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KINETICS AND MECHANISMS OF THE REDUCTION OF *trans*-TETRACYANOHYDROXOBROMOPLATINATE(IV) AND ITS PROTONATED FORM BY SOME INORGANIC ANIONS [*,†]

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CONTENTS

A. INTRODUCTION

The interest in inner-sphere electron-transfer mechanisms for Pt(II)-catalyzed substitution on Pt(IV) complexes [1] and mechanisms for reduction of

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[*] Dedicated to the memory of Wayne Keith Wilmarth.

[†] Taken, in part, from the PhD thesis of Y.-T. Fanchiang, University of Southern California, 1976.

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Pt(IV) complexes by transition metal complexes and simple inorganic substrates [2] has prompted our study of the reduction of Pt(IV) complexes by several inorganic substrates. Our preceding paper [3] in this series describes the oxidation of $S_2O_3^{2-}$ by *trans*-$Pt(CN)_4Br(OH)^{2-}$ in solutions of $pH > 11$. In this paper we report the results of studies of the oxidation of I^-, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$ and CN^- by *trans*-$Pt(CN)_4Br(OH)^{2-}$ and its protonated form, *trans*-$Pt(CN)_4Br(H_2O)^-$. The purpose is to demonstrate the generality of the Br^+ transfer mechanism reported earlier [3] and identify the effects of reducing agent and *trans* ligand on the reaction rate. 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.

B. EXPERIMENTAL

(i) Materials

$Na_2Pt(CN)_4 \cdot 3H_2O$ was obtained from D.F. Goldsmith Inc., and was used as received. $Na_2S_4O_6 \cdot 2H_2O$ used in this work was obtained from K & K Labs. Solutions of $Pt(CN)_4Br(OH)^{2-}$ were prepared by base hydrolysis [4] of *trans*-$Pt(CN)_4Br_2^{2-}$. Br^--free solutions of $Pt(CN)_4Br(OH)^{2-}$ and/or $Pt(CN)_4Br(H_2O)^-$ were prepared by adding a stoichiometric amount of Br^--free hypobromite to a $Pt(CN)_4^{2-}$ solution. The Br^--free hypobromite solutions were generated as described in the literature [5]. All other chemicals were commercially available reagent grade and used without further purification. All studies involving SO_3^{2-} were performed under an atmosphere of N_2.

(ii) Stoichiometric studies and reaction products

Stoichiometries of reactions of the Pt(IV) complexes with SCN^-, $S_2O_3^{2-}$, CN^- and SO_3^{2-} were studied with a Cary 14 Spectrophotometer using a 10-fold excess of Pt(IV) complex over the reducing anion. The stoichiometry of the reaction of the Pt(IV) complex with I^- was measured in the presence of a large excess of I^- (ca. 0.5M) by determining the amounts of I_3^- formed. For these experiments the oxidative addition of I_3^- to $Pt(CN)_4^{2-}$ can be ignored [6].

The platinum product was identified by comparing its UV–VIS spectrum with that of an authentic sample of $Pt(CN)_4^{2-}$. The BrCN formed in the reduction of Pt(IV) complex by CN^- was determined by iodometric titration [7]. The $S_4O_6^{2-}$ formed in the reduction of Pt(IV) complex by $S_2O_3^{2-}$ was determined spectrophotometrically [8].

(iii) Kinetic measurements

pH measurements were made using a Beckman Research Model pH Meter equippped with a Beckman glass electrode and a silver–silver chloride electrode. Calibrations of the H^+ concentration of various buffer solutions were made according to the method described by Hitchcock and Peters [9].

All kinetic measurements were made at 255 nm with a large excess of reducing anion over Pt(IV) complex in order to provide the pseudo-first-order condition. The rates of those reactions having a half-life > 5 s were measured by monitoring the absorbance changes with a Cary 14 spectrophotometer. Reactions with a half-life < 5 s were followed by a stopped-flow spectrophotometer. All reactions were studied at 25.0 ± 0.1°C and 0.10M ionic strength (maintained with $NaClO_4$). The pH was controlled in the range 6–13 using NaOH or an appropriate buffer. Reproducibility of the data was generally better than 5%.

C. RESULTS

(i) Stoichiometries

Under the conditions of the kinetic studies both $Pt(CN)_4Br(OH)^{2-}$ and its protonated form, $Pt(CN)_4Br(H_2O)^-$, are reduced quantitatively to $Pt(CN)_4^{2-}$ by CN^-, I^-, SCN^-, $S_2O_3^{2-}$ and SO_3^{2-}. The moles of Pt(IV) reduced per mole of reducing anion at various pH values and with Pt(IV) in excess are listed in Table 1 for all of the anions.

For several of the reducing anions, the oxidized product was detected in final reaction solutions containing excess reducing anion. Based on the detection of these oxidized products, the quantitative conversion of Pt(IV) to $Pt(CN)_4^{2-}$ and the results of the mole ratio determinations we can identify the stoichiometries of the reactions whose kinetic behavior is under study here.

For the reduction of $Pt(CN)_4Br(H_2O)^-$ by iodide ion the I_2 formed was determined from the spectrum of I_3^- in the final reaction solution. The yield

TABLE 1

Moles of Pt(IV) reduced per mole of reducing agent at various pH values

Reducing agent:	CN^-		I^-	SCN^-			$S_2O_3^{2-}$		SO_3^{2-}	
pH:	12	10	8.8	12	8.8	5.2	13–11 [a]	7.2	12	7.2
Mole ratio:	1.02	1.00	0.49	3.93	3.23	3.00	4.0–0.50	0.54	1.00	0.96

[a] See ref. 3.

was 98%. The chemical reaction is thus

$$\mathrm{Pt(CN)_4Br(H_2O)^- + 3I^- \rightarrow Pt(CN)_4^{2-} + I_3^- + H_2O} \tag{1}$$

The oxidation of the SO_3^{2-} results in the formation of SO_4^{2-}. This was demonstrated by the precipitation of $BaSO_4$ on addition of $BaCl_2$ to the final reaction solution. Addition of $BaCl_2$ to appropriate control solutions yielded no $BaSO_4$. The reaction can be described as

$$\mathrm{Pt(CN)_4Br(OH)^{2-} + SO_3^{2-} + OH^- \rightarrow Pt(CN)_4^{2-} + SO_4^{2-} + Br^- + H_2O} \tag{2}$$

The quantitative determination of the products of the oxidation of $S_2O_3^{2-}$ in solutions of various pH has already been described [3]. Two sulfur-containing products are formed with the distributions determined by the ratio $[S_2O_3^{2-}]/[OH^-]$. The reactions leading to these products are

$$\mathrm{Pt(CN)_4Br(H_2O)^- + 2S_2O_3^{2-} \rightarrow Pt(CN)_4^{2-} + S_4O_6^{2-} + Br^- + H_2O} \tag{3}$$

at $pH \leq 9$

$$\begin{aligned}&\mathrm{4Pt(CN)_4Br(OH)^{2-} + S_2O_3^{2-} + 6OH^-}\\ &\quad\mathrm{\rightarrow 4Pt(CN)_4^{2-} + 2SO_4^{2-} + 5H_2O + 4Br^-}\end{aligned} \tag{4}$$

at $pH \geq 11$

The reduction of both $Pt(CN)_4Br(OH)^{2-}$ and $Pt(CN)_4Br(H_2O)^-$ by CN^- produces BrCN. This was determined by iodometric titration. The yield (5 min after mixing the reactants and ca. 10 half-lives) was low (17%) and was observed to decrease with time (none remained 20 min after mixing). This is apparently due to base hydrolysis of the BrCN to form OCN^- in solutions of pH 7.67. Analogous oxidation of CN^- by $Pt(CN)_4Br_2^{2-}$ was studied at pH 5.57, and 2 min after mixing a 99.5% yield of BrCN was measured. By 5 min after mixing this was reduced to 93% [10]. We formulate the reactions as:

$$\mathrm{Pt(CN)_4Br(OH)^{2-} + CN^- + OH^- \rightarrow Pt(CN)_4^{2-} + OCN^- + Br^- + H_2O} \tag{5}$$

at $pH \geq 10$

$$\mathrm{Pt(CN)_4Br(OH_2)^- + CN^- \rightarrow Pt(CN)_4^{2-} + BrCN + H_2O} \tag{6}$$

at $pH \leq 7$

The reduction of the Pt(IV) complexes by SCN^- results in the formation of SO_4^{2-}, again detected by the precipitation of $BaSO_4$. The increase in the mole ratio [Pt(IV)]/[reducing anion] from 3.0 to 4.0 at high pH is compatible with an increased contribution from the reduction of the Pt(IV) by-product, CN^-, according to reactions 7 and 8. It should be noted that at $pH \geq 11$, CN^- reduces the Pt(IV) complex at a rate ca. 10 times faster than SCN^-, while at pH ≤ 7, HCN reduces the Pt(IV) complex at a rate only 0.0020 times as fast as SCN^-. Also, both SO_4^{2-} and HCN are products of oxidation of SCN^- by other complexes [11]. The reactions are thus described as:

$$3Pt(CN)_4Br(H_2O)^- + SCN^- + H_2O \rightarrow 3Pt(CN)_4^{2-} + SO_4^{2-} + HCN + 3Br^- + 7H^+ \quad (7)$$

at pH ≤ 7

$$4Pt(CN)_4Br(OH)^{2-} + SCN^- + 6OH^- \rightarrow 4Pt(CN)_4^{2-} + SO_4^{2-} + OCN^- + 4Br^- + 5H_2O \quad (8)$$

at pH ≥ 11

(ii) Acid dissociation constant of $Pt(CN)_4Br(H_2O)^-$

An unsuccessful attempt was made to determine K_a for $Pt(CN)_4Br(H_2O)^-$ spectrophotometrically. An alkaline solution of $Pt(CN)_4Br(OH)^{2-}$ was adjusted to pH 0.30 with $HClO_4$. The solution was free of bromide ion in order to eliminate formation of *trans*-$Pt(CN)_4Br_2^{2-}$ in acidic solution. A slow spectral change occurs, with the final solution showing a maximum absorbance at 236 nm. We conclude that the complex which is formed is not $Pt(CN)_4Br(OH_2)^-$ but perhaps some form of dimer. The rate of the reaction is too slow for proton transfer and is second order in [Pt(IV)] ($k = 10.6\ M^{-1}\ s^{-1}$ at 25°C). Extrapolation to time zero shows that there is no significant spectral change due to protonation of the OH^- ligand. This prevents us from making a spectrophotometric measurement of the acid dissociation constant.

Two values have however been obtained in kinetic studies of the Br_2 oxidation of $Pt(CN)_4^{2-}$. Jones and Skinner report a value of 0.025 obtained from a stopped-flow study [4] and Mason reports a value of 0.05 in a simple spectrophotometric study [12]. Although both of these values were determined at 1.0M ionic strength rather than the 0.10M used in this study we have used the 0.025 value in our calculations recognizing that although the reaction conditions are somewhat different the use of the literature value for K_a would not be expected to affect significantly the conclusions of this work.

(iii) Kinetic measurements and reaction mechanisms

In all cases, the reduction of $Pt(CN)_4Br(OH)^{2-}$ and its protonated form by CN^-, I^-, SCN^-, $S_2O_3^{2-}$ and SO_3^{2-} are first order in Pt(IV) and, with the exception of the $S_2O_3^{2-}$ reaction under certain conditions, first order in reducing anion according to:

$$\frac{d[Pt(CN)_4^{2-}]}{dt} = \frac{-d[Pt(IV)]}{dt} = k_0[\text{substrate}][Pt(IV)] \quad (9)$$

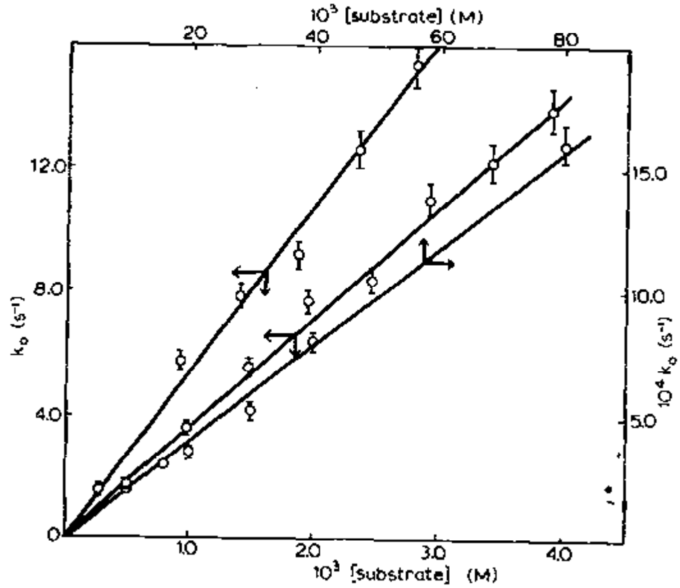

Fig. 1. Variation of k_0 with concentration of reducing agent: upper curve SO_3^{2-} with $[OH^-] = 9.96 \times 10^{-3}$M; middle curve I^- with $[OH^-] = 1.95 \times 10^{-7}$M; and lower curve SCN^- with $[OH^-] = 1.58 \times 10^{-3}$M. Error bars represent ±5% uncertainties.

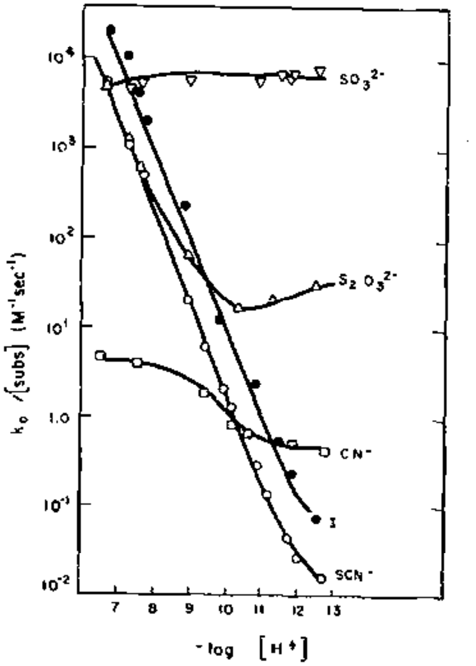

Fig. 2. Variation of k_0/[substrate] vs. $-\log[H^+]$.

The reaction rates are all independent of added $Pt(CN)_4^{2-}$. The linear dependence on substrate concentration is illustrated in Fig. 1. As previously described the order in $S_2O_3^{2-}$ is variable under conditions of changing stoichiometry. The data shown in the figure are for a solution of $[OH^-] = 5.5 \times 10^{-8}$M where the only product is $S_4O_6^{2-}$ and the stoichiometry is independent of $[S_2O_3^{2-}]$.

Values of k_0 are pH dependent for all substrates with three types of kinetic behavior observed. The second-order rate constants, k_0, are plotted versus pH in Fig. 2. For the reactions of SCN^- and I^- the kinetic behavior is described by the empirical rate law of eqn. 10. Here, K_a represents the acid dissociation constant of $Pt(CN)_4Br(H_2O)^-$.

$$\frac{d\left[Pt(CN)_4^{2-}\right]}{dt} = \left\{a + \frac{b[H^+]}{K_a}\right\}[\text{substrate}][Pt(IV)] \tag{10}$$

On the basis of the reaction stoichiometries and kinetic behavior, and because of the indication of Br^+ transfer in the CN^- and $S_2O_3^{2-}$ reactions, the mechanisms for reduction of $Pt(CN)_4Br(OH)^{2-}/Pt(CN)_4Br(H_2O)^-$ by SCN^- and I^- are formulated as occurring via Br^+ transfer to the reducing anion by both the hydroxo- and aquo- complexes.

(a) I^- reaction

$$Pt(CN)_4Br(H_2O)^- \overset{K_a}{\rightleftharpoons} Pt(CN)_4Br(OH)^{2-} + H^+ \tag{11}$$

$$Pt(CN)_4Br(OH)^{2-} + I^- \xrightarrow{k_1} Pt(CN)_4^{2-} + IBr + OH^- \tag{12}$$

$$Pt(CN)_4Br(OH_2)^- + I^- \xrightarrow{k_2} Pt(CN)_4^{2-} + IBr + H_2O \tag{13}$$

$$IBr + 2I^- \rightarrow I_3^- + Br^- \tag{14}$$

(b) SCN^- reaction

$$Pt(CN)_4Br(H_2O)^- \overset{K_a}{\rightleftharpoons} Pt(CN)_4Br(OH)^{2-} + H^+ \tag{11}$$

$$Pt(CN)_4Br(OH)^{2-} + SCN^- \xrightarrow{k_1} Pt(CN)_4^{2-} + BrSCN + OH^- \tag{15}$$

$$Pt(CN)_4Br(H_2O)^- + SCN^- \xrightarrow{k_2} Pt(CN)_4^{2-} + BrSCN + H_2O \tag{16}$$

$$3Pt(CN)_4Br(OH)^{2-} + BrSCN + 7OH^- \xrightarrow{\text{fast}}$$

$$3Pt(CN)_4^{2-} + SO_4^{2-} + OCN^- + 4Br^- + 5H_2O \tag{17}$$

$$2\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{BrSCN} + 5\mathrm{OH^-} \xrightarrow{\text{fast}}$$

$$\times 2\mathrm{Pt(CN)_4^{2-}} + \mathrm{SO_4^{2-}} + \mathrm{HCN} + 3\mathrm{Br^-} + 3\mathrm{H_2O} \tag{18}$$

These equations lead to the rate law

$$\frac{\mathrm{d}\left[\mathrm{Pt(CN)_4^{2-}}\right]}{\mathrm{d}t} = \left\{\frac{k_1 K_a + k_2[\mathrm{H^+}]}{K_a + [\mathrm{H^+}]}\right\}[\text{substrate}][\mathrm{Pt(IV)}] \tag{19}$$

which in the pH range of this study (6–13) simplify to eqn. 10. The constants k_1 and k_2 were determined by a least-squares fit of the kinetics data to eqn. 19. These are listed in Table 2. Equation 19 and the least-squares constants were then used to calculate theoretical values for k_0 which are plotted as the solid lines in Fig. 2. The uncertainties in Table 2 represent the standard deviations.

The thiosulfate reaction shows very similar kinetic behavior with the added complication of a variable stoichiometry in the region of $\mathrm{pH} > 10$ which causes a corresponding change in the rate of consumption of Pt(IV). The kinetic data for the $\mathrm{S_2O_3^{2-}}$ reaction are accommodated by the expression [3]

$$\frac{\mathrm{d}\left[\mathrm{Pt(CN)_4^{2-}}\right]}{\mathrm{d}t} = \left\{\mathrm{a}\alpha + \frac{\mathrm{b}[\mathrm{H^+}]}{K_a}\right\}[\text{substrate}][\mathrm{Pt(IV)}] \tag{20}$$

where

$$\alpha = \frac{4(0.031)[\mathrm{OH^-}] + \left[\mathrm{S_2O_3^{2-}}\right]}{0.031[\mathrm{OH^-}] + \left[\mathrm{S_2O_3^{2-}}\right]} \tag{21}$$

A mechanism consistent with this kinetic behavior, and our earlier studies at $\mathrm{pH} > 11$ of the $\mathrm{S_2O_3^{2-}}$ reaction, is depicted in the following equations. The additional feature of this mechanism is the competition by $\mathrm{S_2O_3^{2-}}$ and $\mathrm{OH^-}$ for the intermediate $\mathrm{BrS_2O_3^-}$ observed when $10^{-3} < [\mathrm{S_2O_3^{2-}}] < 1$ which leads to the change in reaction stoichiometry.

(c) $S_2O_3^{2-}$ reaction

$$\mathrm{Pt(CN)_4Br(H_2O)^-} \overset{K_a}{\rightleftharpoons} \mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{H^+} \tag{11}$$

$$\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{S_2O_3^{2-}} \xrightarrow{k_1} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrS_2O_3^-} + \mathrm{OH^-} \tag{22}$$

$$\mathrm{Pt(CN)_4Br(H_2O)^-} + \mathrm{S_2O_3^{2-}} \xrightarrow{k_2} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrS_2O_3^-} + \mathrm{H_2O} \tag{23}$$

$$\mathrm{BrS_2O_3^-} + \mathrm{OH^-} \xrightarrow{k_3} \mathrm{HOS_2O_3^-} + \mathrm{Br^-} \tag{24}$$

$$BrS_2O_3^- + S_2O_3^{2-} \xrightarrow{k_4} S_4O_6^{2-} + Br^- \tag{25}$$

$$HOS_2O_3^- + 3Pt(CN)_4Br(OH)^{2-} + 6OH^- \xrightarrow{\text{fast}}$$

$$3Pt(CN)_4^{2-} + 2SO_4^{2-} + 3Br^- + 5H_2O \tag{26}$$

and from ref. 3

$$k_3/k_4 = 0.031 \pm 0.002 \tag{27}$$

The rate expression derived for this mechanism is

$$\frac{d\left[Pt(CN)_4^{2-}\right]}{dt} = \left\{\frac{k_1K_a\alpha + k_2[H^+]}{K_a + [H^+]}\right\}[\text{substrate}][Pt(IV)] \tag{28}$$

where

$$\alpha = \frac{4(0.031)[OH^-] + [S_2O_3^{2-}]}{0.031[OH^-] + [S_2O_3^{2-}]} \tag{21}$$

which reduces to eqn. 20 at pH > 5. Using the least-squares constants determined for eqn. 28 the solid line of Fig. 2 was calculated. The constants k_1 and k_2 are listed in Table 2.

The kinetic behavior for the reactions of the Pt(IV) complexes with CN^- and SO_3^{2-} are more complex than observed for the I^- and SCN^- reactions because of the possibility of protonation of the reducing anions in the reaction media ($K_{HCN} = 6.17 \times 10^{-10}$M [13]; $K_{HSO_3^-} = 6.20 \times 10^{-8}$M [14]). Accordingly, kinetic data for the reductions by CN^- and SO_3^{2-} which are

TABLE 2

Kinetic parameters for the reduction of $Pt(CN)_4Br(OH)^{2-}$ and $Pt(CN)_4Br(H_2O)^-$ by some inorganic anions [a]

Anion	k_1 (M^{-1} s^{-1})		k_2 (M^{-1} s^{-1})	
SCN^-	$(3.30 \pm 0.14) \times 10^{-3}$	(= a/4) [b]	$(1.42 \pm 0.28) \times 10^{8}$	(= b/3) [b]
I^-	$\sim 2.8 \times 10^{-2}$	(= a)	$(2.04 \pm 0.66) \times 10^{9}$	(= b)
$S_2O_3^{2-}$	$(1.48 \pm 0.02) \times 10^{1}$		$(4.6 \pm 0.4) \times 10^{8}$	(= b)
CN^-	$(4.85 \pm 0.25) \times 10^{-1}$	(= a)	$k_2K_{HCN} + k_1' \cdot K_a =$ $(1.02 \pm 0.10) \times 10^{-1}$	
SO_3^{2-}	$(6.74 \pm 0.27) \times 10^{3}$	(= a)	$k_2K_{HSO_3^-} + k_1' \cdot K_a =$ $(1.94 \pm 0.26) \times 10^{2}$	

[a] Temperature 25°C; $\mu = 0.1$M ($NaClO_4$).

[b] The factors of 1/4 and 1/3 reflect the stoichiometries of the reaction between the Pt(IV) complex and SCN^-.

plotted in Figs. 1 and 2 can be expressed by the empirical rate law

$$\frac{\mathrm{d}\left[\mathrm{Pt(CN)}_4^{2-}\right]}{\mathrm{d}t} = \frac{\mathrm{a}K_\mathrm{a}K + (\mathrm{b}K + \mathrm{a}K_\mathrm{a})[\mathrm{H}^+]}{K_\mathrm{a}(K + [\mathrm{H}^+])}[\mathrm{substrate}][\mathrm{Pt(IV)}] \qquad (29)$$

where K represents the acid dissociation constants for HCN and HSO_3^-. A mechanism consistent with this expression, the detection of BrCN and the preceding results is as follows.

(d) CN^- reaction

$$\mathrm{Pt(CN)_4Br(H_2O)^-} \overset{K_a}{\rightleftharpoons} \mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{H^+} \qquad (11)$$

$$\mathrm{HCN} \overset{K}{\rightleftharpoons} \mathrm{CN^-} + \mathrm{H^+}$$

$$\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{CN^-} \xrightarrow{k_1} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrCN} + \mathrm{OH^-} \qquad (30)$$

$$\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{HCN} \xrightarrow{k_1'} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrCN} + \mathrm{H_2O} \qquad (31)$$

$$\mathrm{Pt(CN)_4Br(H_2O)^-} + \mathrm{CN^-} \xrightarrow{k_2} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrCN} + \mathrm{H_2O} \qquad (32)$$

$$\mathrm{Pt(CN)_4Br(H_2O)^-} + \mathrm{HCN} \xrightarrow{k_2'} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrCN} + \mathrm{H_3O^+} \qquad (33)$$

and at $pH \geq 11$

$$\mathrm{BrCN} + 2\mathrm{OH^-} \xrightarrow{\text{fast}} \mathrm{Br^-} + \mathrm{OCN^-} + \mathrm{H_2O} \qquad (34)$$

(e) HSO_3^- reaction

$$\mathrm{Pt(CN)_4Br(H_2O)^-} \overset{K_a}{\rightleftharpoons} \mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{H^+} \qquad (11)$$

$$\mathrm{HSO_3^-} \overset{K}{\rightleftharpoons} \mathrm{SO_3^{2-}} + \mathrm{H^+} \qquad (35)$$

$$\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{SO_3^{2-}} \xrightarrow{k_1} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrSO_3^-} + \mathrm{OH^-} \qquad (36)$$

$$\mathrm{Pt(CN)_4Br(OH)^{2-}} + \mathrm{HSO_3^-} \xrightarrow{k_1'} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrSO_3^-} + \mathrm{H_2O} \qquad (37)$$

$$\mathrm{Pt(CN)_4Br(H_2O)^-} + \mathrm{SO_3^{2-}} \xrightarrow{k_2} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrSO_3^-} + \mathrm{H_2O} \qquad (38)$$

$$\mathrm{Pt(CN)_4Br(H_2O)^-} + \mathrm{HSO_3^-} \xrightarrow{k_2'} \mathrm{Pt(CN)_4^{2-}} + \mathrm{BrSO_3^-} + \mathrm{H_3O^+} \qquad (39)$$

$$\mathrm{BrSO_3^- + 2OH^- \overset{fast}{\rightarrow} SO_4^{2-} + Br^- + H_2O} \tag{40}$$

for which the rate law which follows can be derived.

$$\frac{\mathrm{d}\left[\mathrm{Pt(CN)_4^{2-}}\right]}{\mathrm{d}t} = \left\{ \frac{k_1 K_a K + k_2 K[\mathrm{H^+}] + k_1' K_a [\mathrm{H^+}] + k_2' [\mathrm{H^+}]^2}{(K_a + [\mathrm{H^+}])(K + [\mathrm{H^+}])} \right\} \times [\text{substrate}][\mathrm{Pt(IV)}] \tag{41}$$

This can be simplified for $[\mathrm{H^+}] \ll K_a$ to the form of eqn. 29. As before we have fit the kinetic results to the theoretical rate expression (41) in order to obtain the rate constants and, in turn, used these to calculate the solid lines of Fig. 2 in order to illustrate the correspondence between theory and experiment. Unfortunately, the kinetic results prevents independent determinations of k_2 and k_1' and so the values of $k_2 K + k_1' K_a$ are listed in Table 2. These can be used however to identify upper limits for the rate constants k_2 and k_1'. For the $\mathrm{CN^-}$ reaction, $k_2 < 1.6 \times 10^8$ $\mathrm{M^{-1}\ s^{-1}}$ and $k_1' < 4$ $\mathrm{M^{-1}\ s^{-1}}$, and for the $\mathrm{SO_3}^{2-}$ reaction, $k_2 < 3 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ and $k_1' < 7.6 \times 10^3$ $\mathrm{M^{-1}\ s^{-1}}$. These limits are compatible with the other data reported in Table 2.

D. DISCUSSION

On the basis of stoichiometry and kinetics, it has been suggested that the reduction of *trans*-$\mathrm{Pt(CN)_4Br(OH)^{2-}}$ by $\mathrm{S_2O_3^{2-}}$ in alkaline solution proceeds via $\mathrm{Br^+}$ transfer to produce $\mathrm{BrS_2O_3^-}$ as an intermediate [3]. The same bromine-bridging mechanism has been suggested for the Pt(II)-catalyzed substitution reactions of Pt(IV) complexes [1]. A similar mechanism is adopted for all substrates studied here. The detection of BrCN for the reduction of *trans*-$\mathrm{Pt(CN)_4Br(OH)^{2-}}$ and/or *trans*-$\mathrm{Pt(CN)_4Br(H_2O)^-}$ by $\mathrm{CN^-}$ at $\mathrm{pH} \le 7$ lends strong support for the $\mathrm{Br^+}$-transfer mechanism. In addition, IBr [15], BrSCN [16] and $\mathrm{BrS_2O_3^-}$ [17] are known species, although relatively unstable.

The distinguishing feature of Table 2 is the difference in magnitude of k_1 and k_2. Another feature of Table 2 is that the magnitude of k_1 spans a range of 10^6 from $\mathrm{SCN^-}$ to $\mathrm{SO_3^{2-}}$, while k_2 only spans a range of 10 *. Studies of the rates of reduction of some *trans*-$\mathrm{PtL_2X_4}$ complexes (where L = pyridine, piperdine, methyl and ethylamine or dimethyl and diethylsulfide; X = Cl or Br) with $\mathrm{SCN^-}$, $\mathrm{I^-}$, $\mathrm{SeCN^-}$ and $\mathrm{S_2O_3^{2-}}$ by Peloso et al. [2] came to the conclusion that bond-making between the reducing agents and the halide

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* Y.-T. Fanchiang, PhD thesis, University of Southern California, 1976.

ligand was small. Their conclusion was based on the observation that relative effects on the reaction rates of different reducing anions are independent of the platinum complexes. This conclusion, however, it not necessarily correct, since the independence of the platinum complex may merely reflect that the contribution of the bond-making to the activation energy is similar in all reactions studied. Indeed, by the studies of redox reactions of *trans*-$Pt(CN)_4X_4^{2-}$ with I^- (where X = Cl or Br), Poe et al. concluded that the amount of Pt–X bond-breaking and X–I bond-making in the activated complex is quite large [6]. Results in Table 2 show that when the ligand in the *trans* position is OH^-, the reaction rates largely depend on the nature of the substrates. This reflects that the bond-making between reducing anion and bromide-bridging ligand is important for a strong-field *trans* ligand. When the *trans* ligand is protonated, then the reaction rate is relatively independent of the nature of the reducing anion. This reflects that bond-making between the substrate and bromide ligand is relatively unimportant for a weak-field *trans* ligand such as H_2O.

The important role that non-bridging ligands play in one-equivalent inner-sphere redox reactions has long been recognized [18,19]. In the reductive elimination reactions of Pt(IV) complexes of the present study, it can be seen that as the bridging ligand moves away from oxidant towards reductant, simultaneously, the *trans* ligand moves away from oxidant in the opposite direction during the course of reaction. Since the two electrons transferred to the Pt(IV) complex would be accepted in the d_{z^2} orbital in the transition state the availability of the d_{z^2} orbital would be increased by an outward movement of the *trans* ligand. For a relatively strong-field *trans* ligand, OH^-, this movement does not provide dominant energy to the activation energy. However, when it is protonated, the outward movement of H_2O would dominate the bond-making of Br–substrate or bond-breaking of Pt–Br in the transition state to result in a relative independence of the nature of the reducing anion.

Finally, it should be noted that the four in-plane *cis* ligands of the Pt(IV) complex may also play an important role in the movements of bridging ligand and leaving ligand, which would significantly affect the reduction rates. Poe et al. have reported that I^- reduces $PtBr_4I(OH)^{2-}$ with a second-order rate constant of 0.26 M^{-1} s^{-1}, while I^- reduces $PtBr_4I(H_2O)^-$ with a rate constant of 0.60 M^{-1} s^{-1} at 17.1°C [20]. Reduction of $PtBr_5(OH)^{2-}$ and $PtBr_5(H_2O)^-$ by inorganic reducing anions could be suitable for the study of the *cis*-effect for this type of reductive elimination reactions.

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