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KINETICS FOR THE RATE OF EXCHANGE OF BROMIDE WITH CIS-DIBROMODIAMMINEPLATINUM(II)

by

David Ronald Gano

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I. INTRODUCTION

The present study is concerned with the kinetics of exchange of the bromide ligands in cis-dibromodiammine-platinum(II) with free bromide ion in aqueous solutions. A continuing series of investigations in this laboratory have served to characterize a number of the halo and halo-ammine complexes of platinum(II) (1,2,3,4,5,6,7,8,9,10,11,12,13). Since ligand replacement rates of many Pt^{II} complexes are conveniently measurable at room temperature, their kinetics have been extensively studied. The rather unusual square-planar coordination which they exhibit, has added to interest in their behavior. It is generally accepted that the mechanism for these replacement reactions is associative (14). Thus if a ligand X is replaced by ligand Y, group Y may first attack at an axial position of the square complex. The coordination in the transition state is then approximately trigonal bipyramidal with X, Y, and L (where L is the ligand originally trans to X) in the equatorial plane. Such a mechanism path accounts for the retention of configuration of the product, i.e., group Y is trans to L in the product. The kinetics for such a process is second order, first order in complex and in Y. However, alternatively a solvent nucleophile may attack the complex initially in the same manner as above. Sometimes the presence of this intermediate is readily evident as in the case of $PtCl_3(H_2O)^-$ (1). Frequently, however, the solvent molecule is rapidly replaced by Y and only inappreciable fractions of the solvated complex is formed. If these two paths carry appreciable fractions of the reaction, the kinetic expression for the replacement process will be

$$\text{Rate} = (k_1 + k_y[Y])[\text{complex}] \qquad (I.1)$$

where k_1 and k_y are first and second order rate constants respectively and the square brackets represent concentrations. Such a rate law was originally observed by Rich and Taube for the $AuCl_4^-$-Cl^- system and such kinetic behavior is considered normal for platinum(II) complexes. In recent studies of the exchange of Br^{82} in the $PtBr_4^{2-}$-Br^- system, an exception to this normal behavior was found which required a term, $k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-]$ in the rate expression. Clearly, the transition state required a dimer species.

Another recent investigation has shown that the exchange of $Pt(dien)Br^+$ with Br^- was catalysed by $PtBr_4^{2-}$, and that the exchange of Br^- with $PtBr_4^{2-}$ was catalysed by $Pt(dien)Br^+$ (12). (dien is diethylenetriamine) It was of interest to investigate other bromide systems to see if this abnormal behavior would occur in additional cases, and <u>cis</u>-$Pt(NH_3)_2Br_2$ was chosen for study. Before possible $PtBr_4^{2-}$ catalysis could be investigated it was necessary to fully characterize the exchange of the <u>cis</u>-$Pt(NH_3)_2Br_2$-Br^- system alone.

A. Rate Determining Factors in Platinum(II) Complexes

1. Trans effect

The rate of substitution of a ligand in a square planar complex is strongly dependent on the nature of the ligand <u>trans</u> to it in the complex. This is one of the most dramatic of all the phenomena associated with Pt^{II} complexes, for it spans several orders of magnitude. Langford and Gray, in a recent review of square planar complexes, provided the following order of decreasing <u>trans</u> influence for a number of ligands (14): $CO, CN^-, C_2H_4, PMe_3, PEt_3, H^- > CH_3^- > C_6H_5^-, SC(NH_2)_2, NO_2^-, I^-, -SCN^- > Br^-, Cl^- > Py, NH_3, OH^-$. The <u>trans</u> effect was once considered well explained by the π-bonding theory of Chatt <u>et</u> <u>al</u>. and of Orgel (15,16,17). It stressed stabilization by π- bonding of the activated complex, which was assumed to have a trigonal bipyramidal structure. The π-bonding theory, however, could not explain the high <u>trans</u> influences of H^- and CH_3^- ligands which were discovered only shortly after the π-bonding theories had gained wide acceptance. Langford and Gray (14) have proposed a σ-bonding theory to explain the high trans influence of H^-, CH_3^- and PR_3. (R is an alkyl or aryl group.) They observed that the leaving group and the trans group must share a p-orbital and reported results from calculations which showed that valence orbitals of H^-, CH_3^-, and PR_3 have unusually large overlap with a Pt 6pσ orbital. Furthermore they state that the driving force is the moving away of the leaving group to provide more p-orbital for the large overlap with the trans group. Since the trans effect has been repeatedly and thoroughly reviewed in recent years, it will not be discussed in any further detail (18,19,20).

2. Cis effect

A kinetic effect, which was dependent on the ligands cis to the leaving group, was first reported by Grinberg (21). Other evidence for a cis effect was found by Tucker et al., in an investigation of the chloro-ammine complexes of Pt^{II} (10). They concluded that for ligands which are weak trans directors, more attention should be given to the cis effect.

3. Steric hindrance

Steric hindrance of the axial positions of the complex by bulky groups on the ligands, has been found to decrease both k_1 and k_y.

4. Nature of leaving and entering groups

The reaction of $Pt(dien)X^+ + Py \rightleftharpoons Pt(dien)(Py)^+ + X^-$, has been studied to give information about the effect of different leaving groups on the rate of substitution (22). In this study it was established that the best leaving group of those studied was NO_3^-, and that the order of decreasing rates for the respective leaving groups was $NO_3^- > H_2O > Cl^- \approx Br^- > I^- > N_3^- > -SCN^- > -NO_2^- > CN^-$.

It has also been established that the good entering groups are also high in the trans effect series. In fact, if the entering groups are placed in order of decreasing values of k_y, the order is very nearly the same as the trans effect order (14).

5. Solvent

The coordinating properties of the solvent determine to some extent the magnitudes of k_1 and k_y. For a solvent which coordinates strongly with Pt^{II}, the k_1 term is more important. The k_y term becomes more important for those solvents which coordinate weakly with Pt^{II} (14).

6. Charge

The magnitude of the charge on the complex whether positive or negative, has little effect on k_1 (10,1,3). There appears to be some effect on the k_y path, however (23). Gray and Olcott discovered that $k_y[NO_2^-] > k_y[Cl^-]$ with Pt(dien)Br^+ as substrate, but $k_y[Cl^-] > k_y[NO_2^-]$ with Pt(dien)$(OH_2)^{2+}$ as substrate.

B. Bromide Ligand Exchange

Grinberg and Filinov performed the first study of isotopic exchange with radioactive bromide in the systems $PtBr_4^{2-}$ and $PtBr_6^{2-}$ in 1939 (24). They established that the exchange proceeds at a measurable rate and that all four bromide ligands of $PtBr_4^{2-}$ and all six bromide ligands of $PtBr_6^{2-}$ participate in the exchange. A year later Grinberg reported the occurrence of rapid exchange for acido complexes of Pt^{II} and also for cis-$Pt(NH_3)_2Br_2$ (25). In an investigation of $PtX_4^{2-} + X^-$, Grinberg and Nikoskaya found that for $X^- = CN^-$, I^-, Br^-, and Cl^-, that the rate of exchange decreased in the order listed. ($CN^- > I^- > Br^- > Cl^-$) Furthermore, this was the order of decreasing stability of the platinum(II) complexes (26). Grinberg and Shagisultanova reported a more careful study of the $PtBr_4^{2-}$-Br^- exchange system in which they concluded that most of the exchange proceeded through an aquation mechanism for the concentration range covered in their experiments. At higher concentrations of complex, they speculated that a path higher order in complex might be operative. They found no bromide dependent path (27).

In 1959, Grinberg and Shagisultanova reported their investigation of the isotopic exchange of Br^- with $Pt(NH_3)Br_3^-$. They found, as expected, that there were two types of coordinated bromide in the system (28).

The following year these authors attempted the investigation of the isotopic exchange of Br^- with cis- and trans-$Pt(NH_3)_2Br_2$ (29). Because of difficulties in finding a separation method for Br^- and cis-$Pt(NH_3)_2Br_2$, (also the trans-complex) the exchange between $PtBr_4^{2-}$ and cis-$Pt(NH_3)_2Br_2$ was followed. The $PtBr_4^=$ was separated from the exchange solution by precipitation as $[Pt(NH_3)_4^{2+}][PtBr_4^{2-}]$. With equal concentrations of cis-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ of 6.7×10^{-4} M., Grinberg and Shagisultanova observed 67 per cent exchange after 20 minutes. (This corresponded to a time of half-exchange of about 13 min.) The trans-complex exchanged much faster. Grinberg explained these rapid exchange rates by a trading of bromide ligands between ion pairs of the type: $[Pt(NH_3)_2Br(H_2O)^+][PtBr_3(H_2O)^-]$. It seems possible, however, that this may also have been a case of mutual catalysis such as the one which was observed by Teggins and Martin in the

$Pt(dien)Br^+$-$PtBr_4^{2-}$ system (12).

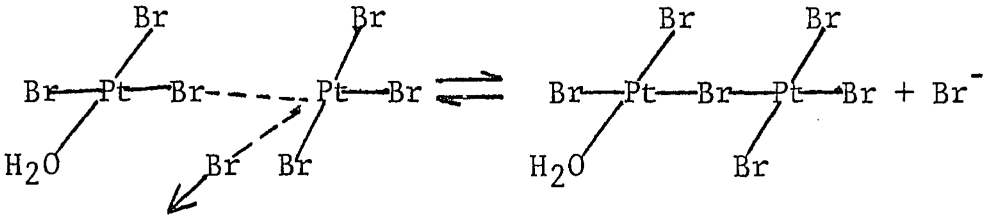
In a study of the kinetics of exchange of Br^- with $Pt(py)Br_3^-$, Grinberg and Shagisultanova found that a Br^- trans to another Br^- exchanged more rapidly than the Br^- trans to pyridine (py) by approximately a factor of 10. No rate law was reported for this system however.

Equilibrium quotients for the aquation of $PtBr_4^{2-}$, cis-$Pt(NH_3)_2Br_2$, and trans-$Pt(NH_3)_2Br_2$ were reported by Grinberg and Shagisultanova (30). At 25°C., for the cis-complex, they obtained a value of 1.8×10^{-3} M. They did not consider the possibility of a second aquation process.

Teggins *et al*. investigated the exchange of Br^- with $PtBr_4^{2-}$ over a wide concentration range. They found that the exchange was characterized by the following complex rate law:

$$\text{Rate}=k_1[PtBr_4^{2-}]+k_2[PtBr_3(H_2O)^-]+k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-]. \quad (I.2)$$

k_1 describes the aquation reaction for $PtBr_4^{2-}$, k_2 can be attributed to the aquation of $PtBr_3(H_2O)^-$ and k_d characterizes the exchange that proceeds via the dimer transition state. The values of k_1, k_2, and k_d at 25°C. were reported to be 2.2×10^{-4} sec^{-1}, 2.2×10^{-4} sec^{-1}, and .22 sec^{-1} M^{-1} respectively. The authors proposed the mechanism involving a dimer transition state shown in Equation I.3 to account for the k_d term.



(I.3)

This is an unusual path for exchange in Pt^{II} systems. The only previous finding of a similar exchange expression was in the study performed by Lokken and Martin for the $Pt(C_2H_4)Cl_3^-$ system (9).

In a study of $Pt(dien)Br^+$, Teggins and Martin found that this complex obeyed the normal rate law for Pt^{II} complexes. However, if $PtBr_4^{2-}$ were added to the system, the rate of exchange was enhanced, and it was necessary to add another term, $k_a[Pt(dien)Br^+][PtBr_4^{2-}]$, to the rate law in order to characterize the exchange satisfactorily. In addition, these authors found that the rate of exchange of $PtBr_4^{2-}$ with Br^- increased in the presence of $Pt(dien)Br^+$, and that a term $k_a'[Pt(dien)Br^+][PtBr_4^{2-}]$, was needed to account for the higher rate of exchange of $PtBr_4^{2-}$ in the presence of $Pt(dien)Br^+$.

Because of the similarity of the <u>cis</u>-$Pt(NH_3)_2Cl_2$ to the corresponding bromo-complex, it is relevant to consider features of this system which were characterized by Reishus and Martin in 1961 for comparison to the present work (6).

They found that the chloride dependent path was essentially unmeasurable, and that most of the exchange must proceed by the aquation of the complex. The equilibrium constants, K_1 and K_2, for the aquation were defined as $K_1=[Pt(NH_3)_2Cl(H_2O)^+][Cl^-]/[Pt(NH_3)_2Cl_2]$ and $K_2=[Pt(NH_3)_2(H_2O)_2{}^{2+}][Cl^-]/[Pt(NH_3)_2Cl(H_2O)^+]$. The values of K_1 and K_2 were found to be 3.3 x 10^{-3} M. and 4 x 10^{-5} M. respectively at 25°C. Rate constants for the exchange via the aquation reactions were also reported. At 25°C., k_1 and k_2 were found to be 2.5 x 10^{-5} sec^{-1} and 3.3 x 10^{-5} sec^{-1}. These results have proved considerably different from the cis-$Pt(NH_3)_2Br_2$ system. This will be discussed in section V.

The exchange of Cl^- and $Pt(C_2H_4)Cl_3{}^-$ was studied by Lokken and Martin (9). The rate law found for this system was Rate = $k_c[Pt(C_2H_4)Cl_3{}^-] + k_c'[trans\text{-}Pt(C_2H_4)Cl_2(H_2O)] + k_d[Pt(C_2H_4)Cl_3{}^-][trans\text{-}Pt(C_2H_4)Cl_2(H_2O)]$. The value of k_c', 2.8 x 10^{-5} sec^{-1}, was approximately a factor of 10 greater than the value of k_c, 2.9 x 10^{-6} sec^{-1}. These rate constants characterized the exchange that occurred via the aquation paths. The value obtained for k_d, the dimer path, was 8.6 x 10^{-3} sec^{-1} M^{-1}.

II. EXPERIMENTAL

A. Materials

1. Platinum

The platinum used in this work was obtained from J. Bishop and Company as platinum wire. It was certified to be 99.99% pure. Since a trace of iridium in the platinum compounds might have a catalytic effect in the reactions studied, the iridium content was reduced to approximately 20 ppb (31) by a procedure which has been discussed by previous workers (20). This procedure was primarily repeated recrystallizations of K_2PtBr_6.

2. Cis-$Pt(NH_3)_2Br_2$

K_2PtBr_4 was made from the purified K_2PtBr_6 by the addition of a stoichiometric amount of $K_2C_2O_4$. Approximately 200 ml. of distilled water was added to the mixture which was then warmed in a water bath to about 80°C. After about 4 hrs. the solution was cooled in an ice bath and filtered to remove any unreacted K_2PtBr_6. The amount of K_2PtBr_4 was estimated and 2 moles of ammonium acetate was added for every mole of the complex. Also, KBr was added until the KBr concentration was approximately 4 times that of the complex. This mixture was heated over a water bath at about 80°C. for 4 hrs. or until the color of the solutions had transformed from a brownish-red to a yellow-gold. Insoluble crystals of the *cis*-Pt$(NH_3)_2Br_2$ were usually visible at this point. The solution and crystals were cooled in an ice bath, subsequently filtered, and washed with a large amount of cold water. The complex was recrystallized twice from hot water containing an excess of KBr to prevent loss of the compound from aquation. After the last recrystallization the compound was washed again with much cold water to remove soluble KBr which was added in the recrystallization step. The compound was finally dried in an oven at about 70°C. for not less than 6 hrs. The analysis for Pt and Br^- yielded 49.6% and 40.6% respectively; calculated values were 50.1% and 41.1%.

3. Ion exchange resins

Analytical reagent grade IRA-400 anion exchange resin and IR-120 cation exchange resin were used in these experiments. The 20-50 mesh resins were obtained in the chloride and hydrogen forms respectively. The IRA-400 was converted to the nitrate cycle by passing a 5% solution of sodium nitrate through the resin. Since it was very important that all the chloride be removed from the resin in these experiments, the effluent was tested for chloride in the following manner: A quantity of the effluent was evaporated to about one-fourth of its original volume. A few drops of 0.1 N.

$Hg_2(ClO_4)_2$ solution was added. If no precipitate formed, the resin was considered satisfactory for use. The IR-120 was converted to the sodium form with a 5% $NaNO_3$ solution also. When the effluent was found to be neutral to pHydrion paper, the resin was judged to be completely converted.

4. Water

Tap distilled water, which was redistilled from alkaline permanganate, was distilled again. The water used to prepare all solutions used for kinetics studies of this thesis was subjected to this treatment.

5. Mercury(I) perchlorate

$Hg_2(ClO_4)_2$ was prepared in this laboratory by the usual method of reacting mercury, mercury(II) oxide, and perchloric acid (32).

6. Bromine-82

The 35-hr. Br^{82}, tracer for these studies, was produced in the "rabbit" of the Ames Laboratory 5 megawatt research reactor. Aqueous solutions of NH_4Br were sealed in partially evacuated quartz tubes and irradiated. The samples were generally allowed to "cool" for about 3 days following irradiation to permit the 4.5-hr. Br^{80m} to decay, and also because they were too active for convenient handling.

7. Additional reagents

All other chemicals for this work, such as the $NaNO_3$ used to adjust the ionic strength and the KBr used in the exchange solutions, were reagent grade chemicals.

B. Equipment

1. Ion exchange columns

The ion exchange columns were generally 1.5 cm. in diameter and about 50 cm. in length. They were fitted with sintered glass filters for rapid flow. The resin bed, however, was only 15 cm. deep. The volume of resin necessary for complete separation of the free bromide from the complexed was determined by passing a solution containing KBr and $NaNO_3$ through the resin bed. The KBr was labelled with Br^{82}. The volume of resin was adjusted until less than 0.1% of the tracer bromide came through the column.

2. Filtration equipment

The Hg_2Br_2 samples were collected on round filter disks for counting. Adams has described the chimney-type filtration device used to collect these samples (33).

3. pH meter and electrodes

A Corning pH meter, Model 12, was utilized for the potentiometric titrations by which the equilibrium quotients for aquation were evaluated. The Model 12 instrument has an expanded scale, which provides a very good estimate of the third decimal place. A Beckman #40498 glass electrode served as the indicator electrode. The reference electrode was a Beckman calomel electrode with saturated KCl. For the bromide ion determinations, an Orion #94-35-00 specific ion electrode was used in conjunction with a calomel reference.

4. Balances

All weighings were performed on either an Ainsworth "Right Aweigh" single pan balance or an Ainsworth type DLB chainomatic balance.

5. Constant temperature baths

The temperature of the solutions was maintained to $\pm$ .1°C. in a Sargent constant temperature bath. The bath was equipped with a Philadelphia microset thermoregulator, a Sargent S pn 2770 controller, and a Sargent type NS1-12 circulator-heater.

6. Radioactivity counting equipment

The gamma rays of the Br^{82} were counted with a thallium activated NaI crystal coupled to a photomultiplier tube. A RIDL 400 channel analyser, Model 34-12B, was utilized to record the spectrum of the pulse heights from the photomultiplier tube. The crystal was housed in a lead brick shield to reduce the background counts produced by cosmic rays and stray radiation. A typical spectrum for Br^{82} is shown in Fig. 1. The energies of the gamma rays counted were 0.554, 0.619, 0.777, 0.827, and 0.70 Mev respectively.

7. Spectrophotometer

All absorption spectra were recorded by means of a Cary, Model 14, spectrophotometer. In general, the solutions were contained in 10 cm. silica cells. However in some cases 1 cm. cells were used.

C. Procedures

1. Analysis of cis-$Pt(NH_3)_2Br_2$

The amount of platinum in a preparation was determined gravimetrically after thermal decomposition. The bromide was determined by a modified Volhard titration (34). Absorption spectra were recorded for all preparations of the complex. An absorption maximum for the complex occurred at 318 mμ. A minimum in the spectrum occurred at 275 mμ. These values were in agreement with those reported in the literature (35). The peak to valley absorbance ratio served as a criterion of purity. Values for this ratio were consistently 1.39:1 or slightly greater. Fig. 2 illustrates the absorption spectrum of the compound. The aquation of the complex has a rather dramatic effect on the spectrum as is shown in the figure.

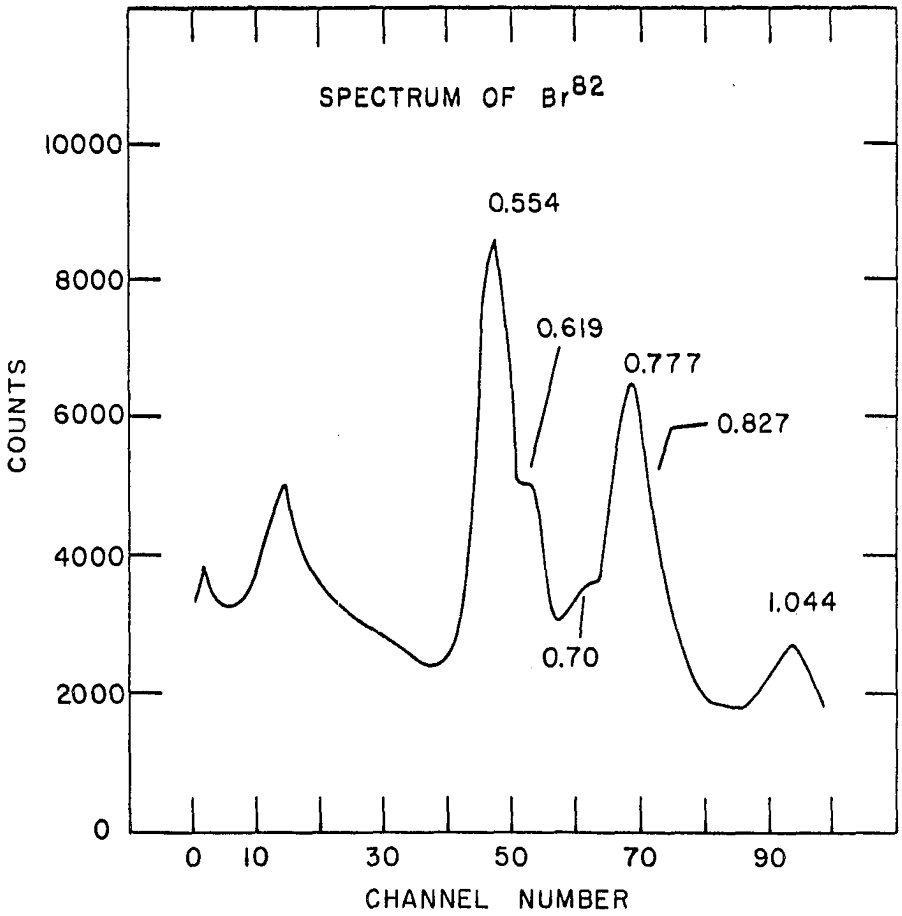


Fig. 1. A typical gamma-ray spectrum of Br^{82} showing the energies of the gamma-rays in Mev's

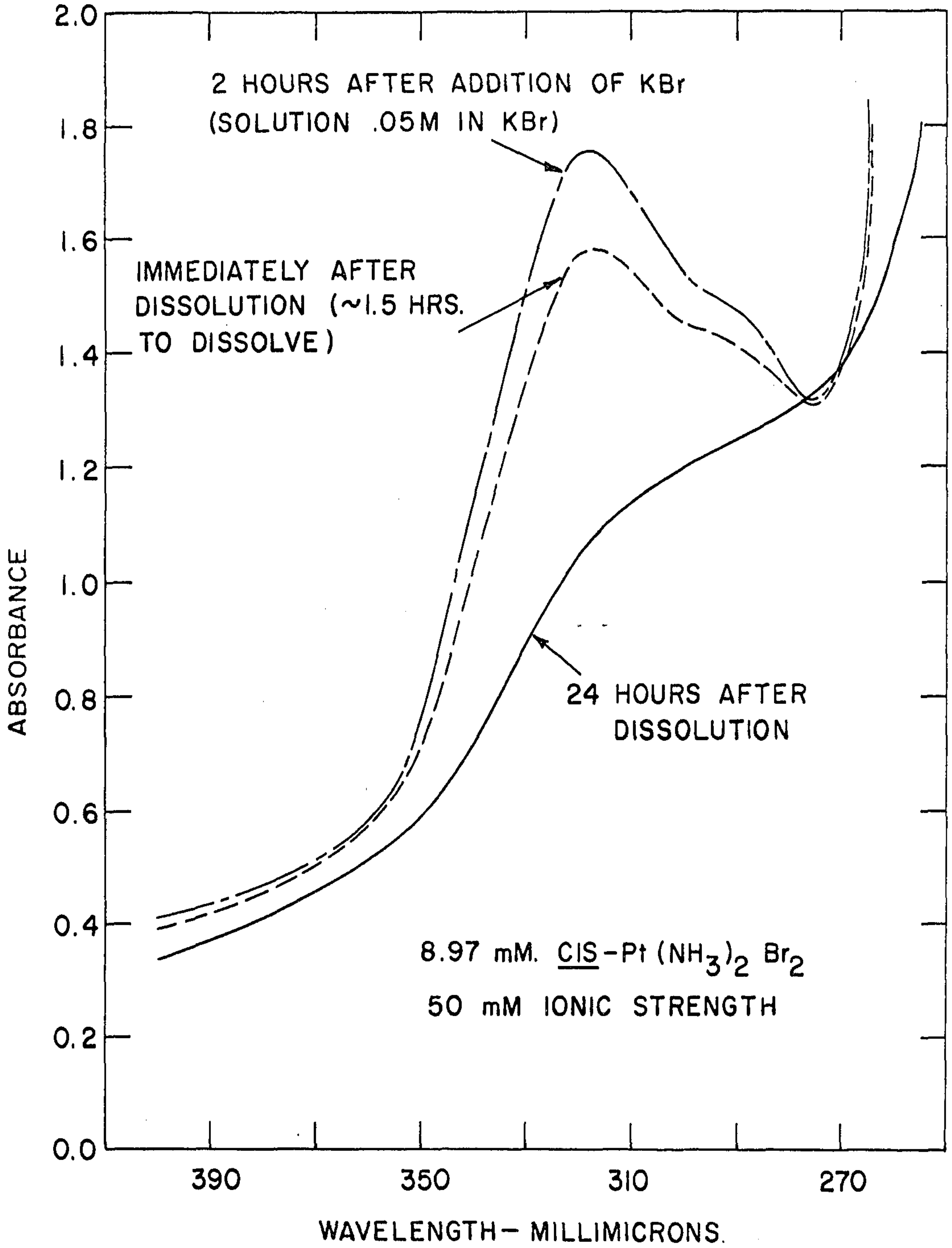


Fig. 2. Absorption spectrum of <u>cis</u>-Pt$(NH_3)_2Br_2$ in 0.05 M. KBr; ϵ = 198 $M^{-1}cm^{-1}$ in 0.1 M. KBr

Because of this effect all spectra were generally recorded in .1 N. KBr, which suppresses the aquation. The effect of the KBr is likewise obvious.

2. Determination of the aquation equilibrium quotients

The extent of equilibrium aquation of cis-$Pt(NH_3)_2Br_2$ was determined by titration of the weak acids, cis-$Pt(NH_3)_2Br(H_2O)^+$ and cis-$Pt(NH_3)_2(H_2O)_2^{2+}$, with NaOH. The recent development of the specific ion electrode provides another means for evaluating the equilibrium quotients. In this method the bromide released to solution by the aquation process was indicated by the electrode. The electrode was calibrated prior to each determination by a standard solution of KBr adjusted to ionic strength 0.05 M. by the addition of $NaNO_3$.

Solutions of complex for the equilibrium quotient determinations were prepared by dissolving the requisite amount of complex and enough $NaNO_3$ to give an ionic strength of 0.05 M. in water. The solutions were thermostated at the desired temperature for at least 48 hrs. before any titrations were performed or bromide ion concentrations determined. Since a change in the absorption spectrum was observed in those solutions exposed to light, all solutions were prepared in volumetric flasks which were wrapped with opaque tape to exclude light. The equilibrium titre was determined by potentiometric titrations. An aliquot of each solution was titrated rapidly in order to locate approximately the end-point of the titration. This end-point was located from the second derivative of the pH with respect to volume of NaOH (36). Then 5 to 6 points were determined in the region of the equivalence point by adding all the NaOH quickly to a fresh aliquot of the solution. The second derivative was determined for these points and the final titre was calculated from these "single-point" titration data. This method minimized errors caused by hydrolysis of the complex, which continued during the contact with the NaOH. Fig. 3 is an example of a titration curve obtained by these methods.

The specific ion electrode proved a better means for determining the equilibrium quotients, because it disturbed the system less. Unfortunately, such a unit was not available until quite late in this investigation. The specific ion electrode provides a measure of the concentration of bromide, which was exactly equivalent to the titre obtained from the pH titrations. (The calculation of the equilibrium quotients from the equilibrium titre will be discussed in the calculations section.)

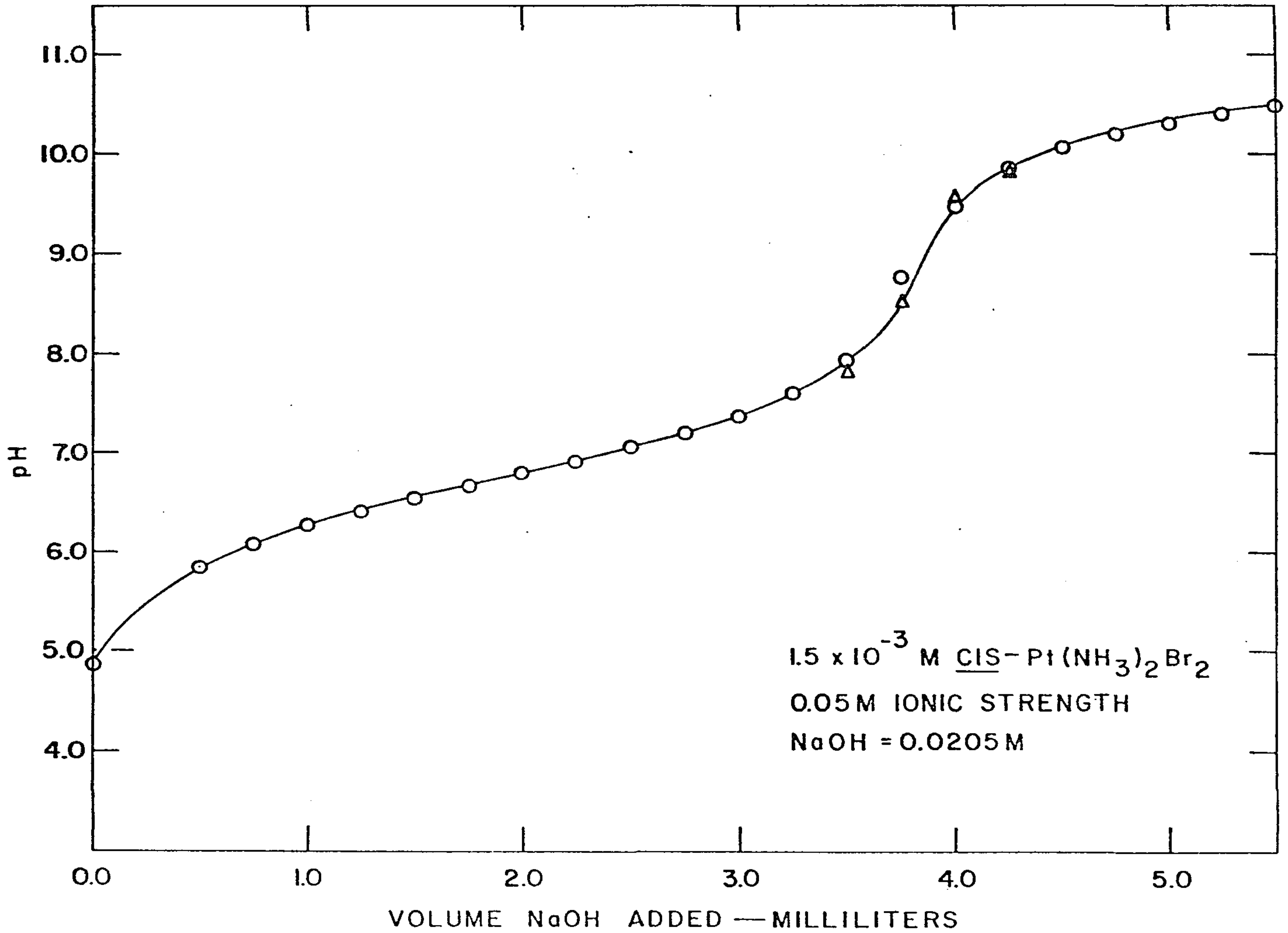


Fig. 3. A titration curve of the type obtained in the equilibrium quotient evaluations

3. Determination of the anation rate constants for cis-$Pt(NH_3)_2Br(H_2O)^+$

Since the value of the anation rate constant was desired at 0.05 M. ionic strength, solutions were prepared at essentially zero ionic strength, and allowed to age at 25°C. until there was no change in the absorption spectrum. An amount of KBr, calculated to give a solution 0.05 M. in KBr, was added to the equilibrium solution of complex. The absorbance of the solution was recorded at various times until the attainment of equilibrium was indicated by no further change in the absorbance. The absorbance at this point was taken as A_{∞} in the calculations for the rate constant. A_0 was the value of the absorbance before any KBr was added to the solution.

4. Separations and determination of specific activity

The bromide tracer was separated from the complex by anion exchange resin in the nitrate form. A fraction of the complex was eluted by approximately 125 ml. of wash water. In the experiments where the amount of $Pt(NH_3)_2Br(H_2O)^+$ was significant, the effluent from the anion exchange column was passed immediately through a cation exchange column. This column absorbed the $Pt(NH_3)_2Br(H_2O)^+$, and permitted the $Pt(NH_3)_2Br_2$ to pass through.

The effluent from the columns was evaporated to about

50 ml. in the presence of aqueous ammonia in order to strip the coordinated bromide from the complex. The solution was acidified with HNO_3, and Br^- was precipitated with $Hg_2(ClO_4)_2$. The Hg_2Br_2 precipitate was collected on previously weighed filter paper disks and allowed to dry after washing with water, alcohol, and ether. In order to correct for changes in the weight of the filter papers caused by humidity changes, filter paper tares were carried through the same processes as those that contained the samples (37). After the weights of the samples were determined, the samples were mounted on cardboard squares and counted. The specific activity, S, was calculated for each sample by applying a decay correction to the counting rate and dividing by the weight of the sample. The equilibrium exchange samples could be determined at any time during the exchange, and were treated in exactly the same manner as the other samples except they were not passed through the columns to remove the radioactive bromide. The specific activity determined for these equilibrium exchange samples will be referred to as S_∞.

5. Isotopic exchange

Solutions of KBr, cis-$Pt(NH_3)_2Br_2$, and sufficient $NaNO_3$ to adjust the ionic strength to 0.05 M. were prepared in volumetric flasks. As for the equilibrium quotient determinations, the volumetric flasks were wrapped with opaque tape to exclude light. The solutions were aged in a constant temperature bath in order that aquation equilibrium be achieved prior to the initiation of the exchange. A small volume of an aqueous solution of NH_4Br^{82} was added to the equilibrated solution of complex to initiate exchange. The volume of the tracer-containing solution added was usually 200 microliters and the amount of Br^- never exceeded 1% of the Br^- already in the solution.

If good results are to be obtained in isotopic exchange experiments, there must be available a means of separating the tracer cleanly from the complex. This was a very difficult problem in the case of cis-$Pt(NH_3)_2Br_2$. The logical choice was to add a 1% excess of $AgNO_3$ or $Hg_2(ClO_4)_2$ to precipitate the free bromide. These procedures failed because, apparently the complex exchanges bromide quite rapidly with the precipitate. Anion exchange resins were used successfully for the analogous cis-$Pt(NH_3)_2Cl_2$ and for the $Pt(dien)Br^+$ systems (6, 12). In the latter case it was possible to collect the effluent from the resin, and then to count Br^{82} from an aliquot of it. This, however, was unsuccessful in the present case. The complex was not eluted quantitatively from the anion exchange resin with an amount of wash water that was practical to use. Eluents other than H_2O could not be used, because they are generally good coordinating agents which would replace the bromide in the complex. A larger excess of H_2O would have been prohibitive, because even though the aquation rate of the complex is slow, the amount of $Pt(NH_3)_2Br(H_2O)^+$ would have increased significantly during these longer time periods. The procedure described in the preceding section was finally adopted.

The exchange studies of solutions which contained an appreciable amount of $Pt(NH_3)_2Br(H_2O)^+$ revealed that a plot of $\log(1-S/S_\infty)$ versus time was not linear. Since all the cis-$Pt(NH_3)_2Br_2$ did not come through the resin, and virtually all the $Pt(NH_3)_2Br(H_2O)^+$ was expected to come through, the ratio of cis-$Pt(NH_3)_2Br_2$ to $Pt(NH_3)_2Br(H_2O)^+$ would not be the same as that ratio calculated from the equilibrium quotient for the aquation. Since there appeared to be no means of determining precisely the amount of cis-$Pt(NH_3)_2Br_2$ and $Pt(NH_3)_2Br(H_2O)^+$ that came through the anion resin, the $Pt(NH_3)_2Br(H_2O)^+$ was removed by a second ion exchange separation, this time with cation resin. In these cases the effluent activity was taken to be just that of the cis-$Pt(NH_3)_2Br_2$ species. Illustrated by Fig. 4 is an experiment in which the $Pt(NH_3)_2Br(H_2O)^+$ concentration was negligible. Fig. 5 exhibits a case in which there was an appreciable amount of $Pt(NH_3)_2Br(H_2O)^+$ present. Finally, in Fig. 6, a case in which the $Pt(NH_3)_2Br(H_2O)^+$ was removed by cation exchange resin is illustrated.

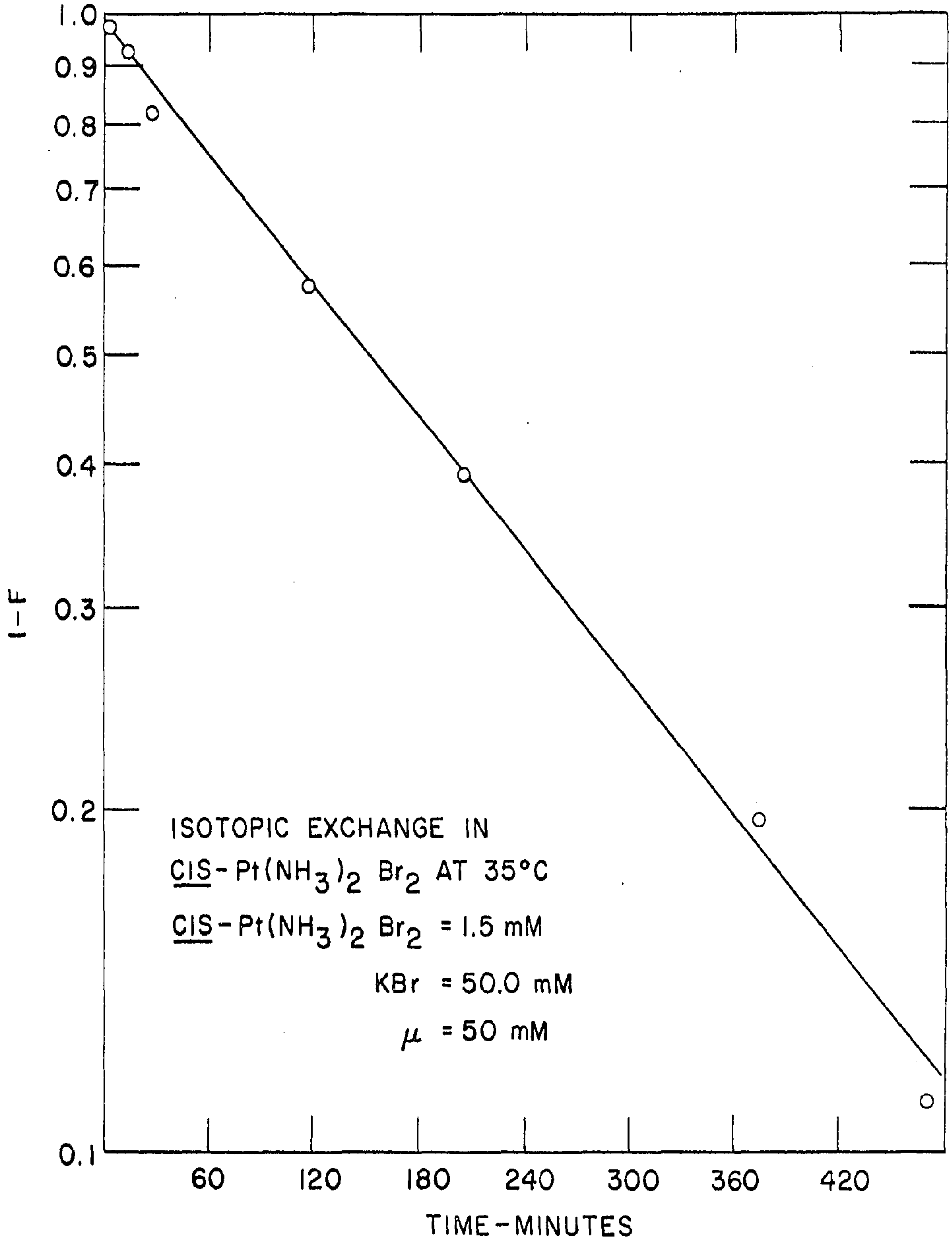


Fig. 4. A typical "high-bromide" experiment

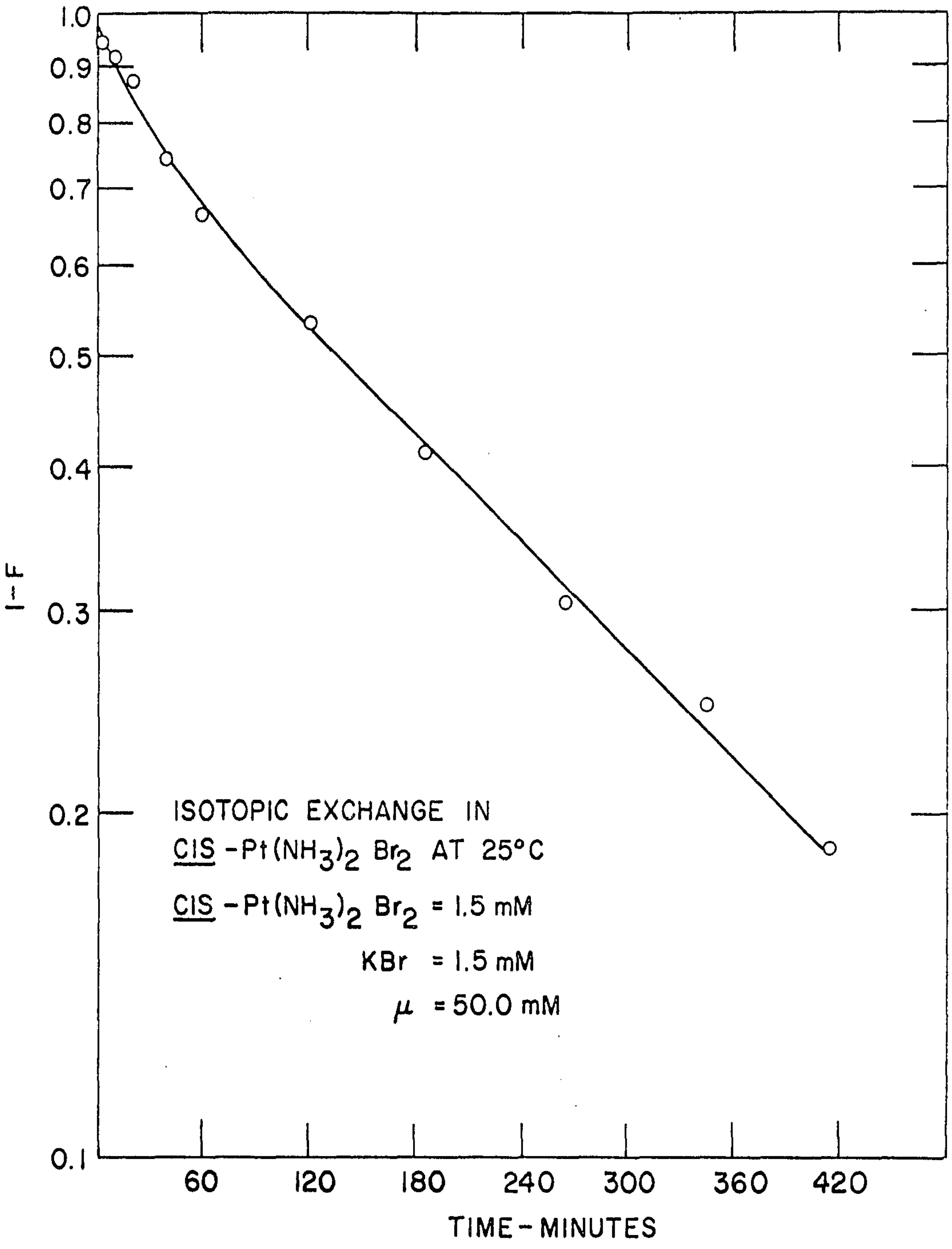


Fig. 5. A typical "low-bromide" experiment

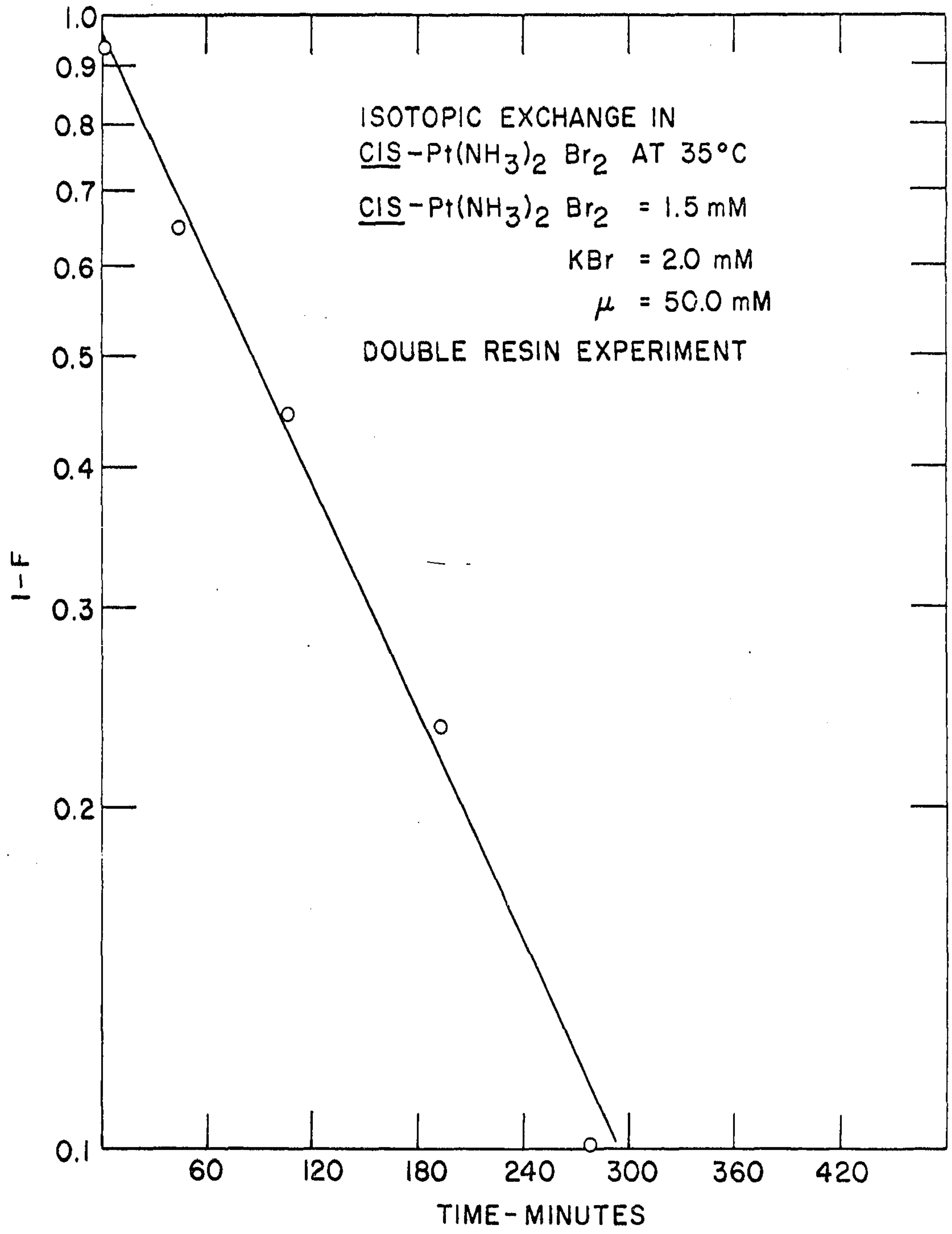


Fig. 6. A "low-bromide" experiment in which the $Pt(NH_3)_2Br(H_2O)^+$ has been removed by cation exchange resin

III. TREATMENT OF DATA

A. Equilibrium Quotients

All of the halo complexes and halo-ammine complexes studied to date in this laboratory react with water to form complexes in which one or more of the halide ligands is replaced by the water. There was no evidence that cis-$Pt(NH_3)_2Br_2$ might be any exception. The expected aquation reactions can be illustrated by Equations III.1 and III.2.

$$\text{\underline{cis}-}Pt(NH_3)_2Br_2 + H_2O \underset{k-1}{\overset{k_1}{\rightleftarrows}} Pt(NH_3)_2Br(H_2O)^+ + Br^- \qquad \text{(III.1)}$$

$$Pt(NH_3)_2Br(H_2O)^+ + H_2O \underset{k-2}{\overset{k_2}{\rightleftarrows}} Pt(NH_3)_2(H_2O)_2^{2+} + Br^- \qquad \text{(III.2)}$$

Equilibrium quotients for reactions III.1 and III.2 were defined as:

$$K_1=[Pt(NH_3)_2Br(H_2O)^+]_\infty [Br^-]_\infty /[Pt(NH_3)_2Br_2]_\infty \qquad \text{(III.3)}$$

$$K_2=[Pt(NH_3)_2(H_2O)_2^{2+}]_\infty [Br^-]_\infty / [Pt(NH_3)_2Br(H_2O)^+]_\infty \qquad \text{(III.4)}$$

The square brackets indicate that the enclosed are concentrations and the ∞ subscripts indicate that these are equilibrium concentrations. T, the equilibrium titre, is defined by Equation III.5.

$$T = [Pt(NH_3)_2Br(H_2O)^+]_\infty + 2[Pt(NH_3)_2(H_2O)_2^{2+}]_\infty \qquad \text{(III.5)}$$

From Equations III.3, III.4, and III.5 it can be shown that

$$K_1(b+T)(a-T) + K_1K_2(2a-T) = T(b+T)^2, \qquad \text{(III.6)}$$

where a is the concentration of complex initially added and b is the initial concentration of Br^-. The values of K_1 and K_2 were determined from the data of two experiments by the simultaneous solution of two equations of the form III.6. After values of K_1 and K_2 were calculated, their validity at other concentrations of added complex could be tested by solving III.6 for T and comparing it with the value obtained experimentally. Although this relationship between the equilibrium quotients and the titres was derived for the $PtCl_4^{2-}$ system, it can also apply to the present system because the aquation of only two of the Cl^-s were considered to be appreciable. Since the equilibrium quotients were determined at the constant ionic strength, 0.05M., they were assumed to be constants for all present studies where this ionic strength was maintained. For further details on the calculation of equilibrium quotients of this nature see Sanders and Martin (5).

B. Rate Constant for the Anation of cis-$Pt(NH_3)_2Br(H_2O)^+$

An approximate value of k_{-1} was obtained from a spectrophotometric experiment in which the change in the absorbance at the wavelength of the absorption max., 318 mμ, was followed after the addition of a known amount of KBr. Assuming the $Pt(NH_3)_2(H_2O)_2{}^{2+}$ concentration to be negligible, the differential equation for the change of $[\underline{cis}\text{-}Pt(NH_3)_2Br_2]$ with time is

$$d[\underline{cis}\text{-}Pt(NH_3)_2Br_2]/dt = -k_1[\underline{cis}\text{-}Pt(NH_3)_2Br_2 + k_{-1}[\underline{cis}\text{-}Pt(NH_3)_2Br_2]_o[Br^-]_o + k_{-1}[\underline{cis}\text{-}Pt(NH_3)_2Br_2][Br^-]_o \qquad (III.7)$$

The zero subscripts mean that these are total Pt^{II} concentrations. The Br^- concentration will be considered a constant, $[Br^-]_o$, here because it is present in such large excess. The integrated form of this equation is

$$\ln \frac{(-k_1[\underline{cis}\text{-}Pt(NH_3)_2Br_2]_o)}{k_{-1}[Br^-]_o[\underline{cis}\text{-}Pt(NH_3)_2Br_2]_o - (k_1+k_{-1}[Br^-]_o)[\underline{cis}\text{-}Pt(NH_3)_2Br_2]}$$

$$= -(k_1+k_{-1}[Br^-]_o)t \qquad (III.8)$$

With the aid of the equilibrium expression, $k_1/k_{-1}[Br^-]_o = ([\underline{cis}\text{-}Pt(NH_3)_2Br_2]_o - [\underline{cis}\text{-}Pt(NH_3)_2Br_2]_\infty)/[\underline{cis}\text{-}Pt(NH_3)_2Br_2]_\infty$

Equation III.8 can be rearranged to give

$$\ln \frac{[\underline{cis}\text{-}Pt(NH_3)_2Br_2]_o - [\underline{cis}\text{-}Pt(NH_3)_2Br_2]_\infty}{[\underline{cis}\text{-}Pt(NH_3)_2Br_2] - [\underline{cis}\text{-}Pt(NH_3)_2Br_2]_\infty} = (k_1+k_{-1}[Br^-]_o)t. \qquad (III.9)$$

The concentration terms may be replaced by absorbances since they are related by the expression, $A = \epsilon lc$, where ϵ is the molar absorption index, l is the length of the cell and c is the molar concentration. Therefore the quantity, $\log(A_\infty - A)/$

$(A_\infty - A_0)$, can be plotted versus time and the time of half-reaction taken from the plot. k_{obs}, $0.693/t_{\frac{1}{2}}$, is equal to $k_1 + k_{-1}[Br^-]$. When the concentration of Br^- was 50 mM., k_1 was considered to be negligible in comparison to $k_{-1}[Br^-]$, and the value for k_{-1} was calculated from the relationship, $0.693/t_{\frac{1}{2}}[Br^-]$. If the Br^- concentration was lower, then an approximate value of k_1 was calculated from the equilibrium quotient and the approximate value of k_{-1} which was calculated assuming k_1 was negligible. The value for k_1 was then subtracted from $.693/t_{\frac{1}{2}}$, and a new value for k_{-1} was obtained by dividing the result by the Br^- concentration.

C. Isotopic Exchange Equations

It was not possible to use the usual McKay equation to calculate the rates of exchange in this study (38). This equation applies to systems for which only two species are exchanging the isotopically tagged element. The present system has appreciable concentrations of at least three species: Br^-, <u>cis</u>-$Pt(NH_3)_2Br_2$, and $Pt(NH_3)_2Br(H_2O)^+$. The non-linearity of the graphs of $\log(1 - S/S_\infty)$ versus time, in the experiments in which there was an appreciable amount of $Pt(NH_3)_2Br(H_2O)^+$, indicated that some of the bromide ligands were exchanging at a faster rate than others.

The method, which was adopted for treating the exchange data, consisted of writing possible differential equations describing the rate of increase of bromide activity in each species. The rates were functions of rate constants and concentrations of exchanging species. These equations were integrated numerically by the IBM 360/50 computer of the Iowa State University Computer Center. These integrations provided calculated values of S at different times, from which values of $\log(1 - S/S_{\infty})$ were plotted *versus* time by the computer together with the experimental evaluations. Values of the rate constants were varied in a search for calculated curves. If necessary, the differential equation rate laws could be modified in an attempt to improve the fit to the data.

Consider the Equations III.1 and III.2. A set of differential equations can be written for the isotopic exchange *via* the reversible aquation reactions.

Let $Pt(NH_3)_2Br_2$ = conc. of complex at time t

U = conc. of Br^{82} in atoms/ml. in the *cis*-$Pt(NH_3)_2Br_2$ at t

V = conc. of Br^{82} in atoms/ml. in the $Pt(NH_3)_2Br(H_2O)^+$ at t

B = conc. of Br^{82} in atoms/ml. in the non-coordinated Br^-

I = total conc. of Br^{82}, atoms/ml., in the solution

$S_U = U/[Pt(NH_3)_2Br_2]$

$S_V = V/[Pt(NH3)_2Br(H_2O)^+]$

$S_B = B/[Br^-] = (I-U-V)/[Br^-]$

The differential equations describing the rate of increase of U and V exhibited by III.1 and III.2 are

$$dU/dt = -2R_1S_U + R_1(S_B+S_V) \tag{III.10}$$

$$dV/dt = -R_2S_V + R_2S_B + R_1(S_U-S_V) \tag{III.11}$$

where R_1 is $k_1[Pt(NH_3)_2Br_2]$ and R_2 is $k_2[Pt(NH_3)_2Br(H_2O)^+]$. The form of these equations, after making the appropriate substitutions, become:

$$dU/dt = -2k_1[Pt(NH_3)_2Br_2]U/2[Pt(NH_3)_2Br_2] + k_1[Pt(NH_3)_2Br_2] \left[(I-U-V)/[Br^-] + V/[Pt(NH_3)_2Br(H_2O)^+]\right] \tag{III.12}$$

$$dV/dt = -k_2V + k_2[Pt(NH_3)_2Br(H_2O)^+](I-U-V)/[Br^-] + k_1\ U/2 - k_1[Pt(NH_3)_2Br_2]V/[Pt(NH_3)_2Br(H_2O)^+] \tag{III.13}$$

The experimental values of S were either $U/Pt(NH_3)_2Br_2$ if the double resin separation was used or $(U+V)/([Pt(NH_3)_2Br_2]$ $[Pt(NH_3)_2Br(H_2O)^+])$ if the single resin separation was used and there was no fractionation. The computer program contained a provision for comparing experimental curves and calculated curves for experiments in which the $[Pt(NH_3)_2Br(H_2O)^+]$

was believed to be preferentially separated. This was accomplished by altering the value of $F, S/S_{\infty}$, which the computer used to generate the calculated curves. The calculated F was $(U+V)/(U_{\infty}+V_{\infty})$ for the case in which only the anion resin was used and no fractionation occurred. To account for fractionation, the form of F was changed to $(CU+DV) / (CU_{\infty}+DV_{\infty})$.

Even though the experimental graphs were not straight lines in every case, it was possible to compare the calculated curve with the experimental curve by a comparison of their times of half-exchange. The differential equation set considered initially did not characterize the exchange satisfactorily at all. Therefore, in addition to the 1st and 2nd "aquation" paths, an additional process was considered. This had a second order mechanism, 1st order in Br^- and 1st order in $Pt(NH_3)_2Br_2$. The contribution of this exchange path was included by adding a term, $R_3(S_B-S_U)$ to Equation III.10. (R_3 is $k_B[Br^-][Pt(NH_3)_2Br_2]$). The experimentally observed times of half-exchange could be predicted reasonably well if this three term rate law was utilized by the proper selection of rate constants. In addition to these, one other possibility for exchange was considered. Since a "dimer" transition state had been observed in a similar exchange system, it seemed possible to be operative in this system. This "dimer" could provide a means of exchange not only for the cis-$Pt(NH_3)_2Br_2$ but also for the $Pt(NH_3)_2Br(H_2O)^+$. Therefore, provision was made in the computer program to add this term to both III.10 and III.11. Thus it was possible to have two rate constants for this means of exchange. The terms which were added were $R_4(S_B-S_U)$ and $R_5(S_B-S_V)$. R_4 was $k_{d1}[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br(H_2O)^+]$ and R_5 was $k_{d2}[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br(H_2O)^+]$.

D. Numerical Integration of Differential Equation

The Runge-Kutta (39) method of numerical integration was employed for the integration of the differential equations. For a pair of simultaneous equations of the type

$$\frac{dx}{dt} = f_1(t,x,y)$$

$$\frac{dy}{dt} = f_2(t,x,y)$$

the increments in x and y for the first interval in t are found from the following formulas:

$$k_1 = f_1(t_o,x_o,y_o)\Delta t,$$

$$k_2 = f_1(t_o + \frac{\Delta t}{2}, x_o + \frac{k_1}{2}, y_o + \frac{\ell_1}{2})\Delta t$$

$$k_3 = f_1(t_o + \frac{\Delta t}{2}, x_o + \frac{k_2}{2}, y_o + \frac{\ell_2}{2})\Delta t$$

$$k_4 = f_1(t_o + \Delta t,\ y_o + k_3,\ y_o + \ell_3)\Delta t$$

$$\Delta x = 1/6(k_1 + 2k_2 + 2k_3 + k_4)$$

$$\ell_1 = f_2(t_o,\ x_o,\ y_o)\Delta t,$$

$$\ell_2 = f_2(t_o + \frac{\Delta t}{2},\ x_o + \frac{k_1}{2},\ y_o + \frac{\ell_1}{2})\Delta t,$$

$$\ell_3 = f_2(t_o + \frac{\Delta t}{2},\ x_o + \frac{k_2}{2}\ ,\ y_o + \frac{\ell_2}{2})\Delta t,$$

$$\ell_4 = f_2(t_o + \Delta t,\ x_o + k_3,\ y_o + \ell_3)\Delta t,$$

$$\Delta y = 1/6(\ell_1 + 2\ell_2 + 2\ell_3 + \ell_4)$$

The increments for the succeeding intervals are computed in exactly the same way except that t_o, x_o, y_o are replaced by t_1, x_1, y_1 as the computation is advanced through intervals in t. The inherent error in this method is estimated at $(\Delta t)^5$. Thus the smaller the interval chosen, the less the inherent error.

IV. RESULTS

A. Equilibrium Quotients

There are several phenomena associated with solutions of cis-$Pt(NH_3)_2Br_2$ in water which indicate that "aquation" of the complex occurs. The pH of its solution slowly decreased with time, the conductivity increased with time, and the absorption spectrum of the complex exhibited a decrease of the absorption at 318 mμ with time. If KBr was added to the solution, the spectrum would revert very nearly to its initial form. A set of absorption spectra, exhibiting these changes, is displayed in Fig. 2.

A means of calculating equilibrium quotients for the aquation from the observable, equilibrium titre, was discussed in section III. The observed equilibrium titres are compiled in Table 1. Also tabulated in Table 1, are calculated values of equilibrium titres, which provided a test of the equilibrium quotients over the concentration range studied. It should be noted that an appreciable amount of $Pt(NH_3)_2(H_2O)_2^{2+}$ is indicated by the fact that the titre is greater than the concentration of complex in the .204 mM. experiment. Additional support was given for this second aquation by the fact that if only one equilibrium was considered, the equilibrium quotient obtained increased as the concentration of complex approached the most dilute values studied. The equilibrium quotients for the two temperatures studied are reported in Table 2.

Table 1. Observed titres used to calculate K_1 and K_2 and calculated titres, a test of the consistency of the quotients

Temp., °C.	Initial *cis*-$Pt(NH_3)_2Br_2$ M.x10^{-3}	Titres M.x10^{-3} Obsd.	Calcd.
25	1.50	0.89	--
	0.75	0.55	0.56
	0.806	0.58	0.59
	0.534	0.45	--
	0.204	0.23	0.22
35	0.20	0.25	0.25
	0.50	0.48	0.48
	1.00	0.80	0.76
	1.50	1.03	1.00
	2.00	1.20	1.19
	1.823	1.12	--
	0.329	0.355	--

Table 2. Values for first and second aquation equilibrium quotients

Temp. °C.	K_1, moles/l., x10^3	K_2, moles/l., x10^4	ΔH_1^o	ΔS_1^o
25.0	0.96	0.9	4 Kcal	-0.4 cal/deg
35.0	1.19	1.5		

Analogous to the findings for the cis-$Pt(NH_3)_2Cl_2$, there appears to be an uncertainty in K_1 of about 10% and about 30%-uncertainty in K_2.

B. Anation Rate Constants

The anation rate constants together with the equilibrium quotients provided a value of k_1, which could be compared with the value of k_1 obtained in the exchange experiments. The values found for the anation rate constants are given in Table 3 along with the corresponding values of k_1, which were calculated from the anation constant and the equilibrium quotient.

Table 3. Anation rate constants and values of k_1 which were obtained from the equilibrium quotients and the anation constants

Temp. ^oC.	k_{-1} (anation constant)	k_1
25.0	$3.3x10^{-2}M^{-1}sec^{-1}$	$3.2x10^{-5}sec^{-1}$
35.0	$7.2x10^{-2}M^{-1}sec^{-1}$	$8.6x10^{-5}sec^{-1}$

C. Isotopic Exchange

It was not possible to adequately characterize the exchange of Br^{82} with cis-$Pt(NH_3)_2Br_2$ by consideration of the first and second aquation paths alone. However, when a direct exchange of Br^{82} with cis-$Pt(NH_3)_2Br_2$ was considered in addition to the two aquation paths, the exchange kinetics were characterized rather well. The value of k_2 (second aquation path) determined under these conditions appeared to be abnormally high. In fact, in order to obtain the curvature in the calculated curves, that was found in the experimental plots for the low-bromide, "single resin" experiments, it was necessary for k_2 to be approximately 10 times the magnitude of k_1. (k_1 is the first aquation path)

In previous studies involving aquation of halo-ammine complexes the k_2 rate constant was very nearly equal to k_1. (For cis-$Pt(NH_3)_2Cl_2$, k_1 was $2.5 \times 10^{-5} sec^{-1}$ and k_2 was $3.3 \times 10^{-5} sec^{-1}$.) An alternative to this high value for k_2, was to add a dimer term and reduce the value of k_2 to about the same value as that of k_1. The effect of the second "aquation" on the rate could be measured only indirectly. This was due to the removal of the $Pt(NH_3)_2Br(H_2O)^+$ by the cation exchange resin in the experiments where there was an appreciable concentration of the $Pt(NH_3)_2Br(H_2O)^+$. If the cation exchange resin was not used in these experiments, the fractionation which occurred in the separation procedures made it impossible to obtain any accurate values of k_2 in these experiments. An estimated value for k_2 was found by the addition of fractionation coefficients in the computer program and attempting to fit the experimental curves. By these means a value of k_2 was estimated. Figure 7 shows the fit of experimental data points with the calculated curve. The rate constants in Table 6 were applied to the differential equation set of Equations IV.1 and IV.2 in obtaining this curve. C, the fractionation factor was given a value of 0.85, while D was considered to be 1.00.

In Tables 4 and 5 are reported the observed half-times and the calculated half-times for both mechanisms at 25 and 35 degrees respectively. The values of the rate constants used in generating the calculated curves from which the calculated half-times were taken are reported in Table 6. The exchange was characterized equally well by either of two sets of differential equations. The first set is Equations IV.1 and IV.2.

$$\begin{aligned} dU/dt = {} & k_1[Pt(NH_3)_2Br_2][S_B + S_V - 2S_U] \\ & + k_{Br}[Pt(NH_3)_2Br_2][Br^-]\,[S_B - S_U] \end{aligned} \qquad \text{IV.1}$$

$$\begin{aligned} dV/dt = {} & k_2[Pt(NH_3)_2Br(H_2O)^+][S_B - S_V] \\ & + k_1[Pt(NH_3)_2Br_2][S_U - S_V] \end{aligned} \qquad \text{IV.2}$$

The other differential equation set is the same as IV.1 and

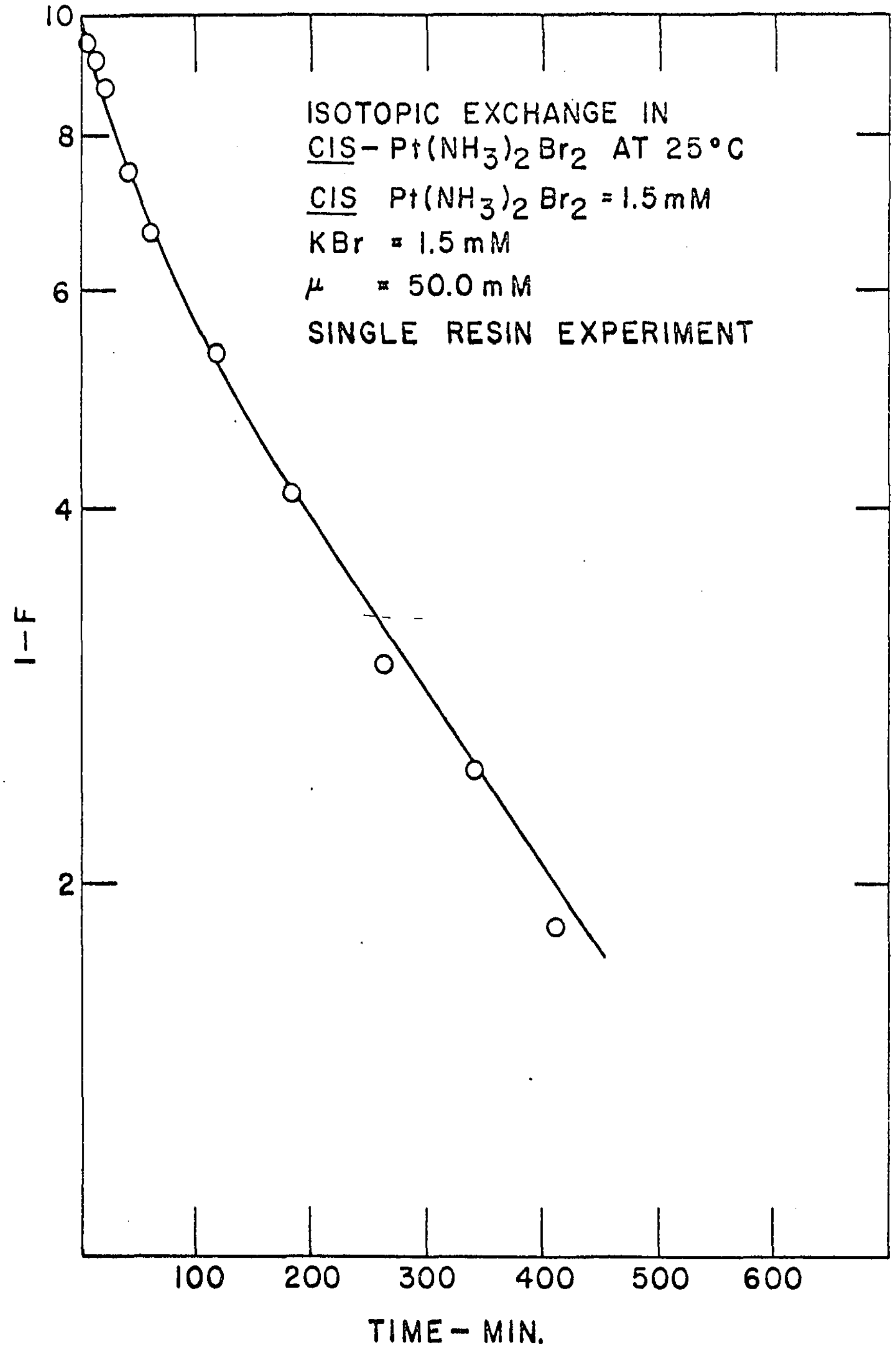


Fig. 7. Calculated curve and experimental points for a "low-bromide" experiment

Table 4. Exchange between bromide and cis-$Pt(NH_3)_2Br_2$ at 25°C

Initial $Pt(NH_3)_2Br_2$ mM.	Initial KBr mM.	Equil. $Pt(NH_3)_2Br(H_2O)^+$ mM.	Equil. $Pt(NH_3)_2(H_2O)^{2+}$ mM.	Time of half-exchange		
				Obsd. min.	Calc.[a] min.	Calc.[b] min.
2.0	2.0	0.539	0.0187	230[c]	234	234
1.5	2.0	0.418	0.0152	265[c]	261	269
1.5	5.0	0.232	0.004	322	307	314
1.5	5.0	0.23	0.004	355[c]	340	345
0.75	2.0	0.22	0.009	388[c]	323	366
1.5	30.0	0.046	---	420[d]	470	469
1.5	10.0	0.13	0.001	420	442	406
1.5	20.0	0.069	---	420	475	464
1.5	50.0	0.028	---	460[d]	440	438
1.5	10.0	0.13	0.001	470[c]	416	418
1.0	2.0	0.29	0.011	300[c]	299	325

[a] Differential equation set given by Equations IV.1 and IV.2.

[b] Equation IV.2 modified by addition of "dimer" term.

[c] "Double resin" experiment.

[d] Average of two experiments.

Table 5. Exchange between bromide and cis-$Pt(NH_3)_2Br_2$ at 35°C.

Initial $Pt(NH_3)_2Br_2$ mM.	Initial KBr mM.	Equil. $Pt(NH_3)_2Br(H_2O)^+$ mM.	Equil. $Pt(NH_3)_2(H_2O)^{2+}$ mM.	Time of half-exchange		
				Obsd. min.	Calc.[a] min.	Calc.[b] min.
1.5	50.0	0.036	---	150	153	149
1.5	30.0	0.057	0.0003	165	163	158
1.5	10.0	0.157	0.0024	140	139	134
1.5	5.0	0.274	0.008	102	105	103
1.0	2.0	0.327	0.021	108[c]	109	116
1.50	2.0	0.471	0.029	89[c]	97	98
2.0	2.52	0.545	0.027	80[c]	92	89
0.75	2.0	0.251	0.017	120[c,d]	119	130
2.0	2.0	0.605	0.035	83[c]	88	86

[a] Differential equation set given by Equations IV.1 and IV.2.

[b] Equation IV.2 modified by addition of "dimer" term.

[c] "Double resin" experiment.

[d] Average of 4 experiments.

Table 6. Rate constants and activation parameters for the rate laws given by Equations IV.1 and IV.2

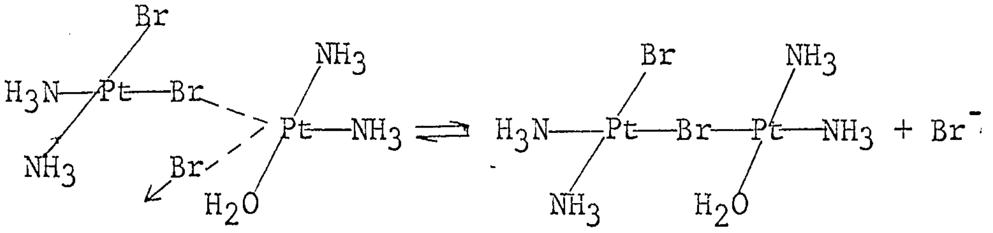
Temp. °C.	Activation parameters	k_1 sec^{-1}	k_2 sec^{-1}	k_{Br} $M^{-1}sec^{-1}$	k_{d2}
Rate law given by IV.1					
25		3.0×10^{-5}	2.0×10^{-4}	3.3×10^{-4}	
35		8.2×10^{-5}	6.0×10^{-4}	1.0×10^{-3}	
For IV.1					
	$\Delta H^{\ddagger}_{25^oC}$	18 Kcal.	19 Kcal.	19 Kcal.	
	$\Delta S^{\ddagger}_{25^oC}$	-20 cal./deg.	-13 cal./deg.	-13 cal./deg.	
Rate law given by IV.2					
25		3.0×10^{-5}	3.0×10^{-5}	3.3×10^{-4}	0.12
35		8.2×10^{-5}	8.2×10^{-5}	1.0×10^{-3}	0.50
For IV.2					
	$\Delta H^{\ddagger}_{25^oC}$	18	18	19	25
	$\Delta S^{\ddagger}_{25^oC}$	-20	-20	-13	20

IV.2 except an additional term,

$$k_{d2}[Pt(NH_3)_2Br(H_2O)^+][Pt(NH_3)_2Br_2][S_B-S_V],$$

is added to IV.2.

A dimer transition state complex, very much like that found by Teggins et al., for the $PtBr_4^{2-}$ system can be proposed to account for the exchange via the k_d path (11). Equation IV.3 illustrates this proposed path.



(IV.3)

V. DISCUSSION

The aquation equilibria for cis-Pt$(NH_3)_2Br_2$ have been described by Equations III.1 and III.2. An uncertainty of approximately 10% seems reasonable for K_1. The average deviation of the calculated titre from the observed titre was about 2%. Also, an uncertainty in the titre of approximately 2% could be calculated if the uncertainties in concentrations and burette readings were additive. From the two simultaneous equations utilized to calculate K_1, it can be shown that 2% errors in the determination of the equilibrium titre will produce an error of about 20% in the value of K_1. This is assuming that these 2% errors in the two values of the titre, used to calculate K_1, combine in such a way to produce the greatest possible error in K_1.

If only one of the titres is changed by 2%, the value found for K_1 is changed by about 5%. The value of K_2, however, was much more uncertain. The maximum error in K_2 appeared to be about 45%. This error is probably 30%. The reason for this large uncertainty in K_2 is the fact that in all the solutions studied, the concentration of $Pt(NH_3)_2(H_2O)_2^{2+}$ was never more than 5-10% of the total platinum concentration. Thus because of its small contribution to the titre, a 2% uncertainty in the titre will have a great effect on the value found for K_2.

Grinberg and Shagisultanova (30) reported a value of 1.8×10^{-3} M. for K_1 at 25°C. They did not indicate the ionic strength for these determinations. They also did not consider the possibility of second aquation. Therefore, it is not surprising that the value for K_1 obtained in this study, 9.6×10^{-4} M. is approximately only one-half of their value.

The anation of $Pt(NH_3)_2Br(H_2O)^+$ provided a means of testing the reliability of the values of k_1 obtained from the isotopic exchange experiments. The error in k_{-1}, the anation rate constant, is estimated to be about 5%. When this is combined with the expected error in K_1, an expected error of about 11% is obtained for the value of k_1 calculated from the anation experiments. The values found for k_1 by this method agreed very well with those obtained from the exchange data. The values obtained from the anation rate data were 3.2×10^{-5} sec^{-1} and 8.6×10^{-5} sec^{-1}. The exchange data provided values of 3.0×10^{-5} sec^{-1} and 8.2×10^{-5} sec^{-1}.

The agreement of k_1 from the anation experiments with the k_1 for the exchange experiments gives added confidence in the k_1 from the exchange data. The half-times of exchange were not very sensitive to small changes in k_2 and k_d. Therefore it is difficult to estimate just how accurately the values of these rate constants are known. Changes in k_1 and k_{Br}, however, produced rather substantial changes in the calculated half-times of exchange. The uncertainty in these constants is estimated to be approximately 10%.

The Russian chemists, who studied cis-$Pt(NH_3)_2Br_2$ in the presence of $PtBr_4^{2-}$, did not report any rate constants (29). Their exchange reactions were considerably faster than those studied here in view of the half-times implied by their data. It appears that the addition of $PtBr_4^{2-}$ to a solution of cis-$Pt(NH_3)_2Br_2$ has a truly dramatic effect upon the exchange rate.

In their study of the Br^- exchange with $PtBr_4^{2-}$, Teggins et al. (11) found k_1 to be 2.2×10^{-4} sec^{-1}. This is much higher than the value found in this study, 3.0×10^{-5} sec^{-1}. It should be pointed out that Br^- is well above NH_3 in the trans effect order. This is likely the reason for the higher value of k_1 for $PtBr_4^{2-}$. Unlike $PtBr_4^{2-}$, a dimer transition term in the rate law was not needed to characterize the exchange of cis-$Pt(NH_3)_2Br_2$ with Br^-. It could be added, however, to account for the apparently excessive rate of exchange of the $Pt(NH_3)_2Br(H_2O)^+$ species. There was no means available for determining just how large k_2 should be and consequently how large k_d. k_2 for the analogous Cl^- system was approximately the same as k_1 for that system. If this was used as a guide line, k_2 for the cis-$Pt(NH_3)_2Br_2$ could be set equal to k_1 for this bromo-complex and a value of k_d determined. It is obvious that the k_d term will contribute most when the concentration of $Pt(NH_3)_2Br(H_2O)^+$ relative to the concentration of complex is the greatest. Therefore the exchange should be studied over the widest concentration range possible. The separation procedure placed a lower limit and the solubility an upper limit on the range that could be studied here.

The values of k_1 for the cis-$Pt(NH_3)_2Cl_2$, $2.5x10^{-5}$ sec^{-1} and the system studied here were very nearly equal. Both leaving groups are trans to NH_3. This gives added evidence that Cl^- and Br^- are about equal in the leaving group series.

Reishus and Martin (6) apparently recovered more of the cis-$Pt(NH_3)_2Cl_2$ from their anion exchange resin than could be recovered from the resin in this study. According to Helfferich, non-electrolytes such as these complexes are sorbed on the resin. Sorbtion is a reversible phenomena and the sorbed substance can be removed from the resin by washing with pure solvent. Apparently the cis-$Pt(NH_3)_2Br_2$ is sorbed more strongly than the chloro-complex. This is possibly due to greater dipole-dipole interaction of the bromo-complex with the solvent; one of the forces of sorbtion.

Lokken and Martin (9), in their study of the isotopic exchange of Cl^- with $Pt(C_2H_4)Cl_3^-$, found that the second aquation rate constant, k_2 for the complex was about 10 times the value of their k_1. The value obtained in the present system is 6 times that of k_1, which is much higher than anything found for the other halo-ammine complexes. While the two systems are by no means similar, this is another case of the rate constant, k_2, being much larger than k_1.

Although the question of the dimer contribution to the k_2 path for exchange still exists, the exchange of Br^- with <u>cis</u>-$Pt(NH_3)_2Br_2$ has now been characterized. It appears that the addition of $PtBr_4^{2-}$ to a solution of this complex will enhance the rate of exchange by a very substantial amount. It should now be possible to determine if the rapid rates of exchange observed by Grinberg and Shagisultanova for this system in the presence pf $PtBr_4^{2-}$ were caused by a swapping process or by mutual catalysis.

VI. SUMMARY

Equilibrium quotients, K_1 and K_2, for the aquation reactions of cis-$Pt(NH_3)_2Br_2$ have been determined at 25 and 35°C. Their values were 9.6×10^{-4} and 9×10^{-5} at 25°C. At 35°C. the values of these quotients were 1.19×10^{-3} and 1.5×10^{-4}.

The isotopic exchange could be characterized equally well by two different kinetic schemes. The first scheme consisted of three paths for exchange of bromide ligands with Br^-. The first of these was the reversible aquation reaction of cis-$Pt(NH_3)_2Br_2$. The rate for this path was $k_1[Pt(NH_3)_2Br_2]$. The second of these paths was a direct exchange of bromide with cis-$Pt(NH_3)_2Br_2$ for which the rate was $k_{Br}[Br^-][$cis-$Pt(NH_3)_2Br_2]$. The reversible aquation of $Pt(NH_3)_2Br(H_2O)^+$ was the third path for this kinetic scheme; $k_2[Pt(NH_3)_2Br(H_2O)^+]$ was the rate for this process. Values for the rate constants, k_1, k_2 and k_{Br}, were $3.0\times10^{-5}sec^{-1}$, $2\times10^{-4}sec^{-1}$ and 3.3×10^{-4} $M^{-1}sec^{-1}$ for this first scheme at 25°C. The value of k_2 appeared to be unusually high. It should be noted that the exchange could be characterized equally well if the value of k_2 were given a lower value and another means for exchange of bromide with $Pt(NH_3)_2Br(H_2O)^+$ *via* a "dimer" path were provided. The rate for this path would be $k_{d2}[Pt(NH_3)_2Br(H_2O^+][$cis-

$Pt(NH_3)_2Br_2$]. For this scheme at 25°C. k_1 and k_{Br} retained their same values, but k_2 was now $3x10^{-5}sec^{-1}$ and the additions rate constant, k_{d2}, was 0.12 $M^{-1}sec^{-1}$.

The exchange rates observed here are much slower than those observed by Grinberg and Shagisultanova (29) for the same system in the presence of $PtBr_4^{2-}$. Since the exchange of Br^- and cis-$Pt(NH_3)_2Br_2$ has been characterized, it is now possible to initiate a more thorough study of the effect of $PtBr_4^{2-}$ upon the rate of exchange of the cis-complex. This study should provide an answer to the question of whether the fast rates observed by the Russian scientists were due to a "swapping" process or mutual catalysis.

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