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LIGAND SUBSTITUTION REACTIONS OF PLATINUM(II) COMPLEXES.
CHLORO(DIETHYLENETRIAMINE)PLATINUM(II)-CHLORIDE EXCHANGE

Ph. D. Thesis Submitted to Iowa State University, November 1970

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CHLORO(DIETHYLENETRIAMINE)PLATINUM(II)-CHLORIDE EXCHANGE

by

John Ralph Paxson

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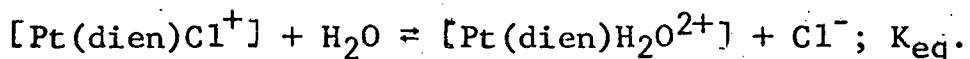
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John Ralph Paxson

ABSTRACT

Kinetics of the isotopic exchange of chloride in chloro-(diethylenetriamine)platinum(II) chloride has been studied using chlorine-36 as the tracer, employing an ion exchange quenching technique and activity determination by a liquid scintillation system. The aquation equilibrium constant was determined by means of titrations of the acidic proton on the H_2O ligand formed according to the reaction:



Titrations of the equilibrated solutions were performed over the range of 10^{-4} M to 10^{-3} M complex concentrations at ionic strengths of 0.100 M and 0.318 M for 25°C and 35°C . For 25°C , $\mu = .100$ M, $K_{\text{eq}} = 1.96 \times 10^{-4}$ M; $\mu = .318$ M, $K_{\text{eq}} = 2.52 \times 10^{-4}$ M. For 35°C , $\mu = .100$ M, $K_{\text{eq}} = 2.09 \times 10^{-4}$ M; $\mu = .318$ M, $K_{\text{eq}} = 2.42 \times 10^{-4}$ M. The isotopic exchange followed the

normal rate law for platinum(II) kinetics:

$$\text{Rate} = [k_1 + k_2(X)] \text{Pt-complex}$$

The exchange was studied over a twenty-fold range of chloride/complex ratios. At 25°C , $\mu = .100 \text{ M}$, $k_1 = 87.4 \pm 2.6 \times 10^{-6} \text{ sec}^{-1}$, $k_2 = 42.3 \pm 5.5 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$. For 35°C , $\mu = .100 \text{ M}$, $k_1 = 258.1 \pm 5.1 \times 10^{-6} \text{ sec}^{-1}$, $k_2 = 136.6 \pm 10.9 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$. The calculated activation parameters are $\Delta H_{\text{aq}}^{\ddagger} = 19.2 \pm .9 \text{ kcal/mole}$, $\Delta S_{\text{aq}}^{\ddagger} = -12.8 \pm 3.1 \text{ cal/mole deg}$; $\Delta H_{\text{Cl}}^{\ddagger} = 20.8 \pm 3.8 \text{ kcal/mole}$, $\Delta S_{\text{Cl}}^{\ddagger} = -4.2 \pm 13.1 \text{ cal/mole deg}$.

I. INTRODUCTION

A. Purpose of the Research

The subject of this investigation was the isotopic exchange reaction of chloro(diethylenetriamine)platinum(II) chloride and chloride ion with radioactive chlorine-36 as the tracer. The $[\text{Pt}(\text{dien})\text{X}^+]$ complexes are considered to be square-planar, with the local symmetry for the Pt^{2+} ion being approximately C_{2v} . There are four ligand σ -valence orbitals (one for each nitrogen and one from X). The metal has the usual 5d, 6s and 6p orbitals.

The diethylenetriamine ligand, dien, has proven valuable in platinum kinetics. This tridentate amine is not displaced at an appreciable rate by even strong nucleophiles. With cations for which a halide occupies the fourth coordination site, there is no complication or ambiguity resulting from successive replacement reactions. In addition, it is possible to compare the kinetic behavior with different leaving groups or with different entering groups for complexes in which the other coordinated positions are identical. In contrast to this simple system, it must be remembered in comparing the rate of isotopic exchange between Br^- and PtBr_4^{2-} with that of Cl^- and PtCl_4^{2-} , one is changing the

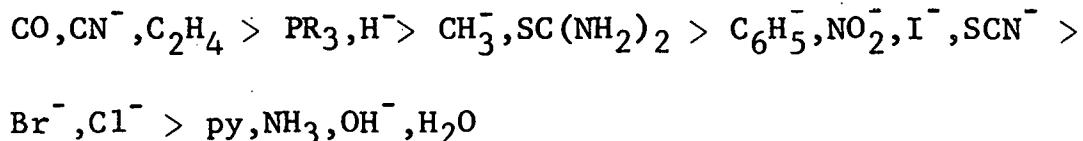
leaving group, the entering group, the cis ligands and the trans ligands. Experience indicates that each of these features influences the rate. The ligand replacement rates for the dien complexes have been especially valuable therefore for systematizing the entering group and the leaving group effects without other influences.

B. Historical Background in Platinum Complexes

In 1844 and 1845 Reiset (1) and Peyrone (2) reported preparation of two isomers of the compound now called dichlorodiammineplatinum(II). Werner (3), in his extensive investigation of coordination complexes, proposed that these are geometric, cis-trans isomers of a square-planar type.

Reihlen (4) disagreed, stating that the so-called trans isomer was actually a dimeric species of the cis compound. The picture was further clouded by Drew's (5) claim to have prepared a third isomer, which was completely incompatible with the square-planar hypothesis. The problem was not completely settled until 1954 with the x-ray diffraction structural determinations by Porai-Koshits (6). Werner's concept, suggested by Jorgensen's work (7) in 1886, was considerably enlarged by the synthetic work of Chernyaev (8). The proposal that ligands in the square plane are more easily replaced

if they are in a trans position to particular ligands which show a strong trans directing influence has been thoroughly tested through synthetic preparations (8) and substitution kinetics (9, p. 351). By correlating the observations from these studies, one can prepare an ordering of ligand trans directing effect, i.e., the ability to labilize the ligands trans to themselves in square-planar complexes. The following order of decreasing trans effect is given by Basolo (9, p. 355):



Recently, Colvin et al. (10) have correlated trans effects, for NH_3 and Cl^- in ammonation reactions, which are consistent within 10% of the experimental values.

The most important theories proposed to explain the trans effect are the polarization, and the σ - and π -bonding theories. Grinberg (11) drew attention to the parallelism between the trans effect order and the polarizability order of the ligands. The rationale is that since platinum carries a positive charge, it 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 of 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. This theory assumes that the trans effect is a consequence of the stability of the reactants rather than of the transition state or intermediate, i.e., that the trans influence of a group operates in the initial complex (ground state) rather than during the course of the reaction (transition state). Although the theory affords an adequate interpretation of many substitution reactions, it does not provide an entirely satisfactory interpretation of the trans effect. The electrostatic-polarization theory does not justify the large trans effect of the CN^- group, which has a polarization close to that of Cl^- .

Chatt et al. (12) and Orgel (13), independently, maintained that groups with greater trans effect also have empty π orbitals, and proposed a π -bonding stabilization of the activated complex. The theory is operative only for ligands

such as C_2H_4 , CO, CN^- and possibly PR_3 . The concept of π -bonding in metal complexes was introduced by Pauling (14, p. 332) in order to account for the short Ni-C bond distances in $Ni(CO)_4$ and also for the large stability of transition metal cyanides as compared to non-transition metal cyanides. A schematic representation of a π bond between Pt and CO is shown in Fig. 1.

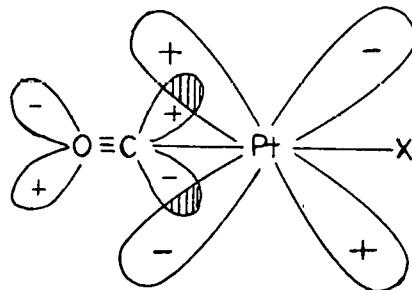


Fig. 1. Schematic representation of a π bond in Pt-CO

A σ -bond is formed by the donation of a pair of electrons from the carbon monoxide σ system to platinum, the π -bond by the overlap of a filled d orbital of platinum and a vacant π^* orbital of carbon monoxide. Thus in the π -bond system, electrons are donated to CO with a resultant reduction of electronic charge on the platinum.

In the π -bonding theory, the activated complex is presumed to have a trigonal bipyramidal structure as shown in

Fig. 2. Chatt et al. (12) emphasized that removal of charge from Pt(II) by π -bonding of L will enhance the addition of the nucleophile and favor a more rapid reaction. Orgel (13) stressed the increased stability of the transition state due to π -bonding because the electron density on Pt(II) is reduced along the Pt-X and the Pt-Y directions. Such an activated complex will lead to retention of configuration and predicts that the properties of Y and L will influence the rate of reaction in a similar way. This explanation also requires that the reactions proceed by a bimolecular displacement mechanism. But the Chatt and Orgel theory does not give an adequate explanation of the large trans effect of H^- and CH_3^- , which have no empty π orbitals but large polarizability.

Bersuker (15) extended Chatt's hypothesis to attempt to explain the π -acceptor properties of negatively charged groups (for example, Cl^- , CN^- , and NO_2^-) and groups which in the free state do not have appropriate vacant π -orbitals. The requirement that a π -bonding system have energetically low-lying and free π -orbitals is fairly rigorous. This is not realized for free groups, particularly negatively charged acid residues. A trans directing group is not free, but

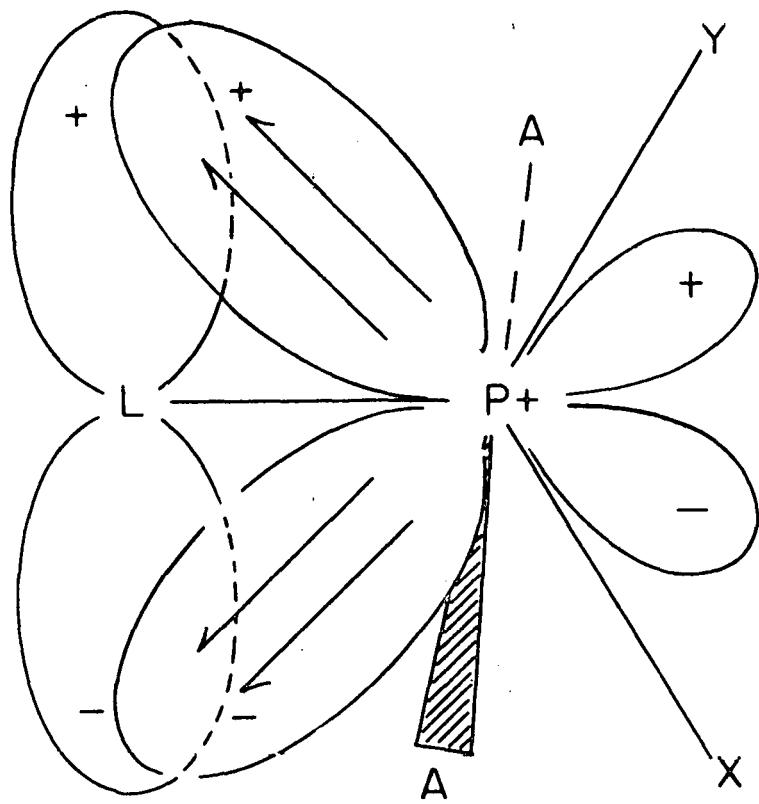


Fig. 2. Structure of the activated complex, PtLXYA_2 in the π -bonding theory. The metal orbital shown is a dp^2 hybrid.

bound in a complex. On complex formation, part of the σ cloud of the ligand is attracted to the central atom with the formation of a donor-acceptor metal-ligand σ bond. Here the trans director group acts as a σ electron donor, so that its electronegativity is increased and the acceptance of electrons into its π -orbital is facilitated considerably. In other words, the trans director, by giving up part of the σ cloud of electrons, lowers its π -orbitals, which become strongly held and capable of accepting electrons. It is obvious that the stronger the σ -donor properties of a given group, the greater the extent to which the electron cloud is transferred to the central atom in molecular σ orbitals and the greater the possibilities for the back transfer of charge from the central atom to the trans directing ligand in π -orbitals. Conversely, the greater the extent to which the electron cloud is accepted in the π -orbitals, the greater the possibilities for the release of σ electrons.

An extention of this is the concept of Oleari et al. (16). They considered particularly (a) distortion to the trigonal bipyramidal as evidenced in overlap integral calculations; (b) transition state stabilization with respect to orbital interaction in irreducible representations with empty

π or σ orbitals on the ligands; and (c) the influence of the leaving group. The predicative property of their theory is an interesting feature. Ligands are considered in pairs. When empty π or σ orbitals are not available on the ligands, the stability priority is: charged pair > charged-neutral pair > neutral-neutral pair. When stabilizing factors, e.g., π orbitals, are available, dominant factors are electrostatic repulsion and transition state stabilization. If the neutral ligand has empty π or σ orbitals, a charged-neutral pair has priority over a charged-charged pair. Once the ordering of pairs is established, the leaving group of the pair is assigned by reference to (a) the negative charge of the ligand; (b) the ability to stabilize the transition state; and finally (c) the solvation energy. The advantage of using such a series of ligand pairs is that one can know which is the most distorted pair and which group of the pair will be replaced. One cannot a priori from the trans effect series alone predict the course of a substitution reaction because one cannot anticipate whether the trans effect or the specific lability will prevail.

Langford and Gray (17) have recently proposed a combined σ - and π -bonding molecular orbital approach to the trans

effect. Their calculations and conclusions did not support Bersuker's contentions. A simplified M.O. diagram for PtCl_4^{2-} in Fig. 3 shows the most stable orbitals as σ bonding located mainly on the four chlorines. The same is true of the π -bonding molecular orbitals, next in order of stability. Then come the anti-bonding partners of these σ - and π -bonding M.O.'s. They are derived from the 5d atomic orbitals of Pt(II) and consist of the four relatively stable M.O.'s, with the order σ_z^* , π_{xz}^* , π_{yz}^* , and π_{xy}^* and the relatively unstable $\sigma_{x^2-y^2}^*$. At higher energy is the p_z orbital, which is not involved in σ bonding and finally the antibonding orbitals $\pi_{x,y}^*$ and σ_s^* .

By using this bonding scheme, it is possible to account for the large trans effect for strong σ -bonding ligands such as H^- and CH_3^- . Remembering the geometries of the atomic orbitals, it is seen that only the p orbitals of the four metal valence orbitals ($d_{x^2-y^2}$, s, p_x and p_y) have trans directional properties. Thus the trans ligand L and the leaving group X in trans- PtA_2LX must share the same σ_x orbital in the overall M.O. arrangements. It follows that a strong σ -bonding ligand L will take on a larger share of the bonding σ_x M.O., leaving a much smaller share for X. This

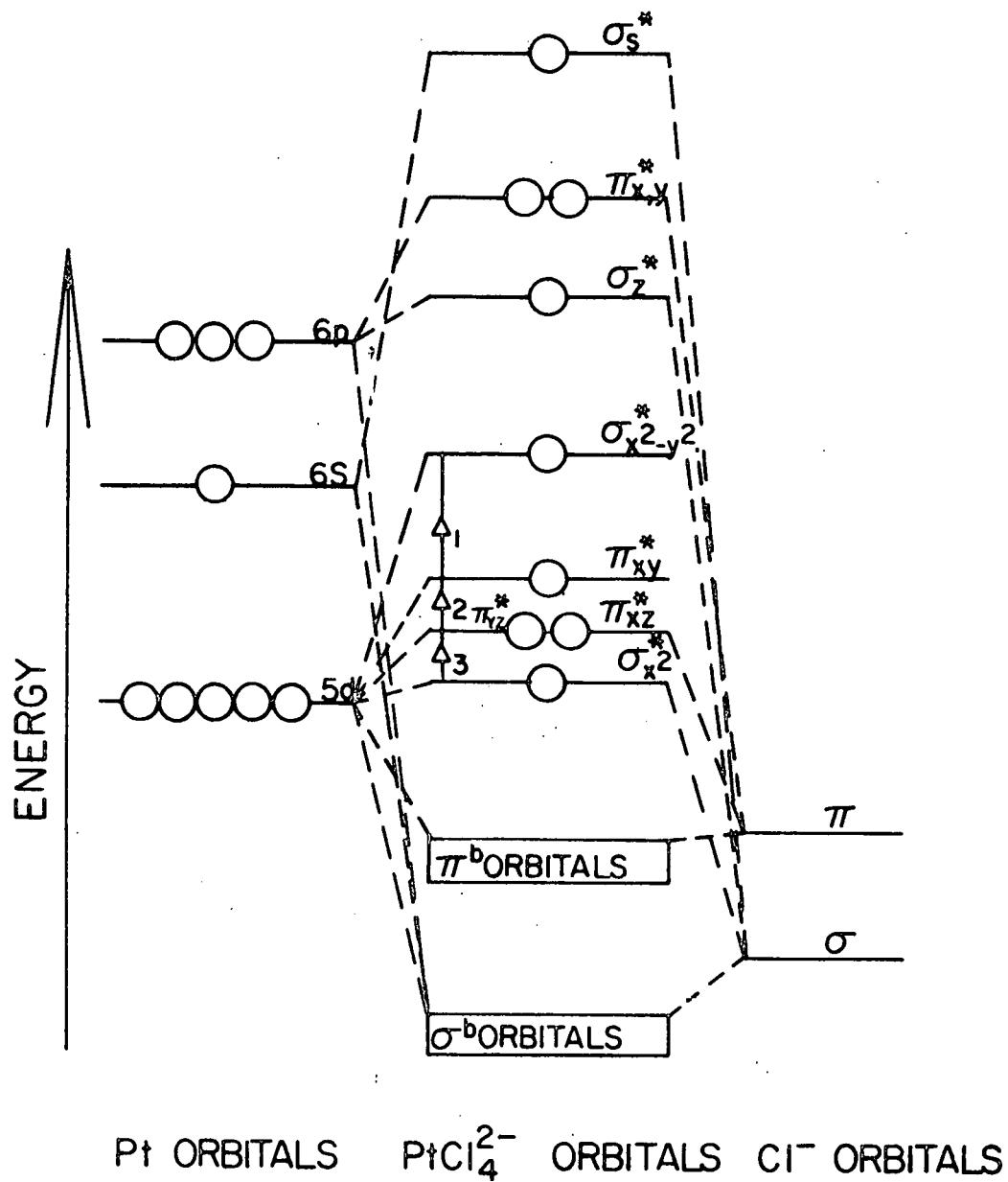


Fig. 3. Relative orbital energies in PtCl_4^{2-}

means that the Pt-X bond is weakened, as was also predicted by the polarization theory. Regardless of the mechanism of substitution, such a result is expected to lead to an increased rate of replacement of X.

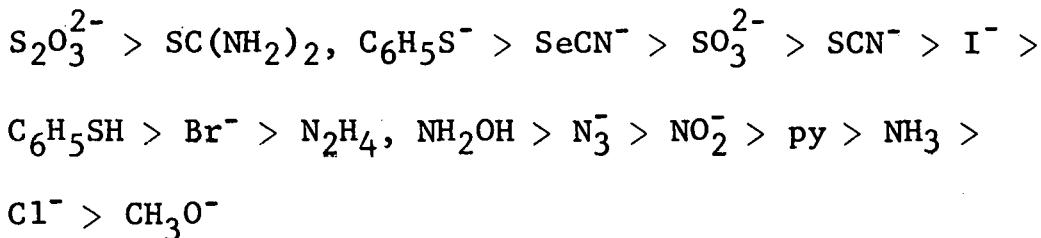
It may be visualized more easily if one simply realizes that a good σ -covalent ligand, such as H^- , will put a great deal of negative charge in the p_x orbital of the metal. This will repel the σ electrons of any ligand in the trans position which must also use the same p_x orbital. Langford and Gray (17, p. 26) offer an additional explanation based on an increase in the stabilization of the trigonal bipyramidal intermediate, because there are more orbitals available for σ -bonding in the trigonal plane than in the square-planar complex. Whereas only one p orbital, p_x , is used to bond the trans ligand L-Pt-X on the x axis of the square-planar complex, the addition of the entering group Y from above the xy plane causes X to move down out of the plane, resulting in an approximate trigonal plane containing Pt, L, X, and Y. This trigonal plane now contains two p orbitals, p_x and p_z , suitable for bonding. Thus, while originally there was only one p orbital bonding two ligands, 50% each, two orbitals now bond three ligands, 66.6% each. Thus good σ -bonding ligands

such as H^- and CH_3^- , which can use the extra p character to enhance the σ structure in the trigonal bipyramidal, will have high trans effects, or a σ -trans effect.

For ligands such as C_2H_4 , CO , and CN^- , the π -bonding theory restated in the context of the M.O. theory explains the π -trans effect (17). Adopting a highly schematic, speculative approach, we may consider that in square-planar $\text{Pt}(\text{II})$ the d_{xz}^* , d_{yz}^* and d_{xy}^* have the proper symmetry for bonding. On the addition of the entering group Y and the formation of a trigonal bipyramidal structure (holding z as the trigonal symmetry axis), four M.O.'s have the proper symmetry: π_{xz}^* , π_{yz}^* , π_{xy}^* and $\pi_{x^2-y^2}^*$. The fact that some of these contribute to the σ bonding system has been neglected. All of these orbitals are shared in π bonding with the three ligands Y, L, and X in the trigonal plane. Thus the trigonal bipyramidal transition state is greatly stabilized if L is capable of accepting electrons from the π^* orbitals of Pt. This then delocalizes electronic charge to the ligands and lowers the energy of the system. Since there are more filled π orbitals (bonding with respect to the ligand, non-bonding with respect to the metal) in the transition state than in the ground state (4 vs. 3), the transition state is stabilized to the greater extent. Thus, the net effect of a good π -acceptor L is to

lower the activation energy for the reaction. Good trans directors fall in one of three categories: (a) strong σ bonding, such as H^- and CH_3^- ; (b) strong π bonding such as C_2H_4 and CO ; and (c) moderate σ and π bonding such as I^- and $\text{SC}(\text{NH}_2)_2$. Ligands such as NH_3 and OH^- that are weak (covalent) σ and π bonders are low in the trans effect series. These opinions are based on a study of the overlap integrals for both sigma and pi bonders. When the overlap between the ligand orbitals involved in σ -bonding and the 6p orbital on platinum was considered, it was found that H^- , PR_3 and CH_3^- have large overlaps. It was found that CO , CN^- and C_2H_4 have large π -bonding overlap when the overlap of appropriate empty stable π^* orbitals with 5d orbitals on platinum was calculated.

Several studies (18,19) have shown a relationship between trans effectiveness and entering group efficiency. From reactions of trans- $\text{Pt}(\text{py})_2\text{Cl}_2$, the following reactivity order is obtained for various entering groups:



Combining this with a similar study of $[\text{Pt}(\text{dien})\text{Br}^+]$ (20),

we obtain an average ligand-reactivity order remarkably similar to the trans effect order. Thus a good trans labilizer is also a good entering group in square-planar substitutions. This is expected for an associative mechanism via a trigonal bipyramidal intermediate, since the trans group and the entering group are in similar positions with respect to the leaving group in the trigonal plane. Whatever stabilization is imparted to the approximately trigonal bipyramidal transition state by a ligand in the trans position can also be imparted to some extent when the ligand is in the entering group position. This is explained by the suggestion that in the trigonal plane of the transition state there are free d electrons available for dative π -bonding to a ligand with empty π^* orbitals. These electrons are in the 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 orbitals which gives many ligands their trans labilizing property, the entering group would be expected to accept these platinum electrons and stabilize the transition state. Poor trans directors, which do not form these partial bonds, are not good entering groups.

A fairly extensive study of relative leaving group rates

has been made using the reaction of pyridine on $[\text{Pt}(\text{dien})\text{X}]^+$ (21). Several significant observations can be made. The order of increasing labilities parallels the order of increasing solution instabilities of the complexes. Leaving groups high in the trans effect series are very slowly replaced. This is consistent with the M.O. trans effect theory, suggesting that good trans labilizers will be strongly bonded to the metal. The negation is not always true. For example, OH^- is a poor trans director, but a poor leaving group also. The strength of the σ -bond derives from a good $\text{Pt}(5\text{d})-\text{OH}$ bond not a $6\text{p}\sigma$ -OH interaction. Another inert leaving group is NH_3 . Apparently the trigonal bipyramidal transition state is relatively high energy when ligands like OH^- and NH_3 occupy one or more positions in the trigonal plane.

More recent studies provide further information relative to the nature of the leaving group and its ease of replacement. Belluco et al. (22) calculated activation parameters for the reactions of thiourea with $[\text{Pt}(\text{dien})\text{X}]^+$. Activation energies increase with decreasing replacement rates: $\text{Cl}^- \sim \text{Br}^- \sim \text{I}^- \ll \text{N}_3^- \sim \text{NO}_3^- < \text{SCN}^- < \text{CN}^-$. Thus, there appears to be two types of leaving groups: (a) ligands which are easily replaced with the rate of substitution almost independent of

the leaving group, and (b) ligands which are more difficult to replace with the substitution rate dependent on the leaving group. These observations can be understood if it is assumed that the mechanism of reaction involves the formation of a five-coordinated intermediate. The reactions can be represented by the reaction profiles of Fig. 4. Profile 1 corresponds to leaving group in category (a). Since the higher activation energy between the ground state and the transition is that with (A) which involves chiefly bond formation with the nucleophile Y and little rupture of the Pt-X bond, the nature of X cannot have a primary effect on the formation of (A).

Profile 2 corresponds to leaving groups in category (b). Now the activation energy between the ground state and the transition state is that with (B). Since this involves primarily a breaking of the Pt-X bond, the rate of replacement will depend on the nature of X.

Implications on the mechanism of substitution can sometimes be drawn from the effect of complex charge on its reaction rate. If a dissociative process, i.e., a separation of charges, is involved, then for an analogous series of complexes the rate will decrease with a decrease of the charge

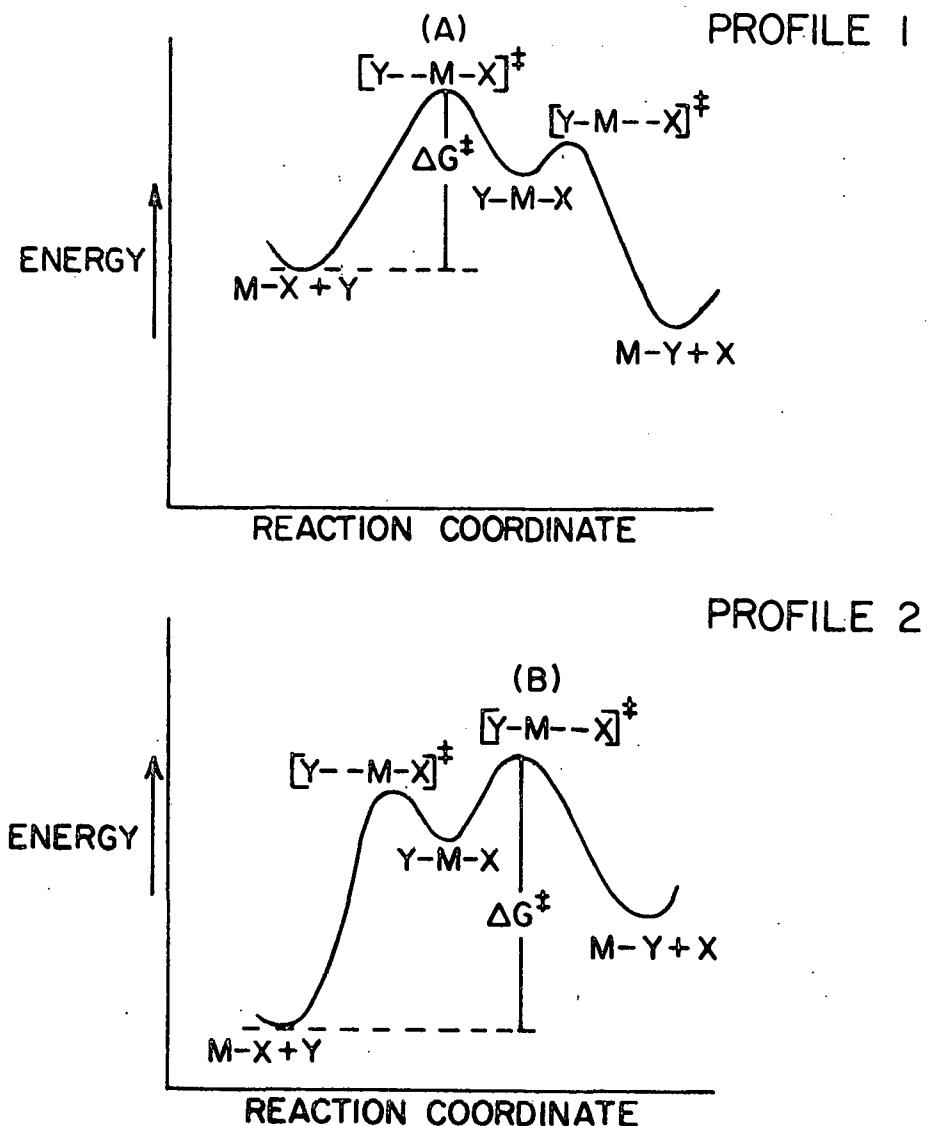
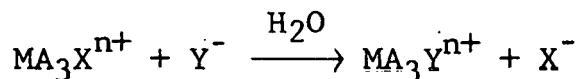


Fig. 4. Reaction profiles (arbitrary scale) for S_N2 mechanism. 1. For $X^- = Cl^-, Br^-, I^-$, the Pt-X bond rupture is kinetically not important. 2. For $X^- = N_3^-, NO_2^-, SCN^-$, the bond rupture of Pt-X is kinetically important. (For displacements on $[Pt(dien)X^+]$)

on the complex. For an associative mechanism, an increase in positive charge requires an increase in reaction rates. For a bimolecular displacement process, the opposing effects of dissociation and neutralization would be of comparable importance and reaction rates would not be affected by the charge on the complex.

Martin (23) and his students have made extensive studies of the hydrolysis of the series PtCl_4^{2-} through $\text{Pt}(\text{NH}_3)_3\text{Cl}^+$. The results show that for a three-unit change in the charge on the complex, the rates of hydrolysis are approximately equal. This indicates that both bond making and bond breaking are important in the transition state. Thus the solvent mechanism, k_1 , like the direct substitution path, k_2 , seems to be a bimolecular displacement process.

These constants are defined for reactions such as:



where in water solution, a two term rate law:

$$\text{Rate} = k_1[\text{MA}_3\text{X}^{n+}] + k_2[\text{MA}_3\text{X}^{n+}][\text{Y}^-]$$

is generally followed, where k_1 and k_2 are first-order and second-order rate constants, respectively. Under pseudo-first-order conditions containing excess Y^- , the experimental first-order rate constant, k_{obs} , is related to the individual

rate constants as shown by $k_{obs} = k_1 + k_2[Y^-]$. This requires that a plot of k_{obs} vs. $[Y^-]$ be linear with an intercept of k_1 for the reagent-independent path and a slope of k_2 for the reagent path. The two-term rate law requires a two path reaction mechanism. The rate constant k_1 is due to slow replacement of X^- by the solvent, which is then rapidly replaced by Y^- . A direct nucleophilic displacement of X^- by Y^- is responsible for k_2 . It then becomes convenient to designate the solvent path k_1 as k_s and the reagent path k_2 as k_y , so that now:

$$k_{obs} = k_s + k_y[Y^-]$$

It should be noted that the k_s pathway does not a priori represent an associative mechanism. This solvent path has been the subject of several substitution studies, which generally indicate a direct displacement mechanism.

Since there is considerable evidence that the solvent path for square-planar substitution involves a direct displacement by the solvent, it is expected that the contribution made by this path to the overall reaction rate would increase with an increase in the coordinating ability of the solvent. Pearson et al. (24) studied solvent effects on the rate of isotopic exchange of chloride with trans- $Pt(py)_2Cl_2$. Good coordinating solvents provide almost entirely a solvent

path for the exchange, $k_1 \gg k_2[\text{Cl}^-]$. The poor coordinating solvents, such as benzene, carbon tetrachloride and sterically hindered alcohols, contribute little to the overall rate of reaction, $k_2[\text{Cl}^-] \gg k_1$. For "good" solvents, k_s increases in the order: $\text{ROH} < \text{H}_2\text{O} \sim \text{CH}_3\text{NO}_2 < \text{DMSO}$. If the role of the solvent were primarily that of solvating the leaving Cl^- , then H_2O rather than DMSO would be more efficient for the reaction. Such would be the case if bond breaking were of primary importance, but the experimental facts argue against this.

Gray and Olcott (25) have designed some clever competition experiments providing direct proof that the solvent acts as a nucleophile in its contribution to the substitution rate in Pt(II) complexes. They examined $[\text{Pt}(\text{dien})\text{X}^+]$ products by determining the anation rates of different Y groups on $[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$. To be consistent with the assignment of k_1 as the aquation rate constant, these rates of Y must be much faster than k_1 or $k_{\text{H}_2\text{O}}$. This is found for all ligands with OH^- being exceptionally rapid. This high hydroxide reactivity is due to a rapid proton transfer, not to the usual ligand replacement. This fact that OH^- is 100% efficient, relative to other ligands, and at the same time relatively

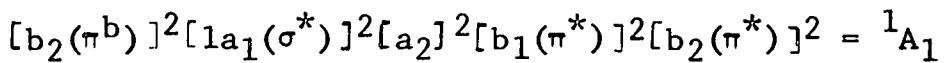
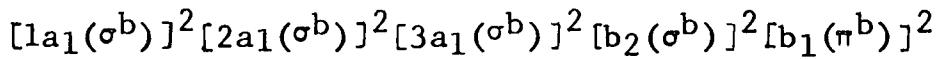
inert to $[\text{Pt}(\text{dien})\text{X}^+]$ allows competition experiments to determine whether or not $[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ is generated directly in the solvent path. The determination of the rate of reaction of $[\text{Pt}(\text{dien})\text{X}^+]$ with OH^- in varying amounts of X^- showed that X^- has no effect on the rate of formation of $[\text{Pt}(\text{dien})\text{OH}^+]$ and the rate constant is the same as $k_{\text{H}_2\text{O}}$. Therefore the solvent assisted dissociative process is discarded because the presence of added X^- would slow the rate due to an equilibrium retardation effect. Reactions of Y^- and OH^- with $[\text{Pt}(\text{dien})\text{X}^+]$ showed that $[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ is not produced in the reagent pathway. The aquo intermediate would be rapidly and completely converted to $[\text{Pt}(\text{dien})\text{OH}^+]$. But if the reagent mechanism is a direct displacement, the initial product would be $[\text{Pt}(\text{dien})\text{Y}^+]$ because Y^- is a better nucleophile than H_2O and therefore $k_y[\text{Y}^-] \gg k_{\text{H}_2\text{O}}$. The initial product would then react slowly to form the stable $[\text{Pt}(\text{dien})\text{OH}^+]$. This rate of formation would be $k_{\text{H}_2\text{O}}$ for the $[\text{Pt}(\text{dien})\text{Y}^+]$. Likewise the rate of initial formation of $[\text{Pt}(\text{dien})\text{Y}^+]$ would correspond to k_y in the absence of OH^- . This is what is found, corroborating a direct reagent displacement mechanism. The trigonal bipyramidal transition state was supported by these experiments. If a square pyramidal transition state and dis-

sociative mechanism led to the aquation of $[\text{Pt}(\text{dien})\text{X}^+]$, then the transition state must have reacted only with the solvent. This is reasonable since association of H_2O to form the square pyramid and subsequent dissociation of X^- would form an aquo-complex intermediate. This would react with the OH^- present to form $[\text{Pt}(\text{dien})\text{OH}^+]$ with a rate constant equal to $k_{\text{H}_2\text{O}}$ for $[\text{Pt}(\text{dien})\text{X}^+]$. But the rate constant found is $k_{\text{H}_2\text{O}}$ for $[\text{Pt}(\text{dien})\text{Y}^+]$. Another inconsistency arises using this model. The first order exchange rate would be faster than the aquation rate if the transition state, with the bond to the leaving group dissociated, could be attacked at that position by the entering group. This rate would then be dependent on the charge on the dissociated intermediate; the higher the charge, the greater would be the rate. This would contradict Martin's (23) findings in the chloroamine series. Therefore the square pyramid could not be the transition state configuration.

C. Spectra and Bonding of $[\text{Pt}(\text{dien})\text{Cl}]^{\text{Cl}}$

The electronic spectra have been assigned by Baddley et al. (26) using a molecular orbital level classification. This level scheme was derived by modifying the general M.O. scheme (27) ($\text{D}_{4\text{h}}$ symmetry with full σ - and π -bonding) for $\text{C}_{2\text{v}}$ symmetry and limited π -bonding. The ground state of the

$[M(dien)X]^{n+}$ complexes is:



The $[M(dien)X]^{n+}$ complexes show a single absorption band of intermediate intensity (ϵ range 200-2000) in the 25,000-40,000 cm^{-1} region. From the level scheme, the band is assigned $b_1, b_2(\pi^*) \rightarrow 2a_1(\sigma^*) [{}^1A_1 \rightarrow {}^1B_1, {}^1B_2]$. The transition involves transferring an electron from a π -molecular orbital, delocalized over M and X, to a $2a_1(\sigma^*)$ orbital, which is essentially the $nd_{x^2-y^2}$ metal orbital. For any M, the band increases in energy in the order of X: $I^- < Br^- < Cl^-$. This is consistent with the assignment of the transition as a partial charge-transfer process, since the stability of $\pi(X)$ is expected to increase $\pi(I) < \pi(Br) < \pi(Cl)$. The charge-transfer is also indicated from a comparison of analogous Pt^{2+} and Au^{3+} complexes. Thus the band for any given X complex shifts to lower energy in going from Pt^{2+} to the better electron acceptor, Au^{3+} . This type of evidence has been used to assign ligand \rightarrow metal charge-transfer in PtX_4^{2-} and AuX_4^- complexes (28). The final observation in favor of the above interpretation is that the $[Pt(dien)OH^+]$ complex does not show the band at all in the spectral region examined.

Table 1 shows the spectral assignments. Figure 5 shows the uv spectrum of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$.

Table 1. The long wavelength electronic transitions in $[\text{Pt}(\text{dien})\text{X}^+]$ complexes

Complex	λ_{max} nm	ν_{max} cm ⁻¹	ϵ_{max}
$\text{Pt}(\text{dien})\text{Cl}^+$	270	37,040	275
$\text{Pt}(\text{dien})\text{Br}^+$	275	36,360	250
$\text{Pt}(\text{dien})\text{I}^+$	300	33,330	500

It is known that the rate of reaction of the saturated system $[\text{Pt}(\text{dien})\text{Cl}^+]$ with pyridine is a factor of 10^3 slower than that of the unsaturated system, $[\text{Pt}(\text{tripy})\text{Cl}^+]$ (21).

The explanation is that for the tripyridal substrate, the aromaticity in the platinum- α -diimine chelate ring enhances the reactivity of the complex. Since there is presumed to be considerable π -bonding in such systems, their reactivity can be attributed to a π -trans effect. Thus one might expect absolute rates difficult, if not impossible, to obtain.

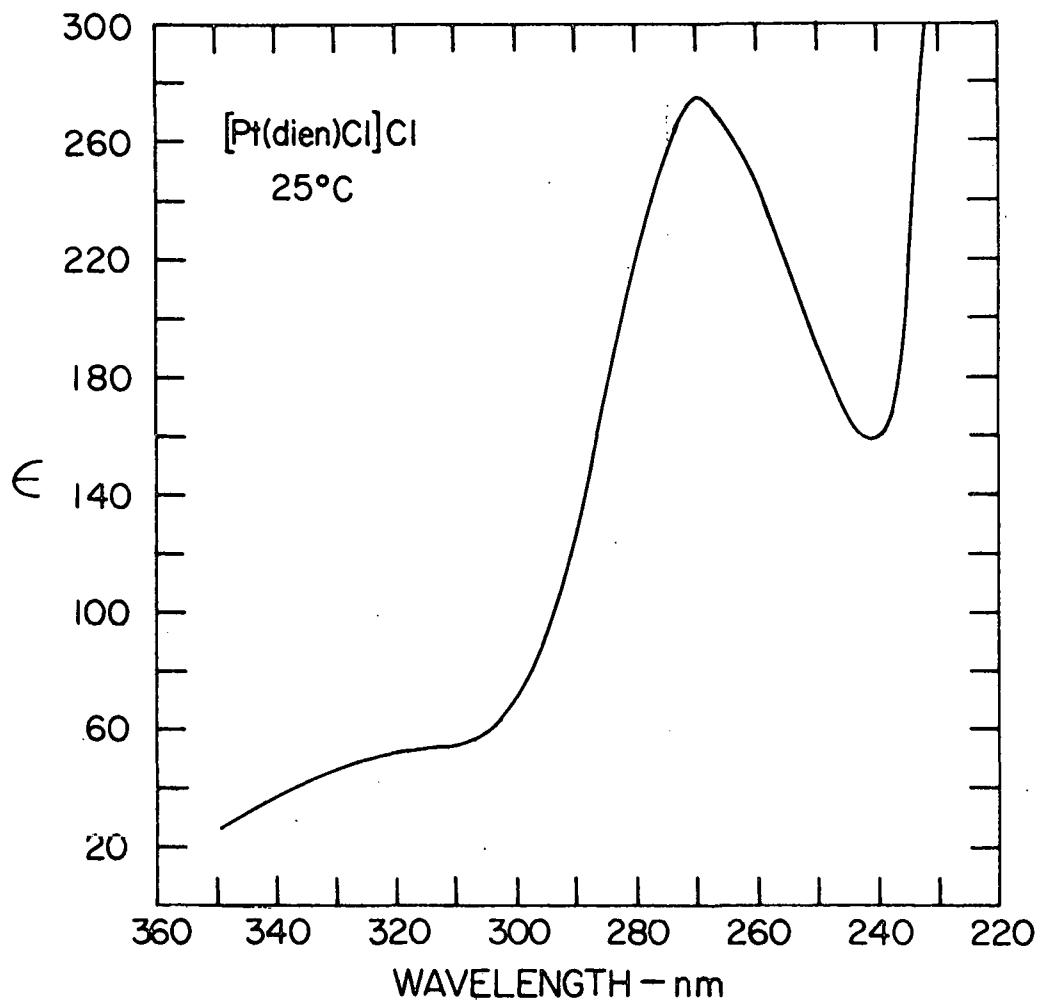
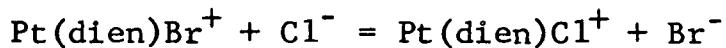


Fig. 5. Ultraviolet spectrum of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ plotted as molar absorptivity, ϵ , in $(\text{M Pt})^{-1} \text{cm}^{-1}$ vs. wavelength in nanometers

D. Origin of the Problem

The equilibrium quotient, K , for the reaction:



is given by the ratio of the second order rate constants:

k_{Cl} (for $[\text{Pt(dien)Br}^+]$) and k_{Br} (for $[\text{Pt(dien)Cl}^+]$). A tracer technique provided this quantity, 0.26 at 25°C , at $\mu = 0.318\text{M}$ in an evaluation of these rate constants (29).

The tracer technique also provided approximate solvation equilibrium quotients at 25°C and $\mu = 0.318\text{M}$ for both $[\text{Pt(dien)Br}]^+$ and $[\text{Pt(dien)Cl}]^+$.

In trying to compare these results with the other reactions of $[\text{Pt(dien)X}]^+$, one encounters one of the most fascinating problems involved in nucleophilic displacements, that of trying to understand what properties of a reagent make it a good nucleophile. There have been several attempts to correlate the extrakineti properties of the reagent with its reactivity. The moderately successful tries are based on the principle of linear free-energy relationships (30, p. 223). Just as there is no one scale of acid-base strengths, there is no one scale of nucleophilic reactivities. The substrate must naturally be considered in any discussion of relative order of nucleophilic strengths. Fortunately there are

several qualitative generalizations available (31,32). The existing kinetic data on many different substrates show that soft (polarizable) nucleophiles are most effective towards soft substrates (class b). Similarly, hard nucleophiles (class a), such as OH^- , are most effective towards hard substrates. Polarizability in the nucleophile is always more important for rates than for equilibria.

Quantitative evaluation of the nucleophilic properties of various reagents generally brings in their basicities toward the proton and a characteristic which may be loosely defined as polarizability or electronegativity. The nature of the electrophilic substrate determines which properties make the greatest contribution. Belluco *et al.* (18) have made the most detailed study of relative reactivity for the monochloro substitution of trans- PtA_2Cl_2 in methanol by various nucleophiles. This study shows that basicity is of little importance since the strongest bases, CH_3O^- and OH^- , are the only reagents that do not compete with the solvent in these displacements. That the reactivity of Y does not correlate with its base strength is to be expected if one considers that the normal pK_a values are for the hard acid H^+ , while the k_y are for the soft acid, Pt(II).

Polarizability, on the other hand, seems to play a major role. The only difficulty is to find a suitable set of numbers to assess quantitatively this polarizability or electronegativity effect. Edwards (33) has shown that a large amount of kinetic and thermodynamic data for organic and inorganic systems can be correlated by equations such as

$$\log (k/k_0) = \alpha P + \beta H$$

$$\log (k/k_0) = \alpha E_n + \beta H$$

where P is a polarizability factor, H is a proton basicity factor defined by $H = 1.74 + pK_a$, and E_n is a redox factor defined by $E_n = E^o + 2.60$, where E^o is the standard oxidation potential for the reagent acting as a reducing agent, i.e., for the reaction: $Y(aq) = 0.5(Y-Y)(aq) + e^-(aq)$, k_0 refers to water, k to the various nucleophiles. For water, H and E_n are zero by definition. For formation constants of complexes, it is found that class (a) metals have large β and class (b) metals have large α . Hard acids are sensitive to the H value of the attacking base (β is large) while soft acids are sensitive to the E_n or P value (α is large). These results are perfectly reasonable examples of the general linear free energy relationship principle. This states that there are linear functions between the logs of rate constants or equi-

librium constants of similar series of related reactions (34). Since the proton is a typical hard acid, it is expected that other hard acids will be sensitive to proton basicity. Soft acids clearly need another scale of basicity, for which E_n and P values are approximations. The disadvantage is that E° values are not known for many common reagents, since the coupled product Y-Y is often incapable of existence.

This suggests that a useful standard scale for soft acids would be a table of stability constants, under standard conditions, for a typical soft acid and a variety of bases. Simpson (35) obtained a number of pK data for the formation constants of various bases with CH_3Hg^+ , a soft acid. A log k_y vs log $K_{\text{CH}_3\text{Hg}^+}$ plot shows as good a correlation as does a plot of log k vs E° for several platinum(II) complexes; but OH^- , or CH_3O^- in methanol, is poorly fitted since at equilibrium it is strongly bound to CH_3Hg^+ , while it is not found to be a nucleophilic group for platinum substitutions.

Since these attempts were unsatisfactory, Belluco et al. (18) decided to use the rate constants for the complex trans- $\text{Pt}(\text{py})_2\text{Cl}_2$ with various nucleophiles as standards. This complex was chosen because data were available for the greatest number of reagents. A set of nucleophilic reactivity con-

stants, n_{Pt} , was defined by:

$$\log(k_y/k_s)_0 = n_{Pt}$$

where k_y and k_s refer to the rate constants for the reaction of trans- $Pt(py)_2Cl_2$ in methanol at 30°C. A plot of $\log k_y$ for other platinum complexes (see Fig. 6) gives reasonably good straight lines in all cases. This suggests the linear free energy relationship:

$$\log k_y = s n_{Pt} + \log k_s$$

The intercepts of plots such as in Fig. 6 are fairly close to measured values of k_s for each substrate.

The constant s is a nucleophilic discrimination factor. A reasonable spread of values, from 0.44 to 1.43 is found. There is a strong inverse correlation between s and k_s . A large value of s goes with a very small k_s . This is reasonable if we interpret k_s as a measure of the "intrinsic" reactivity of the platinum complex, i.e., it is the rate constant for the poorest nucleophile whose effect can be measured in the particular solvent used. If any other nucleophile, such as ClO_4^- , has a rate constant less than the solvent, its kinetic effect will never be measurable. With such a poor nucleophile as the solvent, the greatest burden is put on the complex to reach the activated complex for reaction. If k_s

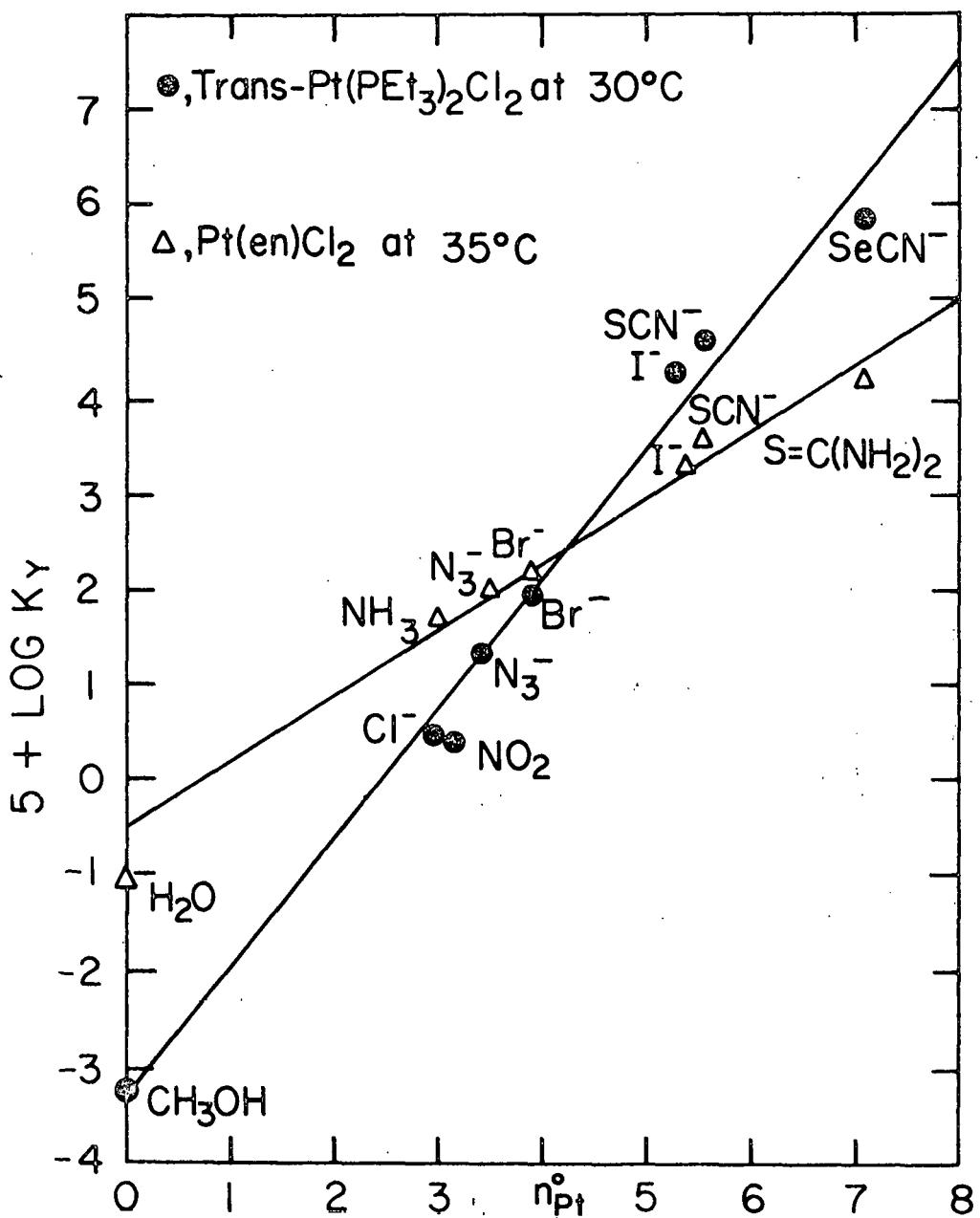


Fig. 6. Correlation of the rates of reaction of Pt(II) complexes with the standard trans-Pt(py)₂Cl₂ for different nucleophiles. \bullet , trans-Pt(Pt₃)₂Cl₂ in methanol at 30°C; Δ , Pt(en)Cl₂ in water at 35°C

is small, this implies that the tendency for the complex to react is small and it will rely more on the nucleophile and therefore be more sensitive to changes in it. Thus arsine and phosphine complexes of platinum(II), with large s values, are sensitive to the nucleophiles while $[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ is not. Bellucco et al. (36) suggested that the nucleophilicity would also be useful in comparisons of different solvents if it were defined for their standard system as:

$$n_{\text{Pt}}^{\text{O}} = \log(k_{\text{y}} M_{\text{O}} / k_s)$$

where M_{O} is the molar concentration (moles/l.) of the solvent. In practice this means all the original n_{Pt} values should be increased by the constant amount 1.39 arising from dividing k_s by 26M, the concentration of methanol. In this way n_{Pt}^{O} is dimensionless. This same study found also that although a solvation effect is important in Pt(II) substitution reactions, it is not the major contribution to reactivity. Data were presented that show the same order of nucleophilic strength maintained, but the spread of reactivity greater in protic than in aprotic solvents.

Before substitution reactions can be compared via the nucleophilicity constants, they should be reduced to common conditions. In most reactions, this means adjusting the rate

constants for ionic strength effects. The rate constant for a reaction, first order in the reactants, A,B..., can be expressed by:

$$k = k^0 \times (\gamma_A \cdot \gamma_B \dots / \gamma_{\pm}) = k^0 \Gamma(\mu)$$

where μ is the ionic strength, γ_A is the activity coefficient of reactant A, etc., and γ_{\pm} the activity coefficient of the transition state term, k^0 is the rate constant at zero ionic strength (30, p. 150). A derivation of this function is presented in Appendix 1. According to this treatment, a rate constant for a reaction between two species, one of which is uncharged, will be independent of ionic strength as was the case for the reference compound used in defining n_{Pt}^0 . The same result can be expected for the reactions of uncharged solvent with charged Pt(II) complexes. As shown by constant k_1 's for various nucleophiles, this is the case. At low ionic strength the function $\Gamma(\mu)$ for a reaction between an anion and $[\text{Pt}(\text{dien})\text{X}]^+$, at 25°C in aqueous solution, is expected to follow the function:

$$\log \Gamma = -1.018 \sqrt{\mu}$$

Chan (37) has reported an investigation of the dependence of rates of substitution in $[\text{Pt}(\text{dien})\text{X}]^+$, where $\text{X} = \text{Cl}^-$ or Br^- , by iodide as a function of ionic strength. Chan's spectro-

photometric kinetic data, provided precise values of k_y over a region of μ from 0.03 to 0.10 M. By plotting $\log k_2$ vs. $\sqrt{\mu}$ for the interval $.17 < \sqrt{\mu} < .32$ M, he obtained a linear plot with slope $-1.05 \text{ M}^{-\frac{1}{2}}$, i.e., the following functional relationship for $\Gamma(\mu)$:

$$\log \Gamma = -1.05 \sqrt{\mu}$$

This slope is somewhat greater than would be expected from the activity coefficients of a 1-1 electrolyte over this ionic strength range (38, pp. 716, 731, 732). Upon application of his empirical expression for $\Gamma(\mu)$ to convert the known rate constants, k_y , to zero ionic strength, it should be recognized that there is a rather dangerous extrapolation of the linear function in both directions from the measured region; however, more complete data are not available. Second order rate constants were converted in this way to zero ionic strength for halide replacement by halides in the (dien)-complexes. The values are collected in Table 2.

The plot of $\log k_2$ vs. n_{Pt}^0 in Fig. 7, for the halide replacement in $[\text{Pt}(\text{dien})\text{Cl}^+]$ and $[\text{Pt}(\text{dien})\text{Br}^+]$ under zero ionic strength conditions is generally consistent with the expected linear behavior. The rate constant for Cl^- with $[\text{Pt}(\text{dien})\text{Cl}^+]$ appears to be the only serious inconsistency

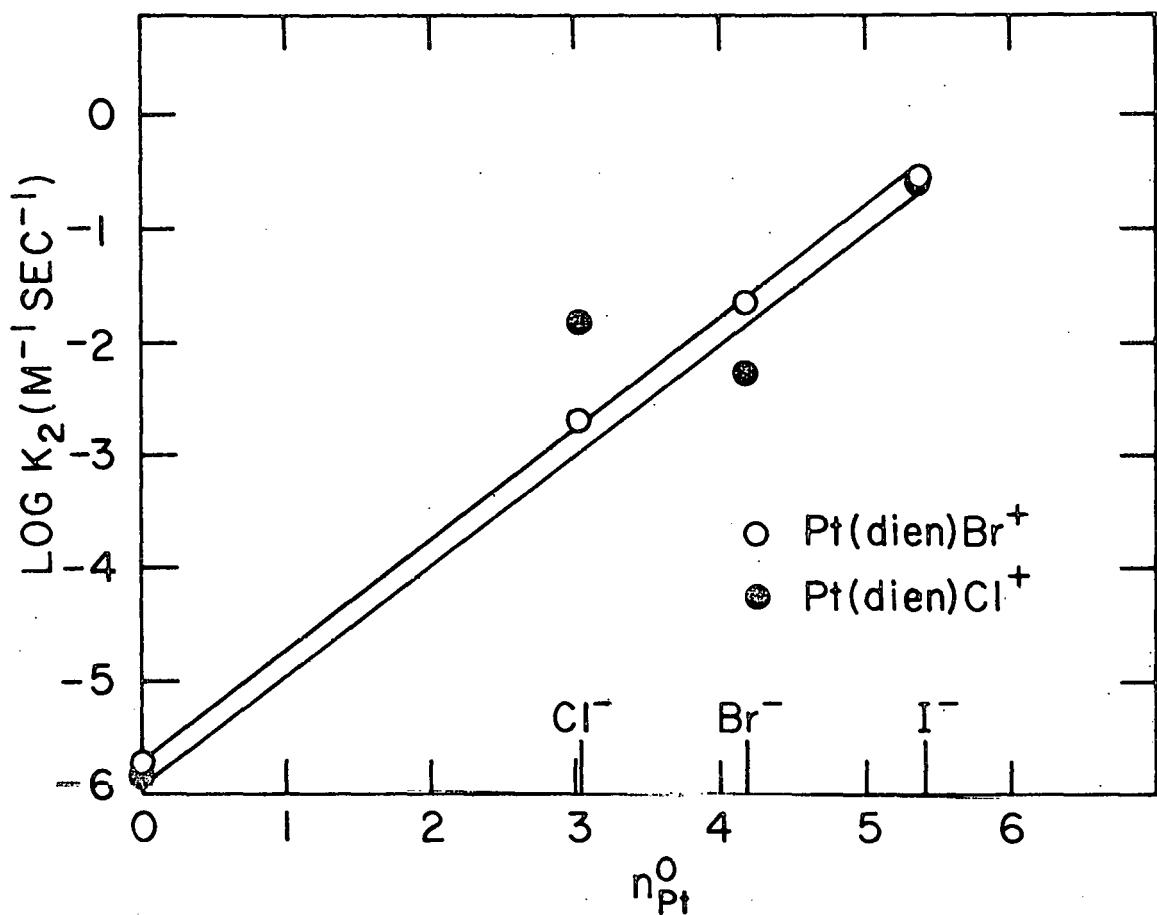


Fig. 7. Typical dependence of the second order rate constant, $k_2 (\text{M}^{-1} \text{ sec}^{-1})$, upon the nucleophilic reactivity constants at 25°C and zero ionic strength

Table 2. Second order rate constants for the replacement of halide ligands of $[\text{Pt}(\text{dien})\text{X}]^+$ by halides. Conversion to ionic strength = 0. Temp = 25°C

Leaving group	entering group	$k_2(\text{sec}^{-1} \text{M}^{-1}) \times 10^4$		
		Cl^-	Br^-	I^-
Cl^-		150 ^a	89 ^b 78 ^a	3200 ^c
Br^-		23 ^b	228 ^d	4200 ^c

^aRef. (17, chapt. 2).

^bRef. (29).

^cRef. (37).

^dRef. (39).

in the set. This rate had been determined by $^{36}\text{Cl}^-$ exchange in which a silver chloride precipitation was used for the separation (20). Silver halide separations have proven unsatisfactory for exchange studies of a number of platinum(II) complexes in this Laboratory. It therefore seemed advisable to reexamine that system.

II. EXPERIMENTAL

A. Materials

1. Platinum

Commercially available platinum contains traces (ca. 20 ppm) of iridium which could act as a catalyst in substitution reactions. Therefore, the platinum was purified by the method of Jowanovitz and co-workers (40). Platinum metal obtained as wire was cut into segments to provide a large surface area and dissolved in aqua regia. The solution was evaporated to near dryness. Repeating the evaporation with frequent addition of HBr drove off HCl and HNO₃, leaving H₂PtBr₆. Addition of KBr to the solution precipitated the slightly soluble, red K₂PtBr₆ as well as K₂IrBr₆ impurity. The precipitate was recrystallized three times from water with total recovery of 98%. This procedure has been shown to yield platinum with .015 ± 0.0021 ppm iridium (41). The purified K₂PtBr₆ was reduced to platinum metal by the dropwise addition of hydrazine to a boiling aqueous solution made strongly alkaline with NaOH.

2. Precursor complexes of platinum

Iridium-free platinum was dissolved in aqua regia. After repeated additions of concentrated HCl and evaporation to near

dryness, a solution of red H_2PtCl_6 was obtained. Addition of excess KCl caused precipitation of insoluble, yellow K_2PtCl_6 (42). This was recrystallized from water.

K_2PtCl_4 was prepared from K_2PtCl_6 by reduction with SO_2 solution (43). This method has the advantage that no salts other than the platinum complex are formed. Thus pure K_2PtCl_4 was obtained.

$[Pt(dien)Br]Br$ was prepared by the methods of Mann (44) and Teggins (39). Using Mann's method, a 2:1 mole ratio of diethylenetriamine trihydrochloride to K_2PtCl_4 in 300 ml of water was boiled under reflux for eight hours. The solution was cooled and a filtrate separated from the resulting copious amounts of KCl. Addition of NaBr allowed the precipitation of light yellow $[Pt(dien)Br]Br$. This was recrystallized from 1N HBr. Purity was indicated by the uv absorption at 275 nm, $\epsilon = 250$ as found by Baddley et al. (26).

The Teggins method (39) utilizes the reaction between $PtBr_4^{2-}$ and dien at a pH of 6. Under these conditions, the reaction is essentially complete in 30 minutes at $25^\circ C$. The K_2PtBr_4 was prepared by refluxing a 1:1.06:0.06 mole mixture of K_2PtBr_6 , $K_2(C_2O_4)$ and $H_2C_2O_4$ in 50 ml of water for four hours. Excess K_2PtBr_6 was removed and the solution used for

the $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ preparation.

3. $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$

The method described by Watt (45) was modified and used for the preparation of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$. To a solution of $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ was added a 2:1 mole ratio of AgNO_3 . The mixture (50 ml) was heated on a steam bath and occasionally stirred for four hours in the dark and filtered. To the filtrate was added a two fold excess of 12 M HCl. After evaporating to 30 ml, the solution was poured with stirring into one liter of a 50-50 mixture of acetone and diethyl ether. A light yellow precipitate separated, was filtered and washed with ether. The product was recrystallized twice from water, washed with ether, air dried for one hour and stored in a desiccator over Anhydrene. Platinum was determined by decomposition of the complex by gradually heating a weighed sample in a platinum boat to about 900°C and maintaining the temperature for several hours. Pt calculated 52.9%, found 52.6%; Cl calculated 19.2%, found 19.1%. Chloride was determined by a gravimetric determination with AgNO_3 (46).

The uv absorption spectrum perhaps provides a better criterion for purity than chemical analysis. Absorption in a valley of such a spectrum reflects the presence of an

impurity. Therefore it is common practice in this Laboratory to use a ratio of absorbances recorded at a maxima and at a minima as indicative of purity. A peak (270 nm) to valley (259.4 nm) of 1.75 was taken as indicating pure complex (>99%).

4. Other chemicals

Technical grade diethylenetriamine was distilled under vacuum through a fractionating column packed with 1/8 inch glass helices. The colorless fraction collected, b.p. 70-71°C (3 mm Hg), was converted to the trihydrochloride by treatment with concentrated hydrochloric acid followed by precipitation with ethanol saturated with HCl. The solid was filtered, washed with ethanol and air dried, m.p. 228-230°C.

LiCl purchased from G. Fredrick Smith Chemical Co. was recrystallized from water. Solutions were standardized by titration of the acid released from an H^+ cation resin by passage of a known aliquot of the LiCl solution. Both tris(hydroxymethyl)aminomethane, (THAM), and NaOH were used as titrating agents. Chloride was determined, as a check of the method, by a $AgNO_3$ precipitation (46).

$LiClO_4$ purchased from G. Fredrick Smith Chemical Co. was recrystallized from water and tested for chloride ion content.

Solutions were standardized as with the LiCl solutions.

1,4-dioxane (#9231) was obtained as a "Baker Analysed" Reagent. Naphthalene was a purified grade from Mallinckrodt Chemical Works. The secondary scintillator was p-bis[2-(5-phenyloxazolyl)]-benzene, (POPOP), scintillation grade, from New England Nuclear Corp. The primary scintillator was 2,5-diphenyloxazole, (PPO), from New England Nuclear Corp.

Chlorine-36 was supplied as 2 N HCl³⁶, 99% pure, by New England Nuclear Corp.

Amberlite IRA-400 was purchased from the Rohm and Haas Company in cubic foot quantities, in the chloride form, 16-50 mesh (U.S. standard screens).

Water used was drawn from the Laboratory distilled water tap, redistilled from alkaline permanganate and again distilled through a fractionating column.

All other chemicals were of analytical reagent grade, meeting the specifications for the American Chemical Society.

B. Instruments

Spectra and absorbance measurements were made on a Cary Recording Spectrophotometer Model 14 with a hydrogen lamp light source. All measurements were made in standard silica spectrophotometric cells. Reference solutions contained all

electrolytes and reagents, except the complex, in the same concentrations as the sample solutions. Data were recorded relative to a baseline which had been recorded using the reference solution in both the sample and reference cells.

The hydrolysis acid-base titrations were conducted using a Radiometer SBR2c/ABU1c/TTA3 automatic recording titration apparatus with a 0.2500 ml burette with an accuracy of 1 μ l \pm 0.7%. The titration vessel was equipped with a water jacket for temperature control and with a gas inlet for atmosphere control. A slight positive pressure was maintained in the vessel by passing grade "A" purified nitrogen through an Ascarite-containing tower and then bubbling the gas through the solution and allowing it to escape through the electrode and gas inlet fittings. The reference electrode was a Radiometer saturated calomel #K401, while the indicator electrode was a Radiometer glass electrode #G202c.

Counting of the chlorine-36, 0.714 Mev β^- , was accomplished with a Beckman Liquid Scintillation System equipped with a Model 33 Teletypewriter. The soft-beta counting spectrophotometer has a 200 sample capacity with ambient temperature operation. Beckman PolyQ screw cap scintillation vials #566350 were used.

In standardization titrations, a Model 12 Corning pH meter with a Beckman glass electrode, #40498, and a fiber type calomel reference, #39710, was used.

Precise weighings were made on a Sartorius single pan analytical balance, Model 2404. This balance has a 100 gram capacity, five place, digital read-out capability with precision of ± 0.05 mg.

The constant temperature bath was a Sargent S-84805 controlled by a Precision Scientific #62541 micro-set thermo-regulator. For 25.0°C , a cold tap water cooling coil was employed. The desired temperature was set to agree with the corrected reading on a 0.1°C division thermometer certified by the National Bureau of Standards. The temperature variations at both 25.0°C and 35.0°C were $\pm 0.05^{\circ}$ measured by a Beckman six degree differential thermometer calibrated to 0.01°C .

The volumetric apparatus used in this study met the class A specifications of the National Bureau of Standards.

Timers to read in minutes and hundredths of minutes were obtained from Precision Scientific Company.

An IBM System 360/50 digital computer was used for all least squares calculations. Plots were obtained from a

Cal-Comp Digital Incremental Plotter. This features a liquid ink pen (black ink) which moves in increments of 0.01 inch.

III. PROCEDURES

A. Aquation Equilibria

The concentration equilibrium quotients for the aquation of the $\text{Pt}(\text{dien})\text{Cl}^+$ ion were determined at 25.0°C and 35.0°C by potentiometric titrations of equilibrium solutions. At each temperature, six replicate titrations were run. The NaOH stock solution, made carbonate free (47), was diluted and used under a nitrogen atmosphere. Standardization of the NaOH was effected by titrating solutions of the primary standard, potassium acid phthalate, KHP, of a concentration requiring about one-half of the total burette volume of NaOH for complete neutralization. The standard KHP solutions were prepared with the standard LiClO_4 solution requisite to hold the ionic strength at 0.1 M or 0.318 M.

Calculated amounts of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ were weighed and placed in 200 ml volumetric flasks wrapped with black vinyl tape to exclude light. Also introduced was LiClO_4 solution to bring the ionic strength to 0.1 or .318 M. The flask was then brought to volume with distilled water. The extreme complex solubility permitted rapid dissolution of the sample. After 24 hours equilibration in a constant temperature bath, titrations and standardizations were begun. Aliquots of the

sample solution were introduced into the thermostated reaction vessel which was equipped with a water jacket insulated with asbestos and opaque tape. Transfer time was about one minute. Bubbling nitrogen quickly provided an inert atmosphere. Adjustment of the automatic titrator required 0.5 minutes and titration was complete (~80% titrant delivered) in 0.5-1.0 minutes. Therefore less than three minutes elapsed between commencement and finish of any titration. The technique of simultaneous standardization at the temperature of measurement (the standard KHP solution was also kept in the constant temperature bath) served to compensate for minor changes in NaOH concentration, for small volume errors resulting from the different temperatures studied, and for instrumental drift. With every fourth titration being a standardization, this method gave highly reproducible results. The small errors above were neglected, as were errors arising from possible temperature changes during transfer and titration to the endpoints. The neglect of hydrolysis during the titration was justified since doubling the time interval of titration yielded data identical with the normal shorter times.

B. Isotopic Exchange

Isotopic exchange of chloride in $[\text{Pt}(\text{dien})\text{Cl}^+]$ for solution chloride was studied at 25.0° and 35.0°C using radio-chlorine-36 as a tracer. The platinum concentration dependence in the rate law was investigated with variable platinum concentration at constant free chloride concentration with ionic strength of 0.1 M. Three to five replicate experiments were run at each concentration. The chloride dependence of the rate was tested likewise with variable chloride and constant platinum concentrations.

A calculated amount of $[\text{Pt}(\text{dien})\text{Cl}] \text{Cl}$ was accurately weighed and placed in a 50 ml volumetric flask wrapped with black vinyl electrical tape. Previous experience in this Laboratory has indicated that light induces the decomposition of platinum dien complexes and possibly would affect the isotopic exchange. Therefore light was excluded as much as possible from the reactions. Free chloride was added from standardized solutions (~1-.1 N) of LiCl . Full recognition was taken of the fact that free chloride was also available from the anion of the complex salt. Chloride produced by hydrolysis was neglected at this point. The ionic strength was brought to 0.1 M by the addition of standard (~.9 N)

LiClO_4 solution. After the solution was brought to volume with distilled water, it was equilibrated 24-48 hours in a constant temperature bath. Ten milliliters were removed and saved for spectrophotometric studies. Radiochlorine-36 was added to the remaining forty milliliters as 2 N HCl^{36} . The 10-20 λ 's added changed neither the volume nor the chloride concentration to any measurable extent. A timer was started when the "spike" of activity was added. After the flask was inverted ten times and returned to the temperature bath, the process of withdrawing one milliliter aliquots and quenching the timed withdrawals by passage through an anion exchange column was begun. The first sample was taken within one minute of the start of the experiment. The anion exchange columns were prepared from Amberlite IRA 400, 16-50 mesh in the perchlorate form. The resin was prepared by converting the chloride form to perchlorate form using 5% perchloric acid as the eluent in a column conversion (48). The three liters of resin required about 18 liters of eluent. Completion of conversion was confirmed by testing the effluent for chloride with AgNO_3 . The converted resin was ready to use after washing with deionized water for 20-30 minutes. The resin was used within 24 hours of conversion. Individual

columns were prepared from 14 mm I.D. pyrex tubing cut to 60 cm lengths. Tygon tubing with a screw clamp was used as a delivery system to 250 ml beakers. Glass wool was used as a support for the resin bed and as a plug to prevent resin swirling when solutions were added. Columns were 50 cm long utilizing about 77 cm³ of resin, including the void space.

It was considered that some problem might arise due to inefficiently or varyingly packed columns. Several experiments were conducted using both a gravity method and a vibrator method of column packing. The gravity method involved pouring a resin slurry into the column and allowing the resin bed to settle and pack by gravity. The vibrator method involved the application of an electric hand vibrator to the column exterior as an aid in packing. Comparisons of column heights on common samples treated by both methods indicated the same packing by both methods.

Sample addition and washing techniques were optimized for permitting rapid introduction of the sample into the resin bed with a minimum of dilution. The sample was drained into the resin column (with the time noted), followed by several small washings with distilled water (total volume \leq 5 ml), then elution with 95 ml of water was conducted by connecting

a filled separatory funnel to the resin column. As the last of the eluent passed into the glass wool atop the column, elution was stopped and the time noted.

The effluent was collected in a 250 ml beaker containing 5-6 drops of ~1.0 N LiCl solution. The solution was evaporated to 5 ml and transferred with washing to 20 ml scintillation vials. The extra LiCl was used to minimize the loss of chlorine-36 through possible evaporation of HCl. With the added chloride, the active chloride was a small percentage of the total; thus it would be a small percentage of any loss. The liquid in the scintillation vials was evaporated to near dryness using a water bath with an air stream directed into the vial. The sample was then brought to one milliliter volume with distilled water.

Fifteen milliliters of a scintillation solution was added. The scintillation solution was the customary (49) 70 grams of naphthalene for increased efficiency (50), 4.0 grams 3,5-diphenyloxazole as primary scintillator, 0.5 grams of p-bis[2-(5-phenyloxazolyl)]-benzene as secondary scintillator brought to one liter of total solution with 1,4-dioxane. The solution will solubulize 2 ml of water per 15 ml of scintillator. The solution of water and scintillator was shaken a

prescribed number of times to stabilize the quenching influence of oxygen. After a minimum of one hour protection of the samples against light exposure, they were counted with a liquid scintillation counter. Settings were established for a maximum of twenty minutes per each of three countings or one hour total per sample per counting sequence. The sequence was repeated two or three times giving 6-9 twenty minute counting periods per sample. A preset count was used based on a two sigma standard deviation of $\pm 2\%$ or 10,000 total counts. Settings were arranged so that by either method each sample was counted 6-9 times. Calculations were based on these counts with those of background, total activity and C_∞ samples (equilibrium value when the initial "spike" of Cl^{36} is statistically distributed among the system components).

C. Treatment of Data

The data obtained from the liquid scintillation system were as counts per minute per milliliter of original sample solutions. The associated two sigma errors were also given. Data were plotted according to the McKay equation (51) as $\ln(1-F)$ vs. time. The fraction of exchange, F , was calculated from the ratio of C_i , the counts per minute per milliliter of

sample at time, t_i , corrected for background, to C_∞ , the counts at equilibrium or time, t_∞ , corrected for background. The error limits on the function $\ln(1-F)$ were calculated by propagating an error of 5% of the C_i count plus .01% of the total activity added to the column. This represents the error in counting plus an error resulting from the failure in column effectiveness for the Cl^- ion. (See Appendix 2 for the derivation of the propagation formula). From the computer graphs of $\ln(1-F)$ vs. t , the half-times, $t_{\frac{1}{2}}$, of the reaction were evaluated. Rates were calculated from the revised McKay equation:

$$\text{Rate} = \frac{\ln 2[(\text{Cl}^- \text{ in complex form})(\text{Total free Cl}^-)]}{t_{\frac{1}{2}}[(\text{Cl}^- \text{ in complex form} + \text{total free Cl}^-)]}$$

The rate law describing normal Pt(II) substitution reactions, first articulated by Rich and Taube (52) and now well substantiated (20,18) is:

$$\text{Rate} = [k_1 + k_2(X)] \text{ Pt-complex}$$

For this equation to valid, little aquation must be apparent and the term [Pt-complex] becomes the unaquated complex concentration. In this isotopic exchange study, the entering group is the leaving group, thus the concentration of X doesn't change. Expressing $k_1 + k_2(X)$ as k_{obs} , the plot of

k_{obs} vs. X yields an intercept k_1 and slope k_2 . The k_1 term is attributed to a rate-determining bimolecular reaction of the complex with the solvent, followed by a rapid replacement of coordinated solvent by the nucleophile. The k_2 term corresponds to a single-stage bimolecular attack on the complex by the nucleophile.

Evaluation of these rate constants at two temperatures enables calculation of the activation parameters, ΔH^\ddagger and ΔS^\ddagger , for each process. By the transition state theory (absolute rate theory) (53), the fundamental equation of the rate constant for an ideal system is:

$$k = \frac{k' T}{h} K^\ddagger \quad (1)$$

where k is the rate constant, k' is Boltzmann's constant; 1.3804×10^{-16} erg molecule $^{-1}$ $^\circ\text{K}^{-1}$, T is the absolute temperature, h is Planck's constant: 6.6252×10^{-27} erg-sec., K^\ddagger is the equilibrium constant involving the reactants and a transition-state complex which is missing one vibrational degree of freedom. Thus strictly speaking, K^\ddagger is not a proper equilibrium constant (it should be multiplied by a translational partition function) although it is usually treated as one.

This equilibrium constant for formation of the transi-

tion-state complex from the reactants is related to the activation parameters by:

$$\Delta F^\ddagger = -RT \ln K^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (2)$$

Combining Equations 1 and 2 we obtain:

$$k = \frac{k' T}{h} \exp\left(-\frac{\Delta F^\ddagger}{RT}\right) = \frac{k' T}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (3)$$

This equation is valid for both constant-volume and constant-pressure systems; however, an interpretation of the temperature dependence of the rate constant cannot be made unless the state of the system is specified. The Arrhenius activation energy, E_a , is defined by:

$$\left(\frac{d \ln k}{d T}\right) = \frac{E_a}{RT^2} \quad (4)$$

In liquid solution, the temperature dependence for the rate constant, defined by Equations 1 and 2 is given by:

$$\left(\frac{d \ln k}{d T}\right) = \frac{\Delta H^\ddagger + RT}{RT^2} \quad (5)$$

Comparing Equations 4 and 5 we have

$$E_a = \Delta H^\ddagger + RT.$$

A procedure for calculating the thermodynamic quantities characterizing the activation process is to plot $\ln(k/T)$ vs. $1/T$. The slope of such a plot is $-\Delta H^\ddagger / R$ at constant pressure. In this study, with only two temperatures, the inte-

grated form of Equation 5 was used:

$$-\frac{\Delta H^\ddagger}{R} = \frac{\ln(\frac{k_{11}}{T_1}) - \ln(\frac{k_{12}}{T_2})}{(T_2 - T_1)/T_1 T_2}$$

where k_{11} is k_1 at T_1 and k_{12} is k_1 at T_2 .

The entropy, ΔS^\ddagger , can be calculated from Equation 3.

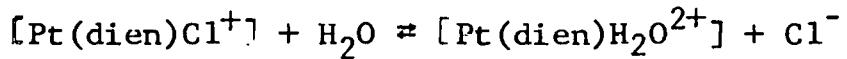
$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln \frac{k h}{k' T}$$

IV. RESULTS AND DISCUSSION

A. Aquation Equilibrium

A typical titration curve for 25 ml samples of aqueous equilibrated solutions of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ is shown in Fig. 8. The endpoint was taken at the inflection point of the curves. This was located by the method of second derivatives (54, p. 552). The values of $(\Delta\text{pH}/\Delta\text{v})$ were obtained and a linear interpolation made to find the final volume. The same method was used in the standardization of NaOH titrant. Table 3 shows the results.

To compare these K_{eq} with others calculable from previous data (29), one must be able to convert between different ionic strengths. If the aquation reaction is represented by:



the aquation equilibrium constant can be described by:

$$a_{\text{q}} K_{\text{eq}} = \frac{a_{\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}} a_{\text{Cl}^-}}{a_{\text{Pt}(\text{dien})\text{Cl}^+}}$$

where the quantities represented are the activities of the specified ions. In terms of the quantities measured in this study, one has:

$$a_{\text{q}} K_{\text{eq}} = a_{\text{q}} K'_{\text{eq}} \frac{\gamma_{\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}} \gamma_{\text{Cl}^-}}{\gamma_{\text{Pt}(\text{dien})\text{Cl}^+}}$$

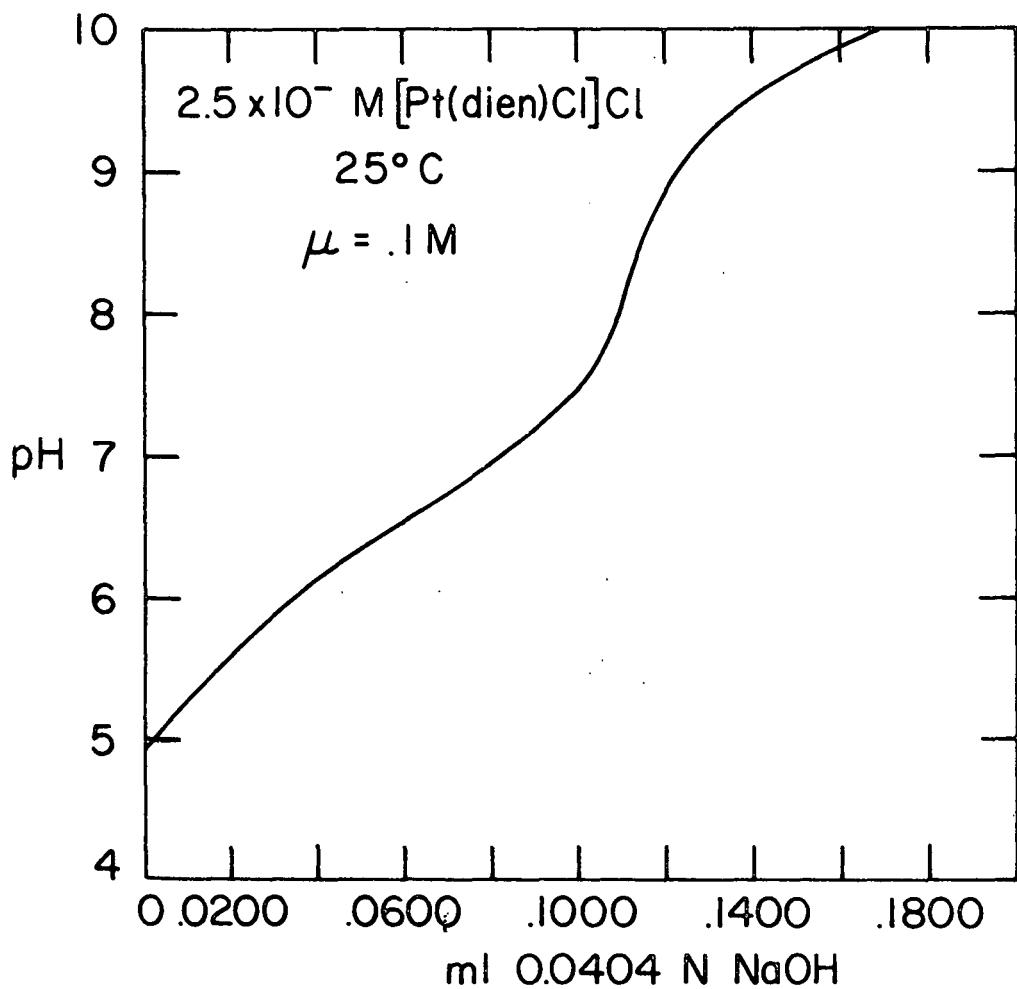


Fig. 8. Typical titration curve for 25.00 ml sample of equilibrated aqueous solutions of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$. 25°C and $\mu = .1 \text{ M}$

Table 3. Results of aquation equilibrium study on $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$

Initial $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ M x 10^4	$\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}$ M x 10^4	Total Cl^- M x 10^4	Final $\text{Pt}(\text{dien})\text{Cl}^+$ M x 10^4	$\text{aq K}_{\text{eq}}^{\text{a}}$ M x 10^4
5 ^{b,c}	1.207	6.207	3.793	1.976
10 ^{b,c}	1.409	11.409	8.591	1.871
25 ^{b,c}	1.726	26.726	23.274	1.982
50 ^{b,c}	1.855	51.855	48.145	1.998
				avg. 1.957
5 ^{d,c}	1.468	6.468	3.532	2.689
10 ^{d,c}	1.736	11.736	8.264	2.465
25 ^{d,c}	2.074	27.074	22.926	2.449
50 ^{d,c}	2.268	52.268	47.732	2.484
				avg. 2.522
5 ^{b,e}	1.264	6.264	3.736	2.119
10 ^{b,e}	1.520	11.520	8.480	2.065
25 ^{b,e}	1.811	26.811	23.189	2.094
				avg. 2.093
5 ^{d,e}	1.373	6.373	3.627	2.413
10 ^{d,e}	1.692	11.692	8.308	2.308
25 ^{d,e}	2.099	27.099	22.901	2.484
				avg. 2.426

^aAll numbers are averages of six or more determinations.

^bIonic strength = .100 M.

^cTemperature = 25°C.

^dIonic strength = .318 M.

^eTemperature = 35°C.

where aqK'_{eq} is the concentration equilibrium quotient in terms of the molar concentration of the species:

$$aqK'_{eq} = \frac{[\text{Pt(dien)}\text{H}_2\text{O}^{2+}][\text{Cl}^-]}{[\text{Pt(dien)}\text{Cl}^+]}$$

The γ_{Cl^-} represents the activity coefficient of the Cl^- ion at the ionic strength used. The other gamma quantities are similarly defined.

Since the activity coefficients of ions are assumed, to a first approximation, to be functions only of the absolute charge on the ions and the ionic strength (38, p. 35), one can make the assumption that $\gamma_{\text{Pt(dien)}\text{H}_2\text{O}^{2+}}$ equals γ_2 for any divalent ion (in moderately dilute solutions) and that $\gamma_{\text{Cl}^-} = \gamma_{\text{Pt(dien)}\text{Cl}^+} = \gamma_1$. Thus one can find systems which yield similar quotients of activity coefficients. Values of the quantity, $\gamma_{\text{C}_2\text{O}_4^{2-}}/\gamma_{\text{HC}_2\text{O}_4^-}\gamma_{\text{Cl}^-}$, which was evaluated for a range of ionic strengths by Pinching and Bates (55) in the potentiometric determination of the ionization constant of oxalic acid, were plotted vs. $\sqrt{\mu}$. γ_1 was taken as γ_+ for HCl in KCl solutions, and γ_1 was assumed equal to $\gamma_{\text{HC}_2\text{O}_4^-}$. Therefore from the data on γ_+ for HCl in KCl solutions (38, p. 575), a value of γ_1 at $\mu = .318$ M was taken to be .725. The value of $\gamma_{\text{C}_2\text{O}_4^{2-}}/\gamma_{\text{HC}_2\text{O}_4^-}\gamma_{\text{Cl}^-}$ at $\mu = .318$ M was indicated

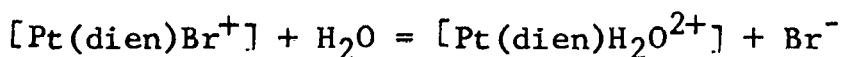
to be 0.493. Therefore multiplying this value by γ_1^2 yields a value of $\gamma_2 = 0.259$. Repeating the process for $\mu = .1 \text{ M}$, one obtains $\gamma_2/\gamma_1^2 = .605$, $\gamma_{\text{Cl}^-} = .788$, giving a $\gamma_2 = .375$.

Assuming that univalent activity coefficients are equal for different ions, the equilibrium constant at any ionic strength can be predicted by multiplying the known concentration K_{eq} for this system at one ionic strength by the quotient $\gamma_2(\mu_2)/\gamma_2(\mu_1)$. In this study, converting from $\mu = .1 \text{ M}$ to $\mu = .318 \text{ M}$ we have:

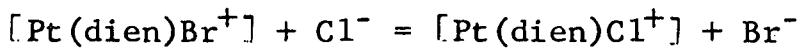
$$\begin{aligned} K_{\text{eq}}(\mu = .318 \text{ M}) &= \frac{K_{\text{eq}}(\mu = .1 \text{ M})\gamma_2(\mu = .318 \text{ M})}{\gamma_2(\mu = .1 \text{ M})} \\ &= 1.96 \times 10^{-4} \text{ M} \times \frac{.375}{.259} \\ &= 2.83 \times 10^{-4} \text{ M} \end{aligned}$$

This is in remarkably good agreement with the experimentally determined value of $2.52 \times 10^{-4} \text{ M}$. Therefore this method seems quite reasonable for use in converting between ionic strengths in this equilibrium system.

From Martin and Bahn (29), we may estimate $a_{\text{aq}} K_{\text{eq}}$ at $\mu = .318 \text{ M}$ for comparison with our value. Considering the following reactions,



and



one may represent the aquation equilibrium quotient for $[\text{Pt(dien)}\text{Cl}^+]$ by:

$$a_{\text{q}} K'_{\text{eq}} = K'_{\text{eqBr}^-} / K'_{\text{eqBr}^- \rightarrow \text{Cl}^-}$$

or:

$$a_{\text{q}} K'_{\text{eq}} = \frac{[\text{Pt(dien)}\text{H}_2\text{O}^{2+}][\text{Br}^-]}{[\text{Pt(dien)}\text{Br}^+]} \times \frac{[\text{Pt(dien)}\text{Br}^+][\text{Cl}^-]}{[\text{Pt(dien)}\text{Cl}^+][\text{Br}^-]} =$$

$$\frac{[\text{Pt(dien)}\text{H}_2\text{O}^{2+}][\text{Cl}^-]}{[\text{Pt(dien)}\text{Cl}^+]}$$

The equilibrium quotient, $a_{\text{q}} K'_{\text{eq}}$, may now be indicated, for $\mu = .318 \text{ M}$, to be:

$$a_{\text{q}} K'_{\text{eq}} = \frac{9.6 \times 10^{-5} \text{ M}}{.26} = 3.69 \times 10^{-4} \text{ M}$$

This is in satisfactory agreement with our value of $2.52 \times 10^{-4} \text{ M}$, if we consider that the aquation equilibrium constant for $[\text{Pt(dien)}\text{Br}^+]$ was very crudely approximated from an ion exchange experiment and the equilibrium constant for the replacement of Br^- in $[\text{Pt(dien)}\text{Br}^+]$ by Cl^- was obtained by a radioactive tracer study with its inherent errors.

A somewhat different result is obtained by using Gray and Olcott's (25) data for the anation reactions of $[\text{Pt(dien)}\text{H}_2\text{O}^{2+}]$. Unfortunately these experiments were not conducted at constant ionic strength. Therefore after reducing each

k_{obs} into its two components: the ionic strength independent k_1 (taken as the intercept of a k_{obs} vs. $[Cl^-]$ plot) and the ionic strength dependent k_2 ; each k_2 was reduced to zero ionic strength. The average, $1.24 M^{-1} sec^{-1}$, was taken and converted to $\mu = .1 M$ by multiplying by a $\gamma_2 = .375$. This new second order rate constant for the anation reaction corresponds to the rate constant for the back reaction in the aquation of $[Pt(dien)Cl^+]$. Since the k_1 term for the aquation of the $[Pt(dien)X^+]$ series is ionic strength independent and fairly constant over a number of X moieties, it was used without correction. Therefore using $K_{eq} = k_1/k_{-1}$, with $k_1 = .78 \times 10^{-4} sec^{-1}$ and $k_{-1} = .465 sec^{-1} M^{-1}$, an aquation equilibrium constant of $1.68 \times 10^{-4} M$ was calculated. This is in reasonable agreement with our value of $1.96 \times 10^{-4} M$ when the various assumptions made by converting the k_{obs} 's at their widely varying ionic strengths to zero ionic strength are considered.

B. Isotopic Exchange

A typical plot $\ln(1-F)$ vs. time for an isotopic exchange reaction is shown in Fig. 9. The half-life, $t_{1/2}$, can be evaluated from the slope of the plots. Tables 4 and 5 show results of isotopic exchange experiments at $25^\circ C$ and $35^\circ C$

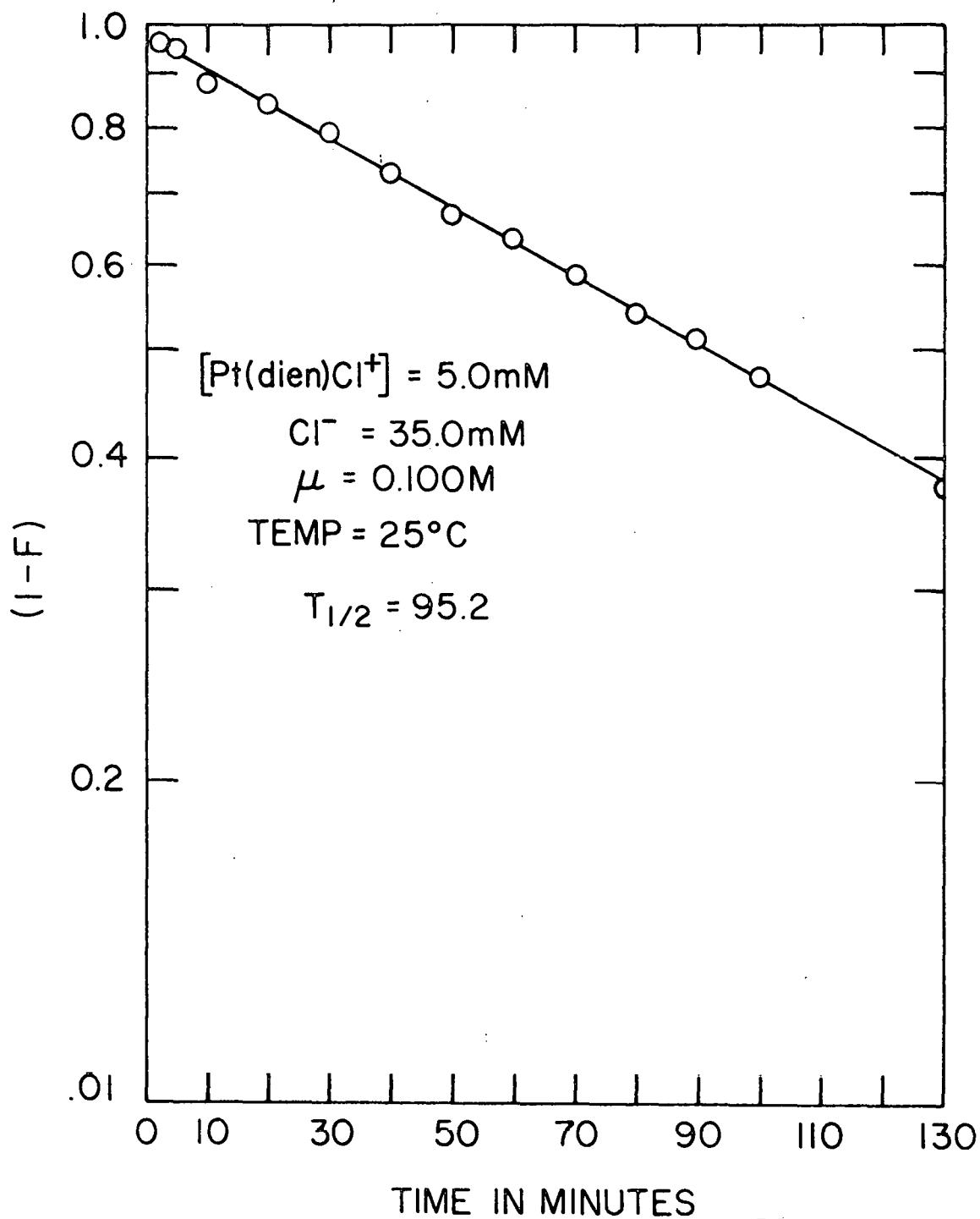


Fig. 9. Typical experiment for the exchange of ^{36}Cl between $[\text{Pt}(\text{dien})\text{Cl}^+]$ and $[\text{Cl}^-]$

Table 4. Rates of reaction of $[\text{Pt}(\text{dien})\text{Cl}]Cl$ with Cl^- in aqueous solutions at 25°C and ionic strength of .1 M

$[\text{Pt}(\text{dien})\text{Cl}^+]$ mM	$[\text{Cl}^-]$ mM	$[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ mM	$t_{\frac{1}{2}}$ (min.)	k_{obs} ($\text{sec}^{-1} \times 10^4$)
.500	12.0	.008	102.0	1.088
			120.8	.919
			104.0	1.067
			113.0	.982
			108.6	1.022
2.000	12.0	.034	105.7	.940
			111.9	.888
			117.7	.844
			115.3	.861
			123.3	.805
5.000	12.0	.085	149.6	.549 ^a
			98.7	.831
			84.4	.976
			82.8	.992
			124.5	.660 ^a
12.000	12.0	.203	67.0	.877
			73.7	.797
			61.0	.963
5.000	35.0	.029	95.8	1.056
			95.2	1.062
5.000	55.0	.018	111.3	.951
			94.3	1.123
5.000	65.0	.016	94.1	1.140
5.000	85.0	.012	101.8	1.072
			92.0	1.187
5.000	100.0	.010	83.9	1.311
			77.9	1.412
			79.1	1.391

^aPoint rejected using Chauvenet's criterion (56, p. 170).

Table 5. Rates of reaction of $[\text{Pt}(\text{dien})\text{Cl}] \text{Cl}$ with Cl^- in aqueous solutions at 35°C and ionic strength of .1 M

$[\text{Pt}(\text{dien})\text{Cl}^+]$ mM	$[\text{Cl}^-]$ mM	$[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ mM	$t_{\frac{1}{2}}$ (min.)	k_{obs} ($\text{sec}^{-1} \times 10^4$)
.500	12.0	.009	40.0	2.77
			42.3	2.62
2.000	12.0	.036	39.0	2.54
			35.0	2.83
5.000	12.0	.091	30.3	2.70
			31.9	2.58
			28.4	2.90
12.000	12.0	.036	21.9	2.68
			21.7	2.71
5.000	35.0	.031	33.8	2.99
			31.2	3.24
			31.7	3.19
5.000	65.0	.017	30.4	3.53
			29.3	3.66
			29.0	3.70
5.000	100.0	.011	28.9	3.81
			28.4	3.87
			28.9	3.81

respectively.

Calculations from these results yield k_1 and k_2 values at different temperatures as shown in Fig. 10. Using these least squares fitted values, the activation parameters are calculable. Table 6 shows the results.

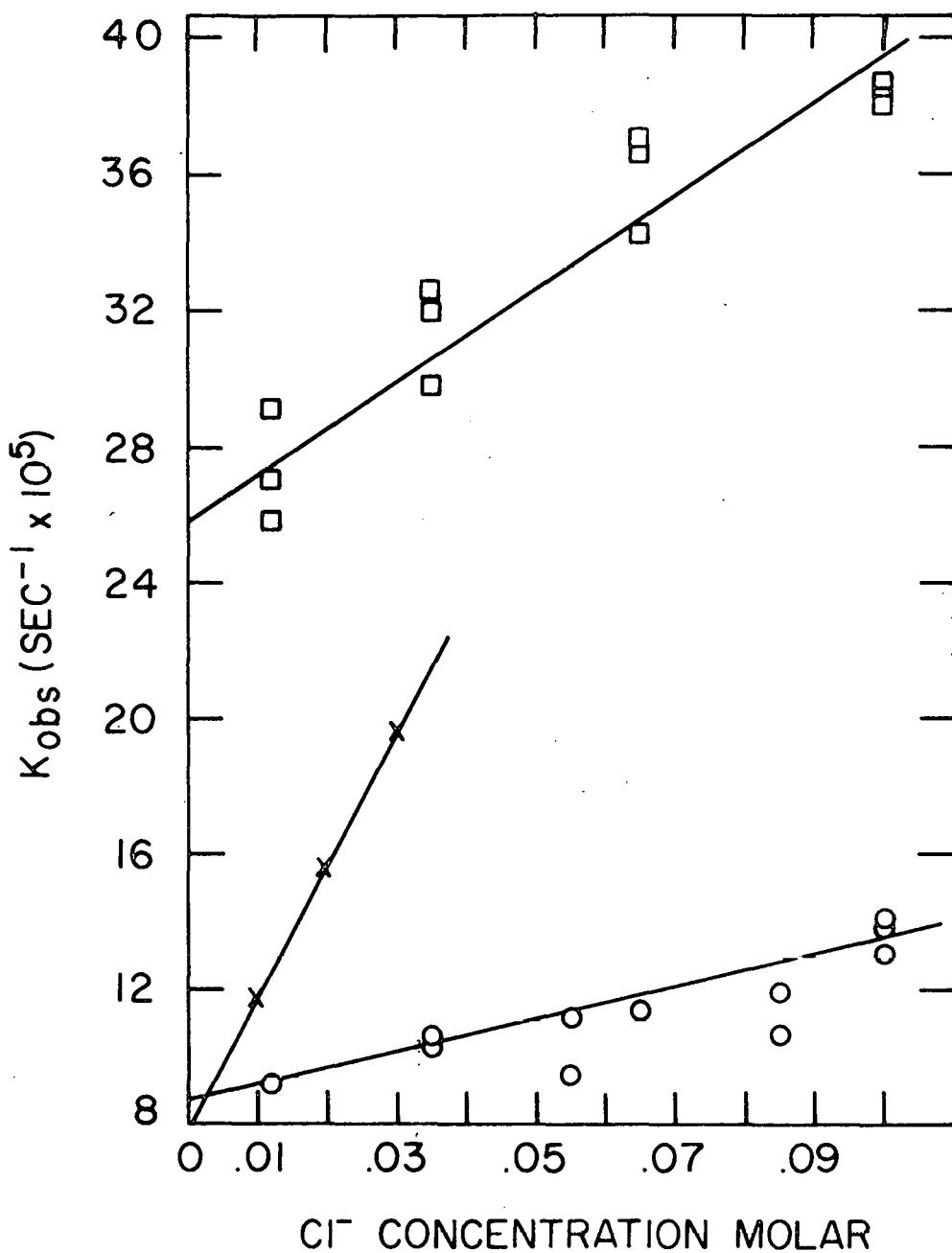


Fig. 10. Plots of k_{obs} vs. $[\text{Cl}^-]$ for the reaction of Cl^- with $[\text{Pt}(\text{dien})\text{Cl}^+]$ at $\mu = .1 \text{ M}$. \circ , This study at 25°C ; \times , Gray (ref. 20) at 25°C ; \square , this study at 35°C

Table 6. Compilation of isotopic exchange results at 25°C and 35°C for the chloride exchange in $[Pt(dien)Cl]Cl$ at $\mu = .100$ M

T	$k_1(\text{sec}^{-1} \times 10^6)$	$k_2(\text{sec}^{-1} \text{M}^{-1} \times 10^5)$
298.2	87.4 ± 2.6	42.3 ± 5.5
308.2	258.1 ± 5.1	136.6 ± 10.9
ΔH^\ddagger (kcal/mole)	$19.2 \pm .9$	20.8 ± 3.8
ΔS^\ddagger (cal/mole deg)	-12.8 ± 3.1	-4.2 ± 13.1

Several observations may be made. The entropy of activation for chloride exchange by the aquation pathway is negative. This is quite normal for Pt(II) kinetics (23), but somewhat surprising for reactions of the type where there is a neutralization of charge in going from the ground state to the transition state. Usually these have positive entropies of activation (30, p. 142). The common explanation is that the uncharged activated complex is less solvated than the charged substrate and reagent. Thus the formation of the transition state is accompanied by an increase in the disorder of the solvent which results in a positive entropy of activation. But for large ions like chloride, where solvation is small, the normal loss of entropy in forming an activated complex

from two reactants in a bimolecular reaction can cancel out the solvation effect. The solvent effect may itself be small in Pt(II) complexes if in the transition state the polarity of the bond between Pt(II) and the entering (and/or leaving) group is large. This would mean that the entering group remains largely charged and solvated to much the same extent as it was in the ground state. But perhaps the best explanation of this anomalous behavior in Pt(II) concerns the trigonal bipyramidal intermediate.

The negative entropy and positive activation enthalpy of the aquation pathway suggests that formation of the transition state is accompanied by a net increase in bonding. Bond making by the nucleophile has proceeded to a considerable degree somewhere between the unstable intermediate trigonal bipyramidal structure and a six-coordinate structure containing complex, nucleophile and solvent; thus the structure is tightened and made more rigid, and a decrease in entropy results. It may be noted that negative values of ΔS° are almost invariably found for equilibria in which there is an increased coordination number of a metal ion (57).

Very little can be said about the entropy for the direct exchange pathway because the number is small with too large

an error to be significant. This is a consequence of the k_2 not being accurately determined (see Fig. 10). But it seems that this value also follows the general trend in Pt(II) kinetics.

Some comparisons can be drawn from the data in Table 7. The behavior of Cl^- and Br^- as leaving groups would seem to be quite similar based on their similar second order rate constants. The reaction rates for $[\text{Pt}(\text{NH}_3)_3\text{Cl}^+]$ are considerably slower than those for $[\text{Pt}(\text{dien})\text{Cl}^+]$. This feature is perhaps due to the restriction of the motion of the amine ligands in the chelate rings, so that the addition of the fifth group to form the transition state is enhanced. The high positive values of the enthalpy and entropy for reactions of $[\text{Pt}(\text{NH}_3)_3\text{Cl}^+]$ are due to the small k_2 value. It is extremely difficult to accurately determine k_2 since it carries very little of the exchange in an isotopic exchange experiment.

A comparison of the two values for the H_2O replacement by Cl^- in $[\text{Pt}(\text{dien})\text{H}_2\text{O}^{2+}]$ should be carefully approached because Gray and Olcott (25) measured this quantity directly under non-equilibrium conditions whereas this study calculated the value from the equilibrium data.

Table 7. Kinetics behavior related to chloride exchange in halo-amine platinum(II) complexes at 25°C and $\mu = .1$ M

Complex	$k_{H_2O} \times 10^5$ sec ⁻¹	$\Delta H_{H_2O}^\ddagger$ kcal mole	$\Delta S_{H_2O}^\ddagger$ cal mole deg	$k_{Cl} \times 10^5$ M ⁻¹ sec ⁻¹	ΔH_{Cl}^\ddagger kcal mole	ΔS_{Cl}^\ddagger cal mole deg
Pt(dien)Cl ⁺	8.7	19	-13	42.3	21	-4
Pt(dien)Br ⁺	13 ^a	20	-17	59.5 ^b	18	-10
Pt(NH ₃) ₃ Cl ⁺	2.6 ^c	18	-18	5 ^c	29	+19
Pt(dien)H ₂ O ²⁺	24 ^d			46500 ^d 42900	19	-7
Pt(NH ₃) ₃ H ₂ O ²⁺				5050 ^c	20	+5

^aRef. (39).

^bRef. (20).

^cRef. (58).

^dRef. (25).

The original impetus for conducting this study was the poor fit of the second order rate constant for the Cl^- exchange with $[\text{Pt}(\text{dien})\text{Cl}^+]$ in a $\log k_2$ vs. n_{pt}^0 plot, Fig. 7. Converting the present value to zero ionic strength, we obtain from Chan's function (37):

$$\begin{aligned}\log \Gamma(\mu) &= -1.05 \text{ M}^{-\frac{1}{2}} \sqrt{\mu} \\ &= -1.05 \text{ M}^{-\frac{1}{2}} \sqrt{1 \text{ M}} \\ &= 1.688 \\ \Gamma(\mu) &= .465\end{aligned}$$

Now:

$$k_2^0 = \frac{k_2}{\Gamma(\mu)} = \frac{42.3 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}}{.465} = 90.0 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$$

Representing this number as $\log k_2^0$, we obtain:

$$\log k_2^0 = -3.042$$

With this number the four points in Fig. 7 for the replacement of chloride fall very closely along a straight line. It may be noted, from Fig. 7, that there is little difference between Cl^- and Br^- as leaving group since straight lines representing their replacement are very close together. This thus confirms our previous observation.

Therefore this ion exchange quenching method of isotopic exchange study has proven valuable in determining elusive rate parameters.

V. RECOMMENDATION FOR FUTURE WORK

Near the completion of this study, a modification of the ion exchange quenching method was developed. The requirements for a clean separation are simply stated:

(1) The method must be fast. We want to quench the reaction rapidly, thus making the time axis in a $\ln (1-F)$ vs. time plot as accurate as possible.

(2) The method must produce efficient separation. Even a .1% error, i.e., the column removes 99.9% of the reactant, could cause a 10% error in the initial points of low activity.

(3) The method must be selective, i.e., we don't want to remove any cation in this case. If the complex cation is removed, we must know that the amount is reproducible. To the extent that the separation is not selective and efficient and that counting statistics are used, the points in an isotopic exchange study are not as accurate as those from another method, like spectrophotometry.

This study used as an efficiency criterion, 99.99%, i.e., .01% of the active chloride was allowed through the column. The separation efficiency was about 95% as determined in two ways: (1) spectrophotometry and (2) by comparing theoretical and experimental C_∞ values.

But this method was deficient in the criterion of speed. The separation was time consuming because of the extreme column length (50 cm³). This length was a result of being limited to LiClO₄ as an ionic strength control because of the solubility problems with other salts in dioxane-based scintillation solutions. The ClO₄⁻ lessens the efficiency of a column, necessitating longer columns. This is a peculiarity of ClO₄⁻ alone, NO₃⁻, CH₃COO⁻ and HCO₃⁻ act normally. The Cl⁻ is difficult to separate from the ClO₄⁻-Cl⁻ combination, but Cl⁻ alone or Cl⁻ in combination with other anions is easily separated.

There are now commercially available solubilizers (Beckman Bio-Solv-3, Isolab Scintisol, Packard Soluene) which allow the use of salt solutions up to 1M. These solutions, not restricted to any particular combination of ions, are solubilized in practical grade toluene-based scintillation solutions using less volume than the dioxane-based solutions.

Since liquid scintillation counting systems should be used with β emitters like ³⁶Cl because of their increased efficiency (100% vs. 10% for Geiger-Muller tubes), these solubilizers are recommended.

The advantages are use of small amounts of activity and use of widely varying ionic strengths at a cost comparable to other methods.

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VIII. APPENDIX 1

Consider a reaction: $A + B = C + D$ with $K^0 = [C][D]/[A][B]$ and rate = $k_f^0[A][B] - k_r^0[C][D]$, then $K^0 = k_f^0/k_r^0$ where the zero superscript indicates the appropriate constants under ideal conditions, such as very low concentrations, and where $[i] = a_i$.

Under non-ideal conditions, where the activity coefficients are no longer unity, and $[i] = a_i/\gamma_i$, the actual equilibrium constant, designated K , is related to K^0 by

$$K^0 = \frac{a_C a_D}{a_A a_B} = \frac{[C][D]}{[A][B]} \times \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} = \frac{K \gamma_C \gamma_D}{\gamma_A \gamma_B}$$

$$K = K^0 \frac{\gamma_A \gamma_B}{\gamma_C \gamma_D} = \frac{k_f}{k_r}$$

$$\frac{k_f^0}{k_r^0} \times \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} = \frac{k_f}{k_r} \quad (1A)$$

How are the individual rate constants of Equation 1A related to the activity coefficient? The correct approach is given by setting the rate proportional to the concentration of the activated complex. By the absolute rate theory:

$$\text{Rate} = \left(\frac{kT}{h}\right) [AB^+] \quad (2A)$$

This corresponds in Pt(II) chemistry to saying that the

limiting rate of reaction is proportional to the concentration of the five-coordinated trigonal bipyramidal transition state. In other words, the limiting rate is the aggregate going over a translational barrier. Therefore we are really concerned with $A + B = (AB^{\ddagger})$.

$$K^{\ddagger} = a_{\ddagger}/a_A a_B = \frac{[AB^{\ddagger}]}{[A][B]} \frac{\gamma_{\ddagger}}{\gamma_A \gamma_B}$$

Consequently, if the rate is proportional to $[AB^{\ddagger}]$,

$$\text{Rate}_f = \left(\frac{kT}{h}\right) \frac{[A][B]}{[AB^{\ddagger}]} K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}}$$

where k = Boltzmann's constant, T is the absolute temperature and h is Planck's constant.

Now:

$$\text{Rate} = \left(\frac{kT}{h}\right) \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}} K^{\ddagger} = k_f(\mu)$$

From standard thermodynamics:

$$\Delta F^{\ddagger} = -RT \ln K^{\ddagger}$$

$$\Delta H^{\ddagger} - T \Delta S^{\ddagger} = \Delta F^{\ddagger} = -RT \ln K^{\ddagger}$$

$$\ln K^{\ddagger} = - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}$$

$$K^{\ddagger} = \exp \left(-\frac{\Delta H^{\ddagger}}{RT} \right) \exp \left(\frac{\Delta S^{\ddagger}}{R} \right)$$

Therefore:

$$k_f(\mu) = \left(\frac{kT}{h}\right) \frac{\gamma_A \gamma_B}{\gamma_{\pm}} \exp(-\Delta H^{\ddagger} / RT) \exp(\Delta S^{\ddagger} / R)$$

If we let $\Gamma(\mu) = \gamma_A \gamma_B / \gamma_{\pm}$

Then:

$$k_f(\mu) = \left(\frac{kT}{h}\right) \exp(-\Delta H^{\ddagger} / RT) \exp(\Delta S^{\ddagger} / R) \Gamma(\mu) = k_f^0 \Gamma(\mu)$$

Finally:

$$k_f^0 = k_f(\mu) / \Gamma(\mu) = k_f(\mu) \frac{\gamma_{\pm}}{\gamma_A \gamma_B} \quad (3A)$$

Equation 3A is the form most often quoted relating rate constants to ionic strength.

IX. APPENDIX 2

In a great number of scientific measurements, quantities sought cannot be measured directly but must be calculated by means of two or more directly measured quantities. It is desirable to know the reliability of such indirectly measured quantities.

Evidently the errors of a calculated quantity depend on the errors of the measured quantities of which it is a function. Their calculation, given the means and the errors of the measured quantities, is based on the following theory of propagation of errors (56).

For the general case where U is a function of X and Y :

$$U = f(X, Y)$$

$$U + u_1 = f(X + x_1, Y + y_1)$$

Using Taylor's expansion:

$$U + u_1 = f(X, Y) + \left(\frac{\partial U}{\partial X}\right)x_1 + \left(\frac{\partial U}{\partial Y}\right)y_1 + \dots$$

$$u_1 = \left(\frac{\partial U}{\partial X}\right)x_1 + \left(\frac{\partial U}{\partial Y}\right)y_1 + \dots$$

$$u^2 = \left(\frac{\partial U}{\partial X}\right)^2 x_1^2 + \left(\frac{\partial U}{\partial Y}\right)^2 y_1^2 + 2\left(\frac{\partial U}{\partial X}\right)\left(\frac{\partial U}{\partial Y}\right) \sum x_1 y_1$$

Since any particular product xy is as likely to be positive

as negative and the summation on that account will tend toward zero, we may say:

$$\sum xy = 0$$

Thus:

$$\sigma_u^2 = \left(\frac{\partial U}{\partial X}\right)^2 \sigma_x^2 + \left(\frac{\partial U}{\partial Y}\right)^2 \sigma_y^2$$

In our case:

$$U(X, Y) = \ln(1-F) = \ln\left(1 - \frac{C}{C_\infty}\right)$$

Therefore:

$$\begin{aligned} \frac{\partial \ln(1-F)}{\partial C_\infty} &= \left[\frac{1}{1 - \frac{C}{C_\infty}} \right] d\left(1 - \frac{C}{C_\infty}\right)_C \\ &= \left[\frac{1}{1 - \frac{C}{C_\infty}} \right] \left[\frac{1}{C_\infty^2} \right] = \left[\frac{C}{(C_\infty - C)C_\infty} \right] \end{aligned}$$

And:

$$\begin{aligned} \frac{\partial \ln(1-F)}{\partial C} &= \left[\frac{1}{1 - \frac{C}{C_\infty}} \right] d\left(1 - \frac{C}{C_\infty}\right)_{C_\infty} \\ &= \left[\frac{1}{1 - \frac{C}{C_\infty}} \right] \left[\frac{-1}{C_\infty} \right] = \left[\frac{-1}{C_\infty - C} \right] \end{aligned}$$

Therefore:

$$\sigma_u^2 = \left(\frac{C}{(C_\infty - C)C_\infty}\right)^2 \sigma_{C_\infty}^2 + \left(\frac{-1}{C_\infty - C}\right)^2 \sigma_C^2$$

This study considered that $\sigma_{C_\infty}^2 = (A \times C_\infty)^2$, where A equals a

total percentage error including the 2σ counting error, the weighing error and volumetric errors. In this study $A = 5\%$. This σ_u^2 was propagated through the calculation of k_{obs} . To calculate k_1 and k_2 , a weighting scheme of equal weights was used because the variation in replicate experiments was too great to justify the use of a weighting scheme based on the use of the standard deviations calculated for each experiment.