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 satisfactory.

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 satisfactory 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

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of solutions at pH ≤ 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 mol·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 MΩ 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 ± 0.5°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 ≤ pH ≤ 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