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Isotopic Exchange of Bromide Ligands in Platinum(II) Complexes. *Cis*-Dibromodiammineplatinum(II)[1]

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The kinetics of the replacement of the bromide ligands for cis-*$Pt(NH_3)_2Br_2$ by H_2O and by $^{82}Br^-$ in water at 25° and 35° have been studied. An ion exchange procedure to remove Br^- was utilized although the conditions had to be rigorously controlled to prevent excessive removal of $Pt(NH_3)_2Br_2$. The first aquation occurs with a first order rate constant of 3.0×10^{-5} sec^{-1} at 25°, $\Delta H^* = 18$ kcal/mole. In addition, a direct second order bromide exchange for* cis-*$Pt(NH_3)_2Br_2$ is measurable, $k_{Br} = 3.3\times10^{-4}$ M^{-1} sec^{-1} at 25°; $\Delta H^* = 18$ kcal/mole. The equilibrium quotients for the replacement of the first and second Br-ligands are $K_1 = 9.6\pm.8\times10^{-4}$ M and $K_2 = 9\pm2\times10^{-5}$ M, respectively.*

Introduction

Studies in this Laboratory on the kinetics of isotopic exchange between bromide and the bromo-ligands of $PtBr_4^{2-}$ and $Pt(dien)Br^+$ have been reported recently.[3,4] Only a fraction of the exchange in each system can be attributed to *normal* nucleophilic ligand substitution reactions for the square-planar platinum(II) complexes, whose characteristics have been summarized in recent reviews.[5,6] The *normal* substitution reactions are considered to involve a direct nucleophilic attack on the platinum complex either by the entering group or by solvent in a rate determining step which is followed by replacement of the solvent by this group. However, in these bromide exchanges the kinetics expressions implied a partial contribution from processes in which two platinum complexes reacted to form the transition state. One interesting consequence was the observation that $Pt(dien)Br^+$ and $PtBr_4^{2-}$ mutually catalyzed the exchange of the other complex with bromide.

Grinberg and Shagisultanova[7] reported that they were unsucessful in applying an ion exchange separation technique to the systems of *cis* or *trans*-$Pt(NH_3)_2Br_2$ with Br^- and could not follow the exchange between these species. They were able to separate the $PtBr_4^{2-}$ anion from the neutral complexes by precipitation procedures. Some fragmentary experimental results with such separations for the exchange between the $Pt(NH_3)_2Br_2$ complexes and $PtBr_4^{2-}$ were reported which indicated a rather rapid exchange of bromide ligands between the two complexes.

The ion exchange technique has previously been successfully applied by Reishus and Martin[8] to Cl^-—*cis*-$(Pt(NH_3)_2Cl_2$ and subsequently had provided quantitative separations for the Br^-—$Pt(dien)Br^+$ system.

We have confirmed Grinberg and Shagisultanova's observation that with $Pt(NH_3)_2Br_2$ a large fraction of the Pt is strongly retained in a conventional anion exchange column. However, by careful control of the ion exchange conditions it has been possible to remove Br^- and still elute 30-50% of the platinum. This procedure appears satisfactory to provide the kinetic description for the isotopic exchange between Br^- and *cis*-$Pt(NH_3)_2Br_2$.

Experimental Section

Materials. The *cis*-$Pt(NH_3)_2Br_2$ was prepared from recrystallized K_2PtBr_6. Neutron activation analyses of the platinum stock have indicated the impurity levels: Ir—15 ppb, Pd—28 ppb, Ag—2.4 ppm. For the preparation of the compound, approximately 40 g of K_2PtBr_6 was added to about 200 ml of a solution of the stoichiometric quantity of $K_2C_2O_4$ to effect reduction to $PtBr_4^{2-}$. The solution was heated in a water bath for 4 hr at 80°C. Subsequently, it was cooled in an ice bath and unreacted K_2PtBr_6 was removed by filtration. To the solution was added 2 moles of ammonium acetate and an additional 2 moles of KBr per mole of $PtBr_4^{2-}$. The KBr served to suppress aquation. The solution was heated to 80° for an additional 4 hr until its color had changed from a dark red brown to a yellow gold and insoluble crystals of *cis*-$Pt(NH_3)_2Br_2$ were visible. The reaction mixture was cooled in ice, and the crystals were collected on a filter and washed with a large volume of cold H_2O. The compound was twice redissolved in a hot KBr solution, recrystallized and finally washed with H_2O.

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[1] Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission.

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[3] J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, 6, 69 (1967).

[4] J. E. Teggins and D. S. Martin, Jr., *Inorg. Chem.*, 6, 1003 (1967).

[5] F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», Wiley, New York, Chapt. 5 (1967).

[6] C. H. Langford and H. B. Gray, «Ligand Substitution Processes», Benjamin, New York, Chapt. 2 (1965).

[7] A. A. Grinberg and G. A. Shagisultanova, *Radiokhim.*, 2, 592 (1960).

[8] J. W. Reishus and D. S. Martin, Jr., *J. Am. Chem. Soc.*, 83, 2457 (1961).

It was dried for not less than 10 hr at 70°. Typical analyses for Pt and Br were 49.6 and 40.6%, respectively, calcd. 50.1 and 41.1%.

For the separation procedures cation exchange resin, Rohm and Haas IR-120, in the Na^+ cycle was used. For the anion exchanges, Rohm and Haas IRA 400 was employed. Originally purchased in the chloride form, it was converted to the nitrate form by elution with $NaNO_3$. The effluent gave no precipitate with 0.1 *M* $Hg_2(ClO_4)_2$ even when its volume had been reduced to one fourth by evaporation.

$Hg_2(ClO_4)_2$ was prepared by the reaction of mercury, mercury(II) oxide and perchloric acid.[9]

The preparation of the 35-hr ^{82}Br tracer in the Ames Laboratory research reactor has been described previously.[3]

All water used in the kinetics studies was drawn from the distilled water tap, distilled from alkaline permanganate and redistilled. Other chemicals were of Analytical Reagent grade.

Equipment. Abosorption spectra of solutions were recorded with a Cary, Model 14, spectrophotometer. For pH measurements a Beckman, Model 40498, glass electrode was employed. Bromide ion activities were measured by means of an Orion, Model 94-35-00, bromide ion electrode. Potentials of these electrodes were recorded by a Corning, Model 12, pH meter.

The radiation from the bromide was counted by means of a 3-in. thallium activated sodium iodide crystal. This was operated with an RIDL, Model 34-12B, 400-channel analyzer and pulses corresponding to the several gamma ray peaks between 0.55 and to 0.83 Mev were recorded.

The IBM 360/40 computer of the Iowa State Computer Center was utilized to test different rate expressions for the isotopic exchange.

Aquation Reactions. There is ample evidence that *cis*-$Pt(NH_3)_2Br_2$ undergoes solvation, presumably in a stepwise fashion according to equations (1) and (2)

$$Pt(NH_3)_2Br_2 + H_2O \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} Pt(NH_3)_2Br(H_2O)^+ + Br^-, K_1 \qquad (1)$$

and

$$Pt(NH_3)_2Br(H_2O)^+ + H_2O \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} Pt(NH_3)_2(H_2O)_2^{2+} + Br^-, K_2 \qquad (2)$$

The complex has very limited solubility, probably less than 5 m*M* in water; and, in addition, the preparations dissolved very slowly so that extensive hydration occurred during the period required for solution. In Figure 1 are shown some spectra of the solutions. The spectrum obtained immediately after dissolution, which required 1.5 hr, had a maximum at about 315 mμ. The striking change in a 24-hr period accompanies the solvation represented by reactions (1) and (2). Upon the addition of a KBr solution to bring Br^- concentration to 0.05 *M*, the maximum which had shifted slightly to 318 mμ was significantly higher than for the spectrum recorded initially.

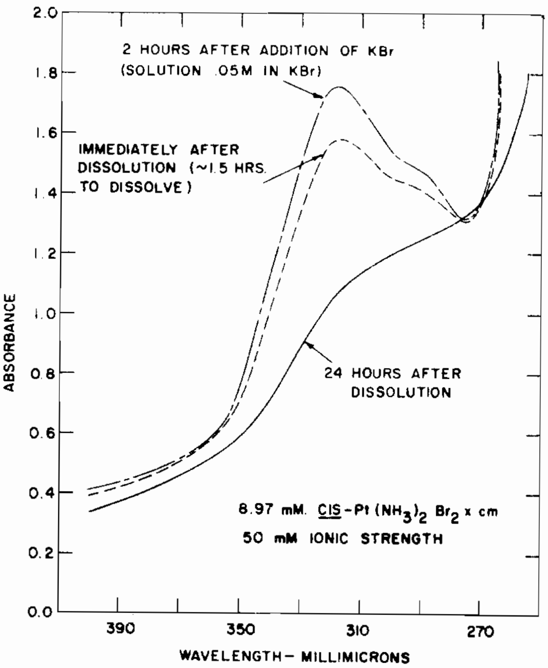

Figure 1. Absorption spectra of solutions of *cis*-$Pt(NH_3)_2Br_2$. Initial and 24-hr spectra obtained with 1.794 m*M* cis-$Pt(NH_3)_2$-Br_2 in 0.050 *M* $NaNO_3$ with a 5.00-cm cell. Final spectrum obtained by diluting this solution to twice its volume with 0.100 KCl and recording the spectrum in a 10.00-cm cell.

During the aquation of the complex there was a drop in the pH and the extent of solvation at equilibrium could be evaluated by the titration of the acidic protons of the complexed H_2O with standard NaOH. An end point occurred at a pH ~9. Titrations were performed after solutions had aged for 48 hr. It is assumed that one proton for each complexed H_2O is titrated so the titer, T, equals $2[Pt(NH_3)_2(H_2O)_2]^{2+} + [Pt(NH_3)_2Br(H_2O)]^+$.

Since neutralization removes the aquo-complexes, additional solvation occurs and the pH drifts downward after each addition of base. Therefore, a fresh sample of the equilibrium solution was taken for each point on the titration curve, and the pH was determined as quickly as possible after the addition of the NaOH and stirring. The titration curve at half-neutralization had a pH of about 7. Since the mono-aquo species, $Pt(NH_3)_2Br(H_2O)^+$ dominates, its dissociation constant is indicated to be $\sim 10^{-7}$ *M*. Before the completion of this work the Orion bromide-ion electrode became available. From the indicated potential of this electrode and a calibration curve, the bromide ion concentration of the equilibrium solutions could be conveniently measured. In a solution of $Pt(NH_3)_2Br_2$ without added bromide, the $[Br^-]$ should equal the titer, T, defined above for the solution. This alternative method gave satisfactory agreement with the titrations and generally was much more convenient.

Neither the titration technique nor the bromide ion electrode were adaptable to evaluation of the initial slope of the hydration. The existence of an extensive second hydration limits the usefulness of a spectrophotometric technique. However, when sufficient

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(9) A. I. Vogel, «Textbook of Quantitative Inorganic Analysis», 3rd ed., Wiley, New York, p. 262 (1961).

KBr to bring the $[Br^-]$ to 0.05 *M* was added to a solution of $Pt(NH_3)_2Br_2$ that had been equilibrated for 48 hr, a single exponential relaxation period was observed for the absorbance at 318 mμ. This relaxation period was primarily associated with the reverse of reaction (1) under the pseudo first-order condition of high bromide.

Ion Exchange Separations. The conditions for the ion exchange separations were critical since large fractions of the platinum were retained by the resin columns. The columns, 50 cm long and 1.5 cm I.D., had beds 15 cm deep of 20-50 mesh resin supported on coarse sintered glass discs for rapid flow. It was determined by means of a KBr solution labeled with ^{82}Br that bromide ion was reduced to 0.1% of its value in a solution which passed through these columns.

It was also apparent that ion exchange beds, in removing from 30 to 50% of the platinum, fractionated the $Pt(NH_3)_2Br_2$ and $Pt(NH_3)_2Br(H_2O)^+$ species. Therefore, the effuent from the anion exchange columns was immediately passed through cation exchange columns to give a pure $Pt(NH_3)_2Br_2$ fraction. However, in high bromide solutions, where very little $Pt(NH_3)_2Br_2(H_2O)^+$ existed, the cation column was not required. Usually, 50 ml sample aliquots were utilized for the ion exchange separations and the columns were immediately washed with 125 ml of H_2O which was added to the effluent.

Evaluation of Isotopic Exchange. For the exchange experiments the desired quantities of KBr, $Pt(NH_3)_2Br_2$, and $NaNO_3$ were weighed into 1-liter volumetric flasks and H_2O was added to the mark. The flasks were then wrapped with opaque tape to exclude light and were allowed to equilibrate for 45 hr in a thermostated bath. The exchange was initiated by the addition of about 200 μl of a solution of NH_4Br tagged with ^{82}Br. The bromide added at this time never exceeded 1% of the bromide present. Aliquots were withdrawn at intervals and subjected to the ion exchange separation. The effluent from the columns with the washing were evaporated to about 15 ml in the the presence of excess NH_3 to replace the complexed bromide. After acidification of the solution, $Hg_2(ClO_4)_2$ was added to precipitate Hg_2Br_2. These precipitates were collected on weighed filter papers; and after their weights were determined, the samples were mountd reproducibly on cardboard squares and counted by the scintillation spectrometer. Thus, the specific activity, S cts.min^{-1} mg^{-1}, corrected for decay, was determined for each sample. For each experiment at least two samples were prepared from solutions which had not passed thorough the resins. The specific activities of these samples served to provide S_∞, and the fraction of exchange for a sample, F, was defined as S/S_∞.

Results

Aquation Equilibria and Kinetics. The evaluation of the equilibrium quotients for reactions (1) and (2) were based on the data in Table I. The equilibrium quotients are related to the titer, T, (or Br^- ion concentration) by the relation[10]

$$K_1T(a-T)+K_1K_2(2a-T)=T^3 \qquad (3)$$

where a = the concentration of $Pt(NH_3)_2Br_2$ added to prepare the solution. The concentration range was limited by the solubility of the compound and by the dilution at which the titrations, or Br^-—electrode potentials could be evaluated with satisfactory accuracy. Values of K_1 and K_2 were calculated from titers at two widely separated concentrations for each temperature. The titers for the other concentrations were calculated from these constants to test the data. Uncertainties in the K's were estimated from the changes which resulted from a change of 1% in one of the titers. At the highest dilutions the titer, T, exceeded a. Hence a significant second aquation was indicated. However, the equilibrium quotients, especially K_2, contained rather large errors because of the limited range of concentration which could be studied and the low concentrations for accurate titrations and bromide ion evaluations.

Table I. Extent of Aquation and the Aquation Equilibrium Quotients, K_1 and K_2. Ionic Strength=0.050 *M*

Initial *cis*-$Pt(NH_3)_2Br_2$ m*M*		Titer or $[Br^-]_\infty$ m*M* Obsd.	Calcd.
	25°		
1.50		0.89	—
0.806		0.58	0.59
0.75		0.55	0.56
0.534		0.45	—
0.204		0.23	0.22
	35°		
0.20		0.25	0.25
0.329		0.355	—
0.50		0.48	0.48
1.00		0.80	0.76
1.50		1.03	1.00
1.823		1.12	—
2.00		1.20	1.19

		K_1	K_2
25°		$9.6\pm .8\times10^{-4}$ *M*	$9\pm2\times10^{-5}$ *M*
35°		$11.9\pm1.0\times10^{-4}$ *M*	$15.\pm3\times10^{-5}$ *M*
ΔH°	=	4 kcal/mol	—
ΔS°	=	-.4 cal/mol deg	—

After a solution of $Pt(NH_3)_2Br_2$ had attained equilibrium with respect to aquation, reactions (1) and (2), the reforming of $Pt(NH_3)_2Br_2$ was followed spectrophotometrically upon the addition of KBr to bring the Br^- concentration to 0.05 *M*. The absorbance at 318 mμ (the wave length of the maximum in the $Pt(NH_3)_2Br_2$ spectrum) approached a limiting value, A_∞, with a single exponential period, τ, of a few minutes, *i.e.*

$$\ln(A_\infty - A) = -t/\tau \qquad (4)$$

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[10] C. I. Sanders and D. S. Martin, Jr., *J.Am. Chem. Soc.*, 83, 807 (1961).

$Pt(NH_3)_2(H_2O)_2^{2+}$ was a minor species; and with the small equilibrium quotient, K_2, k_{-2} is expected to be much greater than k_{-1}. Therefore, the observed relaxation period was considered to be associated primarily with the reaction of Br^- on $Pt(NH_3)_2Br(H_2O)^+$, the reverse of reaction (1). Under these conditions the absorbance of the solution is given by the equation:[11]

$$\ln(A_\infty - A)/(A_\infty - A_o) = -(k_1 + k_{-1}[Br^-])t \qquad (5)$$

Therefore,

$$k_1 + k_{-1}[Br] = 1/\tau \qquad (6)$$

From the observed relaxation periods together with

$$k_1/k_{-1} = K_1 \qquad (7)$$

the rate constants in Table II were calculated.

Table II. Rate Constants for the Reversible Aquation of $Pt(NH_3)_2Br_2$ Ionic Strength=0.050 *M*

Temp. °C	$10^5 \times k_1$ sec^{-1}	$10^2 \times k_{-1}$ $M^{-1}\,sec^{-1}$	
25.0	3.2±0.3	3.3± .02	
35.0	8.6±0.7	7.2±0.5	
ΔH*	17 ±2	14 ±1	kcal/mole
ΔS*	−21 ±3	22 ±2	cal/mole deg

Isotopic Exchange of Bromide Ligands. The conditions for the bromide exchange experiments are included in Table III. Some of the features of two exchange experiments are shown in Figure 2.

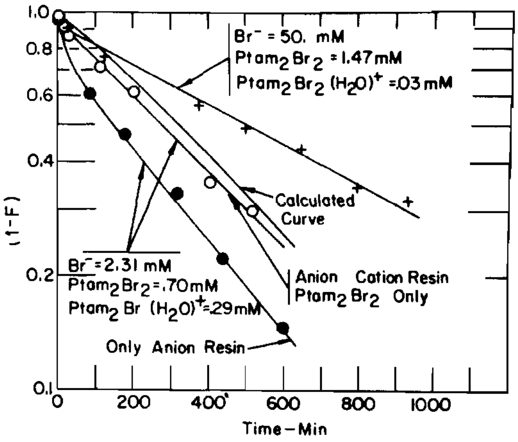

Figure 2. Examples of isotopic exchange experiments at 25°. Ionic strength adjusted to 0.050 *M* by $NaNO_3$. Calculated curve is for scheme I.

First of all, it is apparent that all the curves for (1−F), extrapolated to within a few percent of 1.00 at zero time; therefore the separation of $^*Br^-$ appears quite satisfactory. In high bromide, usually >10 m*M*, the plots of log(1−F) *vs* time were satisfactorily linear so the exchange was conveniently characterized by a slope or half-time of the line. The upper plot in Figure 2 is an example of such. The concentration of $Pt(NH_3)_2Br(H_2O)^+$ was sufficiently small that a cation exchange separation did not alter the exchange curves. However, for exchange experiments with low bromide, as indicated by the lowest curve in Figure 2, the exchange curve was not linear but possessed two distinct periods. When the double resin exchange separation was employed for the same conditions to give (1−F)

Table III. Observed and Calculated Times of Half-exchange for *cis*-$Pt(NH_3)_2Br_2$. Ionic Strength=0.050 *M*

$[Pt(NH_3)_2Br_2]$ Added m*M*	KBr Added m*M*	$[Pt(NH_3)_2Br(H_2O)^+]$ (Equilibrium) m*M*	$[Pt(NH_3)_2(H_2O)_2^{2+}]$ (Equilibrium) m*M*	Time of Half-exchange Obsd. min.	Calcd. Scheme I min.	Calcd. Scheme II min.
25°						
0.75	2.0	0.22	0.009	340	323	366
1.00	2.0	0.29	0.011	300	299	325
1.50	2.0	0.42	0.015	265	261	269
1.50	5.0	0.23	0.004	322 [a]	—	—
1.50	5.0	0.23	0.004	355	340	345
1.50	10.0	0.13	0.001	375 [a]	—	—
1.50	10.0	0.13	0.001	384	442	406
1.50	20.0	0.069	—	425 [a]	475	464
1.50	30.0	0.046	—	465 [a]	470	469
1.50	50.0	0.028	—	460 [a]	440	438
2.00	2.00	0.54	0.019	230	234	234
35°						
0.75	2.00	0.25	0.017	120	119	130
1.00	2.00	0.33	0.021	108	109	116
1.50	2.00	0.47	0.029	89	97	98
1.50	5.00	0.27	0.008	102	105	103
1.50	10.00	0.16	0.002	140 [a]	139	134
1.50	30.00	0.057	—	165 [a]	163	158
1.50	50.00	0.036	—	150 [a]	153	149
2.0	2.00	0.605	0.035	83	88	86
2.00	2.52	0.54	0.027	80	92	89

[a] Anion resin separations only. Calculated values of times of half-exchange are for $Pt(NH_3)_2Br_2$ only.

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(11) A. A. Frost and R. G. Pearson, «Kinetics and Mechanism», Wiley, New York, p. 172-173 (1953).

for only the $Pt(NH_3)_2Br_2$ species, the curves were satisfactorily linear and had somewhat smaller slopes than even the long period of the single resin curve.

It has been concluded therefore that $Pt(NH_3)_2Br(H_2O)^+$ undergoes exchange considerably faster than $Pt(NH_3)_3Br_2$. Since the anion exchange separation may well fractionate the Pt-species by removing significantly greater fractions of $Pt(NH_3)_2Br_2$, it is not possible to evaluate accurately the rate at which activity enters $Pt(NH_3)_2Br(H_2O)^+$. Such exchange rather weakly influences the rate at which activity enters the $Pt(NH_3)_2Br_2$, which was the quantity determined in the double resin separation experiments.

In the treatment of the isotopic exchange with three chemical forms of bromide, rate equations must be written for the entry of labelled bromide into each complex. Since the aquation reactions introduce tagged Br^- into the complexes, the following equations apply for the condition of aquation equilibria.

$$\frac{du}{dt} = k_1[Pt(NH_3)_2Br_2](S_b+S_v-2S_u)+R_{ex-u}(S_b-S_u) \tag{8}$$

and

$$\frac{dv}{dt} = k_1[Pt(NH_3)_2Br_2](S_u-S_v)+k_2[Pt(NH_3)_2Br(H_2O)^+](S_b-S_v) + R_{ex-v}(S_b-S_v) \tag{9}$$

where:

u = Concentration of ^{82}Br in $Pt(NH_3)_2Br_2$. Cts/min 1.

v = Concentration of ^{82}Br in $Pt(NH_3)_2Br(H_2O)$. Cts/min 1.

I = Concentration of total ^{82}Br. Cts/min 1.

S_u = Specific activity of bromide in $Pt(NH_3)_2Br_2 = u/2[Pt(NH_3)_2Br_2]$.

S_v = Specific activity in $Pt(NH_3)_2Br(H_2O)^+ = v/[Pt(NH_3)_2Br(H_2O)^+]$.

S_b = Specific activity of free bromide $= (I-u-v)/[Br^-]$.

The quantities, R_{ex-u} and R_{ex-v}, represented functions of the concentration variables which describe exchange rates in addition to the aquation processes. In practice, various functions could be tested, and the two equations were integrated numerically with the Runge-Kutta method.[12]

From the functions of *u* and *v* the quantity (1–F) was calculated for various trial rate constants. The function log(1–F) computed by this technique is not strictly a linear function of time. However, plots of this function did not possess much curvature. The calculated curves for log(1–F) start from the pont 0 for t=0 whereas the experimental plots extrapolated to a few per cent below this point, as can be seen from the example in Figure 2. Generally, the time of half-exchange for the calculated curve was compared with the half-time indicated by the slope of a straight line drawn for the experimental points. With trial functions of R_{ex-u} and R_{ex-v} a set of rate constants, including k_1 and k_2, for equations (8) and (9) were sought which would give a satisfactory agreement with the observed half-times for the exchange.

The observed half-times for the exchange curves are included in Table III. These half-times vary by only a factor of *ca.* 2 over the concentration range which could be tested. If only the aquation or other first order processes were providing the exchange, a much higher variation would have been observed. It was necessary to include a second order term for the exchange of $[Pt(NH_3)_2Br_2]$, *i.e.*

$$R_{ex-u}=k_{Br}[Pt(NH_3)_2Br_2][Br\ \ ] \tag{10}$$

When this expression was employed for R_{ex-u} together with the values obtained for k_1, it was found that rather high rates were required for dv/dt. This conclusion was also consistent with the high rate of exchange for $Pt(NH_3)_2Br(H_2O)^+$ that was inferred from the single resin experiment in the lowest curve of Figure 2. It was not possible to determine a simple function for R_{ex-v} unambiguously. For example, by simply taking k_2 large enough, a reasonably satisfactory set of halftimes can be calculated, in view of the uncertainties in the experimental values. A set of rate constants, designated as Scheme I in Table IV, was chosen as the best set. The calculated times of half-exchange for this set are tabulated for comparison with the experimental set in Table III. Agreement, which was better than 5% betwen the observed and calculated half-times in all but five of all experiments, seems satisfactory in view of the difficulties inherent in the separation procedure. The values of the rate constants employed are in Table IV together with their activation parameters. This scheme required that k_2 be $7 \times k_1$. The chloride exchange with the chloroammine complexes (reviewed in reference 13) did not generally exhibit such large differences between the first and second aquations for a given complex. Also, since the exchange with other bromo complexes of platinum(II) have involved dimer transition states,[3,4] scheme II was tested in which k_2 was placed equal to k_1 and

$$R_{ex-v}=k_d[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br(H_2O)^+] \tag{11}$$

The times of half-exchange, calculated with the set of rate constants in Table IV, for this scheme are also included in Table III. The calculated values for Scheme II appear equally satisfactory to those calculated with the previous scheme, and it is therefore concluded that the data will not permit a decision between these two schemes. For such a decision exchange experiments are needed at higher concentrations of the complex, and these are precluded by the limited solubility of the compound.

Discussion

Although the exchange rate law for the system cannot be established unambiguously, the rate of exchange is satisfactorily characterized over the range of

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(12) H. W. Richmond, J. Math. Soc. (London), *19*, 31 (1944).

(13) M. A. Tucker, C. B. Colvin, and D. S. Martin, Jr., *Inorg. Chem.*, *3*, 1373 (1964).

Table IV. Rate Constants from the Bromide Exchange Experiments. Ionic Strength = 0.050 *M*

	For Both Schemes		Scheme I	Scheme II	
Temp.	$10^5 \times k_1$ sec^{-1}	$10^4 \times k_{Br}$ sec^{-1} M^{-1}	$10^5 k_2$ sec^{-1} ($k_d = 0$)	$10^5 \times k_2$ sec^{-1}	k_d sec^{-1} M^{-1}
25°	3.0 ± 0.2	3.3 ± 0.3	20	3.0	0.12
35°	8.2 ± 0.7	10 ± 1.0	60	8.2	0.50
ΔH*	18 ± 2	19 ± 2			
ΔS*	–20 ± 3	–10 ± 3			

concentrations it has been possible to attain. Some definite conclusions, however, are possible for the system. The agreement in k_1 between the exchange kinetics and the spectrophotometric studies while not exact was well within the limits of uncertainty. This agreement indicates that the aquation process provides this first order exchange for *cis*-$Pt(NH_3)_2Br_2$. In addition, it appears clear that for $Pt(NH_3)_2Br_2$ there is a second order direct nucleophilic replacement of bromide by bromide ion. The principal ambiguity lies in the rate law for introduction of the tagged bromide into $Pt(NH_3)_2Br(H_2O)^+$.

It is of interest to compare the behavior in the corresponding chloride and bromide system. First of all, the aquation equilibrium constants for aquation of the ligand for bromide are only 0.25 to 0.35 as large as those for chloride, corresponding to a value of *ca.* –0.7 kcal difference in ΔF°. This difference is consistent with the recognized assignment ot Pt^{II} as a Class b ion in the formation of its complexes.[14] The aquation rate constant k_1 of 3.0×10^{-5} sec^{-1} for $Pt(NH_3)_2Br_2$ is scarcely larger than the value of 2.5×10^{-5} sec^{-1} for $Pt(NH_3)_2Cl_2$. The data indicate that the effect of ΔH* for the bromide system, 2 kcal the smaller, is just about balanced by a ΔS* which is 6 cal/deg lower as well. However, the value k_{Br} of 3.3×10^{-4} sec^{-1} M^{-1} is at least six times larger than 5×10^{-5} sec^{-1} M^{-1}, the upper limit for detection for $Pt(NH_3)_2Cl_2$.

The rate of introduction of tagged Br into the $Pt(NH_3)_2Br(H_2O)^+$ appears to be much larger than in the corresponding chloride species since either a k_2, seven times larger than for the chloride system, is needed or else an alternative process occurs. Even with this ambiguity in the rate law, the rate for the exchange appears to be satisfactorily characterized so that the effect of catalysis by other complexes can be studied. Studies of such possible catalysis are planned because Grinberg and Shagisultanova[7] reported such a very rapid exchange of ligand between *cis*-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ and because such catalysis has been observed for the exchange[4] between $Pt(dien)Br^+$ and $PtBr_4^{2-}$.

The difficulties of the ion exchange separation is puzzling in view of its success with the $Pt(dien)Br^+$ and the *cis* and *trans*-$Pt(NH_3)_2Cl_2$ systems. It is tempting to speculate that a Br^- might be added as a labile ligand to give an appreciable concentration of $Pt(NH_3)_2Br_3^-$. This anionic species might be held up sufficiently on the ion exchange columns to interfere with the rapid separation which is required for the exchange. It is postulated that such a labile bromide might be added along the axis normal to the plane of the other ligands. The formation of this square pyramidal configuration would be the first step in the second order bromide exchange process characterized by k_{Br}. However, exchange would not occur unless the complex moved into the trigonal bipyramidal configuration for the transition intermediate.

(14) S. Ahrland, . Chatt, andJ N. R. Davies, *Quart. Rev.* (London), *12*, 265 (1958).