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# Tetrabromoplatinate(II). Acid Hydrolysis and Isotopic Exchange of Ligands with Bromide Ion[1]

BY JOHN E. TEGGINS, DAVID R. GANO, MARY ANN TUCKER, AND DON S. MARTIN, JR.

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The equilibrium constant for the acid hydrolysis of $[PtBr_4]^{2-}$ has been measured at 15, 25, and 40°. Spectrophotometric evidence has indicated the presence of $[Pt_2Br_6]^{2-}$ in the solution. Isotopic exchange rates between the bromide ligands and free bromide have been measured over extensive concentration ranges at the indicated temperatures by the use of $Br^{82}$ tracer. The exchange rate is characterized satisfactorily by the expression

$$R_{ex} = k_1[PtBr_4^{2-}] + k_2[PtBr_3(H_2O)^-] + k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-]$$

The value of $k_1 = 2.2 \times 10^{-4}$ sec$^{-1}$ at 25° describes the aquation reaction for $[PtBr_4]^{2-}$. A value of $k_2 = 2.2 \times 10^{-4}$ sec$^{-1}$ for the aquation of $[PtBr_3(H_2O)]^-$ is determined only approximately. The value of $k_d = 0.22$ sec$^{-1}$ $M^{-1}$ characterizes the formation of a dimer transition state. Evidence is provided that this intermediate is not $[Pt_2Br_6]^{2-}$. There is no evidence for a direct nucleophilic replacement of a bromide ligand by bromide ion.

## Introduction

A systematic analysis of the kinetics for ligand replacement reactions of platinum(II) complexes has indicated that bromide is a stronger nucleophilic reagent than chloride for these systems.[2] In isotopic exchange reactions the nucleophilic agent is chemically identical with the replaced ligand. Accordingly, exchange is generally more rapid in the bromide systems. Earlier work in this laboratory[3] has shown that in solutions of $K_2PtCl_4$ the exchange proceeds by the reversible acid hydrolysis (aquation) of the $[PtCl_4]^{2-}$ ion and the $[PtCl_3(H_2O)]^-$ ion which is present in appreciable concentrations. In particular, a direct or chloride-dependent exchange does not contribute significantly.

Grinberg and Shagisultanova have reported limited exchange studies for the $[PtBr_4]^{2-}$–$Br^-$ system.[4] They concluded that for $[PtBr_4]^{2-}$ the exchange proceeds largely through the intermediate of the aquo ion formation according to eq 1

$$[PtBr_4]^{2-} + H_2O \underset{R_{-1}}{\overset{R_1}{\rightleftharpoons}} [PtBr_3(H_2O)]^- + Br^- \quad K_1 \qquad (1)$$

where $R_1 = k_1[PtBr_4^{2-}]$, $R_{-1} = k_{-1}[PtBr_3(H_2O)^-]\cdot[Br^-]$, and $K_1 = k_1/k_{-1}$ is the equilibrium quotient. This conclusion is modified by their statement, "at higher concentrations of $K_2PtBr_4$, the exchange rate is probably proportional not to the first power of the concentration, but to a higher power."

The present work presents considerably more extensive exchange results which have permitted a more detailed characterization of the exchange kinetics. The rate law indicates that the formation of a dimeric species provides an important route for the exchange which is dominating under some conditions. These exchange studies have been supplemented by spectrophotometric and chemical studies to provide information concerning the possible dimeric species and to test whether the $[Pt_2Br_6]^{2-}$, which can be crystallized from solutions of $[PtBr_4]^{2-}$ as the tetraethylammonium salt,[5] can possibly be the intermediate in the exchange process.

## Experimental Section

**Materials.**—The rubidium salt, $Rb_2PtBr_4 \cdot H_2O$, was utilized because it could be crystallized more conveniently than the more soluble potassium salt. It was prepared from recrystallized $K_2PtBr_6$ in which the iridium content is normally well below the ppm level.[6] Reduction to $K_2PtBr_4$ was effected by a stoichiometric quantity of $K_2C_2O_4$ and the rubidium salt was crystallized by the addition of RbBr. The cation content was determined by an ion-exchange replacement of $Rb^+$ by $H^+$ and titration. Platinum was determined gravimetrically after hydrazine reduction. Bromide was determined by a modified Volhard titration and oxygen by an activation analysis in which the 7.35-sec $^{16}N$, formed by fast neutrons, was counted. *Anal.* Calcd for $Rb_2PtBr_4 \cdot H_2O$: Rb, 24.3; Pt, 27.7; Br, 45.4; O, 2.27. Found: Rb, 24.7; Pt, 27.8; Br, 45.2; O, 2.3.

Tetraethylammonium hexabromodiplatinate(II), $[(C_2H_5)_4N]_2[Pt_2Br_6]$, was prepared by method of Harris, *et al.*[5]

The 35-hr $^{82}Br$ was prepared by irradiating $NH_4Br$ for a few minutes in the "rabbit" of the Ames Laboratory 5-Mw research reactor. The irradiated samples were allowed to age for 1 day to permit the decay of short-lived activities. The β-rays from the $^{82}Br$ were counted by a conventional thin end-window counter and a Nuclear Chicago Corp. Model 186 scaler.

Water for exchange experiments was redistilled from alkaline permanganate. Other materials were of Analytical Reagent grade.

**Procedures.**—Potentiometric titrations were utilized to determine the extent of aquation for the $[PtBr_4]^{2-}$ since the complexed $H_2O$ is measurably acidic. The pH measurements were obtained with a Beckman Model 40498 glass electrode and a Corning Model 12 pH meter. Because the aquation reaction is relatively rapid, the pH readings drifted rapidly. Therefore, each point on the titration curves was determined for a fresh aliquot from an equilibrated solution into which had been added

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1939.

(2) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(3) (a) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *ibid.*, **77**, 2965 (1955); (b) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961).

(4) A. A. Grinberg and G. A. Shagisultanova, *Izv. Akad. Nauk SSSR*, **6**, 981 (1955).

(5) C. M. Harris, S. E. Livingstone, and N. C. Stephenson, *J. Chem. Soc.*, 3697 (1958).

(6) L. S. Jowanovitz, F. B. McNatt, R. E. McCarley, and D. S. Martin, Jr., *Anal. Chem.*, **32**, 1270 (1960).

quickly the indicated quantity of base. The pH for one-half neutralization of the aquo ligand was ~7.9, which indicates that the acid strength is comparable to but slightly weaker than that for the chloroaquo complexes. The end point was taken at pH 9.0.

Ultraviolet spectra for solutions were recorded by means of a Cary Model 14 spectrophotometer. Silica cells were used and the temperature of the cell compartment was maintained at 25 ± 0.1° by water circulated through the cell housing from a thermostat.

For exchange studies the complexes were precipitated as the tetraphenylarsonium salts. These precipitates formed immediately when $[As(C_6H_5)_4]Cl$ was added to solutions containing $[PtBr_4]^{2-}$. From results described later it was concluded that this reagent precipitated $[PtBr_4]^{2-}$ and $[PtBr_3(H_2O)]^-$ without fractionation. However, it was found that the precipitates must be filtered within 30 sec so that exchange between the precipitates and free $Br^-$ might be avoided.

In the majority of exchange experiments solutions were prepared by dissolving weighed amounts of $Rb_2[PtBr_4]\cdot H_2O$ and KBr in a standardized solution of $NaNO_3$, which provided the desired ionic strength. The solutions were placed in flasks wrapped with opaque tape to exclude light and were permitted to equilibrate for several hours in a thermostated water bath. Exchange was initiated by adding a small volume of a solution prepared from the irradiated $NH_4Br$. Changes in solution volume or in bromide concentration were usually less than 1%, although in a few cases they were as high as 2%. Samples were withdrawn at measured intervals for the addition of the $[As(C_6H_5)_4]Cl$ precipitant. Precipitates were filtered within 30 sec by suction onto a filter paper which was supported on a sintered glass disk. The precipitates were washed with ice water, air dried for 20 min, mounted on an aluminum backing, and covered with cellophane tape for counting. Care was exercised to conduct the precipitations reproducibly and to obtain a uniform deposit. Samples were all counted by a conventional end-window Geiger–Mueller counter within 24 hr and corrections for decay were applied. The fraction of exchange, $F_i$, at the separation time $t_i$, was taken as

$$F_i = C_i/C_\infty \qquad (2)$$

where $C_i$ is the counting rate of sample collected at $t_i$ and $C_\infty$ is the average counting rate of two samples in satisfactory statistical agreement which were collected after isotopic equilibrium was established.

In a few instances the exchange was initiated by the addition of active $Br^-$ immediately after the solution was formed. In some others a solution of $Rb_2[PtBr_4]$ in $NaNO_3$ was allowed to equilibrate for several hours, and the exchange was initiated with the addition of a solution of the active $Br^-$ with KBr and $NaNO_3$.

## Results

**Acid Hydrolysis Equilibria.**—The distinct acidity of solutions of $Rb_2[PtBr_4]$, evidenced by the drop of pH to about 4 and the titer for added NaOH, can be attributed to the acidic properties of the aquo ligand formed in the acid hydrolysis, reaction 1. The titration of 10-ml aliquots of an equilibrated 5.00 m$M$ $Rb_2[PtBr_4]$ solution, ionic strength = 0.318 $M$, by the addition of NaOH reached an end point of pH 9.0 for a titer, $T$ = 2.52 mequiv of base/l. With the approximation for the titer, $T$

$$T = [PtBr_3(H_2O)^-] = [Br^-]$$

this result indicated a preliminary value of $K_1 = 2.6 \pm 0.3 \times 10^{-3}$ $M$ (25.0°, $\mu$ = 0.318 $M$). These results are satisfactorily consistent with the value of $3 \times 10^{-3}$ $M$ at 25° reported by Grinberg and Shagisultanova.[7] The equilibrium constant is about one-fifth of the corresponding constant[3b] for $[PtCl_4]^{2-}$. Furthermore with the more rapid pH drift in the titration it was not feasible to attempt an evaluation of the equilibrium constant, $K_2$, for the reaction

$$[PtBr_3(H_2O)]^- + H_2O \rightleftharpoons [PtBr_2(H_2O)_2] + Br^- \quad K_2 \qquad (3)$$

where at equilibrium $[PtBr_2(H_2O)_2]$ would be comprised of *cis* and *trans* isomers. For the chloride system $K_2/K_1 = {}^{1}/_{30}$.[2b] A value of $K_2 = 1 \times 10^{-4}$ $M$ therefore has been assumed to provide estimates of the amounts of $[PtBr_2(H_2O)_2]^-$ which may be encountered in solutions.

**Formation of $[Pt_2Br_6]^{2-}$.**—Harris, *et al.*,[5] have found that in $[N(C_2H_5)_4]_2[Pt_2Br_6]$ the $Pt_2Br_6^{2-}$ exists as a planar ion with a symmetric double bromide bridge. Since salts of this anion can be crystallized from solutions of $PtBr_4^{2-}$, the presence of this species in solution was postulated with equilibrium extablished with respect to reaction 4a. However, reaction 4a in combination with reaction 1 requires that equilibrium also be established for reactions 4b and 4c, as well, each characterized by its individual equilibrium quotient.

$$2[PtBr_4]^{2-} \rightleftharpoons [Pt_2Br_6]^{2-} + 2Br^- \quad K_{da} \qquad (4a)$$

$$[PtBr_4]^{2-} + [PtBr_3(H_2O)]^- \rightleftharpoons [Pt_2Br_6]^{2-} + Br^- + H_2O \quad K_{db} \qquad (4b)$$

$$2[PrBr_3(H_2O)]^- \rightleftharpoons [Pt_2Br_6]^{2-} + 2H_2O \quad K_{dc} \qquad (4c)$$

The dimer species, $[Pt_2Br_6]^{2-}$, can be formed by each of these reactions. The principle of microscopic reversibility requires the reverse of each of these at equilibrium to proceed at the same rate as the corresponding forward reaction. Each of these reactions may however proceed at quite different rates. From the coulombic repulsions between the charged ions it is expected that $\Delta H_{dc}^{\ddagger} < \Delta H_{db}^{\ddagger} < \Delta H_{da}^{\ddagger}$. Reactions 4a and 4b, but not 4c, provide a means of exchange between the free and ligand bromine. Therefore, chemical and spectrophotometric evidence was examined which might provide information concerning the extent and the rate of formation of the $[Pt_2Br_6]^{2-}$ ion.

A sample of $[N(C_2H_5)_4]_2[Pt_2Br_6]$, dissolved in $H_2O$, was passed through a column of Dowex 50 WX 8 cation-exchange resin in the $H^+$ phase. A potentiometric titration with NaOH of the effluent with a platinum concentration of $5.0 \times 10^{-3}$ g-atom of Pt/l. was performed. The titration indicated the presence of free $H^+$ with a concentration of 1.1 ± 0.05 equiv of $H^+$/g-atom of Pt. The weak acid, which was titrated between pH 5.0 and 9.0, amounted to 0.95 ± 0.05 equiv of $H^+$/g-atom of Pt. This result indicates that there is nearly one aquo ligand for each platinum atom.

Water is expected to replace bromide to form the species $[Pt_2Br_5(H_2O)]^-$, but for this species there is an $H_2O$:Pt ratio of only 0.5. The replacement of additional bromides from the dimer species is probably not extensive. Therefore, it appears likely that by the reverse of reaction 4c, the dimer has been largely con-

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(7) A. A. Grinberg and G. A. Shagisultanova, *Zh. Neorgan. Khim.*, **5**, 1895 (1960).

verted into $[PtBr_3(H_2O)]^-$, which became the predominant species. To estimate the concentration of various species in the solution a value of $K_1' = 10^{-3}\ M$, *i.e.*, the same order of magnitude as $K_1$, was assumed for the equilibrium quotient of the reaction

$$[Pt_2Br_6]^{2-} + H_2O \rightleftharpoons [Pt_2Br_5(H_2O)]^- + Br^- \quad K_1' \qquad (5)$$

From the assumed value of $K_2 = 1 \times 10^{-4}\ M$, a value $K_1 = 3 \times 10^{-3}\ M$, and the observed titer the following concentrations were calculated: $[PtBr_3(H_2O)^-] = 3.13$ m$M$, $[PtBr_4^{2-}] = 0.48$ m$M$, $[PtBr_2(H_2O)_2] = 0.68$ m$M$, $[Pt_2Br_6^{2-}] = 0.11$ m$M$, $[Pt_2Br_5(H_2O)^-] = 0.24$ m$M$, and $[Br^-] = 0.47$ m$M$. On the basis of these numbers the equilibrium quotient was estimated for dimerization, $K_{db} = 11\ M^{-1}$. This value was then used to estimate the dimer concentrations which might exist in other solutions. For the equilibrated solution of 5.0 m$M$ $Rb_2PtBr_4$, whose titration was described earlier, the estimate of components becomes: $[PtBr_4^{2-}] = 2.43$ m$M$, $[PtBr_3(H_2O)^-] = 2.32$ m$M$, $[PtBr_2(H_2O)_2] = 0.09$ m$M$, $[Pt_2Br_6^{2-}] = 0.06$ m$M$, $[Pt_2Br_5(H_2O)^-] = 0.02$ m$M$, and $[Br^-] = 2.68 \times 10^{-3}$ m$M$. With the inclusion of these minor species the equilibrium quotient, $K_1$, was unchanged and remained $2.6 \times 10^{-3}\ M$. It is to be emphasized that these computations yield only orders of magnitudes for the concentrations of minor species. However such estimates are valuable for interpretation of the isotopic exchange experiments by providing justification for the evaluation of the concentrations of the dominant species in these systems. Additional values of $K_1$ from titrations at 15 and 40° are in Table I.

Table I

Equilibrium Constant for Aquation of $PtBr_4^{2-}$ and the Rate Constants for the Isotopic Exchange Processes[a]

| Temp, °C | Ionic strength, $M$ | $K_1$, m$M$ | $k_{1\text{-ex}}$, $sec^{-1} \times 10^5$ | $k_{3\text{-ex}}$, $M^{-1}\ sec^{-1}$ |
|---|---|---|---|---|
| 15 | 0.318 | 1.75 | 7 | 0.13 |
| 25 | 0.318 | 2.6 | 22 | 0.22 |
| 25 | 0.100 | 2.8 | 22 | 0.080 |
| 40 | 0.318 | 4.0 | 115 | 0.40 |

[a] $\Delta H_1° = 6$ kcal, $\Delta H_{1\text{-ex}}^{\ddagger} = 19$ kcal, $\Delta H_{3\text{-ex}}^{\ddagger} = 8$ kcal; $\Delta S_1° = +8$ cal/deg, $\Delta S_{1\text{-ex}}^{\ddagger} = -10$ cal/deg, $\Delta S_{3\text{-ex}}^{\ddagger} = -36$ cal/deg.

The absorption spectrum in a 1-cm silica cell was recorded for the effluent from the ion-exchange column in which the $[N(C_2H_5)_4]_2[Pt_2Br_6]$ had been passed through the $H^+$ cation resin. This spectrum is shown as the 0-min curve in Figure 1. The spectrum exhibited a maximum of 0.65 in the optical density curve at 405 m$\mu$. The solution was diluted tenfold and the spectrum was recorded in a 10-cm cell at the time intervals indicated in Figure 1. The maximum decreased to 0.55 over a 200-min period with a half-time of *ca.* 12 min. Calculations, based on the equilibrium quotients estimated above, indicate that $[Pt_2Br_6]^{2-} + [Pt_2Br_5(H_2O)]^-$ in the light path decreased to one-fifth its initial value. The decrease in the optical density can therefore be attributed primarily to the decrease in the concentration of the dimer species, whose average extinction coefficient at 405 m$\mu$ is then indicated to be of the order of 180 $cm^{-1}$ (g-atoms of Pt)$^{-1}$ l. After some solid KBr was added to the cell, the dashed spectrum was recorded, which indicates the formation of $[PtBr_4]^{2-}$. $Rb_2[PtBr_4]\cdot H_2O$ dissolved in dilute HBr exhibits a maximum at 415 m$\mu$ ($\epsilon$ 117 $cm^{-1}\ M^{-1}$). It is apparent that the replacement of $Br^-$ by an $H_2O$ ligand shifts the 415-m$\mu$ band to shorter wavelengths in accordance with the spectrochemical series. An additional shift is expected for $[PtBr_2(H_2O)_2]$, and the extinction coefficient of this species in the 405–415-m$\mu$ region is accordingly expected to lie below that of $[PtBr_3(H_2O)]^-$.

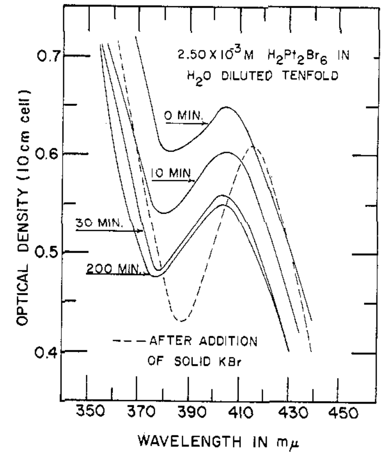


Figure 1.—Spectrophotometric changes when an aged solution of 2.5 m$M$ $H_2Pt_2Br_6$ in a 1-cm cell (0 min) is diluted to 0.25 m$M$ in a 10-cm cell. Dashed curve obtained after the addition of solid KBr. Temperature 25°; $NaNO_3$ added to give ionic strength of 0.318 $M$.

Additional support to this description is offered by the spectral changes which occur when $Rb_2[PtBr_4]$ is dissolved in dilute nitric acid solution. The optical density at 415 m$\mu$ of such a solution is plotted *vs.* time in Figure 2. With an initial concentration of 7.0 m$M$ $[PtBr_4]^{2-}$ the equilibrium state was calculated from the above equilibrium quotients to contain: $[PtBr_4^{2-}] = 3.75$ m$M$, $[PtBr_3(H_2O)^-] = 2.91$ m$M$, $[PtBr_2(H_2O)_2] = 0.09$ m$M$, $[Pt_2Br_6^{2-}] = 0.09$ m$M$, and $[Pt_2Br_5(H_2O)] = 0.03$ m$M$. The optical density decreased slightly in the first few minutes from an initial value of 0.73 and then increased over the period of 1 hr to a steady-state value of 0.82. The initial decrease is attributed to the formation of $[PtBr_3(H_2O)]^-$. As its concentration increased reaction 4b became effective for forming the dimer. The higher extinction coefficient of the dimer then caused the increase in optical density. When $2.40 \times 10^{-2}\ M$ KBr was added at 160 min the optical density reverted to very near its initial value with a half-period of about 6 min.

**Isotopic Exchange.**—Preliminary experiments were performed to evaluate the effectiveness of the separation procedure for the exchange experiments which involved the precipitation of tetraphenylarsonium salts. From a solution containing 50 mg of Pt at a concentration of *ca.* 5 m$M$, which contained approxi-

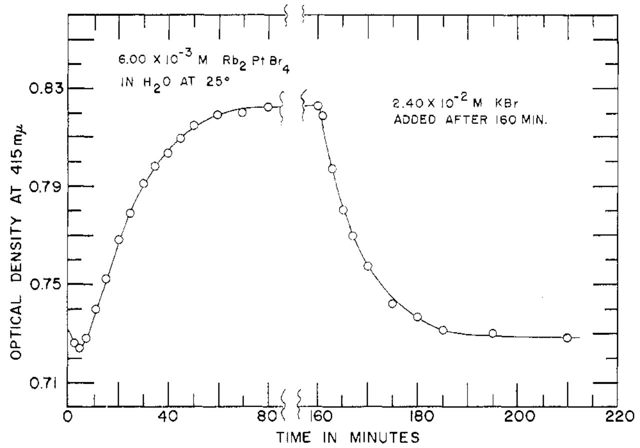


Figure 2.—Changes in optical density after Rb[$PtBr_4$] is dissolved in $H_2O$. Wave length 415 mμ; $NaNO_3$ added to give ionic strength of 0.318 *M*; [$H^+$] = $10^{-3}$ *M*.

mately equal concentrations of [$PtBr_4$]$^{2-}$ and [$PtBr_3(H_2O)$]$^-$, the filtrate from the separation was found to contain a negligible quantity of Pt; estimated <1 mg. It was therefore concluded that this precipitation removed both complex ions.

For satisfactorily reproducible results in the exchange experiments it was found important to filter the precipitates quickly after the addition of the precipitant since apparently a slow exchange occurs between the precipitates and free $Br^-$. In practice, the solutions were filtered within 30 sec from the addition of precipitant. One additional feature was noted. When salts of the [$Pt_2Br_6$]$^{2-}$ anion had been dissolved to yield solutions containing predominantly the [$PtBr_3(H_2O)$]$^-$ ion, the precipitates formed slowly upon the addition of [$As(C_6H_5)_4$]Cl. It is apparently necessary, therefore, for the solutions to contain fairly high concentrations of the [$PtBr_4$]$^{2-}$ species if a precipitate is to form rapidly and remove effectively the platinum complexes.

In the steady-state exchange studies the fractions of exchange were determined for each solution at a series of time intervals which usually covered 70–80% of the exchange. Plots of log (1 − *F*) were satisfactorily linear so that a meaningful exchange half-time could be evaluated from the slopes. The consistency of the points and the zero-time exchange, which in all but the fastest experiment amounted to only a few per cent, indicated a satisfactory separation procedure. The results of three steady-state exchange experiments are shown in Figure 3. Half-times for exchange and the observed zero-time exchange for the various experiments are listed in Table II. Duplicates for a number of these experiments have been performed. In addition to the concentrations of [$PtBr_4^{2-}$]$_0$ and [$Br^-$]$_0$, which were the initial concentrations before aging, the equilibrium concentrations of [$PtBr_3(H_2O)$]$^-$, calculated from the equilibrium quotient, $K_1$, are included in Table I. In some experiments the [$PtBr_3(H_2O)$]$^-$ amounted to as much as 20% of the total platinum. The estimated concentrations of [$PtBr_2(H_2O)_2$] and [$Pt_2Br_6$]$^{2-}$ were always less than 0.2 and 2%, respectively, of the total platinum.

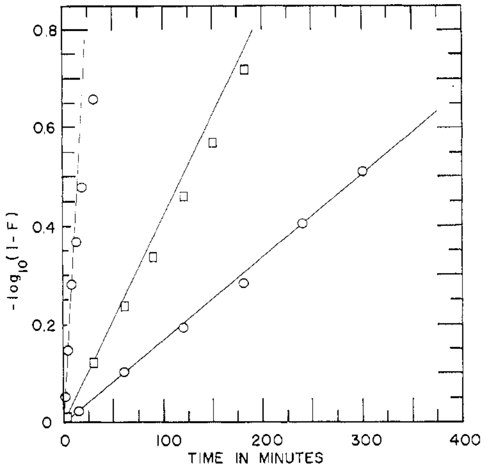


Figure 3.—Log (1 − *F*) *vs.* time for isotopic exchange reactions for aged solutions of [$PtBr_4$]$^{2-}$ and $Br^-$. Temperature 25°; ionic strength 0.318 *M*. Curves were calculated from the rate constants in Table I.

|  | [$PtBr_4^{2-}$]$_0$ | [$Br^-$]$_0$ |
|---|---|---|
| Upper curve | 39.3 m*M* | 26.4 m*M* |
| Middle curve | 5.5 m*M* | 22 m*M* |
| Lower curve | 5.5 m*M* | 200 m*M* |

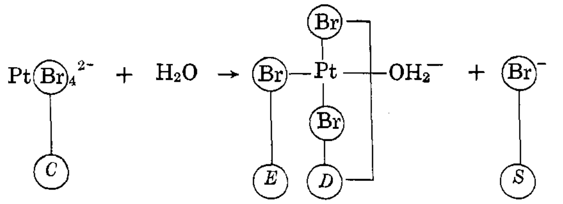
Table II

Isotopic Exchange between [$PtBr_4$]$^{2-}$ + [$PtBr_3(H_2O)$]$^-$ and $Br^-$

| [$PtBr_4^{2-}$]$_0$,[a] m*M* | [$Br^-$]$_0$,[a] m*M* | [$PtBr_3(H_2O)^-$] (steady state), m*M* | % exchange at zero time | Half-time, min Obsd | Half-time, min Calcd | Contribution of $R_{3\text{-ex}}$, % |
|---|---|---|---|---|---|---|
| | | 15°, μ = 0.318 *M* | | | | |
| 2.0 | 30.0 | 0.11 | 2 | 457 | 430 | 16 |
| 5.0 | 29.5 | 0.28 | 2 | 250 | 260 | 33 |
| 10.0 | 30.0 | 0.54 | 2 | 137 | 146 | 49 |
| 20.0 | 30.0 | 1.06 | 4 | 69 | 64 | 65 |
| | | 25°, μ = 0.318 *M* | | | | |
| 2.0 | 200 | 0.027 | 3 | 196 | 197 | 3 |
| 5.5 | 11 | 0.98 | 5 | 43 | 40 | 45 |
| 5.5 | 11 | 0.98<br>(0)[b] | 2 | 50 | . . . | . . . |
| 5.5 | 11 | 0.98<br>(2.53)[b] | 2 | 22 | . . . | . . . |
| 5.5 | 22 | 0.57 | 3 | 74 | 70 | 34 |
| 5.5 | 200 | 0.071 | 4 | 178 | 176 | 6 |
| 10 | 23.5 | 0.96 | 4 | 42 | 44 | 44 |
| 10 | 23.5 | 0.96<br>(0)[b] | 1 | 49 | . . . | . . . |
| 10 | 200 | 0.13 | 3 | 153 | 155 | 11 |
| 20 | 11 | 3.1 | 16 | 8.2 | 8.7 | 73 |
| 20 | 50.3 | 0.98 | 4 | 43 | 42 | 48 |
| 20 | 200 | 0.27 | 3 | 111 | 112 | 21 |
| 31.8 | 12.2 | 4.3 | 0 | 4.6 | 5.1 | 79 |
| 39.3 | 26.4 | 3.2 | 4 | 8.5 | 8.4 | 75 |
| 39.3 | 200 | 0.50 | 4 | 74 | 77 | 33 |
| 56.1 | 66.1 | 2.1 | 4 | 16 | 16.2 | 67 |
| | | 25°, μ = 0.100 *M* | | | | |
| 2.78 | 22 | 0.31 | 2 | 127 | 125 | 9 |
| 5.5 | 22 | 0.61 | 1 | 79 | 80 | 16 |
| 5.5 | 22 | 0.61<br>(0)[b] | 2 | 95 | . . . | . . . |
| 5.5 | 50 | 0.29 | 2 | 142 | 125 | 9 |
| 5.5 | 83.3 | 0.18 | 3 | 150 | 155 | 6 |
| | | 40°, μ = 0.318 *M* | | | | |
| 2.0 | 200 | 0.039 | 0 | 37 | 38 | 1.2 |
| 5.5 | 200 | 0.11 | 0 | 35 | 35 | 3.6 |
| 10.0 | 200 | 0.39 | 1 | 25 | 25 | 12 |
| 20.0 | 200 | 0.39 | 1 | 25 | 25 | 12 |
| 39.3 | 200 | 0.77 | 1 | 18 | 18 | 21 |

[a] Concentrations provided before aging to establish aquation equilibria. [b] Concentrations at start of exchange in a nonequilibrium experiment.

Since appreciable concentrations of $[PtBr_3(H_2O)]^-$ were formed, a rigorous treatment of the exchange kinetics must recognize the four chemical types of bromide as they have been specified in eq 6. The



(6)

symbols $C$, $D$, $E$, and $S$ correspond to the radioactivity concentration in each of the indicated chemical forms in terms of counts $\min^{-1}$ $l.^{-1}$. In general, three differential equations must be specified to describe isotopic exchange in such a four-component system.

The function $(1 - F)$ for such a four-component system under steady-state conditions contains three exponential terms. Since only one exponential period was evident from the experimental exchange curves, the data were first treated with the assumption that specific activities were equal for the three types of complexed bromide, *i.e.*

$$C/4[PtBr_4^{2-}] = D/2[PtBr_3(H_2O)^-] = E/[PtBr_3(H_2O)^-] \quad (7)$$

Such an approximation may be quite close to reality in cases where the bromide ligands undergo exchange at comparable rates or in cases where some process "trades" bromides between the two complexes. It should be noted that the aquation of $PtBr_4^{2-}$, reaction 1, results in the trade of three bromides between complexes for each free bromide ion introduced into the complexes. With the conditions of eq 7 imposed there are only two components, free bromide and complexed bromide, so only a single exponential is needed for $(1 - F)$ which can be treated by the usual McKay equation.[8]

$$R_{ex} = \frac{(\ln 2)(4[PtBr_4^{2-}]_0 - [PtBr_3(H_2O)^-]_\infty)[Br^-]_\infty}{(4[PtBr^{2-}]_0 + [Br^-]_0)\tau_{1/2}} \quad (8)$$

where $\tau_{1/2}$ is the half-time of the exchange. It was evident that the values of $R_{ex}$ obtained by this expression were not consistent with the simple aquation of the complexes or with a combination of aquation and direct exchange which was first order in both complex and bromide.

A very satisfactory fit with the observed values of $R_{ex}$ was obtained by the equation

$$R_{ex} = k_{1\text{-ex}}([PtBr_4^{2-}] + [PtBr_3(H_2O)^-]) + k_{3\text{-ex}}[PtBr_4^{2-}][PtBr_3(H_2O)^-] \quad (9)$$

Values of the rate constants are given in Table I. The calculated values of $\tau_{1/2}$ are included in Table II together with the percentage contribution of the term in $k_{3\text{-ex}}$ to the total exchange rate. The term $k_{1\text{-ex}}\cdot[PtBr_4^{2-}]$ represents largely the aquation rate of $[PtBr_4]^{2-}$ and the value of $k_{1\text{-ex}}$ is considered to provide a good evaluation of $k_1$. However, it should be noted that a rate term proportional to $[PtBr_3(H_2O)^-][Br^-]$ would have this same dependence because of the form of the equilibrium quotient for reaction 1. The term $k_{1\text{-ex}}[PtBr_3(H_2O)^-]$ can result from the aquation of $[PtBr_3(H_2O)]^-$ where $k_2$ also has been set equal to $k_{1\text{-ex}}$. This term never amounted to more than 11% of the exchange rate; therefore $k_2$ is not given precisely and can be only estimated as the same order of magnitude as $k_1$. If the process, described by $R_{3\text{-ex}}$, occurs *via* the formation of the doubly-bridged dimer, $[Pt_2Br_6]^{2-}$, the rate expression indicates that the contribution of reaction 4a is negligible in comparison to that of reaction 4b. The equilibrium constant for reaction 4b can be estimated: $K_{db} = K_{dc}K_1 = 3 \times 10^{-2}$. If $k_{db}$ is placed equal to $k_{3\text{-ex}} = 0.22$ sec$^{-1}$ $M^{-1}$, $k_{-db}$ will be *ca.* 7 sec$^{-1}$ $M^{-1}$ since $k_{-db} = k_{db}/K_{db}$.

The reaction characterized by $k_{-db}$ is believed to have caused the major decrease in optical density in Figure 2 following the addition of KBr at 160 min, as $[Pt_2Br_6]^{2-}$, with a high extinction coefficient, was converted into $[PtBr_4]^{2-}$ and $[PtBr_3(H_2O)]^-$. A pseudo-first-order rate constant for this process would be $k_{-db}[Br^-]$, which would have the value of *ca.* 0.2 sec$^{-1}$. In such a case a half-time of *ca.* 4 sec would apply. Since the observed half-time was 6 min, it has been concluded that the formation of the doubly-bridged dimer is not the process characterized by the term with $k_{3\text{-ex}}$.

The formation of a singly-bridged dimer, in which a bromide from $[PtBr_3(H_2O)]^-$ displaces a ligand from $[PtBr]^{2-}$, illustrated in Figure 4, offers a possible means for the exchange. In this process alone there is no trading of ligands between the complexes other than the aquation, reaction 1. The differential equations for the four-component system in eq 6 incorporating this mechanism in addition to the aquation processes are written as eq 10–13. These equations were solved

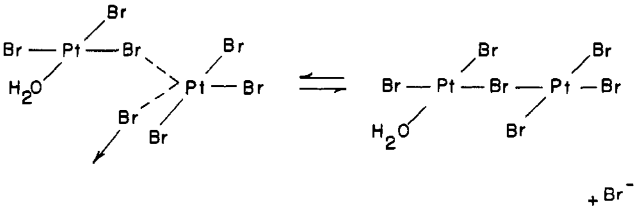


Figure 4.—Possible mechanism for second-order process.

$$\frac{dC}{dt} = -k_1C + k_{-1}[Br^-][PtBr_3(H_2O)^-]\left(\frac{S}{[Br^-]} + \frac{D + E}{[PtBr_3(H_2O)^-]}\right) + k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-]\left(\frac{S}{[Br^-]} - \frac{C}{4(PtBr_4^{2-}]}\right) \quad (10)$$

$$\frac{dD}{dt} = \frac{k_1C}{2} - k_{-1}[Br^-]D + k_c[PtBr_3(H_2O)^-]\left(\frac{S}{[Br^-]} - \frac{D}{[PtBr_3(H_2O)^-]}\right) \quad (11)$$

$$\frac{dE}{dt} = \frac{k_1C}{4} - k_{-1}[Br^-]E + k_t[PtBr_3(H_2O)^-]\left(\frac{S}{[Br^-]} - \frac{E}{[PtBr_3(H_2O)^-]}\right) \quad (12)$$

$$\frac{dS}{dt} + \frac{dC}{dt} + \frac{dD}{dt} + \frac{dE}{dt} = 0 \quad (13)$$

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(8) H. McKay, *Nature*, **142**, 997 (1938).

numerically for the steady-state experiments in Table I by the Runge–Kutta method[9] with the Iowa State University IBM 360-50 computer. For these calculations $k_1 = k_{1\text{-ex}}$, $k_{-1} = k_1/K_1$, $k_t = (^1/_2)k_c = (^1/_3)k_{1\text{-ex}}$, and $k_d = k_{3\text{-ex}}$. Calculated values of $F(t) = (C + D + E)/(C_\infty + D_\infty + E_\infty)$ were plotted. These plots differed so slightly from the single exponentials obtained with the condition of equal specific activity for all bromide ligands that it was not feasible to choose between them on the basis of the experimental exchange data. The rate constants, $k_c$ and $k_t$, characterize the acid hydrolysis of the different types of ligands in $[PtBr_3(H_2O)]^-$. The *trans* effect predicts that $k_c > 2k_t$. However, so long as $k_t + k_c = k_{1\text{-ex}}$, no significant difference in the fraction-exchange curves occurred for any ratio of $k_c/k_t$.

The numerical solutions of eq 10–13 are not restricted to steady-state conditions. These equations can be combined with eq 14 for the rate of change of $[PtBr_3(H_2O)]^-$. The numerical solutions of the complete

$$\frac{d[(PtBr_3(H_2O)^-]}{dt} = R_1 - R_{-1} = k_1[PtBr_4{}^{2-}] - k_{-1}[Br^-][PtBr_3(H_2O)^-] \quad (14)$$

set then yields the fraction of exchange, $F$, as a function of time in a nonequilibrium system. Two such nonequilibrium experiments are illustrated in Figure 5. For the highest curve the solution of $Rb_2[PtBr_4]$ was aged several hours before the addition of $Br^-$ and $[^{82}Br]^-$ to start the exchanges. In the lowest curve the exchange was started immediately upon dissolving the $Rb_2[PtBr_4]$. The middle curve was obtained under the steady-state conditions. The plotted curves were the actual computed solutions. For the upper curve, the estimated quantities of $[PtBr_2(H_2O)_2]$, $[Pt_2Br_5(H_2O)]^-$, and $[Pt_2Br_6]^{2-}$ were presumed to react immediately with $Br^-$ to form $[PtBr_3(H_2O)]^-$, $2[PtBr_3(H_2O)]^-$, and $[PtBr_3(H_2O)]^- + [PtBr_4]^{2-}$, respectively. The resulting $F$ curve then has a positive intercept at zero time. The calculated curves agree satisfactorily with the experimental points, which have also been plotted. These results generally support the role of reversible aquation in providing partially for the exchange process. They do emphasize the necessity for an accurate control and specification of the initial conditions and the chemical system in exchange studies.

Mechanisms other than the one shown in Figure 4 can be written for the second-order process in the exchange. In some of these the "trading" of ligands between the two species may occur or there may be "trading" processes which would be independent of the bromide introduction steps.

The replacement of a ligand in $[PtBr_3(H_2O)]^-$ by a bridging ligand from $[PtBr_4]^{2-}$ may also occur. Such a process introduces $Br^-$ into the minor complexed species, and numerical calculations have shown that this process alone cannot provide the exchange in the absence of the Figure 4 mechanism or an additional "trading" of ligands between the complexes.

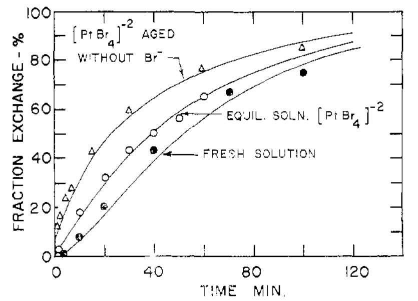

Figure 5.—Fraction exchange *vs.* time for isotopic exchange under nonequilibrium conditions. Solutions prepared from $[PtBr_4{}^{2-}] = 5.5$ m*M* and $[Br^-] = 11$ m*M*. For upper curve $[PtBr_4]^{2-}$ was aged before addition of $Br^-$ and $Br^{*-}$. Middle curve is for equilibrium conditions. For lower curve, $Br^- + Br^{*-}$ was added to freshly dissolved $PtBr_4{}^{2-}$ before aquation was established.

It appears that the higher Coulombic barrier for bringing together two $[PtBr_4]^{2-}$ ions prevents such encounters from providing a significant fraction of the exchange, *i.e.*, greater than 10–20%, since no second-order term in this species was required to describe the exchange rate.

The aquation for $[PtBr_4]^{2-}$ appears to have an activation enthalpy, $\Delta H_{1\text{-ex}}^{\ddagger}$ (Table I), approximately 2 kcal/mole lower than that for $[PtCl_4]^{2-}$. The entropy of activation, $\Delta S_{1\text{-ex}}^{\ddagger}$, is rather similar, amounting to *ca.* −10 eu, compared to −8 eu for $[PtCl_4]^{2-}$. The second-order reaction has a somewhat lower activation enthalpy, $\Delta H_{3\text{-ex}}^{\ddagger}$, of 8 kcal, than the aquation; and the lower entropy change, $\Delta S_{3\text{-ex}}$, of −36 eu is consistent with the interaction of two ions of the same charge sign. The over-all exchange rate expression, given quantitatively by eq 9, confirms the qualitative statement by Grinberg and Shagisultanova[4] that the exchange appears higher than first order in complex.

The resolution of terms in a complex kinetics expression such as eq 9 invariably introduces uncertainties into the kinetics parameters. In this case the value of $k_{3\text{-ex}}$ is strongly dependent upon the concentration of $[PtBr_3(H_2O)]^-$, which must be calculated from $K_1$. The great uncertainties in this equilibrium quotient are therefore directly reflected in the values of $k_{3\text{-ex}}$. However, there appears little doubt that the major portion of the exchange is described by an expression of the form of this equation even though the rate constant $k_{3\text{-ex}}$ may not be accurately determinable.

The dependence of the rate constants upon ionic strength, indicated in Table I, is in line with expectations. Thus, the aquation rate of $[PtBr_4]^{2-}$ for which the transition intermediate bears the same charge as the reactant ion shows negligible dependence upon ionic strength. However, the process characterized by $k_{3\text{-ex}}$, in which two anions coalesce to give the transition intermediate, is strongly accelerated by an increased ionic strength from 0.1 to 0.318 *M*.

It is of interest to note that a second-order term requiring a dimer transition intermediate was found in the rate expression for the exchange of chloride ion with

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[9] J. B. Scarborough, "Numerical Mathematical Analysis," 4th ed, Johns Hopkins Press, Baltimore, Md., 1958, pp 314–319.

the two chlorides *cis* to ethylene in solutions of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$. In this case the chloride *trans* to $C_2H_4$ is virtually labile. This exchange[10] required one term in the rate expression to be $k[Pt(C_2H_4)Cl_3^-]\cdot$[*trans*-$Pt(C_2H_4)Cl_2(H_2O)$]. At 25° $k$ was $8.6 \times 10^{-3}$ $M^{-1}$ $sec^{-1}$, only 4% as large as $k_{3\text{-ex}}$ in the present system. The $\Delta H^{\ddagger}$ was much higher for this chloride system, amounting to 19 kcal, and as expected from the charges of the reacting species the $\Delta S^{\ddagger}$ was much greater as well, amounting to −2 eu. The two *cis* chlorides of Zeise's salt anion are characterized by an exceedingly slow aquation replacement, and this feature may account for the observation of the second-order process, which has not been observed for any other chloride exchange.

Also Grinberg and Shagisultanova[11] reported that *cis*- and *trans*-$[PtBr_2(NH_3)_2]$ each traded Br ligands with $PtBr_4^{2-}$. These were examples of second-order processes that involved two species which were not related by the aquation process. Second-order rate constants which can be inferred from their results were similar in magnitude to $k_{3\text{-ex}}$ of the present study.

There are several instances now in which second-order processes are clearly demonstrated. It appears that the exchange reactions of platinum(II), and possibly substitution reactions as well, may exhibit a complexity which has not been recognized and which will require careful characterization over rather wide concentration ranges.

[10] S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[11] A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, **2**, 592 (1960).

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CONTRIBUTION FROM CENTRO DEI COMPOSTI DI COORDINAZIONE DEL C.N.R., ISTITUTO DI CHIMICA GENERALE, PADUA, ITALY, AND THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON W.C.1, ENGLAND

# The *cis* Effect of the Cyanide Group in Substitution Reactions of Square-Planar Gold(III) Complexes

BY L. CATTALINI, A. ORIO, AND M. L. TOBE

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The kinetics of the displacement of the heterocyclic amine "am" from a series of complexes of the type *trans*-$[Au(CN)_2Cl(am)]^0$ by the reagents $Br^-$, $N_3^-$, and $NO_2^-$ in methanol at 25° have been studied and the usual two-term rate law, rate = $(k_1 + k_2[Y])$[complex], has been observed. The dependence of $k_2$ upon the nature of the entering group indicates that, although Au(III) has a reasonable discrimination ability in these complexes, it is marginally poorer than in the analogous $[AuCl_3am]^0$ series. The nucleophilic power and even the sequence of reactivity depends upon the nature of the leaving group. The changes in behavior that follow the replacement of the two chlorines *cis* to the leaving group by two cyanides are not very large but they indicate that the cyanide group is able to displace more negative charge toward the central gold atom than can chloride. The displacement of "am" from $[AuCl_3am]^0$ by bromide is also reported.

## Introduction

In a previous paper[1] we discussed the kinetic behavior of a series of four-coordinate planar gold(III) complexes of the general type $[AuCl_3am]^0$ (am = a heterocyclic amine) when the neutral ligand "am" was replaced by the anionic nucleophiles $Cl^-$, $NO_2^-$, and $N_3^-$ in methanol at 25.0°. A linear relationship was observed between the basicity of the leaving group and the reactivity (expressed as the logarithm of the second-order rate constant) with respect to chloride substitution, where the entering group acts essentially as a $\sigma$-bonding nucleophile. However, in the reactions with the biphilic reagents $N_3^-$ and $NO_2^-$ the relationship was much more complicated and was explained in terms of $\pi$ bonding and polarization in the transition state.

A number of investigations of the *cis* effect in planar platinum(II) complexes have been reported. In the nucleophilic displacement of chloride from neutral complexes of the type *trans*-$[PtL_2Cl_2]^0$, where the ligands *cis* to the leaving group are able to withdraw charge from the metal into $\pi$ orbitals (*e.g.*, L = $P(C_2H_5)_3$ and $As(C_2H_5)_3$), the nucleophilic discrimination power of the substrate is relatively large.[2] In order to obtain some information about the *cis* effect in nonelectrolyte gold(III) complexes, we have prepared a series of compounds of the type *trans*-$[Au(CN)_2Cl(am)]^0$, and have studied the kinetics of their reactions with $Br^-$, $N_3^-$, and $NO_2^-$ in methanol at 25.0°. This series of complexes differs from that previously studied in that two cyanides are *cis* to the leaving amine instead of two chlorines. It was not possible to study the displacement of the amine by chloride and so, in order to obtain suitable data for comparison, it was necessary to study the reactions of the complexes of the type $[AuCl_3am]^0$ with bromide. It has also been possible to extend the range of basicity over which the leaving group effect could be studied.

## Results

Preliminary experiments indicated that the displacement of the coordinated amine in *trans*-$[Au(CN)_2$-

[1] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

[2] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).