. Usually only 0.01 or 0.02 g of complex would be weighed and diluted to 100 or 200 ml. It was found that in most cases the use of a semi-micro balance and weighings to 0.01 mg substantially improved the precision over that obtainable with weighings to 0.1 mg on an automatic balance. Where weighings to 0.1 mg were sufficient, a chain type balance gave better service than an automatic balance.

It was not necessary to calibrate volumetric flasks or pipettes for the delivery of water, but it was found helpful to standardize pipettes to be used for the delivery of ethanol.

The dimer compound tended to be just a little sticky, so that for the most careful work with small quantities of compound transfer from weighing paper to solution was not entirely satisfactory. Small glass weighing boats were prepared in the shape of a funnel, so that the compound could be rinsed into a volumetric flask with no possibility of loss.

To increase internal consistency in a series of spectra, the solutions were prepared volumetrically from one freshly prepared stock solution of compound, taking care to adjust conditions such that only one pipette was required with volumetric flasks of different sizes. This seemed to give the best results, compared to making a separate weighing for each

solution concentration, or to using several different calibrated pipettes.

Osmometric determination of molecular weights

The molecular weight determination depended upon measuring the concentration of low volatility entities in solution through their lowering of the vapor pressure of the solution. Solvent would condense on the solution of lower vapor pressure and the temperature difference was measured. Two thermistor beads were positioned about 0.5 cm apart over solvent in an insulated compartment, and a drop of solvent would be placed on one, a drop of solution on the other. The temperature difference between the beads was measured by balancing a bridge in such a way as to measure the difference in resistivity between the two beads.

It was essential that there be thermal equilibrium in the compartment, so solvent was added below the beads eight hours before measurements were made. Six syringes were provided in the instrument; solvent and solutions were added to them a few minutes before measurements were made so that the solution would be in approximate thermal equilibrium when drops were placed on the beads. To make a measurement, a drop of solvent would be placed on the reference bead, the sample bead would be washed with a few drops of solvent, and then a syringe containing one of the solutions on which measurements were to be made was lowered into position nearly touching the sample bead. Several drops were put on the bead at intervals



of a few seconds to rinse the pure solvent from it, and then one drop was hung in place and the syringe raised to its rest position. The drop size was such as to double the size of the bead. It was not necessary to wait until the measured resistance difference was stable, but only until the drift was slow enough to permit precise balancing of the bridge. Five minutes was sufficient with the ethanol solvent used, and all readings on sample and reference solutions were made after this time interval. The measured resistance difference was well reproduced on all trials by this procedure.

#### Kinetic study of chloride exchange rate

For each exchange experiment a weighed amount of complex was added to a volumetric flask, the appropriate amount of a stock solution of hydrochloric acid in ethanol was pipetted into the flask, and then ethanol was added to the mark. The complex dissolved after shaking for a few seconds, and the solution was quickly poured into a 250 ml actinic red glass Erlenmeyer flask with a ground glass stopper. The protection from the higher energy light afforded by the red glass was necessary to inhibit decomposition, which is rapid if solutions with no acidity are exposed to the light, and occurs even at moderately high acidity upon exposure to light. It was fortuitous but helpful that solutions which had to be preserved for long periods of time had the highest chloride concentration, and hence the highest acidity.

No attempt was made to control the ionic strength of the exchange reaction solutions, or of ethanol solutions for any other work done. It was difficult to control ionic strength and buffer the acidity because few salts will dissolve in ethanol. At the same time, ion pair effects in ethanol would make it difficult to be sure of the ionic activity in a solution whose nominal ionic strength was known. At no time were any unusual effects or deviations from expected results noted that were likely to be due to changes in the ionic strength.

Difficulty was encountered from changes in the hydrochloric acid content of the stock solution over a long period of time. The solution had been stored in a bottle with a ground glass stopper, at a concentration of about 0.2 N, and it was not expected that further precautions would be needed. This was not the case. A series of experiments had been started just after the stock solution had been made up, so the chloride concentration was not in doubt. A second series had been started several months later, but at the same time the stock chloride had been used in re-checking an equilibrium constant that was particularly sensitive to the chloride ion concentration. Since the value obtained duplicated a value previously determined while working with another freshly prepared stock chloride solution, it was assumed that the chloride concentration had not appreciably changed at this time. A third series of experiments was started shortly before the chloride concentration was checked, so these were assumed to be made

with the stock solution at the new concentration. This left only a few experiments of doubtful validity. The precision of the fit of the data bore out these assumptions. After the instability of the chloride concentration of the stock was noted, the titre of the solution was checked before each new series of experiments was begun.

The chloride concentration of the stock solution was determined by titrating the hydrochloric acid with tris(hydroxymethyl)aminomethane. The ethanol solution was diluted at least ten to one with water so the solution to be titrated was essentially aqueous. A methyl red end-point was used. The solution of standard base was checked occasionally against sulfamic acid, and was found to be stable.

The flasks containing the reaction solution were stored in a water bath at the experimental temperature for aging before the chlorine 36 was added to start the exchange. This aging period was at least four days and in some cases longer than two weeks. The chlorine 36 was added as 2.0 N hydrochloric acid. The maximum solution dilution due to this addition was one percent. The maximum change in the chloride concentration was five percent, and where it was this high the amount of chloride added to start the exchange was included in the calculation of the chloride concentration for the exchange experiment.

For the first few experiments 20 microliters of the chlorine 36 solution was added at full strength as supplied

by the manufacturer. It was later decided to take advantage of the ability to calculate the specific activity of an "infinite time" precipitate from the value of the total activity added to start the exchange. This was done by diluting 0.5 ml of the chlorine solution to 50 ml and adding exactly 1.0 ml of this diluted stock to 100.0 ml of the reaction solution.

The specific activity of the diluted stock solution was determined by quantitative chlorine precipitation as mercury(I) chloride with potassium chloride added as carrier. The size of the aliquot of diluted stock and the amount of potassium chloride added were controlled so that both counting rate and precipitate weight would be comparable to those obtained from an exchange reaction. An experiment was done to ensure that the counting rate of chlorine 36 was essentially the same in the mercury(I) chloride precipitate as in the tetraphenyl--arsonium trichloro(ethylene)platinate(II) precipitate used in the exchange experiments.

Aliquots of the reaction solution were pipetted into ten ml of 0.536 N potassium chloride. This diluted the activity in the labile trans chloride position, quenched the exchange reaction, and ensured that any solvation that had occurred in the trans position was reversed, to permit more complete precipitation. It was found that for reaction solutions of low platinum concentration no precipitate would form unless the high chloride solution was used. In the

reaction solutions of lowest platinum concentration 20 ml of the 0.536 N chloride solution was used to facilitate precipitation.

The tetraphenylarsonium trichloro(ethylene)platinate(II) precipitate was formed by adding 5 to 30 ml of a solution approximately 0.1 N in tetraphenylarsonium acetate to the aliquot of the reaction solution with chloride added.

The volume of the aliquot of the reaction solution was chosen so as to give a precipitate weight between 10 and 40 mg in most cases. It was recognized that there is a dependence of the measured counting rate on the thickness of the precipitate, so an attempt was made to keep the precipitate weight constant over the course of each experiment. Even when this was not successfully done, there was no apparent correlation between precipitate weight and scatter in the data. The volume of the aliquot was always the same within each experiment, and varied from 10.0 ml for experiments most dilute in platinum to 2.0 ml for experiments most concentrated in platinum.

The precipitate was collected with suction on a circular Whatman 52 filter paper about 2.8 cm in diameter. The filter paper was supported on a sintered glass disk, and a glass chimney held in place by rubber bands was placed over the filter paper to contain the solution and precipitate during the filtering operation. The filtrate was washed three times with about 5 ml portions of a dilute solution of

tetraphenylarsonium acetate. The filtrate with its filter paper backing was air dried for at least six hours prior to weighing.

For every three or four sample precipitates collected a tare that had been weighed at the same time as the sample papers were weighed was washed in the same manner as the samples were washed, and set aside to dry with them. The change of weight of this tare was used to compensate for changes in weight of the sample filter papers due to humidity changes. Using this method the precipitates were weighed to within  $\pm 0.2$  mg.

The samples were then taped to square pieces of cardboard about 2 mm thick with wide Mylar cellophane type tape. The cardboard was sandwiched between an aluminum backing and a piece of aluminum with a hole centered over the sample. The aluminum backing was about 1 mm thick. This assembly was clipped together and placed at a controlled distance of about 0.7 cm from the window of a Geiger-Mueller tube with the sample centered under the circular window. The samples were counted from five to thirty minutes, depending on the counting rate, which seldom exceeded 4000 counts/min. A 30 minute background count was taken for each series of samples counted.

## CALCULATIONS

## Calculation of Equilibrium Quotients

The solvation equilibrium quotients were calculated from the absorbtivities of solutions of known total platinum and chloride concentration. For the solvation of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  by water the absorbtivity could be expressed by the equation

$$\text{Absorbtivity} = \epsilon_2[\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})] + \epsilon_3[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] \quad \text{Eq. 4}$$

where  $\epsilon_2$  was the molar absorbtivity of the dichloro species and  $\epsilon_3$  was the molar absorbtivity of the trichloro species. The wavelength was chosen such that there was considerable difference between the molar absorbtivities of the two species. When possible the wavelength was also chosen near a minimum or maximum in the absorption spectrum of one or both species. This minimized the errors in the absorption measurements that were due to small errors in the measurements of the wavelength.

The concentrations of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$  were determined by Eq. 4 and the equation

total platinum concentration =

$$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] + [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})]. \quad \text{Eq. 5}$$

Since the solutions were prepared by dissolving  $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3$  in water with added chloride the chloride concentration at equilibrium could be found from the equation

$$[\text{Cl}^-] = \text{added chloride concentration} + [\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]. \quad \text{Eq. 6}$$

The equilibrium quotient was then calculated by substitution into the expression

$$K_{\text{eq.}} = \frac{[\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})][\text{Cl}^-]}{[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-]}. \quad \text{Eq. 7}$$

The equilibrium quotient for the solvation of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  by ethanol was calculated in an analogous manner, except for Eq. 6. The equilibrium quotient for ethanol solvation was determined from solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in ethanol with added chloride, so the equilibrium chloride concentration was found from the equation

$$[\text{Cl}^-] = \text{added chloride concentration} - [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-]. \quad \text{Eq. 8}$$

#### Calculation of Molecular Weights

The resistance readings from the osmometer bridge were directly proportional to the temperature differences between the solvent and solution on the thermistor beads, and the temperature differences were in general related to the molar concentrations of the solutions through a polynomial in  $\Delta T$ .

In this case, a plot of the resistance readings against the molarity of the standard solutions gave a straight line. This plot was drawn, spanning the range of molarities of sample solutions. The molarities of the samples were obtained directly from the plot after the resistance readings of the samples were obtained. The apparent molecular weights of the species in the solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  were then



immediately available since the weight of dimer per unit volume of solution was known.

#### Calculation of Exchange Kinetic Results

An equation was derived which gave the activity in the cis chloride positions as a function of time, exchange rate, and solution concentrations. Several symbols were defined as they are listed below.

$[Cl^-]_0$  = added chloride concentration (moles  $Cl^-/l$ )

$I$  = total activity in solution (counts/min l)

$U$  = activity in cis position (counts/min l)

$S_s$  = specific activity of free and trans chloride  $= \frac{I - U}{[Cl^-]_0}$

$S_u$  = specific activity of cis chloride =

$$\frac{U}{2(\text{total platinum concentration})}$$

(counts/min l [mole cis  $Cl^-$ ])

$c$  = chloride concentration of solution used to

dilute aliquot before precipitation (moles  $Cl^-/l$ )

$S_p$  = specific activity of precipitate (counts/min mg)

$S_0$  = specific activity of precipitate at time = 0

(counts/min mg)

$S_\infty$  = specific activity of precipitate at a time long

compared to the half-time of exchange (counts/min mg)

$F$  = fraction of exchange  $= S_p/S_\infty$

$R$  = rate of exchange (moles cis chloride/l sec).

The equation determining the specific activity in the cis positions as a function of time was derived as in Eqs. 9 - 11.

$$\frac{dU}{dt} = R(S_s - S_u) = R \left[ \frac{I - U}{[Cl^-]_0} - \frac{U}{2(\text{total platinum concentration})} \right]$$

Eq. 9

$$\frac{dU}{dt} = \frac{RT}{[Cl^-]_0} - \frac{RU(2(\text{total platinum concentration}) + [Cl^-]_0)}{2(\text{total platinum concentration})([Cl^-]_0)}$$

Eq. 10

$$\text{Setting } \alpha = \frac{R(2(\text{total platinum concentration}) + [Cl^-]_0)}{2(\text{total platinum concentration})([Cl^-]_0)}$$

and solving the differential equation gave

$$U = \frac{2(\text{total platinum concentration})I(1 - e^{-\alpha t})}{2(\text{total platinum concentration}) + [Cl^-]_0}$$

Eq. 11

This expression for the activity in the cis position, was related to the specific activity of the precipitate. The specific activity of the precipitate included contributions from cis and trans activity, but the activity in the trans position was much diluted by the addition of aqueous potassium chloride solution to the exchange aliquot just before precipitation.

The derivation of the equation for the specific activity of the precipitate as a function of time was made for the case in which the volume of aliquot was equal to the volume of the diluting chloride solution added. The equation was

derived as in Eqs. 12 - 14.

$$S_p = U + \frac{I - U(\text{total platinum concentration})}{3([Cl^-]_0 + C)(\text{total platinum concentration})} \quad \text{Eq. 12}$$

$$\begin{aligned} S_p &= \frac{U}{3(\text{total platinum concentration})} + \frac{I}{3([Cl^-]_0 + C)} \\ &- \frac{U}{3([Cl^-]_0 + C)} = \frac{I}{3([Cl^-]_0 + C)} \\ &+ \frac{U([Cl^-]_0 + C - (\text{total platinum concentration}))}{3(\text{total platinum concentration})([Cl^-]_0 + C)} \quad \text{Eq. 13} \end{aligned}$$

Substituting the expression for U from Eq. 10

$$\begin{aligned} S_p &= \\ &\frac{I(3[Cl^-]_0 + 2c + 2((\text{total platinum concentration}) - [Cl^-]_0 - c)(e^{-\alpha t}))}{3([Cl^-]_0 + c)(2(\text{total platinum concentration}) + [Cl^-]_0)} \quad \text{Eq. 14} \end{aligned}$$

$S_0$  and  $S_\infty$  were found directly from this equation.

$$S_0 = \frac{I}{3([Cl^-]_0 + c)} \quad \text{Eq. 15}$$

$$S_\infty = \frac{I(3[Cl^-]_0 + 2c)}{3([Cl^-]_0 + c)(2(\text{total platinum concentration}) + [Cl^-]_0)} \quad \text{Eq. 16}$$

1 - F was obtained from  $S_p$  and  $S_\infty$ .

$$1 - F = \frac{2([Cl^-]_0 + c - (\text{total platinum concentration}))}{3([Cl^-]_0 + 2c)} e^{-\alpha t} \quad \text{Eq. 17}$$

The exponential part of the function was used to determine the rate of exchange. The specific activities of the precipitates were divided by the specific activity of the

precipitate taken at "infinite time", and the usual semi-logarithmic plot of  $1 - F$  against time was made. From the definition of  $\alpha$  the rate of exchange equaled

$$\frac{0.693(2(\text{total platinum concentration})([Cl^-]_0))}{(2(\text{total platinum concentration}) + [Cl^-]_0)(t_{1/2})}. \text{ Eq. 18}$$

The values of  $S_0$  and  $S_\infty$  depended upon the total activity added to start the exchange, the relative volumes of aliquot and added chloride solution, and the counting characteristics of the precipitate and counting equipment. The value of  $S_\infty$  was checked on many of the experiments by adding a known amount of activity and using Eq. 16 to calculate the value of  $S_\infty$ . Appropriate changes were made in the equation if the volume of aliquot was not equal to the volume of added chloride solution. The total activity added was in these cases controlled by adding known volumes of a solution of known specific activity to start the exchange. The calculated values of  $S_\infty$  agreed with the experimental values that were found from replicate sampling of the solution at "infinite time".

The theoretical value of the zero time intercept of the  $1 - F$  exchange plot could be calculated from  $S_0$  and  $S_\infty$ . The intercepts were usually between 1.0 and 0.90 and often greater than 0.95. 1.0 was the theoretical upper limit of the intercept. The experimental intercepts agreed with those calculated to within 2 or 3 % in most cases.

A computer program was used to determine a least squares straight line through the points of the  $\log(1 - F)$  against time plot. Each point was assigned a computer calculated weight, based on the following standard deviations.

$$\sigma_{\text{counting rate}} = \frac{(\text{total counts})^{1/2}}{\text{counting time}}$$

$$\sigma_{\text{precipitate weight}} = 0.2 \text{ mg}$$

$$\sigma_{\text{kinetic time}} = 0$$

Program input included the total sample counts and counting time, total background counts and counting time, precipitate weight, and kinetic time for each sample. Since  $\text{Cl}^{36}$  has an exceedingly long half-life, no decay correction was necessary.

The standard deviation in  $1 - F$  was computed from equations found in (67 and 68) relating to the propagation of errors. From this standard deviation the standard deviation of the logarithm of  $1 - F$  was computed, and the weight of the point was taken as  $1/\sigma^2(\log[1 - F])$ . The weights of the first few points were considerably higher than the weights of the points taken toward the end of the exchange, because the fractional deviations of the large values of  $1 - F$  were small.

The experiments with half-times longer than 100 hours were not followed for more than two or three half-times. The experiment with a 1100 hour half-time was followed for

only one half-time. Experimental values of  $S_{\infty}$  were not determined for these experiments. Since the total activity added to start these experiments was not known, a method for estimating the activity at infinite time by an iterative procedure was developed. The last samples taken were used to find a first approximation to  $S_{\infty}$ , and a first approximation to the half-time was found. The value used as an "infinite time" activity was then corrected by the expression

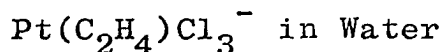
$$S'_{\infty} = \frac{S'_0 - S_0}{1 - e^{-0.693 t/t'_{1/2}}} + S_0 \quad \text{Eq. 19}$$

where  $S'_0$  was the first approximation to  $S_{\infty}$  and  $t'_{1/2}$  was the first approximation to the half-time. A second approximation to the half-time was established from  $S'_{\infty}$  and the process was repeated. The half-time approximation was changed for each iteration, but the value of  $S'_0$  was kept the same, equal to the specific activity of the last sample measured. The iterative process was programmed for the computer. Satisfactory results were obtained. The values of the half-time converged to differences of less than one hour within about twenty iterations for most experiments. No satisfactory convergence was obtained for the experiment with the 1100 hour half-time, so in this case the value for the half-time was taken such that the deviations of the last experimental points from the line were at a minimum value. Since even in this case the fit of the rate of exchange to the rate law

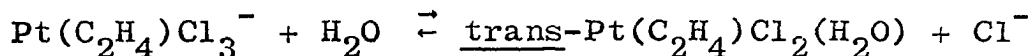
was moderately satisfactory, considerable confidence can be placed in this method of approximating the "infinite time" specific activity value.

## RESULTS

## Solvolysis Equilibrium Quotient of



Leden and Chatt (69) measured the value of the equilibrium quotient for the reaction



by a potentiometric determination of the chloride ion concentration of a solution of the complex in water. They reported a value of  $(3.0 \pm 0.5) \times 10^{-3}$  for  $K_{\text{aquation}}$  at 25 degrees C.

This value was used by Lokken and Martin (56) in a previous study done in this laboratory to characterize the kinetics of cis chloride exchange in  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ . In that study it was mentioned that the value was not as reliable as would have been desirable, but that no better value was available.

It was decided that as a preliminary to the study planned in ethanol solvent an attempt would be made to re-evaluate this quotient, using spectrophotometric techniques.

Since it was assumed that  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  was completely solvated in aqueous solution, the spectrum of this solution was used to determine the molar absorbtivity of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$ . The molar absorbtivity of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in aqueous solution was obtained by dissolving  $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3$  in



an aqueous 0.141 M chloride solution. The molar absorbtivities are shown in Fig. 3.

The equilibrium quotient was determined from the absorbtivities of solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  with various concentrations of added chloride, as shown in Table 3. The total ionic strength in all solutions was 0.318. It was possible to use the values for the molar absorbtivities obtained at 25 degrees C in the 35 degree C study, since the absorbtion bands involved are charge transfer bands, with low temperature coefficients.

A preliminary calculation of the equilibrium constant showed that the concentration of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$  was small in the 0.141 M chloride solutions, and hence the correction for the presence of this species in the determination of the molar absorbtivity of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  was also small.

The values determined for  $K_{\text{aquation}}$  were  $(2.6 \pm 0.2) \times 10^{-3}$  M at 25 degrees C and  $(3.0 \pm 0.3) \times 10^{-3}$  M at 35 degrees C. Using these values the  $\Delta H$  of the reaction was estimated to be  $2.5 \pm 1$  Kcal/mole.

After this study was completed a value of  $K_{\text{aquation}}$  of  $2.5 \times 10^{-3}$  M was published by Allen and Theophanides (70) for this reaction at 25 degrees C. Their study was based on potentiometric measurements of the chloride ion concentration, and they gave values for the solvation equilibrium quotient for several platinum-olefin complexes.

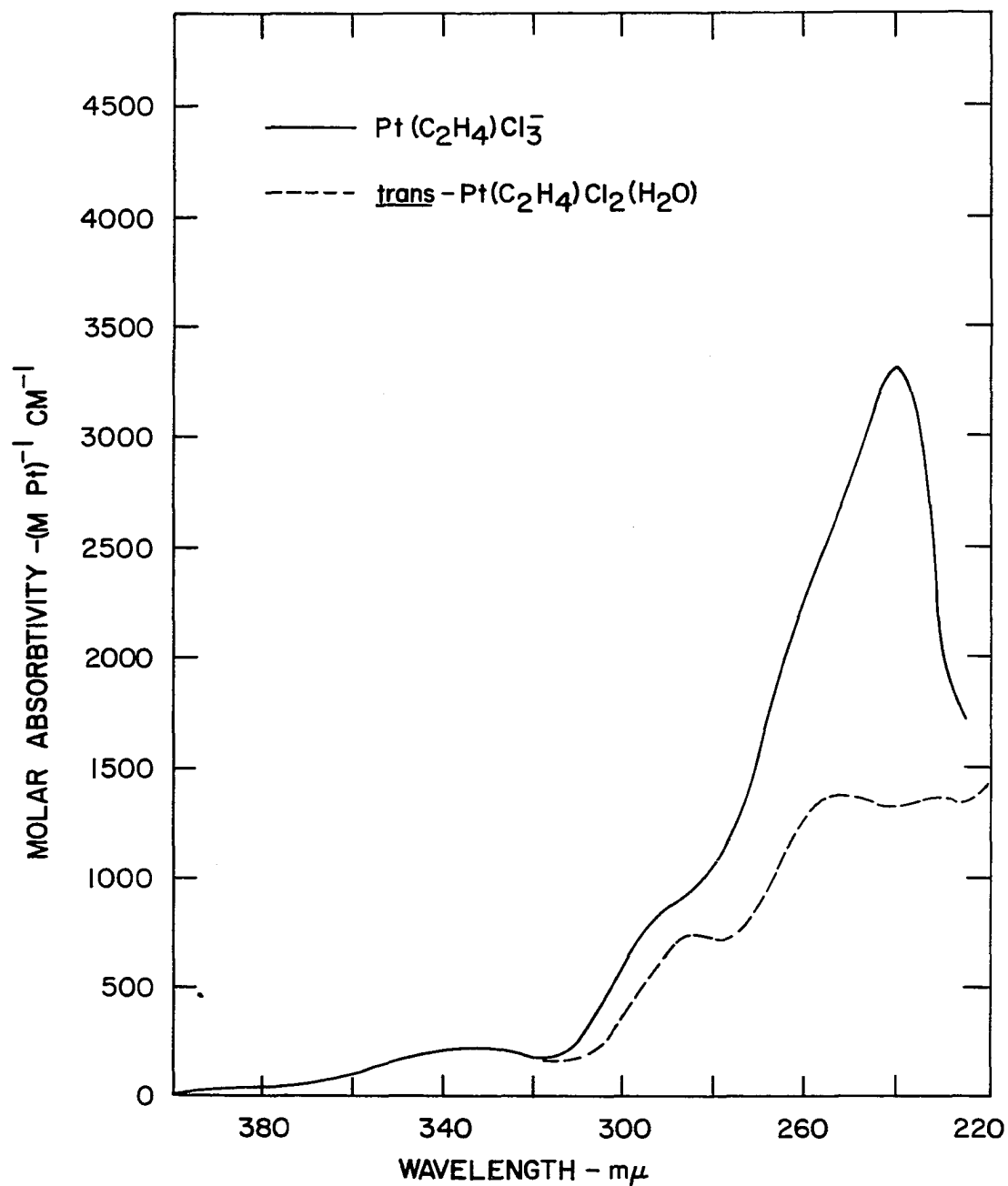


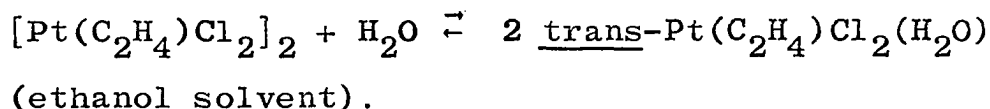
Fig. 3. Molar absorptivities (based on total platinum) of the  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and  $\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$  species in aqueous solution

Table 3. Solvolysis equilibrium constant of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in water

Platinum Concentration (mM)	Added Chloride Concentration (mM)	Absorbtion 2400 A, 1.0 cm cell	$K_{\text{(aquation)}}$ ( $\text{M} \times 10^3$ )
25 degrees C			
4.974	50.25	1.389	2.28
5.008	100.0	1.499	2.49
5.029	50.00	1.648	2.36
5.008	1000.	1.661	2.41
5.000	1410.	1.660	3.09
10.000	0	1.908	2.82
$K_{\text{(aquation)}} = (2.58 \pm 0.21) \times 10^{-3} \text{ M}$			
35 degrees C			
5.071	49.93	1.358	3.01
5.131	100.2	1.521	2.73
10.06	0	1.879	3.32
5.234	49.95	1.415	2.84
5.125	49.95	1.370	3.05
4.990	49.95	1.353	2.79
$K_{\text{(aquation)}} = (2.96 \pm 0.28) \times 10^{-3} \text{ M}$			
$\Delta H = 2.5 \pm 1 \text{ Kcal/mole}$			
$\epsilon(2400 \text{ A}) \text{ for } \text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^- = 3360 \text{ M}^{-1} \text{ cm}^{-1}$			
$\epsilon(2400 \text{ A}) \text{ for } \text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O}) = 1505 \text{ M}^{-1} \text{ cm}^{-1}$			

The Nature of the Solute Species in a  
Solution of Dimer in Ethanol

$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  was synthesized by dissolving  $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in 95 % ethanol, removing the precipitated potassium chloride by filtration, and evaporating the filtrate to dryness. Because the synthesis depended upon crystallization from ethanol, it was expected that the dimer species would predominate in a solution prepared by dissolving dimer in absolute ethanol. Based on this assumption, an attempt was made to measure an equilibrium quotient for the reaction



It was assumed that a spectrum of dimer dissolved in water would give the molar absorptivity of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$ , and that a spectrum of dimer dissolved in absolute ethanol would give the molar absorptivity of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ .

Various amounts of water were added to ethanol to prepare mixed solvents containing between 2 % and 25 % by weight water. Dimer was dissolved in these solvents and spectra were taken of the resulting solutions.

The spectra of the solutions of dimer dissolved in ethanol did change as the percent by weight of water was varied, but no satisfactory equilibrium quotient could be determined. The value of the "equilibrium quotient" that

was calculated changed as the percent by weight of water was changed, and also depended markedly on the wavelength chosen for the calculations.

An experiment was designed to ensure that the differences observed in the "quotients" were real, and not due to experimental error. A wavelength was chosen where the molar absorbtivity of dimer dissolved in water was equal to the molar absorbtivity of dimer dissolved in ethanol. Then the absorbtivities of solutions of constant platinum concentration but different water to ethanol ratios were determined. At 2875 Å the molar absorbtivities of solutions of dimer in water and in ethanol were equal to  $700(\text{M Pt})^{-1} \text{ cm}^{-1}$ . Fig. 4 shows the molar absorbtivities of the platinum species in solution as a function of the weight percent water in the mixed solvent. The maximum molar absorbtivity,  $820(\text{M Pt})^{-1} \text{ cm}^{-1}$ , occurred in a solvent that was 20 % by weight water and 80 % by weight ethanol. The changes in molar absorbtivity were too large and varied too regularly with the composition of the solvent to be explained by experimental error.

There were two possible explanations for these observations. Either there were one or more absorbing species in solution that had not been considered; or the differences in the relative concentrations of ethanol and water in the solvent environment around the platinum species

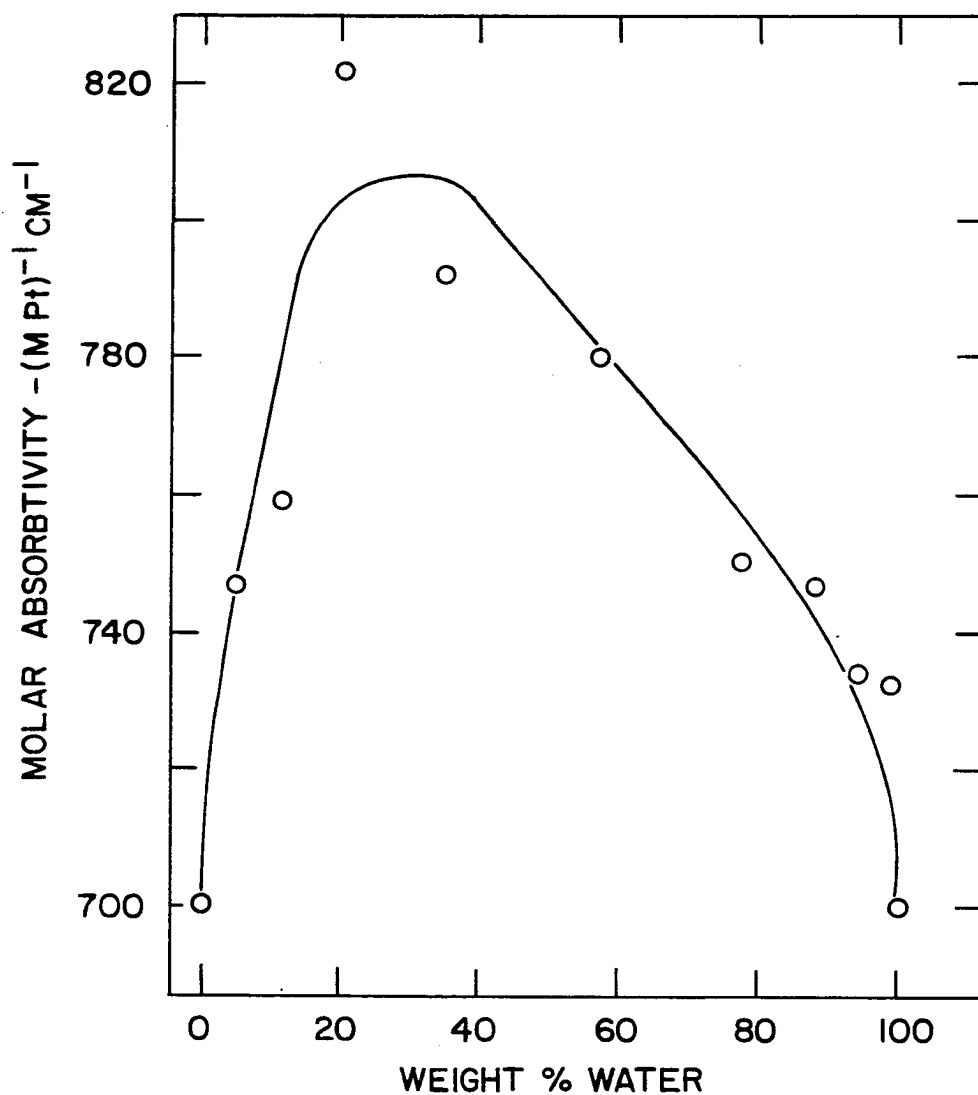


Fig. 4. Change in molar absorbitivity (based on total platinum) of solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in ethanol - water solvent mixtures as a function of the weight percent water.  $287.5 \text{ m}\mu$

led to differences in the absorptivities of these species. The latter explanation was considered the more likely, and if this were the case an equilibrium quotient could not have been determined by this technique.

Since both carbon tetrachloride and cyclohexane should be more inert towards complexing with  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in solution than is ethanol (30), this species alone was expected to be present in these solvents. An attempt was made to obtain spectra of solutions of dimer in these solvents, from which, it was expected, the spectra of the dimer species in solution could be determined with absence of solvating effects.

The dimer dissolved more readily in carbon tetrachloride than in cyclohexane, but even in the latter a  $4 \times 10^{-4}$  M solution could be prepared and the spectrum was recorded from 4000 Å to 2400 Å. Carbon tetrachloride was too opaque to obtain a spectrum in a 10.0 cm cell below 2700 Å, but the spectra of dimer in these two solvents could be compared (Fig. 5) from 4000 Å to 2700 Å. The peak and shoulder which were readily apparent in the spectrum of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  dissolved in carbon tetrachloride were nearly absent from the spectrum of the dimer dissolved in cyclohexane.

It was apparent that either the dimer species was being solvated by one of these solvents, or that there was some weaker interaction between the dimer species and the

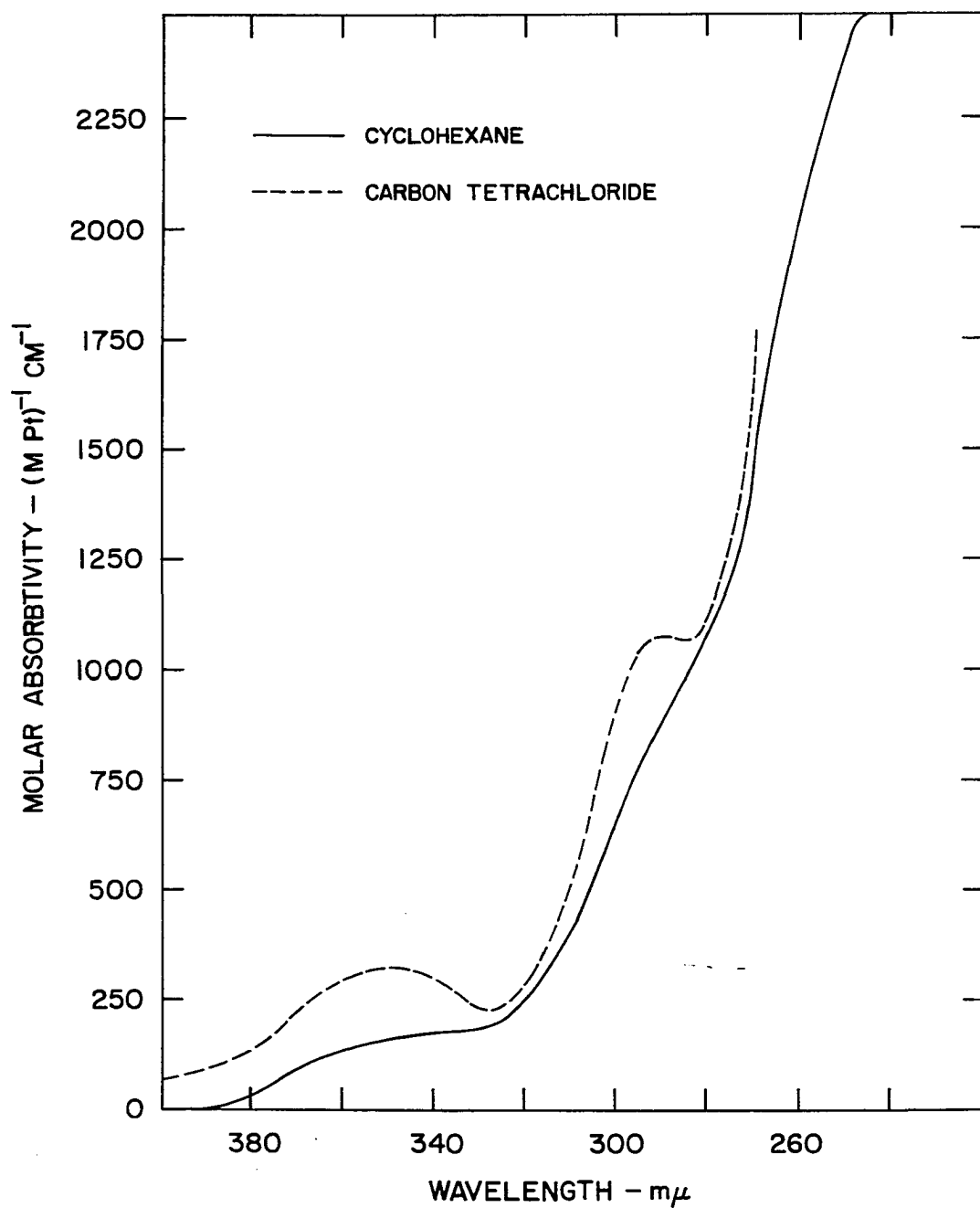


Fig. 5. Molar absorptivities (based on total platinum) of solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in cyclohexane and carbon tetrachloride



solvent that was causing differences in the spectra as the solvent was changed. In either case, it appeared as if an equilibrium constant for the cleavage of the dimer could not be determined from a study in an inert solvent medium with water added as a reagent.

Since there appeared to be some doubt about the extent of interaction between ethanol and  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  an attempt was made to find evidence for a monomer-dimer equilibrium in ethanol solvent. If such an equilibrium existed, more dimer species would be present in a solution of high total platinum than in a solution of low total platinum concentration. This suggested that a test of Beer's Law on solutions of dimer in ethanol would be relevant.

The concentration range that could be investigated with the spectrophotometer was roughly  $2 \times 10^{-2}$  M to  $2 \times 10^{-5}$  M, using 0.1, 1.0, 2.0, 5.0, and 10.0 cm cells. A study was made of solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in ethanol, water and a mixed solvent that was 80 % by weight ethanol and 20 % by weight water. The spectra of the solutions of dimer in the mixed solvent were recorded from 3050 Å to 2750 Å and the spectra of the solutions of dimer in ethanol and in water were recorded from 4000 Å to 2200 Å.

Typical results of the Beer's Law test can be seen in Fig. 6. While there was some apparent deviation from Beer's Law in the ethanol and water solutions below 2600 Å, there

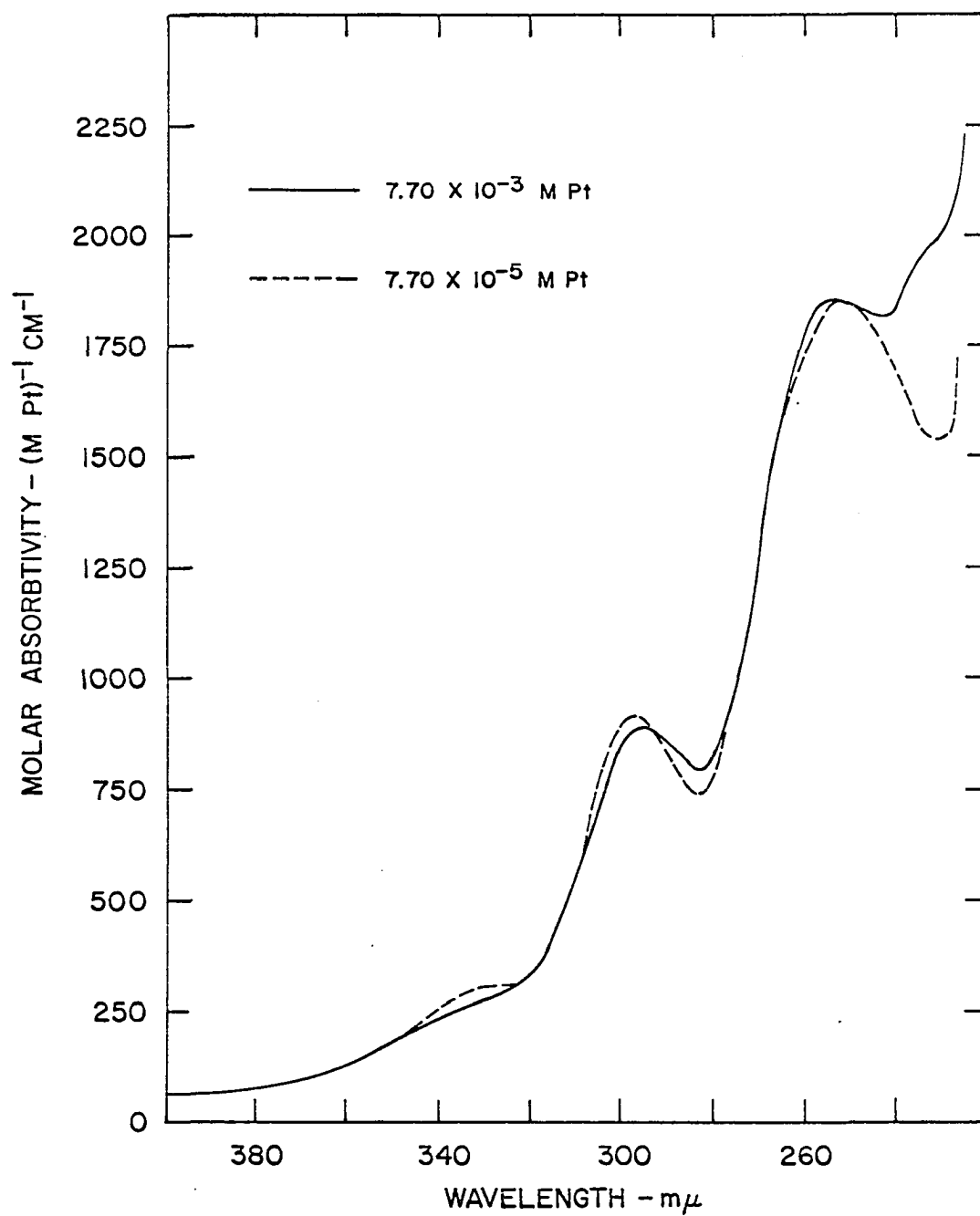


Fig. 6. Beer's Law test of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  dissolved in ethanol

was also difficulty in obtaining reliable spectra in this region. This difficulty was caused by the absorption of excessive light by the solvent when long path length cells were used. For instance, the automatically adjusted slit opened to 0.06 mm at 2500 Å and to 0.1 mm at 2400 Å with a 10.0 cm path length through ethanol. These values compared unfavorably with the usual operating slit width of 0.04 mm obtained with a 1.0 cm path length through water.

It seemed from the results of the study on these three solutions that Beer's Law was obeyed, although the results were to some extent uncertain, because of the difficulties in obtaining good spectra below 2600 Å.

Although it was possible that the complex was present primarily as the dimer species in the  $10^{-4}$  to  $10^{-5}$  concentration range in ethanol and present primarily as trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{H}_2\text{O})$  in the  $10^{-2}$  to  $10^{-3}$  concentration range in the mixed solvent, this was not considered likely, and the possibility arose that the dimer compound was solvated by ethanol as well as by water.

The Beer's Law test on  $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3$  dissolved in ethanol suggested that the spectra were concentration dependent, as shown in Fig. 7. This effect was probably due to the greater solvation of the monomer species in the more dilute solution. It was observed that as the solution became more dilute the spectra more nearly resembled the spectrum of

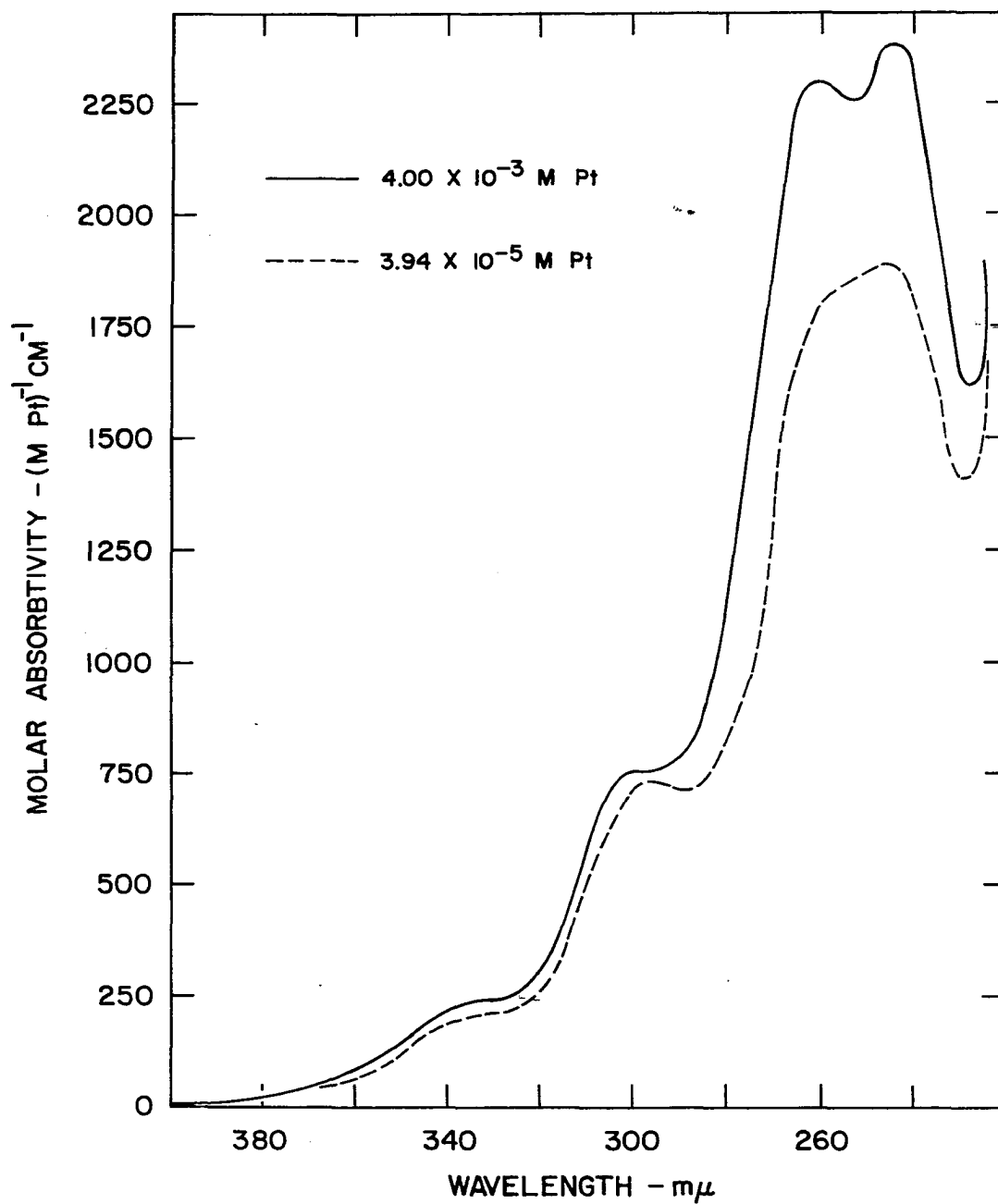


Fig. 7. Beer's Law test of  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$  dissolved in ethanol

dimer dissolved in ethanol. Further, when an equivalent amount of chloride was added to a solution of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  (with the chloride concentration equal to the total platinum and not dimer concentration), the resulting spectrum was the same as the spectrum of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  dissolved in ethanol with the same total platinum concentration.

While this was still negative evidence, and not positive proof, that the dimer was cleaved by ethanol to form two molecules of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ , all of the evidence considered together was convincing. This view was adopted as a working hypothesis.

It was later decided that it was necessary to check this conclusion more thoroughly. The argument would have been strengthened if a Beer's Law test had been made on solutions of dimer in mixed solvents with several varying water to ethanol ratios, but this still would have been only negative evidence for the existence of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ . Also, it was of interest to determine if the dimer species were predominate in solutions more concentrated than the  $10^{-2}$  to  $10^{-3}$  M concentration range that was the maximum possible in the spectrophotometric work.

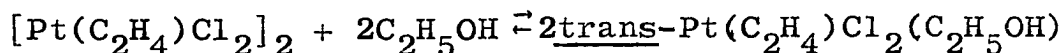
The possibility of making a molecular weight measurement on the platinum complex species present in the ethanol solution was considered. It was found that there was a good possibility for making satisfactory measurements of the

molarity of a solution of dimer in ethanol at room temperature in the 0.010 to 0.025 M total platinum concentration range by using a vapor phase osmometer.

Solutions of benzil in ethanol were used to calibrate the instrument in the 0.004 to 0.025 M concentration range. Dimer was dissolved in ethanol to prepare solutions from 0.010 to 0.025 M on a total platinum basis. The molarity of these solutions was measured.

The results of this experiment are listed in Table 4. While the measured concentrations on a monomer basis were all a little low, indicating that some dimer may have been present, it was apparent that at 0.025 M total platinum the trans-Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH) species predominated, and that 10 % of the total could be set as the upper limit for the amount of platinum present as the dimer species.

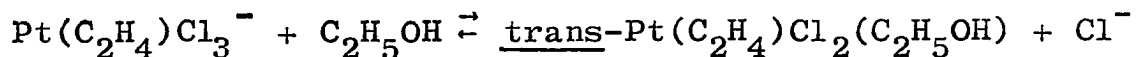
The conclusion reached on the basis of the spectrophotometric evidence was positively confirmed by this molecular weight measurement. The reaction



goes nearly to completion in ethanol if the solution is 0.025 M or less in platinum.

Solvolysis Equilibrium Quotient of Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub><sup>-</sup> in Ethanol

The equilibrium quotient for the reaction



was determined in ethanol solvent by spectrophotometric techniques.

Table 4. Experimental molarity of solutions of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  in ethanol and molecular weight of solute species

Total platinum (mM)	Experimental Molarity (mM)	Molecular Weight of Solute Species (mg. $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2/\text{M ml}$ )
25	23.4	314
20	19.4	303
15	13.8	319
10	8.2	358

M. W. on monomer basis = 294 mg/mole

M. W. on dimer basis = 588 mg/mole

The molar absorbtivity of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$  was obtained from spectra of  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  dissolved in ethanol, and the molar absorbtivity of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in ethanol was obtained by adding 1 part in 500 and 1 part in 1000 of concentrated hydrochloric acid to ethanol and recording several spectra of dimer dissolved in each of these solvents.

Since there was no apparent change in the spectrum of dimer when the hydrochloric acid content of the solvent was changed, it was assumed that the small amount of water introduced was having no effect on the spectra, and that the chloride concentration was high enough to completely reverse the solvolysis reaction.

The molar absorptivities obtained are shown in Fig. 8. The equilibrium constant was calculated from the absorptivities of solutions of dimer in ethanol with various concentrations of chloride ion present, as shown in Table 5. The chloride ion was introduced as concentrated hydrochloric acid. The amount of water introduced with the hydrochloric acid was of the same order of magnitude as the water concentration of the driest ethanol available, and was presumed to have negligible effect on the spectra and equilibrium.

The values obtained for the equilibrium quotients were  $(5.0 \pm 1.2) \times 10^{-5}$  M at 25 degrees C and  $(5.6 \pm 1.5) \times 10^{-5}$  M at 35 degrees C. From these values the  $\Delta H$  of the solvation reaction could be estimated to be of the order of  $2 \pm 6$  Kcal/mole.

The explanation for the lack of precision of the measurements of the solvation equilibrium quotient in ethanol compared to the precision of the measurements of the same equilibrium quotient in water lay in the relative magnitudes of the two quotients. The solvation equilibrium quotient was 50 times smaller for ethanol solvent than for water solvent, and this meant that the minor species was present in smaller amounts, and its concentration was thus more difficult to precisely determine. For instance, if the chloride ion concentration had been made higher than the platinum concentration, the concentration of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$  would have been low. Since the measurements were instead



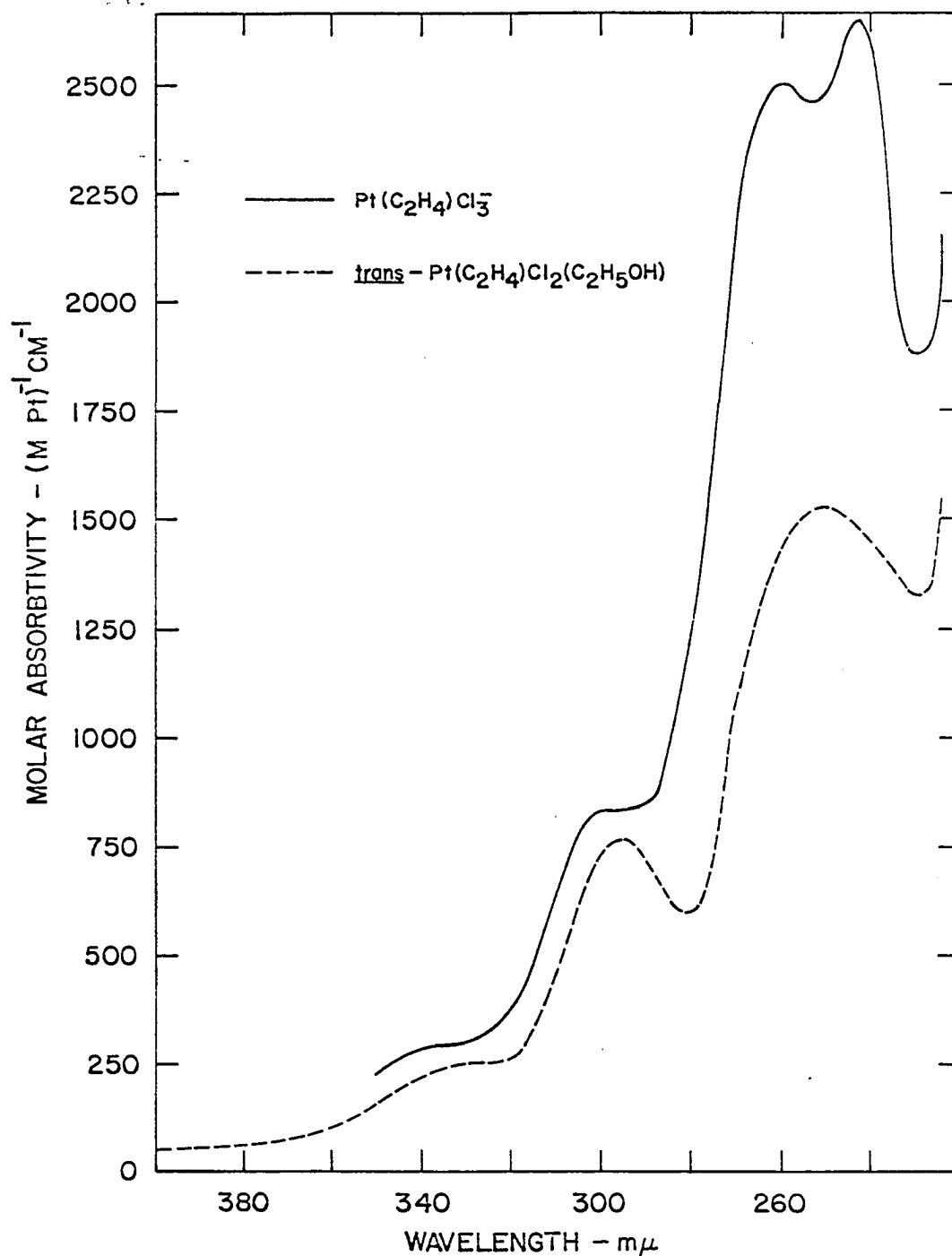


Fig. 8. Molar absorptivities of Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub><sup>-</sup> and trans-Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH) in ethanol solution

Table 5. Solvolysis equilibrium quotient of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in ethanol

Platinum Concentration (M x $10^4$ )	Added Chloride Concentration (M x $10^4$ )	Absorbtion (2600 A, 1.0 cm cell)	$K_{\text{(solvation)}}$ (M x $10^5$ )
25 degrees C			
4	2	0.742	6.84
4	4	0.876	5.29
4	3	0.842	3.23
4	3	0.832	4.18
4	4	0.881	4.83
4	5	0.910	5.56

$$K_{\text{(solvation)}} = (5.0 \pm 1) \times 10^{-5} \text{ M}$$

35 degrees C

3	0.916	0.510	0.424
3	1.83	0.579	0.531
3	2.75	0.614	0.801
4	0.916	0.658	0.464
5	1.83	0.890	0.443
5	2.75	0.950	0.697

$$K_{\text{(solvation)}} = (5.6 \pm 1.5) \times 10^{-5} \text{ M}$$

$$\Delta H = 2 \pm 6 \text{ Kcal/mole}$$

$$\epsilon(2600 \text{ A}) \text{ for } \text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^- = 2522 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\epsilon(2600 \text{ A}) \text{ for } \text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH}) = 1427 \text{ M}^{-1} \text{ cm}^{-1}$$

made with a chloride ion concentration small enough to make the concentrations of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2^-$  ( $\text{C}_2\text{H}_5\text{OH}$ ) the same order of magnitude, the chloride ion concentration was low. Since it was determined by subtracting comparatively large numbers, it was not well known.

### Cis Chloride Exchange Kinetics in $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ in Ethanol

Experiments were performed at 25 and 35 degrees C to measure the rate of the reaction

$$\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2\text{X} + \text{Cl}^{*-} \rightleftharpoons \text{Pt}(\text{C}_2\text{H}_4)\text{Cl}^*\text{ClX} + \text{Cl}^- \text{ (ethanol solvent)}$$

where the chlorides were cis to ethylene, and X was trans to ethylene and represented a labile equilibrium mixture of  $\text{Cl}^-$ ,  $\text{Cl}^{*-}$ , and  $\text{C}_2\text{H}_5\text{OH}$ .

Since the equilibrium quotient for solvation of the labile trans position was small, the amount of solvated species present at equilibrium was small if the total chloride added to the reaction solution exceeded the total platinum concentration. Since the complex was added to solution as  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ , which then was cleaved by ethanol to form trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ , the concentration of this species could be made significantly large relative to the total platinum concentration by keeping the added chloride concentration low. The  $\text{Cl}^{*-}(\text{Cl}^{36})$  used to follow the exchange represented a portion of this added chloride, so in practice the relative concentration of the solvated species could not be made much greater than half the total platinum concentration at 10 mM platinum.

Lokken and Martin (56) found evidence that in water the cis solvation equilibrium quotient was one-tenth the trans solvation equilibrium constant, to an order of magnitude approximation. It would be expected that the same would be true in ethanol. It was assumed that the equilibrium concentration of the cis solvated species was negligible.

The complex concentration, the concentration of the added chloride, and the equilibrium quotient for trans solvation fixed the concentrations of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ . These were assumed to be the platinum species present in measurable amounts at equilibrium. Table 6 lists these concentrations for the exchange experiments performed at 25 and 35 degrees C. Also given are the half-times and rates of exchange that were observed. Figs. 9 and 10 are plots of the exchange data for typical exchange experiments, similar to those drawn by the computer plotter in the determination of the half-life of the exchange.

The chloride concentration was uncertain on experiments 10, 13, 14, 15 and 18 at 35 degrees C, as explained in detail in the section describing experimental procedures. These experiments were started during the period when the stock chloride concentration was changing. The final stock concentration was assumed for these experiments rather than a concentration intermediate between initial and final. The comparison of the fit of these points to the rate law

Table 6. Cis chloride exchange experiments

Total Platinum (mM)	Added Chloride (mM)	trans- (Pt(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) (mM)	Pt(C <sub>2</sub> H <sub>4</sub> )Cl <sub>3</sub> <sup>-</sup> (mM)	t <sub>1/2</sub> (hours)	Exchange Rate (mM/hour)
25 degrees C					
1 2.50	5.70	0.0385	2.46	79.3	0.0233
2 3.75	5.70	0.0940	3.66	30.9	0.0725
3 10.0	4.44	5.60	4.40	0.238	10.6
4 10.0	11.6	0.303	9.70	7.45	0.683
5 15.0	23.0	0.0932	14.9	24.7	0.365
6 25.0	20.8	4.43	20.6	0.408	25.0
7 25.0	45.9	0.0597	24.9	39.5	0.420
35 degrees C					
1 2.50	5.70	0.0423	2.46	15.7	0.118
2 2.50	12.2	0.0141	2.49	88.4	0.0278
3 2.50	45.8	0.00318	2.50	519	0.00602
4 2.50	91.6	0.00155	2.50	631	0.00520
5 2.50	183.2	0.000762	2.50	1108	0.00296
6 3.75	5.70	0.103	3.65	4.07	0.550
7 3.75	18.3	0.0141	3.74	71.5	0.0516
8 <sup>a</sup> 3.75	36.6	0.00628	3.74	332	0.0130

<sup>a</sup>Scatter in kinetic data points

Table 6. cont'd.

Total Platinum (mM)	Platinum (mM)	Added Chloride (mM)	$\frac{\text{trans-}}{\text{Pt}}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ (mM)	$\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ (mM)	$t_{1/2}$ (hours)	Exchange Rate (mM/hour)
9	3.75	73.3	0.00296	3.75	332	0.01420
10 <sup>b</sup>	10.0	4.44	5.60	4.40	0.100	25.2
11	10.0	4.44	5.60	4.40	0.0900	28.0
12	10.0	4.44	5.60	4.40	0.0870	29.0
13 <sup>b</sup>	10.0	11.6	0.285	9.72	2.94	1.73
14 <sup>b</sup>	15.0	23.0	0.102	14.9	7.79	1.16
15 <sup>b</sup>	25.0	20.8	4.45	20.6	0.153	66.7
16	25.0	20.8	4.45	20.6	0.109	93.6
17	25.0	20.8	4.45	20.6	0.132	92.7
18 <sup>b</sup>	25.0	45.9	0.0655	24.9	11.8	1.410

<sup>b</sup>Added chloride concentration uncertain

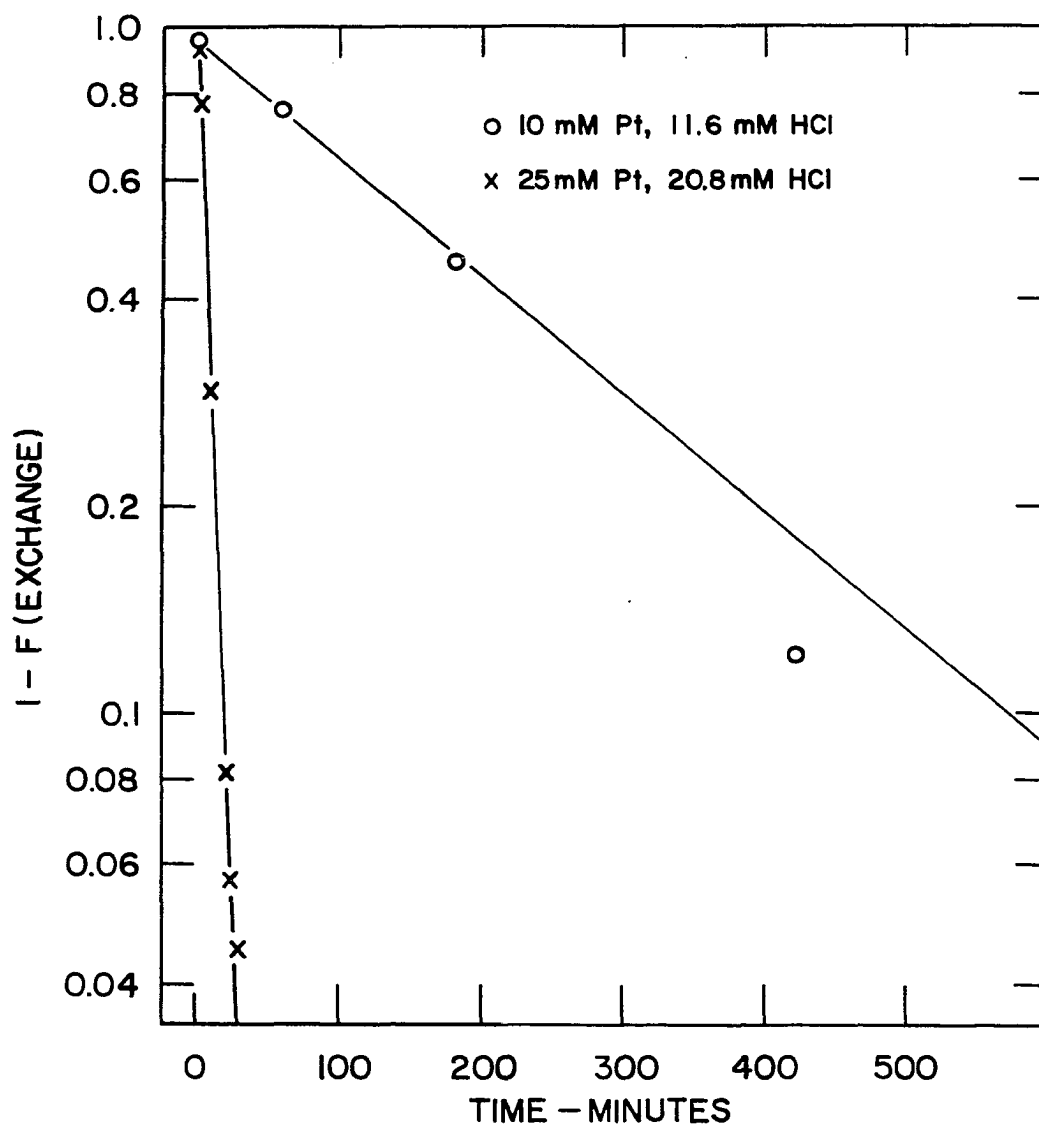


Fig. 9. Typical "fast" cis chloride exchange experiments with high complex and low chloride concentrations

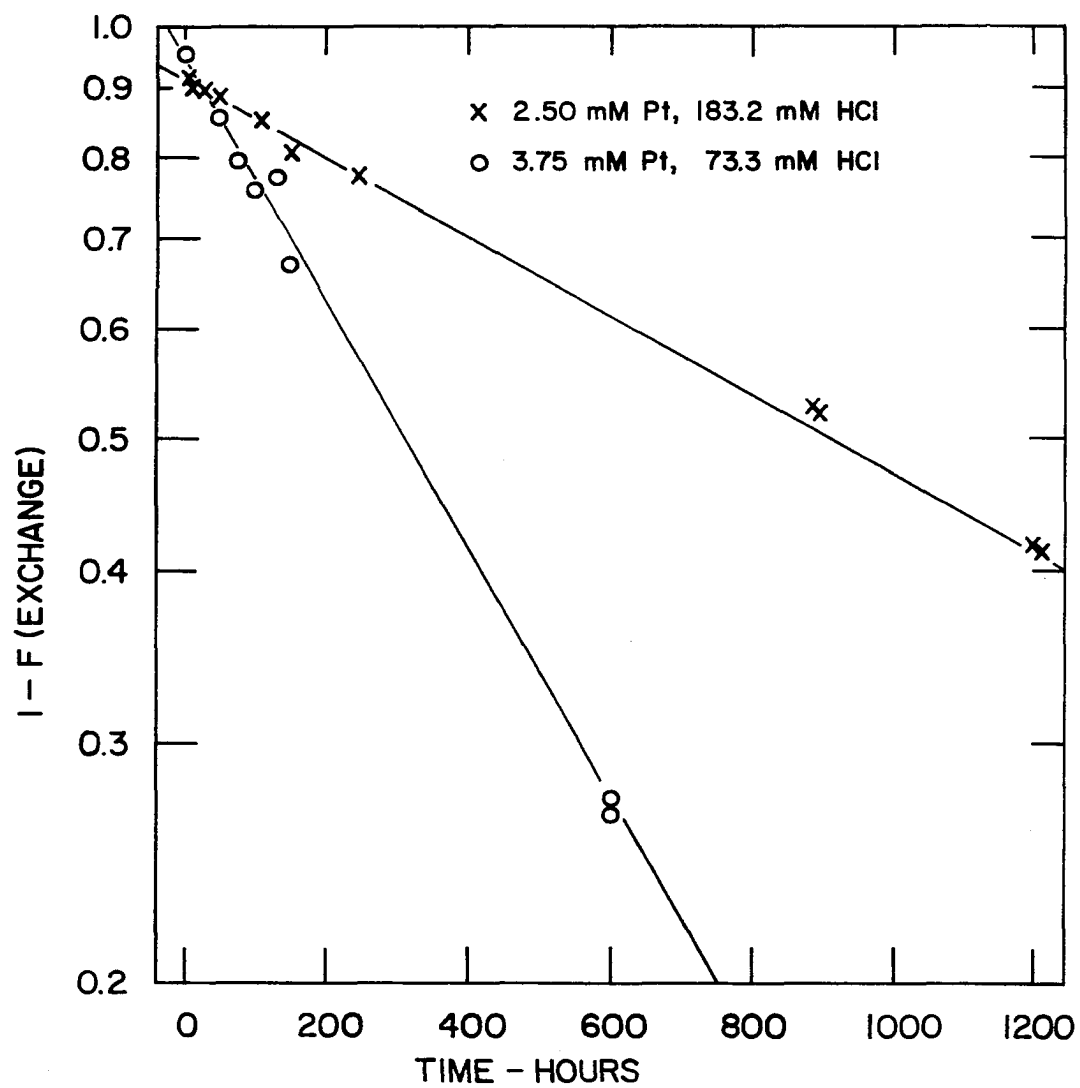


Fig. 10. Typical "slow" cis chloride exchange reactions with low complex and high chloride concentrations



compared to the fit of the experiments where the chloride concentration was well known indicates that this assumption was reasonably valid.

Experiment 8 at 35 degrees C was also uncertain; the scatter in the kinetic data points was considerable and worse than for any of the other experiments.

The calculated rates appeared to be proportional to the product  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$ . To test this fit, the logarithms of the rates and the concentration products were plotted against each other and a least squares straight line was drawn through the points.

Three data sets were treated in this fashion. The least squares slope for the seven experiments at 25 degrees C was  $1.057 \pm 0.032$ . The least squares slope for all eighteen experiments at 35 degrees C was  $0.986 \pm 0.019$ , and the value for the twelve experiments at 35 degrees C in which the most confidence was placed was  $0.992 \pm 0.017$ . These plots are shown in Figs. 11, 12, and 13. Since the experimental slopes were well within two standard deviations of 1.00, no further terms were required in the rate law to adequately fit the data obtained.

It was necessary to determine the best value of  $k$  in the rate law

$$R = k[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]. \quad \text{Eq. 20}$$

No a priori attempt was made to weight each point, as had

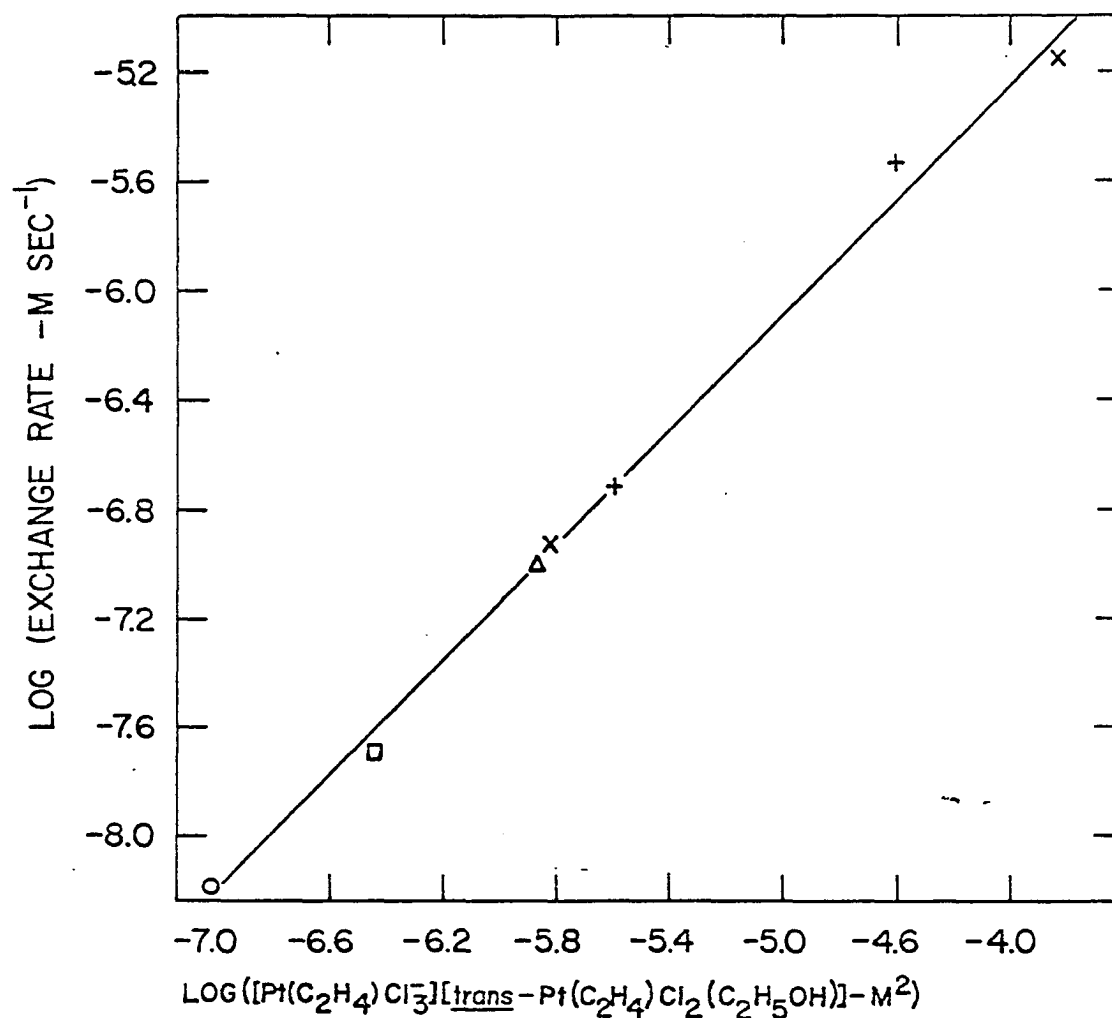


Fig. 11. Correlation of cis chloride exchange rates with the concentration term  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]-\text{M}^2$ . 25 degrees C.  $\circ$  2.50 mM Pt,  $\square$  3.75 mM Pt,  $+$  10.0 mM Pt,  $\Delta$  15.0 mM Pt,  $\times$  25.0 mM Pt

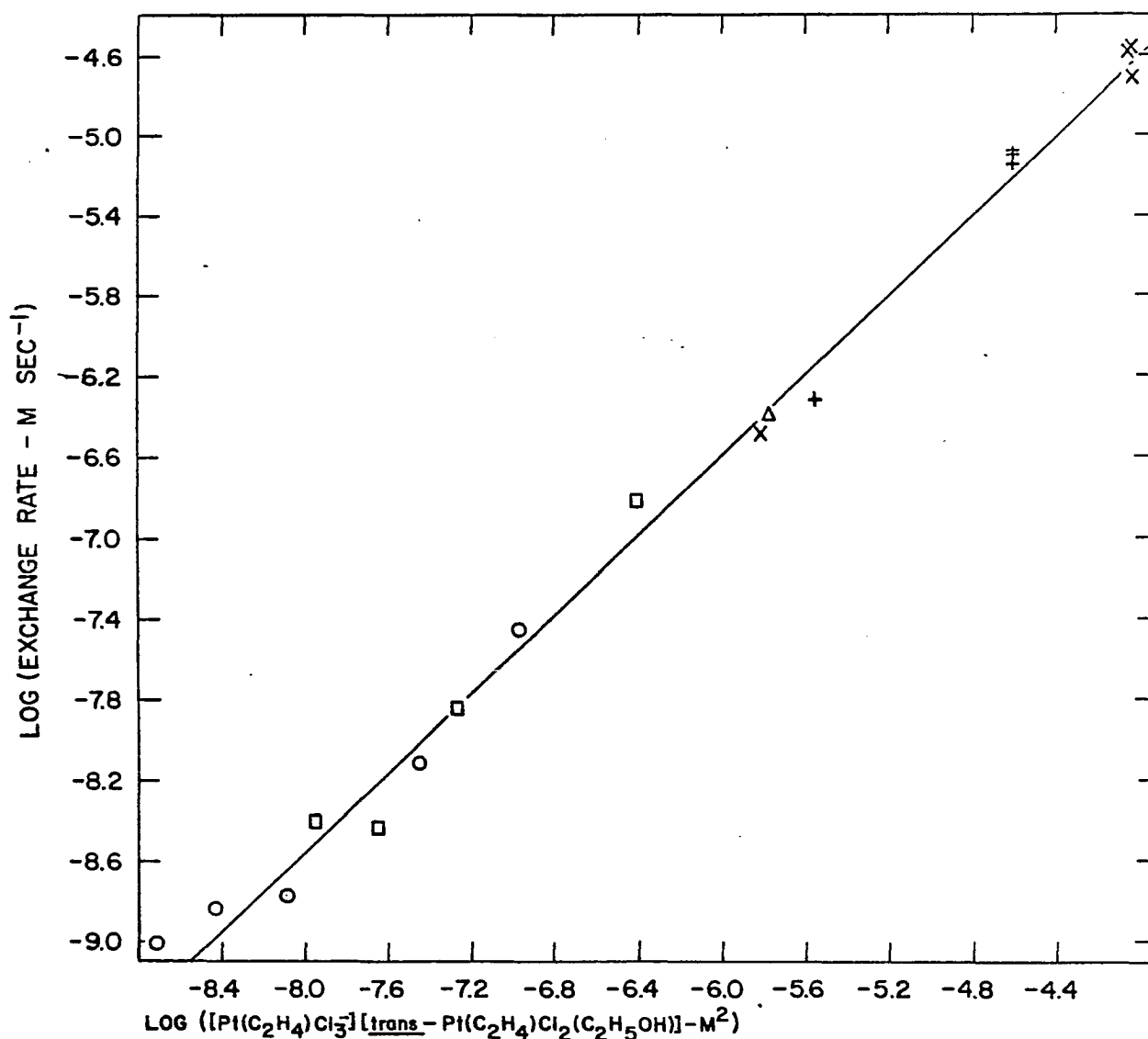


Fig. 12. Correlation of cis chloride exchange rates with the concentration term  $[Pt(C_2H_4)Cl_3^-][trans-Pt(C_2H_4)Cl_2(C_2H_5OH)]$ . 35 degrees C.  $\circ$  2.50 mM Pt,  $\square$  3.75 mM Pt,  $+$  10.0 mM Pt,  $\Delta$  15.0 mM Pt,  $\times$  25.0 mM Pt

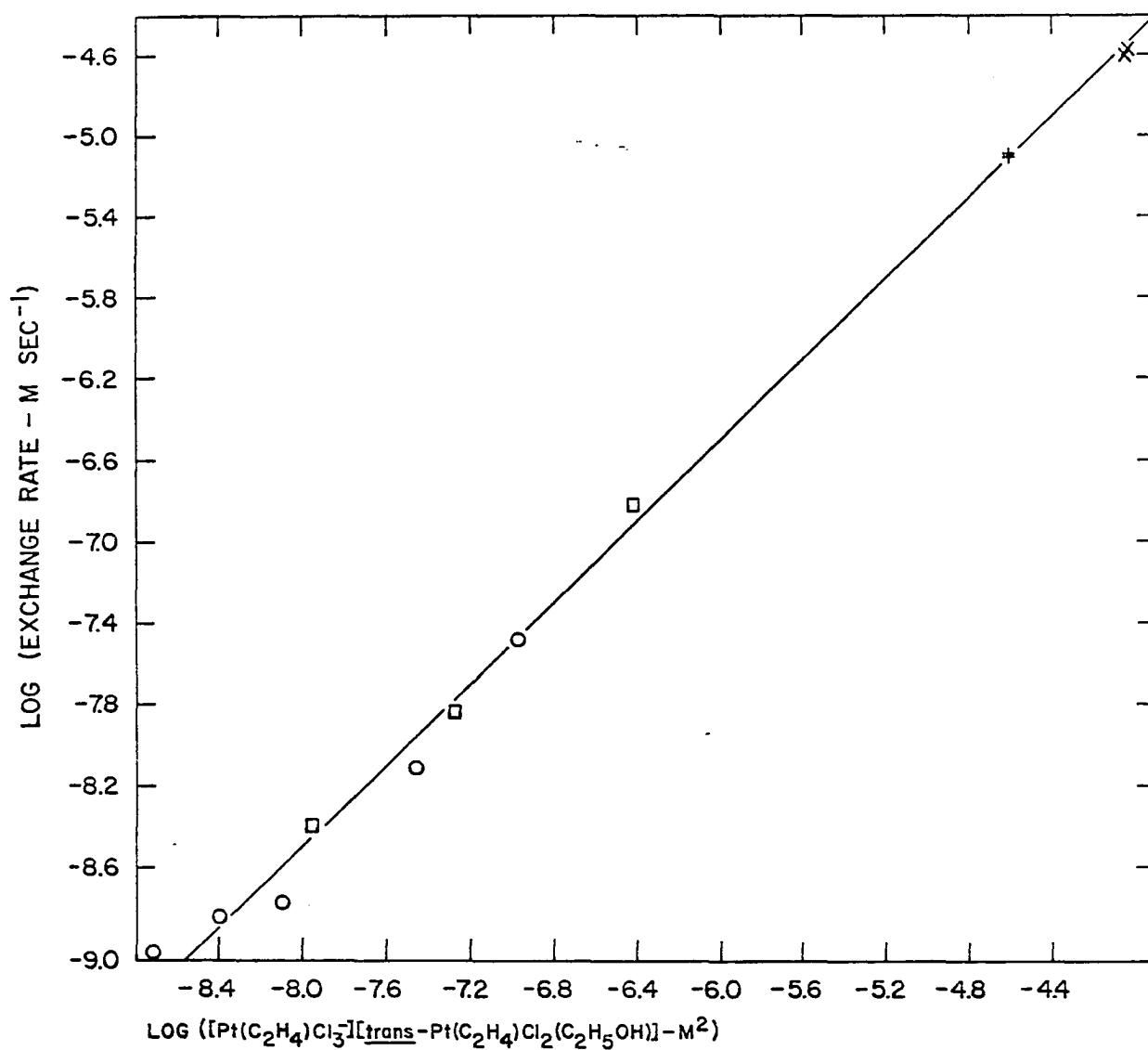


Fig. 13. Correlation of cis chloride exchange rates with the concentration term  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$ . 12 most reliable experiments at 35 degrees C.  $\circ$  2.50 mM Pt,  $\square$  3.75 mM Pt,  $+$  10.0 mM Pt,  $\times$  25.0 mM Pt

been done for the individual data points of each kinetic experiment. It was assumed that there was more error in the determination of the rates than in the concentrations of the platinum species, but the uncertainty in the measured equilibrium quotients for the solvation of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and the possibility of the loss of volatile hydrochloric acid and ethanol from the reaction solutions which were sampled for a month or more precluded assuming there was no error in the concentrations. The chloride concentration was more critical in experiments where it was about the same order of magnitude as the platinum concentration than in experiments where chloride was present in excess. The determination of the rates from "infinite time" specific activities obtained by the iterative procedure was subject to more error than the calculation of the rates from "infinite time" specific activities obtained by sampling the reaction solutions after at least 5 exchange half-times. Also, the rate determinations were less certain for experiments with half-times less than 20 minutes.

An attempt to objectively assign weights to each experiment on the basis of these uncertainties would have been difficult. It was instead assumed that the fractional standard deviations of the rate measurements were equal. It was further assumed that the rate law indicated in Eq. 20 was exact.

With these assumptions the best value of the logarithm of  $k$  was found by plotting the logarithm of the rate against the logarithm of the concentration product, as before. But now the slope of the line through the points was fixed at 1.00, and the best least squares intercept under this restraint was found. This intercept was the logarithm of the best value of the rate constant under these assumptions.

The standard deviation of the intercept was 0.434 times the fractional standard deviation of the rate constant.

It should be noted that while this procedure gave the value of the rate constant without assumption concerning the relative values of the hypothetical fixed standard deviations of the rate measurements and the concentration values, the standard deviation of the rate constant was obtained assuming that the error in the concentration values was small compared to the error in the measurement of the rate. This assumption was not strictly valid, but was probably good to a first approximation.

The rate constant obtained at 35 degrees C with all eighteen experiments included was  $0.272 \pm 0.019 \text{ M}^{-1} \text{ sec}^{-1}$ . With the six least certain experiments excluded the rate constant was  $0.309 \pm 0.020$ . While this standard deviation was slightly higher, the fractional standard deviation was slightly lower. The uncertain experiments at 35 degrees C were not included in the calculations of the constants in

Table 7, which summarizes the results that were obtained.

Table 7. Constants characterizing cis chloride exchange in solutions of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  in ethanol

Temperature (degrees C)	$K_{(\text{solvation})}^a$ (M)	$k^b$ ( $\text{M}^{-1} \text{ sec}^{-1}$ )
25	$5.0 \times 10^{-5}$	$0.0771 \pm 0.0064$
35	$5.6 \times 10^{-5}$	$0.309 \pm 0.020$

$\Delta H^\ddagger = 25 \pm 2 \text{ Kcal/mole}$   
 $\Delta S^\ddagger = 19 \pm 7 \text{ cal/mole deg.}$

$$a_K = \frac{[\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})][\text{Cl}^-]}{[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-]}$$

$$b_k = \frac{\text{exchange rate}}{[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]}$$

It is recognized that the uncertainty in the solvation equilibrium quotient reflected in the rate constant because of the uncertainties in the concentration of species which must be calculated from the equilibrium quotient. However, some assurance can be obtained from the rate data that the measured equilibrium quotients were correct to an order of magnitude approximation. Most, but not all, of the concentrations of trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$  were proportional to the equilibrium quotient. For the experiments where the chloride ion concentration was less than the platinum concentration

the concentration of the solvated complex was nearly independent of the equilibrium quotient. Since the rate data for these experiments fit in well with the other rates obtained, particularly at 35 degrees C, the equilibrium quotients must be within an order of magnitude of their measured values.

The nominal ionic strengths of the reaction solutions ranged from 7.0 to 184 mM. There was a possibility of the formation of ion pairs, and of a rate dependence on the ionic strength. Pearson et al. (30) found evidence for the formation of ion pairs in t-butyl alcohol and other solvents when using a quarternary ammonium chloride salt as a source of chloride ion for platinum complex kinetic studies. However, the difficulty was readily apparent from the observed deviation from a simple rate law. While the possibility of ion pair formation or ionic strength effects in this system could not be excluded, the interpretation of the rate data did not require that they be considered. The fit of the rate data over the broad concentration range studied to a simple rate law was evidence that they were not important.

The experiments with relatively short half-times, less than about fifty hours, were begun only after the reaction solutions had been aged for times long compared to the half-time of the exchange reaction. The experiments with long half-times were aged for about two weeks. This aging



period was in some cases short compared to the half-time of the exchange reaction. Since the experiments for which the aging period was short compared to the half-time of exchange fit the simple rate law, it can be concluded that the reaction solutions came to equilibrium with respect to all species necessary to the exchange path with a half-time shorter than the half-time of exchange.

## CONCLUSIONS

No other rate law exclusively second order in platinum species has been found in the literature. A considerable range of concentrations was investigated in an attempt to measure the contribution of the expected first order solvation term to the exchange. No evidence of a contribution from this path was found, but an upper limit for it was established.

From the assumption that the term  $k_1[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-]$  was not contributing more than half the exchange rate to experiment 5 at 35 degrees C,  $k_1$  cannot be greater than  $1.6 \times 10^{-7} \text{ sec}^{-1}$ . Lokken and Martin (56) measured  $k_1 = 9.7 \times 10^{-6} \text{ sec}^{-1}$  in water. Making similar assumptions an upper limit for the contribution of  $k_1'[\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$  was established that determined an upper limit for  $k_1'$  that was the same order of magnitude as the value of  $9.2 \times 10^{-5}$  that Lokken and Martin measured for the analogous constant in water solution at 35 degrees C.

It must be emphasized that no evidence at all was found for these first order paths in ethanol, they may be considerably smaller than these upper limits which could be established for them.

Basolo (29) lists the effect of solvent on the solvation path rate constant for chloride exchange in

trans-Pt(pyridine)<sub>2</sub>Cl<sub>2</sub>. At 25 degrees C the  $k_1$  in water is 2.5 times the constant in ethanol. Apparently Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub><sup>-</sup> discriminates more between the two solvents since  $k_1$  in water is more than 6 times the  $k_1$  in ethanol.

The other known halide exchange reactions of platinum(II) complexes which involve a kinetic term second order in complex have been discussed in the Introduction. For the two such reactions involving bromide exchange which have been investigated a singly bridged dimer intermediate was proposed. Bromide exchange with PtBr<sub>4</sub><sup>2-</sup> (58) proceeded by a path second order in complex and there was evidence for the formation in solution of the doubly bridged Pt<sub>2</sub>Br<sub>6</sub><sup>2-</sup> dimer. But this evidence indicated that the rate of formation and cleavage of the doubly bridged dimer was too slow to account for the exchange by the second order in complex path. A singly bridged dimer intermediate was proposed. The addition of Pt(dien)Br<sup>+</sup> to solutions of PtBr<sub>4</sub><sup>2-</sup> catalyzed the bromide exchange of both species (60), and in this case only a single bromide bridge between the two species is possible. The entropies of activation of both of these second order in complex exchange constants were negative, which is usual for ligand substitution reactions of platinum(II) complexes.

A doubly bridged dimer intermediate was proposed to account for the second order in complex chloride exchange of Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub><sup>-</sup> in aqueous solution (56). This mechanism

was able to make use of the strong trans directing ability of ethylene in attempting to explain the cis chloride exchange in the complex through the dimer path. The entropy of activation was unusually positive, -2 cal/mole degree for the second order in complex path.

The more positive entropy and enthalpy of activation found for the platinum-olefin system in ethanol compared to the same system in water indicated that the slow step in the mechanistic path might involve the weakening or breaking of a platinum-chloride bond.

If a platinum-chloride bond weakened, with the chloride gaining negative charge and becoming more solvated, the entropy of activation would be expected to be more negative in water than in ethanol, since there is more solvent ordering around the chloride ion in water than in ethanol. The enthalpy of activation would also be more negative in water solution than in ethanol solution because the heat of solvation of chloride is greater in the better ion solvating solvent, and this would compensate for more of the enthalpy required to form the activated complex species.

This net bond weakening in the transition state can be used as an explanation not only of the solvent effect, but also of the unusually positive entropy of activation found for the second order in complex path in water. Belluco et al. (37) have proposed that the usual negative entropies

of activation of ligand substitution reactions of platinum(II) complexes result from net bond strengthening in the transition state. The entropy of activation observed for chloride exchange in the platinum-ethylene complex system through the second order in complex exchange path was found to be only slightly negative. This supports the postulate of net bond weakening in the transition state.

Arguments based on observed entropies and enthalpies of activation cannot be conclusive, since these terms are measured with a fairly large degree of uncertainty. They can, however, be used to support mechanistic arguments if other evidence is not contradicted.

Based on the preceding suggestions, the following mechanistic path is proposed for the second order exchange path of the  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  system. It is postulated that a cis chloride on a  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  species forms a partial bond with the axial position of the platinum atom of a trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$  species, and replaces the solvent trans to the strong trans director, ethylene, forming a singly bridged dimer species.

Since the solvent replaced is trans to ethylene, and is not as stable as a chloride, or bridging chloride, would be in the same position, the formation of the bridge is probably fast once the partial bond is formed with a cis chloride.

If this singly bridged dimer is not first cleaved by solvent, the bridging bond angle will assume the near 90 degree value found in the doubly bridged dimer, and preparatory to forming the second bridge a non-bridging cis chloride of the platinum whose bridging chloride is trans to ethylene will form a partial bond with the axial position of the other platinum atom. If this cis chloride replaces the chloride trans to ethylene on the other platinum atom, and brings the rest of the complex with it as it moves through the XZ plane to its new position, the doubly bridged dimer will be formed. But the direct replacement of one chloride with another is not so favorable nor so fast as the replacement of a solvent by a chloride. The transition state, with a cis chloride of one platinum partially bonded to the axial position of another platinum, may persist for some time.

Since electrons will have been withdrawn from the cis chloride to form the partial bond, the cis chloride-platinum bond will be weakened. Also, electrons will have been withdrawn from the region of the lone-pair orbitals to form the partial bond to the second platinum so that a more favorable situation exists for solvent attack on this cis position. Such solvent attack would tend to move the cis chloride out of the square plane and down to the trans position of the other square plane. The net effect

may be that the cis chloride moves down replacing the trans chloride on the other platinum without taking with it the rest of the complex to form the doubly bridged dimer. The cis position would then be available for the attacking solvent, and the solvent in turn would be quickly replaced by another chloride, completing the cis exchange process. The process is illustrated in Fig. 14.

It is postulated that this breaking of a cis chloride-platinum bond occurs more often than the formation of the doubly bridged dimer.

The strongly negative entropies of activation measured for the second order in complex bromide exchange paths suggest that bond weakening may not be important in these systems. It would be satisfying to postulate one basic mechanism to correlate the second order in complex terms that are being reported for halide exchange reactions of platinum(II) complexes, but apparently more data will have to be accumulated before this can be done.

It would be interesting to determine if the solvent effect on the second order in complex term for the  $\text{PtBr}_4^{2-}$  and  $\text{Pt}(\text{dien})\text{Br}^+$ ,  $\text{PtBr}_4^{2-}$  systems was the same as for the  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  system.

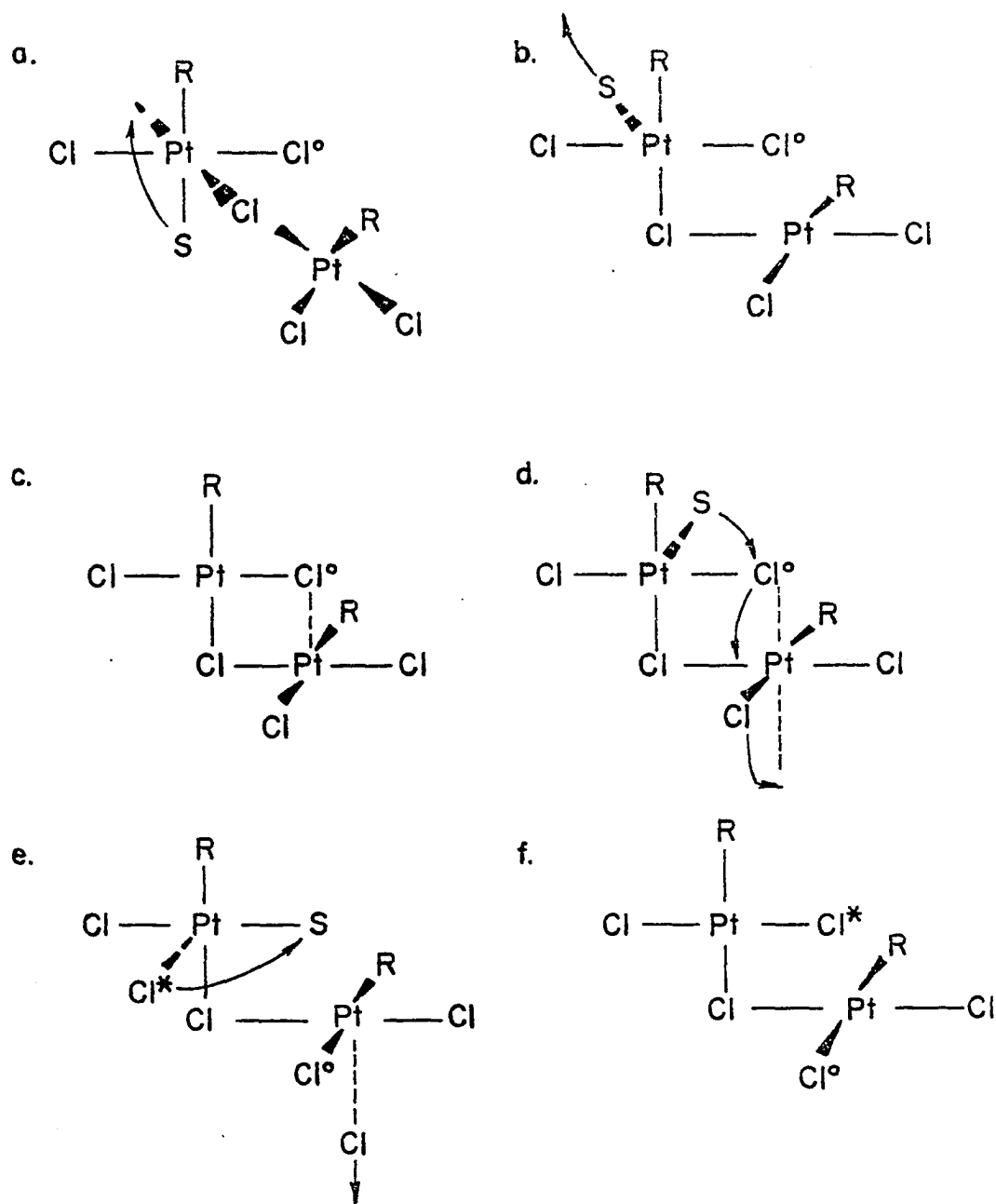


Fig. 14. Formation of singly bridged dimer and cis chloride exchange



## SUMMARY

The solvolysis equilibrium constant of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  was measured to be smaller in ethanol than in water by a factor of 50.  $K_{\text{solvation}}$  in water was  $2.58 \times 10^{-3}$  M at 25 degrees C and  $2.96 \times 10^{-3}$  M at 35 degrees C. The  $\Delta H$  of the reaction was  $2.5 \pm 1$  Kcal/mole.  $K_{\text{solvation}}$  in ethanol was approximately  $5.0 \times 10^{-5}$  M at 25 degrees C and  $5.6 \times 10^{-5}$  M at 35 degrees C. The  $\Delta H$  of the reaction was  $2 \pm 6$  Kcal/mole.

$[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$  was dissociated by ethanol, existing primarily as trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$ . A molecular weight measurement indicated that at 25 mM platinum a maximum of 10 % of the compound was present as the dimer species.

The cis chloride exchange kinetics of a mixture of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$  and trans- $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})$  in labile equilibrium in ethanol solvent were measured. The expression

$$R = k[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-][\text{trans-Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{C}_2\text{H}_5\text{OH})]$$

was sufficient to describe the rate of exchange over a range of nearly  $10^5$  in the rate and a range of 10 in platinum concentration. The constant  $k$  was measured to be  $0.0771 \text{ M}^{-1} \text{ sec}^{-1}$  at 25 degrees C and  $0.309 \text{ M}^{-1} \text{ sec}^{-1}$  at 35 degrees C.  $\Delta H$  of activation was  $25 \pm 2$  Kcal/mole and  $\Delta S$  of activation was  $19 \pm 7$  cal/mole degree at 25 degrees C. No evidence was found for a first order in complex exchange path, which

usually is required to characterize the kinetics of ligand substitution in platinum(II) complexes.

Both the entropy and enthalpy of activation were more positive for the exchange reaction in ethanol than for the same reaction in water solvent. Further, the entropy of activation was more positive in both water and ethanol solvents than is usual for ligand exchange reactions of platinum(II) complexes. Since the usual negative entropy of activation has been ascribed to bond strengthening in the transition state, with relatively small variations due to solvent effects, a mechanism was proposed for this exchange reaction which involved bond weakening in the transition state as the slow step.

The effect of the solvent on the entropy and enthalpy of the reaction indicated that the transition state involved a weakening of a platinum-chloride bond, instead of a weakening of a platinum-solvent bond, and this has been incorporated into the mechanism.

There was not enough evidence to propose this mechanism for other exchange reactions of platinum(II) complexes which proceed in part by a path second order in complex.

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