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The Kinetics of the Silver(i)-induced Oxidation of Chromium(iii) by Peroxodisulphate

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ABSTRACT

Chromium(III) and chromium(VI) compounds play an important role in natural oxidation processes in terrestrial and atmospheric water. During the oxidation of SO_2, peroxodisulphate is formed as an intermediate. In acidic and neutral solutions, peroxodisulphate oxidizes chromium(III) very slowly. This reaction rate is markedly enhanced by silver ions, resulting in a reaction rate that allows the reaction to be studied conveniently under laboratory conditions. The kinetics of the Cr(III)/Ag(I)/$S_2O_8^{2-}$ reaction system were studied as a function of different Cr(III), Ag(I) and $S_2O_8^{2-}$ concentrations, temperature and pressure. The formation of Cr(VI) was observed as a first-order process at high [Cr(III)] and as a zero-order process at low [Cr(III)]. An induction period was observed in both cases. For the first-order process, reaction rates were found to be independent of [Cr(III)], linearly dependent on [Ag^+] and independent of [$S_2O_8^{2-}$]. The activation enthalpy ($\Delta H^{\neq}$) was calculated as 56 ± 5 kJ mol^{-1}, the activation entropy ($\Delta S^{\neq}$) as –136 ± 16 J K^{-1} mol^{-1} and the activation volume as –5.8 ± 0.7 cm^3 mol^{-1}. At low [Cr(III)], the reaction rate was independent of [Cr(III)], linearly dependent on [$S_2O_8^{2-}$] and non-linearly dependent on [Ag^+], reaching a limiting value at high [Ag^+]. The activation enthalpy ($\Delta H^{\neq}$) was calculated as 61 ± 5 kJ mol^{-1}, the activation entropy ($\Delta S^{\neq}$) as –119 ± 15 J K^{-1} mol^{-1} and the activation volume as –1.7 ± 0.1 cm^3 mol^{-1}. A mechanism involving the reversible formation of a silver-peroxodisulphate complex that decomposes into oxidizing intermediates is proposed. The empirical observations can be adequately described by this mechanism.

KEYWORDS

Chromium(III), peroxodisulphate, oxidation, silver.

1. Introduction

Owing to the potential environmental risks associated with the contamination of the environment by hexavalent chromium, it is an area of major concern.[1] Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments and paper and pulp production. The chemistry of chromium tailings from these industries in the environment is rather complex and not fully quantified.[2,3]

It is estimated that South Africa holds about 72% of the world's chromium reserves and is currently one of the largest chromate and ferrochromium, as well as stainless steel producing countries in the world.[4] Mining of chromium unavoidably generates fine particles. This is particularly true for chromite mining in South Africa, where 80% of the ores can be classified as friable.[5] Although chromium has found many useful applications, the impact of the chromium industry on the environment and human health can be extensive and is not fully quantified. Chromium is one of a few elements that can exist in six different positive oxidation states. Kinetic studies involving the oxidation or reduction of chromium compounds are therefore complicated. Industrial effluents and waste are likely to contain only trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), because divalent chromium, Cr(II), is unstable and rapidly oxidizes to Cr(III). Elemental chromium, Cr(0), is also oxidized easily by many natural oxidizing agents like oxygen to Cr(III) unless it is made inactive by superficial oxidation. Hexavalent chromium is considered toxic and a well-established carcinogen, whereas trivalent chromium is a trace nutrient for humans and animals alike.[6–8] It is therefore of environmental importance to increase knowledge on the fate of chromium emissions from industry.

During the metal-catalysed oxidation of SO_2, peroxodisulphate, $S_2O_8^{2-}$, is formed as an intermediate.[9] In acidic and neutral solutions, peroxodisulphate can be used as an oxidant. It is a strong oxidizing agent that decomposes slowly in aqueous solution, resulting in the formation of sulphate radicals, SO_4^{-}. For many reducing agents, oxidation by $S_2O_8^{2-}$ does not proceed at a measurable rate at 25°C, unless a catalyst is present. The reaction rate is markedly enhanced by silver ions, resulting in a reaction rate that enables the reaction to be studied conveniently in the laboratory.[10] The oxidation of Cr(III) by $S_2O_8^{2-}$/Ag(I) has been studied by Yost[11], who reported a relatively fast oxidation of Cr(III) under normal atmospheric conditions.

In this study, we report the detailed kinetics of the oxidation of Cr(III) by $S_2O_8^{2-}$/Ag(I) under relatively mild conditions and determine for the first time the pressure dependence of the reaction. The reaction was studied over a wider range of [Cr(III)], [$S_2O_8^{2-}$] and [Ag(I)], as well as over a longer time scale than before.[11] This proved to reveal vital new mechanistic information for the process.

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2. Materials and Methods

2.1. Materials

Analytical grade reagents with the highest purity level were obtained from different suppliers and used without any further purification. Potassium peroxodisulphate ($K_2S_2O_8$) (Merck), chromium(III) sulphate ($Cr_2(SO_4)_3.6H_2O$) (Merck), silver nitrate ($AgNO_3$) (Aldrich) and sodium perchlorate ($NaClO_4.H_2O$) were used. The pH of reactant solutions was adjusted prior to mixing with stock solutions of sodium hydroxide (NaOH) (SMM) and/or perchloric acid ($HClO_4$) (Merck).

2.2. Methods

A variety of analytical methods can be employed to determine the chromium concentration in aqueous solution.[12] Owing to its relative ease of use and the fact that concentration changes can be monitored as they occur, a direct photometric absorption measurement method was chosen as the standard procedure to monitor the aqueous concentration of Cr(VI). All kinetic experiments were carried out using a Varian Cary 50 Conc UV spectrophotometer, and high pressure experiments were performed using a Shimadzu 2101 UV spectrophotometer. The temperature of all reactant mixtures was kept constant at 40.0 ± 0.1°C. The pH of the various reactants and reaction mixtures was measured with a Metrohm 744 pH meter, fitted with a glass-calomel combination electrode. The KCl solution in the salt bridge was replaced with a corresponding NaCl solution to prevent precipitation of $KClO_4$ in the salt bridge. The pH meter was calibrated daily with standard buffer solutions (pH 4.0, 7.0 and 10.0).

Results and Discussion

3.1. Characteristics of the Cr(III)/$S_2O_8^{2-}$/Ag(I) Reaction System

The Cr(III)/$S_2O_8^{2-}$/Ag(I) reaction system was monitored by following absorbance changes at different wavelengths in the pH range 2 to 5. Typical spectral changes observed during this reaction are shown in Fig. 1.

The UV/visible spectrum for the formation of Cr(VI) shows an absorption band at 350 nm and a shoulder at 440 nm. An isosbestic point at 540 nm is also observed during the reaction followed by a drift after longer reaction times. During this study, the reaction was monitored kinetically by following the absorbance change at 440 nm.

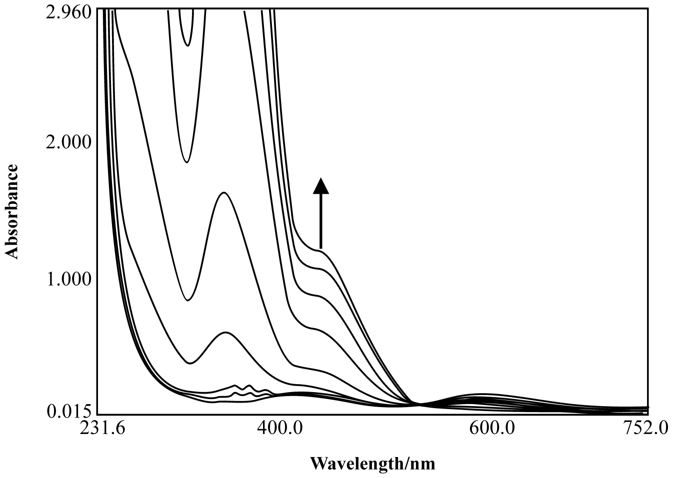

Figure 1. Typical absorbance changes observed during the oxidation of Cr(III) by peroxodisulphate induced by silver(I) ion. [Cr^{3+}] = 0.02 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}; [Ag^+] = 0.02 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C (arrow shows direction of change).

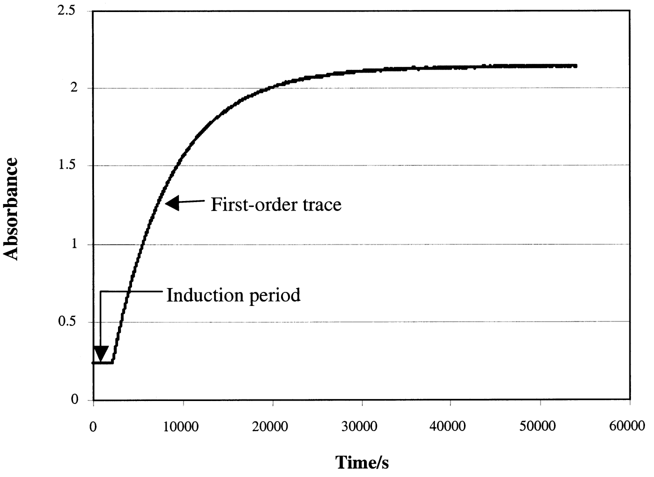

Figure 2. Typical kinetic trace for the silver(I)-induced oxidation of Cr(III) by peroxodisulphate at high [Cr(III)]. [Cr^{3+}] = 0.02 mol dm^{-3}; [Ag^+] = 0.02 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}; λ = 440 nm; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

Two types of kinetic traces were observed during the experiments. At constant pH, temperature, [Ag(I)] and [$S_2O_8^{2-}$], a pseudo first-order process was observed at high Cr(III) concentrations, i.e. 0.02 mol dm^{-3}, whereas a zero-order process was observed at low Cr(III) concentrations, i.e. 0.005 mol dm^{-3}. It follows that the initial [Cr(III)] plays a role in determining the reaction order. Figure 2 shows a typical kinetic trace at a fixed wavelength for the first-order process and Fig. 3 shows a typical kinetic trace for the zero-order process. In both cases, an induction period (*ca.* 1400 s in Fig. 3) occurs before the absorbance changes are observed.

It was decided to proceed with the investigation using two sets of reaction conditions where first- and zero-order behaviour could be studied separately.

3.2. Reaction Stoichiometry

The overall reaction stoichiometry for the oxidation of Cr(III) to Cr(VI) by peroxodisulphate in the presence of Ag^+ ion has been reported as[11]

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O \rightarrow Cr_2O_7^{2-} + 6SO_4^{2-} + 14H^+ \qquad (1)$$

Yost[11] studied the kinetics of this reaction by determining the

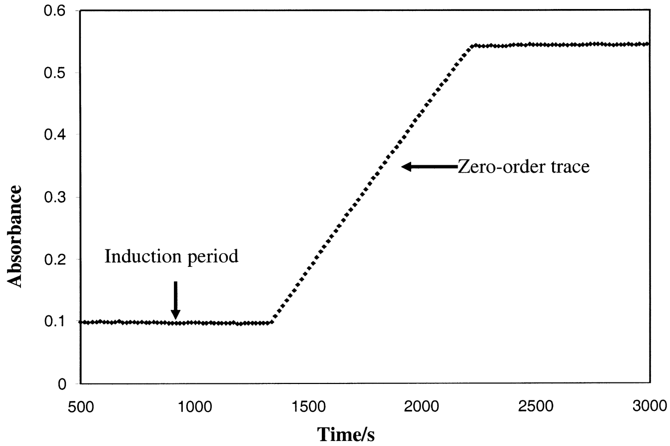

Figure 3. Typical kinetic trace for the silver(I)-induced oxidation of Cr(III) by peroxodisulphate at low [Cr(III)]. [Cr^{3+}] = 0.001 mol dm^{-3}; [Ag^+] = 0.02 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.1 mol dm^{-3}; λ = 440 nm; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

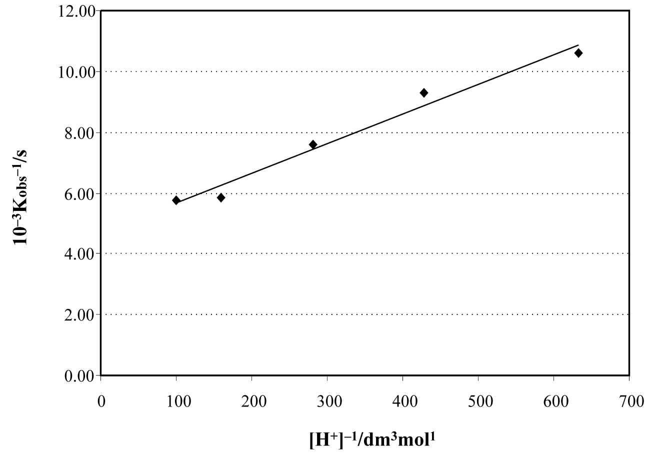

Figure 4. pH dependence of the silver-induced oxidation of Cr(III) by peroxodisulphate. $[Cr^{3+}]$ = 0.01 mol dm^{-3}; $[Ag^+]$ = 0.01 mol dm^{-3}; $[S_2O_8^{2-}]$ = 0.02 mol dm^{-3}; $[HSO_4^-/SO_4^{2-}]$ buffer = 0.10 mol dm^{-3}; T = 40.0 ± 0.1°C.

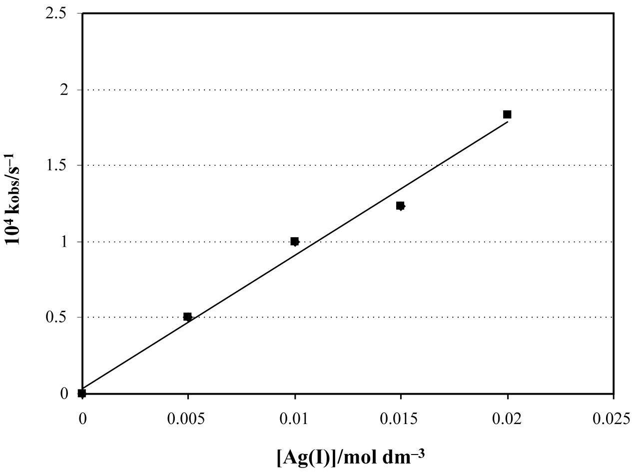

Figure 5. Observed first-order rate constant as a function of $[Ag^+]$ for the $Cr^{3+}/S_2O_8^{2-}/Ag^+$ reaction. $[Cr^{3+}]$ = 0.02 mol dm^{-3}; $[S_2O_8^{2-}]$ = 0.04 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

concentration of Cr(VI) as a function of time by using a titrimetric method. He found that the reaction rate was proportional to [Ag(I)] and to $[S_2O_8^{2-}]$, but independent of the concentration of Cr(III). Ag(III) was considered to participate in the reaction, but no mechanistic details were given.

To determine the effect of pH on the oxidation of Cr(III) by peroxodisulphate induced by silver(I), a bisulphate-sulphate buffered reaction mixture was used. To study any drift in pH due to the formation of reaction products, the pH was measured at fixed [Cr(III)], $[S_2O_8^{2-}]$ and [Ag(I)] before and after the reaction. The pH was found to remain constant during the reaction in the range 2.0 to 2.8 whereas a precipitate was formed at higher pH that prohibited the monitoring of the reaction under such conditions. The first-order rate constant (high Cr(III) concentration range) decreased exponentially with increasing pH. The data could be fitted with a double inverse plot of k_{obs}^{-1} *versus* $[H^+]^{-1}$ as shown in Fig. 4. The remaining kinetic study was therefore conducted at pH 2.8 where the reaction rate could be followed conveniently.

3.3. Kinetic data for the Reaction at High [Cr(III)] (First-order Process)

In all reactions, an induction period was observed during the initial part of the reaction. In order to elucidate the nature of the induction period, experiments were conducted under an argon atmosphere. This resulted in the reduction of the induction period by 10%.

3.3.1. [Cr(III)] dependence

The [Cr(III)] dependence of the reaction was investigated at pH 2.8, $[S_2O_8^{2-}]$ = 0.04 mol dm^{-3} and [Ag(I)] = 0.02 mol dm^{-3}. Results obtained showed that under pseudo-first-order conditions, the observed rate constant did not depend on the initial Cr(III) concentration in the range 0.01 to 0.06 mol dm^{-3}, with an average value of 1.80 ± 0.15 s^{-1} at 40.0°C. All the kinetic traces could be fitted to a first-order model indicating that the process is first-order in terms of [Cr(III)] under these conditions.

3.3.2 $[S_2O_8^{2-}]$ dependence

The $[S_2O_8^{2-}]$ dependence of the reaction was investigated at pH 2.8, [Cr(III)] = 0.02 mol dm^{-3} and [Ag(I)] = 0.02 mol dm^{-3}. Results obtained showed that the observed rate constant does not depend on the $[S_2O_8^{2-}]$ in the range 0.02 to 0.06 mol dm^{-3} with an average value of 1.80 ± 0.15 s^{-1} at 40.0°C.

3.3.3. [Ag(I)] dependence

The [Ag(I)] dependence of the reaction was investigated at pH 2.8 and constant $[S_2O_8^{2-}]$ and [Cr(III)]. Results obtained showed that the observed rate constant depended linearly on [Ag(I)] (Fig. 5), indicating that the reaction is first-order with respect to [Ag(I)]. The straight line shown in Fig. 5 has a zero intercept, indicating that the reaction could not proceed at an observable rate in the absence of silver ion as inducer, since parallel or reverse reactions would have resulted in a non-zero intercept.

3.3.4. Temperature dependence

The temperature dependence of the rate constant, k, of a reaction is given by the Eyring equation:[13]

$$-\frac{\Delta H^{\neq}}{RT}+\frac{\Delta S^{\neq}}{R}=\ln\left(\frac{kh}{k_BT}\right) \qquad (2)$$

where $\Delta H^{\neq}$ = activation enthalpy, $\Delta S^{\neq}$ = activation entropy, R = gas constant, T = temperature, k = measured first-order rate constant, h = Planck constant and k_B = Boltzmann constant.

To determine the effect of temperature on the reaction rate, the reaction was investigated at pH 2.8, over a temperature range from 30 to 50°C, with [Cr(III)] = 0.02 mol dm^{-3}, [Ag(I)] = 0.02 mol dm^{-3} and $[S_2O_8^{2-}]$ = 0.04 mol dm^{-3}. The presentation of the data according to the Eyring equation (2) is shown in Table 1. The activation enthalpy ($\Delta H^{\neq}$) was calculated as 56 ± 5 kJ mol^{-1} and the activation entropy ($\Delta S^{\neq}$) as –136 ± 16 J K^{-1} mol^{-1}. The large negative $\Delta S^{\neq}$ indicates a strongly associative mechanism and a highly ordered transition state.

3.3.5. Pressure dependence

To determine the effect of pressure on the reaction rate, the reaction was investigated at pH 2.8, over a pressure range of

Table 1. Temperature dependence of the silver-induced oxidation of Cr(III) by peroxodisulphate. [Cr(III)] = 0.02 mol dm^{-3}; $[Ag^+]$ = 0.02 mol dm^{-3}; $[S_2O_8^{2-}]$ = 0.04 mol dm^{-3}; pH = 2.8 ± 0.1.

(T ± 0.5)/K	10^4 k/mol dm^{-3} s^{-1}
303	3.66 ± 0.10
308	2.88 ± 0.10
313	1.83 ± 0.20
318	1.14 ± 0.10
323	0.95 ± 0.10

Table 2. Pressure dependence of the Ag(I)-induced oxidation of Cr(III) by $S_2O_8^{2-}$. [Cr(III)] = 0.02 mol dm^{-3}; [Ag^+] = 0.02 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

(p ± 0.10)/MPa	$10^4\ k_{obs}/s^{-1}$
10	1.94 ± 0.20
50	2.12 ± 0.10
90	2.28 ± 0.20
130	2.56 ± 0.10

Table 3. Effect of ethanol as a radical scavenger on the reaction rate. [Cr(III)] = 0.02 mol dm^{-3}, [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}, [Ag(I)] = 0.02 mol dm^{-3}, pH = 2.8 ± 0.1, T = 40.0 ± 0.1°C.

Volume of ethanol/ cm^3 (dm^3 of solution)$^{-1}$	$10^4\ k_{obs}/s^{-1}$
0	1.80 ± 0.10
0.05	1.12 ± 0.10
0.5	0.58 ± 0.20
50.0	0.25 ± 0.10

10–130 MPa, with [Cr(III)] = 0.02 mol dm^{-3}, [Ag(I)] = 0.02 mol dm^{-3} and [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}. Such measurements lead to the determination of $\Delta V^{\neq}$, since the rate constant for a reaction and $\Delta V^{\neq}$ are linked through the equations

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^{\neq}}{RT} \qquad (3)$$

$$\ln k = \ln k_0 - (\Delta V^{\neq}/RT)p \qquad (4)$$

where k and k_0 are the rate constants at pressure p and a pressure of 1 bar (0.1 MPa), respectively, R is the gas constant and T is the absolute temperature. Equation (3) is derived from the standard thermodynamic equations, adapted to transition state theory. Representation of the data according to Equation (4) is shown in Table 2. The activation volume ($\Delta V^{\neq}$) was calculated as –5.8 ± 0.7 $cm^3\ mol^{-1}$.

3.3.6. Effect of a radical scavenger, ethanol, on the reaction rate

The effect of radical scavengers on the reaction rate was investigated before by Prakash *et al.*[14] Acrylamide was used as a radical scavenger and it was found that there was a decrease in the rate constant with increasing concentration of acrylamide, which shows that free radicals are formed that enhance the reaction.

Ethanol is regarded as a suitable scavenger for hydroxo radicals and was therefore chosen as an appropriate radical scavenger to investigate the possible role of radicals in this study. The effect of ethanol on the reaction rate was investigated at pH 2.8 with [$S_2O_8^{2-}$] = 0.04 mol dm^{-3}, [Cr(III)] = 0.02 mol dm^{-3}, [Ag(I)] = 0.02 mol dm^{-3} and temperature = 40.0 ± 0.1°C. Results obtained showed that the observed rate constant decreases with increasing ethanol concentration, confirming that free radicals, presumably $^{\bullet}OH$, play a role in the reaction.

3.4. Kinetic Data for the Reaction at Low [Cr(III)] (Zero-order Process)

Typical kinetic traces as shown in Fig. 3 were obtained in all these cases.

3.4.1. [Cr(III)] dependence

The [Cr(III)] dependence of the reaction was investigated at pH 2.8 with [$S_2O_8^{2-}$] = 0.1 mol dm^{-3} and [Ag(I)] = 0.02 mol dm^{-3}. The results obtained showed that the observed zero-order rate constant did not depend on the Cr(III) concentration in the range 0.001 to 0.005 mol dm^{-3} with an average value of (3.00 ± 0.10) × 10^{-7} mol $dm^{-3}\ s^{-1}$ at 40.0°C.

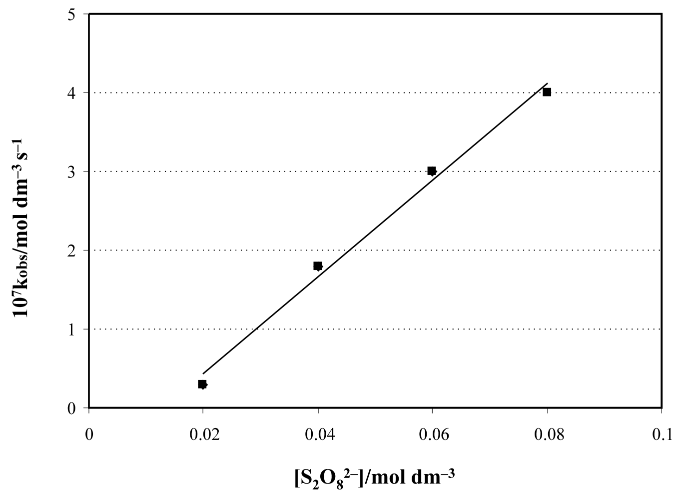

Figure 6. The effect of [$S_2O_8^{2-}$] on the reaction rate of the $Cr^{3+}/S_2O_8^{2-}/Ag^+$ reaction. [Cr^{3+}] = 0.005 mol dm^{-3}; [Ag^+] = 0.02 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

3.4.2. [$S_2O_8^{2-}$] dependence

The [$S_2O_8^{2-}$] dependence of the reaction was investigated at pH 2.8 with [Cr(III)] = 0.005 mol dm^{-3} and [Ag(I)] = 0.02 mol dm^{-3}. Results obtained (Fig. 6) show that the observed rate constant depends on the $S_2O_8^{2-}$ concentration, and increases linearly with increasing [$S_2O_8^{2-}$]. The negative intercept on the y-axis cannot be fully explained, but is probably linked to processes taking place during the induction period by which a decrease in [$S_2O_8^{2-}$] occurs. The intercept on the x-axis is at about 0.015 mol dm^{-3}. This indicates that a substantial concentration of $S_2O_8^{2-}$, almost equal to [Ag(I)], is consumed before the oxidation of Cr(III) is observed.

3.4.3. [Ag(I)] dependence

The [Ag(I)] dependence of the reaction was investigated at pH 2.8 with [$S_2O_8^{2-}$] = 0.1 mol dm^{-3} and [Cr(III)] = 0.005 mol dm^{-3}. Results obtained showed that the observed rate constants depend non-linearly on [Ag(I)] (Fig. 7), and reach a limiting value at high [Ag(I)]. The limiting value is reached when [Ag(I)] equals [$S_2O_8^{2-}$], in agreement with the corresponding observations in 3.4.2

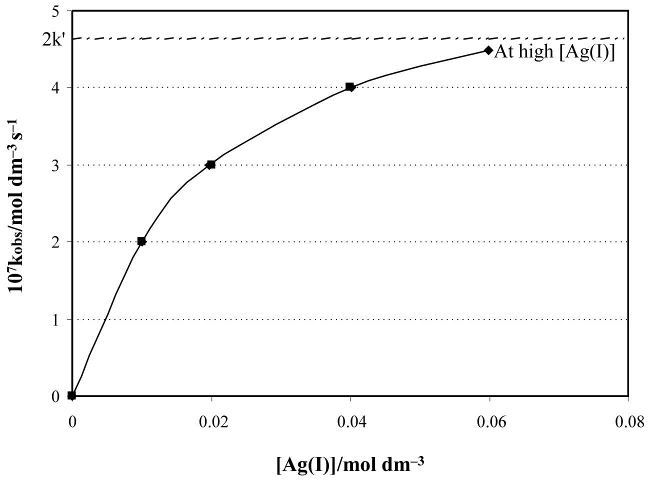

Figure 7. Observed rate constants for the $Cr^{3+}/S_2O_8^{2-}/Ag^+$ reaction as a function of [Ag^+]. [Cr^{3+}] = 0.005 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.1 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

Table 4. Temperature dependence of the silver(I)-induced oxidation of Cr(III) by peroxodisulphate. [Cr(III)] = 0.005 mol dm^{-3}; [Ag^+] = 0.1 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.06 mol dm^{-3}; pH = 2.8 ± 0.1.

(T ± 0.5)/K	10^4 k/mol dm^{-3} s^{-1}
303	5.50 ± 0.10
308	4.58 ± 0.10
313	1.83 ± 0.20
318	1.78 ± 0.10
323	1.26 ± 0.20

3.4.4. Temperature dependence

To determine the effect of temperature on the reaction rate, the reaction was investigated at pH 2.8, over a temperature range of 30 to 50°C, with [Cr(III)] = 0.005 mol dm^{-3}, [Ag(I)] = 0.08 mol dm^{-3} and [$S_2O_8^{2-}$] = 0.06 mol dm^{-3}. A representation of the data according to the Eyring equation is shown in Table 4. The activation enthalpy ($\Delta H^{\neq}$) was calculated as 61 ± 5 kJ mol^{-1} and the activation entropy ($\Delta S^{\neq}$) as –119 ±15 J K^{-1} mol^{-1}. The large negative $\Delta S^{\neq}$ value indicates that under these conditions also the reaction proceeds via an associative mechanism with a highly ordered transition state.

3.4.5. Pressure dependence

To determine the effect of pressure on the reaction rate, the reaction was investigated at pH 2.8, over a pressure range of 10–130 MPa, with [Cr(III)] = 0.005 mol dm^{-3}, [Ag(I)] = 0.08 mol dm^{-3} and [$S_2O_8^{2-}$] = 0.06 mol dm^{-3}. Representation of the data is shown in Table 5. The activation volume ($\Delta V^{\neq}$) was calculated as –1.7 ± 0.1 cm^3 mol^{-1}.

3.5. Discussion of Kinetic Results and Mechanistic Interpretation

The overall stoichiometric reaction for the silver(I)-induced oxidation of chromium(III) to chromium(VI) by peroxodisulphate is given by Yost:[11]

$$2Cr^{3+} + 3S_2O_8^{2-} + 7H_2O \leftrightharpoons Cr_2O_7^{2-} + 6SO_4^{2-} + 14H^+ \qquad (1)$$

He studied the kinetics of this reaction by determining the concentration of the ion $Cr_2O_7^{2-}$ as a function of time by a titrimetric method. Prakash *et al.*[14] also studied the kinetics of the reaction. In both cases the silver-catalysed oxidation of chromium(III) to chromium(VI) by peroxodisulphate anion in sulphuric acid is first-order in silver(I), zero-order in chromium(III) and fractional-order in peroxodisulphate anion. A temperature dependent induction period was observed. Since then, no further kinetic studies on this reaction were reported in the literature. The results obtained in this study are interpreted against this background. The overall reaction (1) is such that a bisulphate/sulphate buffer was employed to control the pH of the solution in the range 2.0 to 2.8.

3.5.1. Induction period

For the studied kinetic processes at high and low [Cr(III)], i.e first- and zero-order reactions, an induction period was always observed. The reactions were performed under an argon atmosphere in order to eliminate any possible oxygen-related oxidation process during the reaction. The following sequence of reactions is proposed:

$$Ag^+ + S_2O_8^{2-} \overset{k_1}{\leftrightharpoons} AgS_2O_8^- \quad \text{fast} \qquad (5)$$

$$AgS_2O_8^- + H_2O \xrightarrow{k_1} Ag^{2+} + {}^{\bullet}OH + SO_4^{2-} + HSO_4- \quad \text{slow} \qquad (6)$$

Table 5. Pressure dependence of the silver-induced oxidation of Cr(III) by peroxodisulphate. [Cr(III)] = 0.005 mol dm^{-3}; [Ag^+] = 0.1 mol dm^{-3}; [$S_2O_8^{2-}$] = 0.06 mol dm^{-3}; pH = 2.8 ± 0.1; T = 40.0 ± 0.1°C.

(p ± 0.10)/MPa	10^4 k_{obs}/s^{-1}
10	1.94 ± 0.10
50	2.12 ± 0.10
90	2.28 ± 0.20
130	2.56 ± 0.10

Based on these reactions it follows that

$$\frac{d}{dt}[Ag^{2+}] = \frac{d}{dt}[{}^{\bullet}OH] = k_1[AgS_2O_8^-]$$

$$= k_1 K_1[Ag^+][S_2O_8^{2-}]$$

$$\text{where } K_1 = \frac{[AgS_2O_8^-]}{[Ag^+][S_2O_8^{2-}]}$$

This reaction scheme predicts a steady build-up of Ag^{2+} and ${}^{\bullet}OH$ that are suggested to account for the induction period. The induction period should decrease with increasing Ag^+ and $S_2O_8^{2-}$ concentrations. One would expect a steady increase in the rate of Cr(VI) formation. However, the induction period ends suddenly (see Fig. 3). This means that Ag^{2+} and ${}^{\bullet}OH$ are used up in the solution, i.e. reduced back to Ag^+ and OH^-. No entirely satisfactory explanation can be given at this stage. This back reaction is probably linked to the oxidation of an impurity, as illustrated by the following generic reactions:

$$Ag^{2+} + X \rightarrow Ag^+ + X^+$$

$${}^{\bullet}OH + X \rightarrow OH^- + X^+$$

where X represents an unknown impurity in the reactant solutions that destroys both Ag^{2+} and ${}^{\bullet}OH$. As soon as the impurity has been used up, then Ag^{2+} and ${}^{\bullet}OH$ can immediately oxidize Cr^{3+} to Cr^{6+}.

3.5.2. Formation of Cr(VI)

Following the induction period, the formation of Cr(VI) can be observed as a first-order process (at high [Cr(III)]:[$S_2O_8^{2-}$]) or as a zero-order process (at low [Cr(III)]:[$S_2O_8^{2-}$]). The proposed overall reaction scheme is as follows:

$$Ag^+ + S_2O_8^{2-} \leftrightharpoons AgS_2O_8^- \quad \text{fast} \qquad (5)$$

$$AgS_2O_8^- + H_2O \xrightarrow{k_1} Ag^{2+} + {}^{\bullet}OH + SO_4^{2-} + HSO_4^- \quad \text{slow} \qquad (6)$$

$$Cr^{3+} + Ag^{2+} \xrightarrow{k_2} Cr^{4+} + Ag^+ \quad \text{slow} \qquad (7)$$

$$Cr^{3+} + {}^{\bullet}OH \xrightarrow{k_3} Cr^{4+} + OH^- \quad \text{slow} \qquad (8)$$

$$3Cr^{4+} \xrightarrow{\text{fast}} Cr^{6+} + 2Cr^{3+}$$

A theoretical rate law for the above-mentioned reaction scheme is:

$$\frac{d[Cr^{6+}]}{dt} = k_2[Cr^{3+}][Ag^{2+}] + k_3[Cr^{3+}][{}^{\bullet}OH] \qquad (9)$$

In order to find expressions for [Ag^{2+}] and [${}^{\bullet}OH$], the steady state approximation is used:

$$\frac{d[Ag^{2+}]}{dt} = 0 = k_1[AgS_2O_8^-] - k_2[Cr^{3+}][Ag^{2+}]$$

$$\therefore k_2[Cr^{3+}][Ag^{2+}] = k_1[AgS_2O_8^-]$$

$$\frac{d[{}^{\bullet}OH]}{dt} = 0 = k_1[AgS_2O_8^-] - k_3[Cr^{3+}][{}^{\bullet}OH]$$

$$\therefore k_3\,[Cr^{3+}][^{\bullet}OH] = k_1[AgS_2O_8^-]$$

Substitution of these expressions in (9) and replacement of $[AgS_2O_8^-]$ leads to:

$$\frac{d[Cr^{6+}]}{dt} = \frac{2k_1K_1[Ag^+][S_2O_8{}^{2-}]}{1+K_1[Ag^+]}$$

$$= \frac{2}{3}\left\{\frac{d[S_2O_8{}^{2-}]}{dt}\right\} \tag{10}$$

Since $[Ag^+]$ is constant, it follows that:

$$\frac{2}{3}\left\{\frac{d[S_2O_8{}^{2-}]}{dt}\right\} = \frac{2k_1K_1[Ag^+][S_2O_8{}^{2-}]}{1+K_1[Ag^+]}$$

$$= k_{obs}[S_2O_8^{2-}] \tag{11}$$

It thus follows from the proposed reaction scheme that under different conditions, different experimental behaviour is possible. Since Ag^+ facilitates a reaction sequence with a lower activation barrier than is needed for the direct oxidation reaction of Cr(III) by $S_2O_8^{2-}$, Ag^+ can be regarded as an inducer or a precursor to the catalyst.

3.5.3. At High [Cr(III)] (first-order process)

Under these conditions, the reaction rate was independent of [Cr(III)]. It follows from Equation 11 that

$$k_{obs} = \frac{2k_1K_1[Ag^+]}{1+K_1[Ag^+]}$$

$$\cong 2\,k_1K_1[\,Ag^+], \text{ since } K_1[Ag^+] < 1.$$

This is in agreement with the experimental results in which k_{obs} varies linearly with $[Ag^+]$ and is independent of $[S_2O_8^{2-}]$. Thus the activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta V^{\neq}$) are for k_1K_1, i.e. for reactions (5) and (6), such that

$$\Delta V_{exp}{}^{\neq} = \Delta V^{\neq}(k_1) + \Delta V(K_1) = -5.8 \text{ cm}^3 \text{ mol}^{-1}$$

$\Delta V^{\neq}(k_1)$ involves electron transfer, i.e. $Ag^+ \rightarrow Ag^{2+}$. This process should result in a small volume decrease as a result of the increase in charge on the silver ion. $\Delta V(K_1)$ involves complex formation, i.e. bond formation and charge neutralization. It is expected that the bond formation would result in a decrease in volume, whereas charge neutralization should result in an increase in volume. The overall effect observed is a negative activation volume, which must result from bond formation and charge concentration effects. In general, negative $\Delta S^{\neq}$ values favour a highly ordered transition state which is in agreement with the negative $\Delta V^{\neq}$ value found for the process.

3.5.4. At Low [Cr(III)] (zero-order process)

At low [Cr(III)], the reaction follows zero-order kinetics, i.e. the reaction rate remains constant as a function of reaction time.

The same mechanism and rate law, Equation (11) proposed before for this process still applies:

$$\frac{2}{3}\left\{\frac{d[S_2O_8{}^{2-}]}{dt}\right\} = \frac{2k_1K_1[Ag^+][S_2O_8{}^{2-}]}{1+K_1[Ag^+]} \tag{12}$$

However, at lower $[Cr^{3+}]$, only partial usage of $S_2O_8^{2-}$ occurs such that the $[S_2O_8^{2-}]$ remains practically constant during the reaction. Equation (12) in this case can be re-written as:

$$\frac{2}{3}\left\{\frac{d[S_2O_8{}^{2-}]}{dt}\right\} = \frac{d[Cr^{6+}]}{dt} = \frac{2k_1K_1[Ag^+]}{1+K_1[Ag^+]} \tag{13}$$

where $k_1' = k_1[S_2O_8^{2-}]$

In equation (13) the reaction rate becomes independent of $[S_2O_8^{2}]$, since it remains constant with time. The net result under these conditions is that the reaction rate varies non-linearly with [Ag(I)] and reaches a limiting value at high [Ag(I)]. The activation parameters were therefore determined at high [Ag(I)] where only the effect of k_1' is observed.

It follows from Fig. 7 that at high [Ag(I)] the reaction rate varies linearly with $[S_2O_8^{2-}]$ since $k_1' = k_1[\,S_2O_8^{2-}]$. The activation parameters determined under these conditions will thus be for k_1 only. It thus follows that:

$$\Delta V_{exp}{}^{\neq} = \Delta V^{\neq}(k_1) = -1.7 \text{ cm}^3 \text{ mol}^{-1}.$$

By combining these results with those obtained under first-order conditions ($\Delta V_{exp}{}^{\neq} = \Delta V^{\neq}(k_1) + \Delta V(K_1) = -5.8$ cm^3 mol^{-1}), it can be concluded that since $\Delta V^{\neq}(k_1) = -1.7$ cm^3 mol^{-1}, $\Delta V(K_1) = -4.1$ cm^3 mol^{-1}.

Thus $\Delta V^{\neq}(k_1)$ can be seen as a small volume collapse due to the charge increase on Ag(I) and $\Delta V(K_1)$ the result of a volume collapse due to complex formation that is larger than the volume increase due to desolvation as a result of charge neutralization associated with this reaction step.

In general, a negative $\Delta S^{\neq}$ is an indication of a highly ordered transition state and this is in agreement with the negative $\Delta V^{\neq}$ data.

3.5.5. Influence of pH

It was found that the formation of Cr(VI) depends on pH, where k_{obs} increases with increasing $[H^+]$ in a non-linear manner. The results in Fig. 4 are typical for a protonation pre-equilibrium that catalyses the reaction progress, which can be described by an equation of the general form

$$k_{obs} = kK[H^+]/(1 + K[H^+])$$

where K represents the protonation constant and k the rate constant for the acid-induced reaction step. It follows that $1/k_{obs} = 1/k + 1/kK[H^+]$. According to Fig. 4, $1/k = (4.7 \pm 0.3) \times 10^3$ s and $1/kK = 9.8 \pm 0.9$ N>s mol dm^{-3} at 40.0°C, from which $K \approx 500$ mol dm^{-3} and $k \approx 2 \times 10^{-4}$ s^{-1}. The magnitude of the protonation constant demonstrates the efficiency of the acid-catalysed process. We suggest that reaction (6) involves a spontaneous acid-induced reaction path for which K represents the protonation of the $AgS_2O_8^-$ complex to facilitate the intramolecular electron transfer reaction.

4. Conclusions

Studying the $Cr^{3+}/S_2O_8^{2-}/Ag^+$ reaction over a longer time period and under different reaction conditions revealed a quite interesting kinetic behaviour. Two different patterns in the kinetic behaviour were observed, which can be explained by the same proposed reaction scheme. The mechanism of the process was further elucidated by determining for the first time all the activation parameters for this process. It was found that the signs and magnitudes of these parameters are in agreement with the proposed reaction mechanism and provide further support for it.

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