

## Short communication

# The reduction of hexavalent chromium by sulphite in wastewater - An explanation of the observed reactivity pattern

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### Abstract

The reduction of Cr(VI) by S(IV) was investigated in buffered aqueous solutions, with the specific goal to establish the reactive Cr(VI) and/or S(IV) species, so that the reactivity pattern of this reaction could be explained. Reaction rates were investigated as a function of [S(IV)], pH and ionic strength. The [S(IV)]-dependence showed that the reaction is second order with respect to the [S(IV)]. From the pH-dependence of the reaction a typical S-shaped curve was obtained. From this curve an apparent  $pK_a$  value was calculated, which indicated that the increase in reactivity at lower pH values can be correlated to the increase in the concentration of the  $SO_2 \cdot H_2O(aq)$  species of S(IV). The effect of ionic strength on the reaction rate supported this theory, since it proved that an interaction involving a neutral molecule (i.e.  $SO_2 \cdot H_2O(aq)$ ) takes place in the rate determining reaction step. In conclusion it can be said that the reactivity vs. pH pattern of this very important industrial and environmental reaction system can now be explained satisfactorily.

### Introduction

In our previous article (Beukes et al., 1999) the reduction of hexavalent chromium by S(IV) (refer to Beukes et al., 1999 for the definition of this term) in wastewater was discussed extensively. It was proven that S(IV) could be used as an effective reducing agent for Cr(VI) in wastewater under specific reaction conditions. There were, however, some experimental observations that could not be explained satisfactorily with either experimental (Beukes et al., 1999) or published results (Brandt and Elding, 1998; Haight et al., 1965; Wawrzenczyk and Cyfert, 1994). To be more precise, the increase in reduction rate with increasing acidity, could not be explained. This can mainly be attributed to the fact that our previous investigation was conducted in unbuffered aqueous media. Since pH-drift made it impossible to measure rate constants accurately, a pH-profile from which a  $pK_a$  value could be derived, could not be constructed. From such a pH-profile it might be possible to determine the reactive S(IV) and/Cr(VI) species. The results reported in this article gives new insight into the above-mentioned problem and offers a feasible explanation.

### Experimental

#### Materials

Analytical grade reagents of the highest purity were obtained from different suppliers and used without any further purification. Sodium metabisulphite ( $Na_2S_2O_5$ ) (BDH) dissolved in water was used as the aqueous source of S(IV). Fresh S(IV) solutions were prepared just prior to measurements. The pH of reaction mixtures between pH 3.5 and 5.5 were kept constant by using suitable buffer solutions (the selection of buffers is discussed later), while the pH

of solutions at  $pH \leq 2.5$  were adjusted prior to mixing by addition of calculated volumes of a stock solution of perchloric acid ( $HClO_4$ ) (BDH). The ionic strength of all solutions was kept constant ( $0.1 \text{ mol} \cdot \text{dm}^{-3}$ ) by addition of calculated volumes of a stock solution of sodium perchlorate ( $NaClO_4 \cdot H_2O$ ) (Merck). Millipore milli-Q deionised water ( $>18 \text{ M}\Omega \text{ cm}$ ) was used to prepare all solutions.

#### Measurements

All kinetic experiments were carried out on an SX-17MV Stopped-Flow spectrophotometer from Applied Photophysics. The temperature of all reagent mixtures was kept constant at  $25 \pm 0.5^\circ\text{C}$  by using a circulating Haake F3 Fisons thermostatic water bath. The pH of solutions was measured with a Hanna Instruments (HI) 9318 pH meter, fitted with an HI 1131 pH electrode and an HI 7669/2 temperature sensor.

Kinetic measurements were conducted at 350 nm, due to the reasons mentioned before (Beukes et al., 1999). The calculations of rate constants were done using the "Applied Photophysics SX-17MV Kinetic Spectrometer Workstation" software package. A modern version of the Marquardt algorithm, based on the routine "Curfit" is used by this program to fit the kinetic runs. A typical kinetic trace, with the fit of the calculated reaction rate superimposed on it, is shown in Fig. 1.

### Results and discussion

#### Selection of a suitable buffer

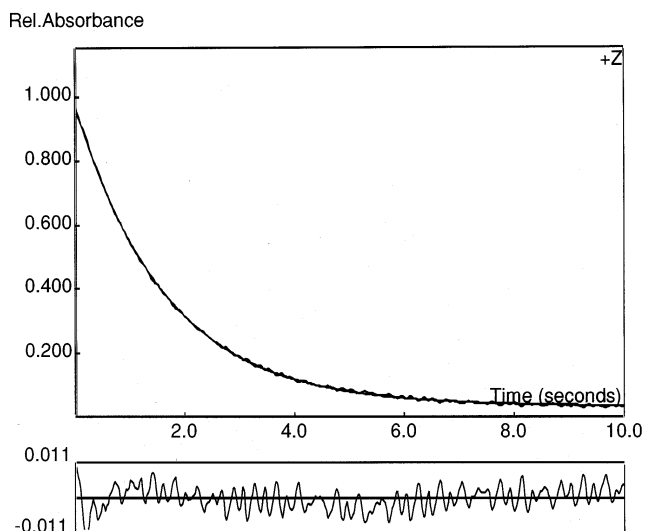
During the reduction of Cr(VI) by S(IV) in unbuffered solutions, pH drift was observed. In order to stabilise the pH, a suitable buffer was required. From earlier investigations (Beukes et al., 1999) it was clear that the pH range of  $1.0 \leq pH \leq 5.5$  would be of importance for a detailed kinetic investigation of the Cr(VI)/S(IV) reaction system. Since negligible pH drift occurred below pH 2.5, a buffer which would be effective from pH 3.0 to 5.5 was required. The sodium acetate/acetic acid buffer was found to be suitable to buffer

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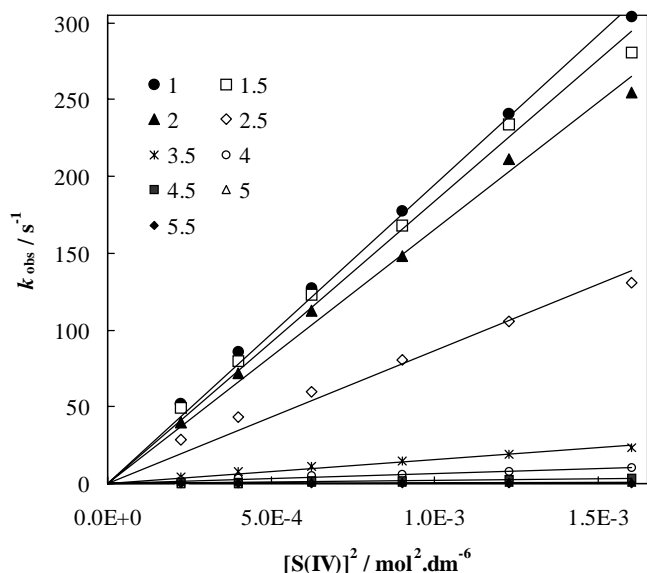
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**Figure 1**

A typical kinetic trace for the Cr(VI)/S(IV) reaction, with the data fitted to a first-order law superimposed on the kinetic trace. The small figure below the kinetic trace shows the deviation of the experimental trace from the fit.  $[Cr(VI)] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ;  $[S(IV)] = 1.5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ;  $\text{pH} = 4.5 \pm 0.1$ ;  $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$ ;  $\lambda = 350 \text{ nm}$



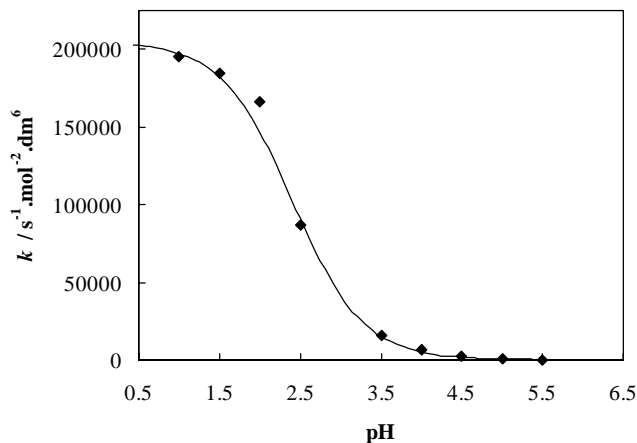
**Figure 2**

Observed rate constants plotted against the square of  $[S(IV)]$ .  $[Cr(VI)] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ;  $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$

the Cr(VI)/S(IV) reaction in the pH range of 3.5 to 5.5, while not interfering with the reaction. Haight et al. (1965) also used the acetate buffer while investigating the Cr(VI)/S(IV) reaction system. The acetate buffer has also been used for other Cr(VI) reactions systems, for instance during the reduction of Cr(VI) by Fe(II) (Buerge and Hug, 1997).

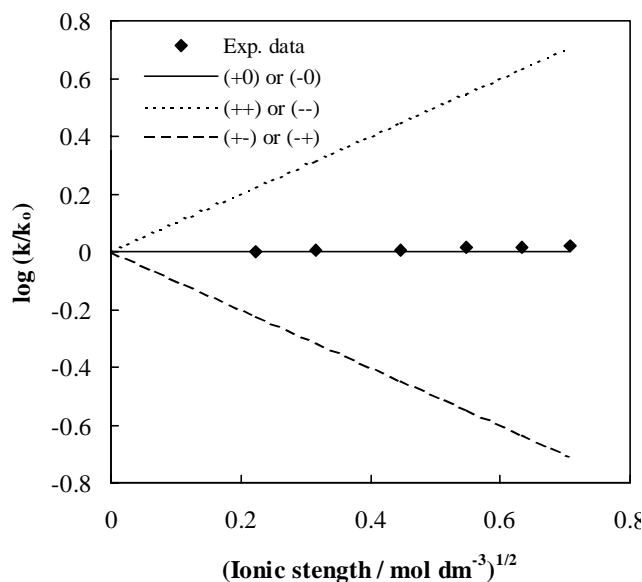
### Kinetic studies

The pH and  $[S(IV)]$ -dependencies of the reaction was investigated over the pH range of 1.0 to 5.5, with the S(IV) concentrations ranging from 30 to 80 times the initial Cr(VI) concentration. It was



**Figure 3**

pH dependence for the Cr(VI)/S(IV) reaction (Marks indicate experimental results, while solid lines indicate computer fit according to equation 1).  $[Cr(VI)] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ;  $[S(IV)] = 1.5 \text{ to } 4.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ;  $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$



**Figure 4**

Effect of ionic strength on the reaction rate.  $[Cr(VI)] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ;  $[S(IV)] = 2.5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ;  $\text{pH} = 4.0 \pm 0.1$ ;  $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$

observed that the measure rate constants ( $k_{\text{obs}}$ ) increased quadratically as the  $[S(IV)]$  increased at a constant pH. This phenomenon persisted over the entire pH range investigated. Haight et al. (1965), as well as Wawrzenczyk and Cyfert (1994) reported that the Cr(VI)/S(IV) reaction is second-order, with respect to the  $[S(IV)]$ . This was confirmed in this study, since a graph of the observed rate constants ( $k_{\text{obs}}$ ) plotted against the square of the  $[S(IV)]$  yielded straight lines through the origin (Fig. 2). This result proves that the second order dependence of the reaction is not only valid over the small pH ranges reported previously by Haight et al. (1965) as well as Wawrzenczyk and Cyfert (1994), but that it remains valid for the entire pH range of  $1.0 \leq \text{pH} \leq 5.5$ .

The pH-dependence of the reaction has previously been studied in an acetate buffered solution (Haight et al., 1965) over the narrow pH range of 4.18 to 5.05 and in a perchloric acid medium

(Wawrzenczyk and Cyfert, 1994) over the pH range of 1.15 to 1.85. These small pH ranges made it impossible to suggest, with any degree of certainty, which S(IV) and/or Cr(VI) species react in the rate determining reaction step(s). By plotting the slopes of the straight lines obtained in Fig. 2 (i.e. the third-order rate constants) against the pH, an S-shaped curve was obtained (Fig. 3). In order to obtain a  $pK_a$  value from this curve, the experimental data were fitted to Eq. (1) by using the non-linear least-squares program, "Table Curve".

$$k = \frac{k_b K_a + k_a [H^+]}{K_a + [H^+]} \quad (1)$$

with:

- $k$  the measure second-order rate constant at a specific  $[H^+]$  ( $[H^+] = 10^{-pH}$ )
- $K_a$  the acid dissociation constant
- $k_a$  the minimum value of  $k$
- $k_b$  the maximum value of  $k$ .

Figure 3 shows the experimental data together with the computer fit (represented by the solid lines) of the data. From the computer fit an apparent  $pK_a$  value of  $2.4 \pm 0.3$  was obtained for the Cr(VI)/S(IV) reaction. This  $pK_a$  is called an apparent  $pK_a$  value, since it is not necessarily the  $pK_a$  of a single species, but could be a combination of the  $pK_a$ 's of different reactive species. This  $pK_a$  value ( $2.4 \pm 0.3$ ) is in reasonable agreement with the first  $pK_a$  of S(IV) ( $pK_a = 1.9$  - Brandt and Van Eldik, 1995), indicating that the  $SO_2 \cdot H_2O(aq)$  species is responsible for the increased reactivity at low pH values. The difference between the apparent  $pK_a$  value and the  $pK_a$  value of  $SO_2 \cdot H_2O(aq)$  can probably be attributed to the fact that  $SO_2 \cdot H_2O(aq)$  is in equilibrium with  $SO_2(g)$  at low pH values. This equilibrium will cause a fraction of the [S(IV)] to be lost to the atmosphere under these conditions, resulting in reaction rates slower than expected. The validity of this hypothesis was confirmed by a calculation which showed that an increase (which represents the amount of S(IV) lost to the atmosphere) in the [S(IV)] of only 2.5% at pH 1.5 and 5.9% at pH 1.0, would result in an apparent  $pK_a$  in full agreement with that reported by Brandt and Van Eldik (1995) for  $SO_2 \cdot H_2O(aq)$ . The reason why these small changes in [S(IV)] have such a strong effect on the apparent  $pK_a$  value, is due to the fact that the reaction rates (which determine the apparent  $pK_a$ ) are exponentially related to the [S(IV)] (see first paragraph under the heading "Kinetic studies").

The effect of ionic strength, on the reaction rate, was investigated at constant [Cr(VI)] and [S(IV)] at pH 4.0. This pH value was chosen, since the kinetic behaviour of the reaction is not likely to be influenced by small changes in the  $pK_a$  values (apparent  $pK_a$ ,  $SO_2 \cdot H_2O$   $pK_a$  and the  $HCrO_4^-$   $pK_a$ ), caused by varying the ionic strength. The results obtained are presented graphically in the format suggested by Atkins (1990) – a graph of  $\log(k/k_0)$  vs.

$\sqrt{\text{ionic strength}}$  (Fig. 4). In such a graph a positive slope of one indicates the interaction of similarly charged molecules, a slope of minus one the interaction of molecules with different charges and no slope an interaction involving a neutral molecule. As can be seen from Fig. 4, the experimental results clearly indicate an interaction involving a neutral molecule. This result suggests that a neutral molecule (i.e.  $SO_2 \cdot H_2O(aq)$ ) reacts in the rate determining reaction step, confirming the findings suggested by the  $pK_a$  determination in the preceding paragraphs.

## Conclusions

Results obtained from investigating the reduction of Cr(VI) by S(IV), as a function of [S(IV)], pH and ionic strength, in buffered aqueous solution proved that the reactivity pattern of the reaction can be described to the speciation of S(IV). In all of the previously published investigations, the authors could only speculate over the reason(s) for the increase in reduction rates at lower pH values. This is the first time that an explanation, backed by experimental proof, for the observed reactivity pattern is published. A better understanding of this reaction system, whether applied to the reduction of Cr(VI) in wastewater (Beukes et al., 1999) or observed in natural systems like the atmosphere (Seigneur and Constantinou, 1995), is therefore possible.

## Acknowledgements

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## References

- ATKINS PW (1990) *Physical Chemistry* (4<sup>th</sup> edn.) Oxford: Oxford Univ. Press. 995 pp.
- BEUKES JP, PIENAAR JJ, LACHMANN G and GIESEKKE EW (1999) The reduction of hexavalent chromium by sulphite in wastewater. *Water SA* **25** 363-370.
- BRANDT C and ELDING LI (1998) Role of chromium and vanadium in the atmospheric oxidation of sulfur(IV). *Atmos. Environ.* **32** 797-800.
- BRANDT C and VAN ELDIK R (1995) Transition metal-catalysed oxidation of sulfur(IV) oxides. Atmospheric-relevant processes and mechanisms. *Chem. Rev.* **95** 119-190.
- BUERGE IJ and HUG SJ (1997) Kinetics and pH dependence of chromium(VI) reduction by iron(II). *Environ. Sci. Technol.* **31** 1426-1432.
- HAIGHT GP, PERCHONOCK E, EMMENEGGER F and GORDON G (1965) The mechanism of the oxidation of sulfur(IV) by chromium in acid solution. *J. Am. Chem. Soc.* **87** 3835-3840.
- SEIGNEUR C and CONSTANTINOUE E (1995) Chemical kinetic mechanism for atmospheric chromium. *Environ. Sci. Technol.* **29** 222-231.
- WAWRZENCZYK M and CYFERT M (1994) Kinetics of sulphite oxidation by Cr(VI) in acid media. *Pol. J. Chem.* **68** 1615-1620.

