Coordination Chemistry Reviews, 51 (1983) 125–139
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE $Pt(CN)_4(OH)Br^{2-}$ OXIDATION OF $S_2O_3^{2-}$ AND $S_4O_6^{2-}$ *

W.K. WILMARTH, RICHARD DOOLY and J.E. BYRD **

Department of Chemistry, University of Southern California, Los Angeles, CA 90007 (U.S.A.)

(Received 7 April 1983)

CONTENTS

A. INTRODUCTION

Very little is known about the mechanisms of the oxidation of simple non-metallic reducing agents by Pt(IV) complexes. The available data [1–3] consists primarily of the studies by Peloso, Dolcetti, and Ettorre of the oxidation of $SeCN^-$, SCN^-, I^-, and $S_2O_3^{2-}$ using a series of Pt(IV) complexes with the general formula PtL_2Cl_4 or PtL_2Br_4, where $L = R_2S$, R_3As, R_3P or amines.

In the present paper we present kinetic and stoichiometric studies of the $Pt(CN)_4(OH)Br^{2-}$ oxidation of $S_2O_3^{2-}$ and $S_4O_6^{2-}$. The products formed in

---

* Dedicated to the memory of Wayne Keith Wilmarth.

** Author to whom correspondence should be directed. Present address: Department of Chemistry, California State College, Stanislaus, Turlock, CA 95380, U.S.A.

the oxidation of $S_2O_3^{2-}$ are $Pt(CN)_4^{2-}$, Br^-, and a mixture of $S_4O_6^{2-}$ and SO_4^{2-}, with the relative yields of $S_4O_6^{2-}$ and SO_4^{2-} being dependent upon the concentration ratio $[S_2O_3^{2-}]/[OH^-]$. These observations are interpreted in terms of a reaction mechanism in which $S_2O_3^{2-}$ is initially converted to a reactive intermediate, $BrS_2O_3^-$, which reacts competitively with $S_2O_3^{2-}$ and OH^- to initiate processes which ultimately generate $S_4O_6^{2-}$ and SO_4^{2-}, respectively. It has been suggested [4] that $BrS_2O_3^-$ is formed as a reactive intermediate in the Br_2 oxidation of $S_2O_3^{2-}$, a reaction which also produces $S_4O_6^{2-}$ and SO_4^{2-} in variable yield. However, the Br_2 oxidation is rather complex and the detailed chemistry of $BrS_2O_3^-$ was not as well defined as it is in the present study. Likewise, a recent study of the oxidation of $S_2O_3^{2-}$ by BrO_2^- showed similar stoichiometric behavior but the nature of the intermediates was not determined [5].

The rate of oxidation of $S_4O_6^{2-}$ was found to be first order in $[S_4O_6^{2-}]$, first order in $[OH^-]$, and zero order in $[Pt(CN)_4(OH)Br^{2-}]$. The rate-determining step in this reaction seems to involve the nucleophilic attack of OH^- on a sulfur atom of $S_4O_6^{2-}$, a process which generates the reactive intermediates $S_2O_3^{2-}$ and $HOSSO_3^-$ which are rapidly oxidized to SO_4^{2-} by $Pt(CN)_4(OH)Br^{2-}$.

B. EXPERIMENTAL

(i) *Materials*

With the exception of the *trans*-$Pt(CN)_4(OH)Br^{2-}$ and $NaClO_4$, all of the chemicals used in this study were commercially available and used as received. Solutions of *trans*-$Pt(CN)_4(OH)Br^{2-}$ were prepared by adding the appropriate amount of standardized Br_2 solution to a solution of $Na_2Pt(CN)_4$. This generates a solution of *trans*-$Pt(CN)_4(OH_2)Br^-$ via the reaction [6]:

$$Pt(CN)_4^{2-} + Br_2 + H_2O \rightarrow trans\text{-}Pt(CN)_4(OH_2)Br^- + Br^-$$

Adjustment of the pH of the solution with NaOH to pH > 11 results in complete conversion of $Pt(CN)_4(OH_2)Br^-$ to $Pt(CN)_4(OH)Br^{2-}$. Any $Pt(CN)_4Br_2^{2-}$ formed by substitution of Br^- for the H_2O in the complex is also rapidly converted to $Pt(CN)_4(OH)Br^{2-}$ [7,8]. The platinum concentrations in the resulting solutions were confirmed by reducing the Pt(IV) with SO_3^{2-} to $Pt(CN)_4^{2-}$ and comparing the resulting UV–VIS spectrum with the known spectrum of $Pt(CN)_4^{2-}$.

Solutions of $NaClO_4$ used to adjust the ionic strength were prepared by dissolving triply recrystallized $NaClO_4$ (prepared by neutralization of conc. $HClO_4$ with Na_2CO_3) in doubly distilled water.

The $Na_2S_4O_6 \cdot 2H_2O$ used in this study was obtained from K and K Laboratories. The number of waters of hydration was determined by drying a sample of the material to constant weight (24 h) at 105°C, and the purity was determined by titration of the acid liberated on addition of excess $HgCl_2$ [9]. Duplicate determinations showed the material to be $100.2 \pm 0.4\%$ pure. Titration with I_2 for determination of $Na_2S_2O_3$, a likely impurity in $Na_2S_4O_6$, indicated less than 0.3% present. This test is necessary because $S_2O_3^{2-}$ also reacts with $HgCl_2$ to generate acid [9].

(ii) Apparatus

Absorbance measurements were made with a Cary Model 14 recording spectrophotometer equipped with a thermostatted cell compartment. The rates of those reactions having half-lives of > 5 s were measured by monitoring the absorbance change accompanying the reaction with this spectrophotometer. Reactions with half-lives of < 5 s were followed using a stopped-flow spectrophotometer equipped with a deuterium lamp. In this instrument the reactants, mixing chamber, and observation tube were held at constant temperature with circulating water.

pH measurements were made using a Beckman Research Model pH meter equipped with Beckman E-3 glass and frit junction calomel electrodes. The KCl in the calomel electrode was replaced with saturated NaCl solution to prevent precipitation of $KClO_4$ when the electrodes were immersed in solutions containing $NaClO_4$. In all cases the $[OH^-]$ was determined from the measured pH by comparison with a calibration curve prepared using solutions of known $[OH^-]$ and 0.10M ionic strength.

(iii) Analysis of product solutions for SO_4^{2-}, $S_3O_6^{2-}$ and $S_4O_6^{2-}$

In order to test for the presence of SO_4^{2-} in the product mixtures, 10^{-3} M solutions of both $Pt(CN)_4(OH)Br^{2-}$ and $S_2O_3^{2-}$ were prepared. After 1 h, saturated $Ba(ClO_4)_2$ solution was added dropwise until a milky white precipitate formed. This remained on acidification. A blank experiment in which the product, $Pt(CN)_4^{2-}$, was substituted for $Pt(CN)_4(OH)Br^{2-}$ showed no precipitate with identical treatment.

The method of analysis for $S_3O_6^{2-}$ and $S_4O_6^{2-}$ in the product solutions was essentially the same as that of Trudinger et al. [10] i.e., cyanolysis of the polythionate using KCN solution to form SCN^-, followed by addition of a strongly acidic solution of ferric ion and measurement of the absorbance at 460 nm due to the $FeSCN^{2+}$ formed. The cyanolysis of $S_4O_6^{2-}$ was found to be complete in less than 15 min at room temperature while the corresponding reaction of $S_3O_6^{2+}$ takes place only at higher temperature and over extended time intervals (100°C, 45 min). After several initial experiments showed an absence of $S_3O_6^{2-}$ in our product solutions only the $S_4O_6^{2-}$ analysis was carried out.

As a result of the apparent instability [11] of $S_4O_6^{2-}$ in our product solutions (pH 11–12; $\mu = 0.10$M; $[Pt(CN)_4^{2-}] \cong 1 \times 10^{-4}$M; $[S_2O_3^{2-}] = 5 \times 10^{-4}$ to 3×10^{-3}M and $[Br^-] \cong 2 \times 10^{-4}$M) it was necessary to compensate for the 10–15% decomposition by using $S_4O_6^{2-}$ solutions as standards. The reaction solutions on which analyses were performed were prepared by injection of an $S_2O_3^{2-}$ solution into a solution of $Pt(CN)_4(OH)Br^{2-}$ (typically 1.0×10^{-4}M, adjusted to the desired pH at 0.10M ionic strength). This solution was rapidly shaken and allowed to react for 15 min, a time sufficient for complete reduction of the $Pt(CN)_4(OH)Br^{2-}$ to $Pt(CN)_4^{2-}$. Following cyanolysis and addition of ferric ion, the yield of $S_4O_6^{2-}$ from the oxidation of the $S_2O_3^{2-}$ could be calculated by comparison of the $FeSCN^{2+}$ absorbance with that obtained from standard solutions of $S_4O_6^{2-}$ in synthetic product mixtures subject to identical treatment.

(iv) Spectrophotometric titration

The stoichiometry in the presence of an excess of $Pt(CN)_4(OH)Br^{2-}$ was determined by spectrophotometric titration. Aliquots of a solution of $S_2O_3^{2-}$ were added to a series of identical solutions of $Pt(CN)_4(OH)Br^{2-}$ (pH 11.0; $[Pt(IV)]_0 = 7.0 \times 10^{-5}$M) and the UV spectrum measured after 16 h to determine the number of moles of $Pt(CN)_4^{2+}$ formed per mole $S_2O_3^{2-}$ added. Corrections were made for the concomitant base reduction of the $Pt(CN)_4(OH)Br^{2-}$.

(v) Kinetic measurements

The solutions for the kinetic measurements were prepared by rapidly mixing solutions of $S_2O_3^{2-}$ (6×10^{-5} to 1×10^{-2}M) with solutions of $Pt(CN)_4(OH)Br^{2-}$ (2.5×10^{-5} to 1.0×10^{-4}M) either in a spectrophotometer cell or in the mixing chamber of the stopped-flow spectrophotometer. The solutions were always equilibrated in a water bath at 25° prior to mixing and in all cases the ionic strength of the final solution was 0.10M ($NaClO_4$). The pH of the solution was measured on completion of the reaction. The extent of reaction as a function of time was determined by monitoring the absorbance due to $Pt(CN)_4^{2-}$ at its maximum at 255 nm ($\varepsilon_{Pt(CN)_4^{2-}} = 1.09 \times 10^4 M\ cm^{-1}$; $\varepsilon_{Pt(CN)_4(OH)Br^{2-}} = 2.10 \times 10^3 M^{-1}\ cm^{-1}$).

C. RESULTS

(i) Oxidation of $S_2O_3^{2-}$

(a) Kinetic studies

The measurements were all carried out at 25° and with the ionic strength adjusted to 0.10 by addition of NaOH and $NaClO_4$. The variations in the concentrations of both $S_2O_3^{2-}$ and OH^- covered the approximate ranges 3×10^{-4} to 0.10M. In each experiment $S_2O_3^{2-}$ was present in sufficient excess so that its concentration was essentially constant during the course of the reaction. Under these conditions the rate was found to be pseudo first order in $Pt(CN)_4(OH)Br^{2-}$. Numerical values of a pseudo-first order rate constant, k_0, which is defined by eqn. 1, were evaluated from the slopes of the plots of log absorbance vs. time.

$$\frac{-\mathrm{d}\ln\left[\mathrm{Pt(CN)_4(OH)Br^{2-}}\right]}{\mathrm{d}t} = k_0 \tag{1}$$

These plots were generally linear for at least three half-lives and the values of k_0 reproducible in replicate experiments to ±5%. The values of k_0 were independent of the concentration of either $Pt(CN)_4^{2-}$ or Br^-.

The significance of our moderately complex kinetic results may be understood more readily if we indicate at this point that to within the limit of error they all conform to the expression:

$$k_0 = a\left[S_2O_3^{2-}\right]\left(\frac{4b\left[OH^-\right] + \left[S_2O_3^{2-}\right]}{b\left[OH^-\right] + \left[S_2O_3^{2-}\right]}\right) \tag{2}$$

The numerical values of a (14.8 ± 0.2) and b (0.031 ± 0.002) were obtained by computer-assisted non-linear least-square analysis of the data. The uncertainties assigned to a and b are the standard deviations obtained in this least-square analysis.

Equation 2 may also be written as eqn. 3, a form which indicates that $k_0/[S_2O_3^{2-}]$ is a function of the ratio $[S_2O_3^{2-}]/[OH^-]$:

$$k_0 = a\left[S_2O_3^{2-}\right]\left(\frac{4b + \left[S_2O_3^{2-}\right]/\left[OH^-\right]}{b + \left[S_2O_3^{2-}\right]/\left[OH^-\right]}\right) \tag{3}$$

Either eqn. 2 or 3 may be replaced by the valid approximations $k_0 = a[S_2O_3^{2-}]$ and $k_0 = 4a[S_2O_3^{2-}]$ in the limiting concentration regions where $[S_2O_3^{2-}]/[OH^-] \gg 4b$ and $[S_2O_3^{2-}]/[OH^-] \ll b$, respectively. In each of these limiting conditions the rate law is found to be zero order in $[OH^-]$, first order in $[S_2O_3^{2-}]$, and, of course, first order in $[Pt(CN)_4(OH)Br^{2-}]$, as it is in all experiments. Under all other conditions the rate law will appear to be complex with the order, with respect to either $[S_2O_3^{2-}]$ or $[OH^-]$, variable and frequently less than unity.

It is convenient to divide the experiments into two groups which will be considered separately. The initial objective in the group 1 experiments was to determine the order with respect to $[S_2O_3^{2-}]$ by systematically varying its concentration at each of four different fixed OH^- concentrations. The

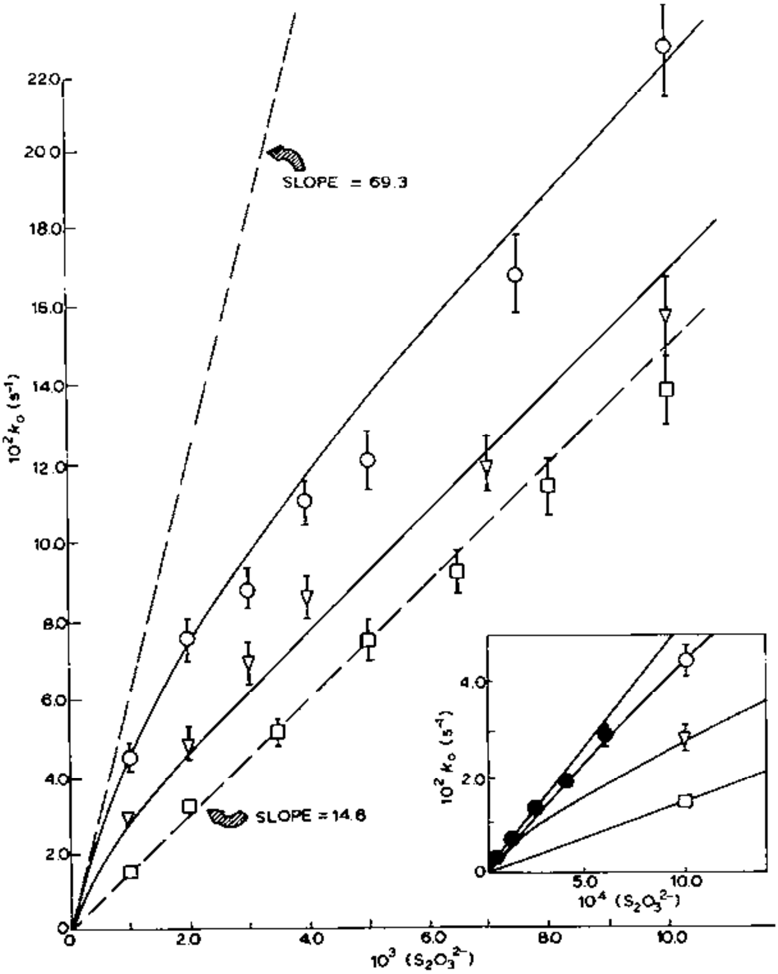

Fig. 1. Variation of k_0 with $[S_2O_3^{2-}]$ at four concentrations of OH^-: $[OH^-] = 9.87 \times 10^{-2}$M (●); 6.16×10^{-2}M (○); 1.38×10^{-2}M (▽); and 3.16×10^{-4}M (□); T = 25.0°C, ionic strength, 0.10M.

results are presented in Fig. 1 as a plot of k_0 vs. the $S_2O_3^{2-}$ concentration. The error bars in this and subsequent figures are based on a typical irreproducibility of ±5%. The solid lines represent calculated values obtained from eqn. 1 and the numerical values of a and b listed above. The lower and upper dashed lines, whose slopes differ by a factor of four, represent the limiting behavior given by the simpler approximate equations $k_0 = a[S_2O_3^{2-}]$ and $k_0 = 4a[S_2O_3^{2-}]$, respectively.

The results which are represented in Fig. 1 as the lower open squares provide an important clue to one limiting form of the rate law since they all fall on the lower dotted line and conform to the equation $k_0 = a[S_2O_3^{2-}]$. They were carried out at the relatively large values of the ratio $[S_2O_3^{2-}]/[OH^-]$ which fall in the range 3.2–32 and conform to the limiting restriction $[S_2O_3^{2-}]/[OH^-] \gg b$. All of the other results plotted in Fig. 1 were obtained at much lower values of the ratio $[S_2O_3^{2-}]/[OH^-]$.

In order to confirm the order with respect to $[S_2O_3^{2-}]$ and remain within the constraints of 0.10M ionic strength, it is necessary to use such low concentrations of $S_2O_3^{2-}$ that the points would not be distinguishable on the scale of the larger plot. These points ($[OH^-] = 9.87 \times 10^{-2}$M) are plotted in the inserted graph in Fig. 1 together with the lowest points of the other concentrations of hydroxide ion. Again, the lines represent the calculated values of k_0 using the non-linear least-squares values of a and b. The solid circles represent experiments in which $0.031 \gg [S_2O_3^{2-}]/[OH^-]$. These results conform to the equation $k_0 = 4a[S_2O_3^{2-}]$.

The second group of experiments were carried out to provide additional information about the order with respect to $[OH^-]$ and the overall form of the rate law. They consist of four series of experiments with each series representing a systematic variation of the OH^- concentration at each of four fixed and relatively low $S_2O_3^{2-}$ concentrations. All of these results are presented in Fig. 2 as a plot of k_0 vs. the OH^- concentration.

The intercept values of k_0 in Fig. 2, which represent values of k_0 extrapolated to zero OH^- concentration, vary linearly with the $S_2O_3^{2-}$ concentration and conform to the equation $k_0 = a[S_2O_3^{2-}]$. If these intercepts had been plotted in Fig. 1, they would have fallen on the lower dotted line along with the open square points because of the large value of $[S_2O_3^{2-}]/[OH^-]$. The extrapolated values of k_0 thus provide additional evidence that there is a limiting region at low alkalinity where the rate is zero order in $[OH^-]$.

Examination of Fig. 2 indicates that as the OH^- concentration is increased at any given $S_2O_3^{2-}$ concentration the order with respect to $[OH^-]$ drops below unity.

At the lowest $S_2O_3^{2-}$ concentration, the order with respect to $[OH^-]$ actually decreases to zero at OH^- concentrations well below 0.10M, the

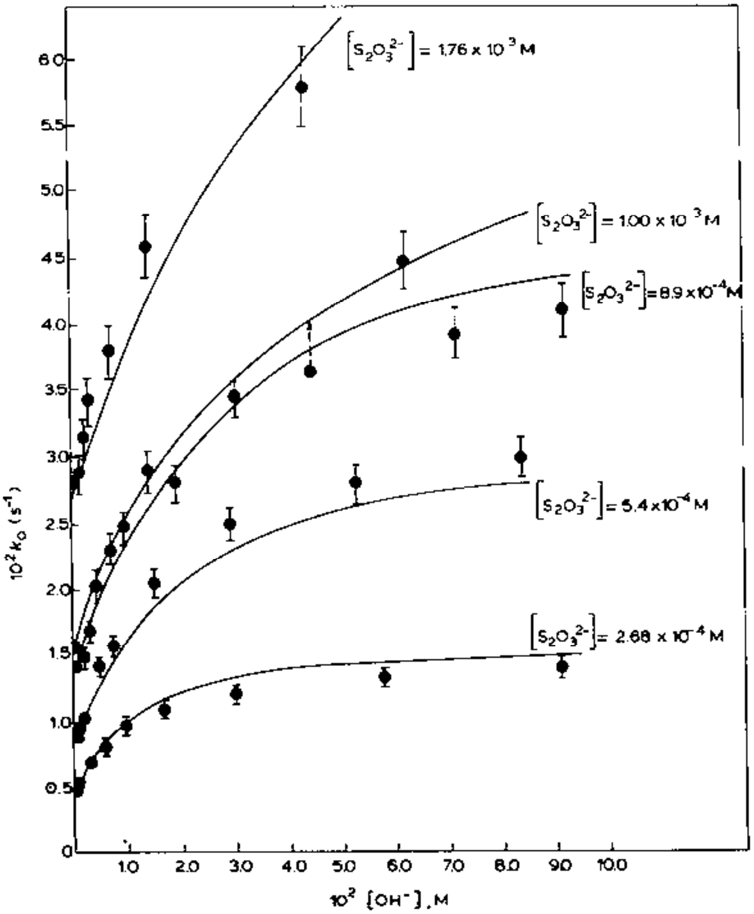

Fig. 2. Variation of k_0 with [OH^-] at five concentrations of $S_2O_3^{2-}$.

maximum concentration which could be employed without an increase in ionic strength. In these experiments, which are represented by the lowest curve in Fig. 2, the "plateau" values of k_0 at high OH^- concentration are greater by a factor of four than the intercept value extrapolated to zero OH^- concentration. Moreover, if this plateau value of k_0 had been plotted in Fig. 1, it would have fallen on the upper dotted line calculated from the expression $k_0 = 4a[S_2O_3^{2-}]$. Unfortunately, the values of k_0 in Fig. 2, at other than the lowest $S_2O_3^{2-}$ concentration, do not become zero order in [OH^-] in the attainable range of OH^- concentration, but the general shape of the curves is compatible with the idea that the plateau values of k_0 obtained by extrapolation to higher OH^- concentrations would be larger than the intercept value by a factor of four.

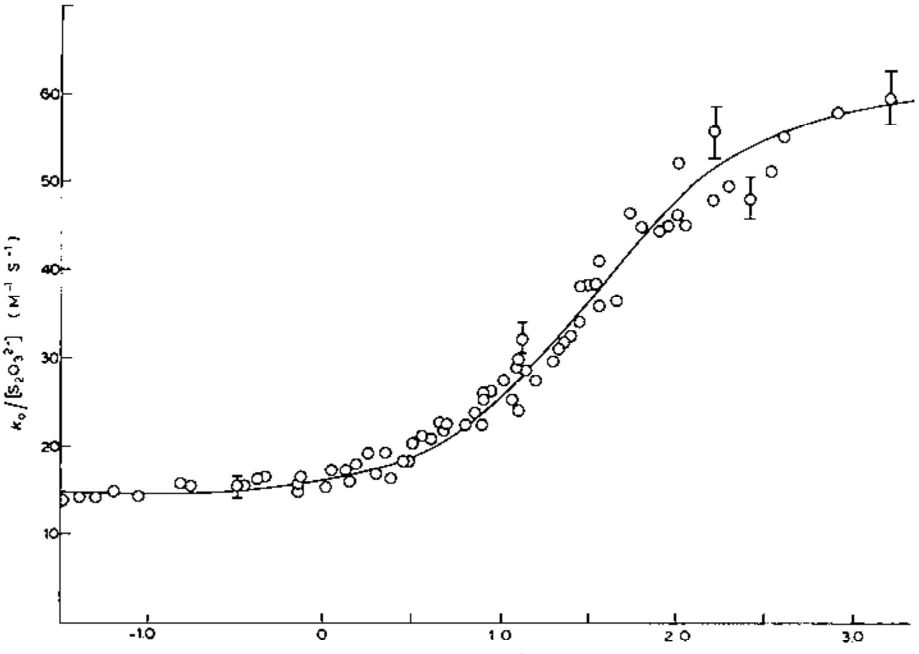

Fig. 3. Plot of $k_0/[S_2O_3^{2-}]$ vs. $-\log[S_2O_3^{2-}]$ for the oxidation of $S_2O_3^{2-}$ by $Pt(CN)_4(OH)Br^{2-}$.

In presenting the kinetic results we have emphasized the data which provide major evidence for the two limiting forms of the rate law. However, the most compelling test of the applicability of eqns. 2 and 3 is the overall agreement between experiment and calculated values of k_0 which are represented by the solid lines in Figs. 1 and 2. The fit of the kinetic experiments to eqns. 2 and 3 is likewise evident in Fig. 3, a plot of $k_0/[S_2O_3^{2-}]$ vs. $-\log[S_2O_3^{2-}]/[OH^-]$ for all 79 of the kinetic experiments. These encompass a range of concentrations of OH^- from 1.00×10^{-4} to 9.87×10^{-2}M, of concentrations of $S_2O_3^{2-}$ from 6×10^{-5} to 1.0×10^{-2}M and of the ratio $[S_2O_3^{2-}]/[OH^-]$ from 32 to 6×10^{-4} (a factor of greater than 50000). For these 79 experiments the average deviation from the calculated values (solid line) is 6.2% and random in nature. Alternatively, the satisfactory agreement is demonstrated by the standard deviations represented by the uncertainties in the numerical values of *a* and *b*.

(b) Stoichiometry

The stoichiometry of the reaction is variable, depending on the relative

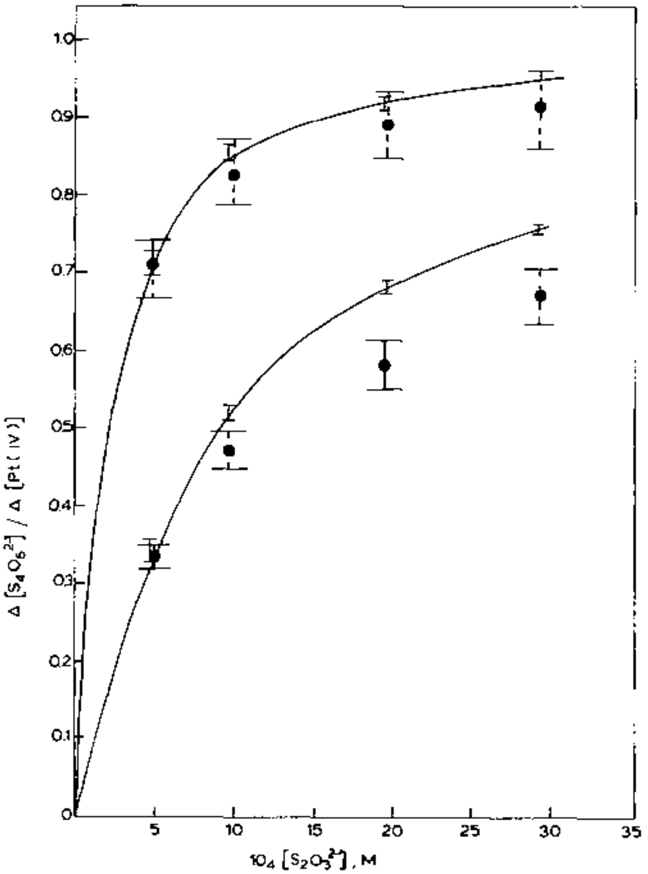

Fig. 4. Variation of the ratio of moles of $S_4O_6^{2-}$ formed per mole of $Pt(CN)_4(OH)Br^{2-}$ consumed as a function of $[S_2O_3^{2-}]$ at pH 11.12 (upper curve) and pH 11.86 (T = 25.0°C, ionic strength = 0.10M).

concentrations of $S_2O_3^{2-}$ and OH^-. The two major sulfur-containing products are SO_4^{2-} and $S_4O_6^{2-}$ which could be formed in essentially quantitative yield depending on the reaction conditions. The reduction product of $Pt(CN)_4(OH)Br^{2-}$ is $Pt(CN)_4^{2-}$ irrespective of whether SO_4^{2-} or $S_4O_6^{2-}$ is the major product. When a spectrophotometric titration was carried out by adding suitable amounts of $S_2O_3^{2-}$ to separate aliquots of $Pt(CN)_4(OH)Br^{2-}$ solution and monitoring the absorbance of the product, $Pt(CN)_4^{2-}$, a sharp endpoint was observed at the molar ratio $S_2O_3^{2-}/Pt(CN)_4(OH)Br^{2-}$ of 1 : 4 (±5%). The presence of sulfate as reaction product was indicated by formation of a milky white precipitate on addition of $Ba(ClO_4)_2$ to product solutions as described in Section B.

In the experiments in which $S_4O_6{}^{2-}$ was an important product, $S_2O_3{}^{2-}$ was present in excess and the spectrophotometric titration technique was no longer applicable. However, it was possible to determine the amount of $S_4O_6{}^{2-}$ formed and the amount of unreacted $S_2O_3{}^{2-}$ present after the reaction was complete by the alternative but somewhat less accurate analytical procedure outlined in Section B. The results are presented in Fig. 4 as a plot of the product ratio $[S_4O_6{}^{2-}]/[Pt(CN)_4^{2-}]$ vs. the initial $S_2O_3{}^{2-}$ concentration (before reaction). The solid lines in Fig. 4 are theoretical curves based on assumed reaction mechanisms discussed in more detail in Section D.

Thus the values of the product ratio, the moles of $Pt(CN)_4Br(OH)^{2-}$ consumed per mole of $S_2O_3{}^{2-}$ undergoing reaction, should be 4 and 0.5 for reactions 4 and 5, respectively:

$$4Pt(CN)_4(OH)Br^{2-} + S_2O_3{}^{2-} + 6OH^- \rightarrow 4Pt(CN)_4^{2-} + 2SO_4^{2-} + 5H_2O + 4Br^- \quad (4)$$

$$Pt(CN)_4(OH)Br^{2-} + 2S_2O_3{}^{2-} \rightarrow Pt(CN)_4^{2-} + S_4O_6^{2-} + OH^- + Br^- \quad (5)$$

(ii) Oxidation of $S_4O_6{}^{2-}$

The stoichiometry was determined at pH 11 in a spectrophotometric titration with the $Pt(CN)_4(OH)Br^{2-}$ present in excess, but at a concentration of only 7.0×10^{-5}M. After 77 h the consumption ratio $\Delta[Pt(CN)_4(OH)Br^{2-}]/\Delta[S_4O_6{}^{2-}]$ was found to be 6.4, a result somewhat below the expected value of 7.0 for the reaction:

$$S_4O_6{}^{2-} + 7Pt(CN)_4(OH)Br^{2-} + 13OH^- \rightarrow 4SO_4{}^{2-} + 7Pt(CN)_4{}^{2-} + 7Br^- + 10H_2O$$

The rate of oxidation of $S_4O_6{}^{2-}$ was studied at 25° and at an ionic strength of 0.10 over the range of OH^- concentration from 0.0012 to 0.085M. The kinetic behavior is far less complex than observed for $S_2O_3{}^{2-}$. The reaction is first order in $[S_4O_6{}^{2-}]$, first order in $[OH^-]$, and zero order in $[Pt(CN)_4(OH)Br^{2-}]$, i.e.,

$$\text{rate} = k[S_4O_6{}^{2-}][OH^-]$$

The numerical value of k was found to be 0.0146 $M^{-1}\ s^{-1}$. Even in the most rapid reactions the rate of $S_4O_6{}^{2-}$ oxidation was very much slower than that of the $Pt(CN)_4(OH)Br^{2-}$ oxidation of $S_2O_3{}^{2-}$, and thus $S_4O_6{}^{2-}$ did not contribute significantly to the reduction of $Pt(CN)_4(OH)Br^{2-}$ in the studies of $S_2O_3{}^{2-}$ oxidation.

D. DISCUSSION

(i) Oxidation of $S_2O_3^{2-}$

Our studies impose two restrictions upon the possible choice of mechanism. Firstly, the activated complex which is formed in the rate-determining step must have a chemical composition which, apart from an unknown number of solvent molecules, is given by the formula $[Pt(CN)_4(OH)Br \cdot S_2O_3]^{4-}$. Secondly, the mechanism must include the formation of a reaction intermediate which subsequently reacts irreversibly and in a competitive fashion with $S_2O_3^{2-}$ and OH^-. Moreover, these competitive reactions must initiate processes which lead ultimately to the formation of either $S_4O_6^{2-}$ or SO_4^{2-}.

The following mechanism, which we shall refer to as Scheme 1, is compatible with these restrictions and, in addition, seems to us to be more plausible than other possible alternatives:

$$Pt(CN)_4(OH)Br^{2-} + S_2O_3^{2-} \xrightarrow{k_1} Pt(CN)_4^{2-} + OH^- + BrS_2O_3^- \quad \text{rate determining} \tag{6}$$

$$BrS_2O_3^- + S_2O_3^{2-} \xrightarrow{k_2} S_4O_6^{2-} + Br^- \tag{7}$$

$$BrS_2O_3^- + OH^- \xrightarrow{k_3} HOS_2O_3^- + Br^- \tag{8}$$

$$HOS_2O_3^- + 3Pt(CN)_4(OH)Br^{2-} + 6OH^- \rightarrow 2SO_4^{2-} + 3Br^- + 3Pt(CN)_4^{2-} + 5H_2O \tag{9}$$

Scheme 1

assuming only the usual steady-state approximation one may readily derive the rate law:

$$-\frac{d \ln[Pt(CN)_4(OH)Br^{2-}]}{dt} = k_1[S_2O_3^{2-}]\left(\frac{4(k_3/k_2)[OH^-] + [S_2O_3^{2-}]}{(k_3/k_2)[OH^-] + [S_2O_3^{2-}]}\right)$$

and identify the kinetic parameters evaluated in Section B as $k_1 = a = 14.8 \pm 0.2$ and $k_3/k_2 = b = 0.031 \pm 0.002$.

Furthermore, this mechanism predicts a variable reaction stoichiometry as observed and summarized in Fig. 4. Indeed, it predicts quantitatively the results of the stoichiometry measurements. Using the mechanism in Scheme 1, eqns. 10 and 11 can be derived:

$$\frac{\Delta[S_4O_6^{2-}]}{\Delta[Pt(CN)_4^{2-}]} = \left(\frac{4k_3}{k_2}\frac{[OH^-]}{[S_2O_3^{2-}]} + 1\right)^{-1} \tag{10}$$

$$\frac{\Delta[SO_4^{2-}]}{\Delta[Pt(CN)_4^{2-}]} = \left(\frac{k_2}{2k_3}\,\frac{[S_2O_3^{2-}]}{[OH^-]} + 2\right)^{-1} \tag{11}$$

Equation 10 can then be used with $k_3/k_2 = 0.031 \pm 0.002$ and the appropriate values of $[OH^-]$ and $[S_2O_3^{2-}]$ to calculate the theoretical stoichiometries (solid lines) for comparison with the experimental stoichiometries plotted in Fig. 4. Substitution of the initial $S_2O_3^{2-}$ concentrations in eqns. 10 and 11 would introduce an error in the calculated product ratios, since the $S_2O_3^{2-}$ concentration decreases continuously during the course of the reaction. What was done instead was to reduce this error to an acceptable value by using a corrected $S_2O_3^{2-}$ concentration to calculate the product ratios, using eqns. 10 and 11 for each of 10 successive 10% reaction increments. The initial $S_2O_3^{2-}$ concentration was used to calculate the SO_4^{2-} and $S_4O_6^{2-}$ concentrations produced in the first 10% of the reaction. These values were then used to calculate a $S_2O_3^{2-}$ concentration applicable for the second 10% of the reaction, etc. The final theoretical values of the ratio $\Delta[S_4O_6^{2-}]/\Delta[Pt(CN)_4^{2-}]$ represented by the solid line in Fig. 4 were obtained by summing the 10 values of $\Delta[S_4O_6^{2-}]$ and dividing by the total $\Delta[Pt(CN)_4^{2-}]$.

In the above mechanism eqn. 9 is meant to carry only stoichiometric significance. Our studies provide no information about its detailed mechanism. However, it presumably occurs in a number of steps, since it involves a net consumption of three $Pt(CN)_4(OH)Br^{2-}$ ions. Fission of the sulfur–sulfur bond, which must occur at some point, may well involve hydrolysis of $O_2SSO_3^{2-}$, a reaction [12] which is known to generate SO_3^{2-}. Such a process would be compatible with our mechanism, since we [13] have found that $Pt(CN)_4(OH)Br^{2-}$ oxidizes SO_3^{2-} much more rapidly than it does $S_2O_3^{2-}$.

The most interesting question which must be faced in the formulation of the mechanism is the identity of the reactive intermediate to which we have assigned the formula $BrS_2O_3^-$. Formation of $BrS_2O_3^-$ in reaction 6 may be visualized as the formal transfer of Br^+ from $Pt(CN)_4(OH)Br^{2-}$ to the sulfur atom of $S_2O_3^{2-}$. This type of formal transfer of Br^+ from a Pt(IV) complex to an oxidizable substrate is a well documented aspect of Pt(IV) chemistry. It occurs most commonly when the substrate is a Pt(II) complex [14]. Transfer of Br^+ is probably also involved in the oxidation of various ligands [3] by complexes of the types PtA_2Cl_4 and PtA_2Br_4, where A is a neutral ligand such as $S(C_2H_5)_2$, $P(C_2H_5)_3$, etc., but the presence of reactive intermediates in these reactions have not been demonstrated.

In the more obvious alternatives to Scheme 1 the formula $BrS_2O_3^-$ can be replaced by the general formula $XS_2O_3^{n-}$ where X can be OH or a Pt(IV) complex. For the alternative, where X is OH, eqn. 6 would be replaced by a process in which OH^+ would be formally transferred from $Pt(CN)_4(OH)Br^{2-}$ to $S_2O_3^{2-}$. There are at least two objections to this alternative. First, all of the available studies of Pt(IV) chemistry [13,14] suggest that transfer of Br^+ occurs much more rapidly than that of OH^+. This is readily understandable since Br, unlike OH, has low lying unfilled *d* orbitals which could be utilized in a transition state in which the group undergoing transfer is simultaneously bonded to both Pt(IV) and substrate molecule. Second, such a mechanism would result in a rate expression significantly different from that which we observed.

(ii) *The $Pt(CN)_4(Br)OH^{2-}$ oxidation of $S_4O_6^{2-}$*

The $Pt(CN)_4(Br)OH^{2-}$ oxidation of $S_4O_6^{2-}$ differs markedly from the analogous oxidation of either $S_2O_3^{2-}$ or SCN^- in that the overall rate is independent of the $Pt(CN)_4(Br)OH^{2-}$ concentration. The form of the rate law indicates that the rate-determining step must involve the reaction of $S_4O_6^{2-}$ and OH^- in a process which generates reactive intermediates which are ultimately oxidized to SO_4^{2-} by $Pt(CN)_4(Br)OH^{2-}$. A mechanism which is compatible with the rate law is given by the following sequence of reactions:

$$S_4O_6^{2-} + OH^- \xrightarrow{k_2} HOSSO_3^- + S_2O_3^{2-}\ (\text{slow}) \tag{12}$$

$$\begin{aligned}3Pt(CN)_4(Br)OH^{2-} + HOSSO_3^- + 6OH^- &\rightarrow 3Pt(CN)_4^{2-} + 3Br^-\\ &+ 2SO_4^{2+} + 5H_2O\ (\text{fast})\end{aligned} \tag{13}$$

$$\begin{aligned}4Pt(CN)_4(Br)OH^{2-} + S_2O_3^{2-} + 6OH^- &\rightarrow 4Pt(CN)_4^{2-} + 2SO_4^{2-}\\ &+ 4Br^- + 5H_2O\ (\text{fast})\end{aligned} \tag{14}$$

In this mechanism, reaction 12 is the rate-determining step which generates the reactive intermediates $HOSSO_3^-$ and $S_2O_3^{2-}$. The overall net reactions of unknown mechanism with $Pt(CN)_4(Br)OH^{2-}$ are given by eqns. 13 and 14.

Reaction 12 may be viewed as a nucleophilic attack by OH^- on $S_4O_6^{2-}$ and the subsequent breaking of a sulfur–sulfur bond. Reaction 15, an alternative method of rupture of the sulfur–sulfur bond, may also contribute to a minor extent in the overall reduction of $Pt(CN)_4(Br)OH^{2-}$, since the reaction products may also react rapidly with $Pt(CN)_4(Br)OH^{2-}$.

$$S_4O_6^{2-} + OH^- \rightarrow SO_3^{2-} + HOSSSO_3^- \tag{15}$$

However, there is a variety of evidence that supports the assumption that reaction 15 is much slower than reaction 12. For example, $S_2O_3^{2-}$ reacts with $S_4O_6^{2-}$ in parallel reaction paths to displace both $S_2O_3^{2-}$ and SO_3^{2-}. The $S_2O_3^{2-}$ displacement reaction [15], which has been studied using ^{35}S-labelled $S_2O_3^{2-}$, is immeasurably rapid. By contrast, the rate of reaction 15 is readily measurable [16].

The reaction mechanism under consideration provides an interesting example of how the rate of a rapidly reversible reaction may be measured by adding a scavenger which reacts rapidly and quantitatively with reactive intermediates. It is evident that reaction 12 must be occurring even in the absence of $Pt(CN)_4(Br)OH^{2-}$. However, under these latter conditions the thermal degradation of $S_4O_6^{2-}$ is much slower than the rate of the $Pt(CN)_4BrOH^{2-}$ oxidation of $S_4O_6^{2-}$. This difference in rate carries the implication that the regeneration of $S_4O_6^{2-}$ by reaction of $HOSSO_3^-$ and $S_2O_3^{2-}$ in the reverse of reaction 12 is a very efficient process. However, it is clearly a process which does not compete with the scavenger action of $Pt(CN)_4(Br)OH^{2-}$ in the reactions which initiate the overall processes given by eqns. 13 and 14.

REFERENCES

1 H.R. Ellison, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 83 (1961) 3943.
2 A. Peloso, G. Dolcetti and R. Ettorre, Inorg. Chim. Acta, 1 (1967) 403.
3 For a recent review see A. Peloso, Coord. Chem. Rev., 10 (1973) 123.
4 R.O. Griffith and R. Irving, Trans. Faraday Soc., 45 (1949) 563.
5 C.L. Lee and M.W. Lister, Can. J. Chem., 57 (1979) 1524.
6 W.R. Mason, Inorg. Chem., 10 (1971) 1914.
7 C.E. Skinner and M.M. Jones, J. Am. Chem. Soc., 91 (1969) 4405.
8 C.E. Skinner and M.M. Jones, ibid., 91 (1969) 1984.
9 R.R. Jay, Anal. Chem., 25 (1953) 288.
10 D.P. Kelly, L.A. Chambers and P.A. Trudinger, Anal. Chem., 41 (1969) 898.
11 O.A. Nietzel and M.A. de Sesa, Anal. Chem., 27 (1955) 1839.
12 E. Hayon, A. Treinin and J. Wilf, J. Am. Chem. Soc., 94 (1972) 47 and references cited therein.
13 J.E. Byrd and W.K. Wilmarth, unpublished results.
14 For a review see W.R. Mason, Coord. Chem. Rev., 7 (1972) 241.
15 See the chapter by J.L. Kice, in J.O. Edwards (Ed.), Inorganic Reaction Mechanisms, Part II. Interscience, 1972.
16 O. Foss and I. Kringlebotn, Acta Chem. Scand., 15 (1961) 1608.