# KINETICS OF REDUCTION OF TRANSITION METAL IONS BY SODIUM TETRAHYDROBORATE

ABSTRACT

**MANASH DAS GUPTA, M.Sc.**
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

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## ABSTRACT

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 focussed attention on the efficacy of sodium tetrahydroborate as a reagent capable of effecting the reduction of inorganic substrates, such as transition metal ions.

The purpose of this investigation has been to study the kinetic features of the reduction of transition metal ions by sodium tetrahydroborate, and to establish mechanistic pathways for such reduction reactions. During the course of the reduction of transition metal ions by sodium tetrahydroborate, attempts were also made to design novel methods for the preparation of some transition metal 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 transition metal ions by sodium tetrahydroborate, at constant ionic strength, has been studied. The transition metal ions which have been used for the purposes of reduction have included:

1. Titanium(IV) and Zirconium(IV) : Chapter 1.
2. Vanadium(V) : Chapter 2
3. Chromium(VI), molybdenum(V) and tungsten(VI) : Chapter 3.
4. Manganese(VII) : Chapter 4.
5. Iron(III), Cobalt(III), ruthenium(III), rhodium(III) and nickel(II) : Chapter 5.
6. Copper(II) and silver(II) : Chapter 6
7. Cerium(IV) : Chapter 7.

The stoichiometry of the individual reduction reactions, was determined as follows: Reaction mixtures containing the transition metal ion ($M^{n+}$, where n was the highest common oxidation state of the metal) and an excess of sodium tetrahydroborate, taken in water, with the requisite amounts of acid (or alkali) and sodium perchlorate, were allowed to react to completion at the particular temperature. The transition metal ion which was left was analysed, spectrophotometrically, at the corresponding $\lambda_{max}$ for the particular transition metal ion.

During the kinetic runs, the progress of all the reduction reactions were followed, spectrophotometrically, by observing the disappearance of the transition metal ion species at its $\lambda_{max}$. In some cases ($Mn^{VII}$ - $BH_4^-$) and

$Ag^{II}$ - $BH_4^-$ systems), the progress of the reaction was monitored by observing the formation of the intermediate species at its $\lambda_{max}$, followed by its conversion to the final product.

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 additional calculated amounts 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 transition metal ion 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 concentration, in each case, was plotted against the respective pH. The plots were linear, indicating the first order dependence of the rate on the hydrogen ion concentration. In the case of metal ions such as manganese(VII) and silver(II), the reactions were observed to occur in two steps. For the reduction of manganese(VII) by sodium tetrahydroborate, the steps involved were:

(i) the reduction of $Mn^{VII}$ to $Mn^{VI}$; and

(ii) the subsequent reduction of $Mn^{VI}$ to $Mn^{IV}$.

For the reduction of silver(II) by sodium tetrahydroborate, the two steps involved were:

(i) the reduction of $Ag^{II}$ to $Ag^{I}$; and

(ii) the subsequent reduction of $Ag^{I}$ to $Ag^{O}$.

For the reduction of nickel(II) by sodium tetrahydroborate, it was observed that the pH of the medium played a significant role in determining the course of the reduction reaction and the nature of the final product formed. At pH = 8.0, the nickel(II) was reduced to nickel boride, $Ni_2B$, and boric acid. At pH = 12.0, the nickel(II) was reduced to nickel boride ($Ni_2B$) and boric acid, with the additional formation of metallic nickel, indicating that the nickel(II) had been reduced to the nickel(O) species.

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.

Variations in the ionic strength of the medium did not have any effect on the rates of these reduction reactions.

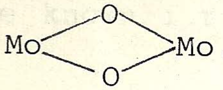
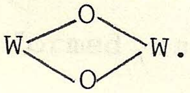
This was consistent with the observation that, since the reactions were performed using high concentrations of acid or base, these would predominate over the ionic strength of the medium.

During the process of the reduction of some transition metal ions, such as manganese(VII) and silver(II), by sodium tetrahydroborate, the presence of the intermediate species was detected by spectral methods. In the case of the reduction of $Mn^{VII}$ by $NaBH_4$, the intermediate species formed was $Mn^{VI}$. This was detected and characterised by e.s.r. spectroscopy, which indicated a paramagnetic species. A spectral scan of the reaction mixture was performed, within 1 min of the initiation of the reaction, in the range 350nm to 800 nm. A sharp absorption peak was observed at 595 nm, indicating the presence of the $Mn^{VI}$ intermediate species. During the reduction of $Ag^{II}$ by $NaBH_4$, the intermediate $Ag^{I}$ ion was detected and characterised, spectrally. A spectral scan in the range 300 nm to 900 nm showed a sharp absorption peak at 375 nm, indicating the presence of the intermediate $Ag^{I}$ species.

Reduction of the transition metal ions by sodium tetrahydroborate had resulted in the formation of the lower stable oxidation state of the metal ion, and boric acid. The lower stable oxidation state of the metal thus formed, in each reduction reaction, was characterised by chemical and spectral methods.

Titanium(IV) was reduced to titanium(III), which was characterised by its typical absorption peak at 300nm and by e.s.r. spectroscopy, wherein the observed paramagnetic character was lower than that expected for a species containing one electron per atom. Zirconium(IV) was reduced to zirconium(III), and its characterization by e.s.r. spectroscopy indicated low paramagnetic character, thought to be typical of Zr-Zr bond formation due to dimerisation.

Vanadium(V) was reduced to vanadium(IV), which was characterised by chemical and spectral methods. A typical absorption peak at 755 nm was observed for the vanadium(IV) species.

Chromium(VI) was reduced to chromium(III), which was characterised by chemical methods. A spectral scan performed in the range 350 nm to 800 nm did not show any absorption peak at 390 nm, indicating that a chromium(V) intermediate species could not be detected, under the present experimental conditions. Molybdenum(VI) was reduced to molybdenum(V), and the i.r. analysis of this final product gave a peak in the region 900-1000 $cm^{-1}$, indicating an oxo-molybdenum(V) species having a terminal Mo=O moiety. A weak band at 487 $cm^{-1}$ and a strong band at 675 $cm^{-1}$ indicated symmetrical and antisymmetrical vibrations, respectively, for a bridge-type structure,  . This was observed to be paramagnetic in character. The $Mo^{V}$ species formed as the final product of reduction, was further characterised by its typical absorption peak at 685 nm. Tungsten(VI) was reduced to tungsten(v), and the i.r. analysis of this final product gave a peak at 1000 $cm^{-1}$, indicating an oxo-tungsten(V) species having a terminal W=O moiety. A weak band at 468 $cm^{-1}$ and a strong band at 684 $cm^{-1}$, indicated symmetrical and anti-symmetrical vibrations, respectively, for a bridge-type structure,  . This was observed to be paramagnetic in character. The $W^{V}$ species formed as the final product of reduction, was also characterised by its typical absorption peak at 765 nm.

Manganese(VII) was reduced in two steps:

(i) reduction of $Mn^{VII}$ to $Mn^{VI}$; and

(ii) reduction of $Mn^{VI}$ to $Mn^{IV}$.

The formation of $Mn^{VI}$ as the intermediate species was characterised by its sharp absorption peak at 595 nm, and by its paramagnetic character, as observed by e.s.r. spectroscopy. The $Mn^{IV}$ species formed, as the final product, was characterised by chemical and spectral methods. The oxidation state of manganese in the final product was determined chemically, and was found to be +4, indicating that the final product of the reduction process was $Mn^{IV}$, that is, $MnO_2$. The $Mn^{IV}$ species thus formed was further characterised by i.r. analysis, wherein the i.r. spectrum of this $Mn^{IV}$ species was identical with that of the known i.r. spectrum of manganese dioxide ($MnO_2$).

Iron(III) was reduced to iron(II), which was characterised by chemical methods. Cobalt(III) was reduced to cobalt(II), which was characterised by chemical methods. Ruthenium(III) was reduced to ruthenium(II), which was characterised by chemical and spectral methods. Spectral analysis gave a band of low intensity at 295 nm, and a sharp peak at 192 nm, which were both assigned to the presence of the ruthenium(II) species. E.S.R. spectroscopy of the ruthenium(II) species, formed as the final product of the reduction reaction, did not show any paramagnetic behavior. This was consistent with the diamagnetic nature of ruthenium(II) complexes due to a $t_{2g}^{6}$ configuration. Rhodium(III) was reduced to rhodium(I) which was characterised by chemical and spectral methods. E.S.R. spectroscopy of the rhodium(I) species, formed as the final product of the reduction reaction, did not show any paramagnetic behavior. This was consistent with the diamagnetic nature of the rhodium(I) complexes. Nickel(II) was reduced to nickel boride, $Ni_2B$, and metallic nickel, depending on the pH of the reaction.

(i) <u>At pH = 8.0</u>, nickel(II) was reduced to nickel boride, which was characterised by chemical methods.

(ii) <u>At pH = 12.0</u>, nickel(II) was reduced to nickel boride, $Ni_2B$, and metallic nickel, $Ni^{o}$. The oxidation state of metallic nickel($Ni^{o}$) was confirmed by determining the oxidation state of nickel chemically, which was found to be zero.

An electron micrograph of the final product showed the presence of crystals of metallic nickel, against a background of amorphous nickel boride, $Ni_2B$.

Copper(II) was reduced to copper(I), which was characterised by chemical and spectral methods. The oxidation state of copper in the final product was chemically determined to be $+1(Cu^I)$. The i.r. spectrum of the cuprous hydride, formed as the final product of the reduction reaction, showed an intense peak at 521 $cm^{-1}$, which could be 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 the cuprous hydride. Silver(II) was reduced in two steps:

(i) the reduction of $Ag^{II}$ to $Ag^I$; and

(ii) the reduction of $Ag^I$ to $Ag^o$.

The formation of silver(I), as the intermediate species, was characterized by spectral methods. A spectral scan of the reaction mixture was performed, within 1 min of the initiation of the reaction, between 300nm and 900nm. This showed an absorption peak at 375 nm, which was due to the presence of the silver(I) intermediate species. The further reduction of the silver(I) intermediate gave a silver species, which was shown, chemically, to be metallic silver $(Ag^o)$.

Cerium(IV) was reduced to cerium(III), which was characterised by chemical and spectral methods. The oxidation state of the final product, obtained from the reduction of cerium(IV), was shown chemically to be +3($Ce^{3+}$). A spectral scan of the product solution was carried out between 180nm and 900nm. This colourless solution showed an absorption peak at 250nm, which was due to the presence of the cerium(III) species.

The reduction of all these transition metal ions by sodium tetrahydroborate in acid or alkaline medium, had resulted in the formation of the lower stable oxidation state of the respective transition metal ion, and in the formation of boric acid as the only other product. The boric acid, formed as the only other product of the respective reduction reactions, was isolated and characterized by chemical and spectral methods. The i.r. spectrum of the boric acid formed at the end of the reaction was recorded, and compared with the i.r. spectrum of known boric acid, and found to be identical. This confirmed the presence of boric acid in the final product.

Since the rates of these reactions were dependent on the concentrations of both, tetrahydroborate 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 transition metal ion with the activated boron complex. This would involve the reaction of the boron intermediate with either a transition 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

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

The intermediate species, $BH_3OH^-$, could be considered as a probable intermediate boron species. Experimental evidence for the formation of intermediate boron compounds could not be obtained. However, earlier investigations had provided evidence for the existence of such intermediates, from the reactions of diborane with ice and with the "bound water" in silica gel. These boron intermediates differed in reducing capacity, 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.

It has been shown that molecular hydrogen reacts homogeneously with a number of metal ions in solution, reducing them to a lower oxidation state. It has also been suggested that the intermediate, $H^+BH_4^-$, undergoes a fast conversion to molecular hydrogen. This molecular hydrogen, generated from the $H^+BH_4^-$ intermediate species, could actually react with the transition metal ion, reducing it to a lower oxidation state, with the concomitant formation of boric acid. The reaction mechanism could be represented as follows:

$$H^+BH_4^- \longrightarrow \frac{1}{2} B_2H_6 + H_2 \qquad (3)$$

$$H_2 + M^{x+} \longrightarrow M^{(x-n)+} + H^+ \qquad (4)$$

$$\frac{1}{2} B_2H_6 + 3H_2O \longrightarrow B(OH)_3 + 3H_2 \qquad (5).$$

Here, $M^{x+}$ in equation (4) represents the transition metal ion, and $M^{(x-n)+}$ represents the transition metal ion in its reduced form. Equation (4) represents the reduction reaction which may be a one-step or a two-step process.

During the course of this investigation pertaining to the kinetics of the reduction of transition metal ions by sodium tetrahydroborate, attempts were also directed towards exploring novel methods for the preparation and isolation of some compounds of the transition metal ions in their lower oxidation states. These have included methods for the preparation and isolation of compounds such as $VOCl_2.2H_2O$, $VOSO_4$ (anhydrous), and cuprous hydride, CuH.

### (i) $VOCl_2.2H_2O$

Anhydrous bright green $VOCl_2.2H_2O$ had earlier been prepared, and the product was extremely deliquescent. The hydrated compound commercially available was obtained when $V_2O_5$ was treated with concentrated HCl or when $VCl_4$ was subjected to hydrolysis.

The present investigation reports a novel method for the preparation of $VOCl_2.2H_2O$. When vanadium(V) was reduced by $NaBH_4$ in $H_2SO_4$ medium, a blue solution was obtained as the end product. This solution was treated with concentrated HCl and heated, until the complete removal of volatile $H_3BO_3$. This process resulted in the formation of a green-coloured water-soluble compound, $VOCl_2.2H_2O$, which was extracted with hot water and crystallised. The compound was characterized by chemical methods and found to correspond to $VOCl_2.2H_2O$. The i.r. analysis showed a sharp peak at $990cm^{-1}$, corresponding to the V-O stretching frequency. The absence of borate was also confirmed. The isolation and characterization of $VOCl_2.2H_2O$, by this method, constitutes the first report of the preparation of this compound, obtained by the reduction of $V^V$ by $NaBH_4$ in acid medium.

(ii) **$VOSO_4$ (anhydrous)**

When vanadium(V) was reduced by sodium tetrahydroborate in $H_2SO_4$ medium, a blue coloured solution was obtained. This solution was treated for the complete removal of borate, by heating the solution repeatedly with concentrated $H_2SO_4$ and methyl alcohol, until the vapours so produced did not give any green-edged flame when ignited. On completion of this treatment, a green-coloured water-insoluble product was precipitated, when the pH of the solution was less than 2.0. This insoluble product was filtered, washed with water and dried above 100°C. Chemical analysis of this green product confirmed it to be $VOSO_4$. IR analysis showed the V-O stretching frequency at 990cm$^{-1}$. The absence of borate was also confirmed. This method purports to be the first report wherein anhydrous $VOSO_4$ has been obtained by reducing $V^V$ by $NaBH_4$ in acid medium.

### (iii) 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 96.5% (theoretical percentage of copper in CuH = 98.4%). The oxidation number of copper in this product was established to be +1($Cu^+$). The i.r. spectrum of this compound gave an intense peak at 521cm$^{-1}$, which was assigned to the presence of a ...Cu...H...Cu...H... bridge-type structure. Absence of any peaks in the region between 2250cm$^{-1}$ 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 has been prepared by the $NaBH_4$ reduction of any copper(II) compound.

The experimental results of the present kinetic investigation, has helped in unequivocally establishing the significant role of sodium tetrahydroborate as a reagent capable of bringing about the reduction of transition 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 preparation of novel compounds of transition metals. The simplicity of such reduction reactions has thus established the important facets of sodium tetrahydroborate in terms of its capability to reduce transition metal ions, and as a reagent which could be used for the preparation of newer compounds of transition metals.