KINETICS AND MECHANISM OF REDUCTION OF SOME METAL IONS BY SODIUM TETRAHYDROBORATE

SUMMARY.

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There has been continued and sustained interest in establishing the role of sodium tetrahydroborate as a reducing agent, capable of reducing diverse kinds of organic substrates such as aldehydes, ketones, esters and anhydrides. The usefulness of sodium tetrahydroborate as a hydrogen generator has also been recognised. Very few studies have focused attention on the efficacy of sodium tetrahydroborate as a reagent capable of effecting the reduction of inorganic substrates, such as metal ions.

The purpose of this investigation has been to study the kinetic features of the reduction of metal ions by sodium tetrahydroborate, and to establish mechanistic pathways for such reduction reactions. During the course of the reduction of metal ions by sodium tetrahydroborate, attempts were also made to design novel methods for the preparation of some compounds, which were either the final products of such reduction reactions or were the compounds derived from these final products.

The kinetics of reduction of various metal ions by sodium tetrahydroborate, has been studied. The metal ions which have been used for the purposes of reduction have included :

1. Titanium(IV) and Zirconium(IV): Chapter 1
2. Iron (III): Chapter 2
3. Copper (II): Chapter 3
4. Bismuth (V): Chapter 4

Reaction mixtures containing the metal ion (M^{n+}, where n was the common oxidation state of the metal), and an excess of sodium tetrahydroborate, taken in water, containing requisite amounts of acid (or alkali) were allowed to react to completion at the particular temperature. The metal ion which was left was analysed, spectrophotometrically, at the corresponding λ_{max} for the particular metal ion. The individual stoichiometric equations have been shown along with the reactions of each of the metal ions with the reductant (sodium tetrahydroborate).

During the kinetic runs, the progress of all the reduction reactions were followed, spectrophotometrically, by observing the disappearance of the metal ion species at its λ_{max}.

The decomposition of sodium tetrahydroborate, as a function of time, was studied. This enabled the determination of the rate and the extent of hydrolysis of sodium tetrahydroborate, and also helped in the elucidation of the probable mechanistic pathway of the hydrolytic reaction. Since sodium tetrahydroborate underwent hydrolysis in aqueous medium, all the solutions used for the kinetic runs were prepared by dissolving an additional calculated amount of sodium tetrahydroborate, in order to compensate for the loss of any sodium tetrahydroborate due to its hydrolysis.

The rates of all the reduction reactions were found to be dependent on the first powers of the concentrations of both, the metal ions and the tetrahydroborate ions. The rates of the reactions were dependent on the pH of the medium. The logarithm of the rate of disappearance of metal ion divided by the tetrahydroborate ion concentrations, in each case, was plotted against the respective pH. The plots were linear, indicating the first order dependence of the rate on hydrogen ion concentration.

The effect of changes in temperature on the rates of these reduction reactions has been studied, and the activation parameters have been evaluated. The large negative entropies of activation indicated a highly ordered transition state for the reduction reactions, and also supported the observation that the process of electron transfer played a dominant role in these reduction processes.

Reduction of the metal ions by sodium tetrahydroborate had resulted in the formation of the lower oxidation state of the metal ions, and BH_3OH^- ion as the boron intermediate. The metals in their lower oxidation states, formed in each of the reduction reactions, were converted back to the stable oxidation states. The metal ions, in this oxidation state, were characterized by chemical and spectral methods.

Titanium (IV) and zirconium (IV) were reduced to titanium (III) and zirconium (III), respectively. In the final stage, the titanium compound obtained was titanium dioxide (TiO_2), while the zirconium compound obtained was $ZrO_2.2H_2O$. The titanium and zirconium compounds, thus obtained in the +4 state, were characterized by chemical and spectral methods.

Iron (III) was reduced to iron (II), which was characterized as the iron (II) complex, $Fe_4[Fe(CN)_6]_3$, by chemical and spectral methods.

Copper (II) was reduced to copper (I), which was characterized by chemical and spectral methods. The oxidation state of copper in the final product, was chemically determined as Cu(I). The IR spectrum of cuprous hydride (CuH), formed as the final product of the reaction, showed an intense peak at 521 cm^{-1}, which was assigned to the presence of a ...Cu...H...Cu...H... bridge-type structure. The absence of any peaks in the region between

2250 cm^{-1} and 1700 cm^{-1} indicated a low covalent character of CuH.

Bismuth (V) was reduced to bismuth (III), via the bismuth (II) state. In the +2 state, the bismuth compound was isolated as bismuth monoxide (BiO), which was characterized by chemical and spectral analyses. The IR spectrum of BiO showed an intense peak at 970 cm^{-1}, which could be assigned to (Bi=O) stretching, typical of metal-oxygen double bond stretching. The weak band at 500 cm^{-1} was assigned to intramolecular bonding among BiO units through oxygen.

$$...Bi=O...Bi=O...$$

The final state of reduction of bismuth (V) was the bismuth (III) species. In the +3 state, the bismuth compound was isolated as bismuth oxychloride (BiOCl), which was analysed by chemical and spectral methods. IR bands were obtained at 529, 340 and 285 cm^{-1}, which were typical bands for the compound BiOCl.

The reduction of all these metal ions (titanium, zirconium, iron, copper and bismuth), by sodium tetrahydroborate in acid or alkaline medium, had resulted in the formation of the stable oxidation state of the respective metal ions in the final product. The reaction proceeded via an unstable lower oxidation state, with the formation of the boron intermediate, $[BH_3OH]^-$. In the case of each metal ion, the boron compound was isolated as $Na[BH_3OH].H_2O$, and characterised by chemical and spectral analyses.

Since the rates of these reactions were dependent on the concentrations of both, tetrahydroborate (BH_4^-) and hydrogen ion (H^+), the chemical composition of the activated complex could be written as $H^+BH_4^-$. The first step of the reaction was

$$BH_4^- + H^+ \longrightarrow H^+BH_4^- \qquad (1)$$

The mechanistic pathway for the reduction reaction could be visualised by a kinetic scheme consisting of equation (1), followed by consecutive steps involving the reaction of the metal ion with the activated boron complex. This would involve the reaction of the boron intermediate with either a metal ion, or with a hydrogen producing species, such as water. For example, considering the reaction of hexacyanoferrate (III) with $H^+BH_4^-$, the reaction could be written as

$$H^+BH_4^- + 2[Fe(CN)_6]^{3-} + H_2O \longrightarrow BH_3OH^- + 2[Fe(CN)_6]^{4-} + 3H^+ \quad (2)$$

The intermediate species, BH_3OH^-, could be considered as the intermediate boron species. Earlier investigations had provided evidence for the existence of such intermediates, from the reactions of diborane with ice and with "bound water" in silica gel. These boron intermediates differed in their reducing capacities, and the formulae of such intermediates helped to show their reducing capacities. For example, the intermediate $BH(OH)_2^-$, would have three equivalents of reducing capacity, while an intermediate of the type, $BH(OH)_2$, would have a two-electron reducing capacity.

In the present investigation, experimental evidence has been obtained for the formation of BH_3OH^- as the intermediate boron compound.

During the course of this investigation pertaining to the kinetics of the reduction of metal ions by sodium tetrahydroborate, attempts were also directed towards exploring novel methods for the preparation and isolation of some compounds of the metal ions in their lower oxidation states. These have included methods for the preparation and isolation of compounds such as cuprous hydride (CuH), and bismuth monoxide (BiO).

(i) Cuprous Hydride (CuH)

Earlier work had reported the formation of anhydrous cuprous hydride by the reaction of copper(I) and lithium tetrahydroaluminate, in ether-pyridine solvent. In the present investigation, water-insoluble cuprous hydride was prepared by the reduction of copper(II) sulphate by sodium tetrahydroborate in ammonium hydroxide medium. Cuprous hydride was precipitated from the reaction mixture. Chemical analysis established that the percentage of copper in this product was 96.3% (theoretical percentage of copper in CuH = 98.4%). The oxidation number of copper in this product was established to be +1 (Cu^+). The IR spectrum of this compound gave an intense peak at 521 cm^{-1}, which was assigned to the presence of a ---Cu---H---Cu---H--- bridge-type structure. Absence of any peaks in the region between 2250 cm^{-1} and 1700cm^{-1} indicated low covalent character. The chemical and spectral analyses conclusively established the compound to be cuprous hydride, CuH.

This method of preparation of cuprous hydride is perhaps the first reported method wherein cuprous hydride(CuH) has been prepared by the sodium tetrahydroborate reduction of any copper(II) compound.

(ii) Bismuth Monoxide (BiO)

When bismuth (V) was treated with sodium tetrahydroborate ($NaBH_4$),in HCl medium, a purple coloured solution was obtained, which subsequently gave a black precipitate. On work-up, this compound was characterized as BiO (bismuth monoxide), indicating that bismuth was in the +2 state. On treating the black precipitate (BiO) with concentrated hydrochloric acid, a clear solution was obtained. On dilution with water, a milky white suspension was obtained. The precipitate was characterized as BiOCl, which indicated that bismuth(V) was reduced to the +3 state. It can, therefore, be postulated that $NaBH_4$, in HCl medium, was able to reduce bismuth(V) to the bismuth(III) state, via an unstable bismuth(II) intermediate.

The experimental results of the present kinetic investigation have helped in unequivocally establishing the significant role of sodium tetrahydroborate as a reagent capable of bringing about the reduction of metal ions. The importance of the kinetic aspects of such reduction reactions and the significance of the energy factors contributing to the understanding and elucidation of the mechanistic pathways, have been highlighted during the course of this investigation. The present study has also revealed the utility of sodium tetrahydroborate in the prepration of novel compounds of metals in their lower oxidation states. The simplicity of such reduction reactions has thus established the important facets of sodium tetrahydroborate in terms of its capability to reduce metal ions, and as a reagent which could be used for the preparation of newer compounds of metals in their lower oxidation states.