Reduction Kinetics of Chromium(VI) by S(-II) in Alkalescent Aqueous Media

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Abstract

Batch experiments were performed to study the reaction kinetics of chromium(VI) and S(-II) in alkalescent aqueous media with high reactant concentrations. Effects of stirring rate, pH, initial Cr(VI) concentration, temperature and inert substance concentration on Cr(VI) reduction were experimentally investigated. Apparent reaction kinetics were obtained. The apparent activation energy ($E_a$) of the reaction was ca. 30.9 kJ mol$^{-1}$ at temperature range of 303-333 K and the reaction showed positive salt effect in the low inert substance concentration media of 0.025–0.25 mol/L, suggesting that the actual reactants might be HCrO$_4^-$ and HS$^-$. 

Key words: reduction kinetics; chromium(VI); S(-II); high reactant concentrations; alkalescent aqueous media

Introduction

Chromium compounds are widely used in various industries such as electroplating, chromate manufacturing, leather tanning, and wood preservation (PAPP, 2001). Stable chromium in the natural environment mainly comprises hexavalent or trivalent forms. The hexavalent form in the industrial wastes exists in divalent oxyanions, e.g., chromate (CrO$_4^{2-}$) and dichromate (Cr$_2$O$_7^{2-}$). The hexavalent chromium [Cr(VI)] is highly soluble in water and toxic for most organisms due to their strong oxidizing nature (Yassi and Nieboer, 1988) and thus poses a great threat to human health if it released to the environment. Since the trivalent chromium [Cr(III)] is less toxic above pH 5.0, which probably due to its impermeability to biological membranes (Rai and Sass, 1987), it might be a feasible detoxification method by reducing Cr(VI) to Cr(III).

As one of the strongest Cr(VI) reductants, S(-II) has attracted much attention (Schroeder and Lee, 1975; Saleh and Parkerton, 1989; Fude and Harris, 1994; Chulsung and Zhou, 2001; Pettine and Millero, 1994; and Pettine and Barra, 1998). Pettine (Pettine and Millero, 1994; Pettine and Barra, 1998) reported the reduction kinetics of Cr(VI) by Cr$_2$O$_7^{2-}$ in seawater, being described as: $r = -d[S(-II)]/dt = k_0[H^+]^2[Cr(VI)]^2[S(-II)]^Y$. Chulsung (Chulsung and Zhou, 2001) investigated the reaction stoichiometry, kinetics, and mechanism using batch experiments with excess [Cr(VI)] over [S(-II)], and indicated that 1.5 mol of sulfide was required for the reduction of 1 mol Cr(VI), suggesting the following stoichiometry: $2CrO_4^{2-} + 3H_2S + 4H^+ \rightarrow 2Cr(OH)_3(s) + 3S(s) + 2H_2O$. The reaction kinetics could be interpreted by a three-step mechanism which comprised formation of an inner-sphere chromate-sulfide intermediate complex ([H$_2$O$_4$Cr$_{VIS}$]$^2- + 3H_2S + 4H^+ \rightarrow 2CrO_4^{2-} + 3S(s) + 2H_2O$), an intramolecular electron transfer to form Cr(IV) species, and subsequently a fast reactions leading to Cr(III).

Most of the reports on chromium(VI) reduction by S(-II) in aqueous media focus on very low concentration of Cr(VI) and S(-II) ([Cr(VI)], [S(-II)]T << 1 mmol/L, [Cr(VI)] >> [S(-II)]) (Schroeder and Lee, 1975; Saleh, F.Y. and Parkerton, 1989; Fude and Harris, 1994; Chulsung and Zhou, 2001; Yang and Lan, 2005). However, with the development of remediation technologies of Cr(VI) contamination using sulfide as reductant, for example, reducing hexavalent chromium by sulfate-reducing bacteria (Bradley and Anna, 1998; Lloyd and Mabbert, 2001; Cheung and Gu, 2003; Ronald, 2006), it is necessary to investigate the reaction kinetics of chromium(VI) reduction by S(-II) in alkalescent aqueous media with relatively high reactant concentrations. The reaction kinetics could be useful in determining the reaction stoichiometry and evaluating further possible destination of Cr(VI) in the decontamination process, which are very essential for making the optimal remediation choice.

In this work, batch experiments with excess [S(-II)] over [Cr(VI)] were conducted to study the effects of pH, temperature and inert substance concentration on the reaction ki-
netics of chromium(VI) and S(-II) in aqueous media of alka-
lescent condition (pH 7.5~9.3) with high reactant concen-
trations.

Materials and Methods

Chemicals and solution

All chemicals were of guarantee reagent (GR) grade and
purchased from Beijing Chemical Company (China). All so-
lutions were prepared with Milli-Q water, and the glassware
was cleaned with 10 mol/L of HNO₃ and rinsed with Milli-
Q water before use.

Sulfide stock solution was newly prepared with
Na₂S·9H₂O crystal in Milli-Q water before use. Cr(VI) stock
solution was prepared with K₂Cr₂O₇. Phosphate buffer and
borate buffer were prepared for pH 6.5–8.2 and pH 8.2–10.5,
respectively.

Experimental procedures

Quantificational dosages of buffers and 7.31 g of NaCl
were added into a 250 ml flask and purged with high purity
nitrogen for 30 min. Cr(VI) stock solution was added into
the flask, and then constant dosages of sulfide stock solution
was quickly injected into the aqueous phase by pipette. The
solution was of 100 ml with 1.25mol/L of NaCl, initial Cr(VI)
concentration 13.96 mmol/L, and initial S(-II) concentration
1.34 mmol/L. The solution was immediately put on a stirred
bed at speed of 800 r/min. 0.3 ml of samples were sampled
from the reaction system at time intervals and then were im-
mediately injected into color-tubes with alkalescent solution
(pH > 11) to halt the reaction before analysis. A constant
temperature water bath was used to keep the temperature
constant (303K).

Analytical methods

Cr(VI) and sulfide concentrations were determined by
diphenylcarbazide spectrophotometry and methylene blue
spectrophotometry, respectively (APHA, 1992). All the mea-
surements were performed on a UV-2100 spectrophotome-
ter (LabTech, USA).

Results and Discussion

Effect of stirring speed on Cr(VI) reduction

Figure 1 shows the relationship between stirring speed
and Cr(VI) reduction rate constant. It is obvious that the re-

![FIG. 1. Effect of stirring speed on the apparent reaction rate constant at pH 8.12.](image-url)
duction rate increased dramatically with the stirring speed increasing from 0 to 600 r/min, and then remained constant when the stirring speed greater than 600 r/min. Since Cr(VI) could rapidly react with S(-II) at high concentration, the diffusion process might be the rate controlling step of the reaction under the condition of low stirring speed, with slight external diffusion effect after stirring speed was greater than 600 r/min. In the following experiment, the stirring speed was kept at 800 r/min.

Effect of pH on Cr(VI) reduction

The effect of pH on S(-II) oxidation is shown in Figure 2. The logarithm of S(-II) concentration (ln[S(-II)]) had a linear relationship with time (t) under various pH, suggesting a pseudo-first-order reaction. The slope of the linear plots of ln[S(-II)] on time decreased significantly with pH increasing, indicating the decrease in apparent reaction rate constant.

The apparent rate constants (k_{app}) at various pH could be obtained from the slope of the linear plots of ln[S(-II)] on time (t), and the results were presented in Figure 3. The logarithm of the apparent rate constants (ln(k_{app})) decreased significantly following a linear relationship with pH increasing, and the slope was calculated to be −0.870. According to equations 3 and 5, the apparent rate constants (k_{app}) are obtained by multiplying k_0 [Cr(VI)]^{0.87} and [H^+]^{z}, and consequently lg(k_{app}) has a linear relationship with pH (−lg([H^+])) with a slope of −z. Therefore, the value of z, e.g., the order of reaction of H^+, is 0.87 in this system.

Effect of initial Cr(VI) concentration on Cr(VI) reduction

Figure 4 presents the effect of initial Cr(VI) concentration (12.6-40 mmol/L) on the reaction kinetics of Cr(VI) and S(-II) (with initial concentration 1.34 mmol/L) at pH 8.92. It is obvious that Cr(VI) reduction rate increased with the increase in initial Cr(VI) concentration. The plot of lg(k_{app}) versus log[S(-II)] can be described as a straight line with a linear relative coefficient (R^2) of 0.9902, and the slope, e.g., the order of reaction of Cr(VI), 1.6, being different from the first-order reaction respect to [S(-II)] is indicated in former studies (Chulsung and Zhou, 2001, Pettine and Millero, 1994).

Effect of temperature on Cr(VI) reduction

The relationship of rate constants versus temperature can be determined using Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$  

where $k$ is rate constant, $A$ is pre-exponential factor, $R$ is molar gas constant, $T$ is the thermodynamic temperature, $E_a$ is the apparent activation energy of the reaction.

The equation can be described as follows:

$$lgk = -2.303 \frac{E_a}{RT} + \text{constants}$$  

As shown in Figure 5, the reduction rate constant of Cr(VI) increased with the increase in temperature, and the plot of

- **FIG. 3.** Dependence of lg(k_{app}) on pH.
- **FIG. 4.** Dependence of lg(k_{app}) on lg([Cr(VI)]) at pH 8.92.
- **FIG. 5.** Dependence of lg(k_{app}) on 1/T.
In this work, the reactant concentrations are relatively high. Pettine (Pettine and Millero, 1994; Pettine and Barra, 1998) and Chulsung (Zhou, 2001) reported that the rate and mechanism of the reaction were independent on inert substance with concentration lower than 1.0 mol/L at low reactant concentrations. In this work, the reactant concentrations are relatively high (\([\text{Cr(VI)}]_0 = 13960 \text{ mol/L}, [\text{S}(-\text{II})]_0 = 1340 \text{ mol/L}\)), therefore the inert substance might have effect on the Cr(VI) reduction.

Figure 6 described the effect of NaCl concentration on Cr(VI) reduction rate in this system. NaCl concentration lower than 0.35 mol/L had prominent effect on Cr(VI) reduction rate, while slightly effect by the NaCl concentration greater than 0.35 mol/L. In the media with NaCl lower than 0.1 mol/L, the apparent reaction rate increased rapidly with the increase in NaCl concentration and reached the peak at NaCl of about 0.1 mol/L, but then decreased.

**Effect of inert substance on Cr(VI) reduction rate**

The Cr(VI) reduction takes place in aqueous solution containing inert substance which has potential effect on the rate of reaction or reaction mechanism (Jin, 1984). Pettine (Pettine and Millero, 1994; Pettine and Barra, 1998) and Chulsung (Chulsung, 2001) reported that the rate and mechanism of the reaction were independent on inert substance with concentration lower than 1.0 mol/L at low reactant concentrations. In this work, the reactant concentrations are relatively high (\([\text{Cr(VI)}]_0 = 13960 \text{ mol/L}, [\text{S}(-\text{II})]_0 = 1340 \text{ mol/L}\)), therefore the inert substance might have effect on the Cr(VI) reduction.

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**Species involved and final products**

The relationship of the rate constant versus activity coefficient of ions was determined using Brönsted's equation:

\[
\log \frac{k}{k_0} = \log \left( \frac{\gamma_{\text{Cr(VI)}} \gamma_{\text{S}(-\text{II})}}{\gamma_x} \right)
\]

where \(\gamma_{\text{Cr(VI)}}\), \(\gamma_{\text{S}(-\text{II})}\) and \(\gamma_x\) are activity coefficients of Cr(VI), S(-II) and activated complex.

The activity coefficient of ions can be defined by Debye-Hückel's limiting law:

\[
-\log \gamma_i = CZ_i^2 \sqrt{I}
\]

where \(\gamma_i\) and \(Z_i\) are activity coefficient and charge number of reactant \(i\) respectively, \(I\) is the ionic strength, \(C\) is a constant.

Combining equations (9) and (10):

\[
\log \frac{k}{k_0} = -C[Z_{\text{Cr(VI)}}^2 + Z_{\text{S}(-\text{II})}^2] - (Z_{\text{Cr(VI)}} + Z_{\text{S}(-\text{II})})^2 \sqrt{I}
\]

According to equation (11), the reaction shows positive salt effect between reactants with same electric charge. As shown in Figure 6, the reduction rate of Cr(VI) was greatly higher and increased rapidly with the increase in inert substance concentration in the media with inert substance concentration lower than 0.1 mol/L, suggesting the reactants with same electric charge might be involved.

The conversion of the species of S(-II) and Cr(VI) in aqueous media can be described as following equations:

\[
\begin{align*}
\text{H}_2\text{S} & \overset{k_1}{\rightarrow} \text{HS}^- + \text{H}^+ & K_1 &= 10^{-7.05} \\
\text{HS}^- & \overset{k_2}{\rightarrow} \text{S}^{2-} + \text{H}^+ & K_2 &= 10^{-11.95} \\
\text{H}_2\text{CrO}_4 & \overset{k_3}{\rightarrow} \text{H}^+ + \text{HCrO}_4^- & K_3 &= 4.1 \\
\text{HCrO}_4^- & \overset{k_4}{\rightarrow} \text{H}^+ + \text{CrO}_4^{2-} & K_4 &= 10^{-5.9}
\end{align*}
\]

The species of S(-II) and Cr(VI) are strongly dependent on pH. According to equations 12–15, the distribution of species of S(-II) and Cr(VI) could be obtained and shown in Table 1, respectively. Obviously, \(\text{HS}^-\) is the main species of \([\text{S}(-\text{II})]\) at the selected pH and is supposed to be one of the direct reactants for the first order of reaction of S(-II).

Table 1 shows that \(\text{CrO}_4^{2-}\) was the main species of Cr(VI). Cr(VI) concentration is much higher than sulfide concentration in this system. However, higher reaction order of Cr(VI) was obtained, suggesting that \(\text{CrO}_4^{2-}\) might not be the species directly involved in Cr(VI) reduction. Table 1 suggests that \(\text{H}_2\text{CrO}_4\) was trace species of Cr(VI) under the adopted pH condition. Combining the conclusion that the reactants with same electric charge might be involved, the dramatic effect of pH on Cr(VI) reduction rate indicated that the complex of \(\text{H}^+\) and \(\text{CrO}_4^{2-}\), i.e. \(\text{HCrO}_4^-\), might be the directly involved species of Cr(VI).

It is believed that the reduction of Cr(VI) results in the production of Cr(III) species (Deng, 1995), and final product of oxidation of S(-II) could be complicated due to the complex oxidation states of element sulfur. Pettine (Pettine and Millero, 1994; Pettine and Barra, 1998) suggested that sulfate was the major product because very high concentration of sulfate was detected during Cr(VI) reduction with \(\text{H}_2\text{S}\), while Chulsung (Chulsung and Zhou, 2001) confirmed that chromium hydroxide and elemental sulfur were the stable products.
products with transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) measurements.

In the experiment process, a thin layer of ivory-white precipitate was obtained, and it dissolved slowly in the following reaction. Since the chromium hydroxide precipitate is very stable and difficult to generate crystal by the aging of amorphous chromium hydroxide precipitate (Liu, 1994), the layer of ivory-white precipitate might not be the chromium hydroxide precipitate but be the product of S(-II) oxidation, i.e. element sulfur. The slow disappearance of the ivory-white precipitate might attribute to the oxidation of element sulfur generating sulfur species in several oxidation states.

Conclusions

The reaction kinetic of Cr(VI) reduction with Cr(VI) and S(-II), with initial concentration 13.96 mmol/L and 1.34 mmol/L respectively, at pH range of 7.5–9.3, is different from the reported results conducted in relatively low reactant concentrations. The apparent kinetics of chromium(VI) reduction with S(-II) can be described as the following empirical kinetic equation:

\[ r = -\frac{d[S(-II)]}{dt} = k_0[H^+]^{0.37}[Cr(VI)]^{1.6}[S(-II)] \]

The activation energy (E_a) of the reaction is ca. 30.9 kJ/mol at temperature range of 303–333 K, being lower than the reported data, probably resulting from the elimination of diffusion resistance. The reaction presented positive salt effect in the low inert substance concentration media (e.g. 0.025–0.25 mol/L) and the actual reactants were predicted to be HCrO_4^- and HS^-, with chromium hydroxide and elemental sulfur being the hypothesized stable products.

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Author Disclosure Statement

No competing interests exist.

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