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The Replacement of an Ammonia Molecule in Halopentaammineplatinum(IV) Cations by Halide Ions

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Rate constants and activation parameters have been determined for the replacement of one ammonia molecule in $Pt(NH_3)_5I^{3+}$ by Cl^-, Br^-, and I^-. Bromide ion reacts twenty times more rapidly than the other halides at 25.0°. Rate data were also collected on the replacement of an ammonia in $Pt(NH_3)_5Br^{3+}$ by Br^- and in $Pt(NH_3)_5Cl^{3+}$ by Cl^-. All reactions studied were catalyzed by $Pt(NH_3)_4{}^{2+}$, but the reactions of $Pt(NH_3)_5I^{3+}$ also occur by a $Pt(NH_3)_4{}^{2+}$ independent path. The mechanism for the Pt(II) catalyzed process has been postulated to involve a Pt(IV)–halide–Pt(II) bridged intermediate. The rate data indicate that a change of the halogen in the bridging position markedly alters the rate of these reactions. The order of effectiveness in promoting reactions at 25.0° is $I^- > Br^- > Cl^-$ with relative rates of 400,000, 400, and 1.

Introduction

There have been several reports that one ammonia molecule in halopentaammineplatinum(IV) cations can be replaced by a halide ion (eq. 1). Chernyaev and Orlova identify pentaammineplatinum(IV) complexes by

$$Pt(NH_3)_5X^{3+} + Y^- \longrightarrow \textit{trans}\text{-}Pt(NH_3)_4XY^{2+} + NH_3 \qquad (1)$$

means of the observation that they are not readily reduced but can be converted to black insoluble *trans*-$Pt(NH_3)_4I_2I_2$ when treated with an aqueous iodide solution. They have also observed the replacement of ammonia by other halides.[1] Basolo and co-workers[2] reported that chloride exchange in $Pt(NH_3)_5Cl^{3+}$ produced *trans*-$Pt(NH_3)_4Cl_2{}^{2+}$. They have reported rate data for this reaction and have postulated the mechanism outlined in eq. 2–4. The four ammonias which lie in the plane of the complex cations are omitted for simplicity; X and Y represent Cl. The mechanism is consistent with the catalysis by $Pt(NH_3)_4{}^{2+}$ which was

$$Pt^{2+} + Y^- \overset{\text{fast}}{\rightleftarrows} PtY^+ \qquad (2)$$

$$H_3NPtX^{3+} + PtY^+ \rightleftarrows H_3NPtXPtY^{4+} \qquad (3)$$

$$H_3NPtXPtY^{4+} \rightleftarrows NH_3 + Pt^{2+} + XPtY^{2+} \qquad (4)$$

observed in rate studies. This type of mechanism is also consistent with the rate data for a variety of substitution reactions of other platinum(IV) ammine complexes[3] and with data reported in this paper.

The purpose of this study was to investigate how the rate of ammonia replacement in halopentaammineplatinum(IV) complexes is affected by changing the entering ligand (Y) and the bridging group (X). The reactions studied include those in which X = Y = Cl, Br, or I, and those in which X = I and Y is Cl or Br.

Experimental

Preparation of Compounds.—The compounds studied were prepared by methods described in the literature. Chloropentaammineplatinum(IV) nitrate was prepared by conversion of the phosphate salt into the chloride and then into the nitrate.[4] Bromopentaammineplatinum(IV) nitrate was prepared in a similar manner by a conversion of the phosphate salt to the bromide and then into the nitrate.[5] Iodopentaammineplatinum(IV) nitrate was prepared by a method reported by Chernyaev and Orlova.[1] Tetraammineplatinum(II) perchlorate was prepared by converting the chloride salt[6] to the perchlorate by precipitation from an aqueous solution with 72% $HClO_4$ at ice bath temperature. All of these compounds were analyzed for platinum and halide content, and their ultraviolet spectra were recorded. Concentrations of $Pt(NH_3)_4(ClO_4)_2$ solutions were determined by Ce(IV) titration in dilute H_2SO_4 containing 1 *M* NaCl. The Pt(II) solutions were found to be stable for several weeks. The spectra of neutral solutions of some of the Pt(IV) complexes were observed to change slightly during a 24-hr. period. Therefore Pt(IV) solutions were prepared in acidic solution and were used the same day. All halide solutions and $HClO_4$ were prepared using reagent grade materials. Fresh iodide solutions were made every few weeks. The ionic strength of solutions was controlled using a $NaClO_4$ solution prepared from reagent Na_2CO_3 and $HClO_4$.

Kinetic Measurements.—The reactions of halopentaammineplatinum(IV) complexes with halide were followed spectrophotometrically. The $Pt(NH_3)_5Br^{3+}$–Br^- system was studied using a Beckman DB recording spectrophotometer. The $Pt(NH_3)_5Cl^{3+}$–Cl^- system was studied using Beckman DU optics with a Gilford absorbance indicator. The reactions of $Pt(NH_3)_5I^{3+}$ with I^-, Br^-, and Cl^- were all studied using a Cary Model 14 recording spectrophotometer. All of these instruments were equipped with a temperature-controlled cell compartment which maintained a temperature within ±0.1°.

The following method was employed in kinetic runs. Solutions of $Pt(NH_3)_4{}^{2+}$ catalyst, halide, and $NaClO_4$ (if needed) were placed in one beaker, and solutions of $Pt(NH_3)_5X^{3+}$ and acid ($HClO_4$) in another. These reactants were warmed or cooled to the desired temperature, mixed, and then placed in a 1-cm. quartz cell which was immediately placed in the instrument. Spectrophotometric data were taken by recording absorbance changes with time at a selected wave length or by scanning a brief portion of the ultraviolet spectrum at time intervals. All reactions were run under pseudo-first-order conditions. The concentration of halide was maintained sufficiently greater than the Pt(IV) concentration so that the concentration of halide was essentially constant during kinetic runs. The Pt(II) catalyst was regenerated by the reaction and hence its concentration remained constant. All reactions were run in dilute $HClO_4$ media. The purpose of this was to inhibit hydrolysis of the Pt(IV) species

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[1] I. I. Chernyaev and V. S. Orlova, *Russ. J. Inorg. Chem.*, **6**, 653 (1961).

[2] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

[3] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

[4] "Gmelins Handbuch der Anorganischen Chemie," 68D, Verlag Chemie, Weirheim/Bergstrasse, 1957, pp. 480, 484, 491.

[5] Reference 4, pp. 484, 485.

[6] R. N. Keller, *Inorg. Syn.*, **2**, 251 (1946).

in solution and to neutralize the ammonia produced in the reaction.

The reaction of $Pt(NH_3)_5Cl^{3+}$ with Cl^- was followed by reading the absorbance at 260 mμ at time intervals. This wave length was selected because the product *trans*-$Pt(NH_3)_4Cl_2^{2+}$ has a maximum in this region, whereas the reactants have a much smaller absorbance. The reaction was observed to be quite slow at 30° (the fastest reaction studied had a half-life of about 3 days). Studies over periods of several days showed that Cl^- reacts slowly with the $Pt(NH_3)_4^{2+}$ catalyst. Therefore the reactions of this system were followed for less than one half-life. Precipitation of the product $Pt(NH_3)_4Cl_2Cl_2$ after about one-half life also prevented studies over a longer time interval. Rate constants were calculated using an infinite time absorbance determined from the molar absorbtivities of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and $Pt(NH_3)_4^{2+}$ at 260 mμ. Plots of $\ln [A_\infty - A_i]$ *vs.* time gave straight lines with slope equal to the pseudo-first-order rate constant. The kinetic data were self-consistent to within ±10%. Activation parameters were calculated from rate data at three temperatures. The values of ΔH^* in all studies were obtained from plots of $\ln k/T$ *vs.* $1/T$. A linear plot was obtained for this reaction. The values of ΔS^* in all studies were evaluated from ΔG^* determined for each temperature, and ΔH^* using th relation $\Delta S^* = (\Delta H^* - \Delta G^*)/T$.

The reaction of $Pt(NH_3)_5Br^{3+}$ with Br^- was followed by scanning from 330 to 280 mμ at time intervals. The absorbance change at 318 mμ was used to evaluate the pseudo-first-order rate constant (318 mμ corresponds to a maximum in the spectrum of *trans*-$Pt(NH_3)_4Br_2^{2+}$). The infinite time absorbance was taken from the infinite time spectrum of the reaction mixture; rate constants were obtained from plots of $\ln [A_\infty - A_i]$ *vs.* time. This reaction was followed for essentially the entire lifetime of the reactants. The first-order plots were linear, and the rate constants were self-consistent to within ±5%.

The reactions of Cl^-, Br^-, and I^- with $Pt(NH_3)_5I^{3+}$ were followed at 415, 247, and 390 mμ, respectively. The 415 and 390 mμ wave lengths correspond to maxima in the spectra of the products *trans*-$Pt(NH_3)_4ICl^{2+}$ and *trans*-$Pt(NH_3)_4I_2^{2+}$, respectively, whereas 247 mμ corresponds to an isosbestic point for *trans*-$Pt(NH_3)_4IBr^{2+}$ and *trans*-$Pt(NH_3)_4Br_2^{2+}$. It was found necessary to use an isosbestic point in the studies of the $Pt(NH_3)_5I^{3+}$–Br^- system because a subsequent reaction of *trans*-$Pt(NH_3)_4IBr^{2+}$ with Br^- to give *trans*-$Pt(NH_3)_4Br_2^{2+}$ was observed to take place with a rate comparable to that of the initial substitution. By using an isosbestic point for these two species, the change in absorbance with time reflected only the disappearance of starting $Pt(NH_3)_5I^{3+}$. The isosbestic point was determined by scanning the spectrum of a sample of *trans*-$Pt(NH_3)_4IBr^{2+}$ at intervals as it reacted with excess Br^- (to give *trans*-$Pt(NH_3)_4Br_2^{2+}$).

The rate data of the reactions of $Pt(NH_3)_5I^{3+}$ were evaluated using the Guggenheim method.[7] Plots of $\ln [A_{i+t} - A_i]$ (where t = a constant time interval) *vs.* time were linear (for data spanning over six half-lives). The slopes gave the pseudo-first-order rate constant. The rate constants were self-consistent ±5% for the $Pt(NH_3)_5I^{3+}$–I^- system and within ±10% for the $Pt(NH_3)_5I^{3+}$–Br^- and $Pt(NH_3)_5I^{3+}$–Cl^- systems.

It was found that k values calculated from the ratio of the pseudo-first-order rate constants, k_{obsd}, and the $[X^-][Pt(II)]$ product ($k_{\text{obsd}}/[X^-][Pt(II)]$) were not constant for runs at temperatures above 38° for the $Pt(NH_3)_5I^{3+}$–I^- and $Pt(NH_3)_5I^{3+}$–Cl^- systems or above 6° for the $Pt(NH_3)_5I^{3+}$–Br^- system. Plots of $k_{\text{obsd}}/[X^-]$ *vs.* $[Pt(II)]$ were linear, however, and the slopes and intercepts were evaluated. The intercepts were verified by kinetic measurements involving no added Pt(II). The slopes of these plots gave third-order rate constants, k, while the intercepts gave values for the rate constant, k', for the Pt(II) independent reaction. The third-order rate constants can be calculated from values of k_{obsd} and k' (intercept) using eq. 5.

$$k = \{(k_{\text{obsd}}/[X^-]) - k'\}/[Pt(II)] \qquad (5)$$

In all reactions infinite time spectra of the reaction mixtures were virtually identical with known spectra of the *trans*-dihalotetraammineplatinum(IV) complexes. In the case of the $Pt(NH_3)_5Cl^{3+}$–Cl^- system a product was found to precipitate after about one-half-life. Some of this material was collected and its ultraviolet spectrum was found to be identical with that of $Pt(NH_3)_4Cl_2Cl_2$. In the study of $Pt(NH_3)_5I^{3+}$ with Br^-, it was never possible to record an infinite time spectrum of *trans*-$Pt(NH_3)_4IBr^{2+}$ because of its subsequent reaction to form *trans*-$Pt(NH_3)_4Br_2^{2+}$. However, spectra taken during the course of the reaction of $Pt(NH_3)_5I^{3+}$ with Br^- clearly showed the formation of spectral bands at 256 and 340 mμ corresponding to ones observed in the spectrum of *trans*-$Pt(NH_3)_4IBr^{2+}$.

Results

A general rate law for all reactions studied is presented in eq. 6. The $[Pt(NH_3)_4^{2+}]$ independent term was observed only in the reactions of $Pt(NH_3)_5I^{3+}$.

$$d[\textit{trans}\text{-}Pt(NH_3)_4XY^{2+}]/dt = (k[Pt(NH_3)_4^{2+}] + k')([Pt(NH_3)_5X^{3+}][Y^-]) \qquad (6)$$

In these reactions the concentration of $Pt(NH_3)_4^{2+}$ was maintained at a sufficiently high level such that the Pt(II) independent process contributed little to the observed rate. Therefore, k' values are rather inaccurate and additional studies are necessary to ascertain whether a simple second-order rate law adequately describes the Pt(II) independent path. Preliminary studies on the rate of the reaction between Br^- and $Pt(NH_3)_5I^{3+}$ indicate that the Pt(II) independent path is not a pseudo-first-order process in the presence of a large excess of Br^-. The rate, however, was found to be Br^- dependent.

Rate data for the five reactions studied are presented in Table I. A summary of rate constants at 25.0° and the activation parameters is presented in Table II. In the reactions in which ionic strength effects were studied, rates increased as the ionic strength of the reaction mixture was raised. This is consistent with the expected primary salt effect for a reaction having the rate law of the Pt(II) catalyzed process. In the reaction of $Pt(NH_3)_5I^{3+}$ with I^- a fivefold change in H^+ did not alter the reaction rate. In all the reactions good pseudo-first-order kinetics were observed for four or more half-lives. Since from 10 to 50% of the initial H^+ was consumed during the course of these reactions, there must be no appreciable $[H^+]$ dependence in any of the reactions in the slightly acidic reaction medium used. There was no evidence to suggest the reaction rates were influenced by light.

The rate of the reaction between Cl^- and $Pt(NH_3)_5Cl^{3+}$ has been reported[2] to be 6.5×10^{-4} M^{-2} sec.$^{-1}$ at 25.0° and an ionic strength of about 0.06 M. This is in good agreement with our value of 12×10^{-4} M^{-2} sec.$^{-1}$ at a higher ionic strength of 0.32 M. The previous workers reported an activation energy of 16.7 kcal./mole.

Discussion

The rate data collected on the replacement of an ammonia in $Pt(NH_3)_5X^{3+}$ by halide are consistent with the mechanism (eq. 2–4) proposed by Basolo and coworkers for a number of similar reactions.[2,3] However,

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[7] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

TABLE I

RATE DATA

$Pt(NH_3)_5I^{3+} + Cl^- \longrightarrow$ *trans*-$Pt(NH_3)_4ICl^{2+} + NH_3$

[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-2}$	[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-2}$
	15.0°^{a}			25.0°^{a}	
2.0	0.55	2.8	2.0	1.1	5.5
4.0	0.95	2.6	4.0	2.2	5.5
8.0	2.10	2.6	8.0	4.5	5.6
			8.0	2.3^b	5.8
	35.0°^{a,e}		8.0	20.4^c	6.4
2.0	2.0	9.5	8.0	31.8^d	9.9
4.0	3.9	9.5			

$Pt(NH_3)_5I^{3+} + Br^- \longrightarrow$ *trans*-$Pt(NH_3)_4IBr^{2+} + NH_3$

[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-3}$	[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-3}$
	5.8°^{f}			15.0^{f,h}	
1.6	1.4	4.4	1.6	2.0	5.6
3.2	3.0	4.6	3.2	4.1	6.1
4.8	4.8	5.0	4.0	5.1	6.1
4.0	7.0^g	4.4	4.8	5.9	5.9
3.2	5.5^g	4.3	6.4	8.5	6.6
	25.0°^{f,i}		4.0	8.5^g	5.3
0.8	3.0	12.5	4.0	5.7^j	6.8
1.6	4.7	11.6			
3.2	9.2	12.8			
4.0	10.8	12.3			

$Pt(NH_3)_5I^{3+} + I^- \longrightarrow$ *trans*-$Pt(NH_3)_4I_2^{2+} + NH_3$

[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-2}$	[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^3$	*k*, M^{-2} sec.$^{-1}$ $\times 10^{-2}$
	15.5°^{k}			25.0°^{l}	
4.0	1.02	2.5	4.0	1.62^m	4.1
	28.5°^{k}		16.0	2.7^n	6.7
2.0	0.87	4.4	16.0	3.9^o	9.7
4.0	1.69	4.2	12.0	4.6^p	3.8
4.0	1.63^s	4.1	12.0	4.4^q	3.6
8.0	3.3	4.2	12.0	4.2^r	3.5
8.0	1.72^t	4.3		38.5°^{k,u,v}	
16.0	6.7	4.2	4.0	0.66	5.6
16.0	1.60^u	4.0	8.0	1.27	5.8
			12.0	1.83	5.8
				48.5°^{k,u,w}	
			4.0	1.26	7.6
			8.0	1.99	7.3
			12.0	2.74	8.0
			4.0	2.49^t	7.4

$Pt(NH_3)_5Br^{3+} + Br^- \longrightarrow$ *trans*-$Pt(NH_3)_4Br_2^{2+} + NH_3$

[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^4$	*k*, M^{-2} sec.$^{-1}$	[Pt-(NH$_3$)$_4^{2+}$] $\times 10^4$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^4$	*k*, M^{-2} sec.$^{-1}$
	25.0°^{x}			34.6°^{x}	
2.0	3.5^y	10.9	2.0	7.2	22.5
4.0	8.0	12.5			
4.0	16.2^z	12.6		44.4°^{x}	
4.0	3.9^{aa}	12.2	2.0	12.2	38.0
4.0	8.1^{bb}	12.7			
20.0	10.0^{cc}	12.5			
10.0	7.3^{dd}	9.1			

$Pt(NH_3)_5Cl^{3+} + Cl^- \longrightarrow$ *trans*-$Pt(NH_3)_4Cl_2^{2+} + NH_3$

[Pt (NH$_3$)$_4^{2+}$] $\times 10^3$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^6$	*k*, M^{-2} sec.$^{-1}$ $\times 10^3$	[Pt-(NH$_3$)$_4^{2+}$] $\times 10^3$ *M*	k_{obsd}, sec.$^{-1}$ $\times 10^6$	*k*, M^{-2} sec.$^{-1}$ $\times 10^3$
	30.0°^{ee}			40.0°^{ee}	
2.0	1.3	2.0	2.0	3.4	5.2
4.0	2.7	2.1	2.0	1.5^{ff}	4.7
4.0	1.3^{ff}	2.0	4.0	6.5	5.1
	50.0°^{ee}		4.0	3.1^{ff}	4.8
2.0	8.3	13.0			
4.0	7.9^{ff}	12.3			
4.0	16.9	13.3			

[a] $[Pt(IV)] = 8.3 \times 10^{-4} M$; $[Cl^-] = 0.010\ M$; $[H^+] = 5.5 \times 10^{-3}\ M$; $\mu = 0.016\ M$. [b] $[Cl^-] = 5.0 \times 10^{-3}\ M$. [c] $\mu = 0.046\ M$; $[Cl^-] = 0.040\ M$. [d] $\mu = 0.35\ M$; $[Cl^-] = 0.040\ M$. [e] $k' = 0.01\ M^{-1}$ sec.$^{-1}$. [f] $[Pt(IV)] = 4.00 \times 10^{-5}\ M$; $[Br^-] = 2.00 \times 10^{-3}\ M$; $[H^+] = 5.5 \times 10^{-3}\ M$; $\mu = 0.016\ M$. [g] $[Br^-] = 4.00 \times 10^{-3}\ M$. [h] $k' = 0.11\ M^{-1}$ sec.$^{-1}$. [i] $k' = 0.5\ M^{-1}$ sec.$^{-1}$. [j] $[Pt(IV)] = 2.4 \times 10^{-5}\ M$. [k] $[Pt(IV)] = 1.65 \times 10^{-4}\ M$; $[I^-] = 1.00 \times 10^{-2}\ M$; $[H^+] = 1.10 \times 10^{-3}\ M$; $\mu = 0.011\ M$. [l] $[Pt(IV)] = 1.30 \times 10^{-4}\ M$; $[I^-] = 1.00 \times 10^{-2}\ M$; $[H^+] = 5.5 \times 10^{-3}\ M$. [m] $\mu = 0.016\ M$. [n] $\mu = 0.11\ M$. [o] $\mu = 0.20\ M$. [p] $\mu = 0.013\ M$; $[H^+] = 0.00326\ M$. [q] $\mu = 0.012\ M$; $[H^+] = 0.0023\ M$. [r] $\mu = 0.011\ M$; $[H^+] = 0.00093\ M$. [s] $[Pt(IV)] = 8.3 \times 10^{-5}\ M$. [t] $[I^-] = 5.0 \times 10^{-3}\ M$. [u] $[I^-] = 2.5 \times 10^{-3}\ M$. [v] $k' = 0.04\ M^{-1}$ sec.$^{-1}$. [w] $k' = 0.20\ M^{-1}$ sec.$^{-1}$. [x] $[Pt(IV)] = 1.0 \times 10^{-3}\ M$; $[Br^-] = 0.16\ M$; $[H^+] = 5.5 \times 10^{-3}\ M$; $\mu = 0.32\ M$. [y] $\mu = 0.16\ M$. [z] $[Br^-] = 0.32\ M$. [aa] $[Br^-] = 0.08\ M$. [bb] $[Pt(IV)] = 5 \times 10^{-4}\ M$. [cc] $[Br^-] = 0.04\ M$. [dd] $\mu = 0.08\ M$. [ee] $[Pt(IV)] = 2.50 \times 10^{-3}\ M$; $[Cl^-] = 0.32\ M$; $[H^+] = 5.5 \times 10^{-3}\ M$; $\mu = 0.32\ M$. [ff] $[Cl^-] = 0.16\ M$.

TABLE II

RATE CONSTANTS AT 25.0° AND ACTIVATION PARAMETERS

Complex reactant	Halide (Y$^-$)	Temp. range, °C.	ΔH*, kcal./mole	ΔS,* e.u.	*k*, M^{-2} sec.$^{-1}$
$Pt(NH_3)_5I^{3+}$	I^-	15–48	6	−29	3.9×10^{2} [a]
$Pt(NH_3)_5I^{3+}$	Br^-	5–25	8	−15	1.2×10^{4} [a]
$Pt(NH_3)_5I^{3+}$	Cl^-	15–35	11	−10	5.6×10^{2} [a]
$Pt(NH_3)_5Br^{3+}$	Br^-	25–45	10	−19	12.0 [b]
$Pt(NH_3)_5Cl^{3+}$	Cl^-	30–50	18	−13	1.2×10^{-3} [b]

[a] Ionic strength is 0.016 *M*. [b] Ionic strength is 0.32 *M*.

a platinum(II) independent reaction was also observed in reactions of $Pt(NH_3)_5I^{3+}$. The rate of this alternate path, which appears to give products identical with those of the $Pt(NH_3)_4^{2+}$ catalyzed reaction, is relatively slow at room temperature.

Interesting conclusions with regard to the effectiveness of Cl, Br, and I as entering and bridging groups can be drawn from the rate data and activation parameters for the platinum(II) catalyzed substitution reactions. Basolo and co-workers[3] have reported some data of this type, but in virtually all previous studies at least two of the three variables, entering, bridging, and leaving group, were changed. Therefore an unambiguous estimate of individual effects could not be made.

Bromide ion reacts thirty times more rapidly with $Pt(NH_3)_5I^{3+}$ than do chloride or iodide ions. The latter two react at comparable rates. Although the rates of these reactions do not show a regular trend from Cl^- to I^-, the activation enthalpies and entropies do. The data show that at room temperature the rate of replacement of ammonia is not markedly affected by the nature of the entering group. However, this appears to result from compensating changes in ΔH* and ΔS*.

The enthalpies of activation increased as the entering group was changed from I^- to Br^- to Cl^-. This change is consistent with the expected enthalpies of formation of the products $Pt(NH_3)_4I_2{}^{2+}$, $Pt(NH_3)_4IBr^{2+}$, and $Pt(NH_3)_4ICl^{2+}$. In both platinum(II) and platinum(IV) systems iodide forms more stable complexes than other halides. Thermochemical data[8] and equilibrium data on reaction 7[9] show that the

$$PtX_6{}^{2-} + 6Y^- \rightleftharpoons PtY_6{}^{2-} + 6X^- \qquad (X = Cl;\ Y = Br,\ I) \quad (7)$$

replacement of a lighter halide by a heavier one is an exothermic process. The favorable enthalpy has been attributed to solvation effects since the platinum(IV)–halogen bond energies are reported to decrease in the order Pt–Cl > Pt–Br > Pt–I.[9]

The entropies of activation are negative for all three reactions of $Pt(NH_3)_5I^{3+}$; the value of ΔS^* is particularly unfavorable for the reaction with I^-. The net entropy change for these reactions would be expected to be positive, since solvation of products should be less than that of reactants. Moreover, it seems probable that the net bonding interaction is less in the doubly charged product than in the triply charged reactant. The negative entropy must arise from the fact that three independent reactant molecules are assembled and required to take up specific orientations in the activated complex. The relatively large negative ΔS^* values correspond to similar values obtained for reactions of Cr^{2+} with several Cr^{3+} and Co^{3+} complexes; these reactions are thought to occur by a similar inner-sphere oxidation–reduction process.[10,11] The limited ΔS^* data in the literature on reactions of complex ions do not show any consistent trends which would explain the magnitude of ΔS^* for the reaction with I^-. The result might be interpreted as requiring an unusually rigid geometry in the activated complex of this reaction. Taube[11] has suggested that in oxidation–reduction reactions which proceed through a bridged intermediate and have a very small ΔH^* (6 kcal./mole in this case) it is probable that a bridged adduct is formed which has considerable stability. Moreover, he suggested that in this intermediate and in the activated complex there will probably be considerable interaction of d orbitals on the metals with suitable orbitals on the bridging atom. If this delocalization also extends to the entering ligand, such an entering ligand would be expected to lower the ΔH^* of the reaction but increase the rigidity of the activated complex and hence the magnitude of the negative value of ΔS^*. Since I^- is said to be the best π acceptor of the halogens, this could account for the observed ΔS^*.

An examination of the data in Table II gives direct evidence for the contribution of the halogen originally present in the pentaammine to the rate of platinum(II) catalyzed reactions. If the mechanism proposed in eq. 2–4 is correct, this halogen functions as a bridging atom through which electron transfer occurs. The rates of these substitution reactions are strongly dependent on the nature of the bridging atom with the observed order I >> Br >> Cl. The same order is observed in one-electron reductions of $Cr(NH_3)_5X^{2+}$, $Cr(H_2O)_5X^{2+}$, and $Co(NH_3)_5X^{2+}$ (X = Cl, Br, or I) with Cr^{2+}.[10] However, the differences in rate are not as marked in the Co and Cr systems.

The changes in ΔS^* observed when the bridging atom is changed from Cl to Br to I are small and favor a more rapid rate when I is the bridging atom. The changes in ΔH^* are of prime importance in making iodine the most effective bridging atom. The small values of ΔH^* observed when iodine is the bridging atom may result from a relatively favorable enthalpy for formation of a bridged intermediate. The fact that Pt(II) and Pt(IV) iodide complexes are quite stable makes this plausible.

An alternative and perhaps helpful manner of visualizing these reactions is to consider the substitution process as a nucleophilic attack on a coordinated halide by the platinum(II)–halide ion pair (eq. 8). Since iodide ion expands its coordination sphere more readily

$$Y^- \cdots Pt:^+ \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\text{—}Pt\text{—}NH_3{}^{3+} \qquad (8)$$

than the lighter halogens, it would be most susceptible to such a nucleophilic attack; ΔH^* would also be expected to be the least when iodine is the bridging atom.

If one assumes that the entering, bridging, and leaving groups in these substitution reactions of platinum(IV) complexes act independently in producing activation parameters, it is possible to calculate values of $\Delta(\Delta H^*)$ and $\Delta(\Delta S^*)$ produced by individual changes. This type of data could be quite useful in predicting rates of substitution reactions of platinum(IV) complexes. Studies are underway which will extend the present data to other ligands and will provide data on the effect of the leaving group. Additional experiments will also indicate whether values obtained for one set of reactants will apply to others. Preliminary results on tetraammine complexes appear to be in agreement with values of $\Delta(\Delta H^*)$ and $\Delta(\Delta S^*)$ which can be calculated from data in Table II.[12]

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