Kinetics and Mechanism for Oxidation of Dissolved Sulfur Dioxide by Tetracyanodichloroplatinate(IV) in Acidic Aqueous Solution and for Formation and O–S Linkage Isomerization of Sulfitotetracyanochloroplatinate(IV)

Johan Berglund, Robert Voigt, Sture Fronaeus, and Lars I. Elding*

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Received November 30, 1993[⊗]

Oxidation of $SO_2\cdot nH_2O/HSO_3^-/SO_3^{2-}$ by $Pt(CN)_4Cl_2^{2-}$ has been studied at 25 °C and 1.0 M ionic strength in acidic aqueous solution by use of stopped-flow spectrophotometry. The stoichiometry of the reaction is 1:1 according to $Pt(CN)_4Cl_2^{2-} + HSO_3^- + H_2O \rightarrow Pt(CN)_4^{2-} + 2Cl^- + HSO_4^- + 2H^+$. It is first-order with respect to both [Pt(IV)] and [S(IV)]. The pH-dependence in the region $0.3 < pH < 4.5$ is complex and indicates that $Pt(CN)_4Cl_2^{2-}$ is reduced by both HSO_3^- and SO_3^{2-} in two parallel reactions with second-order rate constants $1.3 \pm 0.5\ M^{-1}\ s^{-1}$ and $(4.5 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1}$, respectively. The suggested mechanism involves attack by the incoming nucleophiles on coordinated chloride, followed by inner-sphere two-electron transfer to the metal center and formation of $Pt(CN)_4^{2-}$ and $ClSO_3H$ and $ClSO_3^-$. Chlorosulfuric acid and chlorosulfate(VI) hydrolyze in rapid subsequent reactions to HSO_4^-. The kinetics for reaction between $Pt(CN)_4ClOH^{2-}$ and HSO_3^- has also been studied by use of variable-temperature and high-pressure stopped-flow spectrophotometry in an aqueous medium with $0.3 < pH < 2$ and as a function of ionic strength $0.325 < I < 1.0$ M. This is a three-step process. An oxygen-bonded sulfito complex, $Pt(CN)_4Cl(OSO_2)^{3-}$, is formed rapidly by addition of HSO_3^- to the hydroxo ligand of $Pt(CN)_4ClOH^{2-}$, without breakage of the Pt–O bond. In the second step, this complex undergoes a slower, rate-determining intramolecular linkage isomerization to the thermodynamically more stable S-bonded isomer $Pt(CN)_4Cl(SO_3)^{3-}$, which is reduced rapidly to $Pt(CN)_4^{2-}$ and HSO_4^- in an inner-sphere two-electron process. Rate constants at 25 °C, ΔH^{*}, ΔS^{*}, and ΔV^{*} are for the uptake reaction $(1.68 \pm 0.05) \times 10^{-5}\ M^{-1}\ s^{-1}$, $44 \pm 3\ kJ\ mol^{-1}$, $-7.5 \pm 0.4\ J\ K^{-1}\ mol^{-1}$, and $-9.4 \pm 0.4\ cm^3\ mol^{-1}$ and for the O–S isomerization $4.5 \pm 0.2\ s^{-1}$, $74.4 \pm 0.5\ kJ\ mol^{-1}$, $16.6 \pm 0.1\ J\ K^{-1}\ mol^{-1}$, and $5.3 \pm 0.4\ cm^3\ mol^{-1}$. The positive entropy and volume of activation for the linkage isomerization indicate that this process takes place through an intramolecular rearrangement via a loosely bound transition state, in which the Pt–O bond is weakened before a new Pt–S bond is formed. In all experiments, the concentration of dissolved molecular oxygen remains constant. This is in agreement with the proposed mechanism, according to which electron transfer is completed within the solvent cage and no radical species are released into the bulk solution, starting an autoxidation of S(IV).

Introduction

Most previous studies of oxidation of sulfur(IV) in aqueous solution ($SO_2\cdot nH_2O$, HSO_3^-, SO_3^{2-}) by metal complexes have been performed using one-electron oxidants.[1–21] Both kinetic studies and identification of products have been used for diagnosis of the reaction mechanism.[21] Thus, it has been suggested that production of dithionate requires access to the metal center and indicates inner-sphere processes, whereas sulfate is the only product in outer-sphere oxidations.[21] It has also been shown that the Marcus theory gives good correlations for complexes oxidizing sulfur(IV) by an outer-sphere mechanism.[21] The relatively few examples, where two-electron oxidants have been used, include complexes of Pt(IV), Au(III), Ag(III), and Tl(III).[22–29] The aim of the present study was to elucidate the reaction mechanism for the oxidation of sulfur(IV) by $Pt(CN)_4Cl_2^{2-}$.

In aqueous solution, redox-active metal ions such as Mn(III/II), Fe(III/II), Co(III/II), and Cu(III/II) catalyze the oxidation of sulfur(IV) by dissolved oxygen.[30–32] For instance, the catalysis by manganese(III/II) takes place via a complex chain reaction, involving SO_3^- and SO_5^- radicals.[30] As far as we know there are no reports on autoxidation of sulfur(IV) catalyzed by two-electron

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oxidants. However, Pt(III) has been proposed as an intermediate in a number of previously studied photochemical and redox reactions.[33-37] Accordingly, $Pt(CN)_4Cl_2^{2-}$ could in principle also start a chain reaction by generating SO_3^- radicals. In that case, for an excess of dissolved oxygen, even a small amount of platinum(IV) would be sufficient to oxidize a larger amount of sulfur(IV).

Under some experimental conditions in the present work, a fraction of the $Pt(CN)_4Cl_2^{2-}$ complex was hydrolyzed to $Pt(CN)_4ClOH_2^-$ and $Pt(CN)_4ClOH^{2-}$. Two fast reactions could then be observed on a time scale much shorter than the redox reaction between $Pt(CN)_4Cl_2^{2-}$ and sulfur(IV). These fast reactions have been identified as the formation of an O-bonded sulfito complex followed by an isomerization to the S-bonded isomer, as observed previously for some other inert cobalt(III), chromium(III), rhodium(III), and platinum(IV) complexes.[1-12,22] A kinetic study of these reactions has also been included in the present paper.

Experimental Section

Chemicals and Solutions. $K_2Pt(CN)_4Cl_2$ was synthesized by oxidation of $K_2Pt(CN)_4{\cdot}3H_2O$ with chlorine. First 1.0 g of $K_2Pt(CN)_4{\cdot}3H_2O$ (Johnson Matthey) was dissolved in ca. 5 mL of water. Chlorine, prepared by oxidation of hydrochloric acid (Merck, 37% pa) with $KMnO_4$ (Merck, pa), was bubbled through the solution for ca. 2 h. Excess chlorine was removed from the solution by flushing with nitrogen for ca. 2 h. Crystals of $K_2Pt(CN)_4Cl_2$ were obtained by evaporation of water at ca. 40 °C. They were dried over phosphorous pentoxide in a vacuum desiccator. Stock solutions of ca. 10 mM $K_2Pt(CN)_4Cl_2$ were prepared by dissolving ca. 0.24 g of accurately weighted crystals in 50 mL of water. The UV–vis spectrum of these solutions agreed with that reported earlier[38] for $Pt(CN)_4Cl_2^{2-}$.

Oxygen-free stock solutions of ca. 50 mM sulfur(IV) were prepared by adding ca. 0.65 g of Na_2SO_3 (Merck, pa) to oxygen-free ionic medium in a gas washing bottle, continuously flushed with argon. The stock solutions were prepared fresh daily, and the concentrations were shown to be constant by iodometric titration[39] during the course of the experiments. Secondary sulfur(IV) solutions were prepared from the stock solutions by dilution with air-saturated ionic medium. These solutions were never used more than ca. 1 h. The stability of the diluted aerobic sulfur(IV) solutions was checked several times under different conditions by repeating a kinetic experiment after about 1 h using the same sulfur(IV) solution. At no occasion there was any significant difference between the rate constants obtained.

Perchloric acid (Merck, pa) and an acetate buffer, prepared from equimolar amounts of acetic acid (Merck, pa) and sodium acetate (Merck, pa), were used to adjust the pH. Sodium perchlorate, $NaClO_4{\cdot}H_2O$ (Merck, pa) was used as supporting electrolyte. The ionic strength was 1.0 M in all experiments if nothing else is stated. Water was doubly distilled from quartz.

Apparatus. Spectra were recorded by use of a Milton Roy 3000 diode-array spectrophotometer and thermostatted quartz Suprasil cells. Time-resolved absorption spectra were recorded by use of an Applied Photophysics Bio Sequential SX-17MV, stopped-flow ASVD spectrofluorimeter. The kinetics was followed by use of a modified Durrum–Gibson stopped-flow instrument. All experiments were performed at (25.0 ± 0.1) °C if nothing else is stated. Activation volumes were determined with a Hi-Tech high-pressure stopped-flow spectrophotometer, Model HPSF-56, equipped with a digital pressure indicator.[40] The kinetics was evaluated with an on-line OLIS least-squares minimizing program,[41] Model 4000 Data System Stopped-flow version 9.04, implemented on Victor V286A PC computers. Oxygen concentrations were measured with an Orion Research oxygen electrode, Model 97-08, connected to an Orion Research EA 920 expandable ion analyzer.

Equilibria in the Sulfur(IV) System. The equilibria for the sulfur(IV) system in water can be written as $SO_2{\cdot}nH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (n - 2)H_2O$ ($pK_{a1} = 1.37$, $I = 1.0$ M, 25 °C),[42] $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ ($pK_2 = 6.34$, $I = 1.0$ M, 25 °C),[42] $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ ($pK_3 = 1.15$).[1] The concentration of $S_2O_5^{2-}$ is negligible for the total sulfur(IV) concentrations used. Below, S(IV) denotes the equilibrium mixture of $SO_2{\cdot}nH_2O$, HSO_3^-, and SO_3^{2-}. For hydrogen sulfite there is a tautomeric equilibrium $H{-}SO_3^- \rightleftharpoons HO{-}SO_2^-$ with an equilibrium constant of 4.9 at 25 °C and $I = 1.0$ *m*.[43]

Results

General Observations. An aqueous solution of 5.0×10^{-4} M $Pt(CN)_4Cl_2^{2-}$ in a 30 mM $HClO_4$ and 0.97 M $NaClO_4$ ionic medium was prepared from a fresh stock solution. UV–vis spectra were recorded at intervals of time during 7 days. The first spectrum, collected immediately after preparation, agreed perfectly with the spectrum of $Pt(CN)_4Cl_2^{2-}$ reported earlier.[38] The spectrum changed slowly with time due to hydrolysis of $Pt(CN)_4Cl_2^{2-}$ and subsequent protolysis of the formed aqua complex $Pt(CN)_4ClOH_2^-$ to $Pt(CN)_4ClOH^{2-}$, according to eq 1;

$$Pt(CN)_4Cl_2^{2-} + H_2O \overset{K_1}{\rightleftharpoons} Pt(CN)_4ClOH_2^- + Cl^- \quad (1a)$$

$$Pt(CN)_4ClOH_2^- \overset{K_a}{\rightleftharpoons} Pt(CN)_4ClOH^{2-} + H^+ \quad (1b)$$

cf. Figure 1a. K_a for $Pt(CN)_4ClOH_2^-$ is 4.0×10^{-2} M at $I = 1.0$ M and 25 °C.[38] Below, the total concentration of platinum(IV) is denoted as follows: $[Pt(IV)] = [Pt(CN)_4Cl_2^{2-}] + [Pt(CN)_4ClOH_2^-] + [Pt(CN)_4ClOH^{2-}]$.

The spectrum of the equilibrium solution after mixing equal amounts of a newly prepared solution of platinum(IV) and sulfur(IV) was found to be identical with the spectrum of $Pt(CN)_4^{2-}$ reported earlier.[38] Thus, the final reaction product is $Pt(CN)_4^{2-}$.

When a 4×10^{-4} M platinum(IV) solution prepared from a ca. 2 h old platinum(IV) stock solution is mixed rapidly in the stopped-flow instrument with a 5.9 mM sulfur(IV) solution containing 4.0 mM NaCl, three reactions can be observed at 255 nm ($[HClO_4]$ = 30 mM). They are well resolved in time and can be studied separately. A very fast reaction with half-life of ca. 4 ms gives rise to an increase in absorbance. It is followed by a somewhat slower absorbance decrease with half-life of ca. 0.15 s. The third reaction is much slower with a half-life of ca. 145 s, and the absorbance increases due to the formation of $Pt(CN)_4^{2-}$, which exhibits an absorbance maximum at this wavelength. These reactions can be identified as reactions 2–4. The experiment described above was repeated with the chloride initially present in the platinum instead of the sulfur(IV) solution. The chloride-containing platinum(IV) solution was prepared ca. 90 min before use. Mixing the two solutions now resulted in one single reaction, identified as reaction 4. Spectra were recorded for the platinum(IV) solutions with and without added chloride. They indicate

$$Pt(CN)_4ClOH^{2-} + HSO_3^- \overset{k_a}{\rightleftharpoons} O_2SO{-}Pt(CN)_4Cl^{3-} + H_2O \quad (2)$$

$$O_2SO{-}Pt(CN)_4Cl^{3-} \xrightarrow{k_i} O_3S{-}Pt(CN)_4Cl^{3-} \quad (3)$$

$$Pt(CN)_4Cl_2^{2-} + HSO_3^- + H_2O \rightarrow Pt(CN)_4^{2-} + 2Cl^- + HSO_4^- + 2H^+ \quad (4)$$

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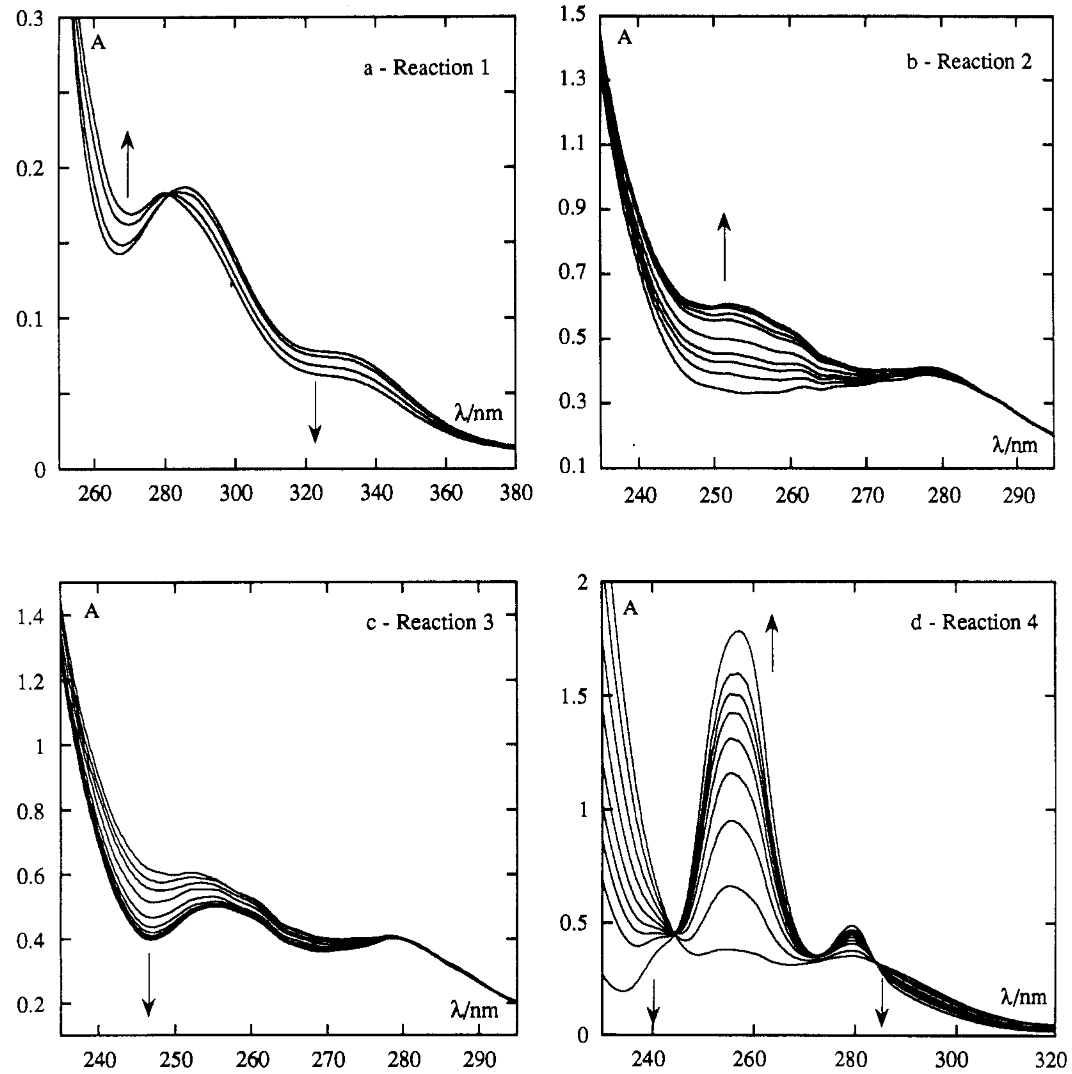

Figure 1. Spectra of a Pt(IV) solution recorded at intervals of time during 7 days and time-resolved spectra recorded during reactions 2–4. Conditions for reaction 1: [Pt(IV)] = 5.0×10^{-4} M, [$HClO_4$] = 30 mM, and [$NaClO_4$] = 0.97 M. The Pt(IV) solution was prepared from a fresh stock solution of $Pt(CN)_4Cl_2^{2-}$. Time after mixing: 0, 23, 76, and 197 h. The first spectrum corresponds to pure $Pt(CN)_4Cl_2^{2-}$. Conditions for reactions 2–4: [Pt(IV)] = 1.9×10^{-4} M, [S(IV)] = 1.5 mM, [$HClO_4$] = 30 mM, I = 1.0 M, and 25 °C. Time after mixing: 0.5, 5, 7, 10, 15, 25, 30, 40, 50, 75 ms (reaction 2); 0.05, 0.1, 0.14, 0.19, 0.29, 0.39, 0.49, 0.59, 0.69, 2.1 s (reaction 3); and 5, 50, 110, 170, 230, 290, 350, 440, 1106 s (reaction 4). The absorbance increases/decreases as a function of time in the direction of the arrows.

that equilibrium 1b is displaced to the left in the presence of chloride. Table 1 summarizes those experiments. *(i)* It is obvious that all observed rate constants are independent of chloride concentration, no matter from which solution the chloride comes. *(ii)* When chloride originates from the sulfur(IV) solutions the changes in absorbance, ΔA, for all three reactions are also independent of the chloride concentration. *(iii)* When the chloride originates from the ca. 90-min-old platinum(IV) solutions, ΔA for reactions 2 and 3 decreases with increasing chloride concentration and ΔA for reaction 4 increases. As can be seen in Figure 1a, the equilibrium mixture $Pt(CN)_4Cl_2^{2-}/Pt(CN)_4ClOH_2^{-}/Pt(CN)_4ClOH^{2-}$ absorbs more strongly at 255 nm than does $Pt(CN)_4Cl_2^{2-}$. This explains the observed ΔA for reactions 2–4 when the equilibria in eq 1 are displaced to the left.

Spectra. Time-resolved spectra for reactions 2 and 3 were recorded by use of the Applied Photophysics stopped-flow spectrophotometer. A ca. 3-h-old 3.8×10^{-4} M Pt(IV) solution was mixed with an equal volume of 3.0 mM S(IV) solution, and kinetic traces were automatically sampled every second nm between 230 and 320 nm. ([H^+] = 30 mM.) The data were processed[44] and time-resolved spectra produced, Figure 1b,c. The change in absorbance during reaction 2 is approximately constant between 245 and 260 nm whereas for reaction 3 there is a maximum change at ca. 246 nm. It should be noted that the spectral changes due to reactions 2 and 3 are superimposed on the spectrum of $Pt(CN)_4Cl_2^{2-}$. The spectral changes due to reaction 4 are displayed in Figure 1d. There are well-defined isosbestic points at 244.5 and 284.5 nm. These spectra were recorded by use of the diode-array spectrophotometer by mixing equal volumes of a freshly prepared solution of 3.8×10^{-4} M Pt(IV) with 2.9 mM S(IV). ([H^+] = 30 mM.)

Stoichiometry. The over-all stoichiometry for the redox process was determined spectrophotometrically at the 255-nm absorbance maximum of $Pt(CN)_4^{2-}$. The measurements were made in an acetate buffer at pH 4.5 where the reduction of platinum(IV) is complete within 1 min under the present conditions and the much slower oxidation of sulfur(IV) by dissolved oxygen does not interfere. Furthermore, chloride was added to the solutions to suppress the hydrolysis of $Pt(CN)_4Cl_2^{2-}$. Solutions with [$Pt(CN)_4Cl_2^{2-}$] = 6.0×10^{-5} M and [S(IV)] < 1.2×10^{-4} M in 0.1 M acetate buffer, 0.2 M NaCl, and 0.7 M $NaClO_4$ were aged for ca. 15 min, and their absorbances measured, Figure 2. Molar absorptivities at 255 nm for $Pt(CN)_4^{2-}$ and [$Pt(CN)_4Cl_2^{2-}$] were determined to be 10 892 and 674 M^{-1} cm^{-1}, respectively, by

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(44) Applied Photophysics Bio Sequential SX-17MV, Sequential Stopped-Flow ASVD Spectrofluorimeter, software manual, Applied Photphysics Ltd. 203/205 Kingston Road, Leatherhead KT22 7PB, UK.

Table 1. Chloride Dependence of Reactions 2–4[a]

reaction	$[Cl^-]$/mM	k_{obsd}/s^{-1}	ΔA	Cl^- origin[b]
2	0	196 ± 12	0.28	sulfur(IV)
	0.025	190 ± 18	0.26	
	0.10	188 ± 8	0.27	
	2.0	207 ± 11	0.25	
	50.0	197 ± 16	0.25	
	0	196 ± 12	0.28	platinum(IV)
	0.050	196 ± 19	0.18	
	0.10	181 ± 17	0.13	
	0.50	183 ± 49	0.05	
	2.0		0	
3	0	4.6 ± 0.2	0.45	sulfur(IV)
	0.025	4.5 ± 0.2	0.45	
	0.10	4.6 ± 0.2	0.45	
	2.0	4.5 ± 0.1	0.45	
	50.0	4.4 ± 0.1	0.45	
	0	4.6 ± 0.2	0.45	platinum(IV)
	0.05	4.8 ± 0.2	0.29	
	0.10	5.3 ± 0.6	0.20	
	0.5		0	
	2.0		0	
4	0	0.045 ± 0.002	0.49	sulfur(IV)
	0.025	0.048 ± 0.002	0.49	
	0.1	0.051 ± 0.005	0.49	
	2.0	0.048 ± 0.002	0.49	
	50	0.048 ± 0.003	0.49	
	0	0.045 ± 0.002	0.49	platinum(IV)
	0.05	0.048 ± 0.001	0.56	
	0.1	0.048 ± 0.001	0.61	
	0.5	0.049 ± 0.006	0.69	
	2.0	0.049 ± 0.001	0.70	

[a] The errors are given as one standard deviation from at least seven measurements for reactions 2 and 3 and from three or four measurements for reaction 4. Conditions: $[Pt(IV)] = 1.98 \times 10^{-4}$ M, $[S(IV)] = 2.93$ mM, $[H^+] = 30$ mM, $I = 1.0$ M, and temperature = 25 °C. [b] The platinum(IV) solutions were prepared ca. 90 min. before use when they contained chloride; cf. text.

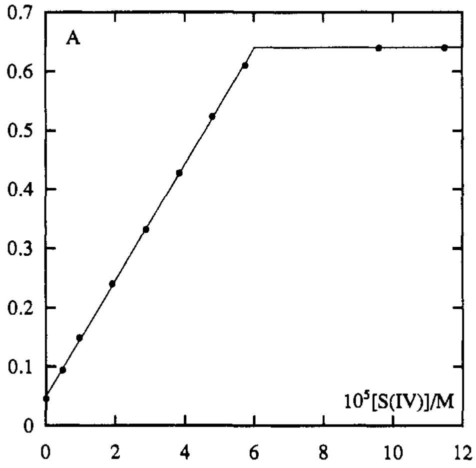

Figure 2. Absorbance at 255 nm for solutions with constant Pt(IV) and increasing S(IV) concentrations. Conditions: $[Pt(IV)] = 6.0 \times 10^{-5}$ M, $[HAc] = [Ac^-] = 0.1$ M, $[Cl^-] = 0.2$ M, $I = 1.0$ M and 25 °C. The lines represent the best fit to data obtained by linear regression analysis and an extrapolation of the absorbance obtained for excess S(IV), respectively.

measuring the absorbance of five different metal solutions for each complex, 3.2×10^{-5} M < $[Pt(CN)_4Cl_2^{2-}]$ < 6.4×10^{-4} M and 1.0×10^{-5} M < $[Pt(CN)_4^{2-}]$ < 1.0×10^{-4} M in the same ionic medium.

The reaction between $Pt(CN)_4Cl_2^{2-}$ and S(IV) can be written as eq 5 where x denotes the stoichiometric coefficient for the reaction and P the product of the oxidized S(IV) species. None

$$Pt(CN)_4Cl_2^{2-} + xHSO_3^- \rightarrow Pt(CN)_4^{2-} + 2Cl^- + P \quad (5)$$

of the possible final products, SO_4^{2-}/HSO_4^- or $S_2O_6^{2-}$, absorb at 255 nm. Equation 6 can then be derived from reaction 5. A/l

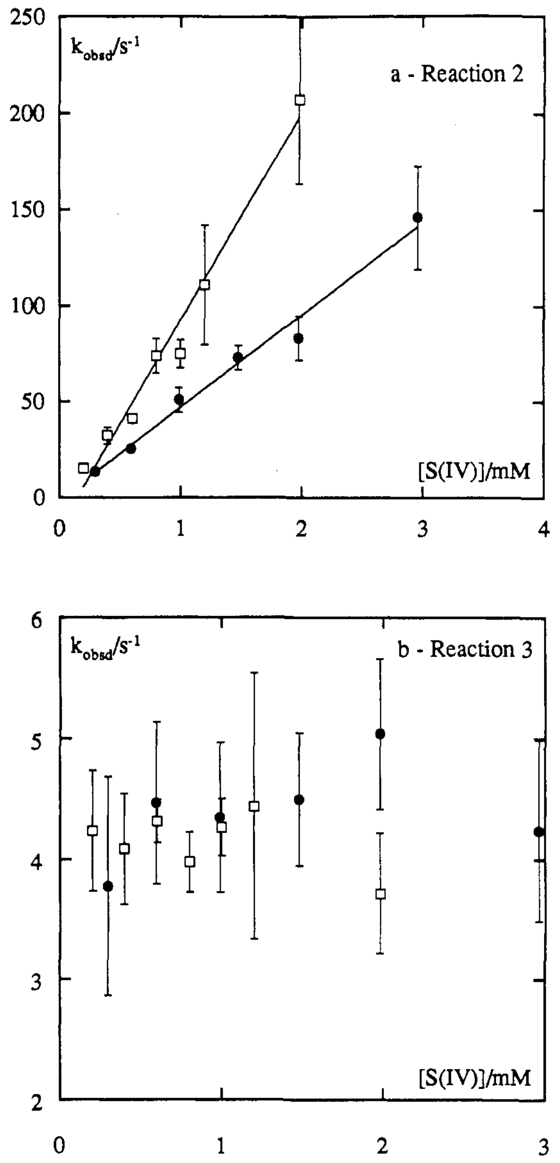

Figure 3. k_{obsd} as a function of [S(IV)] and $[H^+]$ for reactions 2 and 3. Conditions: $[Pt(IV)] = 2.0 \times 10^{-5}$ M, $I = 1.0$ M, $[H^+] = 10$ mM (open symbols) and 30 mM (filled symbols), and 25 °C. The errors are given as one standard deviation from at least seven measurements.

$$A/l = (\epsilon_{Pt(II)} - \epsilon_{Pt(IV)})[S(IV)]_0/x + \epsilon_{Pt(IV)}C_{Pt} \quad (6)$$

denotes the total absorptivity at 255 nm, $[S(IV)]_0$ the added sulfur(IV) concentration and $C_{Pt} = [Pt(CN)_4Cl_2^{2-}] + [Pt(CN)_4^{2-}]$. Using the molar absorptivities for $Pt(CN)_4Cl_2^{2-}$ and $Pt(CN)_4^{2-}$ determined as described above, a stoichiometric coefficient of 1.04 was calculated from the slope of the line in Figure 2. The overall process is therefore best represented by reaction 4 above.

Kinetics, Reactions 2 and 3. The reactions were studied between 245 and 255 nm where the absorbance changes are largest; cf. Figure 1b,c. The kinetics was normally evaluated as two consecutive first-order reactions with sulfur(IV) in at least 10-fold excess over platinum(IV). Reaction 2 is first order with respect to sulfur(IV) while the rate of reaction 3 is independent of the sulfur(IV) concentration, Figure 3. Therefore, at high sulfur(IV) concentrations, it was not feasible to sample enough data points for reaction 2 on a time scale appropriate also for reaction 3. In those cases the reactions were evaluated as first-order reactions by repeating the experiments using two different time bases. Reaction 2 was then complete in less than ca. 0.2 half-life of reaction 3. The rates were studied as a function of excess sulfur(IV) at $[HClO_4] = 10$ mM and 30 mM, Figure 3. The $[H^+]$ dependence was studied in the range 20 mM < $[H^+]$

Table 2. [H^+] Dependence of Reactions 2 and 3[a]

reaction	[H^+]/mM	k_{obsd}/s^{-1}	$10^{-3}\,k/M^{-1}\,s^{-1}$
2	10.0		108 ± 7[b]
	20.0	157 ± 12	79 ± 6
	30.0		48 ± 3[b]
	50.0	85 ± 8	43 ± 4
	75.0	40 ± 6	20 ± 3
	100	30 ± 3	15 ± 1
	300	11.0 ± 0.7	5.6 ± 0.4
	500	5.5 ± 1.1	2.8 ± 0.6
3	10.0	4.1 ± 0.2[c]	
	20.0	4.8 ± 0.3	
	30.0	4.4 ± 0.4[c]	
	50.0	4.7 ± 0.4	
	75.0	4.4 ± 0.3	
	100	4.5 ± 0.5	

[a] The errors are given as one standard deviation from at least seven measurements, except as noted in footnotes *b* and *c*. Conditions: [Pt(IV)] = 1.0×10^{-4} M, [S(IV)] = 1.97 mM, I = 1.0 M, and temperature 25 °C. [b] Results obtained from the slopes of Figure 3a. The errors are given as one standard deviation. [c] Mean values obtained from Figure 3b. The errors are given as one standard deviation.

< 0.95 M with [Pt(IV)] = 9.9×10^{-5} M, [S(IV)] = 1.97 mM, and I = 1.0 M, Table 2. Second-order rate constants obtained as slopes in the linear regression analysis of the data in Figure 3 are also included in Table 2.

The influence of ionic strength I on the rates of reactions 2 and 3 in the range 32.5 mM < I < 1.0 M was studied at constant concentrations of Pt(IV), S(IV), and $HClO_4$ (1×10^{-4} M, 1.46 mM, and 30 mM, respectively). A plot of the logarithm of the observed rate constant for reaction 2, versus $I^{1/2}/(1 + I^{1/2})$ according to eq 7 gives a good linear relation and the product of

$$\log k = \log k_0 + 2Z_aZ_b 0.509 I^{1/2}/(1 + I^{1/2}) \qquad (7)$$

the ionic charges of the reacting species Z_aZ_b = 2.07. The rate constant for reaction 3 is roughly independent of the ionic strength.

No influence of addition of $Pt(CN)_4^{2-}$ could be observed at 5 °C for reaction 2 using [Pt(IV)] = 1.0×10^{-4} M, [$Pt(CN)_4^{2-}$] < 4.0×10^{-5} M, [S(IV)] = 0.96 mM, and [H^+] = 10 mM. This was also true for reaction 3 studied at 25 °C using [Pt(IV)] = 1.95×10^{-4} M, [$Pt(CN)_4^{2-}$] < 1.0×10^{-4} M, [S(IV)] = 3.0 mM, and [H^+] = 30 mM.

The temperature dependence of the rate constants was studied at 5–40 °C and [Pt(IV)] = 1.95×10^{-4} M, [S(IV)] = 3.0 mM, and [H^+] = 30 mM. The enthalpies and entropies of activation given in Table 3 were calculated by use of the Eyring equation, fitted to the data. Good linear plots were obtained.

The volumes of activation for reactions 2 and 3 were determined from the pressure dependence of the observed rate constants. The reactions were followed under pseudo-first-order conditions at 251 and 245 nm respectively with sulfur(IV) in excess. The drive syringes of the high-pressure stopped-flow instrument were loaded with 3.9×10^{-4} M and 6.0 mM solutions of platinum(IV) and sulfur(IV), respectively, and the bomb was sealed and allowed to thermostat at 25 °C for approximately 20 min. The kinetics was followed as a function of pressure between 0.1 and 150 MPa. The ionic strength was 1.0 M and [H^+] = 30 mM. In Figure 4, the natural logarithm of the rate constants is plotted as a function of the applied pressure according to eq 8 where k_0 denotes the

$$\ln k = \ln k_0 - \Delta^{\ddagger} V_0 P/RT \qquad (8)$$

rate constant at ambient pressure, 0.1 MPa. The volumes of activation given in Table 3 were calculated from the slopes of these plots.

Kinetics, Reaction 4. Reaction 4 was followed by monitoring the increase in absorbance at 255 nm where $Pt(CN)_4^{2-}$ exhibits an absorbance maximum, cf. Figure 1d. Pseudo-first-order conditions were applied with sulfur(IV) in at least 10-fold excess. The first few data points of the kinetic traces are influenced by reactions 2 and 3 and were excluded. The rate was studied as a function of excess sulfur(IV) and $HClO_4$ at 25 °C and 1.0×10^{-5} M < [Pt(IV)] < 6.0×10^{-5} M, 2.0×10^{-4} M < [S(IV)] < 7.6×10^{-3} M and 10 mM < [H^+] < 0.5 M, Figure 5. The observed rate constants do not vary with the platinum(IV) concentration in the presence of excess S(IV). The pH dependence was further studied at constant [Pt(IV)] and [S(IV)] (1.95×10^{-5} M and 0.96 mM, respectively) and 5 mM < [H^+] < 50 mM. The second-order rate constants for the different [H^+] values are given in Table 4. The [S(IV)] dependence was also studied at pH 4.5 by use of an acetate buffer under the experimental conditions 2×10^{-5} M < [Pt(IV)] < 4×10^{-5} M, 0.19 mM < [S(IV)] < 18.8 mM, 0.1 or 0.2 M HAc/Ac^- adjusted to I = 1.0 M with $NaClO_4$, Figure 5. Addition of 1×10^{-5} M $Pt(CN)_4^{2-}$ had no significant influence on the rate of reaction using [Pt(IV)] = 2.0×10^{-5} M, [S(IV)] = 2.0 mM in 0.2 M acetate buffer, adjusted to I = 1.0 M with $NaClO_4$.

Oxygen Measurements. The influence of Pt(IV) on the oxidation of sulfur(IV) by dissolved oxygen was studied at pH 2. The concentration of dissolved oxygen during the course of reaction was monitored by use of the oxygen electrode. The reaction was initiated by adding 144 mL of a 2.0×10^{-5} M air-saturated Pt(IV) solution with [O_2] ≈ 2.5×10^{-4} M to an equal volume of a 2.2 mM air-saturated sulfur(IV) solution in a 300-mL BOD sample bottle. The bottle was shaken for a few seconds and the electrode was inserted into the solution, leaving no gas volume above the solution. There was only a small decrease in oxygen concentration after 30 min, attributed to the slow oxidation of sulfur(IV) by oxygen as shown by a blank experiment with the platinum(IV) solution replaced by ionic medium. Spectrophotometric measurements showed that the reduction of platinum (IV) was finished in less than 10 min under those conditions. In a third experiment, the platinum(IV) solution was replaced by a 2.7×10^{-5} M iron(III) solution. After ca. 9 min the dissolved oxygen was completely depleted, due to the iron-catalyzed oxidation of sulfur(IV) by oxygen.[32]

Discussion

The experiments summarized in Table 1 show that it is possible to suppress reactions 2 and 3 by adding chloride to the platinum(IV) solutions. Equilibrium 1 is then displaced to the left, $Pt(CN)_4Cl_2^{2-}$ is the only platinum(IV) species present, and reaction 4 is the only process observed. If $Pt(CN)_4Cl_2^{2-}$ is allowed to hydrolyze slowly, reactions 2 and 3 can also be observed. It is noteworthy that the occurrence of reactions 2 and 3 has no effect whatsoever on the observed rate of the redox reaction 4.

The proposed reaction mechanism is given in Scheme 1. $Pt(CN)_4ClOH^{2-}$ **II** reacts with HSO_3^-, forming the O-bonded sulfito complex **III**, which isomerizes to the S-bonded complex **IV**. The latter complex undergoes fast and quantitative internal electron transfer to $Pt(CN)_4^{2-}$ and HSO_4^-. This means that the reverse reaction 3 can be neglected and that the formation of $Pt(CN)_4^{2-}$ in this process does not disturb the much slower reaction 4. Reaction 3 with rate constant k_i is rate-determining for the formation of $Pt(CN)_4^{2-}$ in this reaction sequence. $Pt(CN)_4Cl_2^{2-}$, **I**, undergoes reductive elimination to the final products, $Pt(CN)_4^{2-}$ and HSO_4^- by two parallel reactions with HSO_3^- and SO_3^{2-}. The details of these reactions are discussed below.

HSO_3^- Addition Reaction 2. Substitution reactions of platinum(IV) complexes are catalyzed by platinum(II).[38,45] Reaction 2 is much faster than ordinary Pt(IV) substitutions and it is not accelerated by the addition of $Pt(CN)_4^{2-}$. Formation of a sulfito complex by an ordinary substitution process is therefore not likely. It is known that sulfito, selenito, and carbonato complexes can be formed by direct reactions between hydroxo or aqua complexes

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Table 3. Activation Parameters for Uptake (2, i, ii, iii) and Isomerization (3, iv, v) Reactions of Various Aqua/Hydroxo Transition-Metal Complexes with HSO_3^-, $HSeO_3^-$, and CO_2

reaction	complex	reactant	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}	ΔV^*/cm^3 mol^{-1}	ref
2	$Pt(CN)_4ClOH^{2-}$	HSO_3^-	44 ± 3	−7.5 ± 0.4	−9.4 ± 0.4	this work[a]
i	$Pt(NH_3)_5OH^{3+}$	HSO_3^-	54.3 ± 5	−10 ± 16		22
ii	$Co(NH_3)_5OH_2^{3+}$	$HSeO_3^-$	56 ± 2	−38 ± 4		42
iii	$Co(NH_3)_5OH^{2+}$	CO_2	64 ± 4	15 ± 13		43
3	$O_2SO{-}Pt(CN)_4Cl^{3-}$ [b]		74.4 ± 0.5	16.6 ± 0.1	5.3 ± 0.4	this work[a]
iv	$O_2SO{-}Pt(NH_3)_5^+$ [b]		15 ± 2	−256 ± 7		22
v	$O_2SO{-}Co(tetren)^+$ [b]		56 ± 4	−124 ± 13		4

[a] The errors are given as standard deviations obtained from linear least-squares analyses. Conditions: $[Pt(IV)] = 2.0 \times 10^{-5}$ M, $[S(IV)] = 3.0$ mM, $I = 1.0$ M. [b] O → S isomerization.

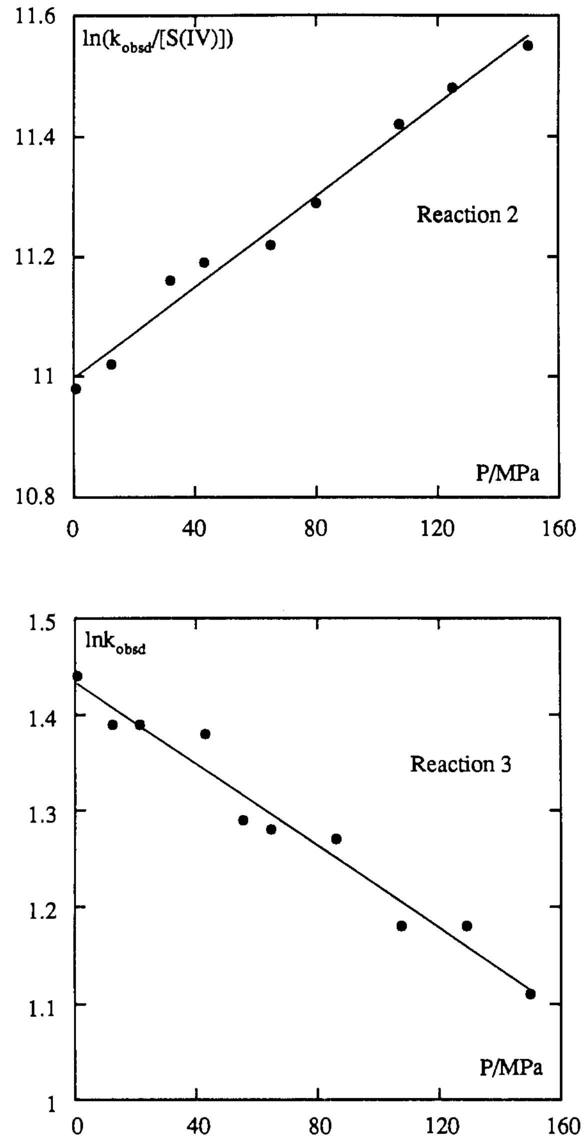

Figure 4. Pressure dependence of reactions 2 and 3. Conditions: $[Pt(IV)] = 2.0 \times 10^{-4}$ M, $[S(IV)] = 3.0$ mM, $[H^+] = 30$ mM, $I = 1.0$ M, and 25 °C.

and dissolved $SO_2(aq)$, $CO_2(aq)$, or $HSeO_3^-$ without breakage of the metal–oxo bond.[1-12,22,46,47] A similar mechanism is probably operating here. The rate of reaction 2 increases with increasing pH and the ionic strength dependence indicates that the reactive species have −2 and −1 charges. These results are in accordance with a process in which $Pt(CN)_4ClOH^{2-}$ and HSO_3^- react to form a sulfito complex without breakage of the Pt–O bond. Reaction 2 is first-order with respect to sulfur(IV) without any

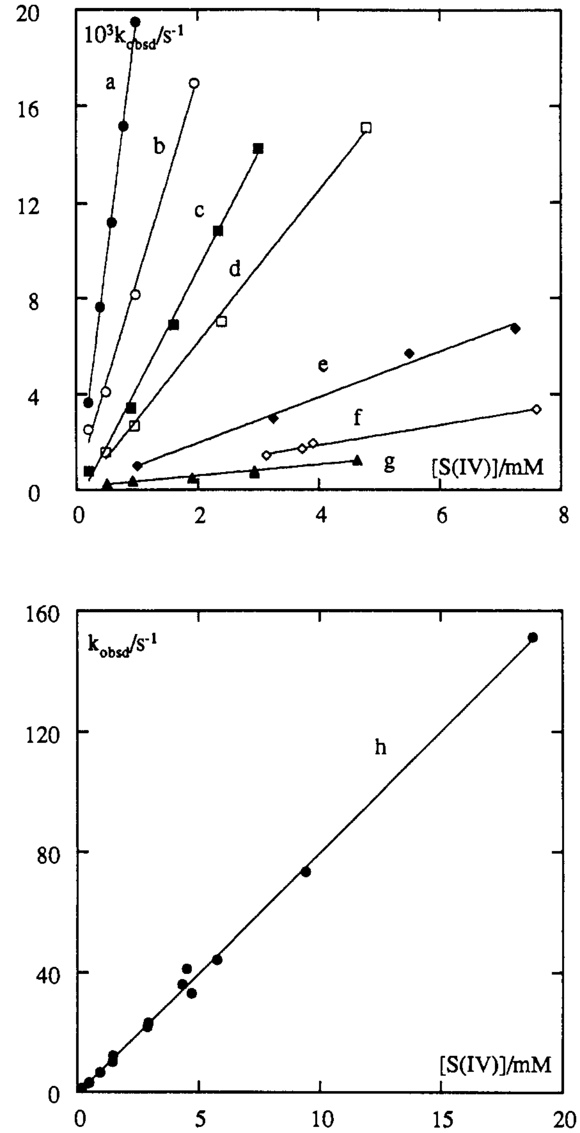

Figure 5. k_{obsd} as a function of [S(IV)] and $[H^+]$ for redox reaction 4. Conditions: $1.0 \times 10^{-5} < [Pt(IV)] < 6.0 \times 10^{-5}$ M, $I = 1.0$ M, and 25 °C. Key: $[H^+] = 10$ mM (a), 20 mM (b), 30 mM (c), 50 mM (d), 0.10 M (e), 0.32 M (f), 0.50 M (g), and [Hac] = [Ac] = 0.1 M and 0.2 M; pH ≈ 4.55 (h).

observable intercept; cf. Figure 3a. This means that the reverse of reaction 2 can be neglected, i.e. the equilibrium of eq 2 is displaced to the right. We then arrive at the rate law of eq 9

$$-d[Pt(CN)_4ClOH^{2-}]/dt = k_{obsd}[Pt(IV)]' \qquad (9a)$$

$$k_{obsd} = k_u[S(IV)]K_aK_{a1}/\{(K_a + [H^+])(K_{a1} + [H^+])\} \qquad (9b)$$

where the total concentration of hydrolyzed $Pt(CN)_4Cl_2^{2-}$ is denoted $[Pt(IV)]' = [Pt(CN)_4ClOH_2^-] + [Pt(CN)_2ClOH^{2-}]$ and the total concentration of sulfur(IV) is $[S(IV)] = [SO_2{\cdot}nH_2O]$

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Table 4. [H$^+$] Dependence of the Redox Reaction 4

[H$^+$]/mM	$10^3 k_{obsd}$/s^{-1}	k/M^{-1} s^{-1}
5.0	41 ± 1	43 ± 1[a]
10.0		20.1 ± 0.4[b]
15.0	9.9 ± 0.3	10.3 ± 0.3[a]
20.0		8.4 ± 0.4[b]
25.0	5.4 ± 0.3	5.6 ± 0.3[a]
30.0		4.9 ± 0.2[b]
40.0	3.6 ± 0.4	3.7 ± 0.4[a]
50.0		3.2 ± 0.1[b]
100		0.95 ± 0.07[b]
316		0.42 ± 0.03[b]
500		0.24 ± 0.02[b]

[a] The errors are given as one standard deviation from three to nine measurements. Conditions: [Pt(IV)] = 1.95 × 10^{-5} M, [S(IV)] = 0.96 mM, I = 1.0 M, and temperature = 25 °C. [b] The second-order rate constants are obtained from the slopes in Figure 5. The errors are given as one standard deviation. Conditions: cf. Figure 5.

+ [HSO_3^-] + [SO_3^{2-}]. In Figure 6, the second-order rate constant, k_{obsd}/[S(IV)], has been plotted as a function of [H$^+$]. The fit of eq 9b to the curve by use of a nonlinear least-squares regression analysis using K_{a1} = 0.043[42] and K_a = 0.040[38] is excellent and gives k_u = (1.68 ± 0.05) × 10^5 M^{-1} s^{-1}. This value is almost 300 times larger than that reported for the reaction between $Pt(NH_3)_5OH^{3+}$ and HSO_3^-, 590 M^{-1} s^{-1}.[22] Harris et al.[10] have also determined the rate constant for addition of HSO_3^- to $Cr(NH_3)_5OH_2^{3+}$ to 5 M^{-1} s^{-1}. Fowless and Stranks[47] have found rate constants of a similar order of magnitude (147 and 281 M^{-1} s^{-1}) for the reaction between $HSeO_3^-$ and $Co(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$, whereas the corresponding hydroxo complexes reacted more slowly with rate constants of 8 and 4 M^{-1} s^{-1}, respectively.

Harris et al. have previously pointed out[22] that the activation parameters for reactions i–iii listed in Table 3 all fall in a narrow range. The oxygen-bonded complexes are all formed by addition of the incoming ligand to the aqua or hydroxo ligands of the metal centers. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for reaction 2 given in Table 3 are similar to the other values which further supports a common mechanism. The volume and entropy of activation for reaction 2 are both negative. Formation of the sulfito complex in this case does not involve breakage of the Pt–O bond, and the activation parameters cannot be interpreted in conventional dissociative/associative terms. Since the hydrogen sulfite ligand is incorporated into the inner coordination sphere of the complex, it seems reasonable that both the volume and entropy of activation should decrease in the activation process, as observed.

Wilmarth and co-workers[23] studied the reactions between *trans*-$Pt(CN)_4Br(H_2O)^-$ and *trans*-$Pt(CN)_4Br(OH)^{2-}$ and several reducing anions, among them SO_3^{2-}. They suggested a mechanism involving an attack by the nucleophiles on coordinated bromide followed by two-electron transfer to the metal center and Br$^+$ transfer to the incoming ligand. In the particular case of SO_3^{2-}, however, a rapid uptake reaction by the hydroxo complex followed by intramolecular isomerization to a sulfur-bonded complex and inner-sphere two-electron transfer similar to our reactions 2 and 3 is an equally probable mechanism that might also fit to their experimental results. On the other hand, it will be difficult to rationalize the fast processes 2 and 3 observed in the present study by a mechanism of the type proposed by Wilmarth et al.,[23] mainly because the reaction product $ClSO_3^-$ is hydrolyzed in a first-order process independent of pH in the pH interval 3.5–9 with a rate constant of 294 s^{-1} at 25 °C[48] which is ca. 120 times faster than the first-order rate constant determined by us for reaction 3, as discussed below.

O–S Isomerization Reaction 3. The rate of reaction 3 is independent of both S(IV) concentration, ionic strength, and pH. This is in accordance with an intramolecular isomerization from an O-bonded to a S-bonded sulfito complex. Platinum(IV) is a soft metal center, and binding to sulfur is preferred. A thermodynamic driving force for the O-bonded complex to isomerize to a more stable S-bonded sulfito isomer is expected. The isomerization rate constant k_i is (4.5 ± 0.2) s^{-1} as calculated from the data in Table 2. Again, this rate constant is much larger, ca. 10^4 times, than the rate constants reported for isomerization of $Co(tetren)(OSO_2)^+$,[4] $Pt(NH_3)_5(OSO_2)^+$,[22] and $Cr(OH_2)_5(OSO_2)^+$,[10] which are 2.7 × 10^{-4}, 5.6 × 10^{-4}, and 1.98 × 10^{-4} s^{-1}, respectively.

Both the volume and the entropy of activation are positive for the isomerization of $O_2SO{-}Pt(CN)_4Cl^{3-}$, cf. Table 3. This might indicate that the isomerization in this case takes place through an intramolecular rearrangement, via a loosely bound transition state in which the Pt–O bond is weakened before a new Pt–S bond is formed. This is expected to give an increase of molar volume and a disorder in the activation process. On the other hand, Harris et al. found negative entropies of activation for the O → S isomerization of $Co(tetren)OSO_2^+$ and $Pt(NH_3)_5OSO_2^{2+}$; cf. Table 3.[4,22] In the case of $Co(tetren)OSO_2^+$, the large negative value was rationalized in terms of an internal S_N2 process.

Redox Process 4. Reduction of platinum(IV) according to reaction 4 was followed with [S(IV)] ≫ [Pt(IV)] by monitoring the increase in absorbance at 255 nm due to formation of $Pt(CN)_4^{2-}$. Formation of $Pt(CN)_4^{2-}$ through the pathway described by reactions 2 and 3 is rapid and does not disturb the observation of reaction 4.

The evaluation according to first-order-kinetics gives perfect fits and the observed rate constants do not vary with the platinum(IV) concentration in the presence of excess sulfur(IV). Furthermore, the rate constant is proportional to the sulfur(IV) concentration, cf. Figure 5, and independent of the chloride concentration, cf. Table 1. The mechanism depicted in Scheme 1 gives the rate law of eq 10.

$$d[Pt(CN)_4^{2-}]/dt = k_{obsd}[Pt(CN)_4Cl_2^-] \qquad (10a)$$

$$k_{obsd} = \frac{[S(IV)K_{a1}]}{[H^+] + K_{a1}}(k_1 + k_2K_{a2}/[H^+]) \qquad (10b)$$

Thus, $k_{obsd}([H^+] + K_{a1})/([S(IV)]K_{a1})$ should be a linear function of 1/[H$^+$]. A fairly good straight line with an intercept k_1 = 1.3 ± 0.5 M^{-1} s^{-1} and a slope k_2K_{a2} = 0.228 ± 0.007 s^{-1} is obtained by use of the data for the [H$^+$] dependence given in Table 4. By use of the literature value[42] pK_a = 6.3, a value of k_2 = 4.5 ± 0.1 × 10^5 M^{-1} s^{-1} can be calculated. From Figure 5h, $k_2 \approx 4.5 \times 10^5$ M^{-1} s^{-1} can be calculated which is in good agreement with the value obtained in more acidic solutions.

Mechanisms for reductive eliminations and ligand assisted- or platinum(II)-accelerated substitutions at platinum(IV) centers have been the subject of some controversy and extensive studies in previous literature, cf. Drougge and Elding[38] and references therein. In all those reactions, partial charge displacement according to eq 11 or complete electron transfer to platinum(II) according to eq 12, ionic charges omitted, is accomplished through

$$Y + Z{-}Pt(IV){-}X \rightarrow Y{\cdots}Z{-}Pt(IV){-}X \qquad (11)$$

$$Y + Z{-}Pt(IV){-}X \rightarrow YZ + Pt(II) + X \qquad (12)$$

an attack on one of the halide ligands Z of the platinum(IV) complex by the reductant Y.[38] Reduction of gold(III) complexes by for instance halide, thiocyanate, sulfite, and platinum(II) takes place according to similar mechanisms.[27,49–52] Equations 11 and

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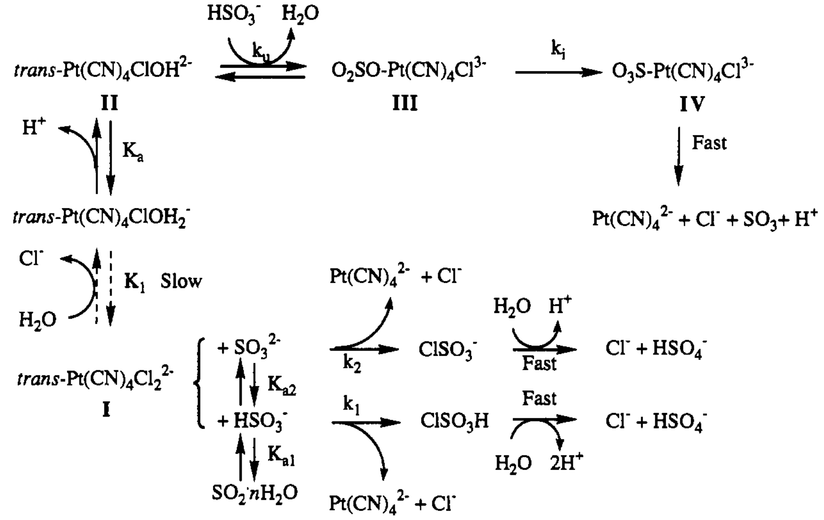
Scheme 1. Proposed Mechanism for Reactions 2–4



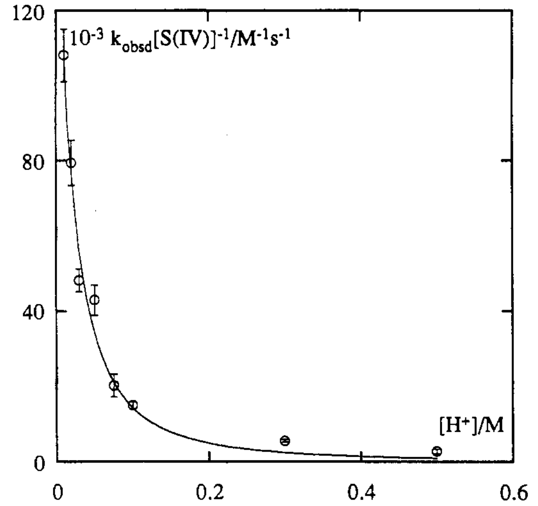
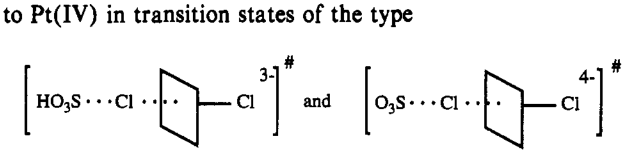


Figure 6. The second-order rate constant of reaction 2 as a function of $[H^+]$. Conditions: cf. Figure 3 and Table 2. The curve represents the best fit of eq 9 obtained by a nonlinear regression analysis to the experimental data. The errors are given as one standard deviation from at least seven measurements.

12 are formally equivalent to two-electron transfer to the metal center followed by transfer of Z^+ to the incoming reductant as suggested by Wilmarth et al.[23]

In analogy with those previous results, the present reduction of *trans*-$Pt(CN)_4Cl_2^{2-}$ by HSO_3^- and SO_3^{2-} is suggested to occur by an attack of HSO_3^- or SO_3^{2-} on a chloride ligand of the complex, followed by chloride bridged two-electron transfer from S(IV) to Pt(IV) in transition states of the type



The chlorosulfuric acid and chlorosulfate(VI) formed as reaction products react rapidly with solvent water, giving Cl^- and HSO_4^- as the final products.[48,53] This mechanism is analogous to that proposed by Wilmarth and co-workers[23] for the reactions between several reducing anions and *trans*-$Pt(CN)_4Br(H_2O)^-$ and *trans*-$Pt(CN)_4Br(OH)^{2-}$, although we favor an electron transfer mediated by chloride instead of Cl^+ transfer. In the present case, the mechanism works also for sulfite as reductant, since the substrate complex does not contain coordinated hydroxide or aqua ligands, suitable for rapid uptake reactions; cf. discussion above. An alternative mechanism involving interaction between the cyanide ligands of the $Pt(CN)_4$ moiety and sulfite, as suggested by Lancaster and Murray[17,18] for $Fe(CN)_5(CNSO_3)^{5-}$, seems much less likely.

Photoinduced oxidation of S(IV) by dissolved oxygen in aqueous solution takes place as a free-radical chain reaction and is very effective.[54] The chain is initiated by generation of sulfite radicals and is propagated by SO_3^-, SO_4^-, and SO_5^- radicals. According to present knowledge, metal-ion catalyzed autoxidation takes place by a similar mechanism in which reaction between a trivalent metal ion, M, and sulfur(IV) initiates the autoxidation, reaction 13.[30–32] Consequently, formation of the SO_3^- radical is the trigger

$$M(III) + HSO_3^- \rightarrow M(II) + SO_3^- + H^+ \qquad (13)$$

of the autoxidation in both systems. The present measurements indicate that Pt(IV) does not initiate such free-radical autoxidation of sulfur(IV), since the concentration of dissolved oxygen remains practically constant for a long period of time after the reduction of Pt(IV). According to the mechanism depicted in Scheme 1, this should be expected since electron transfer is completed within the solvent cage and no radical species are released into the bulk solution.

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Supplementary Material Available: Pseudo-first-order rate constants as a function of ionic strength, temperature, and pressure for reactions 2 and 3, Tables S1–3, respectively (3 pages). Ordering information is given on any current masthead page.

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