

# A kinetic and mechanistic study of the chromium (VI) reduction by hydrogen peroxide in acidic aqueous solutions

W van Niekerk<sup>1</sup>, JJ Pienaar<sup>1\*</sup>, G Lachmann<sup>1</sup>, R van Eldik<sup>2</sup> and M Hamza<sup>2</sup>

<sup>1</sup> School of Chemistry and Biochemistry, North-West University, Potchefstroom Campus, Potchefstroom 2520, South Africa

<sup>2</sup> Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany

## Abstract

The reduction of hexavalent chromium, Cr(VI), by hydrogen peroxide in both buffered and non-buffered aqueous solutions was investigated as a function of concentration, pH, ionic strength, effect of radical scavengers, temperature and pressure. The rate of the reaction between Cr(VI) and hydrogen peroxide exhibited a strong dependence on the pH of the reaction mixture, viz. a decrease in reaction rate with increasing pH from 1.0 to 7.0. For a  $2.5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$  Cr(VI) solution, a  $\text{H}_2\text{O}_2$  concentration of at least 10 times the initial Cr(VI) concentration was required for complete reduction in this pH range. Neither the ionic strength of the reaction mixture, nor the presence of a radical scavenger had an effect on the rate of the rate-determining step. From the temperature dependence of the reaction the activation enthalpy ( $\Delta H^\ddagger$ ) was calculated to be  $10.4 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$  and the activation entropy ( $\Delta S^\ddagger$ ) to be  $-186 \pm 3 \text{ J K}^{-1}\cdot\text{mol}^{-1}$  for the rate-determining step. The volume of activation ( $\Delta V^\ddagger$ ) was found to be  $-6.1 \pm 0.5 \text{ cm}^3\cdot\text{mol}^{-1}$  from the pressure dependence of the reaction rate. The empirical data could be fitted to:  $k_{\text{obs}} = k[\text{H}^+][\text{H}_2\text{O}_2]/(\text{K}_a + [\text{H}^+])$ , with  $k = (48.4 \pm 1.4) \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  and  $\text{K}_a$  the acid dissociation constant of  $\text{H}_2\text{CrO}_4$ . A reaction mechanism in which a Cr(VI)/ $\text{H}_2\text{O}_2$  adduct is formed in the rate determining step, is proposed. The theoretical rate law that can be derived from this mechanism is in agreement with the empirical rate law.

**Keywords:** kinetics, mechanism, chromium (VI), reduction, hydrogen peroxide, activation parameters

## Introduction

Although chromium has found many useful industrial applications, the impact of the chromium industry on the receiving environment is extensive, complicated and not fully quantified. Landfill disposal of waste containing chromium is common practice arising from industrial chromium production as well as chromium utilising industries (Kimbrough et al., 1999). Contaminated landfill sites and industrial effluents are likely to contain only trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). Divalent chromium, Cr(II), is unstable and rapidly oxidised to Cr(III). Elemental chromium, Cr(0), is also oxidised to Cr(III) unless it is stabilised by superficial oxidation.

Hexavalent chromium is considered toxic and carcinogenic (Yassi and Nieboer, 1988), whereas trivalent chromium is a trace nutrient for humans and animals alike (Wong and Trevors, 1988). The industrial and environmental importance of the reduction of Cr(VI) is emphasised by this fact. In the South African context this reduction process is even more important since South Africa is considered the largest chromite and ferrochromium producing country, as well as the 6<sup>th</sup> largest stainless-steel producing country in the world. It is estimated that South Africa holds approximately 72% of the world's chromium reserves (UCT, 2001).

The low solubility of Cr(III) solids (mostly  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}(\text{OH})_3$ ) is likely to be the major reason why Cr(III) generally makes up a small percentage of the total chromium concentration in polluted groundwater (Calder, 1988). Mobilisation of the  $\text{Cr}(\text{OH})_3$  precipitate is slow, unless enhanced by dissolution in strong acidic environments or complexation with organics (Rai et al., 1987). Oxidation of Cr(III) is mostly achieved through  $\text{MnO}_2$ , which acts as a catalyst (Rai et al., 1989).

In contrast, there are no significant solubility constraints in groundwater for Cr(VI) (Rai et al., 1989). When Cr(VI) is transported by groundwater, it may be transformed to and precipitated as Cr(III). However, the reducing capability of a soil is limited to the amounts of reductant (organics, Fe(II), sulphides, etc.) present. Hence excessive chromium loading on soil might not only upset, but destroy the natural balance, giving way to Cr(VI) formation, even if the original load was exclusively Cr(III). Due to the toxicity and carcinogenicity of Cr(VI), the USEPA (2002) has set a drinking water limit for chromium of  $0.05 \text{ mg}\cdot\text{l}^{-1}$  (Calder, 1988). As a result, the removal of Cr(VI) from industrial wastewater has become necessary in order to avoid contamination of water sources.

Despite numerous studies, there are still many uncertainties regarding the kinetics and reaction mechanism of the reduction reactions of Cr(VI). During a survey of relevant scientific literature, the importance of hydrogen peroxide as reducing agent of Cr(VI) became apparent. Hydrogen peroxide is a strong oxidising agent that is commonly used in water purification. The chemistry of hydrogen peroxide and chromium is, however, complex and involves ligand exchange, proton transfer, oligomerisation, and redox reactions (Baloga, 1961).

Several investigations have been conducted on the reduction of Cr(VI) by  $\text{H}_2\text{O}_2$  (Moore et al., 1966; Orhanovic and Wilkins, 1967; Adams et al., 1968; Bartlett and Quane, 1973; Funahashi et al., 1978; Witt and Hayes, 1982; Perez-Benito and Arias, 1997; Zhang and Lay, 1998; Gili et al., 2002 and Vander Griend et al., 2002). However, the use of buffers and the relatively limited pH range in which these studies were carried out, make the results less applicable for industrial applications. Certain buffers take part in the reaction and have an influence on the reaction rate (Perez-Benito and Arias, 1997). In this study we report the kinetics of the reduction of Cr(VI) by  $\text{H}_2\text{O}_2$  over a wide pH range (1.0 to 7.0) as a function of numerous rate-determining factors that include for the first time the pressure dependence from which the volume of activation can be calculated.

\* To whom all correspondence should be addressed.

☎ +27 18 299-2301; fax: +27 18 299-2447;

e-mail: [Kobus.Pienaar@nwu.ac.za](mailto:Kobus.Pienaar@nwu.ac.za)

Received 16 May 2006; accepted in revised form 13 August 2007.

## Materials and methods

### Materials

Analytical grade (AR) reagents were bought from different suppliers and used without any further purification. Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) (UniLab) was used as the aqueous source of Cr(VI).  $\text{H}_2\text{O}_2$  solutions were prepared by dilution of 30% hydrogen peroxide (Merck). Since hydrogen peroxide is unstable in water, all solutions were standardised with cerium(IV) sulphate ( $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) (Merck) (Vogel, 1989). At  $\text{pH} < 3.5$  the pH of reactant solutions was adjusted prior to mixing with stock solutions of sodium hydroxide (NaOH) (SMM) and/or perchloric acid ( $\text{HClO}_4$ ) (Merck). At higher pH, the pH drift during the reaction necessitated the use of buffers. Standard acetate and phosphate buffers were used by mixing the appropriate sodium salts (Merck) and acids (Merck). These buffers had a negligible effect on the reaction rate. The ionic strength of all solutions was kept constant at  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  by adding calculated volumes of a stock solution of sodium perchlorate ( $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ) (UniLab) to the reactant solutions. Millipore milli-Q deionised water ( $18 \text{ M}\Omega \cdot \text{cm}^{-1}$ ) was used to make up all solutions.

### Methods

A variety of analytical methods can be employed to determine the chromium concentration in aqueous solution (Vogel, 1989). Due to its relative ease of use and the fact that concentration changes can be monitored as they occur, the direct photometric absorption measurement method was chosen as the standard procedure to monitor the aqueous concentration of Cr(VI). All kinetic experiments at ambient pressure were carried out on a SX-17MV stopped-flow spectrophotometer from Applied Photophysics or a Varian Cary 50 Conc UV spectrophotometer. A custom-built high-pressure stopped-flow system at the Institute for Inorganic Chemistry, University of Erlangen-Nürnberg was used for collecting experimental data at elevated pressure (Van Eldik, 1993). The temperature of all reactant mixtures was kept constant to  $0.1^\circ\text{C}$  at the given temperature with a Haake F3 Fisons thermostatic water bath. The pH of the various reagent solutions and reaction mixtures was measured with a Metrohm 744 pH meter, fitted with a combined glass-calomel electrode. The KCl solution in the salt bridge was replaced by an NaCl solution to prevent precipitation of  $\text{KClO}_4$  in the salt bridge. The pH meter was calibrated daily with standard buffer solutions (pH 4.0, 7.0 and 10.0).

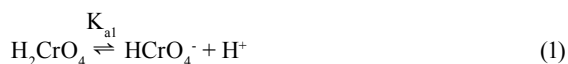
First-order rate constants were calculated with the Olis Kinfit software package and data fitting was performed with the solver module in Excell® (Microsoft®).

## Results and discussion

### Characteristics of the Cr(VI)/ $\text{H}_2\text{O}_2$ reaction system

The reaction of Cr(VI) with hydrogen peroxide depends on the speciation and the redox potentials of the reagents. Experimental conditions were selected by taking these properties into consideration.

Aqueous Cr(VI) can mainly be represented by the following equilibria:



where:

$$\begin{aligned} K_{a1} &= 4.1 \text{ mol} \cdot \text{dm}^{-3} \text{ at } 25^\circ\text{C} \text{ (Perez-Benito and Arias, 1997)} \\ K_{a2} &= 1.26 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \text{ at } 25^\circ\text{C} \text{ and } I = 1.0 \text{ mol} \cdot \text{dm}^{-3} \\ &\text{(Cotton et al., 1999)} \end{aligned}$$

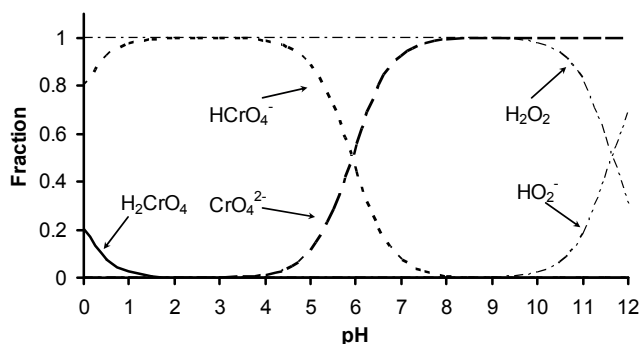
A substantial fraction of dichromate only exists in solution when the total Cr(VI) concentration is higher than  $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ . The total concentration of dissolved chromate in the 6+ oxidation state is referred to as Cr(VI). Since concentrations of  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{NaCr}_2\text{O}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  in dilute aqueous solutions are very low, Cr(VI) can be defined as:

$$[\text{Cr(VI)}] = [\text{H}_2\text{CrO}_4] + [\text{HCrO}_4^-] + [\text{CrO}_4^{2-}] \quad (3)$$

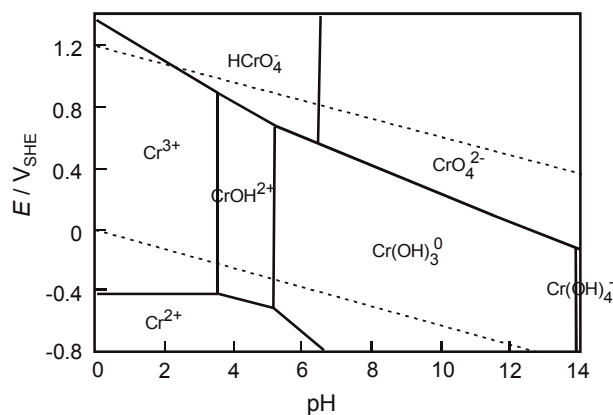
In this paper all results will therefore be discussed in terms of [Cr(VI)].

The important species in the Cr(VI)/ $\text{H}_2\text{O}_2$  system are summarised in Fig. 1. Hydrogen peroxide is a weak acid and  $\text{HO}_2^-$  will form only in significant concentrations at  $\text{pH} > 10$ .  $\text{H}_2\text{CrO}_4$  is a minor species even at pH 1. Over the pH range 1 to 6 the major species is  $\text{HCrO}_4^-$  while  $\text{CrO}_4^{2-}$  becomes the major species at  $\text{pH} > 6$ .

The  $E/V_{\text{SHE}}$ -pH diagram shown in Fig. 2 (Beverkog and Puigdomenech, 1996) provides a generalised depiction of the major aqueous chromium species and redox stabilities under conditions of chemical equilibrium. From the standard electrode potentials given in Fig. 2 it is apparent that Cr(VI) becomes a weaker oxidant as chromic acid de-protonates at higher pH.

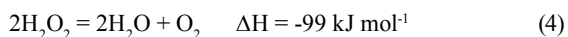


**Figure 1**  
Estimated pH profile for mononuclear Cr(VI) species and hydrogen peroxide species

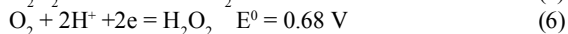
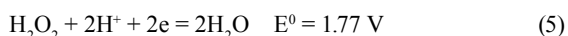


**Figure 2**  
Predominance diagram for dissolved chromium species.  $[\text{Cr}_{\text{aq}}] = 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ ,  $25^\circ\text{C}$  (Beverkog and Puigdomenech, 1996)

H<sub>2</sub>O<sub>2</sub> is thermodynamically unstable:



The standard electrode potentials for Eqs. (5) and (6) show that H<sub>2</sub>O<sub>2</sub> is a strong oxidant, but can also act as a reductant in the presence of very strong oxidants (Cotton et al., 1999):



According to the Nernst equation, this potential will change by -59.2 mV pH<sup>-1</sup> with a change in pH (Rieger, 1994).

### Spectral characteristics of the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction system

Cr(IV) has a distinctive UV/visible spectrum with a large molar absorption coefficient of 1550 dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup> at 350 nm (Wawrzencyk and Cyfert, 1994). In comparison, H<sub>2</sub>O<sub>2</sub> has no usable absorption spectrum. Cr(III), formed during the reduction of Cr(VI) with H<sub>2</sub>O<sub>2</sub> also exhibits a UV/visible spectrum, but with a relatively small molar absorption coefficient of 13.5 dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup> at 350 nm (Wawrzencyk and Cyfert, 1994). Kinetic experiments were therefore carried out in the range 350 to 370 nm (depending on the pH of the reaction mixture) where the absorption by H<sub>2</sub>O<sub>2</sub> and Cr(III) is negligible.

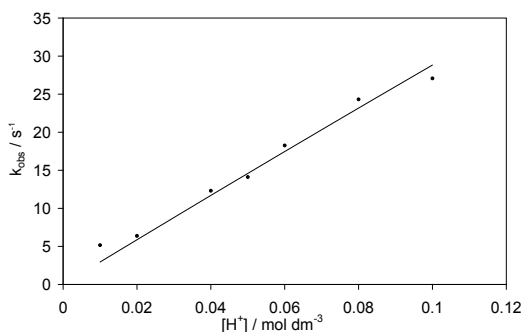
### Effects of pH on Cr(VI) reduction

The influence of pH on the reduction of Cr(VI) by H<sub>2</sub>O<sub>2</sub> was investigated for 2.5 × 10<sup>-4</sup> mol dm<sup>-3</sup> Cr(VI) and 2.5 × 10<sup>-2</sup> mol·dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> solutions.

The observed first-order rate constants for the decrease in [Cr(VI)] as a function of pH, given in Fig. 3, show that the pH of the reaction mixture has a significant effect on the reduction rate.

At pH > 5, very long reaction times together with large H<sub>2</sub>O<sub>2</sub> concentrations were required to reduce Cr(VI) successfully. No further investigations into the reduction of Cr(VI) by H<sub>2</sub>O<sub>2</sub> were therefore conducted at pH > 7.

During this investigation, buffered reaction mixtures were used. Any drift in pH due to the formation of reaction products, would obviously influence the reduction rate. The effect of pH drift on the reaction is reflected by the shapes of the kinetic traces at different pH values. In buffered or non-buffered reaction mixtures where the pH drift was relatively small (pH 3), typical first-order kinetic traces were observed.



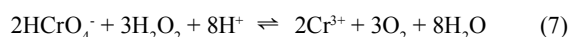
**Figure 3**  
Effect of [H<sup>+</sup>] on the observed rate constants.  
[Cr(VI)] = 2.5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>; [H<sub>2</sub>O<sub>2</sub>] = 2.5 × 10<sup>-2</sup> mol·dm<sup>-3</sup>;  
T = 25.0 ± 0.1 °C

### Reagent concentration dependence

#### [H<sub>2</sub>O<sub>2</sub>] dependence

As shown in the previous section, the initial pH of the reaction mixture is of great importance for effective reduction of aqueous Cr(VI) by H<sub>2</sub>O<sub>2</sub>. The optimum range for Cr(VI) reduction by H<sub>2</sub>O<sub>2</sub> seems to be at low pH values. From the distribution curve of the different Cr(VI) and H<sub>2</sub>O<sub>2</sub> species (Fig. 1), it is clear that the largest changes in speciation occur between pH 4 and 7. At pH = 3.0, there is only one Cr(VI) species, HCrO<sub>4</sub><sup>-</sup>, and one hydrogen peroxide species, H<sub>2</sub>O<sub>2</sub>, present in high concentration and no buffer is needed since no significant pH drift occurs at this pH value during the reaction. pH = 3.0 was therefore chosen as an appropriate pH to investigate the required dosage of H<sub>2</sub>O<sub>2</sub>.

Perez-Benito and Arias (1997) as well as Funahashi et al. (1978) accounted for the stoichiometry of the reaction of Cr(VI) with H<sub>2</sub>O<sub>2</sub> in terms of two overall reactions:

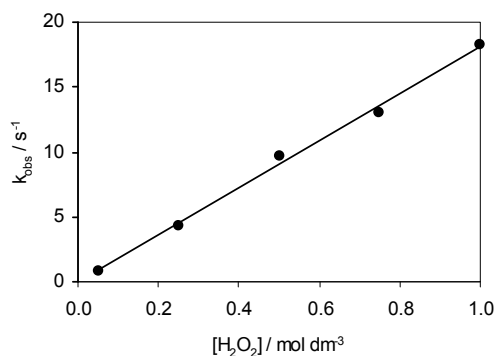


An excess of H<sub>2</sub>O<sub>2</sub> will favour both reactions. Practically an excess of at least 10 times the [Cr(VI)] of H<sub>2</sub>O<sub>2</sub> is required for effective reduction of aqueous Cr(VI). This dosage is efficient over a wide pH range (Fig. 1).

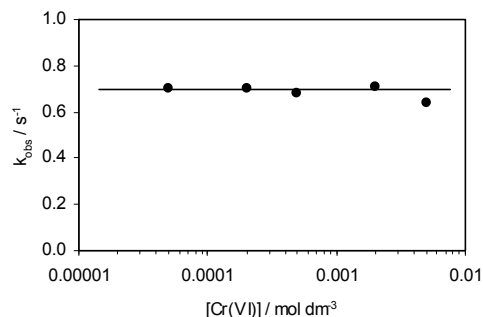
It was also found that the reaction rate has a first-order dependence on the [H<sub>2</sub>O<sub>2</sub>] (see Fig. 4).

#### [Cr(VI)] dependence

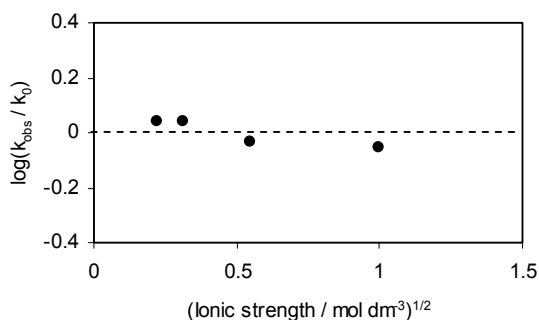
Under pseudo-first-order conditions the observed rate constants showed a zero-order dependence on the [Cr(VI)] (see Fig. 5).



**Figure 4**  
Observed first-order rate constants for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction as function of [H<sub>2</sub>O<sub>2</sub>]. [Cr(VI)] = 2.5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>;  
I = 0.1 mol·dm<sup>-3</sup>; T = 25.0 ± 0.1 °C; pH = 3.0 ± 0.1



**Figure 5**  
Observed first-order rate constants for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction as function of [Cr(VI)]. [H<sub>2</sub>O<sub>2</sub>] = 2.5 × 10<sup>-2</sup> mol·dm<sup>-3</sup>;  
I = 0.1 mol·dm<sup>-3</sup>; T = 25.0 ± 0.1 °C; pH = 3.0 ± 0.1



**Figure 6**

Graphical representation of the experimental data for the ionic strength dependence of the rate constants for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction. [Cr(VI)] = 2.5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>; [H<sub>2</sub>O<sub>2</sub>] = 2.5 × 10<sup>-2</sup> mol·dm<sup>-3</sup>; T = 25.0 ± 0.1°C; pH = 3.0 ± 0.1

### Ionic strength dependence

The effect of ionic strength on the rate of the reaction was investigated at constant [Cr(VI)] and [H<sub>2</sub>O<sub>2</sub>] at pH 3. This pH value was chosen again since here the speciation of Cr(VI) and H<sub>2</sub>O<sub>2</sub> changes slightly with changes in pH (Fig. 1). The results are given in Fig. 6 by using the well-known Eq. (9) that is derived from the Debye-Hückel limiting law (Atkins and De Paula, 2006) by plotting of  $\log(k_{\text{obs}}/k_0)$  vs.  $\sqrt{\text{ionic strength}}$ . In such a plot the interaction of two single charged molecules of the same charge (i.e. a reaction between singly charged cations or anions) will be represented by a slope of 1, two singly charged molecules with opposite charge (i.e. a reaction between a cation and an anion) by a slope of -1 and the interaction involving a neutral molecule will have a slope of zero.

$$\log k_{\text{obs}} = \log k_0 + 2AZ_A Z_B \sqrt{I} \quad (9)$$

From Fig. 6 it can be seen that the slope does not deviate much from zero. This is an indication of uncharged particles involved in the rate-determining step of the process. By considering the distribution of the reagent species (Fig. 1) for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> system, a reaction between H<sub>2</sub>CrO<sub>4</sub>/HCrO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub> is possible under these conditions.

### Effect of radical scavengers

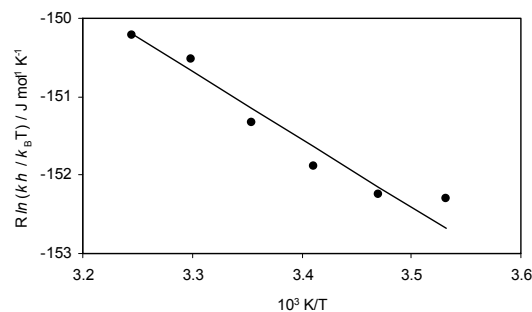
Several authors have already speculated about the possible role of radical scavengers in the reduction of Cr(VI) by H<sub>2</sub>O<sub>2</sub> (Moore et al., 1966; Adams et al., 1968; Funahashi et al., 1978 and Shi et al., 1994). However, the effect of radical scavengers was not investigated in more detail in the mentioned studies. Compounds such as ethanol and tertiary-butanol have in the past been used as radical scavenger in metal/H<sub>2</sub>O<sub>2</sub> systems. Some of these radical scavengers are more effective with respect to hydroxyl radicals than others. Ethanol is regarded as an effective scavenger for hydroxyl radicals (Deister and Warneck, 1990) and was therefore chosen to investigate the role of radicals in the Cr(VI)/H<sub>2</sub>O<sub>2</sub> system.

### Temperature dependence

The temperature dependence of a first-order rate constant,  $k_{\text{obs}}$ , of a reaction can be described by the Eyring equation (Eq. (10)) (Atkins and De Paula, 2006):

$$-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} = \ln\left(\frac{kh}{k_B T}\right) \quad (10)$$

% Ethanol	$k_{\text{obs}} / \text{s}^{-1}$
0.0	0.676 ± 0.002
2.0	0.675 ± 0.002
3.5	0.655 ± 0.001
5.0	0.625 ± 0.003



**Figure 7**

Graphical representation of the temperature dependence of the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction according to the Eyring equation. [Cr(VI)]<sub>initial</sub> = 2.5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>; [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub> = 2.5 × 10<sup>-2</sup> mol·dm<sup>-3</sup>; I = 0.1 mol·dm<sup>-3</sup>; pH = 3.0 ± 0.1

where:

- $\Delta H^\ddagger$  the activation enthalpy
- $\Delta S^\ddagger$  the activation entropy
- $R$  the gas constant
- $T$  the absolute temperature
- $k$  the rate constant
- $h$  the Planck constant
- $k_B$  the Boltzmann constant

The reaction was investigated at pH = 3.0 over the temperature range from 10 to 35°C in the presence of an excess H<sub>2</sub>O<sub>2</sub>.

$\Delta H^\ddagger$ , was calculated from the slope and the activation entropy,  $\Delta S^\ddagger$ , from the intercept of a straight line in Fig. 7.

$$\begin{aligned} \Delta H^\ddagger &= 8.7 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta S^\ddagger &= -122 \pm 4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

### Pressure dependence

The volume of activation,  $\Delta V^\ddagger$ , can be obtained from the pressure dependence of a rate constant, which can be expressed as:

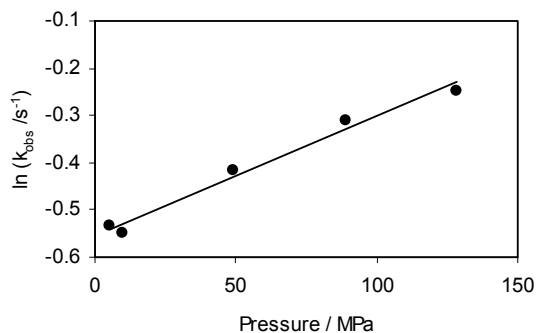
$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (11)$$

A plot of  $\ln k$  vs. pressure is shown in Fig. 8.

From the slope of the plot,  $\Delta V^\ddagger$  was estimated to be  $-6.2 \pm 0.5 \text{ cm}^3\cdot\text{mol}^{-1}$ . The rate constant clearly increases with increasing pressure, which is coupled to a negative volume of activation. This is an indication of an associative process, which can be correlated with a bond formation reaction in the rate-determining step.

### Discussion of kinetic data

The experimental data in Fig. 3 were fitted to the empirical equation that is expected for a rate-determining reaction that is



**Figure 8**

Influence of pressure on the observed rate constants for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction.

$$[\text{Cr(VI)}] = 2.5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}; [\text{H}_2\text{O}_2] = 2.5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}; \\ I = 0.1 \text{ mol}\cdot\text{dm}^{-3}; T = 25.0 \pm 0.1^\circ\text{C}; \text{pH} = 3.0 \pm 0.1$$

preceded by an acid-base equilibrium:

$$k_{\text{obs}} = k'[\text{H}^+]/(K_a + [\text{H}^+]) \quad (12)$$

where:

$k'$  is a first-order rate constant

$K_a$  a deprotonation constant

In order to account for the increase in reaction rate with decreasing pH, one needs to consider the speciation of both Cr(VI) and H<sub>2</sub>O<sub>2</sub> under the selected reaction conditions. The dominant Cr(VI) species are H<sub>2</sub>CrO<sub>4</sub> at pH < 0, HCrO<sub>4</sub><sup>-</sup> at pH 1 - 6 and CrO<sub>4</sub><sup>2-</sup> at pH > 6. From the electrode potentials given in Fig. 2, it is apparent that the increase in reaction rate with decreasing pH can be attributed to H<sub>2</sub>CrO<sub>4</sub> which is the strongest oxidant of the aqueous Cr(VI) species. From Fig. 1 it is apparent that the increase in reaction rate with decreasing pH observed for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction, does not depend on the H<sub>2</sub>O<sub>2</sub> speciation. H<sub>2</sub>O<sub>2</sub>, and not HO<sub>2</sub><sup>-</sup>, is the reactive hydrogen peroxide species under the selected experimental conditions.

The dependence of  $k_{\text{obs}}$  on the H<sup>+</sup> concentration can be accounted for by Eq. (12). As long as [H<sup>+</sup>] is much lower than  $K_a$  a linear relation between  $k_{\text{obs}}$  and [H<sup>+</sup>] will be observed. This is the case up to [H<sup>+</sup>] = 0.1 mol·dm<sup>-3</sup> as seen in Fig. 3, which means that  $K_a$  is much larger than 0.1. The deviation from linearity in Fig. 3 is too small to calculate reliable values for both  $K_a$  and  $k'$ . The value for  $K_{a1}$  = 4.1 mol·dm<sup>-3</sup> reported by Perez-Benito and Arias was used to calculate  $k' = 1210 \pm 36 \text{ s}^{-1}$ .

From the concentration dependence studies it follows that the observed rate constant is not a function of the initial [Cr(VI)]. However, there is a linear dependence on the initial [H<sub>2</sub>O<sub>2</sub>] under pseudo-first-order conditions. A proposed mechanism for the Cr(VI)/H<sub>2</sub>O<sub>2</sub> reaction system should satisfy the first-order dependence in [H<sub>2</sub>O<sub>2</sub>] and the zero-order dependence in [Cr(VI)] in the rate law. Hence it follows that:

$$k_{\text{obs}} = k[\text{H}^+][\text{H}_2\text{O}_2]/(K_a + [\text{H}^+]) \quad (13)$$

by comparing Eq. (12) and Eq. (13), it follows that:

$$k' = k[\text{H}_2\text{O}_2]$$

From the data reported in Fig. 3 it follows that  $k = k'/[\text{H}_2\text{O}_2] = (48.4 \pm 1.4) \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . This rate law correlates with all experimental results. The success to fit the experimental data with  $K_{a1}$  indicates that H<sub>2</sub>CrO<sub>4</sub> is responsible for the increased

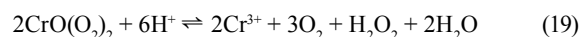
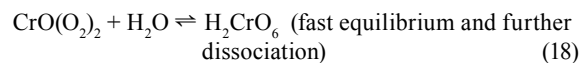
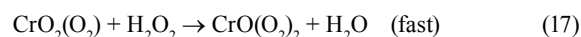
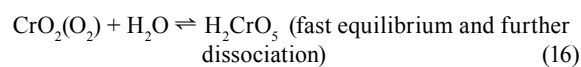
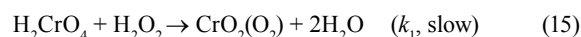
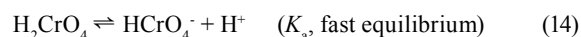
reactivity at low pH. No mathematical fit of the experimental data was possible when  $K_{a2}$  was used instead. A negligible difference in reaction rate for the reduction of Cr(VI) by H<sub>2</sub>O<sub>2</sub> in reaction mixtures with different ionic strength also indicates the presence of a neutral molecule (H<sub>2</sub>CrO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub>) in the rate-determining step. The Cr-OH bond is labile to undergo substitution as indicated by the observation that a weak ligand such as sulphate can replace OH to form a Cr(VI) sulphate complex (Cotton et al., 1999).

The participation of free radicals in at least the rate-determining step(s) can be eliminated due to the fact that the presence or absence of a radical scavenger had no effect on the reduction rate of Cr(VI).

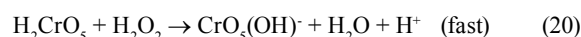
The large negative value of  $\Delta S^\ddagger$  indicates an associative reaction mechanism. On the other hand the small  $\Delta H^\ddagger$  is in accordance with the high lability of the Cr(VI)-OH bond which facilitates substitution by a peroxy group. From the pressure dependence study the volume of activation ( $\Delta V^\ddagger$ ) of  $-6.1 \pm 0.5 \text{ cm}^3\cdot\text{mol}^{-1}$  was calculated, which also points to an associative substitution process (see Discussion). It follows from the values of  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$  that the transition state is highly ordered, since a negative activation entropy and a negative activation volume were observed. This also supports the idea that bond formation occurs during the rate-determining step.

### Suggested mechanism

The following reaction scheme, which is in agreement with all experimental observations, is proposed for the redox process:



The first step Reaction (14) represents the deprotonation equilibrium, followed by the rate-determining formation of the Cr(VI)/H<sub>2</sub>O<sub>2</sub> adduct in Reaction (15). A similar reaction step was proposed by Moore et al. (1966), Orhanovic and Wilkins (1967) and Funahashi et al. (1978). During this reaction an activated complex is formed via a substitution process that can either have an associative or dissociative character (see further discussion). Although there is still a difference of opinion, most authors agree that the intermediate formed during this reaction is the blue peroxochromium(VI) complex CrO(O<sub>2</sub>)<sub>2</sub>. Eqs. (18) and (20) represent the formation of the violet peroxochromium(VI) species, HCrO<sub>6</sub><sup>-</sup>, in slightly acidic or neutral solutions (Witt and Hayes, 1982).



The rapid formation of this compound has no effect on the rate law. Apart from the last step in the proposed mechanism, formation of the blue and violet intermediates probably progresses via a common mechanism.

If it is taken into account that Eq. (15) is the only rate-determining step that contributes significantly to the overall reaction rate, the rate law can be written as:

$$r = k_1[\text{H}_2\text{O}_2][\text{H}_2\text{CrO}_4] \quad (21)$$

The concentration of  $\text{H}_2\text{CrO}_4$  is given by:

$$[\text{H}_2\text{CrO}_4] = [\text{Cr(VI)}]_{\text{T}}[\text{H}^+]/(\text{K}_a + [\text{H}^+]) \quad (22)$$

Substitution of Eq. (22) in (21) gives:

$$r = k_1[\text{Cr(VI)}]_{\text{T}}[\text{H}_2\text{O}_2][\text{H}^+]/(\text{K}_a + [\text{H}^+]) \quad (23)$$

from which it follows that:

$$k_{\text{obs}} = k_1[\text{H}_2\text{O}_2][\text{H}^+]/(\text{K}_a + [\text{H}^+]) \quad (24)$$

This theoretical rate law (Eq. (24)) is in agreement with the empirical rate law (Eq. (13)). According to the proposed reaction scheme, the reported activation parameters are for the overall second-order rate constant  $k_1/\text{K}_a$ . Thus, in terms of the experimental volume of activation,  $\Delta V_{\text{exp}}^{\ddagger} = \Delta V^{\ddagger}(k_1) - \Delta V(\text{K}_a)$ , it consists of contributions associated with the formation of  $\text{H}_2\text{CrO}_4$  and the subsequent substitution process. During the protonation of  $\text{HCrO}_4^-$  in Eq. (14), charge neutralisation and a decrease in electrostriction are expected to cause a significant volume increase. Thus it is reasonable to expect a significantly negative value for  $\Delta V(\text{K}_a)$  for the deprotonation equilibrium such that  $-\Delta V(\text{K}_a)$  will make a significant positive contribution to  $\Delta V_{\text{exp}}^{\ddagger}$ . Since the experimentally observed volume of activation is significantly negative, it follows that  $\Delta V^{\ddagger}(k_1)$  must be even more negative to compensate for the expected positive contribution from  $-\Delta V(\text{K}_a)$ . This suggests that the rate-determining step (Eq. (15)) must involve significant bond formation that is associated with a decrease in the partial molar volume and therefore a negative volume of activation (Van Eldik et al., 2000). At this stage it is not possible to assign a definite value to  $\Delta V^{\ddagger}(k_1)$  since  $\Delta V(\text{K}_a)$  is not known. However, we can conclude that hydrogen peroxide definitely enters the coordination sphere of  $\text{H}_2\text{CrO}_4$  in an associative manner, made possible through the protonation of  $\text{HCrO}_4^-$ . In terms of the structure of  $\text{CrO}_4^{2-}$ , protonation of the strongly coordinated oxo ligands leads to the formation of less strongly bound hydroxo ligands which can then be displaced in  $\text{H}_2\text{CrO}_4$  in an associative manner.

## Conclusions

From the presented results the following conclusions can be drawn:

- The pH of the reaction mixture has a strong effect on the reduction rate of Cr(VI) by  $\text{H}_2\text{O}_2$
- During the non-buffered reduction of Cr(VI) by  $\text{H}_2\text{O}_2$ , a pH drift occurs which influences the reduction process
- Fast and complete reduction of Cr(VI) is favoured at low  $\text{pH}_{\text{initial}}$  ( $1.0 \leq \text{pH}_{\text{initial}} \leq 4.0$ )
- At  $\text{pH}_{\text{initial}} > 7.0$  a very large excess of  $\text{H}_2\text{O}_2$  is required for the effective reduction of Cr(VI)
- The concentration of  $\text{H}_2\text{O}_2$  required for effective reduction of Cr(VI) seems to be in the order of  $[\text{H}_2\text{O}_2] = 100 \times [\text{Cr(VI)}]$  for  $1.0 \leq \text{pH}_{\text{initial}} \leq 4.0$
- The proposed reaction mechanism is valid over a wide pH range ( $1 < \text{pH} < 7$ )

- New information acquired through the pressure dependence study supports the proposed reaction mechanism
- The rate law satisfies the experimental data and corresponds with the empirical rate law
- Calculation of the rate constants for the process is of significant value in terms of environmental impacts. Since the reaction can be an important reduction path for released Cr(VI) compounds in the atmosphere, the results of this study are relevant for industrial applications.

Although hydrogen peroxide would usually not be considered as the primary reductant for the removal of chromates, this study has shown that a hydrogen peroxide treatment of an acid effluent could simultaneously decrease the environmental impact of chromates.

## Acknowledgements

Financial support from Eskom TRI, Eskom HR, NRF and THRIP is gratefully acknowledged.

## References

- ADAMS AC, CROOK JR, BOCKHOFF F and KING EL (1968) The preparation and properties of peroxychromium(III) species. *J. Am. Chem. Soc.* **90** 5761-5768.
- ATKINS PW and DE PAULA J (2006) *Physical Chemistry* (8th edn.). Oxford: Oxford University Press. 1064 pp.
- BALOGA MR and EARLEY JE (1961) The kinetics of the oxidation of Cr(III) to Cr(VI) by hydrogen peroxide. *J. Am. Chem. Soc.* **83** 4906-4909.
- BARTLETT BL and QUANE D (1973) Tetraperoxychromate(V)-diperoxychromate(VI) equilibrium in basic aqueous hydrogen peroxide solutions. *Inorganic Chem.* **12** 1925-1927.
- BEVERSKOG B and PUIGDOMENECH I (1997) Revised Pourbaix Diagrams for chromium at 25 - 300°C. *Corrosion Sci.* **39** (1) 43-57.
- CALDER LM (1988) Chromium contamination of groundwater. In: Nriagu, O.J. and Nieboer E (eds.) *Chromium in the Natural and Human Environments*. New York: Wiley. 215-229.
- COTTON FA, WILKINSON G, MURILLO CA and BOCHMANN M (1999) *Advanced Inorganic Chemistry* (6th edn.). New York: Wiley-Interscience. 1355 pp.
- DEISTER U and WARNECK P (1990) Photo-oxidation of  $\text{SO}_3^{2-}$  in aqueous solution. *J. Phys. Chem.* **94** 2191-2198.
- FUNAHASHI S, UCHIDA F and TANAKA M (1978) Reactions of hydrogen peroxide with metal complexes. 3. Thermodynamic and kinetic studies on the formation, dissociation and decomposition of peroxochromium(VI) complexes in acid media. *Inorg. Chem.* **17** 2784-2789.
- GILI P, MEDEROS A, LORENZO-LUIS PA, DE LA ROSA EM and MUNOZA (2002) On the interaction of compounds of chromium(VI) with hydrogen peroxide. A study of chromium(VI) and (V) peroxides in the acid-basic pH range. *Inorg. Chim. Acta* [Web:] <http://www.elsevier.com/locate/ica> (Accessed on 21 Feb. 2002).
- KIMBROUGH DE, COHEN Y, WINER AM, CREELMAN L and MABUNI C (1999) A critical assessment of chromium in the environment. *Crit. Rev. Environ. Sci. Technol.* **29**: 1-46. [Web:] [http://polysep.ucla.edu/Publications/view\\_papers.htm](http://polysep.ucla.edu/Publications/view_papers.htm) (Accessed on 14 March 2001).
- MOORE P, KETTLE SFA and WILKINS RG (1966) The kinetics of formation of blue peroxychromic acid in aqueous solution. *Inorg. Chem.* **5** 466-467.
- ORHANOVIC M and WILKINS RG (1967) Kinetic studies of the reactions of peroxy compounds of chromium(VI), vanadium(V) and titanium(IV) in acid media. *J. Am. Chem. Soc.* **89** 278-282.
- PEREZ-BENITO JF and ARIAS C (1997) A kinetic study of the chromium(VI)-hydrogen peroxide reaction. Role of the diperoxychromate(VI) intermediates. *J. Phys. Chem.* **101** 4726-4733.

- RAID, EARY LE and ZACHARA JM (1989) Environmental chemistry of chromium. *Sci. Tot. Environ.* **86** 15-23.
- RAI D, SASS BM and MOORE DA (1987) Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorg. Chem.* **26** 345-349.
- RIEGER PH (1994) *Electrochemistry* (2<sup>nd</sup> edn.), Chapman and Hall. 483 pp.
- SHI X, MAO Y, KNAPTON AD, DING M, ROJANASAKU Y, GANNETT P, DALAL N and LUI K (1994) Reaction of Cr(VI) with ascorbate and hydrogen peroxide generates hydroxyl radicals and causes DNA damage: role of a Cr(VI)-mediated Fenton-like reaction. *Carcinogenesis* **15** 2475-2478.
- UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA) (2002) *National Primary Drinking Water Regulations*. [Web:] <http://www.epa.gov/safewater/dwh/c-ioc/chromium.html> (Accessed on 16 Jan. 2002).
- UNIVERSITY OF CAPE TOWN (UCT), Graduate School of Business. (2001) A Perspective on the South African Mining Industry in the 21<sup>st</sup> Century. An independent report. Chamber of Mines of South Africa Publication. [Web:] <http://www.bullion.org.za/bulza/pgs/onpub.htm> (Accessed on 20 March 2001).
- VANDER GRIEND DA, GOLDEN JS and ARRINGTON CA(Jr) (2002) Kinetics and mechanism of chromate reduction with hydrogen peroxide in base. *Inorg. Chem.* **41** 70042-7048.
- VAN ELDIK R, GAEDE W, WIELAND S, KRAFT J, SPITZER M and PALMER DA (1993) Spectrophotometric stopped-flow apparatus suitable for high-pressure experiments to 200 MPa. *Rev. Sci. Instrum.* **64** 1355-1357.
- VAN ELDIK R, DÜCKER-BENFER C and THALER F (2000) Inorganic and bioinorganic reaction mechanisms: Application of high-pressure techniques. *Adv. Inorg. Chem.* **49** 1-58.
- VOGEL AI (1989) *Vogel's Textbook of Quantitative Chemical Analysis* (5<sup>th</sup> edn.). Essex: Longman Scientific and Technical. 877 pp.
- WITT SN and HAYES DM (1982) Kinetics and mechanism of the formation of violet peroxychromate in aqueous solution. *Inorg. Chem.* **21** 4014-4016.
- WONG PTS and TREVORS JT (1988) Chromium toxicity to algae and bacteria. In: Nriagu OJ and Nieboer E (eds.) *Chromium in the Natural and Human Environments*. New York: Wiley. 305-315.
- YASSI A and NIEBOER E (1988) Carcinogenicity of chromium compounds. In: Nriagu OJ and Nieboer E (eds.) *Chromium in the Natural and Human Environments*. New York: Wiley. 443-495.
- ZHANG L and LAY PA (1998) EPR spectroscopic studies on the formation of chromium(V) peroxo complexes in the reaction of chromium(VI) with hydrogen peroxide. *Inorg. Chem.* **37** 1729-1733.
-

