Kinetics and mechanism of the reduction of enneamolybdonickelate(IV) by iodide

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Abstract

The kinetics and mechanism of the reduction of enneamolybdonickelate(IV) by iodide in acid aqueous solution was studied by spectrophotometry. The reaction rate increases, as the concentration of H⁺ increases and with temperature. It shows that the reaction rate law is:

$$\frac{d[Ni^{IV}_M]}{dt} = k_{obs}[Ni^{IV}_M]_T$$

The reaction rate constants and activation parameters of the rate-determining steps were evaluated. A mechanism related to the reaction is proposed.

Introduction

Heteropolyacids and their salts are known to act as acidic and re oxidation–reduction of heteropolyacids and heteropolyacid salts are instructive because of their use as redox catalysts. However, most authors have paid attention to studying the catalytic activity of heteropolyanions and their salts, having Keggin and/or Dawson structures [4–7], in which the heteroatom is coordinated to four oxygen atoms in a tetrahedral arrangement. No papers have reported on other types of heteropolyanions applied as catalysts. Ammonium enneamolybdonickelate(IV) $\{([NH_4]_6[NiMo_9O_{32}]6H_2O)\}$ is a Waugh-type heteropolyacid salt in which nickel is coordinated to six oxygen atoms in a slightly distorted octahedral arrangement. Each of these oxygen atoms is coordinated to three molybdenum atoms and each molybdenum atom is also surrounded by six atoms albeit in a very distorted octahedral geometry. Figure 1 illustrates the structure of the enneamolybdonickelate ion cluster. It can oxidize substances, including organic and inorganic reagents [8]. Very few references to the kinetics and mechanism of this-type heteropolyacid salts have been found. A study on the kinetics and mechanism of the reduction of enneamolybdonickelate(IV) by iodide may throw some light on the Waugh structure of heteropolyacids and their salts as catalysts.

Experimental

Materials

Ammonium enneamolybdonickelate(IV) (Ni^{IV}_M) was prepared by the method described earlier [9]. Solutions of KI (AR) were prepared by directly weighing the samples, then checking on the purity was carried out by the titration method against thiosulfate. KNO₃ was used for adjusting the ionic strength. All reactants were prepared by dissolving in doubly distilled water degaerated with nitrogen.

Test for free radical

Generation of free radicals during the course of the reaction was confirmed by polymerization of acrylonitrile (AR) in the solution. No precipitate was produced after adding a certain amount of MeCN to mixed solutions of the reactants 60 min later.

Kinetic measurements

Kinetic measurements were made in a UV-265 spectrophotometer (made in Japan) equipped with a thermostatic cell holder. The appropriate amount of oxidative and reductive solution were placed in the thermostatic bath equipped on the UV-265 spectrophotometer for 10 min. The following two kinds of solutions were then mixed. The reaction rates were determined by observing the decrease in absorption at 564 nm, the maximum absorption of Ni^{IV}_M solution, under the conditions in which the concentration of I⁻ is in large excess over that of Ni^{IV}_M. The temperature of the reaction was controlled to 295 ± 0.10 K. The pH value was measured on a pHS-2 model pH-meter. All experiments were carried out in a 99.9% nitrogen atmosphere.

Results and discussion

The order of reaction dependence on Ni^{IV}_M

We obtained the $(A_t - A_\infty)$ values from curves of absorbance $(A_t)$ versus time $(t)$ of the reaction of Ni^{IV}_M
with iodide. The values of $\ln(A_t - A_\infty)$ versus time were plotted in Figure 2. It can be seen that $\ln(A_t - A_\infty)$ versus $t$ is linear. Therefore, the pseudo-first-order reaction dependence on $[\text{Ni}^{IV}_M]$ was confirmed.

*Determining the order of reaction dependence on iodide*

For a given $\text{Ni}^{IV}_M$ concentration, temperature, pH and ionic strength, the rates $\left(-\frac{d_c\text{Ni}^{IV}_M}{dt}\right)$ can be obtained from the $A_t$ versus $t$ curves of the reaction between $\text{Ni}^{IV}_M$ and different concentrations of iodide. Plot of $\ln \left(-\frac{d_c\text{Ni}^{IV}_M}{dt}\right)$ versus $[\text{I}^-]$ is not linear. The slope of the line is 0.13 which indicates that the reaction with respect to $[\text{I}^-]$ is of fractional order. This means the $[\text{I}^-]$ is in the numerator and denominator in the fraction. Various fractional orders with respect to $[\text{I}^-]$ were tried. Only $[\text{I}^-]/k_{\text{obs}}$ dependence on the concentration of $[\text{I}^-]$ increases linearly (Figure 3). Therefore, there may be a pre-equilibrium.

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**Fig. 1.** The structure of the enneamolybdenickelate(IV) cluster.

**Fig. 2.** Dependence of $\ln(A_t - A_\infty)$ on $t$.

**Fig. 3.** Relation between $[\text{I}^-]/k_{\text{obs}}$ and concentration of iodide ($[\text{I}^-]$).