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Ligand substitution of platinum(II) complexes: The

cis-dibromodiammineplatinum(II)-bromide-tetrabromoplatinate(II) system

by

George Fox Vandegrift III

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

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INTRODUCTION

The subject of this investigation was bromide exchange in the three component system - $\underline{cis}$-Pt$(NH_3)_2Br_2$ - Br^- - $PtBr_4^{2-}$. In 1960, Grinberg and Shagisultanova reported a limited study of what they believed to be direct exchange between $PtBr_4^{2-}$ and $\underline{cis}$- or $\underline{trans}$-Pt$(NH_3)_2Br_2$ (1). Later work by Teggins and Martin, where the Pt(dien)Br^+ - Br^- -$PtBr_4^{2-}$ system was studied, concluded that there was no direct exchange between the platinum complexes but rather that one complex assisted the other in bromide exchange with solution (2). They speculated that exchange between Pt$(NH_3)_2Br_2$ and $PtBr_4^{2-}$ was also one of mutual catalysis of exchange with free bromide which had formed from the solvation processes. The object of this investigation was to determine if this speculation was correct.

Over the years a coherent model for substitution in platinum(II) square planar complexes had evolved. This same model has been successfully extended to other low spin d^8 systems such as complexes of Ni(II), Pd(II), Au(III), Rh(I), and Ir(I). Because of their convenient reaction times, platinum(II) complexes have supplied the bulk of our knowledge about the kinetics of d^8 square planar complexes, acting as a slow motion prototype of the other d^8 systems mentioned.

Developments leading to this model have been traced by a series of excellent review articles or chapters (3, 4, 5, 6, 7). The mechanism has been generally agreed to be associative with either attack by the entering group, $\underline{Y}$, or a solvent molecule, $\underline{S}$, on one of the faces of the square plane. The transition state is believed to approximate a trigonal bipyramid, with $\underline{X}$ (the leaving group), $\underline{Y}$ (or $\underline{S}$), and the group previously

trans to X in the trigonal plane. When Y (or S) enter the plane, X is
placed in the labile axial position of the plane and is subsequently
lost. If the entering group Y is in great excess of X and the replacement
of solvent by Y is rapid enough as to make the concentration of the
solvated complex insignificant. The rate expression for substitution of
X by Y is:

$$\text{Rate} = (k_s + k_y[Y])[Pt-X] . \tag{1}$$

There was a strong correlation found between Pearson's concept of
"hard and soft" acids and bases and the magnitude of k_y for various
nucleophiles (8). The nucleophilic ordering for platinum(II), a "soft
acid", was quite different than that of "hard acid" organic substrates.
Generally, the more polarizable the group the better it was as a
nucleophile. Belucco, et al. proposed that the ratio of k_y/k_s would serve
as a useful measure of reactivity toward platinum(II) complexes for various
nucleophiles (9). The system picked for their standard was trans-
$[Pt(py)_2Cl_2]$ in methanol at $30^\circ C$ where py is pyridine. The nucleophilic
reactivity constants, N^o_{Pt} are defined by the equation:

$$N^o_{Pt} = \log k_y/k_s' \tag{2}$$

for this system (k_s' equaling k_s divided by the concentration of methanol
in methanol. This had to be done so that a second order rate constant, k_y,
could be compared to another second order constant.) The following is a
partial list of N^o_{Pt} values reproduced from reference (6, p. 399).
$(C_2H_5)_3P(8.85) > C_6H_5S^-(7.10) > CN^-(7.0) > I^-(5.42) > Br^-(4.18) > N_3^-(3.58)$
$> Cl^-(3.04) > CH_3CO_2^-(<2.4)$. This list illustrates the point that it is
not proton base strength but rather "softness" of the nucleophile which

makes it more reactive toward platinum(II) substitution.

For an associative mechanism, as is generally accepted for Pt(II) substitution, it would seem that leaving group effects would be minimal. However, Gray and Olcott, who followed a series of experiments of the type:

$$Pt(dien)X^+ + py \longrightarrow Pt(dien)py^{2+} + X^-, \tag{3}$$
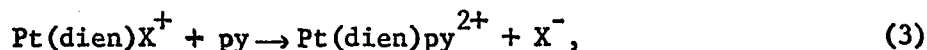
found the startling effect that the spread in rate constants for the series of X^- leaving groups studied was over a range of 10^6 (10). The rate constants decreased in the following order of $\underline{X}^-$: $NO_3^- > H_2O > Cl^- > Br^- > I^- > N_3^- > \underline{S}CN^- > NO_2^- > CN^-$. This result does not necessarily mean that the generally accepted associative mechanism is incorrect, but it does require that Pt-$\underline{X}$ bond breaking make a contribution comparable to Pt-$\underline{Y}$ bond formation. That is to say, depending on the platinum complex and the entering group $\underline{Y}$ studied, the process (bond formation or bond breaking) with the higher activation energy would be rate determining.

Steric effects lend a great deal of support to an associative mechanism. If bulky ligands were attached cis or trans to the leaving group, it would be expected, that if the mechanism were associative, steric hindrance would cause a decrease in rate; whereas, steric acceleration is the rule for a dissociative process. It has also been shown that cis blocking is much more effective than placing a bulky group trans to the leaving group. This gives strong evidence in favor of a trigonal bipyramid intermediate over one which is square pyramidal.

Isotopic exchange, where $\underline{X}$ is replaced by the chemically identical species $\underline{Y}$, allows one to work in a much wider concentration range and to

leave the psuedo first order range to which most substitution kinetics are limited. This is possible because as long as there are only two forms of $\underline{X}$ exchanging, no matter what the concentrations of the reacting species or how many terms of their order in the rate expression, a plot of $\ln(1-F)$ vs time, F being the fraction of exchange, will be linear with slope equaling a known constant x the rate of exchange. The basis for this statement was published by McKay in 1938 (11).

$$\text{Rate of Exchange} = \frac{\left[\text{conc. of X in Pt}\right]\left[\text{conc. of X in soln}\right]}{\left[\text{Total conc. of X}\right]} \text{ x slope} \tag{4}$$

By varying concentrations of each species in solution and observing effects on the calculated rate, the form of the rate law may be established.

Several anomalies to the normal platinum(II) behavior have now been observed because of the lower entering group concentrations studied by isotopic exchange which could not be easily handled by conventional kinetics (2, 12, 13, 14, 15). Before discussing these anomalies, it seems appropriate to retreat and chronicalize developments in isotopic bromide exchange.

Grinberg and Filinov performed the first recorded study of radio-active bromide exchange in 1939 (16). Radioactive Br^- tracer was obtained from neutron irradiation of $C_2H_4Br_2$ followed by its being shaken with aqueous KBr. The KBr^* was then left to equilibrate in solution with $PtBr_4^{2-}$ or $PtBr_6^{2-}$. From this work it was found that all four positions of $PtBr_4^{2-}$ and all six positions of $PtBr_6^{2-}$ were equivalent.

In 1940, Grinberg published another paper extending these earlier works to other systems (17). Two systems of interest to the investigation,

$$K_2PtBr_4 + KBr^* \rightleftharpoons K_2PtBr_4^* + KBr \tag{5}$$

and

$$K_2PtBr_4^* + \underline{cis}\text{-}Pt(NH_3)_2Br_2 \rightleftharpoons K_2PtBr_4 + \underline{cis}\text{-}Pt(NH_3)_2Br_2^*, \tag{6}$$
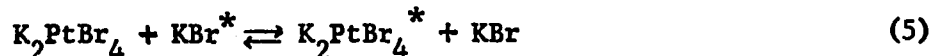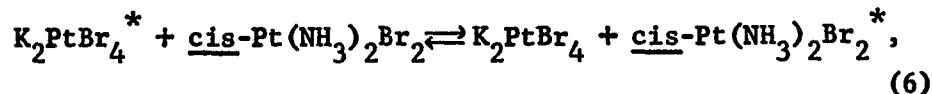
were mentioned. Although no numbers were reported. It was mentioned that both $PtBr_4^{2-}$ and $PtBr_6^{2-}$ exchanged easily with solution and that in the latter system, interchange of bromide between the complexes proceeded rapidly.

In 1949, and in greater detail in 1951, this same author with Nikol'skaya reported a study of the reaction:

$$PtX_4^{2-} + X^{*-} \rightleftharpoons Pt\overset{*}{X}_4^{2-} + X^-, \tag{7}$$

where they found a correlation between thermodynamic stability and rate of exchange (18, 19). For $X^- = CN^-$, I^-, Br^-, and Cl^-, it was found that both thermodynamic stability and rate of exchange decreased in the order $(CN^- > I^- > Br^- > Cl^-)$.

In 1955, Grinberg and others published two more papers concerning $PtBr_4^{2-}$-Br^- exchange (20, 21). From this more careful study, they concluded that most of the exchange proceeded through an aquation mechanism for the concentration range studied. Some other interesting conclusions were that the "age" of solution effected the exchange rate and that impurities had a catalytic effect. They speculated that although they found a first order dependence of $\left[PtBr_4^{2-}\right]$, "... at higher concentrations of $PtBr_4^{2-}$ the exchange rate is probably proportional not

to the first power of the concentration but to a higher power." They
were essentially correct; however, at the concentration range they had
used ($[PtBr_4^{2-}]$ = 2.7 - 16.5mM; $[Br^-]$ = 22 - 132 mM), it was not for
lack of $PtBr_4^{2-}$ that the higher order dependence was not observed but
because of the high bromide concentration range studied.

It was not until 12 years after Grinberg's statement on the seemingly
anomalous behavior of $PtBr_4^{2-}$-Br^- exchange kinetics, that the publication
by Teggins, et al. characterized this higher order term (12). The
mechanism proposed for the dimer term in the exchange rate law:

$$Rate = k_1[PtBr_4^{2-}] + k_2[PtBr_3(H_2O)^-] + k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-] \quad (8)$$

(k_1 = 2.2 x 10^{-4} sec^{-1}, $\Delta H^{\neq}$ = 19 kcals/mole, $k_2 \approx k_1$, and

k_d = .22 M^{-1} sec^{-1}, $\Delta H^{\neq}$ = 9 kcals/mole at 25°C and

μ = .1)

was:
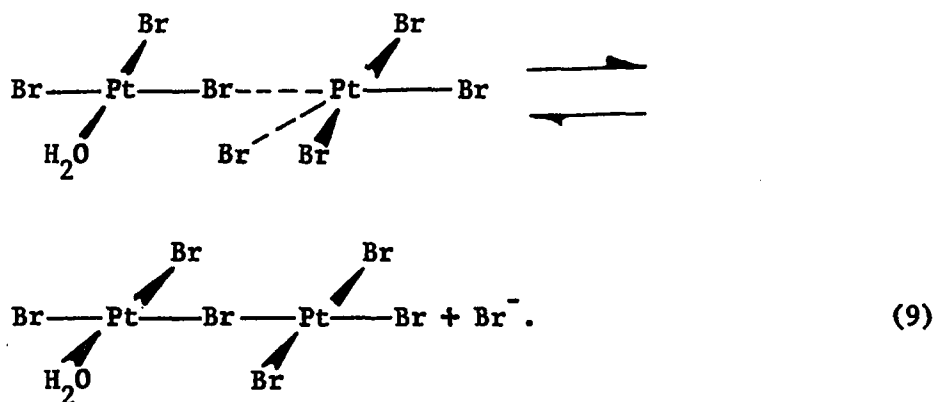
The high bromide concentrations used by Grinberg suppressed the aquation
of $PtBr_4^{2-}$ and kept the contribution of this term to the exchange rate
small.

In 1959, Grinberg and Shagisultanova reported an investigation of $Pt(NH_3)Br_3^- -Br^-$ exchange and in 1961, one of $Pt(py)Br_3^- -Br^-$ exchange. They found, as expected, that there were two types of coordinated bromide in both of the complexes (22, 23).

The next year, as mentioned previously, the same authors reported a study of bromide exchange between $PtBr_4^{2-}$ and both cis or trans $Pt(NH_3)_2Br_2$ (1). They had initially attempted a study of $Pt(NH_3)_2Br_2^- -Br^-$ exchange but found, as did Gano several years later, that an ion exchange separation of Br^- from $Pt(NH_3)_2Br_2$ was not quantitative, and hence not useful, and precipitation of bromide with $AgNO_3$ was not satisfactory. Precipitation of $PtBr_4^{2-}$ with $Pt(NH_3)_4^{2+}$, as they had used many times before, was the method of separating the two complexes. A half time of only 10 minutes was observed at $25^\circ C$ when the concentrations of $PtBr_4^{2-}$ and cis-$Pt(NH_3)_2Br_2$ were equal at 0.51 mM. The exchange between $PtBr_4^{2-}$ and the trans-$Pt(NH_3)_2Br_2$ complex was faster yet. Grinberg explained these rapid rates as a trading of ligands between ion pairs of the type: $[Pt(NH_3)_2Br(H_2O)^+][PtBr_3(H_2O)^-]$.

The unusual path for exchange observed in the $PtBr_4^{2-} -Br^-$ system was the first reported for bromide exchange in a platinum(II) system; however, a similar rate expression was observed for $Pt(C_2H_4)Cl_3^- -Cl^-$ exchange by Lokken and Martin in 1963 (14). The rate expression for exchange between the cis chlorides on the complex and free Cl^- was determined as:

$$R_{ex} = k_c[Pt(C_2H_4)Cl_3^-] + k_c'[Pt(C_2H_4)Cl_2(H_2O)] \qquad (10)$$
$$+ k_d[Pt(C_2H_4)Cl_3^-][Pt(C_2H_4)Cl_2(H_2O)]$$

(at 25°C k_c = 2.9 x 10^{-6} sec^{-1}, $\Delta H^{\neq}$ = 21 kcals/mole; k_c' 2.8 x 10^{-5} sec^{-1}, $\Delta H^{\neq}$ = 22 kcals/mole; k_d = 8.6 x 10^{-3} M^{-1} sec^{-1}, $\Delta H^{\neq}$ = 19 kcals/mole).

The chloride ligand <u>trans</u> to ethylene was virtually labile, establishing equilibrium in less than 2 minutes. The first two terms in the rate expression are normal aquation terms seen to some degree for all platinum(II) complexes. The last term however could only be explained by the formation of a dimer. They considered this term to be exchange between free chloride and the known dimeric molecule <u>trans</u>-di-μ-chlorodichlorobis(ethylene)diplatinum(II):

(11)
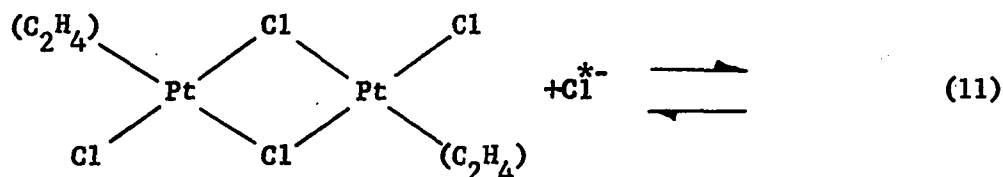
followed by breakage of the bridged structure.

Pearson and Muir reported a study of cleavage rates of halogen-bridged platinum(II) complexes with amines four years later (24). For the reaction

$$+2a = 2PtaLX_2, \qquad (12)$$
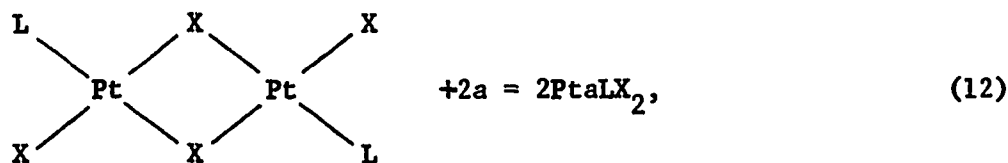
they found a normal platinum(II) substitution rate expression

$$\text{rate} = (k_1 + k_2[Y])\ \text{complex.}$$

Lokken and Martin's work is easily explained through a similar mechanism; the slow step being formation of the dimer species (which is the reverse of the cleavage step).

$$Pt(C_2H_4)Cl_3^- + Pt(C_2H_4)Cl_2(H_2O) \rightleftharpoons Pt_2(C_2H_4)_2Cl_4 + Cl^{*-} + H_2O \qquad (13)$$
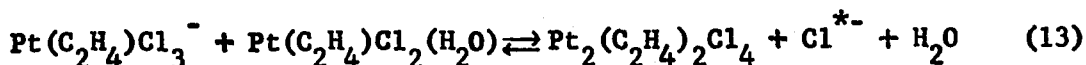
Chloride exchange results in ethanolic solutions of $[Pt(C_2H_4)_2Cl_4]$ were reported by McMane and Martin in 1968 (15). Chloride exchange between free chloride in solution and the chlorides cis to (C_2H_4) in the two monomeric species $Pt(C_2H_4)Cl_3^-$ and trans-$Pt(C_2H_4)Cl_2(C_2H_5OH)$ (which are the predominant species in solution at the concentrations studied) was characterized by the rate expression:

$$R_{ex} = k_d[Pt(C_2H_4)Cl_3^-][trans-Pt(C_2H_4)Cl_2(C_2H_5OH)] \qquad (14)$$

(at $25°C$ $k_d = 7.7 \times 10^{-2}$ M^{-1} sec^{-1}, $\Delta H^{\neq} = 25$ kcal/mole). The proposed mechanism for exchange is in essence similar to that suggested by Lokken and Martin previously. However, because of the higher activation entropy of the formation of this dimer species in comparison to that of the former (19 compared to -2e.u.), a singly bridged dimer with loss of a solvent molecule accompanying the formation of that bridge is proposed as the rate determining step.

In a study of $Pt(dien)Br^+$ bromide exchange, Teggins and Martin found this system obeyed the normal platinum(II) rate law:

$$R_{ex} = (k_1 + k_2[Br^-])[Pt(dien)Br^+] \qquad (15)$$

(at $25°C$ $k_1 = 1.3 \times 10^{-4}$ sec^{-1}, $\Delta H^{\neq} = 20$ kcals/mole; $k_2 = 5.9 \times 10^{-3}$ M^{-1} sec^{-1} $\Delta H^{\neq} = 16$ kcals/mole) (2). However, when $PtBr_4^{2-}$ was added to its solutions, it was found that exchange was enhanced, and the rate law had to be expanded to include a term

$$k_d[PtBr_4^{2-}][Pt(dien)Br^+].$$

It was also found that the rate of bromide exchange in $[PtBr_4^{2-}]$ was

increased by what was within experimental error the same term (at 25°C

k_d = .20 M^{-1} sec^{-1}, $\Delta H^{\neq}$ = 15 kcals/mole). It was their opinion, based on

the data that had been collected, that bromide was not traded between the

two complexes. One complex merely assisted the other through a weak

bromide bridge to exchange with solution.

A study of the isotopic exchange of cis-$Pt(NH_3)_2Br_2$ was reported by

Gano, et al. in 1968 (13). It was found that the exchange data could be

characterized equally well by two rate expressions. The first of these

expressions was:

$$R_{ex} = (k_1 + k_{Br}[Br^-])[Pt(NH_3)_2Br] + k_2[Pt(NH_3)_2Br(H_2O)^+] \qquad (16)$$

(at 25° k_1 = 3.0 x 10^{-5}, sec^{-1} $\Delta H^{\neq}$ = 18 kcals/mole, k_{Br} = 3.3 x 10^{-4}

sec^{-1}, $\Delta H^{\neq}$ = 19 kcals/mole, k_2 = 2 x 10^{-4} sec^{-1}).

The second expression was as the first but the value of k_2 was made

less and a fourth term

$$k_d[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br(H_2O)^+]$$

was added (at 25°C k_2 = 0.3 x 10^{-4} sec^{-1}, k_d = .12 M^{-1} sec^{-1}).

Now that a separation procedure for the neutral complex cis-

$Pt(NH_3)_2Br_2$ from both Br^- and $PtBr_4^{2-}$ had been made available, Grinberg's

observation on $Pt(NH_3)_2Br_2$ - $PtBr_4^{2-}$ exchange could be tested and

compared to the results of the $Pt(dien)Br^+$ - $PtBr_4^{2-}$ system.

EXPERIMENTAL

Materials

Platinum

It has long been suspected that iridium impurity has a marked effect on platinum's chemical behavior (25). Because of this effect and suspicions that other platinum metals (Ru, Os, Rh, Pd, Ag, Au) may also affect the chemical reactions and kinetics of platinum, there have now been three separate neutron activation analyses of platinum out of this group (25, 26, 27). All three of these studies have agreed that the method suggested by Jowanovitz, et al. (25) for purifying platinum of these impurities has been successful to some degree for the metals observed. The results of these studies may be found in Table 1.

Table 1. Extent of impurity of other metals in platinum

Metal	Commercial platinum Wire μg/g Pt.	"Purified" platinum μg/g Pt.
Ir (25)	19.0	.04
Ir (26)	4.30	.015
Pd (26)	18.0	.028
Ag (26)	7.1	2.4
Os (27)	.13	.032
Ru (27)	1.04	.044

A triple recrystallization with a yield of 97% per recrystallization of the dipotassium salt of hexabromoplatinate (IV) was the basis for the purification.

Rb_2PtBr_4
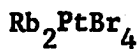
Sixty grams of purified K_2PtBr_6 was stirred vigorously with 250 ml of water containing an equi-molar amount of $K_2C_2O_4$ at 75-85°C on a heater-stirrer for 4-6 hours. Heating at higher temperatures causes decomposition and the formation of platinum black. The volume of the solution was allowed to decrease through evaporation so that by the end of this period it was less than 100 ml. The color of the liquor had turned from red to dark brown.

The solution was then cooled in a brine solution to remove all unreacted K_2PtBr_6 from solution. After filtering, RbBr was added to the mother liquor and precipitation of Rb_2PtBr_4 followed immediately. The product was filtered from solution and recrystallized from .2 M RbBr. Approximately 2 ml of .2 M RbBr solution were needed to dissolve 1 g of Rb_2PtBr_4 at 70°C.

Purity was tested spectrophotometrically by a peak to valley absorbance ratio criterion. Rb_2PtBr_4 was recrystallized until the ratio of the peak (at 415 nm) to the valley (at 387 nm) was constant. The value of this ratio was 1.38 ± .03 in .05 M KBr solution. A visible spectrum of this complex may be found in Figure 1.

A determination of the chemical composition of Rb_2PtBr_4 was performed by a thermal gravimetric analysis (TGA). A typical trace is portrayed in Figure 2. The first weight loss, beginning at ca. 450°C was caused by
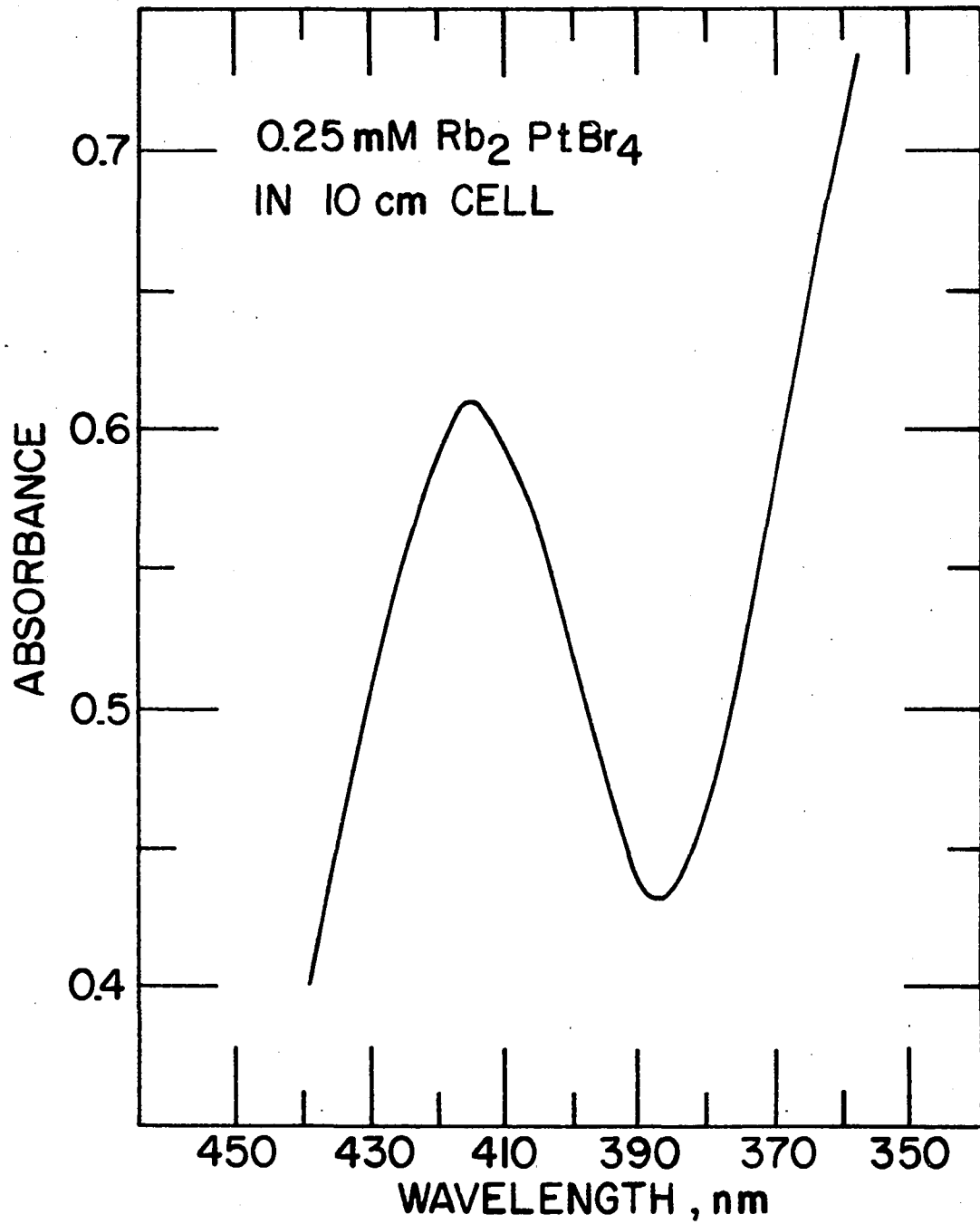
Figure 1. Absorption spectrum of Rb_2PtBr_4 in .1 M KBr
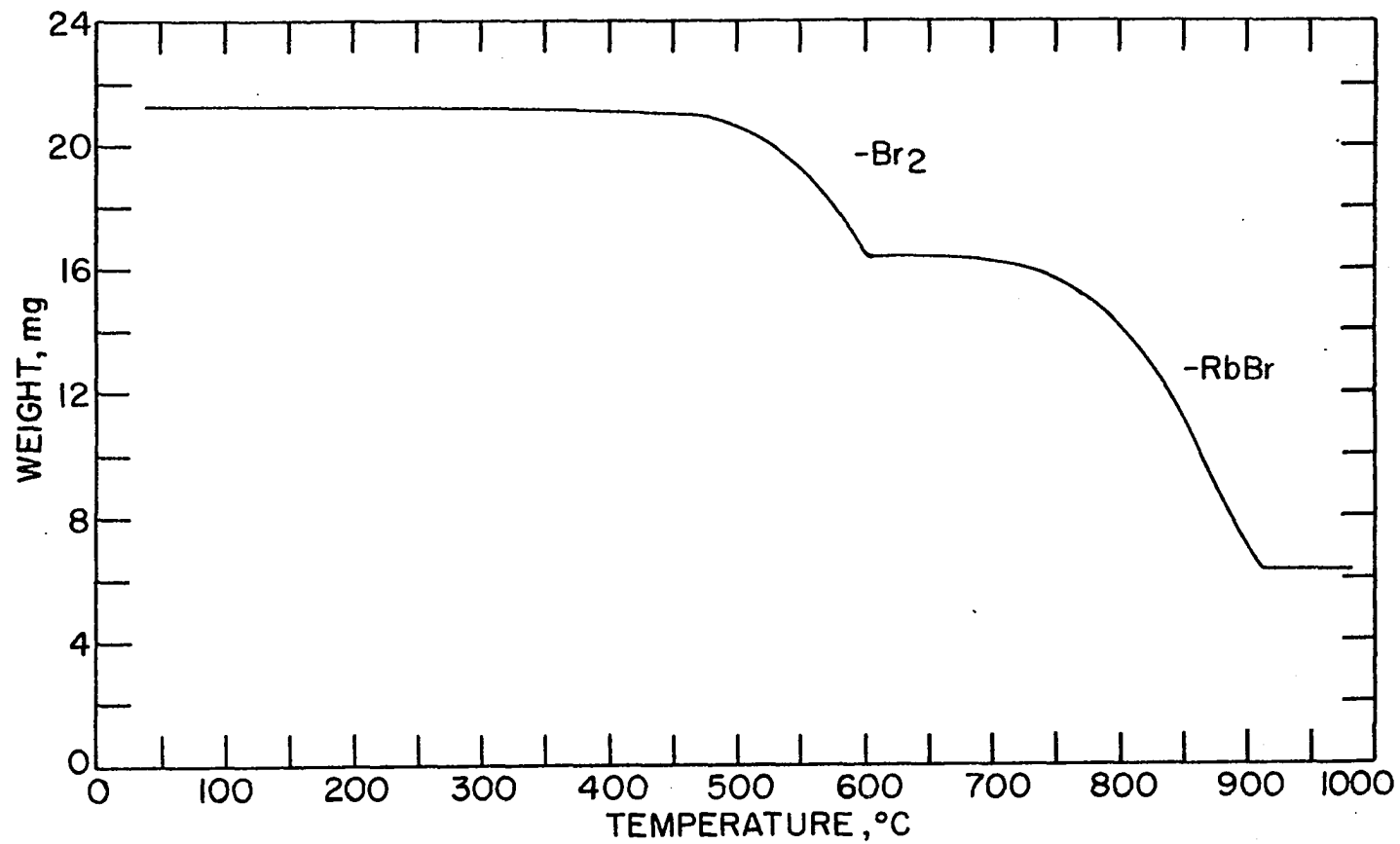
Figure 2. A typical thermogravimetric analysis of Rb_2PtBr_4

disappearance of Br_2 - as evidenced by a red condensation on the cool end of the tube. At ca. 700°C loss of RbBr began. By 950°C all that remained was platinum metal.

obs. Pt = 29.3   calc. = 28.4%

obs. Br_2 = 23.2%   calc. = 23.4%

obs. RbBr = 47.5%   calc. = 48.2%

It should be noted that Rb_2PtBr_4 is slowly air oxidized and should be recrystallized every few months to retain purity. The presence of water and more specifically an acid solution accelerates this reaction. It was observed that when RbBr was added to a solution of H_2PtBr_4 which had been allowed to stand several days in the air, an insoluble residue was collected from the recrystallization of Rb_2PtBr_4. The substance was analyzed by TGA and the formula that best fit the compositions was Rb_2PtBr_6. It was also observed that an insoluble residue forms in basic solutions of Rb_2PtBr_4. After wet Rb_2PtBr_4 was dried in an oven at 85°C for eight hours, only a 10% recovery was made.

Cis-Pt$(NH_3)_2Br_2$

K_2PtBr_4 was prepared as described previously for the preparation of Rb_2PtBr_4. However, this time after the cold solution was filtered to remove unreacted K_2PtBr_6, 2 moles of ammonium acetate and 4 moles of potassium bromide were added for every mole of complex estimated to be in solution. The solution was diluted to obtain the 250 ml of original solution and was stirred while being heated at 85°C. Approximately four hours later, the reaction was complete, the solution having changed from

a dark brown to faint yellow. Golden yellow needles of $\underline{cis}$-Pt$(NH_3)_2Br_2$ were also evident.

The solution and crystals were cooled in an ice bath. After being filtered, the crystals were washed with a large volume of cold H_2O to dissolve any salts which co-precipitated with the insoluble platinum complex. The impure compound was then recrystallized from .1 M KBr solution (solubility at 75°C, $\underline{ca}$. 5 g $\underline{per}$ liter; the yield of recrystallization was 85-90%). A peak to valley ratio was also used as a criterion of purity for Pt$(NH_3)_2Br_2$. The ratio of the absorbance for the peak at 318 nm, to that of the valley at 275 nm, was $1.42 \pm .01$ when the compound was considered pure. The molar absorbitivity at the 318 nm peak was determined to be 201 M^{-1} cm^{-1}. A spectrum of the d to d transition range of cis-Pt$(NH_3)_2Br_2$ may be found in Figure 3. After recrystallization, the compound was allowed to dry for at least 15 hours at 75°C.

A TGA was also performed on cis-Pt$(NH_3)_2Br_2$. Unfortunately, it was not the powerful tool as in the case of Rb_2PtBr_4. Since ammonia and Br_2 left simultaneously on heating to 275°C, the only parameter that could be derived was the percentage platinum in the complex; % determined = 50.0% vs calculated value = 50.1%. A potentiometric analysis for bromide was undertaken. Ammonia was used to strip bromide off the platinum. After acidification and the solution diluted to a known volume the bromide concentration was measured with a calibrated bromide active electrode; ave. Br found: 40.9%, calculated: 41.1%.

It should be noted that the compound is usually orange-brown after recrystallization. Although the yellow form may also be found, it changes
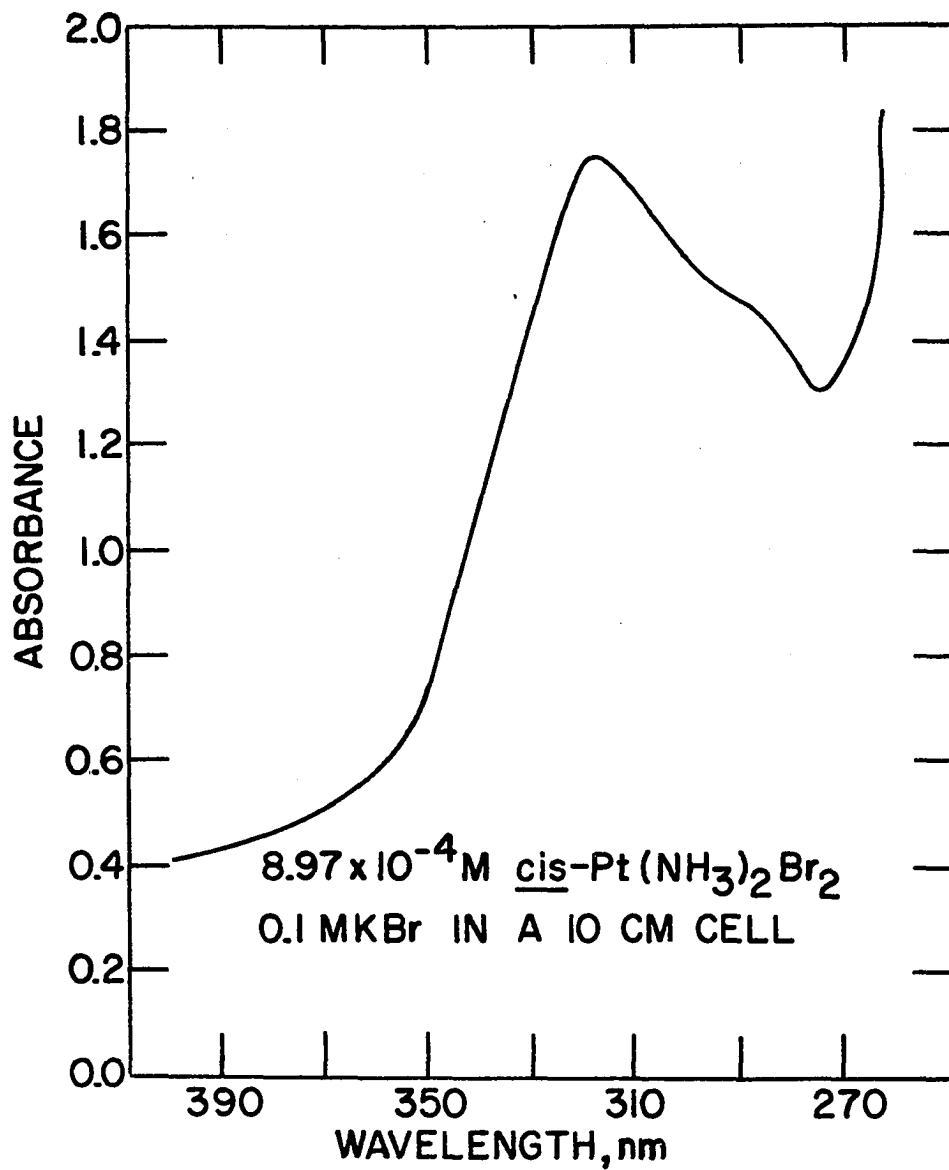
Figure 3. Absorption spectrum of <u>cis</u>-Pt(NH$_3$)$_2$Br$_2$ in .1 M KBr

spontaneously into the other with a darker color.

Rubidium bromide

Rubidium perchlorate, purchased from the G. Frederick Smith Chemical Co., was dissolved in large quantities of hot water (1 lb. in 8-12 liters of boiling water) and poured through a bed (70 cm deep and 7 cm in diameter) of Amberlite IRA-400 anionic exchange resin, previously converted to the bromide form. The effluent was collected and boiled down to 500 ml. At this point the solution was cooled and filtered. No unconverted $RbClO_4$ was observed; the solution was then slowly heated to evaporate the remaining liquid. The caked RbBr was ground by a mortar and pestle and dried in an oven at $120^{\circ}C$ overnight.

Mercury (I) perchlorate

$Hg_2(ClO_4)_2$ was prepared by the standard method of reacting mercury, mercury (II) oxide, and perchloric acid (28).

Ion exchange resin

Amberlite IRA-400, 20-50 mesh, was purchased from the Rohm and Haas Company in cubic foot quantities in the chloride form. The resin was converted to the nitrate form by passing a 5% solution of $NaNO_3$ through the resin until chloride was no longer detectable by precipitation with $Hg_2(ClO_4)_2$. Twenty-five percent excess of the volume was then eluted through the column. The resin was initially back washed to remove any foreign matter or broken resin beads and washed with water for an hour after elution to remove $NaNO_3$ and NaCl (29).

Water

All water used was distilled from permanganate to remove organic impurities.

Radioactive bromide (Br^{82})

Br^{82}, with a half life of 35.5 hours, was produced in a rabbit of the Ames Laboratory 5 megawatt research reactor. A sample of 0.5 ml of 10 mg/ml aqueous solution of NH_4Br was sealed under vacuum in a quartz tube for irradiation. After 15 hours of irradiation in a flux of 4.2 x 10^{13} cm^{-2} sec^{-1}, the sample was left to cool for three days to permit the 4.5 hour Br^{80m} and other short lived activities to decay.

Additional reagents

All of the remaining chemicals used were analytical reagent grade, meeting the specifications of the American Chemical Society.

Equipment

Ion exchange columns

The columns themselves were Pyrex glass, 1.5 cm internal diameter and 40 cm long, and tapered at the lower end where 10 cm lengths of tygon tubing were forced over them. A screw clamp was used to close off the tubing. A ball of glass wool rested at the bottom of each column and 18 cm of ion exchange resin was placed over it, with a second layer of spun glass at the top. It was found by Gano that this much resin removed more than 99.9% of free bromide at the concentration range at which both his and this work were performed (30).

Filtration equipment

The Hg_2Br_2 samples were collected on circular filter disks in a chimney filter described by Adams (31). This system was modified for precipitation of $[As(C_6H_5)_4]_2[PtBr_4]$. It was found necessary to filter the solutions as quickly as possible after precipitation was performed. To meet this objective a two way stopcock was connected to the outlet of the filter flask. One tube led from the stopcock to an aspirator, the other led to a needle valve which in turn was connected to an air jet on the lab bench. When the stopcock was in the second position a slight positive pressure was kept inside the flask, thus keeping any liquid above the filter paper from draining into the flask. When the stopcock was in the other position the system worked as an ordinary suction filter flask apparatus.

pH meter and bromide active electrode

A Corning pH meter, Model 12, was used for bromide determination in conjunction with an Orion #94-35-00 specific ion electrode and a Beckman #39710 fiber type calomel reference electrode.

Balance

Precise weighings were performed on a Sartorius single pan analytical balance, Model 2404, having a 100 gram capacity, five place digital read-out capacity with a precision of $\pm$ .05 mg.

Constant temperature bath

The temperature of solutions was controlled at both 25 and 35°C to $\pm$ .05° in a Sargent constant temperature bath, equipped with a Philadelphia

microset thermoregulator, a Sargent Spm 2770 controller and a Sargent

type NS1-12 circulator-heater. At 25°C a constant head apparatus was

utilized to run cooling water through a copper coil place in the bath;

this was not necessary at 35°C.

Gamma ray counting equipment

Gamma rays were counted by a thallium activated NaI crystal coupled

to a photomultiplier tube. An RIDL 400 channel analyzer, Model 34-12B,

was utilized to record the spectrum of counts vs energy as generated from

the photomultiplier tube. The crystal was housed in a lead brick shield to

reduce background radiation. A typical spectrum of Br^{82} recorded by this

instrument is shown in Figure 4. The sum of the counts between channels

40 and 80 was used in calculating the specific activity of bromide in

exchange samples.

Spectrophotometer

All spectra and absorbance measurements were recorded by a Cary,

Model 14, spectrophotometer. Standard silica spectrophotometric cells

were used for all measurements. When temperature control was necessary,

a special cell block was employed which had thermostated water from a

constant temperature bath pumped through it.

Automatic titrator

A radiometer SBR2c/ABU1c/TTA3 automatic recording titrator apparatus

with a .2500 ml burette with an accuracy of 1 μl$\pm$ .07% was utilized for

all acid-base titrations. The titration vessel was equipped with a water

jacket, which was lined with asbestos and opaque tape, for temperature
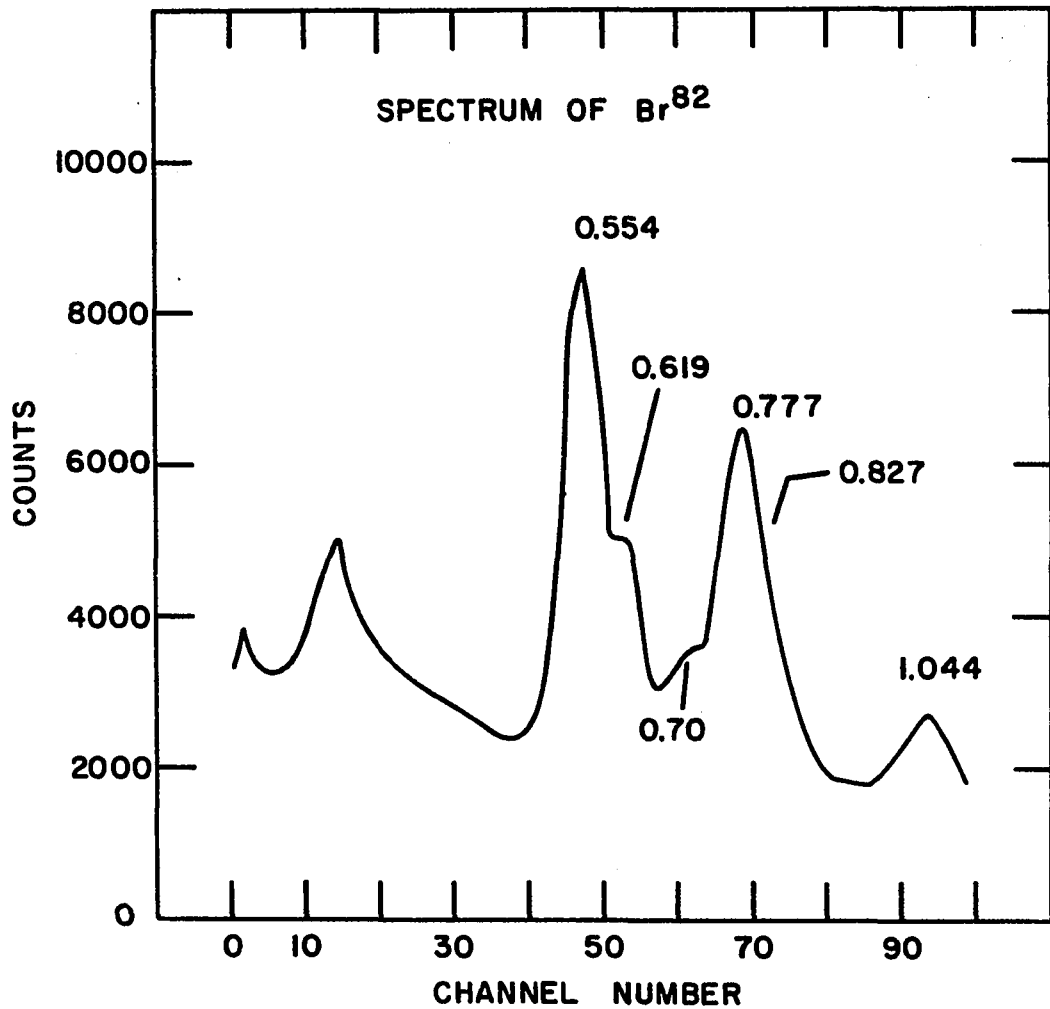
Figure 4. A typical gamma-ray spectrum of Br^{82} showing the energies of the gamma-rays in MeV's

control and a gas outlet from which grade "A" purified nitrogen was introduced into the system, to provide a positive pressure in the vessel and to exclude carbon dioxide. The reference electrode was a Radiometer saturated calomel #K401 electrode; the indicator electrode was a Radiometer #G202c glass electrode.

Thermogravimetric analyzer

Thermogravimetric analyses were performed on a Dupont 950 thermogravimetric analyzer used in conjunction with a Dupont 950 differential thermal analyzer. The system is capable of operating within a temperature range of ambient temperature to $1200^{\circ}C$.

Computation equipment

An IBM 360/50 digital computer was used for all programable calculations. Plots were prepared by a Cal-Comp Digital Incremental Plotter, which plotted directly from computer magnetic tape output.

Timers

Precision Scientific Company timers, which indicate intervals to .01 minutes, were used.

Procedures

Determination of aquation equilibrium quotients

The concentration equilibrium quotients for aquation of cis-$Pt(NH_3)_2Br_2$, cis-$Pt(NH_3)_2Br(H_2O)^+$ and $PtBr_4^{2-}$ were determined at $25^{\circ}C$ and $35^{\circ}C$ by potentiometric titrations of equilibrium solutions having an ionic strength of .05 M. Some 14 solutions, having varying amounts of Br^- and

complex concentrations, were titrated at least 6 times each at both temperatures. Primary standard grade potassium acid phthalate was used to standardize the base.

Three stock solutions were prepared by weighing out calculated amounts of the platinum complex, KBr, and $NaNO_3$. One solution contained the highest concentration of the platinum complex and of potassium bromide desired and enough $NaNO_3$ to attain an ionic strength of .05 M. The second contained the highest concentration of the platinum complex desired and enough sodium nitrate to bring the solution up to .05 M ionic strength. The third solution was a .05 M solution of $NaNO_3$. From these stocks, solutions of varying complex and bromide concentrations were prepared. All solutions were stored in volumetric flasks, wrapped with black vinyl tape to exclude light, in a constant temperature bath for two days.

Two solutions were prepared from primary standard grade potassium acid phthalate, KHP, with concentrations midway among the predicted titers of the platinum solutions. These also were kept at constant temperature for two days. The NaOH stock solution, made carbonate free (32), was diluted and used under a nitrogen atmosphere.

Titrations were conducted in sets. Two or three standardizations and then 6-8 titrations of one of the platinum complex solutions were performed, followed by the next set until all of the solutions had been titrated. All titrations at a given temperature for one complex were performed on the same day.

The procedure for a titration was the following. An aliquot of solution (usually 10 ml) was removed from the taped flask and emptied into a titration vessel which had been previously warmed in a constant

temperature bath. The titration vessel was then surrounded by the water

jacket and the electrodes with the stirrer and gas outflow line were put

into the solution. The titration was then begun and was complete in less

than half a minute. The solution was discarded, the titration vessel

washed and put to dry in an oven, the electrodes washed and dried with

tissue, another vessel put into the constant temperature bath and the

procedure repeated again for the next sample. The total time elapsed from

the time the aliquot was removed until the end of the titration was less

than one and one half minutes.

A few titrations were run at 1/2 the normal speed to see if any

additional aquation was proceeding during the titrations. The end points

were the same at the slower speed, meaning this effect was minimal. Blank

solutions (those containing only .05 M $NaNO_3$) were titrated like any of the

other solutions and were later used to adjust the observed titers.

Aquation kinetics ($PtBr_4^{2-}$)

The aquation rate constant of $PtBr_4^{2-}$ in the presence of an

equilibrated solution of $Pt(NH_3)_2Br_2$ was performed at $25^\circ C$ and $35^\circ C$ by

a spectrophotometric method. Experiments were initiated by addition of

solid Rb_2PtBr_4 to solution and followed for at least five half lives so

that Guggenheim plots could be utilized in finding the observed rate

constant.

A 1.5 mM solution of cis-$Pt(NH_3)_2Br_2$ (maintained at an ionic strength

of .05 M with $NaNO_3$) was prepared and left to equilibrate in the dark for

56 hours in a constant temperature bath. After this period a base line

was run of the solution in one cm cells placed in both the reference and sample compartment. The cells were balanced so that at 268 nm, where there is a peak in the $PtBr_4^{2-}$ spectrum, the absorbance was 0.0. The spectrophotometer was then "held on" this wavelength. The aquation reaction was then followed by observing the disappearance of the peak. The change of absorbance at 268 nm between that at 2 minutes into the reaction and five half lives later was ca. 0.5. This method was based on the procedure followed by Elding, who performed an aquation rate study of $PtBr_4^{2-}$ in the presence of varying concentrations of HBr (33). Figure 5 was copied directly from Elding's publication. Although the ionic strength medium was different (his was .5 M with $HClO_4$), there was no observable difference between the spectra shown and what was observed in this work.

Two hundred ml of the solution was separated from the rest and put into an amber glass stopper Erlenmeyer flask. The reaction was begun when enough solid Rb_2PtBr_4 was added to the solution to make it .1 mM. The solid crystals, which were weighed precisely, were placed in a 100 ml flask. Part of the 200 ml of solution was poured into the smaller flask with the crystals, swirled until the crystals were dissolved returned to the larger flask and inverted until the solution was homogeneous. The timer was begun when it appeared that ca. half of the Rb_2PtBr_4 was dissolved, thus putting a 5 to 10 second uncertainty in the initial time. After washing the sample spectrophotometric cell several times with the solution, it was filled and returned to the thermostated cell block. The trace of absorbance vs time was begun at this time -- some two minutes into the reaction. The reaction was then followed for over five half times so a Guggenheim plot of
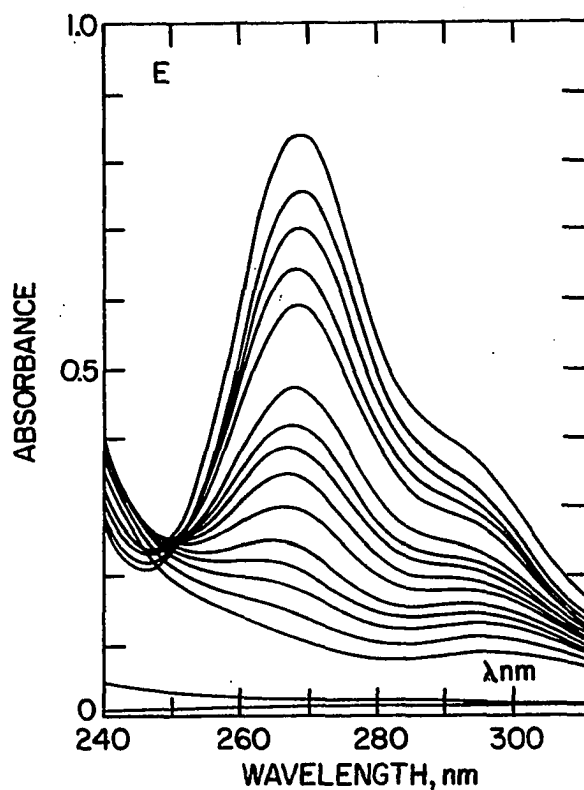
Figure 5. Absorption spectra of solutions of K_2PtBr_4, equilibrated at
25°C, having C_{Pt} = 9.99 x 10^{-5} (M) and the following total
concentrations of bromide (from above): 100.4, 10.40, 6.40,
4.40, 3.40, 2.000, 1.600, 1.400, 1.200, 1.000, 0.800, 0.700,
0.600, 0.500, and 0.400 mM. The top curve represents
approximately the spectrum of $PtBr_4^{2-}$ (98% of the platinum is
present as this species). The two bottom curves represent the
absorbance or solutions containing (a) HBr (0.100 M) and
$HClO_4$ (0.400 M) and (b) $HClO_4$ (0.500 M). The cell thickness
was 1 cm. The blank contained 0.500 M $HClO_4$. Thus, the top
curve should be corrected, for the absorbance of free
bromide.

$\ln(A_t - A_{t+\tau})$ vs time could be drawn.

Isotopic exchange - cis-Pt(NH$_3$)$_2$Br$_2$

An aliquot of $\overset{*-}{Br}$ was added to equilibrated solutions and its distribution into Pt(NH$_3$)$_2$Br$_2$ was determined by following the reaction at various intervals. For the determinations, an ion exchange procedure was employed to remove both Br$^-$ and PtBr$_4^{2-}$ from solution. Bromide was then stripped from the complex by ammonia and precipitated as Hg$_2$Br$_2$ by the addition of Hg$_2$(ClO$_4$)$_2$. The samples of Hg$_2$Br$_2$ were weighed and counted on a NaI crystal. Exchange was followed in both the presence and absence of PtBr$_4^{2-}$. Two types of experiments were possible when PtBr$_4^{2-}$ was present. In the first case PtBr$_4^{2-}$ was initially tagged with active bromide in the second it was not. Bromide exchange experiments were performed at both 25° and 35°C.

Exchange in the absence of Rb$_2$PtBr$_4$

Calculated amounts of cis-Pt(NH$_3$)$_2$Br$_2$, KBr, and NaNO$_3$ were weighted to the nearest .1 mg and placed in a 1000 ml volumetric flask. After the flask was filled to the line with distilled water, it was wrapped with black vinyl electrical tape. The solution was stirred for 12-18 hours on a magnetic stirrer and then left to equilibrate for 24-48 hours in a constant temperature bath.

The timer was started when 50λ of radioactive tracer was added to the flask. This small amount changed neither the volume of the solution nor the concentration of bromide. The flask was inverted again and again for 1/2 a minute. At this point the first fraction was removed by pouring

about 75 ml of solution into a 150 ml beaker. The volumetric flask was
then returned to the constant temperature bath to await removal of the
next fraction. The reaction was quenched by passage through an ion
exchange resin in the nitrate form. The negatively charged bromide ions
were exchanged in the resin for nitrate. When the last of the 75 ml of
solution was at the top of the resin bed, the time was recorded and
elution with distilled water, used to wash out the 150 ml beaker, was
begun. Washing and elution was continued until 300 ml of solution were
collected in the 400 ml beaker at the bottom of the column. Fifty ml of
concentrated aqueous ammonia and 4-6 glass beads were put into the beaker.
It was covered with Fisher Speedy Vap watch glass and put on a hot plate
to evaporate. A period of ca. 1 1/2 minutes elapsed between the time the
fraction was withdrawn until the time was recorded. The time lapse of the
entire process was 6 minutes. Succeeding points were treated in the same
manner.

Infinity-time samples were taken any time during the run by removing
a small volume of the solution (the volume depending on the concentration
of the species containing bromide), adding water, and dividing it into 4
different beakers. Ammonia and glass beads were added and they were put
on a hot plate to evaporate as any other sample. This method could be
utilized because the specific activity of bromide in all forms is equal at
infinite time. This means that since the sum of the activity of bromide in
all forms divided by the weight of the bromide in all forms will remain
constant throughout the run, the specific activity of $Pt(NH_3)_2Br_2$ at
infinite time will equal the combined specific activity of bromide in all

forms at any time.

The solutions were evaporated while boiling on the hot plate, adding ammonia intermittently, until their volume had diminished to 50 ml. The ammonia was added for two purposes, firstly to strip the bromide off of the platinum complex

$$Pt(NH_3)_2Br_2 + 2NH_3 \longrightarrow Pt(NH_3)_4^{2+} + 2Br^- \tag{17}$$
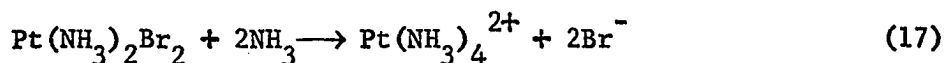
and secondly to maintain a high pH of the solution so there would be no loss of bromide through evolution of HBr.

After the solutions had cooled and were filtered to remove the glass beads, they were acidified with concentrated nitric acid. Precipitation of Hg_2Br_2 was initiated by the addition of a few drops of .1 M $Hg_2(ClO_4)_2$ solution. The beakers were then stored in the dark for several hours so that the precipitate could settle.

The precipitates were collected on previously weighed filter disks and allowed to dry for no less than four hours after washing with water, ethanol, and ether. Four tare disks, which also had been weighed previously, were carried through the same processes as those which contained the samples (34). The tare weights were of the order of 1 to 20% of those of the samples depending on atmospheric conditions.

After the weight of each sample was determined, the filter disks were mounted on cardboard squares, and counted for 1 to 30 minutes (the time differential being so that at least 10,000 disintegrations would be observed). The time each count was begun was noted. Because of the relatively short half life of Br^{82} (35.5 hours), a decay correction was applied to the counting rate of each sample. The specific activity of

each sample was determined by dividing each counting rate by the weight of the sample.

Anion exchange resins were used successfully for the analogous cis-Pt$(NH_3)_2Cl_2$ and several other neutral and positively charged platinum(II) complexes without this complicated and time consuming precipitation procedure (2, 35, 36, 37). In these systems it was possible to collect the effluent from the resin and then count Br^{82} from an aliquot of it. Gano found that such a procedure was unsuccessful in this system, however (30). The complex was not eluted quantitatively from the column with any practical amount of wash water. Hence, the procedure described herein, as slightly modified from Gano's, was adopted.

Exchange in the presence of Rb$_2$PtBr$_4$

When $PtBr_4^{2-}$ was initially untagged the procedure is exactly as described as above with the exception that a calculated amount of Rb$_2$PtBr$_4$ was also weighed and entered in the flask along with Pt$(NH_3)_2Br_2$, KBr, and NaNO$_3$.

When $PtBr_4^{2-}$ was initially tagged a slightly modified procedure was needed. The amount of Rb$_2$PtBr$_4$, KBr, and NaNO$_3$ needed for the correct concentrations of a 1,000 ml volume were weighed and the flask was filled to the line with water. After these salts were completely dissolved and the solution was made homogeneous by stirring, 200 ml of the solution was transferred to a 250 ml amber erlenmeyer flask fitted with a glass stopper. The calculated amount of Pt$(NH_3)_2Br_2$ was then washed into the 1,000 ml volumetric flask with ca. 150 ml of the solution which had been initially

separated. This washing was made necessary by the hydrophobic nature of cis-$Pt(NH_3)_2Br_2$. The solution containing $Pt(NH_3)_2Br_2$ was stirred until the complex was completely dissolved and then left in a constant temperature bath. To the remaining 50 ml was added 50λ of tagged bromide; this solution was then also left in a constant temperature bath for 48 hours to equilibrate.

The timer was activated at the instant the two solutions were mixed. From that point the procedure was as previously described.

Isotopic exchange - $PtBr_4^{2-}$

The incorporation of radioactive bromide into $PtBr_4^{2-}$ was observed with and without the presence of $Pt(NH_3)_2Br_2$ at 25° and 35°C. A precipitation technique was used to quench the reaction; $[As(C_6H_5)_4]Cl$ removed both $PtBr_4^{2-}$ and $PtBr_3(H_2O)^-$ from solution. The precipitated samples were quickly filtered and allowed to dry for later radioactivity counting on a NaI crystal.

Exchange in the absence of $Pt(NH_3)_2Br_2$

A solution containing the proper amounts of Rb_2PtBr_4, KBr, and $NaNO_3$ was prepared in a 100 ml volumetric flask. So that duplicate runs could be performed, half of the solution was transferred to a second 100 ml volumetric flask. Both flasks were wrapped with opaque tape to exclude light. The solutions were allowed to equilibrate 24-36 hours.

The timer was activated when a 10λ "spike" of radioactive bromide was added to the flask. After inverting the flask ten times, the flask

was returned to the constant temperature bath and 2 ml aliquots were removed at intervals for analysis. The reaction was quenched by precipitation of $PtBr_4^{2-}$ + $PtBr_3(H_2O)^-$ upon the addition of a 10% solution of ϕ_4AsCl. It was found essential to separate the solution as quickly as possible from the precipitates so that exchange between the precipitates and free Br^- might be avoided. The procedure used to accomplish filtration in less than 15 seconds after precipitation follows. The tetraphenyl-arsonium chloride solution was kept cold by storing its flask in an ice bath. Two ml of the solution was withdrawn and placed on the filter paper inside the chimney filter. A slight positive pressure was kept in the filter flask so the solution would remain over the filter paper. Another 2 ml pipette was utilized for the removal of an aliquot from the reaction vessel. The precipitation was instantaneous when the second solution was dropped over the ϕ_4AsCl solution. The precipitate was filtered, washed with ice cold water, and then allowed to dry. Infinity time samples were removed after ten half lives and treated as any other sample.

When all samples were collected, they were taped to cardboard squares and counted in the same manner as were Hg_2Br_2 samples used for $Pt(NH_3)_2Br_2$ exchange experiments.

Exchange in the presence of $Pt(NH_3)_2Br_2$

When $Pt(NH_3)_2Br_2$ was initially untagged the procedure was exactly as above but $Pt(NH_3)_2Br_2$ was also added to solution and because of its limited solubility the flask had to be stirred for 12-18 hours to dissolve all of the complex. Infinity times were taken when the much slower bromide-

exchanger, cis-Pt$(NH_3)_2Br_2$ had reached isotopic equilibrium. The system was not in isotopic equilibrium until this time.

In experiments where Pt$(NH_3)_2Br_2$ was initially tagged, a 100 ml solution was prepared containing Pt$(NH_3)_2Br_2$, KBr, and NaNO$_3$. After complete dissolution, 51 ml were removed from the flask and the amount of Rb$_2$PtBr$_4$ needed to prepare a 50 ml solution of the concentration of PtBr$_4^{2-}$ desired was added to the flask containing 49 ml of solution. To the flask containing 51 ml of solution, 50$^\lambda$ of bromide tracer was added. Both flasks were allowed to equilibrate for 3-4 days. Active bromide exchange was initiated when 1 ml of tagged bromide solution was discharged with a syringe into the flask containing the 49 ml of PtBr$_4^{2-}$ solution. After this point the procedure was the same as that when no Pt$(NH_3)_2Br_2$ was present.

Treatment of Isotopic Exchange Data

Cis-Pt$(NH_3)_2Br_2$ exchange

The specific activity of each sample was calculated by dividing the counting rate in counts per minute by the weight in grams of Hg$_2$Br$_2$ in that sample. The fraction of exchange of that sample, F, was then calculated by dividing the specific activity of that sample by the average specific activity of the infinity samples. The function ln(1-F) was then plotted vs time.

PtBr$_4^{2-}$ exchange

The specific activity of each sample was determined directly from counting rate data and was in units of cpm/2 ml of solution. The ratio

of the specific activity of each sample and that of the average infinite

time specific activity was F, the fraction of exchange. The function

ln(1-F) was then plotted against time.

A weighted least squares program was utilized to find a "best fit"

straight line through the experimental data. The log (1-F) values were

weighted in proportion to $1/\sigma^2$ by an error propagation which assumed a 5%

error in the counting rate and a .5 mg weighing error on each sample

(including the infinity-time samples). Although this method sounded

reasonable, the earlier points (those with a small F value) were weighted

much higher than later ones. Intuitively this large range of weights

(in some cases over five powers of ten) seemed unreasonable.

It was determined that there was an average variation in the intercept

of the log (1-F) vs time plots of ca. .01 throughout the 50 or so

experiments that were performed. This .01 variation in log (1-F) was then

propagated with the other assumed errors to find a new set of weights for

each experiment. The weights calculated in this manner seemed more

reasonable (varying only over 2 powers of 10) to the actual spread of the

observed points.

TREATMENT OF DATA AND RESULTS

Aquation Equilibria

Cis-Pt(NH$_3$)$_2$Br$_2$

Although the first and second aquation equilibrium quotients of
cis-dibromodiammineplatinum(II) (defined in Equations 18 and 19) had
already been determined under the same conditions as this work was
performed, it was felt that better values could be obtained because of the
new automatic titration system which was now available.

$$\text{Pt(NH}_3)_2\text{Br}_2 + \text{H}_2\text{O} \xrightarrow{K_{1(a)}} \text{Pt(NH}_3)_2\text{Br(H}_2\text{O)}^+ + \text{Br}^- \tag{18}$$

$$\text{Pt(NH}_3)_2\text{Br(H}_2\text{O)}^+ + \text{H}_2\text{O} \xrightarrow{K_{2(a)}} \text{Pt(NH}_3)_2(\text{H}_2\text{O})_2^{2+} + \text{Br}^- \tag{19}$$
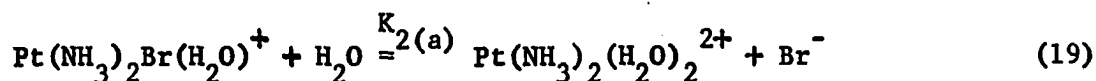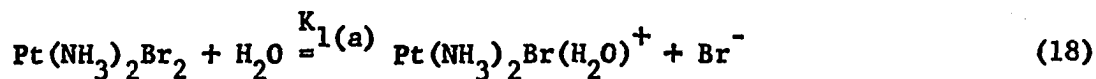
Before this instrument's arrival each point on the potentiometric
titration curve was determined by a separate sample. This procedure was
required because the aquation reaction formed more of the hydrolized
species as a manual titration was continued. It was thus impossible to
find the true equilibrium concentration of the aquated complexes using a
single solution. In this previous procedure an amount of base was added
to a solution. After a short but fixed time to allow electrode equilibra-
tion the pH was read and the solution was discarded. To a fresh solution
a larger amount of base was added; this new pH read and so on. Gano's
values (30) are reported below:

at 25° $\quad K_{1(a)} = 9.6 \pm .8 \times 10^{-4}$ M $\quad K_{2(a)} = 9 \pm 2 \times 10^{-5}$ M

at 35° $\quad\quad\quad = 11.9 \pm 1.0 \times 10^{-4}$ M $\quad\quad = 15 \pm 3 \times 10^{-5}$ M

A typical titration curve of a 20 milliliter equilibrated aqueous solution of $Pt(NH_3)_2Br_2$-Br^- is presented in Figure 6. At $25°C$ the pK_a of $Pt(NH_3)_2Br(H_2O)^+$ was ca. 7 -- the same value as reported by Gano, et al. -- the pK_a had dropped to ca. 6.5 at $35°C$. The pK_a is defined as the base 10 logarithm of the inverse of the equilibrium quotient for the dissociation of the acid under study. It was determined as the pH at the half neutralization point of the titrations.

The second derivative method was utilized in finding neutralization points, which are in fact the inflection point of the curves (38, p. 552). An example of the procedure follows for the titration curve shown in Figure 6 and Table 2. The pH was read from the recorded titration curve every 2% units around the end point and then a linear interpolation was made between the two where the $\Delta^2 pH$ changed sign.

Table 2. Second derivative method for finding the end point of an acid base neutralization as performed on the titration curve shown in Figure 6; temperature = $25°C$; $[NaOH]$ = 1.07×10^{-4} mmoles/% vol.; 100% = .25 ml

Volume (%)	pH	ΔpH	$\Delta^2 pH$	End Pt
27	7.60			
		30		$\% V = 29 + 2\ (\frac{10}{24})$
			+10	
29	7.90			= 29.83
		40		
			-14	
31	8.30			
		26		
33	8.56			

Figure 6. A typical titration of <u>cis</u>-Pt(NH$_3$)$_2$Br$_2$ solution. Base strength = 1.07 x 10^{-4} moles/% (.0429M)

When the NaOH solution was standardized with KHP, it was possible to use 1% divisions because of the sharpness of the end point.

It was found that because of the small amount of acid titrated and the fact that the pH at the end point was always greater than 8.0 a blank had to be subtracted from the amount of base used to neutralize the acid. This blank is explained as the amount of base needed to bring a solution containing none of the complex to the pH of the end point. This is, in fact, the method with which it was assessed. In the case of the typical experiment, the blank was 3.6%. The titer for this typical experiment was then equal to

$$\frac{(29.8 - 3.6\%) \times 1.07 \times 10^{-4} \text{ mMoles/}\%}{2 \times 10^{-2}1} = .140 \text{ mM.}$$

The equilibrium quotients, $K_{1(a)}$ and $K_{2(a)}$, may be represented in terms of the concentrations the species involved for a specific ionic strength.

$$K_{1(a)} = \frac{[Pt(NH_3)_2Br(H_2O)^+][Br^-]}{[Pt(NH_3)_2Br_2]} \qquad (20)$$

$$K_{2(a)} = \frac{[Pt(H_2O)_2^{2+}][Br^-]}{[Pt(NH_3)_2Br(H_2O)^+]} \qquad (21)$$

The procedure in determining these equilibrium quotients from titers was presented by Sanders and Martin (39) in 1960. Following is the derivation.

$$a = \text{Total } [Pt(NH_3)_2Br_2]_0 = [Pt(NH_3)_2Br_2] + [Pt(NH_3)_2(H_2O)^+]$$
$$+ [Pt(NH_3)_2(H_2O)_2^{2+}] \qquad (22)$$

$$b = \text{bromide added to solution initially} \qquad (23)$$

T = titer = total acid in solution

$$= \left[Pt(NH_3)_2 Br(H_2O)^+ \right] + 2\left[Pt(NH_3)_2(H_2O)^{2+} \right] \quad\quad (24)$$

$\left[Br^- \right]$ = total bromide in solution

$$= b + T \quad\quad (25)$$

From the equilibrium quotients the concentrations $\left[Pt(NH_3)_2 Br(H_2O)^+ \right]$ and $\left[Pt(NH_3)_2(H_2O)_2^{2+} \right]$ can be expressed as functions of $\left[Pt(NH_3)_2 Br_2 \right]$ and $\left[Br^- \right]$:

$$T = \left[Pt(NH_3)_2 Br_2 \right] \left(\frac{K_{1(a)}}{\left[Br^- \right]} + \frac{2 K_{1(a)} K_{2(a)}}{\left[Br^- \right]^2} \right) \quad\quad (26)$$

$$a = \left[Pt(NH_3)_2 Br_2 \right] \left(1 + \frac{K_{1(a)}}{\left[Br^- \right]} + \frac{K_{1(a)} K_{2(a)}}{\left[Br^- \right]^2} \right) \quad\quad (27)$$

From these expressions for T and a

$$\frac{T}{a} = \frac{\dfrac{K_{1(a)}}{\left[Br^- \right]} + \dfrac{2 K_{1(a)} K_{2(a)}}{\left[Br^- \right]^2}}{1 + \dfrac{K_{1(a)}}{\left[Br^- \right]} + \dfrac{K_{1(a)} K_{2(a)}}{\left[Br^- \right]^2}} = \frac{\left[Br^- \right] K_{1(a)} + 2 K_{1(a)} K_{2(a)}}{\left[Br^- \right]^2 + \left[Br^- \right] K_{1(a)} + K_{1(a)} K_{2(a)}} \quad\quad (28)$$

When the expression for $\left[Br^- \right]$ of (25) is substituted into Equation (28), rearrangement yields:

$$T \cdot \left[(b + T)^2 + (b + T) K_{1(a)} + K_{1(a)} K_{2(a)} \right] = a \left[(b + T) K_{1(a)} + 2 K_{1(a)} K_{2(a)} \right] \quad\quad (29)$$

Further rearrangement of terms yields:

$$T^3 + (2b + K_{1(a)}) T^2 + (b^2 + K_{1(a)} b + K_{1(a)} K_{2(a)} - K_{1(a)} a) T$$
$$+ (-K_{1(a)} ab - 2 K_{1(a)} K_{2(a)} a) = 0 \quad\quad (29')$$

Equation (29) is a function of three variables (a, b, and T) and two

parameters $(K_{1(a)}$ and $K_{1(a)}K_{2(a)})$. A computer program written by Ronald

Coley (40) was designed to perform a weighted least squares analysis of

aquation equilibria of a disubstitutable complex. The method of least

squares adjustment applied was a minimization of the sum of the weighted

squares of the differences between the experimentally determined and the

least squares adjusted value of T. This program was only designed, however,

on the basis of two variables (a and T) with no provision for addition or

variation of free bromide. It seemed that high added bromide concentrations

experiments were quite important since at high bromide the second aquation

would be suppressed so that $K_{1(a)}$ could be measured independently and

therefore with greater assurance. With the guidance of a paper by Wentworth

(41), the computer program was redesigned to handle three variables.

Following in Tables 3 and 4 are the results of aquation equilibria study

at 25° and 35°. The equilibrium quotients for the aquation reactors along

with their standard thermodynamic quantities calculated through the standard

equations:

$$\Delta H^{\circ} = R(\ln K_{\alpha}/K_{\beta})(\frac{T_{\beta} T_{\alpha}}{T_{\beta}-T_{\alpha}}) \tag{30}$$

$$\Delta G^{\circ} = R\, T\, \ln K^{\circ} = -RT \ln K + RT \ln \Gamma_{(\mu)} \tag{31}$$

and $$\Delta S^{\circ} = \frac{-\Delta G^{\circ} + \Delta H^{\circ}}{T}, \tag{32}$$

where $\Gamma_{(\mu)} = \Pi\gamma$ products$/\Pi\gamma$ reactants and the γ's were estimated by the

procedure described by Coley (40), are found in Table 5.

Table 3. Aquation equilibria of $Pt(NH_3)_2Br_2$ results at $25^{\circ}C$; a and b are
as defined in Equations 22 and 23

| a(mM) | b(mM) | T(mM) | | % Diff |
		Obsd.	Calcd.	
1.500	0.00	0.8825	0.8938	1.265
1.500	2.00	0.4760	0.4831	1.463
1.500	5.00	0.2700	0.2691	0.332
1.500	10.00	0.1490	0.1517	1.754
1.500	20.00	0.0828	0.0804	3.024
1.500	30.00	0.0567	0.0546	3.859
1.500	40.00	0.0436	0.0413	5.509
1.500	50.00	0.0349	0.0332	4.994
1.200	0.00	0.7609	0.7682	0.950
0.900	0.00	0.6364	0.6290	1.177
0.750	0.00	0.5572	0.5525	0.847
0.600	0.00	0.4802	0.4703	2.103
0.375	0.00	0.3421	0.3316	3.174
0.150	0.00	0.1784	0.1635	9.122

Teggins, et al. (12) investigated the aquation equilibria of

tetrabromoplatinate(II) at $25^{\circ}C$ and ionic strengths of .318 and .1 M.

They were only able to find a $K_{1(c)}$ term although there was spectrophoto-

metric evidence of not only a $K_{2(c)}$ term but also dimerization equilibrium.

Grinberg and Shagisultanova (42) had previously reported a value for $K_{1(c)}$

Table 4. Aquation equilibria of $Pt(NH_3)_2Br_2$ results at 35^oC; a and b are as defined in Equations (22) and (23)

a(mM)	b(mM)	T(mM) Obsd.	Calcd.	% Diff
1.50	0.00	0.955	0.9762	2.173
1.20	0.00	0.827	0.8382	1.338
0.90	0.00	0.684	0.6858	0.258
0.75	0.00	0.603	0.6024	0.105
0.60	0.00	0.520	0.5127	1.419
0.45	0.00	0.413	0.4147	0.408
0.30	0.00	0.311	0.3055	1.792
0.15	0.00	0.187	0.1786	4.719
1.50	1.50	0.630	0.6286	0.230
1.50	3.00	0.462	0.4494	2.803
1.50	6.00	0.267	0.2796	4.519
1.50	9.00	0.204	0.2013	1.354
1.50	15.00	0.139	0.1284	8.261

Table 5. Aquation equilibrium quotients for $Pt(NH_3)_2Br_2$ at μ = .05 M

	$K_{1(a)}$	$K_{2(a)}$
25°	$1.13 \pm .02 \times 10^{-3} M$	$4.2 \pm .6 \times 10^{-5} M$
35°	$1.40 \pm .02 \times 10^{-3} M$	$7.5 \pm .6 \times 10^{-5} M$
ΔH^o	$3.9 \pm .2$ kcals/mole	10 ± 3 kcals/mole
ΔG^o	$3.38 \pm .04$ kcals/mole	$5.1 \pm .9$ kcals/mole
ΔS^o	$1.7 \pm .8$ e.u.	16 ± 13 e.u.

in 1960. Elding (33) has recently also reported a value at 25° and 35°.

The values for these different determinations of the first aquation

equilibrium quotient of $PtBr_4^{2-}$, $K_{1(c)}$ as defined in Equation (30), may

be found in Table 6.

$$PtBr_4^{2-} + H_2O \overset{K_{1(c)}}{=} PtBr_3(H_2O)^- + Br^-$$ (33)

$$PtBr_3(H_2O)^- + H_2O \overset{K_{2(c)}}{=} PtBr_2(H_2O)_2 + Br^-$$ (34)
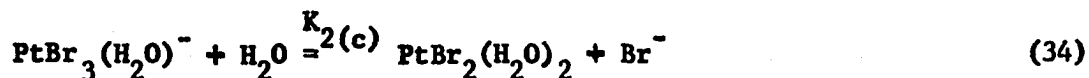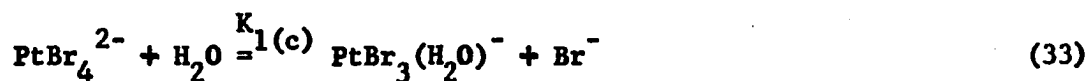
Table 6. Values of the first aquation equilibrium quotient of $PtBr_4^{2-}$ determined by different workers

Workers	$K_{1(c)}$ x 10^3 M	μ(Ionic strength) M	Temperature ^OC
Teggins, et al. (12)	2.6	.318	25°
	2.8	.1	25°
G. and S. (42)	3	--	25°
Elding (33)	1.8	.5	25°
	2.6	.5	35°

The technique for measuring the aquation equilibria of $PtBr_4^{2-}$ was

the same as described for $Pt(NH_3)_2Br_2$, and the titration curve were of

the same nature. The only difference being that the pK_a for $PtBr_3(H_2O)^-$

is ca. 7.5 at 25° and 7.0 at 35^OC. The effect of the higher pK_a values

was to flatten out the curves and make end point determinations more

difficult.

At 25° only a $K_{1(c)}$ term was found. When a $K_{1(c)}$ - $K_{2(c)}$ fit was

attempted, $K_{2(c)}$, defined by Equation (34), was calculated to be a negative

value. When the $K_{1(c)}$ only fit was applied there was little loss of agreement between calculated and experimental values of titer and there was no significant change in the value of $K_{1(c)}$.

At $35^{\circ}C$, a positive $K_{2(c)}$ was calculated when a $K_{1(c)}$- $K_{2(c)}$ fit was applied to the titration data. There was a noticeably less satisfactory fit when $K_{2(c)}$ was neglected. Elding (33) reported the values of $K_{2(c)}$ at both 25° and $35^{\circ}C$.

$$K_{2(c)} = 2.5 \pm .03 \times 10^{-4} M \quad 25^{\circ} \tag{35}$$

$$K_{2(c)} = 3.6 \pm .03 \times 10^{-4} M \quad 35^{\circ} \tag{36}$$

The reason a second aquation equilibrium quotient was found at $35^{\circ}C$ and not at $25^{\circ}C$ could be that although the standard practice was to perform titrations 2 days after the solutions were prepared, because of technical difficulty the solutions were stored in the dark for ca. two weeks before titration in the case of the $35^{\circ}C$ work. This is the amount of time Elding stored his solutions. The value of $K_{2(c)}$ he reported is more than three times the value found by this author. Since there is no ionic strength dependence for this reaction (Equation 34), the differing values are most likely caused by the differing methods of determination (potentiometric vs spectrophotometric). Tables 7 and 8 record the results of titrations of $PtBr_4^{2-}$ solutions at 25° and $35^{\circ}C$. The equilibrium constants and their thermodynamic parameters are found in Table 9.

Table 7. Aquation equilibria of $PtBr_4^{2-}$ results at 25^oC; a and b are as defined in Equations (22) and (23) but for the $PtBr_4^{2-}$ system

a (mM)	b (mM)	T (mM)		% Diff
		Obsd.	Calcd.	
3.00	0.00	1.670	1.7737	5.847
3.00	1.60	1.370	1.4065	2.597
3.00	3.00	1.150	1.1467	0.291
3.00	6.00	0.860	0.8200	4.872
3.00	12.00	0.550	0.5105	7.734
3.00	15.00	0.470	0.4277	9.878
3.00	18.00	0.370	0.3677	0.633
3.00	24.00	0.280	0.2866	2.313
3.00	30.00	0.220	0.2347	6.244
6.00	30.00	0.480	0.4660	3.001
4.80	30.00	0.360	0.3739	3.706
2.40	30.00	0.190	0.1880	1.070
1.20	30.00	0.100	0.0943	6.085

Table 8. Aquation equilibria of $PtBr_4^{2-}$ results at 35^oC; a and b are as defined in Equations (22) and (23) but for the $PtBr_4^{2-}$ system

a (mM)	b (mM)	T (mM)		% Diff
		Obsd.	Calcd.	
2.00	0.00	1.496	1.5258	1.955
1.50	0.00	1.198	1.2321	2.769
1.00	0.00	0.900	0.9027	0.299
0.80	0.00	0.770	0.7584	1.526
0.60	0.00	0.636	0.6052	5.090
0.40	0.00	0.470	0.4380	7.313
0.20	0.00	0.249	0.2481	0.351
2.00	1.50	1.165	1.2045	3.283
2.00	3.00	0.999	0.9861	1.310
2.00	4.50	0.878	0.8311	5.641
2.00	6.00	0.721	0.7150	0.839
2.00	7.50	0.631	0.6264	0.726
2.00	15.00	0.391	0.3832	2.028
2.00	30.00	0.150	0.2141	29.941

Table 9. Aquation equilibrium quotients for $PtBr_4^{2-}$ at $\mu = .05$ M

	$K_{1(c)}$	$K_{2(c)}$
25°	$2.56 \pm .04 \times 10^{-3}$ M	--
35°	$3.59 \pm .12 \times 10^{-3}$ M	$1.1 \pm .2 \times 10^{-4}$
ΔH^o	$6.1 \pm .5$ k cals/mole	--
ΔG^o	$3.77 \pm .05$ k cals/mole	--
ΔS^o	8 ± 2 e.u.	--

Bromide Exchange

<u>At 25°</u>

If the bromide concentration is maintained at a high level to suppress aquation, bromide is found in solution predominantly in the three forms: $Pt(NH_3)_2Br_2$, Br^-, and $PtBr_4^{2-}$. The symbols a, b, and c are used for the total concentration added to solution of <u>cis</u>-$[Pt(NH_3)_2Br_2]$, Br^-, and $[PtBr_4]^{-2}$ respectively, i.e.,

$$a = [Pt(NH_3)_2Br_2] + [Pt(NH_3)_2Br(H_2O)^-] + [Pt(NH_3)_2(H_2O)_2^{2+}] \qquad (37)$$

$$b = [Br^-] - [PtBr_3(H_2O)^-] - [Pt(NH_3)_2Br(H_2O)^+] - 2[Pt(NH_3)_2(H_2O)_2^{2+}]$$
$$(38)$$

$$c = [PtBr_4^{2-}] + [PtBr_3(H_2O)^-]. \qquad (39)$$

The first term in each equation is suitably approximated by the respective symbol, a, b, or c, when the bromide concentration is above .02 Molar.

As a solution is allowed to equilibrate, bromide in each of the three forms will exchange with bromide in the other two. When dynamic equilibrium is attained, the rate by which bromide moves from one form into another will be equal to the rate in which it returns. The following diagram depicts the situation in the system under study.

$$Pt(NH_3)_2Br_2 \quad \overset{R_{ac}}{\underset{R_{ac}}{\rightleftharpoons}} \quad PtBr_4{}^{2-} \tag{40}$$

$$R_{ab} \diagdown \diagdown R_{ab} \qquad\qquad R_{bc} /\!\!/ R_{bc}$$

$$Br^-$$
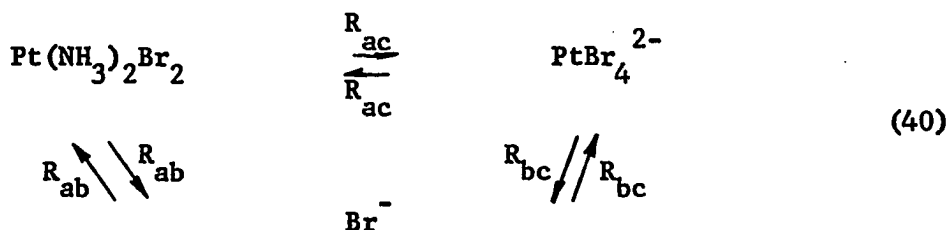
R_{ab} = rate that bromide is exchanged between $Pt(NH_3)_2Br_2$ and free

bromide   moles liter^{-1} sec^{-1}

R_{bc} = rate that bromide is exchanged between $PtBr_4{}^{2-}$ and free

bromide   moles liter^{-1} sec^{-1}

R_{ac} = rate that bromide is exchanged between the two complexes.

moles liter^{-1} sec^{-1}

Two independent differential equations are needed to describe isotopic exchange in such a three component system:

$$\frac{du}{dt} = R_{ab}(S_s - S_u) + R_{ac}(S_v - S_u) \tag{41}$$

$$\frac{dv}{dt} = R_{bc}(S_s - S_v) + R_{ac}(S_u - S_v) \tag{42}$$

where

u = concentration of activity (^{82}Br) in $Pt(NH_3)_2Br_2$ cpm/l

v = concentration of activity (^{82}Br) in $PtBr_4{}^{2-}$ cpm/l

I = total concentration of activity (^{82}Br)   cpm/l

S_u = specific activity of bromide in $Pt(NH_3)_2Br_2$ = u/2a

S_v = specific activity in $PtBr_4^{2-}$ = $v/4c$

S_s = specific activity of free bromide = $(I-u-v)/b$

The Runge-Kutta method of numerical integration (43, pp. 362, 363) was performed on this pair of differential equations for various concentrations of a, b, and c and initial tagging situations. From these calculations the curves of log(1-F) vs time were generated for both species, where:

$$F_u = \frac{u-u_0}{u_\infty-u_0} \qquad\qquad u_0 = u \text{ at time} = 0 \qquad (43)$$

$$u_\infty = u \text{ at time} = \infty$$

$$F_v = \frac{v-v_0}{v_\infty-v_0} \qquad\qquad v_0 = v \text{ at time} = 0 \qquad (44)$$

$$v_\infty = v \text{ at time} = \infty$$

Because of the nature of the system, F is not a simple fraction of exchange associated with a linear logarithmic function. It is not restricted to values between 0 and 1 and in many cases may be greater than 1.

It was found that the generated curves of ln(1-F) were very nearly linear for the time studied, so little was lost in comparing calculated and experimental times of half exchange. In this system times of half exchange for u are defined as the time when $F_u = \frac{1}{2}$; times of half exchange will be symbolized by $t_{\frac{1}{2}}$. The following is the basis for this method and that of the computer program written to execute it:

$$\frac{du}{dt} = f_1(t,u,v) \qquad (45)$$

$$\frac{dv}{dt} = f_2(t,u,v) \qquad (46)$$

The increments in u and v are found as follows:

$$k_1 = f_1(t_0, u_0, v_0)\Delta t \tag{47}$$

$$k_2 = f_1(t_0 + \frac{\Delta t}{2}, u_0 + \frac{k_1}{2}, v_0 + \frac{j_1}{2})\Delta t \tag{48}$$

$$k_3 = f_1(t_0 + \frac{\Delta t}{2}, u_0 + \frac{k_2}{2}, v_0 + \frac{j_2}{2})\Delta t \tag{49}$$

$$k_4 = f_1(t_0 + \Delta t, u_0 + k_3, v_0 + j_3)\Delta t \tag{50}$$

$$\Delta u = \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \tag{51}$$

$$j_1 = f_2(t_0, u_0, v_0)\Delta t \tag{52}$$

$$j_2 = f_2(t_0 + \frac{\Delta t}{2}, u_0 + \frac{k_1}{2}, v_0 + \frac{j_1}{2})\Delta t \tag{53}$$

$$j_3 = f_2(t_0 + \frac{\Delta t}{2}, u_0 + \frac{k_2}{2} m v_0 + \frac{j_2}{2})\Delta t \tag{54}$$

$$j_4 = f_2(t_0 + \Delta t, u_0 + k_3, v_0 + j_3)\Delta t \tag{55}$$

$$\Delta v = \frac{1}{6}(j_1 + 2j_2 + 2j_3 + j_4). \tag{56}$$

Succeeding points are found by:

$$t_i = t_{i-1} + \Delta t_{i-1} \tag{57}$$

$$u_i = u_{i-1} + \Delta t_{i-1} \tag{58}$$

$$v_i = v_{i-1} + \Delta t_{i-1}. \tag{59}$$

Before it was possible to employ the Runge-Kutta method on the differential Equations (41) and (42) it was necessary to find approximate values for the three rates of bromide exchange: R_{ab}, R_{bc}, and R_{ac}. The next section will describe how these rates were estimated so the Runge-Kutta method could be employed for further refinement.

R_{ab}, the rate that bromide is exchanged between $Pt(NH_3)_2Br_2$ and free bromide, may be considered the sum of two terms:

$$R_{ab} = R_{ab}{}^o + R_{ab}{}'. \tag{60}$$

$R_{ab}{}^o$ is the rate that bromide exchanges with $Pt(NH_3)_2Br_2$ in the absence of $PtBr_4{}^{2-}$. As was mentioned previously, an expression for $R_{ab}{}^o$ was proposed by Gano, et al. (13) but the fit of this function was not very satisfactory at high bromide concentrations. Because the larger fraction of this work was performed in the region of high bromide, the $R_{ab}{}^o$ terms used here were determined experimentally. $R_{ab}{}'$ is a term which includes involvement of $PtBr_4{}^{2-}$ with bromide exchange between that in solution and on $Pt(NH_3)_2Br_2$. This value may be estimated from the series of experiments where at zero time only the bromide and not $PtBr_4{}^{2-}$ is tagged with radioactive tracer.

$$\frac{du}{dt} = R_{ab}(S_s - S_u) + R_{ac}(S_v - S_u) \tag{41}$$

Initially both S_u and S_v are zero; therefore, at zero time:

$$\frac{du}{dt} = R_{ab}S_s^o \qquad\qquad S_s^o = \frac{I}{b} \tag{61}$$

$$S_\infty = \frac{u_\infty}{2a} = \frac{I}{2a+b+4c} \tag{62}$$

$$\text{or}\quad I = \frac{2a+b+4c}{2a}\, u_\infty \tag{63}$$

Substitution of the expressions for S_s^o and I into Equation (61) yields

$$\frac{du}{dt} = R_{ab}\frac{2a+b+4c}{2ab}\, u_\infty \tag{64}$$

$$\frac{d(u/u_\infty)}{dt} = \frac{dF_u}{dt} \quad\text{since } u_0 = 0 \tag{65}$$

therefore

$$R_{ab} = \left(\frac{2ab}{2a+b+4c}\right)\left[\frac{dF_u}{dt}\right]_{t=0}.$$ (66)

It is also true that

$$\left[\frac{dF_u}{dt}\right]_{t=0} = -\left[\frac{d\ln(1-F)}{dt}\right]_{t=0}.$$ (67)

This means that R_{ab} may be determined from the initial slope of $\ln(1-F)$ vs time plot of exchange data. Experimentally it was established that these functions appeared linear beyond one time of half exchange. Figure 7, which is a $\ln(1-F)$ vs time plot of a typical data set from this type of experiment, bears this out. The dashed line through the points is a linear weighted least squares fit which was previously described. Hence, these rates were calculated using the formula:

$$R_{ab} = \frac{2ab(.693)}{(2a+b+4c)t_{\frac{1}{2}}}.$$ (68)

At one bromide concentration according to Gano, et al. (13) the form of R_{ab}^{o} would be

$$k_{ab}^{o}\left[Pt(NH_3)_2Br_2\right].$$ (69)

R_{ab}' was assumed to have the form

$$k_{ab}'\left[Pt(NH_3)_2Br_2\right]\left[PtBr_4^{2-}\right].$$ (70)

Table 10 coordinates rate calculated using Equation (68) with variations in the tetrabromoplatinate(II) concentration when a and b were held constant at 1.5 and 30 mM throughout this set of experiments. The bottom line in Figure 8 is a plot of these values. According to the assumed rate law,
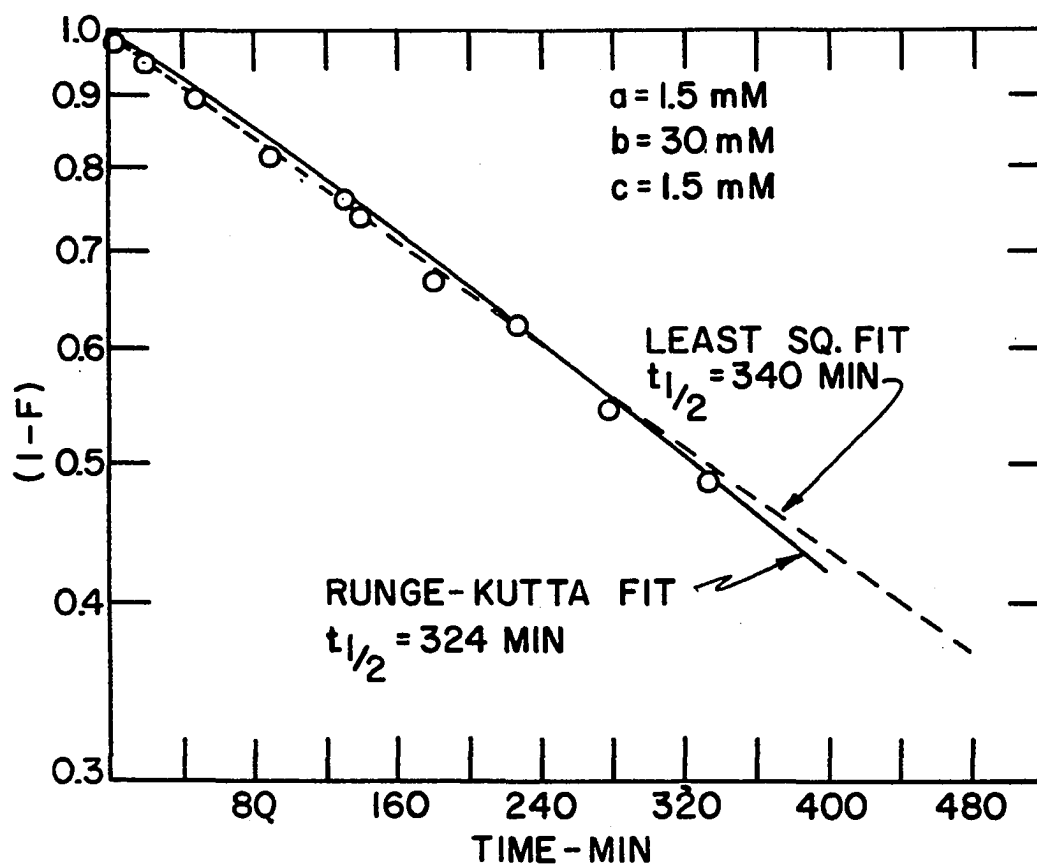
Figure 7. A typical isotopic exchange experiment where activity was followed going into $Pt(NH_3)_2Br_2$, $PtBr_4^{2-}$ was initially untagged ($S_v^o = 0$)

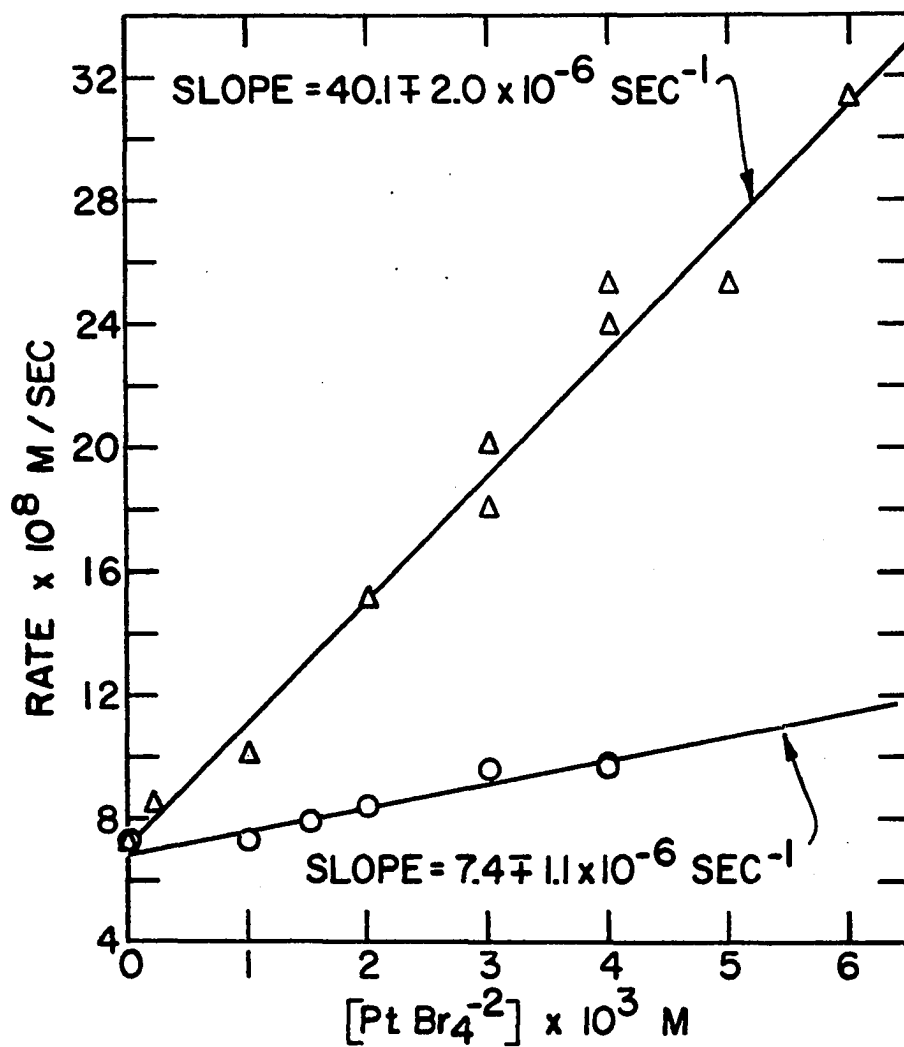Figure 8. Rates of bromide exchange at 25°C vs $[PtBr_4^{2-}]$; a = 1.5 mM; b = 30 mM. O: S_v^o = 0; Rate = R_{ab}. Δ: S_v^o = S_s^o; Rate = R_{ab} + R_{ac}

$$\text{the slope} = k_{ab}' \left[\text{Pt(NH}_3)_2\text{Br}_2\right]$$

$$= 7.4 \pm 1.1 \times 10^{-6} \text{ sec}^{-1} \tag{71}$$

$$\text{and the intercept} = R_{ab}^{o}. \tag{72}$$

From this set of experiments

$$k_{ab}' = 4.9 \pm .7 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}. \tag{73}$$

Table 10. Bromide exchange of $Pt(NH_3)_2Br_2$ vs $\left[\text{PtBr}_4^{2-}\right]$ at $25^{\circ}C$. $S_v^o = 0$; b = 30 mM; a = 1.5 mM

$\left[\text{PtBr}_4^{2-}\right]$ mM	$t_{\frac{1}{2}}$ min	$R_{ab} \times 10^8$ M sec^{-1}
0	436 ± 6	7.2 ± .1
1.0	387 ± 12	7.3 ± .2
1.5	340 ± 5	7.8 ± .1
2.0	304 ± 4	8.4 ± .1
2.5	386 ± 7	8.5 ± .2
3.0	240 ± 11	9.7 ± .4
4.0	219 ± 8	9.7 ± .4

Two additional sets of experiments were needed to establish $Pt(NH_3)_2Br_2$ participation in R_{ab}'. The first of these was a set of experiments where a was varied and b and c were held constant at 30 and 3 mM. The upper line in Figure 9 is a plot of R_{ab} calculated from these experiments vs
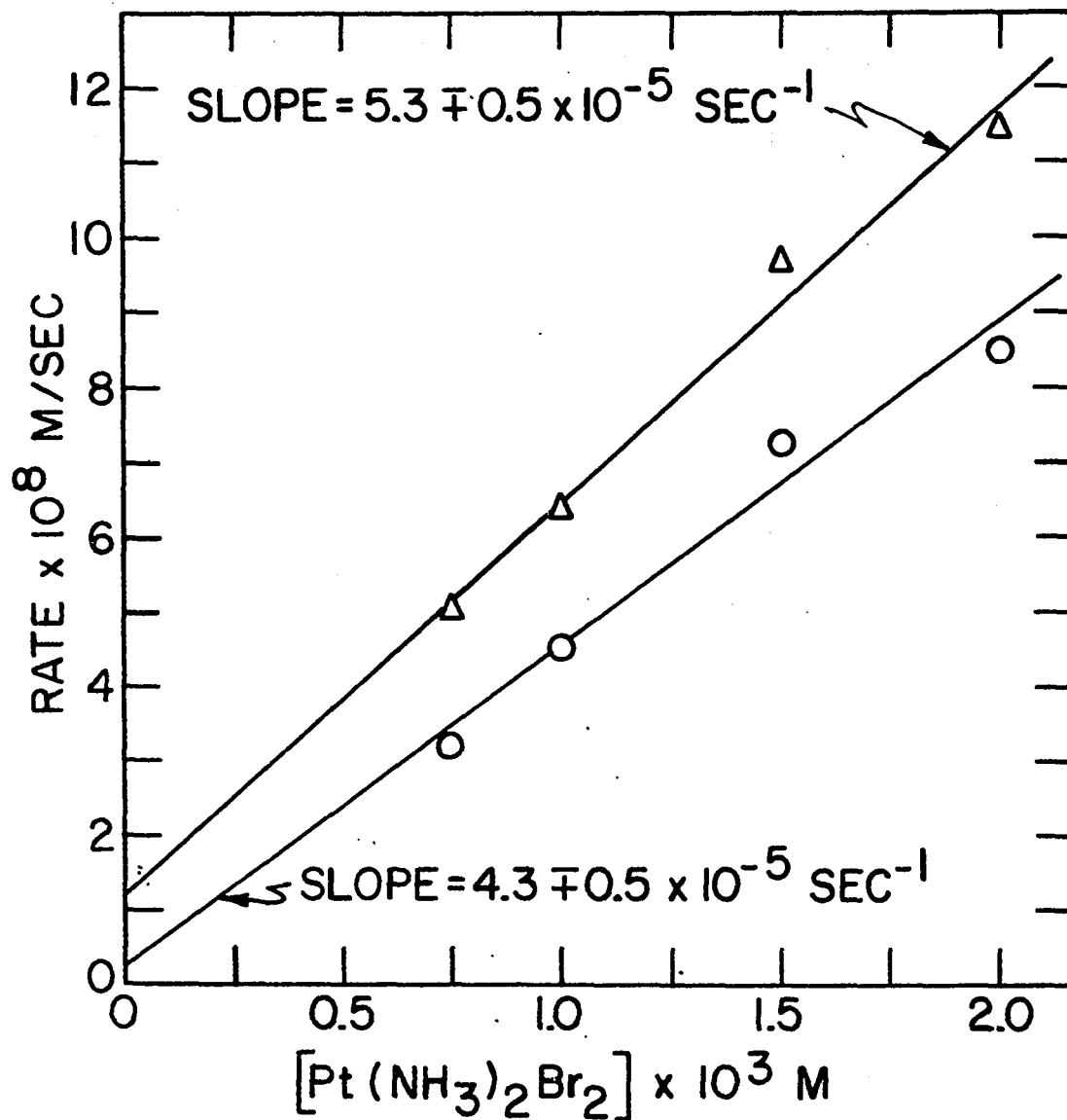
Figure 9. Rate of $Pt(NH_3)_2Br_2$-Br^- exchange at 25^oC vs $[Pt(NH_3)_2Br_2]$; $b = 30$. O, $c=o$. $\triangle$, $c = 3$ mM; $S_v^o = 0$

$\left[Pt(NH_3)_2Br_2\right]$.
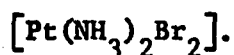
$$\text{The slope} = k_{ab}^{\,o} + k_{ab}^{\,'} \left[PtBr_4^{\,2-}\right]$$

$$= 5.3 \pm .5 \times 10^{-5} \text{ sec}^{-1}.$$

(74)

The second set of experiments was similar to the first in all things but the concentration of $PtBr_4^{\,2-}$, c in this set of experiments is zero. The lower line in Figure 9 is a plot of $R_{ab}^{\,o}$ vs $\left[Pt(NH_3)_2Br_2\right]$. Table 11 coordinates rates and concentrations for the two best experiments that are plotted in Figure 9.

Table 11. Bromide exchange of $Pt(NH_3)_2Br_2$ at $25^{\circ}C$ and $\mu = .05$ M vs $\left[Pt(NH_3)_2Br_2\right]$. $S_v^o = 0$ and $b = 30$ mM

$\left[Pt(NH_3)_2Br_2\right]$ mM	$\left[PtBr_4^{\,2-}\right]$ mM	$t_{\frac{1}{2}}$ min	Rate x 10^8 M sec^{-1}
.75	0	510 ± 6	3.24 ± .04
.75	3.0	240 ± 5	4.99 ± .10
1.0	0	478 ± 21	4.53 ± .20
1.0	3.0	254 ± 20	6.34 ± .50
1.5	0	436 ± 6	7.23 ± .10
1.5	3.0	240 ± 11	9.64 ± .44
2.0	0	471 ± 50	8.52 ± .90
2.0	3.0	264 ± 12	11.41 ± .52

The slope $= k_{ab}^{\ o}$

(75)

$$= 4.3 \pm .5 \times 10^{-5} \ sec^{-1}.$$

Subtracting the slope of the upper line from that of the lower one produces a value of

$$k_{ab}{}' = \frac{1 \pm 1 \times 10^{-5}}{[PtBr_4{}^{2-}]}$$

(76)

$$= 3 \pm 3 \times 10^{-3} \ M^{-1} \ sec^{-1},$$

which is consistent to the value produced by the R_{ab} vs $[PtBr_4{}^{2-}]$ plot $(4.9 \pm .7 \times 10^{-3})$ within the large experimental error. In a closer examination of Figure 9, it can be noted that the intercept of these lines should be zero. The intercept of the upper line would correspond to a catalyzed rate of bromide exchange in $Pt(NH_3)_2Br_2$ where there is no $Pt(NH_3)_2Br_2$ in the transition state. Because of the large error in this intercept $(1.2 \pm .7 \times 10^{-8})$, however, one should not speculate why it exists but rather if it exists.

The first term in the pair of differential equations (41 and 42) may now be given an approximate value:

$$R_{ab} = R_{ab}{}^{o} + 4.9 \times 10^{-3} \ a \ c.$$

(77)

For an estimation of R_{ac}, a set of experiments was performed in which the initial specific activity of the tetrabromoplatinate(II) was not zero but rather was equal to the specific activity of the free bromide in solution $(S_v^{o} = S_s^{o})$.

Looking again at Equation (41)

$$\frac{du}{dt} = R_{ab}(S_s - S_u) + R_{ac}(S_v - S_u), \qquad (41)$$

$$\text{at } t = 0 \quad S_s^o = \frac{I-v_o}{b} = S_v^o = \frac{v_o}{4c} = \frac{I}{b+4c} . \qquad (78)$$

With the assumption that the specific activities of Br^- and $PtBr_4^{2-}$ remain

equal throughout the run; or they both equal $\frac{I-u}{b+4c}$, the equation may be

simplified to:

$$\frac{du}{dt} = (R_{ab} + R_{ac})(\frac{I-u}{b+4c} - \frac{u}{2a}) \qquad (79)$$

This is an approximation, but a very good one. There are two reasons

for this. First, the amount of bromide present in $Pt(NH_3)_2Br_2$ is small

compared to the total bromide. In an average solution, $a = 1.5$ mM, $b = 30$

mM, $c = 3$ mM, $2a$ is only one-fifteenth of the total bromide (3/45). The

specific activity of the two other species may only vary from $\frac{I}{b+4c}$ to $\frac{14}{15}I/$

$(b+4c)$. The second reason is that bromide exchanges some 5 to 10 times

faster between $PtBr_4^{2-}$ and free bromide than between $Pt(NH_3)_2Br_2$ and free

bromide. This faster exchange rate keeps the specific activities of Br^-

and $PtBr_4^{2-}$ relatively similar as $Pt(NH_3)_2Br_2$ robs activity from both.

Rearrangement of (79) yields

$$\frac{du}{dt} = (R_{ab} + R_{ac})\left[\frac{I}{b+4c} - \frac{(2a + b + 4c)u}{2a(b+4c)}\right] \qquad (80)$$

the equation is now in the form

$$\frac{dx}{dt} = \beta + \alpha x, \text{ which may be integrated to:} \qquad (81)$$

$$\frac{\ln(\beta + \alpha u)}{-\alpha} \bigg|_0^u = (R_{ab} + R_{ac})t \qquad (82)$$

$$\ln\left[\frac{I}{b+4c} - \frac{(b+4c+2a)u}{2a(b+4c)}\right] - \ln\left[\frac{I}{b+4c}\right] = \frac{b+4c+2a}{2a(b+4c)}\left[R_{ab} + R_{ac}\right]t \qquad (83)$$

$$\ln\left[1 - \frac{u/2a}{I/(2a+b+4c)}\right] = -\frac{b + 4c + 2a}{2a(b + 4c)}(R_{ab} + R_{ac})t \qquad (84)$$

$$I/(2a + b + 4c) = u_\infty/2a \qquad (85)$$

$$\ln(1 - u/u_\infty) = -\frac{b + 4c + 2a}{2a(b + 4c)}(R_{ab} + R_{ac})t \qquad (86)$$

$$\text{at } F_u = 1/2 \quad R_{ab} + R_{ac} = \frac{\ln 2 \times 2a(b + 4c)}{(2a + b + 4c)t_{\frac{1}{2}}} \qquad (87)$$

Figure 10 is a ln(1-F) vs time plot of a typical experiment of this type.

From Table 12 and Figure 8, this time the upper line, the result can be seen that when rates calculated in this manner from experimental times of half exchange are plotted against the concentration of tetrabromo-platinate(II) present (a = 1.5 mM; b = 30 mM), a straight line fit produces a slope = $40.1 \pm 2.0 \times 10^{-6}$ sec^{-1}. If it is assumed that R_{ac} is of the form

$$R_{ac} = k_{ac}[Pt(NH_3)_2Br_2][PtBr_4^{2-}], \qquad (88)$$

the slope is equal to

$$(k_{ab}' + k_{ac})a;$$

$$\text{or} \quad k_{ac} = \frac{\text{slope}}{a} - k_{ab}' \qquad (89)$$

$$= 22 \pm 2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}.$$

It would then appear that R_{ac}, the second and fourth terms in the pair of differential equations (41 and 42), was now approximately known. However, a bromide dependence study was undertaken which showed k_{ac} to be a complex rate constant containing an inverse bromide concentration dependence:

$$k_{ac} = k_{ac}' + \frac{k_{ac}''}{[Br^-]}. \qquad (90)$$
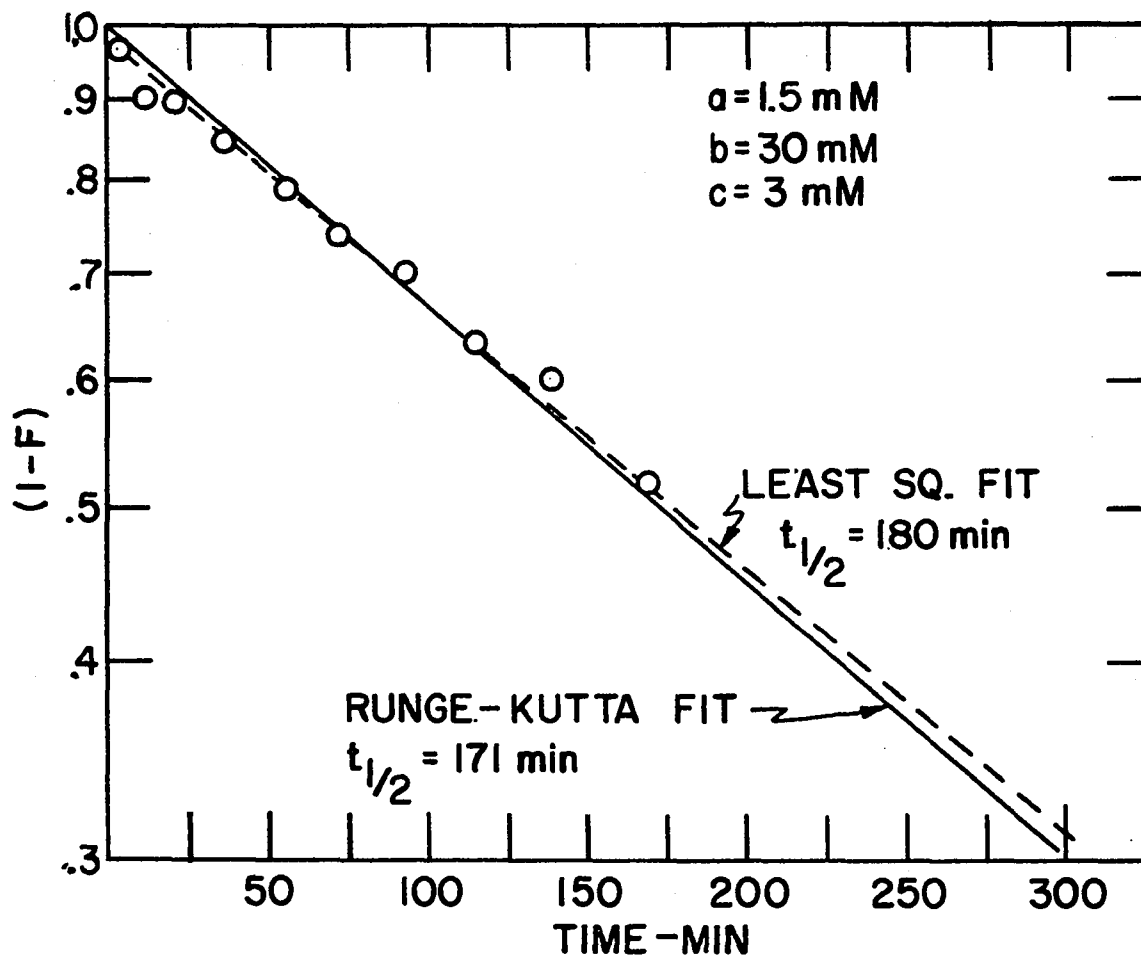
Figure 10. A typical isotopic exchange experiment at $25^{\circ}C$ where activity was followed growing into $Pt(NH_3)_2Br_2$. $PtBr_4^{2-}$ was initially tagged $(S_v^{o} = S_s^{o})$

Table 12. Bromide exchange of $Pt(NH_3)_2Br_2$ at $25^{\circ}C$ and $\mu = .05$ M vs $[PtBr_4{}^{2-}]$. $S_v^o \approx S_s^o$; a = 1.5 mM; b = 30 mM

$[PtBr_4{}^{2-}]$ mM	$t_{\frac{1}{2}}$ (min)	$(R_{ab} + R_{ac}) \times 10^8$ M sec^{-1}
0	436 ± 6	7.2 ± .1
.2	377 ± 23	8.4 ± .6
1.0	318 ± 11	10.0 ± .4
2.0	213 ± 2	15.1 ± .1
3.0	162 ± 5	20.0 ± .6
	180 ± 12	18.0 ± 1.2
4.0	129 ± 9	25.2 ± 1.9
	136 ± 5	23.9 ± 1.0
5.0	130 ± 6	25.2 ± 1.2
6.0	105 ± 2	31.3 ± .6

In this set of experiments both a = 1.5 mM and c = 3 mM were held constant. The initial specific activity of free bromide ions and $PtBr_4{}^{2-}$ were equal $(S_v^o = S_s^o)$. The results of these experiments may be found in Table 13. Figure 11 is a plot of these results. $R_{ab}{}'$ plus R_{ac}, calculated in the same fashion as above from experimental times of half exchange, is the ordinate; $[Pt(NH_3)_2Br(H_2O)^+]$, which at high bromide concentrations is proportional to $1/[Br^-]$, is the abscissa.

Table 13. Bromide dependence of bromide exchange of $Pt(NH_3)_2Br_2$ at $25^{\circ}C$ and μ = .05 M.
a = 1.5 mM; $S_v^o = S_s^o$

$[Br^-]$ mM	$[Pt(NH_3)_2Br(H_2O)^+]$ mM	$[PtBr_4{}^{2-}]$ mM	$t_{\frac{1}{2}}$ min	$R_{ab}{}^o \times 10^8$ M sec^{-1}	$R_{ab} + R_{ac} \times 10^8$ M sec^{-1}	$R_{ab}{}' \times R_{ac} \times 10^8$ M sec^{-1}
2^a	.358	0	265 $\pm$ 8	5.4	--	--
		3	31 $\pm$ 2	--	82.4	77.0
10	.143	0	375 $\pm$ 8	6.9	--	--
		3	89 $\pm$ 2	--	32.8	25.0
20	.079	0	420 $\pm$ 11	7.0	--	--
		3	141 $\pm$ 3	--	21.9	14.9
30	.054	0	436 $\pm$ 6	7.2	--	--
		3	171 $\pm$ 9	--	19.3	12.1
41	.040	0	441 $\pm$ 29	7.2	--	--
		3	199 $\pm$ 8	--	16.3	9.1

[a]Value not plotted in Figure 11.
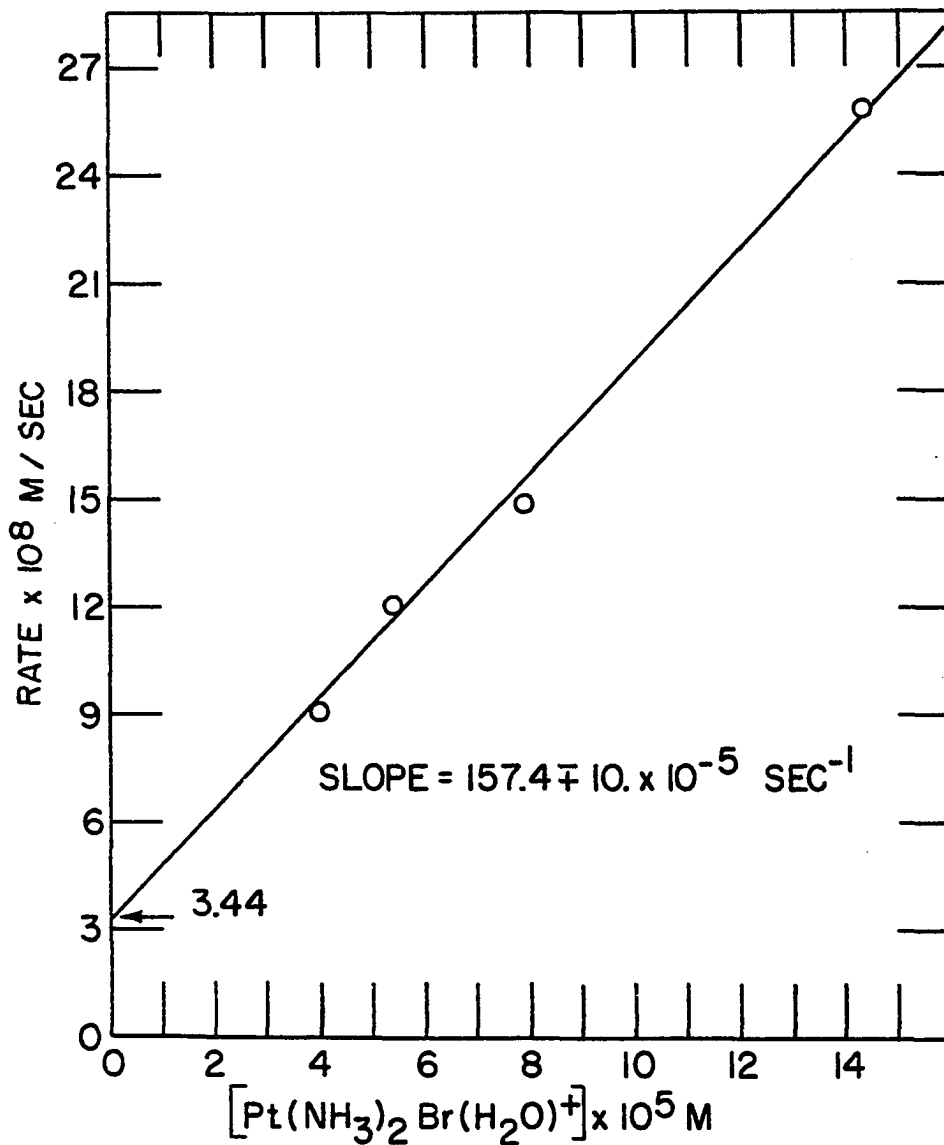
Figure 11. $[R_{ab}{}' + R_{ac}]$ vs the concentration of $Pt(NH_3)_2Br(H_2O)^+$ present at $25^\circ C$; $c = 3mM$; $a = 1.5$ mM; $S_v^o = S_s^o$

The intercept $= (k_{ab}' + k_{ac}')a\ c$ (91)

$$= 3.4 \pm .8 \times 10^{-8} \text{ M/sec}$$

The slope $= \dfrac{k_{ac}'' \times c}{K_a}$ (92)

$$= 157 \pm 10 \times 10^{-5} \text{ sec}^{-1}.$$

From this information and that previously described ($k_{ab}' = 4.9 \times 10^{-3}$ M^{-1} sec^{-1}), the value of R_{ac} that was introduced into the differential equations (41 and 42) for a first approximation was

$$R_{ac} = (2.7 \times 10^{-3} + \frac{5.9 \times 10^{-4}}{b})a\ c.$$ (93)

There is one further term in the cycle [Equation (40)] to be determined, viz; R_{bc} - the rate that free bromide in solution exchanges with the bromide ligands of $PtBr_4^{2-}$. R_{bc} was also considered of the form

$$R_{bc} = R_{bc}^o + R_{bc}',$$ (94)

but experiments where $PtBr_4^{2-}$ was followed in the presence of initially untagged $Pt(NH_3)_2Br_2$ gave no detectable increases in R_{bc} when $Pt(NH_3)_2Br_2$ was present. The value of R_{bc} which was used in the pair of differential equations (41 and 42) for Runge-Kutta refinement was equal to R_{bc}^o. Teggins, et al. (12) determined this rate at .318 and .1 M ionic strength; however, this work was performed at .05 M ionic strength. This meant that a rate expression for $PtBr_4^{2-}$ bromide exchange had to be found. Because of the high bromide concentrations at which the greater part of experiments were performed the second order term as reported by Teggins,

$$k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-],$$

was negligible. R_{bc}^o could be fit by the function

$$R_{bc}^o = k_{bc}\left[PtBr_4^{2-}\right] \tag{95}$$

Experimental rates of exchange, calculated by the standard McKay equation:

$$R_{bc}^o = \frac{4c \times b \times \ln2}{(b + 4c)t_{\frac{1}{2}}}, \tag{96}$$

are presented in Table 14 and plotted vs $\left[PtBr_4^{2-}\right]$ in Figure 12.

$$k_{bc} = 2.12 \pm .07 \times 10^{-4} \ sec^{-1} \tag{97}$$

This is experimentally equivalent to Teggins' value of $2.2 \times 10^{-4} \ sec^{-1}$ determined at both .318 M and .1 M ionic strength.

Table 14. Isotopic exchange between solution bromide and $PtBr_4^{2-}$ at $25°C$ and $\mu = .05$ M

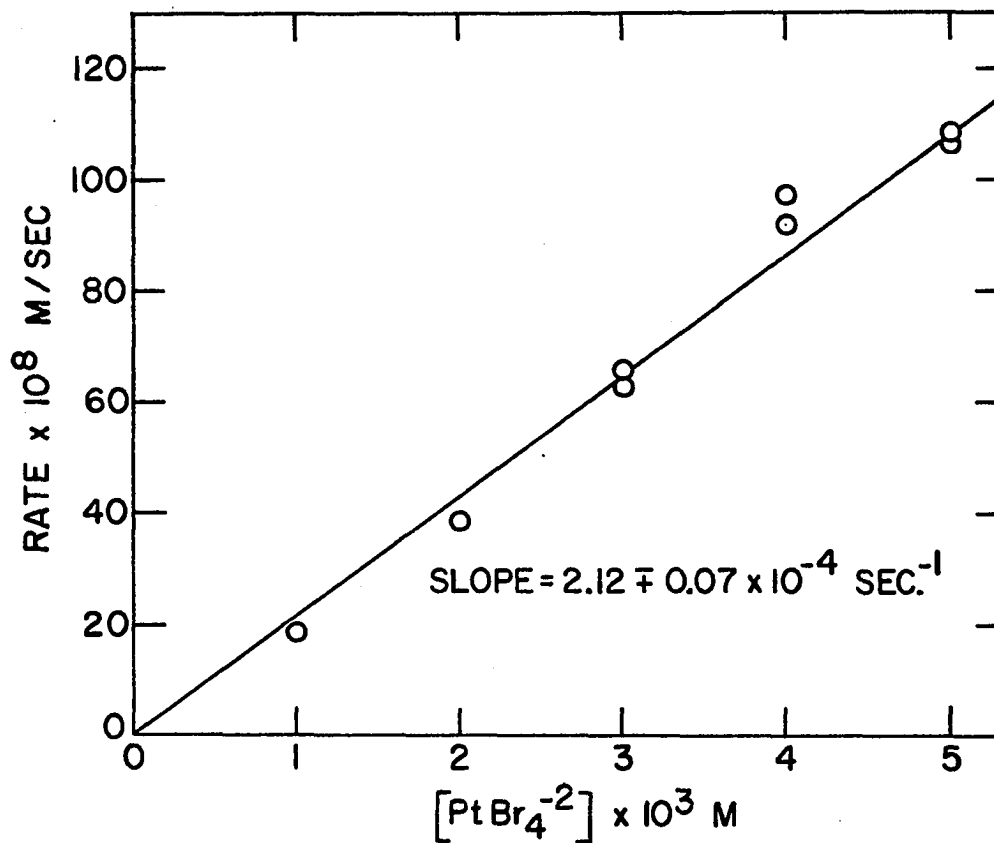| $\left[PtBr_4^{2-}\right]$ mM	$\left[Br^-\right]$ mM	$t_{\frac{1}{2}}$ min	Rate $\times$ 10^8 M sec^{-1}
1.0	30	217 $\pm$ 8	18.8 $\pm$ .7
2.0	30	188 $\pm$ 5	38.8 $\pm$ 1.3
3.0	30	151 $\pm$ 2	65.8 $\pm$ .8
		157 $\pm$ 3	63.0 $\pm$ 1.2
4.0	30	124 $\pm$ 4	97.3 $\pm$ 3.4
		131 $\pm$ 4	92.1 $\pm$ 3.4
5.0	30	129 $\pm$ 8	107.2 $\pm$ 6.7
		127 $\pm$ 3	108.9 $\pm$ 2.9
3.0	20	112 $\pm$ 2	77.4 $\pm$ 1.2
3.0	41	166 $\pm$ 2	64.1 $\pm$ .7

Figure 12. Rate of bromide exchange of $PtBr_4^{2-}$ at $25^{\circ}C$ and $\mu = .05$ M vs concentrations of Rb_2PtBr_4; b = 30 mM

Refinement of rate parameters by Runge-Kutta method

Now that all three rates of bromide exchange in the pair of differential equations (41 and 42), the times of half exchange could now be calculated by numerical integration with the computer and compared to those experimentally determined.

The form of the differentials is then:

$$\frac{du}{dt} = (R_{ab}{}^{o} + .49 \times 10^{-2}ac)\left[\frac{I-u-v}{b} - \frac{u}{2a}\right] \tag{98}$$

$$+ (.27 \times 10^{-2} + \frac{.59 \times 10^{-3}}{b}) \ ac \ \left[\frac{v}{4c} - \frac{u}{2a}\right]$$

$$\frac{dv}{dt} = 2.12 \times 10^{-4}c \ \left[\frac{I-u-v}{b} - \frac{v}{4c}\right] \tag{99}$$

$$+ (.27 \times 10^{-2} + \frac{.59 \times 10^{-3}}{b})ac \ \left[\frac{u}{2a} - \frac{v}{4c}\right]$$

Table 15 coordinates data used to find an inverse bromide dependence in the rate that bromide ligands are traded between the two complexes. In these experiments the specific activity of $PtBr_4{}^{2-}$ was initially equal to that of the free bromide $(S_v^o = S_s^o)$; $\left[Pt(NH_3)_2Br_2\right] = 1.5$ mM and $\left[PtBr_4{}^{2-}\right]$ = 3 mM.

Table 16 coordinates a set of experiments with varying concentrations of $PtBr_4{}^{2-}$ while $\left[Br^-\right]$ and $\left[Pt(NH_3)_2Br_2\right]$ were held constant at 30 mM and 1.5 mM respectively. The specific activity of bromide and $PtBr_4{}^{2-}$ were equal at zero time $(S_v^o = S_s^o)$.

Table 15. Pt$(NH_3)_2Br_2$ isotopic exchange at $25°C$ where $S_v^o = S_s^o$; a = 1.5 mM; c = 3 mM; μ = .05 M (bromide variation)

[Br⁻] mM	$t_{\frac{1}{2}}$ (min) Exp.	$t_{\frac{1}{2}}$ (min) Calcd.	$R_{ab}^o \times 10^8$ M sec⁻¹	$R_{ab}' \times 10^8$ M sec⁻¹	$R_{ac} \times 10^8$ M sec⁻¹	% Diff
2	31 ± 2	31	5.40	2.20	74.84	0.0
10	89 ± 2	86	6.00	2.20	25.93	-3.4
20	141 ± 3	133	7.00	2.20	14.18	-5.7
30	180 ± 12 162 ± 5 (171 ± 9) ave.	165	7.22	2.20	9.94	-3.5
41	199 ± 8	191	7.22	2.20	7.61	-4.0

Table 16. $\left[Pt(NH_3)_2Br_2\right]$ exchange at $25°C$ where $S_v^o = S_s^o$; a = 1.5 mM; b = 30 mM; μ = .05 M ($\left[PtBr_4^{2-}\right]$ variation)

[PtBr₄²⁻] mM	$t_{\frac{1}{2}}$ (min) Exp.	$t_{\frac{1}{2}}$ (min) Calcd.	$R_{ab}^o \times 10^8$ M sec⁻¹	$R_{ab}' \times 10^8$ M sec⁻¹	$R_{ac} \times 10^8$ M sec⁻¹	% Diff
.2	377 ± 23	388	7.22	.15	.67	+ 2.9
1.0	318 ± 12	280	7.22	.73	3.33	-11.9
2.0	213 ± 2	208	7.22	1.47	6.64	- 2.3
3.0	171 ± 9	165	7.22	2.20	9.94	- 3.5
4.0	129 ± 9 136 ± 5 (134 ± 7) ave.	137	7.22	2.94	13.32	+ 2.3
5.0	130 ± 6	118	7.22	3.67	16.49	- 9.2
6.0	105 ± 2	103	7.22	4.41	19.74	- 1.9

The information pertaining to Table 16 and 17 are the same except in Table 17 the specific activity of $PtBr_4^{2-}$ was initially zero ($S_v^o = 0$).

Table 17. $Pt(NH_3)_2Br_2$ exchange at 25^oC where $S_v^o = 0$; a = 1.5 mM; b = 30 mM; $\mu = .05$ M ($[PtBr_4^{2-}]$ variation)

$[PtBr_4^{2-}]$	$t_{\frac{1}{2}}$ (min)		$R_{ab}^o \times 10^8$	$R_{ab}' \times 10^8$	$R_{ac} \times 10^8$	% Diff
mM	Exp.	Calcd.	M sec^{-1}	M sec^{-1}	M sec^{-1}	
1.0	387 ± 12	328	7.22	.73	3.33	-15.2
1.5	340 ± 5	294	7.22	1.10	4.98	-13.5
2.0	304 ± 4	266	7.22	1.47	6.64	-12.5
2.5	286 ± 7	244	7.22	1.84	8.29	-14.7
3.0	240 ± 11	224	7.22	2.20	9.94	- 6.7
4.0	219 ± 8	193	7.22	2.94	13.22	-11.9

In Table 18 experiments with varying amounts of $Pt(NH_3)_2Br_2$ present are coordinated. Again $PtBr_4^{2-}$ was not tagged at zero time.

Table 18. $Pt(NH_3)_2Br_2$ exchange at 25^oC where $S_v^o = 0$; c = 3mM; b = 30 mM; $\mu = .05$ M ($[Pt(NH_3)_2Br_2]$ variation)

$[Pt(NH_3)_2Br_2]$	$t_{\frac{1}{2}}$ (min)		$R_{ab}^o \times 10^8$	$R_{ab}' \times 10^8$	$R_{ac} \times 10^8$	% Diff
mM	Exp.	Calcd.	M sec^{-1}	M sec^{-1}	M sec^{-1}	
.75	240 ± 5	246	3.23	1.10	4.97	+ 2.5
1.0	254 ± 20	236	4.55	1.47	6.63	- 7.1
1.5	240 ± 11	224	7.22	2.20	9.94	- 6.7
2.0	264 ± 12	235	8.52	2.94	13.24	-10.6

The fit in Tables 15 - 18 is promising of better things but not good.

The calculated times of half exchange are low -- especially so for

experiments where the initial specific activity of $PtBr_4^{2-}$ was zero. The

next four tables, 19 - 22, coordinate the same experiments as the first

four. In this case, however, the approximated bromide exchange rates

were revised to $R_{ab}' = 0$ and $R_{ac} = .76 \times 10^{-2} + .59 \times 10^{-3}/b$.

Table 19. $Pt(NH_3)_2Br_2$ exchange at $25^\circ C$ where $S_v^o = S_s^o$; a = 1.5 mM, c = 3 mM; μ = .05 M ([Br$^-$] variation)

[Br$^-$]	$t_{\frac{1}{2}}$ (min)		$R_{ab}^o \times 10^8$	$R_{ac} \times 10^8$	% Diff
mM	Exp.	Calcd.	M sec^{-1}	M sec^{-1}	
2	31 $\pm$ 2	31	5.40	77.09	0.0
10	89 $\pm$ 2	87	6.00	28.18	- 2.2
20	141 $\pm$ 3	134	7.00	16.43	- 5.2
30	171 $\pm$ 9	167	7.22	12.19	- 2.3
41	199 $\pm$ 8	192	7.22	9.86	- 3.5

Setting R_{ab}' equal to zero seemed to enhance the fit between

experimental and calculated times of half exchange in all instances but

Table 13. Remembering Figure 10 and the discussion generated by the non-

zero intercept of the rate in the presence of $PtBr_4^{2-}$, one may see the

manifestations of this nonagreement. It appears that some experimental,

but not discovered, error has been involved. Since the catalysis effect

was negligible when $PtBr_4^{2-}$ was not tagged, this set of experiments does

Table 20. Pt$(NH_3)_2Br_2$ exchange at $25°C$ where $S_v^o = S_s^o$; a = 1.5 mM, b = 30 mM; μ = .05 M ($[PtBr_4^{2-}]$ variation)

$[PtBr_4^{2-}]$ mM	$t_{\frac{1}{2}}$ (min) Exp.	$t_{\frac{1}{2}}$ (min) Calcd.	$R_{ab}^o \times 10^8$ M sec^{-1}	$R_{ac}^o \times 10^8$ M sec^{-1}	% Diff
.2	377 ± 23	389	7.22	.82	+ 5.8
1.0	318 ± 12	281	7.22	4.08	-11.6
2.0	213 ± 2	209	7.22	8.14	- 1.9
3.0	171 ± 9	167	7.22	12.19	- 2.3
4.0	133 ± 7	138	7.22	16.22	+ 3.8
5.0	130 ± 6	118	7.22	20.24	- 9.2
6.0	105 ± 2	103	7.22	24.24	- 1.9

Table 21. Pt$(NH_3)_2Br_2$ exchange at $25°C$ where $S_v^o = 0$; a = 1.5 mM, b = 30 mM; μ = .05 M ($[PtBr_4^{2-}]$ variation)

$[PtBr_4^{2-}]$ mM	$t_{\frac{1}{2}}$ (min) Exp.	$t_{\frac{1}{2}}$ (min) Calcd.	$R_{ab}^o \times 10^8$ M sec^{-1}	$R_{ac}^o \times 10^8$ M sec^{-1}	% Diff
1.0	387 ± 12	350	7.22	4.08	- 9.6
1.5	340 ± 5	321	7.22	6.11	- 5.6
2.0	304 ± 4	298	7.22	8.14	- 2.0
2.5	286 ± 7	279	7.22	10.16	- 2.4
3.0	240 ± 11	261	7.22	12.19	+ 8.7
4.0	219 ± 8	234	7.22	16.22	+ 6.8

Table 22. $Pt(NH_3)_2Br_2$ exchange at $25°C$ where $S_v^o = 0$; $b = 30$ mM, $\mu = .05$ M ($[Pt(NH_3)_2Br_2]$ variation)

$[Pt(NH_3)_2Br_2]$ mM	$t_{\frac{1}{2}}$ (min) Exp.	Calcd.	R_{ab}^o x 10^8 M sec^{-1}	R_{ac} x 10^8 M sec^{-1}	% Diff
.75	240 ± 5	285	3.23	6.10	+18.7
1.0	254 ± 20	274	4.55	8.13	+ 7.9
1.5	240 ± 11	261	7.22	12.19	+ 8.8
2.0	264 ± 12	275	8.52	16.24	+ 4.2

not change the overall mechanistic scheme. What it does do, however, is to show the experimental errors involved in a system such as this.

Further refinements in the value of R_{ac} led to lowering of R_{ac}', as defined in Equation (90), from $.76$ x 10^{-2} to $.6$ x 10^{-2} M^{-1} sec^{-1}. The value of k_{ac}'', also defined in Equation (90), remained the same at $.59$ x 10^{-3} sec^{-1}. The procedure for refining these two values consisted of changing one value or the other and comparing calculated and observed times of half exchange. A minimization of the sum of the percent differences between calculated and observed times of half exchange (with their signs) was used for the criterion of "best fit". Only experiments where $PtBr_4^{2-}$ was tagged initially $(S_v^o = S_s^o)$ were considered. In experiments where $S_v^o = 0$, the effects of trading between the two complexes was minimal and thus also should be these experiments' effects on the value of R_{ac}. Table 23 correlates experimental and calculated times of

Table 23. A listing of all experiments that followed $Pt(NH_3)_2Br_2$ exchange with bromide and $PtBr_4^{2-}$ at $25^\circ C$ and $\mu = .05$ M

a mM	b mM	c mM	$R_{ab} \times 10^8$ $M\ sec^{-1}$	$R_{ac} \times 10^8$ $M\ sec^{-1}$	S_v^o	$t_{\frac{1}{2}}$ (min) Exp.	Calcd.
.75	30	0	3.2	--	--	510	--
.75	30	3	3.2	5.7	0	240	289
1.0	30	0	4.5	--	--	478	--
1.0	30	3	4.5	7.7	0	254	278
1.5	2	0	5.4	--	--	265	--
1.5	2	3	5.4	76.4	S_s^o	31	31
1.5	10	0	6.0	--	--	375	--
1.5	10	3	6.0	27.5	S_s^o	89	89
1.5	20	0	7.0	--	--	420	--
1.5	20	3	7.0	15.7	0	208	215
1.5	20	3	7.0	15.7	S_s^o	141	138
1.5	30	0	7.2	--	--	436	--
1.5	30	.2	7.2	.8	S_s^o	377	391
1.5	30	1	7.2	3.8	0	387	352
1.5	30	1	7.2	3.8	S_s^o	318	287
1.5	30	1.5	7.2	5.8	0	340	324
1.5	30	2.0	7.2	7.7	S_s^o	213	215
1.5	30	2.0	7.2	7.7	0	304	300
1.5	30	2.5	7.2	9.6	0	286	281
1.5	30	3.0	7.2	11.5	S_s^o	171	172
1.5	30	3.0	7.2	11.5	0	240	264
1.5	30	4.0	7.2	15.3	S_s^o	134	144
1.5	30	4.0	7.2	15.3	0	219	236
1.5	30	5.0	7.2	19.0	S_s^o	130	124
1.5	30	6.0	7.2	22.8	S_s^o	105	108
1.5	41	0	7.2	--	--	441	--
1.5	41	3	7.2	9.1	S_s^o	199	200
2.0	30	0	8.5	--	--	471	--
2.0	30	3	8.5	15.3	0	264	279

half exchange using the "best fit" values of R_{ac} for all experiments following $Pt(NH_3)_2Br_2$ exchange at $25^{\circ}C$.

Formally, R_{ac}, the rate bromide is traded between the two complexes, could be resolved by watching activity grow into $PtBr_4^{2-}$. Practically, this method has little merit. For example, in a solution with concentrations of $[PtBr_4^{2-}]$, $[Pt(NH_3)_2Br_2]$, and $[Br^-]$ of 3, 1.5 and 30 mM, $R_{bc} = 63.7 \times 10^{-8}$ M sec^{-1} whereas $R_{ac} = 11.5 \times 10^{-8}$ M sec^{-1}. The rate of trading is only 15% of the total exchange rate. Of course, R_{ac} could be increased by lowering the bromide concentration but the second order term $kd[PtBr_4^{2-}][PtBr_3(H_2O)^-]$ in R_{bc} becomes important as this is done; thus complicating the rate equation as well as increasing R_{bc}. The concentration of $Pt(NH_3)_2Br_2$ cannot be increased above 2.0 mM because of its limited solubility. At this concentration, R_{ac} would only be 20% of the total exchange rate. A limited number of experiments following $PtBr_4^{2-}$ exchange were performed however. They will be found listed in Table 24 with their calculated times of half exchange.

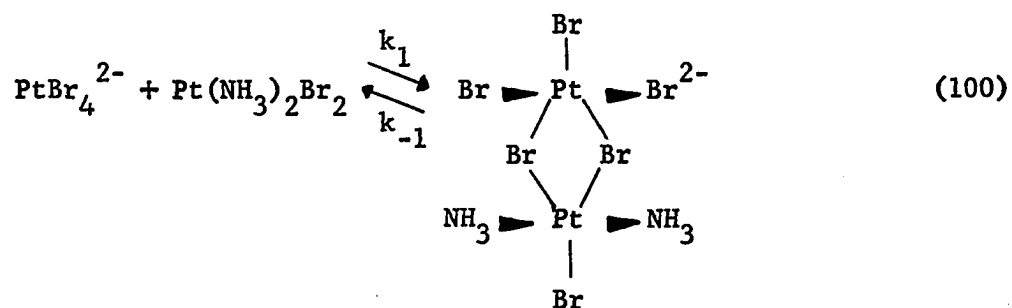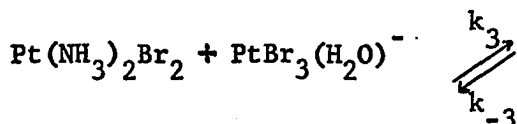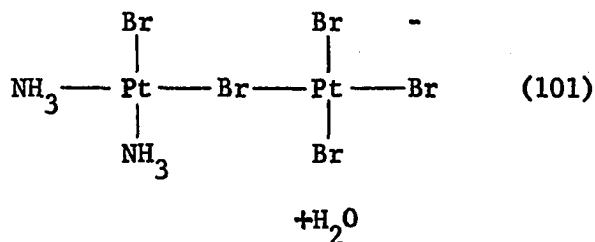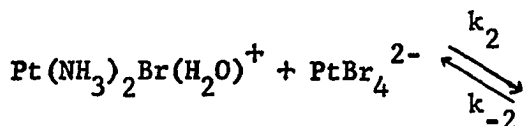From these results the following mechanism was postulated.

$$PtBr_4^{2-} + Pt(NH_3)_2Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad (100)$$

Table 24. $PtBr_4^{2-}$ exchange at $25^{\circ}C$ and $\mu = .05$ M in the presence of 1.5 mM $[Pt(NH_3)_2Br_2]$

c mM	b mM	S_u^o	$t_{\frac{1}{2}}$ Exp.	Calcd.
3	30	0	140 ± 2	145
3	30	S_s^o	131 ± 4	134
3	20	0	104 ± 2	102
4	30	0	136 ± 3	134

$$Pt(NH_3)_2Br(H_2O)^+ + PtBr_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$

$$(101)$$

$$Pt(NH_3)_2Br_2 + PtBr_3(H_2O)^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$$

The k_1 path is a clear case of exchange involving no net reaction. Trading takes place half the time the intermediate is formed. However, the second part of the mechanism is not so simple. The k_2 - k_{-3} path provides aquation for $Pt(NH_3)_2Br_2$ and anation for $PtBr_3(H_2O)^-$; the k_3 - k_{-2} path, aquation for $PtBr_4^{2-}$ and anation for $Pt(NH_3)_2Br(H_2O)^+$. Because catalysis may not shift equilibrium there is a relationship between these rate constants and the first aquation equilibrium constants for

$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$.

At equilibrium:

$$k_2\left[Pt(NH_3)_2Br(H_2O)^+\right]\left[PtBr_4^{2-}\right] = k_{-2}\left[Pt(NH_3)_2Br_5^-\right] \tag{102}$$

and

$$k_3\left[Pt(NH_3)_2Br_2\right]\left[PtBr_3(H_2O)^-\right] = k_{-3}\left[Pt(NH_3)_2Br_5^-\right]. \tag{103}$$

From these two equations

$$\frac{k_2}{k_3}\left(\frac{\left[Pt(NH_3)_2Br(H_2O)^+\right]}{\left[Pt(NH_3)_2Br_2\right]} \times \frac{\left[PtBr_4^{2-}\right]}{\left[PtBr_3(H_2O)^-\right]}\right) = \frac{k_{-2}}{k_{-3}} \tag{104}$$

The first aquation equilibrium constant for $Pt(NH_3)_2Br_2$

$$K_{1(a)} = \frac{\left[Pt(NH_3)_2Br(H_2O)^+\right]\left[Br^-\right]}{\left[Pt(NH_3)_2Br_2\right]} \tag{105}$$

and the first aquation equilibrium constant for $PtBr_4^{2-}$

$$K_{1(c)} = \frac{\left[PtBr_3(H_2O)^-\right]\left[Br^-\right]}{\left[PtBr_4^{2-}\right]}. \tag{106}$$

thus $\quad \dfrac{k_2}{k_3}\left(\dfrac{K_{1(a)}}{\left[Br^-\right]}\right)\left(\dfrac{\left[Br^-\right]}{K_{1(c)}}\right) = \dfrac{k_{-2}}{k_{-3}} \tag{107}$

or $\quad k_2\, k_{-3}\, K_{1(a)} = k_3\, k_{-2}\, K_{1(c)}. \tag{108}$

The next step was to test the prediction of catalysis for the aquation of $PtBr_4^{2-}$ by $Pt(NH_3)_2Br_2$. The rate equation was derived in the following way.

$$PtBr_4^{2-} + H_2O \underset{k_{cb}}{\overset{k_{bc}}{\rightleftharpoons}} PtBr_3(H_2O)^- + Br^- \tag{109}$$

$$PtBr_4^{2-} + Pt(NH_3)_2Br(H_2O)^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pt(NH_3)_2Br_5^- - \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} PtBr_3(H_2O)^-$$
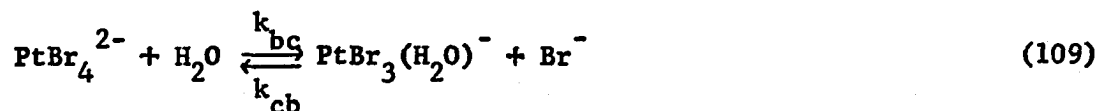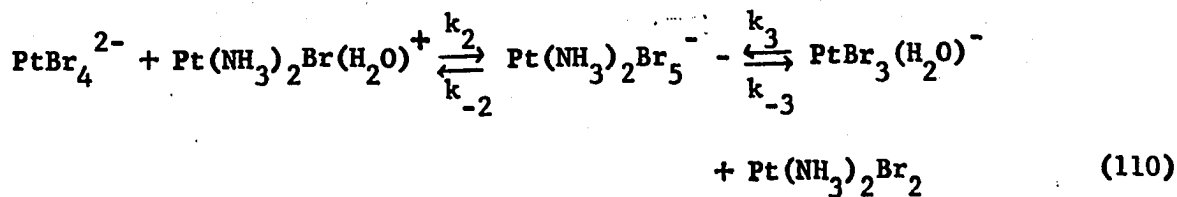
$$+ Pt(NH_3)_2Br_2 \qquad (110)$$

$$x = \left[PtBr_3(H_2O)^-\right] \qquad (111)$$

$$c-x = \left[PtBr_4^{2-}\right] \qquad (112)$$

$$a = 1.5 \text{ mM} = \left[Pt(NH_3)_2Br_2 \text{ originally added to solution}\right] \qquad (113)$$

$$n = \left[Pt(NH_3)_2Br_2\right] = .62 \text{ mM} \qquad (114)$$

$$m = \left[Pt(NH_3)_2Br(H_2O)^+\right] = .82 \text{ mM} \qquad (115)$$

$$b = \left[Br^-\right] = .88 \text{ mM} \qquad (116)$$

$$\frac{dx}{dt} = k_{bc}[c-x] - k_{cb}[x][b] + k_2[c-x][m] - k_{-2}\left[Pt_2(NH_3)_2Br_5^-\right] \qquad (117)$$

The steady state approximation for $Pt_2(NH_3)_2Br_5^-$ requires

$$\frac{d\left[Pt(NH_3)_2Br_5^-\right]}{dt} \approx 0 \qquad (118)$$

$$= k_2[c-x][m] + k_3[x][n] - [k_{-2} + k_{-3}]\left[Pt_2(NH_3)_2Br_5^-\right]$$

$$\therefore \left[Pt_2(NH_3)_2Br_5^-\right] \approx \frac{k_2[c-x][m] + k_3[x][n]}{k_{-2} + k_{-3}} \qquad (119)$$

The substitution of the value of $\left[Pt_2(NH_3)_2Br_5^-\right]$ in (119) into (117) leads to:

$$\frac{dx}{dt} = k_{bc}[c-x] - k_{cb}[x][b] + k_2[c-x][m] - \frac{k_{-2}}{k_{-2}+k_{-3}} (k_2[c-x][m] + k_3[x][n]) \qquad (120)$$

$$\frac{dx}{dt} = k_{bc}[c-x] - k_{cb}[x][b] + \frac{k_{-3}k_2}{k_{-2}+k_{-3}} [c-x][m] - \frac{k_{-2}k_3}{k_{-2}+k_{-3}} [x][n] \qquad (121)$$

$$\frac{dx}{dt} = -(k_{bc} + k_{cb}[b] + \frac{k_{-3}k_2}{k_{-2}+k_{-3}}[m] + \frac{k_{-2}k_3}{k_{-2}+k_{-3}}[n])[x]$$

$$+ (k_{bc} + \frac{k_{-3}k_2}{k_{-2}+k_{-3}}[m])[c] \qquad (122)$$

This equation is then in the form:

$$\frac{-dx}{dt} = \beta + \alpha x \qquad (123)$$

where:

$$\alpha = -(k_{bc} + k_{cb}[b] + \frac{k_{-3}k_2}{k_{-2}+k_{-3}}[m] + \frac{k_{-2}k_3}{k_{-2}+k_{-3}}[n]) \qquad (124)$$

and

$$\beta = (k_{bc} + \frac{k_{-3}k_2}{k_{-2}+k_{-3}})[c]. \qquad (124')$$

which is integrable:

$$-\frac{1}{\alpha} \ln(\frac{\beta+\alpha x}{c}) = t \quad c = \text{constant of integration} \qquad (125)$$

The following method, the Guggenheim approximation, allows one to

eliminate the constant of integration when the initial and infinity values

of x are not known (44, p. 49).

At t = t

$$\exp[-\alpha t] = \frac{\beta+\alpha x_t}{c} ; \qquad (126)$$

at t = t + τ

$$\exp[-\alpha(t+\tau)] = \frac{\beta+\alpha x_{t+\tau}}{c}. \qquad (127)$$

From (126) and (127):

$$\exp[-\alpha t] - \exp[-\alpha(t+\tau)] = \frac{\alpha}{c}(X_t - X_{t+\tau}). \qquad (128)$$

Rearrangement of 128 yields:

$$\exp\left[-\alpha t\right]\left[1 - \exp(-\alpha\tau)\right] = \frac{\alpha}{C}(X_t - X_{t+\tau}). \tag{129}$$

When the natural logarithm of each term is taken and the constants

presented as one term, the expression is in the form:

$$-\alpha t = \ln(X_t - X_{t+\tau}) + C' \tag{130}$$

$$C' = -\ln\left\{\frac{C}{\alpha}[1 - \exp(\alpha\tau)]\right\}. \tag{130'}$$

Therefore, a plot of $\ln(A_t - A_{t+\tau})$ vs time will be linear with a slope of

$-\alpha$, the sum of the apparent first order forward and reverse rate constants.

It is suggested that the value of τ should be two or three times as great

as the half-life period of the reaction for accuracy. The larger the

difference between A_t and $A_{t+\tau}$ the better defined is the slope of the

generated line.

The first two terms in $-\alpha$, $k_{bc} + k_{cb}[.88]$ was found equal to

$2.8 \pm .2 \times 10^{-4}$ sec^{-1}. The value of k_{cb} $(8.3 \pm 1.4 \times 10^{-2}$ M^{-1} sec$^{-1})$ was

determined by taking the ratio $k_{bc}/K_{1(c)}$, the forward rate constant for

the Equation (109) divided by the equilibrium quotient for that same

reaction. For the value of the last two terms, a return to exchange rate

results is needed. It was found that the trading rate involving an

inverse bromide dependence was equal to $\dfrac{.59 \times 10^{-3}}{[Br^-]} \left[PtBr_4^{2-}\right]\left[Pt(NH_3)_2Br_2\right]$

M sec^{-1}. In terms of the mechanism, the rate that active bromide entered

$Pt(NH_3)_2Br(H_2O)^+$,

$$\frac{d\left[Pt(NH_3)_2Br_2{}^*\right]}{dt} = k_{-3}\left[Pt_2(NH_3)_2Br_5{}^*\right]$$

$$= k_{-3}\frac{(k_2\left[PtBr_4^{2-}\right]\left[Pt(NH_3)_2Br(H_2O)^+\right])}{k_{-2} + k_{-3}} \tag{131}$$

$$= \frac{k_{-3} \, k_2}{k_{-2} + k_{-3}} \frac{K_{1(a)}}{[Br^-]} \left[PtBr_4^{2-} \right] \left[Pt(NH_3)_2 Br_2 \right].$$

Therefore,

$$\frac{k_{-3} \, k_2}{k_{-2} + k_{-3}} K_{1(a)} = k_{ac}''; \quad k_{ac}'' = .59 \times 10^{-3} \text{ sec}^{-1} \tag{132}$$

$$\frac{k_{-3} \times k_2}{k_{-2} + k_{-3}} = .52 \pm .04 \text{ M}^{-1} \text{ sec}^{-1} \tag{133}$$

For reasons stated previously from which Equation (108) was devised,

$$\frac{k_3 \, k_{-2} \, K_{1(c)}}{k_{-2} + k_{-3}} = k_{ac}'' \tag{134}$$

$$\frac{k_3 \, k_{-2}}{k_{-2} + k_{-3}} = .23 \pm .02 \text{ M}^{-1} \text{ sec}^{-1}. \tag{135}$$

The sum of the last two terms in the aquation rate constant then are:

$$.52 \left[.82 \times 10^{-3} \right] + .23 \left[.62 \times 10^{-3} \right] \tag{136}$$

$$= .57 \times 10^{-3} \text{ sec}^{-1}$$

The predicted observed rate constant at 25°C for aquation of $PtBr_4^{2-}$ in the presence of 1.5 mM $Pt(NH_3)_2Br_2$ would then be $(.28 + .57) \times 10^{-3}$ or $8.5 \times 10^{-4} \text{ sec}^{-1}$. Two experiments were run under these conditions.

$$k_{obs}(1) = 4.90 \pm .07 \times 10^{-4} \text{ sec}^{-1} \tag{137}$$

$$k_{obs}(2) = 4.96 \pm .03 \times 10^{-4} \text{ sec}^{-1} \tag{138}$$

Figure 13 is a plot of the $(A_t - A_{\tau + t})$ vs time for one of these runs.

There is no doubt that aquation of $PtBr_4^{2-}$ was catalyzed, but it is just as certain it does not explain all of the exchange between the complexes. It appears that the mechanism must now be expanded:
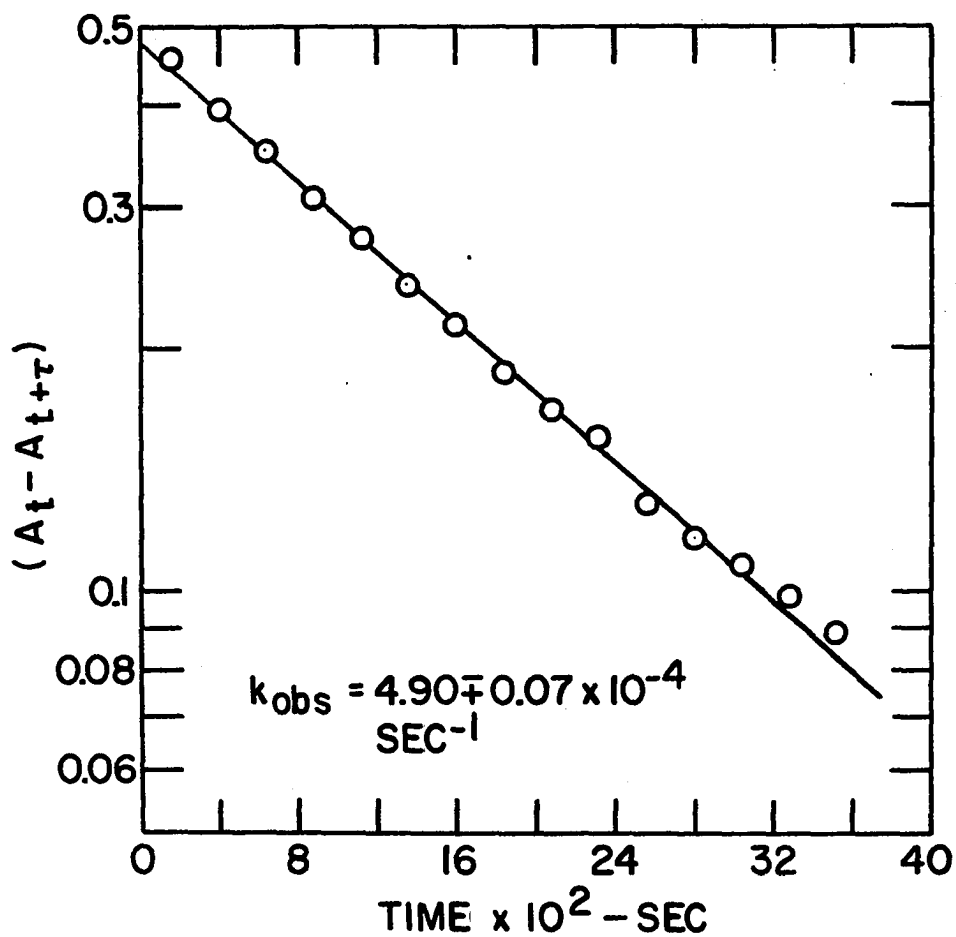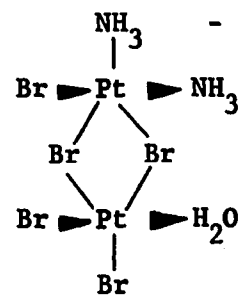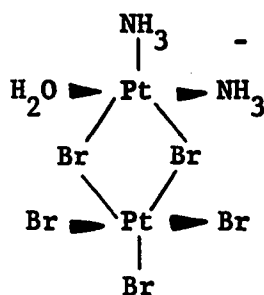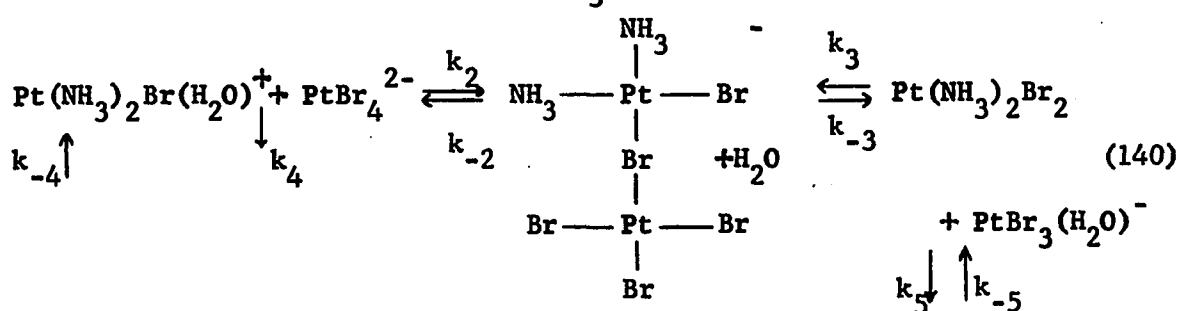
Figure 13. Guggenheim plot of spectroscopic data for the aquation of $PtBr_4^{2-}$ in the presence of cis-$Pt(NH_3)_2Br_2$ at $25°C$ and $\mu = .05$ M; a = 1.5 mM, c = .1 mM, b = 0. Changes in absorbance were observed at 268 nm

$$PtBr_4^{2-} + Pt(NH_3)_2Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

(139)

$$Pt(NH_3)_2Br(H_2O)^+ + PtBr_4^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} Pt(NH_3)_2Br_2$$

(140)
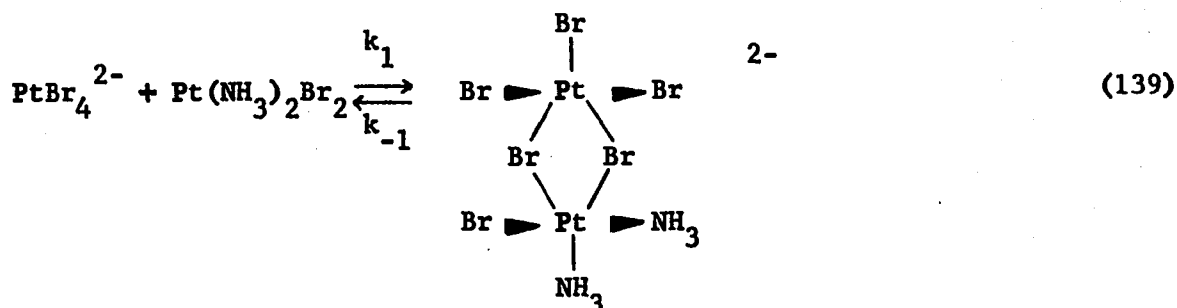
and/or
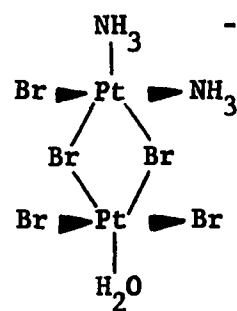
There is no way kinetically to distinguish between these three possible intermediates formed from paths 4 and 5, but the sum of these rate constants may be found by first finding what $\dfrac{k_2 k_{-3}}{k_{-2}+k_{-3}}$ and $\dfrac{k_3 k_{-2}}{k_{-2}+k_{-3}}$

really are.

$$-\alpha- (k_{bc} + k_{cb}[Br^-]) = (4.9 - 2.8) \times 10^{-4} = \frac{k_2 k_{-3}}{k_{-2}+k_{-3}}[.82] + \frac{k_3 k_{-2}}{k_{-2}+k_{-3}}[.62]$$

(141)

$$\frac{k_2 k_{-3}}{k_{-2}+k_{-3}} = \frac{K_{1(c)}}{K_{1(a)}} \frac{k_3 k_{-2}}{k_{-2}+k_{-3}}$$

(142)

Solution of these two simultaneous equations provides values of $\frac{k_2 k_{-3}}{k_{-2}+k_{-3}} =$

$.20 \pm .03$ M^{-1} sec^{-1} and $\frac{k_3 k_{-2}}{k_{-2}+k_{-3}} = .09 \pm .02$ M^{-1} sec^{-1}. Therefore, the

combined first order rate constant for paths 4 and 5 equals:

$$k_{ac}'' - \frac{k_2 k_{-3}}{k_{-2}+k_{-3}} K_{1(a)} = .59 \times 10^{-3} - .20 \times 1.13 \times 10^{-3}$$

(143)

$$= .33 \times 10^{-3} \ sec^{-1}$$

The rate of trading through routes 4 and 5

$$= \frac{\frac{1}{2}(K_a k_4 + k_c k_5)}{[Br^-]} [PtBr_4^{2-}][Pt(NH_3)_2 Br_2]$$

(144)

$$= \frac{.33 \times 10^{-3}}{[Br^-]} [PtBr_4^{2-}][Pt(NH_3)_2 Br_2]$$

The complexity of the reaction required to account for the collected

data at $25^\circ C$ should be emphasized. This is best done by summarizing what

has been learned, and the speculation which lead to the proposed

mechanism.

1. There is no measurable catalysis of bromide exchange between

$Pt(NH_3)_2 Br_2$ and solution bromide by the presence of $PtBr_4^{2-}$.

2. There is no measurable catalysis of bromide exchange between

$PtBr_4^{2-}$ and solution bromide by the presence of $Pt(NH_3)_2 Br_2$.

3. The rate that active bromide enters $Pt(NH_3)_2Br_2$ is enhanced by $PtBr_4^{2-}$ but only through a trading mechanism. The limited results of $PtBr_4^{2-}$ exchange in the presence of $Pt(NH_3)_2Br_2$ support this contention.

4. Although there is some trading of bromide ligands between the complexes themselves the far greater share of exchange has an inverse bromide dependence, suggesting bromide exchange between $PtBr_4^{2-}$ and $Pt(NH_3)_2Br(H_2O)^+$ and between $Pt(NH_3)_2Br_2$ and $PtBr_3(H_2O)^-$.

5. An Anation-Aquation catalysis (which appears formally as a trading of water molecule for a bromide ion) accompanies some 40% of the exchange.

6. The rate equation for trading of bromide ligands between the two complexes is

$$R_{ac} = (k'_{ac} + \frac{k''_{ac}}{[Br^-]})[PtBr_4^{2-}][Pt(NH_3)_2Br_2] \qquad (145)$$

where

$$k'_{ac} = \tfrac{1}{2} k_1 \qquad (146)$$

and

$$k''_{ac} = \frac{k_2 k_{-3}}{k_{-2}+k_{-3}} K_{1(a)} + \tfrac{1}{2} K_{1(a)} k_4 + \tfrac{1}{2} K_{1(c)} k_5 \qquad (147)$$

7. At $25^\circ C$, $k'_{ac} = 6 \times 10^{-3}$ M^{-1} sec^{-1}, $k''_{ac} = 5.9 \times 10^{-4}$ sec^{-1}, $k_1 = 1.2 \times 10^{-2}$ M^{-1} sec^{-1}, $\frac{k_2 k_{-2}}{k_{-2}+k_{-3}} = .20$ M^{-1} sec^{-1}, and $[K_{1(a)}k_4 + K_{1(c)}k_5] = .66 \times 10^{-3}$ sec^{-1}.

At $35^\circ C$

The same types of experiments described for 25° were performed at $35^\circ C$. Table 25 and Figure 14 correlate rate of $Pt(NH_3)_2Br_2$ bromide
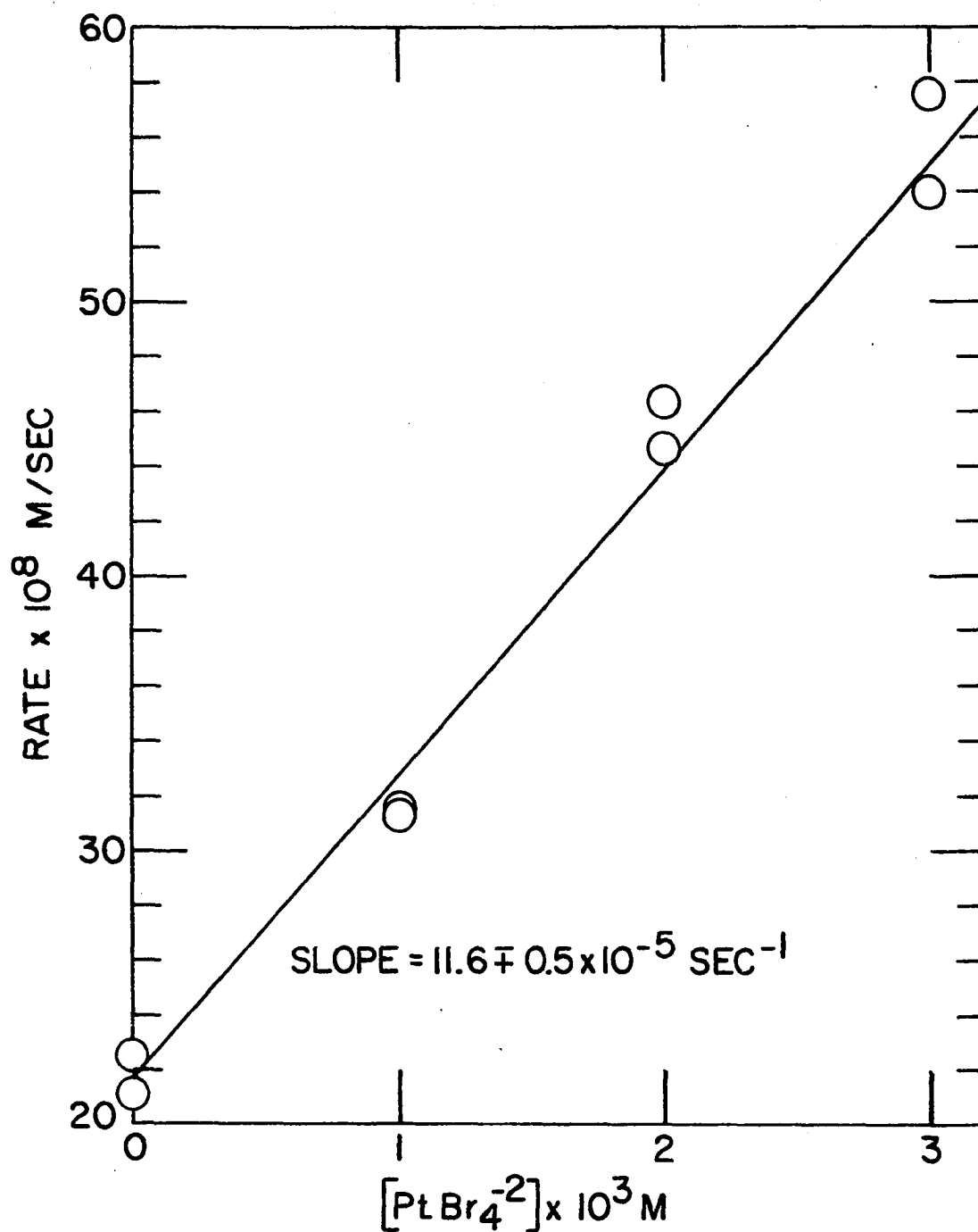
Figure 14. $[R_{ab} + R_{ac}]$ at $35^{o}C$ and $\mu = .05$ M vs $[PtBr_4^{2-}]$; a = 1.5 mM, b = 30 mM; $S_v^o = S_s^o$

exchange for experiments where $PtBr_4^{2-}$ concentration was varied while a and b remained constant at 1.5 and 30 mM; $S_v^o = S_s^o$. The slope of the line $(k_{ac}[Pt(NH_3)_2Br_2])$ equaled $11.6 \pm .5 \times 10^{-5}$ sec^{-1}.

Table 25. $Pt(NH_3)_2Br_2$ exchange at 35^oC and $\mu = .05$ M vs $PtBr_4^{2-}$; a = 1.5 mM; b = 30 mM; and $S_v^o = S_s^o$

$[PtBr_4^{2-}]$ mM	$t_{\frac{1}{2}}$ min	Rate x 10^8 M sec^{-1}
0	150 $\pm$ 4	21.1 $\pm$ .6
	140 $\pm$ 3	22.5 $\pm$ .5
1	101 $\pm$ 2	31.6 $\pm$ .7
	102 $\pm$ 2	31.3 $\pm$ .7
2	69 $\pm$ 2	44.3 $\pm$ 1.1
	72 $\pm$ 1	44.6 $\pm$ .6
3	60 $\pm$ 1	54.0 $\pm$ .9
	56 $\pm$ 1	57.6 $\pm$ .3

Table 26 and Figure 15 correlate rates of exchange with varying $[Br^-]$ concentration (again, rate is actually plotted against $[Pt(NH_3)_2Br(H_2O)^+]$). The derived rate equation for 3 mM $[PtBr_4^{2-}]$ and 1.5 mM $[Pt(NH_3)_2Br_2]$ was

$$R_{ac} = (4. \pm 4.) \times 10^{-8} + (45. \pm 6. \times 10^{-4}) [Pt(NH_3)_2Br(H_2O)^+] \quad (148)$$
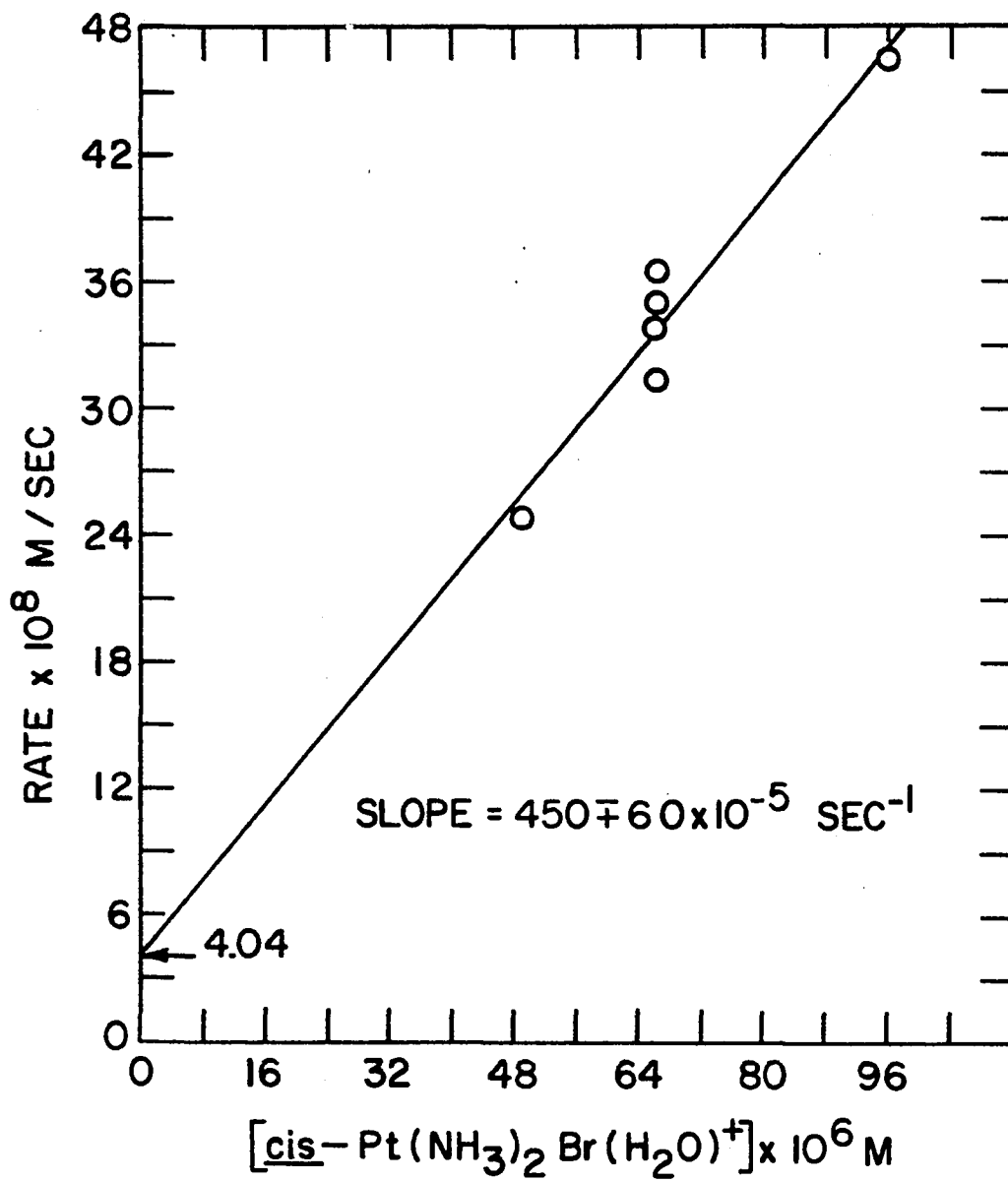
Figure 15. R_{ac} at $35^{\circ}C$ and $\mu = .05$ M vs $[Pt(NH_3)_2Br(H_2O)^+]$; a = 1.5 mM; c = 3 mM; $S_v^o = S_s^o$

The figure shows a plot with y-axis labeled "RATE x 10^8 M/SEC" ranging from 0 to 48, and x-axis labeled "$[\underline{cis}-Pt(NH_3)_2 Br(H_2O)^+]x 10^6$ M" ranging from 0 to 96. The plot shows SLOPE = $450 \mp 60 \times 10^{-5}$ SEC^{-1} with a y-intercept arrow marked 4.04.

Table 26. The bromide dependence of $Pt(NH_3)_2Br_2$ exchange at $35^{\circ}C$ and $\mu = .05$; a = 1.5 mM and $S_v^o = S_s^o$

$[Br^-]$ mM	$[Pt(NH_3)_2Br(H_2O)^{-1}]$ mM	$[PtBr_4^{2-}]$ mM	$t_{\frac{1}{2}}$ min	$R_{ab}^o \times 10^8$ M sec^{-1}	$R_{ab} + R_{ac} \times 10^8$ M sec^{-1}	$R_{ab}' + R_{ac} \times 10^8$ M sec^{-1}
20	.096	0	137 ± 1	21.4 ± .2	--	--
		3	45 ± 1	--	68.0 ± 1.0	46.6 ± 1.2
30	.066	0	150 ± 4	21.1 ± .6		
			140 ± 3	22.5 ± .5	--	--
		3	60 ± 1		54.0 ± 1.9	33.9 ± 1.5
						31.5 ± 1.4
			56 ± 1	--	57.6 ± .3	36.5 ± .9
						35.1 ± .8
41	.049	0	144 ± 3	22.4 ± .5	--	--
		3	69 ± 1	--	47.3 ± .4	24.9 ± .8

Put into the more standard form of Equation (145)

$$R_{ac} = (.90 \times 10^{-2} + \frac{2.10 \times 10^{-3}}{[Br^-]})[PtBr_4{}^{2-}][Pt(NH_3)_2Br_2] \qquad (149)$$

R_{bc}, the rate the bromide is exchanged between $PtBr_4{}^{2-}$ and free bromide, was also needed at $35°$. The results used to determine this value are found in Table 27 and Figure 16. The rate constant, k_{bc}, was determined to be $7.35 \pm .9 \times 10^{-4} \sec^{-1}$.

Table 27. Rates of $PtBr_4{}^{2-}-Br^-$ exchange at $35°C$ and $\mu = .05$ M; b = 30 mM

$[PtBr_4{}^{2-}]$ mM	$t_{\frac{1}{2}}$ min	$R_{bc} \times 10^8$ M sec^{-1}
2	48 ± 2	15.4 ± .6
2	52 ± 2	14.1 ± .6
3	46 ± 1	21.6 ± .4
3	44 ± 1	22.4 ± .2
3	45 ± 1	22.0 ± .6
4	49 ± 4	24.6 ± 1.8
4	46 ± 3	26.2 ± 1.6
4	36 ± 1	36.1 ± .5
4	41 ± 1	·29.5 ± .4

With this information the Runge-Kutta method of numerical integration was then performed on the differential rate equations (41 and 42):
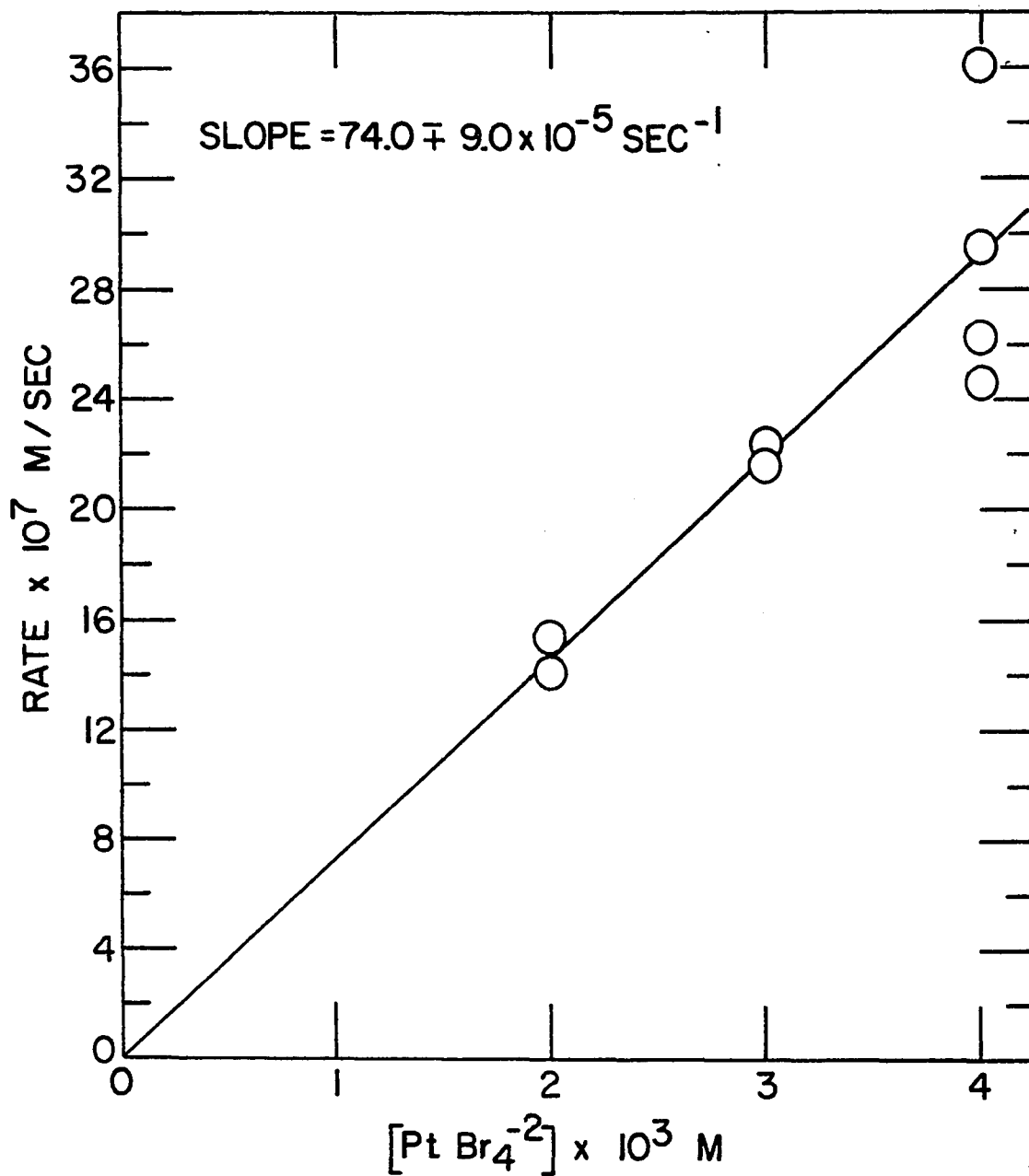
Figure 16. $PtBr_4^{2-}-Br^-$ exchange at $35^\circ C$ and $\mu = .05$ m vs $[PtBr_4^{2-}]$; b = 30 mM

$$\frac{du}{dt} = R_{ab}^{\ o} \left[\frac{I-u-v}{b} - \frac{u}{2a}\right]$$

$$+ (.9 \times 10^{-2} + \frac{2.1 \times 10^{-3}}{b})ac \left[\frac{v}{4c} - \frac{u}{2a}\right] \tag{150}$$

$$\frac{dv}{dt} = 7.35 \times 10^{-4}c \left[\frac{I-u-v}{b} - \frac{v}{4c}\right]$$

$$+ (.9 \times 10^{-2} + \frac{2.1 \times 10^{-3}}{b})ac \left[\frac{u}{2a} - \frac{v}{4c}\right] \tag{151}$$

Table 28 correlates the half times of exchange calculated from this method with those experimentally determined.

Table 28. Correlation of times of half exchange calculated by Runge-Kutta method and those experimentally determined at 35°C and $\mu = .05$ M; $a = 1.5$ mM and $S_v^o = S_s^o$ throughout

$[PtBr_4^{2-}]$ mM	$[Br]$ mM	$t_{\frac{1}{2}}$ (min) Exp.	Calcd.	% Diff	$R_{ab} \times 10^8$ M sec^{-1}	$R_{ac} \times 10^8$ M sec^{-1}
1	30	101 ± 2 102 ± 2	94	-7.3	21.83	11.79
2	30	69 ± 2 72 ± 1	70	-1.4	21.83	23.51
3	30	60 ± 1 56 ± 1	56	-3.4	21.83	35.15
3	20	45 ± 1	44	-2.2	21.33	50.05
3	41	69 ± 1	66	-4.3	22.33	26.94

A better fit may be obtained if R_{ac} is revised to

$$(.9 \times 10^{-2} + \frac{1.9 \times 10^{-3}}{[Br]})ac.$$

Table 29 correlates experimental and calculated times of half exchange for all experiments performed at $35^{\circ}C$ which followed $Pt(NH_3)_2Br_2$ exchange.

The aquation of $[PtBr_4^{2-}]$ in the presence of cis-$Pt(NH_3)_2Br_2$ was also followed at $35^{\circ}C$. Three duplicate runs were followed with a total cis-$Pt(NH_3)_2Br_2$ concentration of 1.5 mM:

$$k_{obs}(1) = 16.1 \pm .3 \times 10^{-4} \text{ sec}^{-1} \tag{152}$$

$$k_{obs}(2) = 16.4 \pm .2 \times 10^{-4} \text{ sec}^{-1} \tag{153}$$

$$k_{obs}(2) = 16.4 \pm .6 \times 10^{-4} \text{ sec}^{-1} \tag{154}$$

having an average k_{obs} of $16.3 \times 10^{-4} \text{ sec}^{-1}$.

The uncatalyzed terms in the observed aquation rate constant, $k_{bc} + k_{bc}/K_{1(c)}$, were equal to $9.4 \pm .2 \times 10^{-4} \text{ sec}^{-1}$, thus giving a value for the catalysis rate constant at $35^{\circ}C$ of $6.9 \pm .6 \times 10^{-4}$. From the procedure demonstrated previously at $25^{\circ}C$ it was determined

$$\frac{k_2 k_{-3}}{k_{-2} + k_{-3}} = .62 \pm .08 \text{ M}^{-1} \text{ sec}^{-1}; \tag{155}$$

$$\frac{k_3 k_{-2}}{k_{-2} + k_{-3}} = .24 \pm .03 \text{ M}^{-1} \text{ sec}^{-1}; \tag{156}$$

and $\frac{1}{2}(K_{1(a)}k_4 + K_{1(c)}k_5) = 1.0 \pm .4 \times 10^{-3} \text{ sec}^{-1}$ \hfill (157)

If

$$k_1 = 2 k_{ac} \tag{158}$$

$$= 1.8 \times 10^{-2} \ M^{-1} \ sec^{-1} \text{ -- from Equation (149) is added to}$$

the above list all the rate constants defined at $25^{\circ}C$ have been

determined at $35^{\circ}C$.

Table 29. A listing of all experiments that followed $Pt(NH_3)_2Br_2$ exchange with bromide and $PtBr_4^{2-}$ at $35^{\circ}C$ and $\mu = .05$

a mM	b mM	c mM	$R_{ab} \times 10^8$ M sec^{-1}	$R_{ac} \times 10^8$ M sec^{-1}	S_v^o	$t_{\frac{1}{2}}$ (min) Exp.	Calcd.
1.5	20	0	21.3	--	--	137	--
1.5	20	3	21.3	45.7	S_s^o	45	46
1.5	30	0	21.8	--	--	145	--
1.5	30	1	21.8	10.8	S_s^o	102	97
1.5	30	2	21.8	21.5	S_s^o	71	73
1.5	30	3	21.8	32.2	S_s^o	58	59
1.5	41	0	22.3	--	--	144	--
1.5	41	3	22.3	24.8	S_s^o	69	69

Activation parameters

The evaluation of the rate expressions at two temperatures allows

activation parameters for the various pathways to be calculated. The

equations used to find them were:

$$\frac{\Delta H^{\neq}}{R} = \frac{\ln(k_1/T_1) - \ln(k_2/T_2)}{(T_2-T_1)/T_1T_2},$$

where k_1 is the rate constant at temperature T_1, and k_2 is the rate constant at temperature T_2, and

$$\Delta S^{\neq} = \frac{\Delta H^{\neq}}{T} + R \ln \frac{kh}{\kappa T},$$

where R is the ideal gas constant in calories per degree K, k is the rate constant at temperature T, h is Planck's constant: 6.6252×10^{-27} erg-sec., and κ is Boltzmann's constant: 1.3804×10^{-1} ergs per molecule per degree K. Table 30 is a compilation of rate constants for exchange and their thermodynamic parameters.

The activation parameters appear typical of Pt(II) square planar substitution (46). The activation parameters reported above for k_{bc} may be compared to those reported by Teggins, et al., $\Delta H^{\neq}$ = 19 kcals/mole, $\Delta S^{\neq}$ - 10 cal/degree; which are consistent within experimental error. Because of the large errors associated with k_1 it is difficult to make comparisons; however it is gratifying to see how well its activation parameters compare to those of the dimer rate constant in $PtBr_4^{2-}$ exchange: $\Delta H^{\neq}$ = 8 kcals; $\Delta S^{\neq}$ = -36 cal/deg.

Table 30. Isotopic exchange rate constants at 25° and 35° and their thermodynamic parameters

Rate constant	Value at 298.2°K	Value at 308.2°K	$\Delta H^{\ddagger}$ kcals moles^{-1}	$\Delta S^{\ddagger}$ Cal/ degree
k_{bc} (sec^{-1})	$2.12 \pm .07 \times 10^{-4}$	$7.35 \pm 0.9 \times 10^{-4}$	22	-6
k_1 (M^{-1} sec^{-1})	$1.2 \pm .4 \times 10^{-2}$	$1.8 \pm 1.8 \times 10^{-2}$	7	-45
$\dfrac{k_2 k_{-3}}{k_2 + k_3}$ (M^{-1} sec^{-1})	$.20 \pm .03$	$.62 \pm .08$	20	--
$\dfrac{k_3 k_{-2}}{k_2 + k_3}$ (M^{-1} sec^{-1})	$.09 \pm .02$	$.24 \pm .03$	20	--
$k_4 K_a + K_5 k_c$ (sec^{-1})	$.66 \pm .50 \times 10^{-3}$	$2.0 \pm .8 \times 10^{-3}$	20	--

DISCUSSION

Although it might seem appropriate to compare Grinberg's reported times of half exchange with those calculated in the computer program used to fit experimental data by a Runge-Kutta curve, this exercise would be fruitless for the following reasons. There was no bromide added to his solutions; at the concentrations used, this would mean that both $Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ were almost entirely in their monoaquo form and in the case of $Pt(NH_3)_2Br_2$ there would be a considerable amount of $Pt(NH_3)_2(H_2O)_2^{2+}$ at equilibrium. Since solutions were only allowed to equilibrate for 2 to 3 hours, however, equilibrium was not reached. (Aquation of $PtBr_4^{2-}$-$t_{\frac{1}{2}} \sim 55$ minutes; Aquation of $Pt(NH_3)_2Br_2$ - $t_{\frac{1}{2}} \sim 300$ minutes.) It is impossible therefore to know the concentrations of each species at the beginning of the run, and for that matter, during the run since they were varying. Also, at this low bromide concentration range the approximations that were made in handling the high bromide system in the present work would be completely inadequate.

It has now been determined that the exchange that Grinberg reported in 1960 was in fact trading of bromide between the two complexes (1).

It was further found that although there is exchange between the two complexes themselves, the greater part of the exchange was between the pairs $\left[Pt(NH_3)_2Br_2\right]\left[PtBr_3(H_2O)^-\right]$ and $\left[Pt(NH_3)_2Br(H_2O)^+\right]\left[PtBr_4^{2-}\right]$. Some 40% of the trading between these pairs is accompanied by an anation-aquation catalysis (which appears formally as a trading of a bromide ion for a water molecule). The proposed mechanism, Equations (139) and (140), used to explain the complex nature of this exchange, contains

intermediates which are quite similar to those found in mechanisms proposed for other second order rate terms containing two complex concentration terms, which were in the Introduction (2, 12, 14, 15, 30). The one large distinction is that there was no measurable exchange between the intermediates proposed for this system and halide in solution. It can be seen, however, that in every other proposed mechanism, there is a step where the bridging halide loses its identity as a ligand of one of the complexes. When this occurs, the bond may be broken from either direction and trading is accomplished.

Since in all of these systems but one, trading of halide between the two complexes in the transition state could not be observed because the activity entering these two complexes was not measured independently, it is impossible to tell if this or the $Pt(dien)Br^+$ - $PtBr_4^{2-}$ system is out of line. There is no doubt some catalysis of bromide with solution in this system is just too small to measure. Could it be that in these other systems, halide is traded between the complexes, say, 1,000 times faster than the dimer is exchanging halide with solution? It then seems fruitful to study other bromide systems of this type. The trans-$Pt(NH_3)_2Br_2$ - Br^- - $PtBr_4^{2-}$ is currently under study in this laboratory. The $Pt(dien)Br^+$ - Br^- - $Pt(NH_3)_2Br_2$ system seems ideal for another.

Perhaps a trend could be found to explain why there is this difference in this system and that of $Pt(dien)Br^+$ - $PtBr_4^{2-}$. With the recent developments in Pt(II) complexes' use as cancer inhibitors and more and more metal complexes appearing in biochemical research, it may be that such knowledge could have an especially practical use in the near future.

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