The Base Hydrolysis of the *trans*-Dibromotetracyanoplatinate(IV) Ion

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Abstract: In basic media one of the bromides of *trans*-$Pt(CN)_4Br_2^{2-}$ is replaced by a hydroxide ion. A study of the rate of this reaction reveals a two-term rate law given by the equation $-d[Pt(CN)_4Br_2^{2-}]/dt = [Pt(CN)_4Br_2^{2-}] \cdot (k_1[OH^-] + k_2[Br^-])$. The second term becomes significant when the ratio $[Br^-]/[OH^-]$ is $\geq 10^4$. The hydroxide term exhibits a dependence on the anion of the salt used to control the ionic strength. The bromide ion term exhibits no pH dependence (over the relatively small pH range of 8–9 examined). Different mechanisms are proposed for the two terms; the first appears to involve a dissociative process, while the second term results from assistance by the bromide ion. The value of k_1 at 25° in 1.0 *M* KNO_3 is $6.9 \times 10^3\ M^{-1}\ min^{-1}$, and the value of k_2 at 25° is $2.5 \times 10^{-1}\ M^{-1}\ min^{-1}$. The reaction is reversible with an equilibrium constant of 6.98×10^4. The reaction is not accelerated by the addition of $Pt(CN)_4^{2-}$.

Many substitution reactions in platinum(IV) complexes have been studied, and a variety of mechanisms have been reported.[2,3] The current study was undertaken after a preliminary investigation of the oxidation of $Pt(CN)_4^{2-}$ by iodine or bromine revealed that the initial oxidation was followed by a slower substitution reaction. This paper reports a study of one aspect of these systems, the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$, represented by the equation

$$trans\text{-}Pt(CN)_4Br_2^{2-} + OH^- \rightleftarrows trans\text{-}Pt(CN)_4Br(OH)^{2-} + Br^- \quad (1)$$

The study focused on the forward reaction for which the rate law given by eq 2 was found. This particular

$$-d[Pt(CN)_4Br_2^{2-}]/dt = [Pt(CN)_4Br_2^{2-}] \times (k_1[OH^-] + k_2[Br^-]) \quad (2)$$

system is of special interest as the conjugate base mechanisms, so frequently invoked to explain substitution reactions accelerated by base, *cannot* be invoked here, and because ion pairing and bridging mechanisms should be less likely from charge considerations. Few SN2 mechanisms have been substantiated in octahedral substitution reactions, and since platinum(IV) has been suggested as a possible center for this type of mechanism,[2] the present system would seem to provide an opportunity to test the occurrence of such a process.

Experimental Section

Preparation of Compounds. Platinum dichloride (5 g) from City Chemical Corp., New York, N. Y., is added to a hot aqueous solution of potassium cyanide (5 g of KCN in 100 ml of water). This gives a ratio of 4 moles of KCN per mole of $PtCl_2$. The solution is evaporated to 15–20 ml over a steam bath and filtered hot. When this is cooled $K_2[Pt(CN)_4]$ precipitates. The product is recrystallized from H_2O, dried under vacuum at 65°, and analyzed.

Anal. Calcd for $K_2Pt(CN)_4$: K, 20.73; C, 12.72; N, 14.84. Found: K, 20.73; C, 12.77; N, 14.73.

The addition of an excess of bromine to 50 ml of a hot aqueous solution containing 10 g of $K_2[Pt(CN)_4]$ results in the formation of *trans*-$K_2[Pt(CN)_4Br_2]$. The volume is reduced to 5 ml on a steam bath to expel the excess bromine and because of the high solubility of the dibromide complex. The product was recrystallized from H_2O and dried under vacuum at 40° prior to use and analysis. The carbon, nitrogen, and bromine analyses of these complexes were performed by Galbraith Laboratories, Knoxville, Tenn.

Anal. Calcd for $K_2[Pt(CN)_4Br_2]$: K, 14.56; C, 8.94; N, 10.43; Br, 29.75. Found: K, 14.40; C, 8.70; N, 10.29; Br, 29.67.

Spectral Measurements. The detailed features of the spectra of the complexes involved were obtained from ultraviolet and visible spectral measurements made on a Cary 14 recording spectrophotometer with 1.00-cm quartz cells. The spectra of *trans*-$K_2[Pt(CN)_4Br_2]$ were run in 2×10^{-2} *M* $HClO_4$ to repress hydrolysis.

Rate Measurements. The rate data were obtained by the use of three methods. The pH-Stat studies to establish the rate of base consumption were carried out with a Radiometer automatic titrator. The amount of base (0.01 *M* KOH) added to the solution was taken to be equal to the amount of *trans*-$Pt(CN)_4Br_2^{2-}$ reacted. The procedure for a run was as follows. The titrator was standardized at the desired temperature with standard buffer. Then 100 ml of 1.0 *M* KNO_3 solution was added to a thermostated jacketed beaker and the electrodes were placed in the solution to allow them to come to temperature equilibrium. The pH of the solution was then adjusted to the desired value, and a weighed sample of *trans*-$K_2[Pt(CN)_4Br_2]$ was added. The base solution was added from a 10-ml buret calibrated to 0.05 ml. During the reaction N_2 was bubbled through the solution to prevent the titration of CO_2, which would otherwise be absorbed from the air.

Spectrophotometric measurements to establish the rate of disappearance of *trans*-$Pt(CN)_4Br_2^{2-}$ were made using a Beckman DU spectrophotometer at 342 mμ which corresponds to an absorbance maximum of *trans*-$Pt(CN)_4Br_2^{2-}$. The product has a small absorbance in this region, and the concentration of *trans*-$Pt(CN)_4Br_2^{2-}$ during the reaction with OH^- is given by the relationship

$$[trans\text{-}Pt(CN)_4Br_2^{2-}] = \frac{Abs^{342} - ([trans\text{-}Pt(CN)_4Br_2^{2-}]_i \times 260)}{880}$$

where Abs^{342} is the absorbance of the reaction solution at 342 mμ. These studies were carried out in red light using 100-ml flasks placed in a constant-temperature bath adjusted to ±0.1° Care was taken to exclude light from the reaction mixture, and each reading on the spectrophotometer was made from a fresh sample to avoid any effect of light on the rate.

Pseudo-first-order conditions were obtained by buffering the reaction mixture at the desired pH with 0.1 *M* H_3BO_3 buffer (pH 8, 9, and 10) and with 0.02 *M* KH_2PO_4 buffer (pH 7). The ionic strength was fixed at 1.0 *M* with KNO_3 (except where otherwise

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[1] Du Pont Teaching Fellow, 1967–1968.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 237 ff.

[3] B. Corian and A. J. Poe, *J. Chem. Soc., A*, 1633 (1967), and references therein.

stated). The pH value of each solution was determined on a Radiometer pH 4 meter reading to 0.01 pH unit that had been standardized with standard buffers at each temperature used. All reagents used were ACS grade except for the H_3BO_3 which was USP grade. The H_3BO_3 solution was filtered through a Millipore filter apparatus before use.

Rate data on the release of bromide ion from *trans*-$Pt(CN)_4Br_2^{2-}$ were obtained directly by use of a bromide ion electrode (Orion Research, Inc., Cambridge, Mass.) in conjunction with a saturated KCl–calomel electrode and a Radiometer pH 4 meter. Solutions were buffered at a pH of 8 with 0.1 *M* H_3BO_3 buffer to obtain pseudo-first-order conditions. The ionic strength was controlled at 1.0 *M* with KNO_3. Standard KBr solutions were made up in the same medium to establish a calibration curve. The concentration of bromide ion can be found at any time by measuring the emf of an aliquot of the reaction mixture and comparing this value with the calibration curve.

Concentration *vs.* time data were treated by using a first-order or a reversible first-order rate expression. Pseudo-first-order rate constants were evaluated graphically. The second-order rate constants for the first term of the rate law (k_1) were calculated by dividing the pseudo-first-order rate constant obtained in each individual run by the hydroxide ion concentration measured for that run. The second-order rate constants for the second term (k_2) were obtained from a linear least-squares determination of the slope of a plot of the first-order rate constant *vs.* [Br^-] from runs with added bromide.

Activation parameters for the first term of the hydrolysis were evaluated by using a linear least-squares treatment of rate constants (k_1) obtained at 10, 20, 25, and 30° in 1.0 *M* KNO_3 and in 1.0 *M* KOAc. The activation parameters for the second term were obtained from rate constants (k_2) at 10, 15, 20, and 25° using a linear least-squares treatment.

Equilibrium Measurements. Equilibrium data on reaction 1 were obtained by use of spectrophotometric measurements, bromide ion concentration measurements, and pH measurements on solutions containing *trans*-$Pt(CN)_4Br_2^{2-}$, Br^-, and OH^-. The concentration of the dibromotetracyanoplatinate(IV) ion can be obtained from the relationship given previously. The solutions were kept out of light and thermostated at 25°. The equilibrium constant for reaction 1′ was obtained by dissolving *trans*-K_2-[$Pt(CN)_4Br_2$] in distilled water and measuring the pH of the solution at equilibrium. The equilibrium constant for (1) can be

$$\textit{trans-}[Pt(CN)_4Br_2]^{2-} + H_2O \rightleftarrows \textit{trans-}[Pt(CN)_4BrOH]^{2-} + Br^- + H^+ \quad (1')$$

obtained from that for equilibrium 1′ by dividing $K_{1'}$ by K_{H_2O}.

Reaction with Phenol and Aniline. Measurements were made on the change in absorbance at 342 mμ when phenol and aniline are added to solutions of the *trans*-dibromotetracyanoplatinate(IV) ion. All solutions were 0.01 *M* in either phenol or aniline, 0.01 *M* in perchloric acid, and 5 × 10^{-4} *M* in *trans*-$Pt(CN)_4Br_2^{2-}$. A comparison was made of the decomposition of *trans*-$Pt(CN)_4Br_2^{2-}$ by aniline or phenol in 0.5 *M* sodium bromide and with no bromide added. One solution containing phenol and one containing aniline in addition to the other reagents as above were made 0.5 *M* in sodium bromide and 8 × 10^{-4} *M* in $Pt(CN)_4^{2-}$ to find the effect of $Pt(CN)_4^{2-}$ on the rate of decomposition. Reagent blanks were also prepared which contained all reagents except the platinum complexes.

Results

The visible and ultraviolet spectra of *trans*-K_2[$Pt(CN)_4Br_2$] exhibit peaks at 342 and 240 mμ, both of which follow Beer's law. The 240-mμ peak is somewhat affected by the addition of sodium perchlorate used to control the ionic strength. When the spectrum of the complex is run in 1.0 *M* KBr, the absorbance of the peak at 240 mμ is significantly decreased. At the same time there is a small increase in absorbance in the region between the 240- and 342-mμ peaks although no peak was evident (Figure 1). The extinction coefficients for the *trans*-$Pt(CN)_4Br_2^{2-}$ ion are as follows: in aqueous solution (pH 1.7), ε^{342} 1.14 × 10^3, ε^{240} 4.25 × 10^4; in 1.0 *M* $NaClO_4$ (pH 1.7), ε^{240} 4.35 × 10^4; in 1.0 *M* KBr (pH 1.7), ε^{240} 4.00 × 10^4.

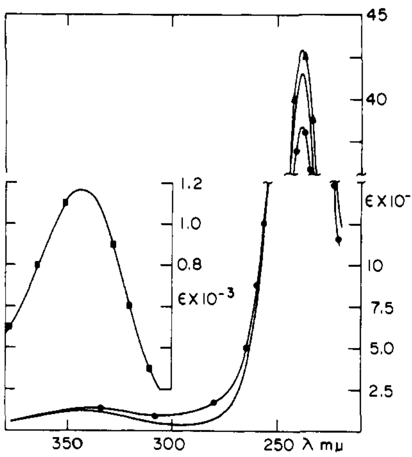

Figure 1. The ultraviolet spectra of 4 × 10^{-5} *M* *trans*-$Pt(CN)_4Br_2^{2-}$ in aqueous solution (——), in 1.0 *M* $NaClO_4$ (▲), and in 1.0 *M* KBr (●); the ultraviolet spectrum of 5 × 10^{-4} *M* *trans*-$Pt(CN)_4Br_2^{2-}$ in aqueous solution (■).

The spectrophotometric results indicated that at a pH of 9 one bromide was completely hydrolyzed. Bromide ion electrode and pH-Stat results showed that as much as 10% of the second bromide ion on *trans*-$Pt(CN)_4Br_2^{2-}$ was hydrolyzed at a pH of 9 after 2 days. Since all data followed pseudo-first-order behavior assuming the release of one bromide ion for at least three half-lives, the release of the second bromide was considered to be unimportant in these studies. The hydrolysis rate was found to be sensitive to light and variations in the medium.

The kinetic data for the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ in 1.0 *M* KNO_3 are given in Table I. The reaction was found to be first order in *trans*-$Pt(CN)_4Br_2^{2-}$ and first order in hydroxide ion. The second-order rate constants (each representing an average of two to five runs) show no variation within experimental error over the pH range 7–9. The average value of k_1 for all runs (excluding the pH-Stat data) is 6.94 × 10^3 M^{-1} min^{-1} with a standard deviation of 0.36 × 10^3. A relatively large experimental error would be expected in the second-order rate constants because of the lack of precision in the measurement of the hydroxide ion concentration even with the use of a pH meter measuring to ±0.01 pH unit. This error would be at least 5%, which is added to normal variations in rate data.

Table I. Rate Data in 1.0 *M* KNO_3 at 25°

Method	[$Pt(CN)_4Br_2^{2-}$], *M*	pH	k_1, M^{-1} min^{-1}
Spectrophotometric	5 × 10^{-4}	9	6.53 × 10^3
Spectrophotometric	8 × 10^{-4}	9	6.48 × 10^3
Spectrophotometric	5 × 10^{-4}	8	6.80 × 10^3
Spectrophotometric	5 × 10^{-4}	8.5	7.00 × 10^3
Spectrophotometric	8 × 10^{-4}	8	7.30 × 10^3
Spectrophotometric	5 × 10^{-4}	7	7.34 × 10^3
Br^- electrode	8 × 10^{-4}	8	7.40 × 10^3
pH-Stat	8 × 10^{-4}	9	8.12 × 10^3

There is some variation in the rate data gathered by different methods. The rather large difference between the pH-Stat data and those obtained with the spectrophotometer and bromide ion electrode may be due to one or all of several causes. First the problem of the accuracy of base concentration measurements, mentioned above, is compounded by the use of the automatic titrator with its pH-measuring device. Secondly, the solutions in the pH-Stat work are unbuffered, while the spectrophotometric and bromide ion electrode data were gathered using a 0.1 M H_3BO_3 buffer, thus introducing the possibility of a medium effect. Thirdly, the jacketed beaker used in the pH-Stat work was not completely covered so there may have been some light present, while the other data were collected using conditions where no light would be present.

It was found that the rate of reaction was affected to some extent when the anion of the salt used to adjust the ionic strength was changed. The results of a study of this effect are given in Table II.

Table II. Second-Order Rate Constants in Various Salt Solutions and Activation Parameters (μ = 1, 25°), Measured Spectrophotometrically

Media	pH	k_1, M^{-1} min^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, cal/(mole deg)
1.0 M KNO_3	7-9	6.94×10^3	26.4	38.3
1.0 M KOAc	8-9	5.12×10^3	30.2	50.5
0.33 M K_2SO_4	9	5.37×10^3		
1.0 M $NaNO_3$	9	6.70×10^3		
1.0 M $NaClO_4$	8.5	6.15×10^3		

The addition of KBr to the reaction mixture (while maintaining the ionic strength constant) produced a much larger effect on the reaction rate. It was found that the pseudo-first-order rate constant exhibited a dependence that was proportional to the bromide ion concentration and independent of the hydroxide ion concentration over the small pH range of 8-9 (Figure 2). This indicates that the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ can also occur by a path that is first order in bromide ion, first order in *trans*-$Pt(CN)_4Br_2^{2-}$, and zero order in hydroxide ion in addition to the path that is first order in the complex and first order in hydroxide ion. A rate law for the hydrolysis reaction consistent with this behavior is given by eq 2. A summary of the second-order rate constants for the bromide-dependent term along with the activation parameters are presented in Table III.

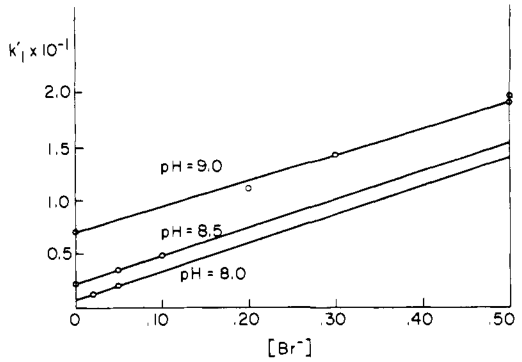

Figure 2. A plot of k_1' *vs.* [Br⁻], where k_1' is the pseudo-first-order rate constant found for the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ at constant pH. The ionic strength was 1.0 and the temperature was 25.0° in all cases.

Table III. Rate Constants and Activation Parameters for the Bromide-Dependent Term (μ = 1.0, 25°)

[Br⁻] range	pH	k_2, M^{-1} min^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, cal/(mole deg)
0.0–0.5 M KBr	9.0	2.58×10^{-1}	13.7	−24.4
0.0–0.1 M KBr	8.5	2.55×10^{-1}		
0.0–0.05 M KBr	8.0	2.77×10^{-1}		

Table IV gives rate data for the reaction under a variety of conditions. The addition of $Pt(CN)_4^{2-}$ had little effect on the rate, while the addition of $[Pt(NH_3)_4]Cl_2$ causes the reaction to go to completion in less than 1 min at pH 8. $IrCl_6^{2-}$ accelerates the reaction, and this is not due to the chloride which has been released by the hydrolysis of $IrCl_6^{2-}$, as chloride ion at this concentration has no effect on the rate. The reaction is accelerated slightly by the room lights and to a greater extent by the light in a DU spectrophotometer. KI (1.0 M) reduced the dibromide complex very quickly; 0.1 M NaSCN seemed to reduce the complex rather rapidly although no indication of any $(SCN)_2$ was found.

Table IV. The Effect of Various Additives and Light on the Rate of Reaction (1.0 M KNO_3, 25°)

Conditions	k_1, M^{-1} min^{-1}
5×10^{-4} M $K_2[Pt(CN)_4]$	6.50×10^3
5×10^{-4} M $[Pt(NH_3)_4]Cl_2$	Very fast
1×10^{-4} M $IrCl_6^{2-}$	1.71×10^4
1×10^{-4} M $IrCl_6^{2-}$ + 0.5 M KBr	1.6×10^{-1} (k_{obsd})
6×10^{-4} M Cl^-	6.60×10^3
In room light	7.88×10^3
In DU light	1.24×10^4
1.0 M KI	Reduction
0.9 M KNO_3, 0.1 M SCN^-	Very fast or reduction

Reaction 1 was found not to proceed to completion at pH 7 or below. The results of an equilibrium study of the reaction are given in Table V.

Table VI gives data on the decrease in *trans*-$Pt(CN)_4Br_2^{2-}$ concentration with time when phenol or aniline is present under conditions where the platinum complex is otherwise stable. The addition of bromide ion has a pronounced effect on the rate of *trans*-$Pt(CN)_4Br_2^{2-}$ decomposition. It can be seen also that the decomposition rate is greater in 0.01 M aniline than in 0.01 M phenol. The addition of $Pt(CN)_4^{2-}$ to the solution slows the decomposition.

Discussion

There are several features of the hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ in basic media which must be incorporated in any satisfactory set of mechanisms for the processes involved. These are: (1) the first-order hydroxide ion dependence of the bromide-independent path, (2) the first-order bromide ion dependence of the hydroxide ion independent path, (3) the considerable effect of added salts (presumably *via* their anions) on the reaction rate, (4) the absence of any acceleration by $Pt(CN)_4^{2-}$ and the powerful catalysis by $Pt(NH_3)_4^{2+}$, (5) the equilibration of products and reactants under practically all of the conditions examined. Also (6) the rate of bromide release, hydroxide consumption, and *trans*-$Pt(CN)_4Br_2^{2-}$

Table V. Equilibrium Data (25°)

$[Pt(CN)_4Br_2]$, M	pH	$[Br^-]$ added, M	K_1[a]	Method
5×10^{-4}	7	0 (0.05 M phosphate)	4.1×10^4	Spectrophotometric
5×10^{-4}	7	0.01 (0.05 M phosphate)	6.5×10^4	Spectrophotometric
5×10^{-4}	7	0.1 (0.05 M phosphate)	4.6×10^4	Spectrophotometric
5×10^{-4}	6.3	0 (1.0 M phosphate)	6.3×10^4	Spectrophotometric and Bromide ion electrode
5×10^{-4}	5.3	0 (0.4 M phthalate)	1.3×10^5[b]	
2×10^{-3}	4.03	0	4.27×10^4	Spectrophotometric, pH meter
1×10^{-3}	4.17	0	4.40×10^4	
5×10^{-4}	4.24	0	4.32×10^4	Spectrophotometric, pH meter
8×10^{-4}	3.42	0 (1.0 M $NaClO_4$)	8.82×10^4[b]	Spectrophotometric
5×10^{-4}	9.0	0.5 (0.05 M KNO_3)	6.16×10^4	Spectrophotometric
5×10^{-4}	9.0	0.2 (0.8 M KNO_3)	6.20×10^4	Spectrophotometric
5×10^{-4}	8.04	0.02 (0.98 M KNO_3)	8.75×10^4	Spectrophotometric
5×10^{-4}	8.04	0.05 (0.95 M KNO_3)	6.66×10^4	Spectrophotometric
5×10^{-4}	8.49	0.1 (0.9 M KNO_3)	6.70×10^4[b]	Spectrophotometric
5×10^{-4}	8.50	0.05 (0.95 M KNO_3)	6.81×10^4[b]	Spectrophotometric
5×10^{-4}	6.94	0 (1.0 M KNO_3)	6.94×10^4	Spectrophotometric
		Av	6.98×10^4	
		Std dev	2.32×10^4	

[a] $K_1 = [trans\text{-}Pt(CN)_4Br(OH)^{2-}][Br^-]/[trans\text{-}Pt(CN)_4Br_2^{2-}][OH^-]$. [b] Duplicates.

Table VI. Effect of Aniline and Phenol on *trans*-Dibromotetracyanoplatinate(IV)

Reagent	Added $[Br^-]$, M	t	Abs^{342}	$[Pt(CN)_4Br_2^{2-}]_t$, M
0.01 M phenol	0	Upon mixing	0.570	5×10^{-4}
		5 hr	0.570	5×10^{-4}
		4 days	0.550	4.82×10^{-4}
0.01 M phenol	0.5	Upon mixing	0.540	4.74×10^{-4}
		5 hr	0.054	4.74×10^{-5}
		4 days	0.012	~ 0
0.01 M aniline	0	Upon mixing	0.580	5.09×10^{-4}
		5 hr	0.450	3.95×10^{-4}
		4 days	0.162	1.42×10^{-4}
0.01 M aniline	0.5	Upon mixing	0.490	4.30×10^{-4}
		5 hr	0.003	~ 0
		4 days	0.007	~ 0
0.01 M phenol + 8×10^{-4} M $Pt(CN)_4^{2-}$	0.5	Upon mixing	0.618	5.4×10^{-4}
		5 hr	0.282	2.47×10^{-4}
0.01 M aniline + 8×10^{-4} M $Pt(CN)_4^{2-}$	0.5	Upon mixing	0.608	5.4×10^{-4}
		5 hr	0.008	~ 0

disappearance are all very nearly the same in the absence of added bromide ion; and (7) the *trans*-$Pt(CN)_4Br_2^{2-}$ complex is decomposed in the presence of aniline or phenol with added bromide under conditions where no decomposition occurs in the absence of aniline and phenol. When no bromide is added to the same solution the platinum complex decomposes much more slowly. If solutions are 8×10^{-4} M in $Pt(CN)_4^{2-}$, the decomposition is slowed somewhat.

Numerous mechanisms have been proposed for the substitution reactions of platinum(IV). The *trans*-dihalotetraammineplatinum(IV) cations undergo substitution reactions which are catalyzed by the tetraammineplatinum(II) action *via* a bridged intermediate.[2,4] These reactions apparently do not proceed by an uncatalyzed path at an appreciable rate. Our results showed one very important difference from those of Mason, Berger, and Johnson, in that the addition of the related platinum(II) complex, $Pt(CN)_4^{2-}$, to the reaction mixture had no effect on the rate of hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$. However, the addition of $Pt(NH_3)_4^{2+}$ did cause rapid hydrolysis of $Pt(CN)_4Br_2^{2-}$ presumably *via* a mechanism involving a halogen-bridged intermediate. The lack of a catalytic reaction in the presence of $Pt(CN)_4^{2-}$ may well be due to the unfavorable electrostatic interactions involved in bringing a *trans*-$Pt(CN)_4Br_2^{2-}$ ion up close to a $Pt(CN)_4^{2-}$ ion. The only way in which this might be facilitated is by means of ion pairs with cations or a bridging cation, but neither of these would lead to a suitable transition state. In the absence of such cations the intermediate would have a net charge of -4. There is evidence[5] that the hydrolysis and chloride-exchange reactions of $PtCl_6^{2-}$ are catalyzed by $PtCl_4^{2-}$, but detailed rate data are not available on these processes. Catalysis of the chloride exchange in $PtCl_6^{2-}$ by a platinum(III) species has been proposed to explain the retardation of exchange by oxidizing and reducing agents and its acceleration by light.[6,7] In the present case, the rate of hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ is accelerated by the addition of Ir(IV) to the reaction mixture. These results indicate that catalysis by a reduced species, such as Pt(III), is unlikely.

It is probable that a more conventional mechanism

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(4) W. R. Mason, III, E. R. Berger, and R. C. Johnson, *Inorg. Chem.*, **6**, 248 (1967).

(5) R. Dreyer, I. Dreyer, and D. Rettig, *Z. Physik. Chem.* (Leipzig), **224**, 199 (1963).

(6) R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).

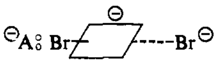
(7) A. J. Poe and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).

may be operative here rather than any of the specialized mechanisms usually utilized in discussion of platinum(IV) reactions. It remains to determine whether an associative or a dissociative mechanism is the more probable. It is also clear from the two-term rate law that a different mechanism is involved in the presence of a large amount of added bromide.

In some recent studies on the reaction of iodide with *trans*-$Pt(CN)_4X_2^{2-}$ (X = Br, Cl) and $PtBr_6^{2-}$, a redox mechanism is postulated.[8,9] The detailed mechanism proposed involves the transfer of X^+ from *trans*-$Pt(CN)_4X_2^{2-}$ to the iodide ion in the rate-determining step. The reduced central metal ion releases the ligand in the *trans* position. The platinum(II) complex is then reoxidized by the halogen molecule, leaving a halide in one *trans* position and adding the new ligand to the second *trans* position. It is possible that a mechanism of this sort is operative in the bromide-dependent term of our system.

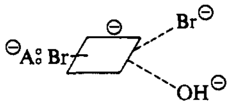
The Hydroxide Term. The term that is first order in hydroxide is characterized by a high positive entropy of activation. Its rate is also altered significantly as the salt used to maintain the ionic strength is varied. The positive entropy of activation suggests that this path involves a dissociative process in which a platinum–bromide bond is stretched to an appreciable extent in the attainment of the transition state. The positive entropy change would then arise from the separation of one ion into two and from the decrease in solvation of the species as the charge is spread over a larger volume.

The effect of various anions on the rate of reaction may also be consistent with a dissociative process.[10,11] The formation of an outer-sphere complex or some other type of aggregation involving two species of negative charge is quite unusual. However, it is possible that the negative charge on *trans*-$Pt(CN_4)Br_2^{2-}$ is concentrated in the plane of the cyanide ligands through back-bonding. In fact, the proposal that Cl^+ is transferred from *trans*-$Pt(CN)_4Cl_2^{2-}$ to I^- in the reduction of this complex by iodide was mentioned above.[9] Further, since the bromide ions have donated an electron pair to form the bond with the central metal, the bromide could be somewhat more electrophilic in nature than a bromide ion. One could then visualize some sort of association of the coordinated bromide and anions in solution which might tend to cause an even greater donation of electron density to the central metal as in with the process leading to an acceleration of the dissociation of the opposite bromide. The rate constant with various anions increases in the order: $OAc^- \sim SO_4^{2-} < ClO_4^- < NO_3^-$. This order *does not* correlate with the nucleophilicity or the basicity of the anions.



The first-order dependence of the hydrolysis rate on hydroxide ion can arise from the necessity that a hydroxide ion be in a position to enter the vacated coordination site for any net reaction to occur. The hydroxide ion would be present as a result of outer-sphere complexation or perhaps be in the solvation shell by virtue of its special relationship to the solvent. In either case, the amount of hydroxide ion in the proper position would be proportional to the hydroxide ion concentration. This process could be described as a dissociative interchange (I_d).[12]

An alternative proposal involves an associative interchange process (I_a) where the transition state is represented by a very loose octahedral wedge. The advantage of such a mechanism is that one might expect a more nucleophilic anion such as acetate or a doubly charged anion such as sulfate to be more strongly associated with a slightly electrophilic center than perchlorate or nitrate ion. The variation in the reaction rate would be explained in terms of a retardation of the basic rate through a decrease in the degree of association of OH^- as a consequence of a reduced electrostatic attraction to the ionic aggregate. In addition, the base dependence can be more explicitly accounted for. However, the large positive entropy of activation cannot be explained as well by the proposed transition state, and we favor the dissociative process.



It should be noted that the variation in rate constant with the different added salts might be accounted for by differences in the activities of the solutions, even though they are all at 1.0 *M* ionic strength. At concentrations greater than 0.01 *M* the activities deviate from the concentrations, and there is no reason to believe this deviation would be similar for the different salts used.

The Bromide Term. A further check on the proposed dissociative nature of the hydrolysis should be found in the effect of bromide ion on the rate of reaction. The rate should be retarded upon addition of bromide ion since the law of mass action would require that the concentration of the five-coordinate intermediate be decreased.

$$Pt(CN)_4Br_2^{2-} \rightleftarrows Pt(CN)_4Br^- + Br^-$$

$$Pt(CN)_4Br^- + OH^- \rightarrow Pt(CN)_4Br(OH)^{2-}$$

It was found, however, that the rate of reaction increased greatly; this is *not consistent with either a dissociative or an associative mechanism.* The enthalpy of activation in 1.0 *M* KBr is about half as great as the enthalpy in 1.0 *M* KNO_3, but the entropy is much different. The degree of solvation, the degree of dissociation, or both have been greatly altered in the transition state then. This coupled with the fact that this reaction path does not appear to be base dependent necessitates a mechanism of a different sort.

Since the reaction is first order in bromide ion, a mechanism involving bromide association seems logical. Again we postulate that the bromide ion bonded to the

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[8] E. J. Bounsall, D. J. Hewkin, D. Hopgood, and A. J. Poe, *Inorg. Chim. Acta*, **1**, 281 (1967).

[9] A. J. Poe and D. H. Vaughan, *ibid.*, **2**, 159 (1968).

[10] T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961).

[11] T. P. Jones and J. K. Phillips, *J. Chem. Soc., A*, 674 (1968).

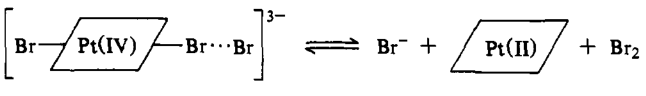
[12] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 1.

platinum is somewhat electrophilic in nature, perhaps similar to a bromine atom. The attack of bromide ion would then correspond to the formation of the tribromide ion. A transition state of this nature would

be consistent with the entropy of activation since entropy would be lost by the association of the attacking bromide ion. The dissociation of the bromide ion being replaced is apparently not as complete in the transition state as in the previous path. The formation of the bromide–bromide linkage would transfer electron density to the central metal, facilitating the release of the opposite bromide accounting for the increased rate. An interesting possibility is that the formal oxidation state of platinum might be +3 in this transition state.

The postulation of a transition state of this nature is not without precedent. Previous work on various reductions of platinum(IV) dihalides by thiocyanate and iodide, among others, has indicated that the reduction takes place by electron transfer through a weak bond formed between the reducing agent and one of the halogens of the substrate.[13] It should be noted that these redox processes are favored when π-acceptor ligands are bonded to the central metal ion.[13c] This may be caused by a net withdrawal of electron density from the halogen facilitating bond formation between the halogen and the attacking nucleophile, in our case, bromide ion.

It is quite possible that the bromide term involves a redox process of the sort mentioned above.[8,9] This is similar to the mechanism that we have postulated except that the electron pair is completely transferred to the central metal ion, and the halogen molecule is released into the solution.



I

(3)

The decomposition of *trans*-$Pt(CN)_4Br_2^{2-}$ when phenol or aniline is added to a solution of the complex and the increased rate of this decomposition when bromide ion is added would be consistent with this equilibrium. However, there are further considerations. Our equilibrium studies (eq 1) were carried out over a wide range of pH values (3–9) and bromide ion concentrations (0–0.5 *M*). Equilibrium 3 and thus equilibrium 1 should be very sensitive to these variations because the bromine produced in equilibrium 3 would be subject to hydrolysis. Using the equilibrium constant given for (4)[14] at pH 8 and 0.01 *M* [Br⁻], for example, the [Br₂]/[HBrO] ratio

$$Br_2 + H_2O \rightleftharpoons HBrO + H^+ + Br^- \qquad K = 5.8 \times 10^{-9} \qquad (4)$$

would be less than 0.02. The resulting shift in equilibrium 1 should show up unless the equilibrium constant for (3) is very small; however, it does not (see Table V). It is unlikely that HBrO acts as an oxidizing agent to prevent the shift in equilibrium for two reasons: (1) the oxidation potential of HBrO (0.76 V)[15] is much lower than bromine and is about the same as the dibromotetracyano complex (~0.7 V, as determined polarographically);[16] (2) we believe that the mechanism available for oxidation to occur is very important in determining the susceptibility of $Pt(CN)_4^{2-}$ to oxidation. For instance, Ce(IV) does not oxidize $Pt(CN)_4^{2-}$ at an appreciable rate even though its oxidation potential is much higher than that of bromine.[17] Bromine has the possibility of coordinating with $Pt(CN)_4^{2-}$ to form I. HBrO would not be expected to have this coordinating ability.

Another important piece of evidence regarding the redox mechanism involves the spectral changes in a solution of *trans*-$Pt(CN)_4Br_2^{2-}$ when bromide ion is added (Figure 1). It is interseting to note that the addition of large amounts of $Pt(CN)_4^{2-}$ to these solutions does not alter the spectral changes due to the bromide addition.[9] This means that an equilibrium of the sort given in eq 1 cannot be the source of the spectral change. A spectral change of this sort might result from the formation of I though.

We must now account for the decomposition of *trans*-$Pt(CN)_4Br_2^{2-}$ in phenol and aniline. It appears that species I could assume much of the character of a bromine molecule while retaining at least a nominal bond to the central metal. This would, in fact, be necessary to account for the acceleration in the rate of release of the *trans* bromide. This species could then function as the brominating agent. Moreover, the difference in the rates of decomposition in phenol and aniline might be explained by assuming that this brominating reagent is not nearly as effective as bromine. Although the relative rates of bromination of phenol and aniline are not available, the σ^+ values for NH_2 and OH substituents[18] indicate that aniline would brominate more easily. Poe postulates that the rate-determining step is the reduction of the platinum complex (or the formation of the halogen molecule) in the redox mechanism.[9] Since both phenol and aniline are brominated very rapidly it would seem that there should be no variation in the rate of decomposition with phenol or aniline. Of course, the variation could be explained by a competition between the reoxidation of tetracyanoplatinate(II) ion and the bromination of the aromatic reagent present. However, since the equilibrium concentration of $Pt(CN)_4^{2-}$ must be very low (see discussion of equilibrium 3) compared to the 0.01 *M* concentration of phenol or aniline and considering that the rates at which phenol and aniline are brominated approach diffusion control, it seems very unlikely that a competition is involved.

As a final test we studied the decomposition of *trans*-$Pt(CN)_4Br_2^{2-}$ in solutions 0.01 *M* in phenol or aniline, 0.5 *M* in sodium bromide, 8×10^{-4} *M* in added $Pt(CN)_4^{2-}$, and 5×10^{-4} *M* in *trans*-$Pt(CN)_4Br_2^{2-}$. The $Pt(CN)_4^{2-}$ should force equilibrium 3 to the left, thereby reducing the amount of bromine available to

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(13) (a) A. Peloso, R. Ethorre, and G. Dolcetti, *Inorg. Chim. Acta*, 1, 307 (1967); (b) A. Peloso and G. Dolcetti, *Coord. Chem. Rev.*, 1, 100 (1966); (c) *J. Chem. Soc., A*, 1944 (1967).

(14) H. A. Liebhafsky, *J. Am. Chem. Soc.*, **56**, 1500 (1934).

(15) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall Inc., New York, N. Y., 1952, p 61.

(16) C. E. Skinner and M. M. Jones, unpublished work.

(17) B. V. Ptitsyn, S. V. Zemskov, and A. V. Nikolaeu, *Dokl. Akad. Nauk USSR*, **167**, 304 (1966).

(18) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 90.

react. Perhaps a better way to say the same thing is that the added $Pt(CN)_4^{2-}$ should prevent the phenol or aniline from competing successfully for the Br_2. Table VI indicates that although the reaction is slowed by a factor of 3 or 4, the decrease in rate is not consistent with competition betwen $Pt(CN)_4^{2-}$ and phenol or aniline.

Summarizing this discussion, (1) the equilibrium data in Table V indicates that if equilibrium 3 occurs the equilibrium constant must be very small; (2) the data for the decomposition of *trans*-$Pt(CN)_4Br_2^{2-}$ (Table VI) would be consistent with equilibrium 3 only if a relatively large concentration of $Pt(CN)_4^{2-}$ were produced by the equilibrium, *i.e.*, the equilibrium constant for 3 was approaching 1; (3) the spectral data are not consistent with equilibrium 3. Thus considering the data we favor a mechanism of bromide-assisted substitution rather than a mechanism involving a redox process.

In conclusion we must admit that the substitution reactions of *trans*-$Pt(CN)_4Br_2^{2-}$ appear to possess some unusual features of their own. Simple mechanisms of the SN1 or SN2 type are obviously inadequate to explain the various factors governing the course of such reactions.

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