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The Mechanism of Bromine Oxidation of Tetracyanoplatinate(II) and Tetraammineplatinum(II) Ions

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The bromine oxidation of $\text{Pt}(\text{CN})_4^{2-}$ in bromide or chloride solutions to give *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ or *trans*- $\text{Pt}(\text{CN})_4\text{BrCl}^{2-}$ and the bromine oxidation of $\text{Pt}(\text{NH}_3)_4^{2+}$ in bromide solution to give *trans*- $\text{Pt}(\text{NH}_3)_4\text{Br}_2^{2+}$ proceed by a two-step process. The first step is a rapid oxidation of the platinum(II) complex to give a bromoaquoplatinum(IV) complex, while the second is a slower water replacement in the platinum(IV) complex by halide. The kinetics of platinum(IV) product formation corresponding to the water replacement step show second-order rate dependence on bromide for the reactions in bromide media. The third-order constant for the formation of *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ at 25° and $\mu = 1.01 M$ is $4.1 \times 10^5 M^{-2} \text{sec}^{-1}$; the value of K_a for the aquocyno complex precursor is 0.050 M . For the formation of *trans*- $\text{Pt}(\text{NH}_3)_4\text{Br}_2^{2+}$ the value of k_3/K_a is 52 $M^{-3} \text{sec}^{-1}$; a lower limit value of $\sim 5 M$ was placed on the value of K_a for the aquoammine complex precursor. The formation of *trans*- $\text{Pt}(\text{CN})_4\text{BrCl}^{2-}$ showed only first-order dependence on chloride. The second-order constant is 4.3 $M^{-1} \text{sec}^{-1}$; the value of K_a for the aquocyno complex precursor is 0.011 M . These results are interpreted in terms of a mechanism which in the case of reactions in bromide solution includes a rapid association of bromide with the bromoaquo complex formed in the rapid oxidative step. The rate law for the formation of *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ also includes a first-order term independent of bromide ion concentration.

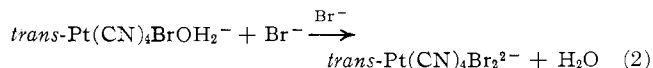
Introduction

A convenient and well-known method for preparing *trans* dihalo complexes of platinum(IV) involves the oxidation of a suitable square-planar platinum(II) complex with halogen in aqueous halide solution according to eq 1 ($X_2 = \text{Cl}_2, \text{Br}_2, \text{or } \text{I}_2$).^{1,2} However, in

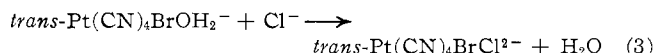


spite of widespread use of these reactions in synthesis of platinum(IV) complexes, little is known about their reaction mechanism. Consequently, the characterization of the reaction path for reactions of the type in eq 1 would be a valuable contribution to platinum(IV) chemistry. Moreover, the reactions of eq 1 are oxidative addition reactions. Reactions of this general type have attracted considerable recent interest.³ For example, oxidative additions to planar complexes of rhodium(I) and iridium(I) are believed to be important in the homogeneous catalysis of certain organic reactions,⁴ such as hydrogenation, olefin polymerization, and olefin isomerization. The mechanistic details for this type of reaction are thus of interest.

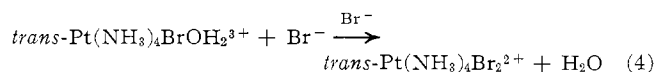
A recent study⁵ of the formation of *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ from the bromine oxidation of $\text{Pt}(\text{CN})_4^{2-}$ in bromide solution indicated that a two-step process is involved: a rapid oxidation of the platinum(II) complex followed by a slower substitution reaction, eq 2. The present



paper reports some additional kinetic studies on this reaction as well as studies of the anation of *trans*- $\text{Pt}(\text{CN})_4\text{BrOH}_2^-$ in chloride solution, eq 3, and of the



anation of *trans*- $\text{Pt}(\text{NH}_3)_4\text{BrOH}_2^{3+}$ in bromide solution, eq 4.



Experimental Section

Preparation of Compounds.—Potassium tetracyanoplatinate(II) trihydrate, $K_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$, and tetraammineplatinum(II) perchlorate, $[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$, were prepared according to literature methods.^{6,7} Purity was determined by elemental analysis and electronic spectra.⁸ All other chemicals were reagent grade. Bromine solutions were prepared fresh with dilute perchloric acid (0.020 M). A bromide analysis was performed on an aqueous solution following repeated extraction with CCl_4 ; the bromide content of the bromine solutions was less than 2%.

Kinetics.—The rate of formation of the platinum(IV) products in eq 2–4 was measured spectrophotometrically as described previously.⁹ Except as noted the ionic strength was maintained at 1.01 M with NaClO_4 . The three reactions studied here were all investigated in the presence of excess halide. Under these conditions the reactions were pseudo first order and appeared to go to completion. Infinite-time spectra in each case were identical with authentic samples of the product platinum(IV) complexes. For each reaction a rapid change in the spectrum of the platinum(II) complex (rate too fast to measure) was followed by a slower change leading to the spectrum of the final platinum(IV) product. Isosbestic points were noted for reaction 2 at 31,700 and 44,250 cm^{-1} and for reaction 3 at 45,400 cm^{-1} . Kinetic experiments generally could be reproduced to within ± 3 –5%; the rate constants reported in the data tables in many cases represent averages of several experiments.

In evaluating the bromide dependence of reaction 2, the $[\text{Br}^-]$ was taken to be the sum of the added bromide and the bromide formed in the initial rapid oxidation step (assumed equal to the initial $[\text{Pt}(\text{II})]$). Least-squares plots of k_{obsd} at constant $[\text{H}^+]$ for reaction 2 vs. $[\text{Br}^-]^2$ were linear with small nonzero intercepts. The slope of these plots corresponds to the third-order reaction characterized by the constant k_3 , whereas the intercept corresponds to the first-order bromide-independent reaction characterized by k_1 . Values of k_3 given in Table I were calculated from these plots together with K_a which was obtained from eq 5.

$$1/(k_{\text{obsd}} - k_1) = (1/k_3[\text{Br}^-]^2) + (K_a/k_3[\text{Br}^-]^2[\text{H}^+]) \quad (5)$$

Least-squares plots of $1/(k_{\text{obsd}} - k_1)$ vs. $1/[\text{H}^+]$ were linear;

(1) See for example the preparation of *trans* dihalo complexes in "Gmelin Handbuch der Anorganischen Chemie," 8th ed, Verlag Chemie, Weinheim/Bergstr., Germany: Vol. 68C, 1939; Vol. 68D, 1957.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 11–14.

(3) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970), and references therein.

(4) L. Vaska, *ibid.*, **1**, 335 (1968); R. Cramer, *ibid.*, **1**, 186 (1968); J. P. Collman, *ibid.*, **3**, 136 (1970).

(5) C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, **91**, 4405 (1969).

(6) Reference 1, Vol. 68C, p 202.

(7) W. R. Mason and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965); R. N. Keller, *Inorg. Syn.*, **2**, 251 (1946).

(8) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

(9) W. R. Mason, *Inorg. Chem.*, **9**, 1528 (1970), and references therein.

values of K_a computed from the slopes and intercepts were self-consistent to within $\pm 16\%$. The calculated values of k_3 were self-consistent to within $\pm 5-6\%$. Rate constants for reaction 3 were evaluated in a similar manner. Least-squares plots of k_{obsd} vs. $[\text{Cl}^-]$ were linear and passed through the origin within experimental error. Values of K_a obtained from eq 6 were self-

$$1/k_{\text{obsd}} = (1/k_2[\text{Cl}^-]) + (K_a/k_2[\text{Cl}^-][\text{H}^+]) \quad (6)$$

consistent to within $\pm 5\%$, and calculated values of k_2 were self-consistent to within $\pm 6\%$. The $[\text{H}^+]$ dependence for reaction 4 was linear up to 0.5 M H^+ (the highest concentration used). Consequently, the constants k_3/K_a were evaluated by dividing k_{obsd} by $[\text{Br}^-]^2[\text{H}^+]$. Values of k_3/K_a were self-consistent to within $\pm 4-5\%$.

Results and Discussion

From spectrophotometric observations, the bromine oxidations of $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{NH}_3)_4^{2+}$ proceed by a two-step process. The first step is rapid and is characterized by the disappearance of the platinum(II) spectrum (which is quite distinctive in the case of $\text{Pt}(\text{CN})_4^{2-}$). This step is consistent with the oxidation of the platinum(II) complex to a platinum(IV) intermediate. The second step is slower, and the spectrophotometric changes observed are consistent with a replacement reaction involving the platinum(IV) intermediate leading to the product complex. These results are in agreement with the earlier investigation⁵ of the bromine oxidation of $\text{Pt}(\text{CN})_4^{2-}$. The first step was reported to be complete in less than 2 msec. Thus the rate studies reported here are all for the second, slower step of the reactions, eq 2-4.

Rate data are presented in Tables I-III. The forma-

TABLE I
RATE DATA

$\text{trans-Pt}(\text{CN})_4\text{BrOH}_2^- + \text{Br}^- \xrightarrow{\text{Br}^-} \text{trans-Pt}(\text{CN})_4\text{Br}_2^{2-} + \text{H}_2\text{O}$					
$10^4[\text{Br}^-],$ M	$10^3k_{\text{obsd}},$ sec ⁻¹	$10^5k_3,$ M ⁻² sec ⁻¹	$10^4[\text{Br}^-],$ M	$10^3k_{\text{obsd}},$ sec ⁻¹	$10^5k_3,$ M ⁻² sec ⁻¹
25.0 ^{a,c}			15.0 ^{b,d}		
0	0.38 ^d	...	4.0	7.57 ^r	2.6
1.5	2.52 ^d	4.0	5.0	10.8 ^r	2.6
2.5	5.26 ^d	4.3	6.0	14.5 ^s	2.5
3.0	6.78	4.2	7.5	21.4 ^s	2.5
4.0	11.2	4.3	5.0	10.8 ^s	2.6
5.0	16.0	4.1	35.0 ^{b,t}		
6.0	21.9	4.0	2.0	8.09	7.6
6.75	27.5	4.0	3.0	14.5	8.1
7.5	33.6 ^d	4.0	5.0	30.4	7.4
5.0	8.76 ^{g,h}	3.9			
5.0	23.1 ^{f,i}	4.3			
5.0	27.9 ^j	3.8			
2.5	7.75 ^{g,k}	4.3			
2.5	10.8 ^{g,l}	4.3			
2.5	12.8 ^{g,m}	4.1			
5.0	17.7 ⁿ	4.2			
5.0	11.5 ^o	2.8			
5.0	4.29 ^p	0.9			

^a Added Br^- . $[\text{Total Br}^-] = [\text{added Br}^-] + [\text{Pt(II)}]$. ^b $[\text{Pt}(\text{CN})_4^{2-}] = 1.85 \times 10^{-5} \text{ M}$, $[\text{HClO}_4] = 0.0080 \text{ M}$, $[\text{NaClO}_4] = 1.00 \text{ M}$, $K_a = 0.050 \text{ M}$. ^c $k_1 = 9.4 \times 10^{-4} \text{ sec}^{-1}$, $[\text{Br}_2] = 5.4 \times 10^{-4} \text{ M}$. ^d $[\text{Br}_2] = 5.0 \times 10^{-4} \text{ M}$. ^e $[\text{Br}_2] = 2.5 \times 10^{-4} \text{ M}$. ^f $[\text{Br}_2] = 7.5 \times 10^{-4} \text{ M}$. ^g $[\text{Br}_2] = 2.7 \times 10^{-4} \text{ M}$. ^h $[\text{HClO}_4] = 0.0040 \text{ M}$. ⁱ $[\text{HClO}_4] = 0.012 \text{ M}$. ^j $[\text{HClO}_4] = 0.018 \text{ M}$. ^k $[\text{HClO}_4] = 0.014 \text{ M}$. ^l $[\text{HClO}_4] = 0.024 \text{ M}$. ^m $[\text{HClO}_4] = 0.034 \text{ M}$. ⁿ $[\text{Pt}(\text{CN})_4^{2-}] = 3.7 \times 10^{-5} \text{ M}$. ^o $\mu = 0.51 \text{ M}$. ^p $\mu = 0.01 \text{ M}$. ^q $k_1 = 1.33 \times 10^{-3} \text{ sec}^{-1}$. ^r $[\text{Br}_2] = 7.2 \times 10^{-4} \text{ M}$. ^s $[\text{Br}_2] = 6.9 \times 10^{-4} \text{ M}$. ^t $k_1 = 3.1 \times 10^{-3} \text{ sec}^{-1}$, $[\text{Br}_2] = 6.7 \times 10^{-4} \text{ M}$.

tion of the platinum(IV) product in each case is independent of the bromine concentration but is very slow in the absence of added halide ion. A measurable rate was observed for reaction 2 in the absence of added

TABLE II
RATE DATA

$\text{trans-Pt}(\text{CN})_4\text{BrOH}_2^- + \text{Cl}^- \rightarrow \text{trans-Pt}(\text{CN})_4\text{BrCl}^{2-} + \text{H}_2\text{O}$					
$10^3[\text{Cl}^-],$ M	$10^3k_{\text{obsd}},$ sec ⁻¹	$k_2,$ M ⁻¹ sec ⁻¹	$10^3[\text{Cl}^-],$ M	$10^3k_{\text{obsd}},$ sec ⁻¹	$k_2,$ M ⁻¹ sec ⁻¹
25.0 ^a			15.0 ^a		
4.0	7.44	4.4	4.0	3.56 ^k	2.1
4.0	7.58 ^b	4.4	8.0	7.44 ^k	2.2
4.0	7.54 ^c	4.4	12.0	10.5 ^k	2.0
4.0	8.05 ^d	4.7	35.0 ^a		
8.0	14.4 ^d	4.2	4.0	13.2 ^c	7.7
12.0	21.1 ^d	4.1	8.0	25.1 ^c	7.3
16.0	27.2 ^d	4.0	12.0	38.1 ^c	7.4
4.0	4.71 ^e	2.8			
4.0	1.84 ^f	1.1			
4.0	0.30 ^g	...			
4.0	12.7 ^{g,h}	4.4			
4.0	11.0 ^{g,i}	4.4			
4.0	13.4 ^{g,j}	5.6			

^a $[\text{Pt}(\text{CN})_4^{2-}] = 1.85 \times 10^{-5} \text{ M}$, $K_a = 0.0107 \text{ M}$, $[\text{HClO}_4] = 0.0080 \text{ M}$, $[\text{NaClO}_4] = 1.00 \text{ M}$, $[\text{Br}_2] = 5.42 \times 10^{-4} \text{ M}$. ^b $[\text{Br}_2] = 8.13 \times 10^{-4} \text{ M}$. ^c $[\text{Br}_2] = 6.15 \times 10^{-4} \text{ M}$. ^d $[\text{Br}_2] = 7.6 \times 10^{-4} \text{ M}$. ^e $\mu = 0.51 \text{ M}$. ^f $\mu = 0.01 \text{ M}$. ^g $[\text{HClO}_4] = 0.028 \text{ M}$. ^h $[\text{HClO}_4] = 0.018 \text{ M}$. ⁱ $[\text{Pt}(\text{CN})_4^{2-}] = 3.7 \times 10^{-5} \text{ M}$, $[\text{HClO}_4] = 0.016 \text{ M}$. ^j $[\text{Br}_2] = 7.2 \times 10^{-4} \text{ M}$.

TABLE III
RATE DATA

$\text{trans-Pt}(\text{NH}_3)_4\text{BrOH}_2^{3+} + \text{Br}^- \xrightarrow{\text{Br}^-} \text{trans-Pt}(\text{NH}_3)_4\text{Br}_2^{2+} + \text{H}_2\text{O}$					
$10^2[\text{Br}^-],$ M	$10^4k_{\text{obsd}},$ sec ⁻¹	$10k_3/K_a,$ M ⁻² sec ⁻¹	$10^2[\text{Br}^-],$ M	$10^4k_{\text{obsd}},$ sec ⁻¹	$10^2k_3/K_a,$ M ⁻² sec ⁻¹
25.0 ^a			35.0 ^{a,m}		
0	0 ^b	...	1.0	1.46	1.35
2.0	1.70 ^b	5.3	2.0	5.54	1.28
3.0	3.63 ^c	5.0	3.0	13.0	1.33
3.0	3.70 ^d	5.1	45.0 ^{a,m}		
2.0	3.69 ^{e,g}	5.1	1.0	3.26	3.0
2.0	6.06 ^{e,h}	5.4	2.0	12.9	3.0
3.0	3.92 ^{t,i}	5.4	3.0	29.2	3.0
2.0	22.8 ^{f,j}	5.3			
2.0	102.5 ^{f,k}	5.1			
1.0	27.0 ^{f,l}	5.4			
2.0	41.8 ^{f,l}	5.2			
3.0	8.6 ^f	11.9			
1.0	5.77 ^{f,i}	5.3			

^a $[\text{Pt}(\text{NH}_3)_4^{2+}] = 2.19 \times 10^{-5} \text{ M}$, $[\text{HClO}_4] = 0.0080 \text{ M}$, $[\text{NaClO}_4] = 1.00 \text{ M}$. ^b $[\text{Br}_2] = 8.0 \times 10^{-4} \text{ M}$. ^c $[\text{Br}_2] = 7.7 \times 10^{-4} \text{ M}$. ^d $[\text{Br}_2] = 4.8 \times 10^{-4} \text{ M}$. ^e $[\text{Br}_2] = 4.5 \times 10^{-4} \text{ M}$. ^f $[\text{Br}_2] = 6.2 \times 10^{-4} \text{ M}$. ^g $[\text{HClO}_4] = 0.018 \text{ M}$. ^h $[\text{HClO}_4] = 0.028 \text{ M}$. ⁱ $\mu = 0.29 \text{ M}$. ^j $[\text{HClO}_4] = 0.108 \text{ M}$. ^k $[\text{HClO}_4] = 0.500 \text{ M}$. ^l $[\text{HClO}_4] = 0.200 \text{ M}$. ^m $[\text{Br}_2] = 6.7 \times 10^{-4} \text{ M}$, $[\text{HClO}_4] = 0.108 \text{ M}$.

bromide, but the observed rate can be accounted for from bromide formed in the rapid oxidation step together with bromide resulting from a few per cent decomposition of the bromine solutions. The rate data for reaction 2 are consistent with the rate law in eq 7.

$$d[\text{trans-Pt}(\text{CN})_4\text{Br}_2^{2-}]/dt = \{k_1 + k_2[\text{Br}^-]^2[\text{H}^+]/([\text{H}^+] + K_a)\}[\text{trans-Pt}(\text{CN})_4\text{BrOH}_2^-] \quad (7)$$

The value of K_a at 25° and $\mu = 1.01 \text{ M}$ is $0.050 \pm 0.008 \text{ M}$. The constant k_1 , which corresponds to a bromide-independent reaction, was found to be $9.4 \times 10^{-4} \text{ sec}^{-1}$ at 25° and $\mu = 1.01 \text{ M}$ and $[\text{H}^+] = 0.008 \text{ M}$. However, under the conditions used to study reaction 2, this path contributed less than 10% to the overall reaction, except in a few experiments at low $[\text{Br}^-]$. Consequently, the value for k_1 is not precise nor is the hydrogen ion dependence for this path known for certain. This term could result from bromide in the bromine solutions since some reaction is observed in the absence of added bromide. However, the observed rate would require 15% or more bromide in the bromine solutions,

TABLE IV
 RATE CONSTANTS AT 25° AND ACTIVATION PARAMETERS^a

Reactants	ΔH^* , kcal mol ⁻¹	ΔS^* , cal deg ⁻¹ mol ⁻¹	Rate constant (25°)
Pt(CN) ₄ ²⁻ + Br ₂ + Br ⁻	9.3 ± 1.5	-2 ± 4	$k_3 = 4.1 \times 10^5 M^{-2} \text{sec}^{-1}$
Pt(CN) ₄ ²⁻ + Br ₂ + Cl ⁻	10.6 ± 1.0	-20 ± 4	$k_2 = 4.3 M^{-1} \text{sec}^{-1}$
Pt(NH ₃) ₄ ²⁺ + Br ₂ + Br ⁻	15.8 ± 0.5	+3 ± 1	$k_3/K_a = 52 M^{-3} \text{sec}^{-1}$

^a $\mu = 1.01 M$.

which seems unlikely since analysis of the bromine solutions showed less than 2% bromide. Further study of this bromide-independent path is necessary for its proper interpretation.

The data for reaction 3 are consistent with the rate law in eq 8. The value of K_a at 25° and $\mu = 1.01 M$

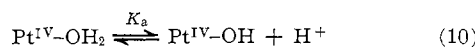
$$d[\text{trans-Pt(CN)}_4\text{BrCl}^{2-}]/dt = k_2[\text{Cl}^-][\text{H}^+][\text{trans-Pt(CN)}_4\text{BrOH}_2^-]/([\text{H}^+] + K_a) \quad (8)$$

is $0.0107 \pm 0.0005 M$. The data for reaction 4 are consistent with the rate law in eq 9. Since the rates

$$d[\text{trans-Pt(NH}_3)_4\text{Br}_2^{2+}]/dt = k_3/K_a[\text{Br}^-]^2[\text{H}^+][\text{trans-Pt(NH}_3)_4\text{BrOH}_2^{3+}] \quad (9)$$

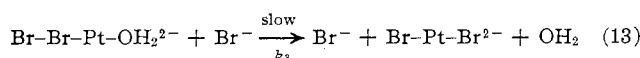
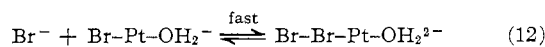
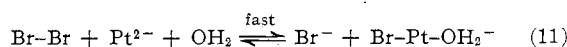
were linear in $[\text{H}^+]$ up to the highest $[\text{H}^+]$ employed (0.50 M), only a lower limit estimate of K_a is possible; its value must be $> \sim 5 M$.

The rate laws in eq 7-9 may be interpreted if one assumes that the rapid oxidation step involving bromine and platinum(II) produces an aquoplatinum(IV) complex in which the water molecule is subsequently replaced by halide. The aquo complex will act as an acid characterized by the rapid equilibrium indicated in eq 10. The rate dependence on hydrogen ion may be



explained if a water molecule is replaced more rapidly than a hydroxo ligand. This is supported by the fact that aquo complexes of platinum(IV) are known to be modestly strong acids,¹⁰ and hydroxo platinum(IV) complexes are inert.¹¹ It is noteworthy that the magnitude of K_a for the aquoammine complex of reaction 4 is much larger than for the aquocyano complexes of reactions 2 and 3. This is not surprising in view of the ionic charges expected for these complexes. The value of K_a reported⁵ previously for reaction 2 was 0.025 M which differs slightly from the value found here. The agreement is probably satisfactory in view of the fairly widely differing experimental conditions employed between the present (simple spectrophotometric) and the previous kinetic study (stopped-flow measurements).

The second-order bromide dependence for reactions 2 and 4 but first-order chloride dependence for reaction 3 is curious. A similar second-order bromide dependence was reported⁵ in the earlier study of bromine oxidation of Pt(CN)₄²⁻. The interpretation advanced⁵ involved the process outlined in eq 11-13 (the four

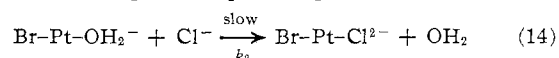


cyano ligands lying in a plane about each platinum

(10) Reference 2, p 32.

(11) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 59 (1962).

complex have been omitted for clarity). The fast oxidative step of eq 11 involves the formation of a bromoaquoplatinum(IV) complex. This is followed by a rapid bromide association to form the Br-Br-Pt-OH₂²⁻ species in eq 12. The rate-determining step is then visualized as a second-order water replacement in eq 13. The pathway outlined in eq 11-13 is consistent with the observed second-order bromide dependence for reactions 2 and 4. However, the first-order chloride dependence indicates a different behavior for reaction 3. Such behavior is probably best explained by noting that the corresponding chloride association step to form Cl-Br-Pt-OH₂²⁻ is expected to be less favorable. Thus the rate-determining step would likely involve only the bromoaquo complex, eq 14. The different



reacting aquoplatinum(IV) complexes of eq 13 and 14 may account for the difference in the values of K_a measured for reactions 2 and 3, which otherwise should be the same.

The bromide-association process of eq 12 would be favored from an electrostatic point of view for the positively charged ammine complex (ion-pair formation). The association for the negatively charged cyano complex is more difficult to rationalize. Changes in the charge-transfer spectra of the *trans*-Pt(CN)₄Br₂²⁻ ion in bromide solutions have also been interpreted in terms of bromide association.¹² It seems likely that the bromo ligands in these cyano complexes are quite positive, resulting from enhanced positive charge on the platinum due to metal→ligand π bonding to the cyano ligands.

The rate-determining water replacement step in each reaction must be a second-order process to account for the observed rate laws. The intimate features of this step are not clarified by this study, but the process could be either an associative process or an associative interchange.¹³ From the ionic strength dependence of the rates, it is evident that reactions 2 and 3 decrease in rate as the ionic strength is decreased, whereas with reaction 4 an increase in rate is noted. This behavior is consistent with primary salt effects for reactions between reagents of like charge in the first two cases and reagents of unlike charge in the third case and therefore is consistent with the associative transition states visualized.

From temperature-dependence studies, activation parameters were estimated for the slow water-replacement step of each reaction. These parameters are summarized in Table IV along with rate constants at 25°. It should be emphasized that the temperature dependence of these reaction rates also includes contributions from the temperature dependence of K_a . Thus the values of ΔH^* and ΔS^* listed must be con-

(12) A. J. Poe and D. H. Vaughan, *Inorg. Chim. Acta*, **2**, 159 (1968).

(13) See C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, for a discussion of these terms.

sidered as estimates. The lower reactivity of the ammine complex is due to unfavorable activation enthalpy. This is consistent with a degree of bond breaking being important for the aquoammine complex. The difference in reactivity of the aquocyanide complex with bromide and chloride, however, suggests that the entering ligand also plays a role in activation. The associative interchange mechanism thus may provide the best overall picture of the process.

The third-order rate constant for reaction 2 reported previously is $1.2 \times 10^5 M^{-2} \text{sec}^{-1}$ at 25° and $\mu = 1 M$, somewhat lower than that reported here. The

reason for this difference is not known. There are few additional data for comparison with the water-replacement rates reported here since many platinum(IV) reactions proceed by redox pathways involving platinum(II).⁹ This type of path appears excluded here because of the presence of excess bromine and, therefore, a very low concentration of platinum(II).

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Boron-Nitrogen Compounds. XL.^{1a} The Vibrational Spectrum of *B*-Trifluoroborazine

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The vibrational spectrum of *B*-trifluoroborazine, $(-\text{BF}-\text{NH}-)_3$, has been investigated and an assignment of fundamentals is proposed. The data are supported by a study of the infrared spectrum of $(-\text{BF}-\text{ND}-)_3$ and compare favorably with a normal-coordinate analysis of *B*-trifluoroborazine. The effect of boron-bonded fluorine on the electronic structure of the borazine ring is discussed.

Introduction

Recently, the vibrational spectra of borazine^{2,3} and some *B*-trihaloborazines⁴ were reinvestigated. The results of these studies suggested a smaller BN force constant than previously reported for borazines⁵⁻⁷ and also indicated that chlorine or bromine substitution at the boron sites exerts little or no mesomeric or inductive effects on the borazine ring system. Therefore, it seemed appropriate to extend this study to include the *B*-trifluoroborazine molecule. In this latter compound inductive effects should be most pronounced if they play any significant part in the nature of the BN ring bonding of borazines.

The structure of *B*-trifluoroborazine has been studied by electron diffraction⁸ and by X-ray analysis.⁹ The infrared spectrum in the sodium chloride region¹⁰ and the Raman spectrum¹¹ have been reported previously and these spectral data are in agreement with the results of the present investigation.

In the present work the infrared and Raman spectra of *B*-trifluoroborazine and the infrared spectrum of

its *N*-perdeuterated derivative are reported and assignments of the fundamental modes of vibration are suggested. The latter are in consonance with the results of a normal-coordinate analysis which also illustrates significant coupling of vibrations involving motions of the BF group.

Experimental Data

B-Trifluoroborazine, $(-\text{BF}-\text{NH}-)_3$, was prepared by the reaction of *B*-trichloroborazine with titanium tetrafluoride.¹² The *N*-perdeuterated compound was obtained from the dehydrofluorination of $\text{F}_3\text{B} \cdot \text{ND}_3$.¹³

Infrared spectra were recorded on the gas phase (10-cm cell with cesium iodide windows at autogeneous pressure and ambient temperature) and the solid material with a Perkin-Elmer Model 621 infrared spectrometer using cesium iodide windows.

The Raman spectrum of *B*-trifluoroborazine was obtained from the solid and from a solution in carbon disulfide with a Cary Model 81 Raman spectrometer and with a Jarrell-Ash double monochromator using a Spectrophysics 50-mW He-Ne laser operating at 6328 Å as the exciting device. In all cases the listed frequency values are the averages of several recordings and the instruments were operated at normal conditions.

Computer calculations were performed on an IBM 360-65 computer at the University of Kentucky Computing Center. The programs, which use the Wilson *FG* technique¹⁴ for setting up the vibrational secular equation, were written by Schachtschneider.¹⁵

Assignment of Fundamentals

In analogy to borazine, the *B*-trifluoroborazine molecule can be assumed to be planar and having D_{3h} symmetry. Recent X-ray work⁹ has illustrated, however,

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