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Base-Promoted Reduction of *trans*-Dibromotetracyanoplatinate(IV) and Hypobromous Acid Oxidation of Tetracyanoplatinate(II). Kinetics and Mechanisms[†][1]

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The rate laws for reactions i and ii in aqueous solution at 25 °C, $\mu = 0.10$ M, and $[OH^-] = 0.010–0.10$ M have been found to be $d[Pt(CN)_4^{2-}]/dt = k_1[Pt(CN)_4Br_2^{2-}][OH^-]$ and $-d[Pt(CN)_4^{2-}]/dt = k_2[Pt(CN)_4^{2-}][OBr^-]_{tot}/[OH^-]$, respectively, with $k_1 = 26 \pm 1.3\ M^{-1}\ s^{-1}$ and $k_2 = 0.18 \pm 0.015\ s^{-1}$: (i) *trans*-$Pt(CN)_4Br_2^{2-} + 2OH^- \rightleftharpoons Pt(CN)_4^{2-} + Br^- + OBr^- + H_2O$; (ii) $Pt(CN)_4^{2-} + OBr^- + H_2O \rightleftharpoons$ *trans*-$Pt(CN)_4Br(OH)^{2-} + OH^-$. At $[OH^-] \geq 0.010$ M, the reactions can be studied consecutively, with reaction ii following the more rapid reaction i. Values of quotients for reactions i and ii have been estimated to be 0.41 and $(1.1 \pm 0.10) \times 10^5$, respectively. Their reaction mechanisms and the related base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ are discussed.

Introduction

Ligand substitution reactions of platinum(IV) complexes are of considerable mechanistic interest. In the presence of platinum(II) complexes, the reactions are believed to involve a 2-equiv redox switch between the Pt(II) and Pt(IV) complexes.[2] In the absence of platinum(II) complexes, the reactions are believed to proceed via a reductive elimination of the Pt(IV) complex followed by a rapid reoxidation of the formed Pt(II) complex. This was called an REOA mechanism.[3] Thus, a key feature of the substitution reactions of platinum(IV) complexes is a 2-equiv redox reaction.[4]

Reaction between *trans*-$Pt(CN)_4Br_2^{2-}$ and OH^- has been studied by Skinner and Jones, and a bromide-assisted substitution mechanism was proposed.[5] Their work has been criticized by Poe and Vaughan[3c] in that it was possible for the base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ to occur via an REOA mechanism. However, no experimental data were provided to support this criticism. In this report we present kinetic and mechanistic study on the base-promoted reduction of *trans*-$Pt(CN)_4Br_2^{2-}$ and HOBr oxidation of $Pt(CN)_4^{2-}$. Our study provides evidence that base hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ at pH ≥12 can be readily interpreted in terms of an REOA mechanism.

Experimental Section

Materials. In this report all of the Pt(IV) complexes that are discussed are trans isomers. Therefore, the designation of trans in the prefix of the Pt(IV) complex will be omitted. $Na_2Pt(CN)_4 \cdot 3H_2O$ was obtained from Goldsmith Chemical & Metal Corp. and was used as received. The halide-free hypohalite solutions were prepared and standardized according to the literature.[6] It was known that OBr^- has a tendency to disproportionate and produce bromate ion.[7] However, it was found that the stock solution of OBr^- was quite stable in alkaline solution ($[OH^-] = 0.50–1.0$ M) when it was prepared and kept at ca. 0 °C. All the hypohalite solutions used in this study were halide-free. The $Na_2Pt(CN)_4Br_2$, $Na_2Pt(CN)_4Cl_2$, and $[(CH_3)_4N]_2[Pt(CN)_4BrCl]$ complexes were prepared and characterized according to the methods of Chernyaev et al.[8] Addition of an equivalent amount of Br_2 or NaOBr to a $Pt(CN)_4^{2-}$ solution at pH 10 resulted in a platinum complex that has been identified as $Pt(CN)_4Br(OH)^{2-}$.[5] It was found that the solutions of $Pt(CN)_4Br(OH)^{2-}$ are most stable at pH 10. All other chemicals except for $NaClO_4$ were reagent grade and were used as received.

Reaction Products. The platinum products were identified by comparing their UV–vis spectra with that of an authentic sample of $Pt(CN)_4^{2-}$ and of the $Pt(CN)_4Br(OH)^{2-}$ complex generated by base hydrolysis of $Pt(CN)_4Br_2^{2-}$ at pH 10.[5]

Equilibrium Constant Measurements. The equilibrium constant for the OBr^- oxidation of $Pt(CN)_4^{2-}$ is expressed in eq 2. At equilibrium, the concentration of $Pt(CN)_4^{2-}$ can be calculated from eq 3. ϵ_1^{255} is the molar absorptivity of $Pt(CN)_4^{2-}$ at 255 nm ($1.1 \times 10^4\ M^{-1}\ cm^{-1}$).[9] ϵ_2^{255} is the molar absorptivity of $Pt(CN)_4Br(OH)_2^-$ at 255 nm ($2.0 \times 10^3\ M^{-1}\ cm^{-1}$). C_1 is the initial concentration of $Pt(CN)_4^{2-}$. C_2 is the initial concentration of $Pt(CN)_4Br(OH)^{2-}$. b is the path length of the quartz cell.

$$Pt(CN)_4^{2-} + OBr^- + H_2O \rightleftharpoons Pt(CN)_4Br(OH)^{2-} + OH^- \quad (1)$$

$$K_{eq} = \frac{[Pt(CN)_4Br(OH)^{2-}][OH^-]}{[Pt(CN)_4^{2-}][OBr^-]} \quad (2)$$

$$[Pt(CN)_4^{2-}]_{eq} = \frac{(A^{255}/b) - \epsilon_2^{255}(C_1 - C_2)}{\epsilon_1^{255} - \epsilon_2^{255}} \quad (3)$$

Absorbance of OBr^- at 255 nm can be neglected. Concentrations of $Pt(CN)_4Br(OH)^{2-}$ and OBr^- at equilibrium were calculated from their initial concentrations and $[Pt(CN)_4^{2-}]_{eq}$.

Kinetic Measurements. All kinetic measurements were made at 255 nm (absorbance maximum of $Pt(CN)_4^{2-}$] or 342 nm (absorbance maximum of $Pt(CN)_4Br_2^{2-}$] under pseudo-first-order conditions with platinum complexes in deficiency. Reactions with a half-life >5 s were followed with a Cary 14 spectrophotometer. Reactions with a half-life <5 s were followed by a stopped-flow spectrophotometer. All rate measurements were performed at 25 ± 0.10 °C, 0.10 M ionic strength (maintained with $NaClO_4$), and $[OH^-] = 0.010–0.10$ M. The pseudo-first-order rate constants were obtained from the slopes of plots of log $(A_t - A_\infty)$ vs. time. These plots were linear for at least 4 half-lives. It should be noted that Na_2CO_3 was also present in the halide-free hypohalite solutions. The effect of the presence of CO_3^{2-} has not been examined, but we assume that it would not affect significantly the conclusions of this work.

Results

Initial Observations. Addition of 10^{-4} M $Pt(CN)_4Br_2^{2-}$ or $Pt(CN)_4BrCl^{2-}$ to an alkaline solution ($[OH^-] = 10^{-3}–10^{-1}$ M) resulted in formation of $Pt(CN)_4^{2-}$. The $Pt(CN)_4^{2-}$ complexes were then slowly oxidized to $Pt(CN)_4Br(OH)^{2-}$. Addition of 10^{-4} M $Pt(CN)_4Cl_2^{2-}$ to a 1 M hydroxide solution resulted in partial formation of $Pt(CN)_4^{2-}$ (ca. 60%), but no $Pt(CN)_4Cl(OH)^{2-}$ was formed. These results, together with observations that OBr^- reacts with $Pt(CN)_4^{2-}$ to form $Pt(CN)_4Br(OH)^{2-}$, while there is no observable reaction between $Pt(CN)_4^{2-}$ and OCl^- in alkaline so-

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Table I. Calculated Values of the Equilibrium Constant for Reaction 1 at μ = 0.10 M, $[OH^-]$ = 0.10 M, and 25 °C

$10^5 \times [Pt(CN)_4^{2-}]_{eq}$, M	$10^5 \times [OBr^-]_{eq}$, M	$10^4 \times [Pt(CN)_4Br(OH)^{2-}]_{eq}$, M	$10^{-5}K_{eq}$
1.8	3.9	7.0	1.0
1.7	3.8	7.0	1.1
1.7	3.5	6.2	1.1
1.5	3.3	6.3	1.3

Table II. Kinetic Data of the Reaction of $Pt(CN)_4Br_2^{2-}$ with OH^-[a]

$[OH^-]$, M	$[Br^-]_{added}$, M	k_{obsd}, s^{-1}	$[OH^-]$, M	$[Br^-]_{added}$, M	k_{obsd}, s^{-1}
1.00×10^{-2}	none	0.24	5.00×10^{-2}	1.00×10^{-2}	1.5
3.00×10^{-2}	none	0.92	5.00×10^{-2}	2.00×10^{-2}	1.4
5.00×10^{-2}	none	1.2	5.00×10^{-2}	3.00×10^{-2}	1.4
8.00×10^{-2}	none	2.3	5.00×10^{-2}	4.00×10^{-2}	1.2
1.00×10^{-1}	none	2.8	5.00×10^{-2}	5.00×10^{-2}	1.2
5.00×10^{-2}	none	1.6			

[a] Conditions: $[Pt(CN)_4Br_2^{2-}] = 4.00 \times 10^{-5}$ M; μ = 0.10 M (maintained with $NaClO_4$); temperature 25 °C.

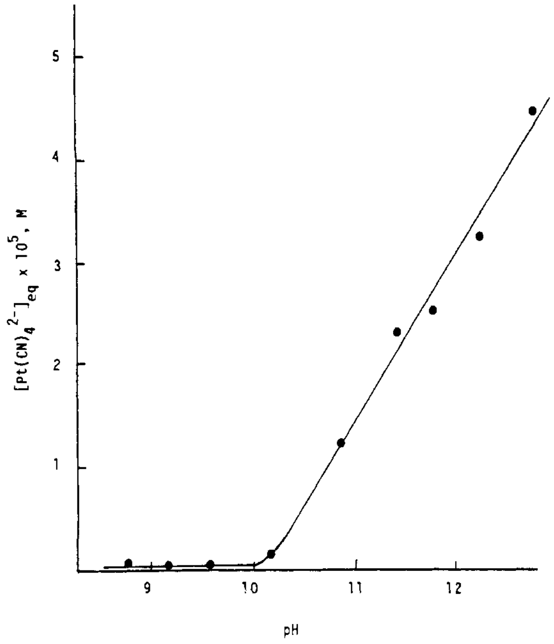


Figure 1. Plot of the calculated concentrations of $Pt(CN)_4^{2-}$ at equilibrium vs. pH values.

lution ($[OH^-] = 10^{-2}$–10^{-1} M), suggest that the reactions between $Pt(CN)_4XY^{2-}$ and OH^- at pH ≥11 can be described as

$$Pt(CN)_4Br_2^{2-} + 2OH^- \rightleftharpoons Pt(CN)_4^{2-} + OBr^- + Br^- + H_2O \rightleftharpoons Pt(CN)_4Br(OH)^{2-} + OH^- + Br^- \quad (4)$$

$$Pt(CN)_4BrCl^{2-} + 2OH^- \rightleftharpoons Pt(CN)_4^{2-} + OBr^- + Cl^- + H_2O \rightleftharpoons Pt(CN)_4Br(OH)^{2-} + OH^- + Cl^- \quad (5)$$

$$Pt(CN)_4Cl_2^{2-} + 2OH^- \rightleftharpoons Pt(CN)_4^{2-} + OCl^- + Cl^- + H_2O \quad (6)$$

Equilibrium Constant Measurements. With use of eq 3, $[Pt(CN)_4^{2-}]$ values at equilibrium in mixtures of equimolar amounts of $Pt(CN)_4^{2-}$ and OBr^- (6.7×10^{-5} M) as a function of pH were calculated. These values are plotted in Figure 1. Table I lists the calculated values of the equilibrium constant obtained at 0.10 M NaOH. Four similar runs were performed. Accordingly, the equilibrium constant for reaction 1 is estimated to be (1.1 ± 0.10) × 10^5 at 25 °C, μ = 0.10 M ($NaClO_4$). This value was confirmed by adding a separately prepared $Pt(CN)_4Br(OH)^{2-}$ to the mixture of $Pt(CN)_4^{2-}$ and OBr^-.

Table III. Kinetic Data of the Reaction of $Pt(CN)_4^{2-}$ with HOBr[a]

$[OBr^-]_{tot}$, M	$[OH^-]$, M	k_{obsd}, s^{-1}	$[OBr^-]_{tot}$, M	$[OH^-]$, M	k_{obsd}, s^{-1}
1.00×10^{-3}	0.100	1.6×10^{-3}	4.30×10^{-3}	0.0226	2.7×10^{-2}
3.57×10^{-3}	0.100	6.4×10^{-3}	4.30×10^{-3}	0.0413	1.6×10^{-2}
5.35×10^{-3}	0.100	1.0×10^{-2}	4.30×10^{-3}	0.0538	1.3×10^{-2}
7.13×10^{-3}	0.100	1.5×10^{-2}	4.30×10^{-3}	0.0662	1.1×10^{-2}
8.92×10^{-3}	0.100	1.8×10^{-2}	4.30×10^{-3}	0.0787	8.5×10^{-3}
1.07×10^{-2}	0.100	2.2×10^{-2}			

[a] Conditions: $[Pt(CN)_4^{2-}] = 5.60 \times 10^{-5}$ M; μ = 0.10 M (maintained with $NaClO_4$); temperature 25 °C.

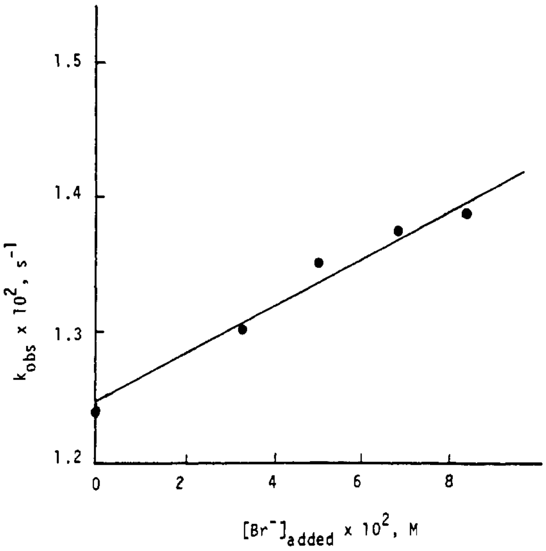
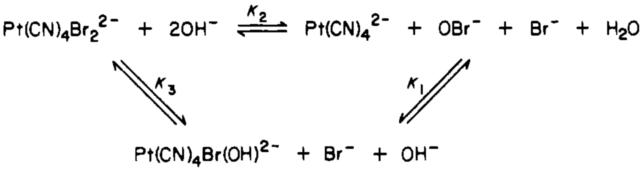


Figure 2. Plot of K_{obsd} vs. $[Br^-]$ added for the oxidation of $Pt(CN)_4^{2-}$ by hypobromite.

Scheme I



Kinetic Measurements. (a) Reaction between $Pt(CN)_4Br_2^{2-}$ and OH^-. The reaction was monitored at 342 nm with OH^- in large excess over Pt(IV). Under this condition, $Pt(CN)_4Br_2^{2-}$ was quantitatively reduced to $Pt(CN)_4^{2-}$. The slow reoxidation of $Pt(CN)_4^{2-}$ to $Pt(CN)_4Br(OH)^{2-}$ does not interfere with the reaction under investigation. The kinetic data are listed in Table II. Plots of k_{obsd} vs. $[OH^-]$ yield a straight line with a zero intercept (not shown), indicating that the reaction is first order in OH^-. Accordingly, the rates of reaction between $Pt(CN)_4Br_2^{2-}$ and OH^- can be expressed by eq 7 with $k_1 = 26 \pm 1.3$ M^{-1} s^{-1}.

$$\frac{d[Pt(CN)_4^{2-}]}{dt} = k_1[OH^-][Pt(CN)_4Br_2^{2-}] \quad (7)$$

It was found that k_{obsd} for the base-promoted reduction of $Pt(CN)_4Br_2^{2-}$ decreases slightly with the addition of NaBr to the reaction mixture. This is most likely due to a medium effect.[10]

(b) Reaction between $Pt(CN)_4^{2-}$ and HOBr. The reaction between $Pt(CN)_4^{2-}$ and OBr^- was followed by the absorbance decrease at 255 n, with OBr^- in at least 10-fold excess over $Pt(CN)_4^{2-}$. Under this condition, $Pt(CN)_4^{2-}$ was quantitatively oxidized into $Pt(CN)_4Br(OH)^{2-}$. The kinetic data obtained at various $[OBr^-]_{tot}$ and $[OH^-]$ are listed in Table III.

Data shown in Table III can be expressed by eq 8, with k_2 = 0.18 ± 0.015 s^{-1}.

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[10] Linck, R. G. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974**, *9*, 173.

$$-\frac{d[Pt(CN)_4^{2-}]}{dt} = \frac{k_2[OBr^-]_{tot}[Pt(CN)_4^{2-}]}{[OH^-]} \qquad (8)$$

The effect of added Br^- on the reaction rates between $Pt(CN)_4^{2-}$ and OBr^- are plotted in Figure 2. This effect will be analyzed in the Discussion.

Discussion

The kinetic study on the base hydrolysis of $Pt(CN)_4Br_2^{2-}$ by Skinner and Jones was carried out in the pH range 7–9.[5] Our kinetic study was carried out in the pH range 12–13. At our experimental conditions it is clearly shown that the reaction of $Pt(CN)_4Br_2^{2-}$ with OH^-, which produces $Pt(CN)_4^{2-}$ and OBr^-, is followed by a much slower reoxidation of $Pt(CN)_4^{2-}$ by OBr^-. Consequently, at pH ≥12, the base-promoted reduction of $Pt(CN)_4Br_2^{2-}$ and the hypobromous acid oxidation of $Pt(CN)_4^{2-}$ can be studied consecutively. Indeed, the oxidation of $Pt(CN)_4^{2-}$ by OBr^-, the base-promoted reduction of $Pt(CN)_4Br_2^{2-}$, and the base hydrolysis of $Pt(CN)_4Br_2^{2-}$ are all related and can be represented in Scheme I.

The value of K_1 was estimated in the present work as 1.1×10^5 (25 °C, $\mu = 0.10$ M). The value of K_3 was reported by Skinner and Jones as 4.6×10^4 (25 °C, $\mu = 0.10$ M).[5] Accordingly, K_2 ($= K_3/K_1$) is calculated as 0.41. Note should be made that Scheme I is a simplified case, and the reactions involved may be far from elementary reactions. Therefore, it may be meaningless to calculate the specific rates for the backward reactions from the reaction quotients and the forward rate constants. It should also be noted that the experimental conditions of the present study are very different from those used by Skinner and Jones (pH 7–9, relatively high Br^- concentrations).[5] Consequently, it is not clear whether mechanistic results of the present study can be extrapolated to those conditions.

On the basis of stoichiometries and kinetics, it has been suggested that the reduction of $Pt(CN)_4Br(OH)^{2-}/Pt(CN)_4Br(H_2O)^-$ by SCN^-, $S_2O_3^{2-}$, I^-, SO_3^{2-}, or CN^- in aqueous solution proceeds via an inner-sphere Br^+-transfer mechanism.[4b,c] In some cases, the Br^+-transfer products, such as BrCN, were detected directly. A similar mechanism is adopted for the base-promoted reduction of $Pt(CN)_4Br_2^{2-}$ studied here. Thus, kinetic data shown in Table II can be expressed by Scheme II.

Scheme II

$$Pt(CN)_4Br_2^{2-} + OH^- \overset{k}{\rightleftharpoons} [Br\text{--}Pt(CN)_4\text{--}Br\text{--}OH^{3-}] \rightleftharpoons Pt(CN)_4^{2-} + HOBr + Br^- \qquad (9)$$

$$HOBr + OH^- \overset{K_a}{\rightleftharpoons} OBr^- + H_2O \qquad (10)$$

Scheme II involves the formation of a bridged intermediate (or activated complex), $Br\text{--}Pt(CN)_4\text{--}Br\text{--}OH^{3-}$, followed by a rapid Br^+ transfer from the platinum metal center to OH^-. In Scheme II, k equals k_1 of eq 7.

The empirical rate law for the oxidation of $Pt(CN)_4^{2-}$ by OBr^- is expressed in eq 8 and can be interpreted within the framework of Scheme III. Reaction 12 is considered the rate-determining step and can be viewed as the formation of the bridged intermediate $H_2O\text{--}Pt(CN)_4\text{--}Br\text{--}OH^{2-}$, followed by a cleavage of the Br–OH bond to produce $Pt(CN)_4Br(H_2O)^-$. This mechanism would lead to rate law 14. The value of K_a, the acid dissociation constant of HOBr, was reported as 2×10^{-9} M.[7] Accordingly, k' is estimated to be 2.0×10^{-6} s^{-1}. In Scheme III, $k'K_w/K_a$ equals k_2 of eq 8.

Scheme III

$$OBr^- + H_2O \overset{K_w/K_a}{\rightleftharpoons} HOBr + OH^- \qquad (11)$$

$$H_2O\text{--}Pt(CN)_4^{2-} + HOBr \xrightarrow{k'} H_2O\text{–}Pt(CN)_4Br^- + OH^- \qquad (12)$$

$$H_2O\text{–}Pt(CN)_4Br^- + OH^- \rightarrow Pt(CN)_4Br(OH)^{2-} + H_2O \qquad (13)$$

$$-\frac{d[Pt(CN)_4^{2-}]}{dt} = \frac{k'K_w[OBr^-]_{tot}[Pt(CN)_4^{2-}]}{K_a[OH^-]} \qquad (14)$$

In the presence of high Br^- concentration, it was observed that k_{obsd} for the OBr^- oxidation of $Pt(CN)_4^{2-}$ increased when Br^- concentration was increased (Figure 2). A probable explanation for the bromide dependence shown in Figure 2 is a parallel oxidation of $Pt(CN)_4^{2-}$ by Br_2OH^-. Eigen et al. have reported that Br_2OH^- has a stability constant[11]

$$\frac{[Br_2OH^-]}{[HOBr][Br^-]} = 1 \qquad (15)$$

Combined with eq 11, this leads to

$$[Br_2OH^-] = [HOBr][Br^-] = \frac{K_w[Br^-][OBr^-]_{tot}}{K_a[OH^-]} \qquad (16)$$

All together, the rates for the hypobromous acid oxidation of $Pt(CN)_4^{2-}$ can be expressed by eq 17 with $k' = 1.6 \times 10^{-6}$ s^{-1} and $k'' = 2.6 \times 10^{-6}$ M^{-1} s^{-1}.

$$-\frac{d[Pt(CN)_4^{2-}]}{dt} = (k' + k''[Br^-])\frac{K_w[OBr^-]_{tot}[Pt(CN)_4^{2-}]}{K_a[OH^-]} \qquad (17)$$

From the value of K_1 of reaction 1 and the emf of the half-reaction[12]

$$HOBr + 2e^- \rightleftharpoons OH^- + Br^- \qquad E° = 0.92 \text{ V}$$

One can calculate the emf of the half-reaction

$$Pt(CN)_4^{2-} + Br^- + OH^- \rightleftharpoons Pt(CN)_4Br(OH)^{2-} + 2e^- \qquad E° = 0.77 \text{ V}$$

The potential of the following half-reaction has been determined by Morgan and Jones:[13]

$$Pt(CN)_4^{2-} + 2Br^- \rightleftharpoons Pt(CN)_4Br_2^{2-} + 2e^- \qquad E° = -0.75 \text{ V}$$

This datum indicates that the emf of an unknown $Pt(CN)_4(OH)_2^{2-}$ is equal to or less than −0.17 V:

$$Pt(CN)_4^{2-} + 2OH^- \rightleftharpoons Pt(CN)_4(OH)_2^{2-} + 2e^-$$

An attempt to synthesize $Pt(CN)_4(OH)_2^{2-}$ was carried out by Levy.[14] He used H_2O_2 to oxidize $Pt(CN)_4^{2-}$, but formation of a mixed-valent platinum complex was observed.

In summary, we have presented evidence that, at $[OH^-] \geq 0.01$ M, the base-promoted reduction of $Pt(CN)_4Br_2^{2-}$ and the oxidation of $Pt(CN)_4^{2-}$ by hypobromous acid may be studied consecutively, with the latter reaction following the more rapid former reaction. This observation is consistent with an REOA mechanism for the base hydrolysis of $Pt(CN)_4Br_2^{2-}$ in alkaline solution. However, whether results of the present study can be extrapolated to base hydrolysis of $Pt(CN)_4Br_2^{2-}$ at low pH remains to be seen.

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Registry No. *trans*-$Pt(CN)_4Br_2^{2-}$, 20756-58-5; $Pt(CN)_4^{2-}$, 15004-88-3; HOBr, 13517-11-8.

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