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

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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 2.5×10^{-4} mol·dm^{-3} Cr(VI) solution, a H_2O_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 ($\Delta H^{\neq}$) was calculated to be 10.4 ± 0.5 kJ·mol^{-1} and the activation entropy ($\Delta S^{\neq}$) to be -186 ± 3 J K^{-1}·mol^{-1} for the rate-determining step. The volume of activation ($\Delta V^{\neq}$) was found to be -6.1 ± 0.5 cm^3·mol^{-1} from the pressure dependence of the reaction rate. The empirical data could be fitted to: $k_{obs} = k[H^+][H_2O_2]/(K_a + [H^+])$, with $k = (48.4 \pm 1.4) \times 10^3$ dm^3·mol^{-1}·s^{-1} and K_a the acid dissociation constant of H_2CrO_4. A reaction mechanism in which a Cr(VI)/H_2O_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 6th 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 Cr_2O_3 and $Cr(OH)_3$) 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 $Cr(OH)_3$ 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 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 mg·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, olimerisation, and redox reactions (Baloga, 1961).

Several investigations have been conducted on the reduction of Cr(VI) by H_2O_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 H_2O_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.