Table I. Infrared Data (cm^{-1}) for π-Bonded Cyclopentadienylchromium Aquo and Chloro Complexes

$[(\eta^5\text{-}C_5H_5)Cr(OH_2)_n](BF_4)_2$	$NH_4[C_5H_5CrCl_3]$	range for $(\eta^5\text{-}C_5H_5)M^a$
3100	3157	(C-H) 3115-3012
1432	1405	(C-C) 1447-1400
$1090^{b,c}$	1114	(C-H) 1126-1097
	1010	(C-H) 1017-998
838	851	(C-H) 850-712
	839	
	813	

[a] H. P. Fritz, *Chem. Ber.*, 92, 780 (1959). [b] Broad, asymmetric. [c] BF_4^- has a broad band at 1100 cm^{-1}.

cm^{-1}, which are obscured by broad BF_4^- absorption in the aquo complex. We take the infrared data as good evidence that the C_5H_5 ligand is π-bonded in both chloro and aquo complexes; furthermore, the close similarity in UV-vis spectra is evidence that there are three ligands in the coordination sphere of each complex. The solid obtained by lyophilizing HBF_4 solutions gives a low value for percentage of oxygen in the complex, and we suspect that decomposition of the BF_4^- anion has taken place in concentrated acidic medium leading to formation of fluoride ion, which can replace water.

Preliminary experiments on the rates of reactions of the aquo complex have been performed. On standing under nitrogen at room temperature, a light-sensitive, violet solution of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion gradually becomes turbid and its color changes from violet to bluish gray. Finally a dark brown precipitate separates, and the solution exhibits the UV-vis spectrum of $Cr(OH_2)_6^{3+}$ ion. The first turbidity is apparent to the eye after 1 h, but fluctuating spectrophotometric readings occur before this. In several experiments freshly prepared solutions of the aquo complex were filtered under dinitrogen to remove the polymeric cyclopentadiene and then placed in jacketed spectrophotometric cells (25 °C). Repetitive visible spectra were then taken. Isobestic points, which persisted for about 25 min, were observed at 524 and 342 nm. Approximate values of rate constants were obtained by applying the Guggenheim method[6] to absorbance vs. time data measured before the loss of the isobestic points. A value of 1×10^{-2} s^{-1} for the replacement of the cyclopentadiene ligand was obtained (25 °C, 6 M $HClO_4$). In the other experiments, freshly prepared solutions of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion in 6 M$HClO_4$ were mixed with solutions (I = 6.0 M) that contained chloride ion. When the final solution had a high concentration of chloride ion, (5 M), a rapid color change from violet to blue was noted, and the UV-vis spectrum 5 min after mixing was very similar to that of $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion. In other experiments, freshly prepared solutions of the aquo complex were first filtered to remove polymeric cyclopentadiene and then absorbancies were measured at several wavelengths so that the concentration of the complex could be estimated. A solution that contained HCl and $HClO_4$ (I = 6.0 M) was then prepared so that on mixing, the final solution would contain equal concentrations of the aquo complex and chloride ion. In one typical experiment, the final concentrations were 3.5×10^{-3} M. Even under these low concentration conditions the spectral changes were too rapid to allow accurate determination of rate constants. The UV-vis spectrum 5 min after mixing exhibited maxima at 567 and 430 nm. This represents a red shift of 17 nm for the low-energy maximum and 5 nm for the higher energy and is consistent with the replacement of water by chloride ion in the inner coordination sphere of chromium. It is reasonable to assume that under low concentration conditions the reaction is

$$(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+} + Cl^- \rightarrow (\eta^5\text{-}C_5H_5)Cr(OH_2)_2Cl^+ + H_2O$$

From the data we have obtained, a reasonable lower limit for the second-order rate constant for this reaction is 10 M^{-1} s^{-1} (T = 25 °C, I = 6.0 M, $[H^+]$ = 6.0 M). This value is much larger than rate constants for substitution reactions in classical chromium(III) coordination complexes.

Further kinetic studies on reactions of the $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion are planned, and a stopped-flow apparatus is under construction.

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Registry No. $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_3](BF_4)_2$, 78764-13-3; $NH_4[(\eta^5\text{-}C_5H_5)CrCl_3]$, 78764-14-4; $(\eta^5\text{-}C_5H_5)_2Cr$, 1271-24-5; Cl^-, 16887-00-6.

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(6) E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926).

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Formation and Decomposition of Thiosulfate in the Ferrous Sulfide-Sulfur Dioxide Reaction

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In a series of recent publications, Thom et al.[1-4] proposed a mechanism for the formation of elemental sulfur during the reaction of FeS with aqueous solutions of SO_2 which can be represented by the overall equation (1). In this mechanism,

$$FeS + 2SO_2(aq) \rightarrow FeSO_4 + {}^1/_4S_8 \qquad (1)$$

these authors proposed that SO_2 is first adsorbed on the FeS surface, which subsequently results in the formation of ferrous iron and thiosulfurous acid as shown in eq 2 and 3. This acid

$$FeS + SO_2(aq) \rightarrow FeS{\cdot}SO_2(ads) \rightarrow Fe^{2+} + S_2O_2^{2-} \qquad (2)$$

$$S_2O_2^{2-} + 2H^+ \rightarrow H_2S_2O_2 \qquad (3)$$

then reacts with HSO_3^- to form thiosulfate which then reacts with the sulfoxylate anion to form disulfanedissulfonic acid (eq 4 and 5). Through a series of consequetive reactions,

$$H_2S_2O_2 + HSO_3^- \rightarrow H_2S_2O_3 + HSO_2^- \qquad (4)$$

$$H_2S_2O_3 + HSO_2^- \rightarrow HO_3SS{\cdot}SOH + OH^- \qquad (5)$$

finally elemental sulfur is formed according to eq 6.

$$HS_8{\cdot}SO_3^- \rightarrow S_8 + HSO_3^- \qquad (6)$$

The authors studied this reaction by adding FeS or other sulfide to a solution of Na_2SO_3 in a closed vessel and then by acidifying by HCl to generate SO_2 which then attacks the sulfide. The reaction was monitored by recording the change in pressure and analyzing samples periodically for Fe^{2+},$S_2O_3^{2-}$ ions. The experimental conditions, however, are ill-defined because, depending on the amount of HCl added, the following species will all be present: SO_3^{2-}, HSO_3^-, and SO_2. In all tests,

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(1) G. C. Thom, Thesis, The American University, Washington, 1977; *Diss. Abstr. Int. B*, **38**, 1239-B (1977).

(2) G. C. Thom, P. F. Waters, and A. F. Hadermann, *Inorg. Chem.*, **17**, 1693 (1978).

(3) G. C. Thom, P. F. Waters, A. F. Hadermann, *Hydrometallurgy*, **3**, 373 (1978).

(4) G. C. Thom and P. F. Water, paper presented at the 144th National Meeting of the American Association for the Advancement of Science, Washington, D. C., Feb 1978.

SO_2 pressure increased gradually to a certain value then decreased and finally remained constant. While the metal ion formed immediately after HCl was added, it took about 50 min for $S_2O_3^{2-}$ to form. Further, the start of formation of $S_2O_3^{2-}$ coincided with the maximum pressure of SO_2 thus indicating that the decrease in SO_2 pressure is related to the formation of $S_2O_3^{2-}$ ion.

The authors went further and suggested a general mechanism for the aqueous oxidation of sulfides by other oxidizing agents,[3,4] e.g., O_2 which can be represented by the overall equation (7), where M is a divalent metal. According to these

$$MS + 2H^+ + {}^1/_2O_2 \rightarrow M^{2+} + {}^1/_8S_8 + H_2O \qquad (7)$$

authors reaction 7 takes place along the steps shown in eq 8–10, which are then followed by eq 5 and 6, i.e., elemental

$$MS + O_2 + H^+ \rightarrow M^{2+} + H_2SO_2 \qquad (8)$$

$$M^{2+} + H_2SO_2 \xrightarrow{MS} M^{2+} + H_2S_2O_2(?) \qquad (9)$$

$$H_2S_2O_2 + {}^1/_2O_2 \rightarrow H_2S_2O_3 \qquad (10)$$

sulfur is formed as a result of the decomposition of thiosulfuric acid. However, the authors did not present data for $S_2O_3^{2-}$ content when O_2 is used as an oxidizing agent; they simply extrapolated from their work on the reaction of FeS with aqueous SO_2.

Unfortunately, these authors are unaware of the extensive literature available regarding the mechanism of the aqueous oxidation of sulfides.[5] When applied for the reaction in question, it can be represented by an oxidation–reduction couple as shown in eq 11 and 12, or in general when O_2 is used

$$FeS \rightarrow Fe^{2+} + {}^1/_8S_8 + 2e^- \qquad (11)$$

$$2SO_3^{2-} + 3H_2O + 4e^- \rightarrow S_2O_3^{2-} + 6OH^- \qquad (12)$$

as an oxidizing agent, eq 13 and 14 represent the reaction.

$$MS \rightarrow M^{2+} + {}^1/_8S_8 + 2e^- \qquad (13)$$

$${}^1/_2O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (14)$$

This mechanism stipulates that the dissolution of sulfides is a galvanic process like the corrosion of a metal. Certain regions of the sulfide act as anodic zones (eq 13) while other regions act as cathodic zones (eq 14). Electrons from the anode are transported to the cathode in the solid phase which is a semiconductor. This view was supported by numerous experiments. For example:

(1) Kinetic studies showed that the rate of dissolution of sulfides follows the same law like the corrosion of metals.[5]

(2) Direct experiments on sulfides immersed in a solution solidified by agar showed that cathodic regions are formed on that part of sulfide more accessible to oxygen.[6]

(3) The behavior of two sulfides in contact is not the same as each independently because of galvanic currents.[7,8]

(4) The behavior of a sulfide in contact with a metal powder is not the same as each independently, again, because of galvanic currents.[9]

(5) When a external EMF is imposed on a sulfide immersed in an aqueous solution, the sulfide dissolves according to $MS \rightarrow M^{2+} + {}^1/_8S_8 + 2e^-$. Elemental sulfur remains adhering on the surface of the anode. If it were formed by decomposition of thiosulfuric acid, it should have formed as a fine powder suspended in solution.[10]

(6) Recent tests have shown that even when aqueous oxidation is conducted in ammoniacal medium, elemental sulfur is first formed and could be isolated before it oxidizes further to sulfate via numerous intermediate products. This was achieved by adding an organic solvent for sulfur to separate it as soon as it is formed.[11]

The formation thiosulfate ion reported by Thom et al. is actually due to the reaction between elemental sulfur and sulfite ion.

$$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$$

The sulfite ion is present in the original reaction mixture which was acidified by HCl to form SO_2. The reaction between HCl and Na_2SO_3 does not seem to be a very fast reaction. The curves presented by these authors showing the formation of $S_2O_3^{2-}$ point to the above reaction. Thus at 58.3 °C, $S_2O_3^{2-}$ appeared in solution after 50 min, and when the SO_2 reached its maximum value of about 7 psig, while at 71.9 °C, $S_2O_3^{2-}$ appeared after 45 min; it also appeared when the SO_2 reached its maximum value of about 9 psig. It is evident that the formation of thiosulfate is a secondary reaction which takes place when the SO_2 used is prepared by acidifying sodium sulfite solution to which the solid sulfide is added; i.e., elemental sulfur originally formed at the FeS surface reacts further with SO_3^{2-} in solution at high temperature and pressure to form thiosulfate.

Thom et al. therefore did not contribute to the mechanism of aqueous oxidation of sulfides; they just studied the rate of dissolution of elemental sulfur in sodium sulfite to form sodium thiosulfate. They also studied the rate of reverse reaction when the solution was filtered off the reaction mixture. Their proposed mechanism that thiosulfate ion is responsible for the liberation of elemental sulfur during the aqueous oxidation of sulfides is unfounded.

Registry No. $S_2O_3^{2-}$, 14383-50-7; FeS, 1317-37-9; SO_2, 7446-09-5.

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(6) Thornber, *Chem. Geol.*, **15**, 1–14 (1975); *Chem. Geol.*, **15**, 117–144 (1975).

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