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

SUMMARY.

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Thesis

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.

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CERTIFICATE

I certify that the Thesis entitled "KINETICS AND MECHANISM OF REDUCTION OF SOME METAL IONS BY SODIUM TETRA-HYDROBORATE" submitted by Mrs. SUNITA DASGUPTA, for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She has been duly registered and the Thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree of any other university.

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IN MEMORY OF MY
PARENTS
AND
LATE YOUNGEST BROTHER
SUBHASH

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CONTENTS

INTRODUCTION

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Since its discovery by Schlesinger, Brown and coworkers (1), sodium tetrahydroborate has found wide usage as a powerful reducing agent(2). It is quite stable in basic solution, but liberates hydrogen by reducing the hydronium ion as the pH is lowered. Sodium tetrahydroborate is presently one of the most easily available among many complex metal hydrides. It is easier to handle than lithium tetrahydroaluminate ($LiAlH_4$) and lithiumtetrahydroborate ($LiBH_4$), because of its comparatively lower sensitivity towards moisture (3).

Sodium tetrahydroborate in water or methanol solution was found to be an effective reagent for the conversion of aldehydes and ketones to the corresponding alcohols (4). It was also observed that, whereas acid chlorides were reduced to primary alcohols in non-aqueous media, other substrates such as carboxylic acids, acid anhydrides, esters and nitriles were not affected(4). Schlesinger and coworkers had recognised the potential usefulness of sodium tetrahydroborate as a hydrogen generator. It was also observed to be an excellent reducing agent in aqueous medium(5). Extensive quantitative investigations of its hydrolysis(5), and the subsequent structural(6), spectroscopic(7-9), and polarographic(10) studies indicated that the overall hydrolytic reaction was best represented as :

$$BH_4^- + 4H_2O \longrightarrow B(OH)_3 + OH^- + 4H_2 \qquad (1)$$

In solution, tetrahydroxoborate was the predominant species :

$$B(OH)_3 + OH^- \longrightarrow B(OH)_4^- \qquad (2)$$

The overall equilibrium in aqueous solution may be represented by (11) :

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \qquad (3)$$

Where $K = 110\ dm^6\ mol^{-2}$.

Schlesinger and coworkers had observed that at room temperature, in an unbuffered medium or in the absence of an acidic accelerator, the hydrolysis (equation 1) was extremely restricted, and the percentage of hydrogen liberated was quite small (5). The solution pH was found to be the limiting parameter. The accelerating effects of many acids such as inorganic protic acids, oxalic acid, succinic acid, P_2O_5, Al_2O_3, and B_2O_3 were studied. Organic polyfunctional acids were found to be efficient accelerators, but the reaction became uncontrollable. Attempts were made to establish a qualitative correlation between the efficiency of the accelerator and its acid strength. The accelerator used was B_2O_3. However, an amount of this oxide equal to the amount of BH_4^- was required to give theoretical yields of hydrogen.

The effect of various transition metal salts and many typical metal catalysts (primarily the transition metals), on the rate of hydrolysis of $NaBH_4$, was quantitatively studied (5). Following the earlier work, several other studies have been carried out on the acceleration of BH_4^- hydrolysis by transition metal ions (12-17). However, the results were frequently inconclusive and contradictory. It was also claimed that the rate of hydrolysis of $NaBH_4$ was due to the metal borides formed 'in situ'.

The rate of reduction of ketones by sodium tetrahydroborate in isopropyl alcohol as solvent was studied (18). The reaction followed second order kinetics with the rate constants decreasing in the order : acetone > methyl ethyl ketone > methyl isopropyl ketone > methyl t-butyl ketone. Esters did not undergo reduction by BH_4^- in isopropyl alcohol solvent. However, the reduction of esters was achieved by the addition of LiBr or anhydrous $MgCl_2$ (or $MgBr_2$) to sodium tetrahydroborate taken in dimethyl ether or diethylene glycol (diglyme) as solvent.

A study of the thermodynamic properties of sodium tetrahydroborate(19) revealed that for the reaction at 298 K:

$$NaBH_4(S) \longrightarrow Na^+ + BH_4^-,$$

the standard free energy change was - 5.66 ± 0.07 $kcalmol^{-1}$. The standard free energy of formation of BH_4^- (aqueous) was 28.6 ± 0.1 $kcalmol^{-1}$, and the standard entropy of the ion was estimated as 25.3 ± 1.0 eu. The polarizability of BH_4^- in its alkali salts, was found to be 3.94 Å, and the ionic radius was calculated to be 2.03 Å.

The electronic structure of metal tetrahydroborates has focused attention on the quasi-relativistic study of $M(BH_4)_4$, where M=Zr, Hf, Th and U (20,21). The kinetics of reduction of substituted 4-methyl-thioacetophenones by sodium tetrahydroborate had provided evidence for the steric enhancement of resonance (22). The kinetics of oxidation of 1-hexene by molecular oxygen, in the presence of TPP - MnCl and $NaBH_4$, has been studied (23). The reduction of acetonitrile by sodium tetrahydroborate, catalysed by ruthenium (II), has been reported (24). The nature of activation caused in the presence of rhodium (III) catalyst, as a result of the treatment of rhodium (III) with sodium tetrahydroborate, has been examined(25).

Reviews on the reduction of carbonyl groups by metal tetrahydroborates (26) and by $NaBH_4$, in the presence of lanthanide chlorides (27), have highlighted the importance of $NaBH_4$ as an efficient reducing agent. Sodium tetrahydroborate in mixed solvent (tetrahydrofuran and a protic solvent) showed much higher stereoselectivity than in each individual solvent, in the asymmetric reduction of chiral α-ketoamides(28). The selective reduction of esters and lactones with $NaBH_4$ in mixed solvents, such as t-butanol-methanol and tetrahydrofuran-methanol, has been reported(29).

Amongst the diverse kinds of reactions that the tetrahydroborate ion can undergo is a general method of intercalating a variety of cationic molecules into layered solid matrices. It has been shown that the BH_4^- anion acts as the reductant, and cation intercalation occurred according to the reaction(30):

$$x\ (Cat^+)BH_4^- + A \longrightarrow (Cat^+)_x[A^{x-}] + (\frac{x}{2})B_2H_6 + (\frac{x}{2})H_2$$

which did not give any undesired by-products (31,32). It was also observed that whether a particular cation would enter the lattice of a host material was actually determined by both thermodynamic and kinetic factors (30-33). Theoretical studies have been carried out in order to closely examine the structures of various borane dianions. Protonation of closo-borane dianions $B_nH_n^{2-}$ led to new anions of the $B_nH_{n+1}^-$

type, with flexible structures, and details concerning the dynamic behaviour of such anions were reported (34,35). As part of the efforts to understand and control the formation of nanoscale magnetic materials, studies on the reduction of Fe^{2+} and Fe^{3+} in aqueous and non-aqueous media were carried out(36). It was further observed that the solvent medium (H_2O or diglyme) was important in determining the final product (36). The reduction of Co^{2+} by tetrahydroborate in nonaqueous solutions was reported, and the results showed that the chemistry was very different in aqueous media (37). In this study carried out in nonaqueous media, Co_2B was the primary product in the form of ultrafine particles (37). The reduction of pentaborane with sodium triethyl borohydride produced the disodium salt of hypho-undecahydropentaborate (2-), by a novel hydride addition ; this species was the first hypho-boron hydride dianion (38). Interest in borane cage expansion via the insertion of boron and other main group moieties led to the investigation of the nido-$B_{10}H_{12}$ anion, the most reactive of the known decaborane anions(39). The synthesis and structural characterization of the sodium salts of fluorinated poly (pyrazolyl) borates have been reported (40). Ligand systems have been used in the synthesis of several new copper and silver complexes (40).

The efficacy of sodium tetrahydroborate as a reducing agent in organic synthesis is apparent in the extant chemical literature. Considering the impact that sodium tetrahydroborate has made over the years in the field of organic transformations, not much work has been reported on the kinetic aspects of the reduction of inorganic compounds by this versatile reductant ($NaBH_4$). While attempting to highlight the sustained importance and interest that sodium tetrahydroborate has generated, the present investigation will focus attention on the kinetic features of the reduction of some metal ions by $NaBH_4$, and will suggest plausible mechanistic pathways for such reduction reactions. This present investigation would fulfil the compelling need to explore the reduction reactions of metal ions in general, and would add yet another significant dimension to the reducing potentialities of sodium tetrahydroborate.

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SCOPE OF THE PRESENT INVESTIGATION

SCOPE OF THE PRESENT INVESTIGATION

Sodium tetrahydroborate had been earlier used as an efficient reducing agent in the reduction of various organic substrates. For example, sodium tetrahydroborate in water or methanol solvent was found to be an effective reagent for the conversion of aldehydes and ketones to the corresponding alcohols.

Kinetic studies on the reduction of metal ions by sodium tetrahydroborate has not merited much attention.

The present investigation is a detailed kinetic probe into the reduction of metal ions by sodium tetrahydroborate in aqueous acid and aqueous alkaline.media.

The purpose of this kinetic investigation has been to attempt to extend the scope of this extremely efficient and versatile reducing agent, $NaBH_4$, and to explore and establish mechanistic pathways of reactions involving the reduction of metal ions.

The aims of the present investigation were :

(1) to study the kinetic features of the reduction of metal ions by sodium tetrahydroborate;

(2) to demonstrate the usefulness of sodim tetrahydroborate as a reagent which could bring about the reduction of metal ions; and

(3) to attempt the isolation and characterization of compounds formed during the course of the reduction of metal ions by sodium tetrahydroborate.

In the present investigation, the metal ions which have been reduced by $NaBH_4$, have included : titanium (IV), zirconium (IV), iron (III), copper (II) and bismuth (V).

The progress of all these reduction reactions have been monitored spectrophotometrically, and the orders of the reactions with respect to both, the metal ions and $NaBH_4$, have been determined. The effect of the variation of pH on the rates of the reactions have been studied.

The reactions have been studied over a range of temperatures, and the activation parameters have been evaluated.

For each reduction reaction, the stoichiometry of the reaction has been determined. In each case, the products of the reduction reactions were isolated, identified and characterized by analytical and spectral methods. The oxidation states of the metal ions (formed by the reduction of the respective metal ions by $NaBH_4$) in the end products, in each case, were characterized by chemical and spectral methods.

Based on all these experimental observations and data, the mechanistic pathways for the reduction of all the metal ions by sodium tetrahydroborate in aqueous (acid and alkaline) media, have been postulated.

The present investigation, dealing with the kinetics of reduction of metal ions by sodium tetrahydroborate, would not only establish the credibility of $NaBH_4$ as a reagent capable of effecting such reduction reactions, but would also play a noteworthy role in contributing towards the isolation and characterisation of lower oxidation states of metals. Such reactions, involving the reduction of metal ions by sodium tetrahydroborate, could greatly facilitate the preparation of new compounds to help in the elucidation of synthetic methods and reaction mechanisms.

EXPERIMENTAL

PURIFICATION OF THE MATERIALS AND PREPARATION OF COMPOUNDS

CONDUCTIVITY WATER

Conductivity water was prepared by the following method : tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analysi", sulphuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). The conductivity water thus prepared was utilised for the preparation of all the solutions used in the kinetic determinations.

Reagents

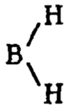
Sodium hydroxide, hydrochloric acid, nitric acid, hydrogen peroxide, potassium hexacyanoferrate(II), sodium thiosulphate, potassium iodide, and cupferron were E. Merck samples. Phosphoric acid, hydrofluoric acid, oxalic acid, ferric ammonium sulphate and ferric chloride were Sarabhai samples. Alizarin-S and phenolphthalein were BDH samples.

Sodium carbonate and mannitol were SD's samples. Methanol and ethanol samples were obtained from the Bengal Chemical Company. Mandelic acid was a Sigma-Aldrich sample.

Sodium tetrahydroborate

Loba Chemical Co. sample was used. This was kept under vacuum to avoid possible decomposition. The purity of the sample was checked by IR analysis. Two sharp peaks were obtained at 2290 cm^{-1} and 1120 cm^{-1}, both being characteristic for $NaBH_4$. They have been assigned as follows (1) :

(i) 2290 cm^{-1} : (B-H) asym stretching

(ii) 1120 cm^{-1} :  deformation.

The (B-H) asym stretching was further split (2380 cm^{-1} and 2220 cm^{-1}). It has been suggested that the splitting was a consequence of the inability of the tetrahedral anion to rotate freely in the crystal lattice (2).

Substrates

Titanium dioxide and zirconyyl chloride were BDH samples, and were used as the source of titanium (IV) and zirconium (IV) respectively. Potassium hexacyanoferrate (III), copper (II) sulphate and sodium bismuthate were E. Merck samples, and were used as the source of iron (III), copper (II) and bismuth (V), respectively.

Preparation of starting materials

(a) Titanium (IV) - peroxo complex

Titanium (IV)- peroxo complex in solution was used as the source of titanium(IV). 2.0 g of titanium dioxide was digested with a minimum amount of hydrofluoric acid in a teflon beaker. When TiO_2 completely went into solution, it was reprecipitated, using a minimum amount of ammonium hydroxide solution. This freshly precipitated TiO_2 was washed several times with water to completely remove the fluoride ions. This was then redissolved (3) in 1 M hydrochloric acid in a 250 ml volumetric flask. 1 drop of hydrogen peroxide was added, when the yellow coloured peroxo complex was formed, which showed a λ_{max} at 380 nm (4). This solution corresponded to 0.1 M strength, with respect to titanium (IV). The solutions of required strengths were prepared as and when necessary.

(b) Zirconium (IV) - alizarin-S complex

Zirconium (IV) - alizarin-s complex in solution was used as the source of Zirconium (IV). 4.86g of zirconyl chloride ($ZrOCl_2$) was dissloved in 1 M hydrochloric acid in a 250 ml volumetric flask, and one drop of an aqueous solution of alizarin-s was added. A pink coloured solution was obtained which showed a λ_{max} at 515 nm (5). This solution corresponded to 0.1M strength, with respect to zirconium (IV). The solutions of required strengths were prepared, as and when necessary.

For each of the metal ions used, the maximum absorption was determined by performing a scan between 180 nm and 900 nm. The λ_{max} for each of the metal ions used are shown in Table 1.

Table 1. Maximum absorption (λ_{max}) for metal ions

Substrate	λ_{max} (nm)
Titanium (IV)	380 (H) (4)
Zirconium (IV)	515 (H) (5)
Iron (III)	420 (N) (6)
Copper (II)	615 (A)
Bismuth (V)	500 (H)

H = HCl; N = NaOH ; A = NH_4OH.

In this investigation, all the optical density measurements were carried out at wave lengths which corresponded to the maximum absorption (λ_{max}).

The IR spectra were recorded on IR 297 and 983 spectrophotometers (Perkin Elmer), using KBr as solvent.

Laser Raman Spectra

The Laser Raman Spectra were recorded on a Spex Ramalog Model 1403 spectrometer. The 4880Å laser line from Spectra Physics Model 165-09 Argon Laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by proton-count processing system. The sample was held in the form of a pellet in KBr. The recording was done at ambient temperature.

Kinetic method

All the standard flasks and vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered. All the glass apparatus used were tested for loss of solvent, and the loss was found to be negligible.

The standard flasks, reaction vessels and the pipettes used were standardised, using conductivity water, and the corrections were found out and applied.

An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperature accurately, with fluctuations of not more than $\pm 0.1^{o}C$. The temperature was recorded by means of an accurate sensitive thermometer, reading to tenths of a degree. The bath liquid was water, covered with a layer of liquid paraffin to minimise evaporation of water and loss of heat due to radiation.

Spectrophotometer

For absorption measurements, an Elico Spectrocol CL-28 model spectrophotometer was used.

Absorption Cells

The absorption cells used were matched glass test tubes (15 ml capacity).

Decomposition of $NaBH_4$ as a function of time

It was thought appropriate to study the decomposition of $NaBH_4$, as a function of time. This would enable the determination of the rate of hydrolysis of $NaBH_4$ and would also throw some light on the probable mechanistic pathway of the hydrolytic reaction.

The hydrolytic reactions of $NaBH_4$ were carried out in the presence of each metal ion, and the rate of the hydrolytic reaction was determined.

The experimental procedure for the reduction of each of the metal ions used was as follows :

$NaBH_4$ was prepared in water, and the solution was kept at the requisite temperature. At definite intervals of time, 5 ml aliquots of this solution were removed, and mixed with 5 ml solution of the metal ion prepared in acidic or alkaline media, and kept at the required temperature. The reaction was followed by measuring the change in the optical density at the previously determined λ_{max}(nm) of the system. The rate constant (k_1) was determined, and the concentration of BH_4^- was calculated from the equation,

$$-\frac{d[M^{n+}]}{dt} = k_1[BH_4^-]$$

where M^{n+} was the metal ion.

A plot of log C (concentration of BH_4^- ions) versus time was found to be linear, which indicated a first order dependence of the reaction on BH_4^- ion concentration.

The reaction was repeated at different temperatures, and the rate constant at each of these temperatures was calculated. The representative data for the Fe^{III}-BH_4^- system has been shown in Table 2.

Plots of log k_1 versus the reciprocal of temperature were linear, and the slope was used to calculate the activation energy of the reaction.

The value of activation energy for the hydrolysis of NaBH4 (for the Fe^{III}-BH_4^- system), was found to be 19 kJ mol^{-1}, which was comparable to that obtained for the reaction involving the reduction of hexacyanoferrate (III) by $NaBH_4$ (19 kJ mol^{-1}).

Table 2. Decomposition of $NaBH_4$ as a function of time, for the Fe^{III}-BH_4 system

Temperature (± 0.1 °C)	Time min	10^2 k_1 (min^{-1})	$[BH_4^-]$ 10^4xM
25	30	22.2	5.55
	60	14.6	3.65
	90	9.6	2.39
30	30	25.4	6.34
	60	16.6	4.15
	90	10.9	2.74
40	30	31.8	7.95
	60	20.7	5.17
	90	13.6	3.40

$[Fe(CN)_6]^{3-}$ = 2.5×10^{-4} M ; NaOH = 1×10^{-2} M ;
λ_{max} = 420 nm

Rate measurements

The required amount of the substrate (metal ion) was weighed out accurately in a 10 ml standard flask and made up in alkali (sodium hydroxide or ammonium hydroxide solution), or in acid (hydrochloric acid), whose strengths had been determined. Sodium tetrahydroborate was weighed out in a 10 ml standard flask, and the solution was prepared in water (or in alkali) whose strength had been determined. Sufficient time was allowed to compensate for any change of heat during dilution. Since it had been observed that sodium tetrahydroborate underwent decomposition in aqueous solution as a function of time, additional calculated amounts of sodium tetrahydroborate were always added to compensate for the loss of $NaBH_4$ due to hydrolysis.

The pH of each solution (substrate and sodium tetrahydroborate) was checked using a pH meter (Control Dynamics, digital model).

The two reacting solutions were separately thermostated at the required temperature for 30 min, under a nitrogen atmosphere. The solutions were then mixed in equal volumes by syringing into the spectrophotometric cell. The reaction mixture was homogeneous throughout the duration of the reaction. The pH of the reaction mixture was checked periodically, during the course of the reaction, and was found to remain constant.

The progress of the reaction was followed by observing the disappearance of the metal ion species at its λ_{max}.

All the kinetic experiments were carried out in duplicate, and the rate constants which were determined were found to be reproducible to within ± 3%.

Calculations

(a) Rate constants

The pseudo-first-order rate constants, k_1, expressed as s^{-1} (or min^{-1}) were calculated from equation (1) :

$$k_1 = \frac{2.303}{t} \log \frac{A_o}{A_t} \qquad (1)$$

where A_o was the initial absorption of the reaction mixture, and A_t was the absorption at time t.

The plots of absorption against time were linear, and extrapolation to zero time gave the values of A_o.

All values of the rate constants were the average of two experiments, with agreement being within ± 3%.

(b) Thermodynamic activation parameters

These parameters were obtained from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows :

(i) Activation energy (E)

From the linear plot of log k_1 against the reciprocal of temperature (T),

$$\text{Slope} = -\frac{E}{2.303R}$$

$$E = -\text{Slope} \times 2.303\ R\ (\text{kJ mol}^{-1})$$

(ii) Frequency factor (A)

$$k_1 = A\ e^{-E/RT}$$

$$\log A = \log k_1 + \frac{E}{2.303RT} \quad (s^{-1})$$

(iii) Enthalpy of Activation ($\Delta H^{\neq}$)

$$\Delta H^{\neq} = E - RT \quad (kJ\ mol^{-1})$$

(iv) Entropy of Activation ($\Delta S^{\neq}$)

$$k_1 = \frac{kT}{h} e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT}$$

$$\Delta S^{\neq} = 2.303 \left[\log k_1 + \frac{\Delta H^{\neq}}{2.303RT} - \log \frac{kT}{h}\right] \quad (JK^{-1}mol^{-1})$$

where k is the Boltzmann constant, and h is the Planck's constant.

(v) Free Energy of Activation ($\Delta G^{\neq}$)

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (kJmol^{-1})$$

Stoichiometry

Reaction mixtures containing the metal ion (M^{n+}, where n was the highest 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).

Product Analysis

(I) The products obtained from the reduction of titanium (IV) and zirconium(IV) respectively, using $NaBH_4$ as the reductant, were isolated and characterised.

(A) Titanium (IV)

(1) Isolation of the products

$2x10^{-3}$ M titanium peroxo complex in 1 M HCl, and $2x10^{-2}$ M $NaBH_4$ in water, were mixed in equal volumes. On mixing, a purple-violet coloured precipitate was formed. The colour gradually changed from purple to white, as the reducing action of $NaBH_4$ ceased. The violet colour was due to the reduction of Ti^{4+} to the Ti^{3+} oxidation state (7). Titanium in the +3 state was gradually converted back to the +4 state, due to the decrease in the reducing action of $NaBH_4$ and aerial oxidation (7). The precipitate was kept overnight, filtered, washed several times to make it free from the boron compound, and dried. The titanium compound thus isolated, was analysed as shown under 2(a) : Chemical analysis, and 2(b): Spectral analysis.

The filtrate obtained was evaporated. Shiny white crystals of the boron compound were obtained. The boron compound was analysed as shown under "Analysis of the Boron Intermediate".

2. Analysis of the Titanium compound obtained in the product.

(a) Chemical Analysis

The compound showed the following characteristic properties :

(i) It was a white powdered solid.

(ii) It was insoluble in all acids, except hydrofluoric acid.

(iii) For the estimation of the percentage of titanium in the compound, the following method was used :

0.151 g of the titanium compound (corresponding to 0.0905 g of titanium) was weighed accurately and dissolved by adding few drops of hydrofluoric acid. Titanium was precipitated as $TiO.H_2O$ by the addition of dilute NaOH solution. The precipitate was filtered and washed several times with water to make it free from alkali, and then dissolved in 3 M HCl.

To the clear solution thus obtained, a slight excess of 6% aqueous solution of cupferron was added with constant stirring, until the curdy precipitate ceased to appear. The precipitate was filtered, washed, dried and ignited along with the filter paper, till a constant weight was obtained. The precipitate was weighed as TiO_2 and the final weight was found to be 0.150 g (which corresponded to 0.089 g of titanium) as against 0.151 g of the titanium compound originally taken. This weight corresponded to 59.5% of titanium in the compound. This value compared favourably, within the limits of experimental error, with the theoretical percentage of titanium present in TiO_2 (60%).

(b) Spectral Analysis

The product sample was analysed spectrally. IR bands were obtained at 335, 530, 571, 647 and 1375 cm^{-1}, which were assigned to ν(Ti-O) stretching (8-13). It has been shown that bands at 335 and 1375 cm^{-1} were typical for TiO_2 (14). It has been established that TiO_2 most commonly existed in rutile form and behaved as a typical transition metal oxide (15). Hence all the IR bands obtained could be assigned to vibrations where (Ti-O) single bond vibrations were predominant. Further, the absence of stretching frequencies in the region 900-1050 cm^{-1} indicated that the titanium compound was not a monomeric species. The Ti=O structural unit was thus not present (16).

From chemical and spectral analyses, the titanium compound obtained was thus confirmed to be TiO_2.

(B) Zirconium (IV)

(1) Isolation of the products

Equal volumes of $2x10^{-3}$ M $ZrOCl_2$ solution in 1 M HCl, and $2x10^{-2}$ M $NaBH_4$ in water, were mixed together. The mixture was evaporated carefully over a water bath. The white gelatinous precipitate obtained was filtered, washed and dried. This compound was probably $ZrO_2 . nH_2O$ (17), and was analysed as shown under 2(a): Chemical analysis and 2(b): Spectral analysis.

The filtrate obtained was evaporated. Shiny white crystals of the boron compound were obtained. The boron compound was analysed as shown under "Analysis of the Boron Intermediate."

2. Analysis of the Zirconium compound obtained in the product.

(a) Chemical analysis

The compound showed the following characteristic properties :

(i) It was a white solid.

(ii) It was insoluble in water, but soluble in dilute acids.

(iii) It showed the presence of two molecules of water.

0.5254 g of the zirconium compound was heated to a constant weight. The final weight of the zirconium compound was found to be 0.4071 g, thus showing the presence of two molecules of water in the compound ($ZrO_2.2H_2O$).

(iv) For the estimation of the percentage of zirconium, the following method was used :

0.201 g of the zirconium compound (corresponding to 0.115 g of zirconium) was weighed accurately and was dissolved in 0.1 M nitric acid (20 ml), and heated for about 10 minutes. The resulting solution was made alkaline by the addition of 0.1 M NaOH solution (30 ml), followed by heating for about 10 min to ensure complete decomposition. The precipitated hydrated zirconium dioxide was filtered off and washed several times with cold water. The gelatinous precipitate was dissolved in 20% HCl (v/v) and 50 ml of 16% aqueous mandelic acid solution was added. The mixture was heated for about 20 minutes. The resulting precipitate was filtered and washed with a hot solution containing 2% of HCl and 5% mandelic acid, dried and weighed as ZrO_2. It was found to contain 0.1144 g of zirconium, as against 0.201g of zirconium compound originally taken. This weight corresponded to 56.4% of zirconium present in the zirconium compound. This value compared favourably, within the limits of experimental error, with the theoretical percentage of zirconium present in $ZrO_2.2H_2O$ (57.2%).

(b) Spectral Analysis

The product sample was analysed spectrally. The IR bands were obtained at 3240 (b), 1614 (m), 974 (s) and 540 (b).cm^{-1}

The bands at 3240 cm^{-1} and 1614 cm^{-1} were assigned to ν(O-H) and δ(H-O-H) respectively (18-21).

The strong band at 974 cm^{-1} was assigned to ν(Zr=O) (22-26).

The broad band at 540 cm^{-1} was probably due to ν(Zr-O) stretching, and could be suggested as intramolecular bonding among ZrO_2 units through the oxygen as shown(23):

$$\text{-------}\overset{\overset{\displaystyle O}{\|}}{Zr}{=}O\text{---------}\overset{\overset{\displaystyle O}{\|}}{Zr}{=}O\text{-------}$$

From chemical and spectral analyses, the zirconium compound obtained was thus found to be $ZrO_2.2H_2O$.

(II) Products obtained from the reduction of Iron(III).

The products obtained by the reduction of Fe^{III} by $NaBH_4$ were characterised.

(1) Isolation of the products

$5x10^{-4}$ M potassium hexacyanoferrate(III), taken in

1×10^{-2} M NaOH solution, and 5×10^{-2} M sodium tetrahydroborate (taken in 1×10^{-2} M sodium hydroxide solution), were mixed in equal volumes at room temperature. The reaction mixture was evaporated to dryness, over a water bath. The residue obtained was digested with a few drops of concentrated hydrochloric acid and recrystallised from hot water. Shiny white crystals, mixed with prussian blue amorphous solid were obtained. This mixture was treated with water and kept overnight. The crystals were dissolved, the prussian blue solid was filtered, washed several times (to make it free from the boron compound), and dried. The iron complex thus isolated was analysed under 2 (a): Chemical analysis and 2 (b): Spectral analysis.

The filtrate obtained was evaporated. Shiny white crystals of the boron compound were obtained. The boron compound was analysed as shown under "Analysis of the Boron Intermediate".

2. (a) Chemical Analysis

The compound showed the following characteristic properties :

(i) It was an amorphous prussian blue solid.

(ii) It was soluble in concentrated HCl and oxalic acid solution.

(iii) When $Ca(OH)_2$ solution was added to a solution of the sample, taken in concentrated HCl, a red precipitate was obtained.

(iv) WHen sodium hydroxide solution was added to a solution of the sample, taken in concentrated HCl, a precipitate of $Fe(OH)_3$ was obtained.

(v) For the estimation of the percentage of iron, the following method was used:

0.025g of the iron complex (corresponding to 0.0114 g of iron) was dissolved in 3 ml of concentrated hydrochloric acid in a 100 ml volumetric flask, and the volume was made up to the mark by diluting with water. 10 ml of this solution was pipetted out, transferred into a conical flask, and two drops of concentrated nitric acid were added. The solution was boiled, neutralised with concentrated sodium hydroxide solution and 3 ml of glacial acetic acid was added. The solution was titrated iodometrically against standardised sodium thiosulphate solution. It was found to contain 0.0112 g of iron, as against 0.025 g of the iron complex originally taken. This weight of iron corresponded to 44.6% of iron in the complex. This value compared favourably, within the limits of experimental error, with the theoretical percentage of iron in the $Fe_4[Fe(CN)_6]_3$ complex (45.5%).

(b) Spectral Analysis

The product sample was analysed spectrally. IR bands were obtained at 500 (m), 602 (s), 736 (m), 1420 (s), 2085 (s), 2100 (s), and 2261 (s) cm^{-1}.

The bands at 500 and 602 cm^{-1} were assigned to ν(Fe-CN) and δ(Fe-CN) respectively (27,29,32). The bands at 2085 and 2261 cm^{-1} were assigned to ν(CN) of the free CN^- ion and ν(CN) coordinated to metal (Fe), respectively

(27-31).

It has been shown that the bands at 500, 602, 736, 1420 and 2100 cm^{-1} were typical for the $Fe_4 [Fe(CN)_6]_3$ complex (33).

From the chemical and spectral analyses, the iron complex obtained was confirmed to be $Fe_4 [Fe(CN)_6]_3$.

(III) Products obtained from the reduction of copper (II).

The products obtained by the reduction of copper(II) by $NaBH_4$ were characterised.

(1) Isolation of the products

$5x10^{-2}$ M $CuSO_4$ in 5 M NH_4OH solution, and $5x10^{-1}$ M $NaBH_4$ in 5 M NH_4OH solution, were mixed in equal volumes. The reaction mixture was allowed to stand at 30°C for 24 h. Coffee-coloured particles were precipitated. The mixture was filtered.

The precipitate was mixed with 50 ml of water and boiled for one hour to dissolve the boron compound. The precipitate was filtered, washed and dried. The copper compound thus isolated, was analysed as shown under 2(a): Chemical analysis and 2(b): Spectral analysis.

The filtrate obtained was evaporated. Shiny white crystals of the boron compound were obtained and analysed as shown under "Analysis of the Boron Intermediate".

2(a) Chemical Analysis

The compound showed the following characteristic properties :

(i) It was a coffee-coloured solid.

(ii) It was soluble in dilute acids (HCl and HNO_3).

(iii) For the estimation of the percentage of copper, the following method was used :

0.136g of the copper compound (corresponding to 0.133g of copper) was mixed with 100 ml of water, and 5 ml of concentrated sulphuric acid was added. The solution was heated till the compound dissolved. A light blue solution was obtained. 10 ml of 5 M NH_4OH was added, and the precipitate formed was redissolved in 5 ml of glacial acetic acid. The mixture was then titrated iodometrically against standardised sodium thiosulphate solution. It was found to contain 0.131 g of copper as against 0.136 g of the copper compound originally taken. This weight corresponded to 96.3% of copper in the compound. This value compared favourably, within the limits of experimental error, with the theoretical percentage of copper present in CuH (98.4%).

(b) Spectral Analysis

The product sample was analysed spectrally. The IR spectra of CuH (in KBr) showed an intense peak at 521 cm^{-1}, which was assigned to the presence of a

---Cu---H---Cu---H---

bridged-type structure. The absence of any peak in the region between 2250 cm^{-1} and 1700 cm^{-1} indicated low covalent character, an observation which finds support from earlier reported work (34-36). The chemical and spectral analyses conclusively established the compound to be cuprous hydride, CuH.

(IV) Products obtained from the reduction of Bismuth (V)

The products obtained by the reduction of bismuth(v) by $NaBH_4$ were characterised.

(1) Isolation of the products

$2x10^{-3}$ M sodium bismuthate solution in 1 M HCl was mixed with $2x10^{-2}$ M $NaBH_4$ solution in water in equal volumes, at room temperature. The reaction mixture turned purple for a very brief period, and subsequently a black precipitate appeared. The precipitate was filtered rapidly, washed several times to make it free from the boron compound, and dried. The bismuth compound thus isolated was analysed as shown under 2(a): Chemical analysis and 2(b): Spectral analysis.

The filtrate obtained was evaporated. Shiny white crystals of the boron compound were obtained, and analysed as shown under "Analysis of the Boron Intermediate".

2(a) Chemical Analysis:

The compound showed the following characteristic properties :

(i) It was a black powder.

(ii) It was soluble in concentrated hydrochloric acid and nitric acid.

(iii) The sample reduced acidified potassium permanganate solution.

(iv) On addition of excess of water to the solution of the sample, a milky white precipitate appeared. The precipitate was kept overnight, filtered, washed and dried. This isolated product (BiOCl) was analysed as shown under 3(a): Chemical analysis, and 3(b): Spectral analysis.

(v) For the estimation of the percentage of bismuth, the following method was used :

0.64 g of the bismuth compound (corresponding to 0.594 g of bismuth) was weighed accurately and dissolved in 3 ml of concentrated nitric acid by warming. The solution was cooled and 6 M NaOH solution was added. Bismuth hydroxide $Bi(OH)_3$, was precipitated out. Sodium hydroxide solution was then added dropwise, till the completion of the precipitation. The precipitate was filtered through a previously weighed sintered crucible (G4), washed repeatedly with water, dried in a vacuum desiccator and weighed accurately as $Bi(OH)_3$. The final weight was found to be 0.728 g (which corresponded to 0.584g of bismuth) as against the bismuth compound originally taken. This weight corresponded to 91.2% of bismuth in the compound. This value compared favourably, within the limits of experimental error, with the theoretical percentage of bismuth (92.8%) present in bismuth monoxide, BiO.

2. (b) Spectral Analysis:

(i) The product sample was analysed spectrally. IR bands were obtained at 970 (s) and 500 (w) cm^{-1}.

The strong band obtained at 970 cm^{-1} was assigned to $\nu(Bi=O)$ stretching, typical of metal-oxygen double bond stretching (37, 38).

The very weak band at 500 cm^{-1} could be due to intramolecular bonding among BiO units (through oxygen),

$$---Bi{=}O---Bi{=}O---$$

(ii) UV Spectra

0.0225 g of the product sample (BiO), corresponding to 10^{-3} M concentration was dissolved in 100 ml of concentrated hydrochloric acid, and the UV spectra was recorded (UV 26, Beckman). The λ_{max} was observed at 300nm, which was attributed to $BiCl_3$ (39),

$$BiO \xrightarrow{conc.HCl} BiCl_3$$

From the chemical and spectral analyses, the bismuth compound obtained was thus confirmed to be BiO (bismuth in the +2 state).

3. Analysis of BiOCl

(a) Chemical Analysis

(i) It was a white amorphous solid.

(ii) It was soluble in concentrated hydrochloric acid. On dilution, a milky white precipitate was formed. This compound was BiOCl.

(b) Spectral Analysis

The product sample (BiOCl) was analysed spectrally. IR bands were obtained at 529 (s), 340 (s) and 285 (s) cm^{-1}.

The band at 529 cm^{-1} was assigned to ν(Bi-O) stretching (37,40), while the bands at 340 cm^{-1} and 285 cm^{-1} were assigned to ν(Bi-Cl) stretching (40,41).

It has been shown that the bands at 529, 340 and 285 cm^{-1} were typical bands for the compound, BiOCl (42).

From chemical and spectral analyses, the bismuth compound obtained under 2 (a) (iv) : chemical analysis, was thus confirmed to be BiOCl (Bismuth in (the +3 state)).

Analysis of the Boron Intermediate

The reaction of sodium tetrahydroborate ($NaBH_4$) with metal ions (titanium, zirconium, iron, copper and bismuth) yielded the identical boron intermediate, BH_3OH^-. During the course of all the reduction reactions involving these metal ions and sodium tetrahydroborate, it was observed that $NaBH_4$, on hydrolysis produced BH_3OH^- ion (43-48). The Na^+ ions present in aqueous acidic or aqueous alkaline solutions combined with negatively charged BH_3OH^- ions to give the compound, $Na^{\delta+}[BH_3OH]^{\delta-}$, which could take up one molecule of water of crystallisation. Therefore, the boron compound which was formed, in the reduction of these metal ions by sodium tetrahydroborate, could be formulated as $Na[BH_3OH].H_2O$.This was characterised by Chemical and Spectral analyses.

(a) Chemical Analysis

(i) A small portion of the recrystallised product was taken in a porcelain dish, mixed with a small amount of concentrated sulphuric acid to make a paste, and 3 ml of methanol was added. The mixture was heated and the vapour was ignited. A green-edged flame was obtained. Therefore, the compound contained boron.

(ii) The melting point of the compound was found to be $160^\circ C$.

(iii) To an aqueous solution of the sample, zinc uranyl acetate solution was added. The appearance of a yellow precipitate indicated the presence of Na^+ ion in the aqueous solution of the compound.

(iv) The molar conductance of the above compound was determined, and was found to be 110 ohm^{-1} cm^2 mol^{-1}.

(v) The percentage of boron in the compound was estimated as boric acid, using the following method :

0.263 g of the boron compound, corresponding to 0.040 g of boron, was weighed accurately, quantitatively transferred to a 100 ml volumetric flask, and the volume was made up to the mark with water. 10 ml of this solution was titrated against 0.1 M HCl using methyl orange as indicator. This volume of HCl consumed (4 ml) corresponded to the volume of HCl required to convert the boron compound (present in 10 ml of the solution), to boric acid. 10 ml of the solution containing the boron compound was taken, 4 ml of 0.1M HCl and 1 g of mannitol were added, and the solution was shaken well until complete dissolution. This solution was then titrated against standardised sodium hydroxide solution (0.025 M), using phenolphthalein as indicator. The calculation was done using the following relationship :

1 ml of 1 M NaOH ≡ 0.06184 g of H_3BO_3

From the volume of NaOH consumed (14.3 ml), the solution was found to contain 0.038 g of boron, as against 0.040 g of boron present in the boron compound originally taken. This weight corresponded to 14.4% of boron in the boron compound. This value compared favourably, within the limits of experimental error, with the theoretical percentage of boron (15.2%) present in the compound, $Na[BH_3OH].H_2O$.

(b) Spectral Analysis

The boron compound was analysed spectrally. IR bands were obtained at 3250 (b), 2528 (w), 2350 (w), 2275(s), 1611 (m), 1451 (s), 1193 (s), 895 (s), 884 (s) and 646 (m)cm^{-1}.

The band obtained at 3250 cm^{-1} has been assigned to ν(O-H) stretching (18-21).

The bands at 2528, 2350 and 2275 cm^{-1} have been assigned to ν(B-H) stretching (49-53).

The bands at 1611, 1451 and 1193 cm^{-1} have been assigned to δ(H-O-H) (18-21), ν(B-OH) (50,54,55), and $\delta(BH_2)$ (50), respectively.

The bands at 884 and 646 cm^{-1} could be attributed to δ(B-H) (52), and δ(B-OH) (54), respectively.

The sharp band obtained at 895 cm^{-1} has been assigned to the B-H link in an apical position (50).

Raman Spectra

Raman lines were obtained at 880 cm^{-1} and 500 cm^{-1}.

The band obtained at 880 cm^{-1} was attributed to BH_2 (wag) (53,56), while the band at 500 cm^{-1} was due to B-H bending (53).

(C) Analysis using the Scanning Electron Microscope

A study of the external morphology of the crystals of the boron intermediate was carried out, using the Scanning Electron Microscope (SEM).

In order to examine the homogeneity and the crystalline character of the boron compound, an electron micrograph of the boron compound was taken (magnification 400

Fig.1. Electron micrograph (magnification 400 times) of the boron compound, obtained on reduction of metal ions by $NaBH_4$.

times, Jeol SM-35CF) at room temperature (Fig.1). The electron micrograph provided evidence for the homogeneity and the crystalline nature of the boron compound. Further, there was the indication that the boron compound existed as a single space species.

Structure of the boron compound

The probable structure of the boron compound could be decided, based on the following considerations :

(i) The hydrogen atoms shared one electron each with the sp^2 hybrid orbitals of boron, forming three covalent bonds with boron.

(ii) The oxygen atom of the OH group could donate its lone pair of electrons to the vacant p orbital of the boron atom, forming one coordinate covalent bond. The boron atom would thus attain a negative charge, which attracts the Na^+ ion present in solution, forming a partially ionic bond between boron and sodium atoms.

(iii) The B-H link in the apical position suggested a tetrahedral structure, with the boron atom being at the centre, and three hydrogen atoms and one OH group at the four corners of the tetrahedron.

(iv) The three hydrogen atoms were attached to the boron atom by bond pairs of electrons. This reduced the electron - electron repulsion, so that the tetrahedron becomes distorted.

The reaction of tetrahydroborate with bismuth in acid solution could thus be expressed by the equation:

$$3[H^{+}BH_4^{-}] + 2Bi^{5+} + 3H_2O \longrightarrow 2Bi^{2+} + 3[BH_3OH]^{-} + 9H^{+} \quad (1)$$

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DISCUSSION

CHAPTER 1

KINETICS OF REDUCTION OF TITANIUM(IV) AND ZIRCONIUM(IV)

1. Titanium

Titanium is the second member of the d-block transition elements, having the configuration $3d^2 4s^2$. Titanium (IV) is the most stable and common oxidation state, and compounds in the lower oxidation states are oxidised to Ti^{IV} by various reagents.

Spectroscopic studies have been carried out on hydrozinium (1+) and hydrazinium (2+) hexafluoro titanates (IV), and on the decomposition of hydrazinium (2+) hexafluorotitanate (IV) difluoride (1). The reaction between Ti^{IV} and pyridylazo-resorcinol reagents has been reported (2). The chemistry of dinitrogen residues has highlighted the synthetic and x-ray crystal structure of the diazenido-complexes of Ti^{IV}, and the organohydrazide derivatives of Ti^{IV}, wherein the overall processes have been represented by the reduction of Ti^{IV} to the Ti^{III} species (3-5). There have been reports on the synthesis and structure of metal- and organometal complexes with Ti^{IV} and

Zr^{IV} ions (6,7). The synthesis, characterization and structural studies of thiolato-bridged Ti^{IV}-Cu^{I} species have suggested the importance of hetero-bimetallic complexes containing d^{10}-d^{0} dative bonds (8). The valence ionisation spectrum of $TiCl_4$(9) and the electronic structure of titanium (IV) halides have been reported (10). Kinetic studies on the reactions of H_2O_2 with various oxotitanium (IV) complexes have provided evidence for an associative mechanistic pathway (11). Peroxo-titanium(IV) porphyrins were formed by the irreversible reactions of metalloporphyrins and peroxide ions (12). The reduction of peroxotitanium(IV) has been studied using S^{IV}, Fe^{II}, Ti^{III}, iodide, thiodiethanol, thioxane and thiourea in acidic solutions (13). The redox reactions of super oxo-titanium (IV) in acidic perchlorate solution have been shown to proceed by a one-equivalent mechanism (14).

Titanium (III) has been used for the reduction of iodo and bromo-penta-ammine ruthenium (III) complexes (15), perchlorate ions (16), substituted methyl phenyl sulphoxides (17), cobalt(III) complexes (18,19), and of malonic acids

(20). Complex formation of Ti^{III} with citric acid has been studied (21). Electron spin resonance and electro-chemical studies of macrocycle pentadienyl Ti^{III} and Zr^{IV} derivatives $[M(\eta^5-C_5H_5)R_2]$, involving chelated phosphino methyl, ($R=CH_2PPh_2$) and phosphino acetate, ($R=O_2CCH_2PPh_2$) ligands have been reported (22). There have been recent reports on the kinetics of the decomposition of peroxy-titanyl (2+) ion in acidic aqueous solution (23), as also on the synthesis and structural characterization of Ti^{o} anions (24).

The synthesis, characterization and catalytic oxidation of oxotitanium (IV) complexes with chiral imines of amino acids was reported. It was shown that these complexes were effective in the catalytic oxidation of sulphides, and in the epoxidation of activated olefins(25). Convenient and high-yield synthesis of many oxochloro organometallic derivatives were attempted, and particular emphasis focused on the monocyclo-pentadienyl oxochloro complexes of titanium (IV). The electronic configuration of such complexes by extended Hückel molecular orbital calculations has been achieved(26). Metal aryl oxides have been found to have useful applications as polymerization catalysts, antioxidants, insecticides and fungicides. The results of studies on the synthesis and characterization of orthochlorophenoxy derivatives of Ti (IV) have been reported (27). The chemistry of organometallic complexes has now become important, owing to the relevance of these compounds to metal-catalysed oxo-transfer reactions, as models for studies of metal-supported interactions, and for the transformation of the hydrocarbons on metal or metal oxide surfaces. The synthesis of the first organometallic heteropolynuclear μ-oxo-complexes containing titanium bonded to oxygen has been reported (28). The reaction of TiO_2 or titanium isopropoxide with glycol, in the presence of alkali metal hydroxides, has been used for the synthesis and structural characterization of soluble titanium glycolatato-complexes (29).

Scanning tunneling microscopy (STM) has been successful in revealing novel insights concerning the surface chemistry on metals and semiconductors. This technique has been used for the atomic-scale imaging of a

TiO_2 (110) surface (30).

Bulky aryl oxide and alkoxide complexes of transition metals have been of continuing interest in organometallic chemistry. The synthesis and crystal structure of trichloro (2, 6-ditertiary butylphenoxo) titanium (IV) was reported, and this complex was shown to be active in olefin polymerization reactions (31).

Zirconium

The common oxidation state of zirconium is 4+. Aquo ions of lower valency states of zirconium are not very well-defined. Zirconium(IV) compounds exhibit high coordination numbers and a great variety of coordination polyhedra.

Complex formation in the zirconium (IV) system has been observed with xylenol orange papaverine perchlorate (32), pyrocatecholazo derivatives (33), and with alkynes (34) and benzidynes (35). There have been reports on the kinetics of ion exchange of some metal amines in hydrous zirconium (IV) oxides (36), as also the kinetics of exchange of some divalent metal ions with phosphosilicates of zirconium (IV) ions (37). Kinetic studies have been carried out on the acid dissociations of the tetrameric ion of zirconium, $[Zr_4(OH)_8\ H_2O]^{8+}$, with particular emphasis on the acid dependence on the rates of such reactions (38). The kinetics of metal-centred rearrangements and the C-N bond rotations in Ti^{IV} and Zr^{IV} in N,N'- dialkyl thiocarbamates have highlighted the stereochemistry of 8-coördinated dodecahedral complexes of the type MX_4Y_4(39,40). Equilibrium studies and redox kinetics of peroxo complexes of zirconium(IV) in acid perchlorate solutions have been reported (41).

The syntheses and ion exchange properties of crystalline zirconium (IV) complexes have been studied (42). Crystal and molecular structures of [dihydro-bis (1-pyrazolyl) borato] dichloro cyclopentadienyl zirconium (IV) have emphasised the importance of mixed borate zirconium (IV) complexes (43). Cationic zirconium (IV) benzyl complexes have gained importance as examples of the one-electron oxidation of d^0 organometallics (44). The synthesis and spectroscopic importance of zirconium phosphate have been reported (45, 46).

The reaction of $ZrOCl_2.8H_2O$ and 2,2'- oxydiacetic acid, in aqueous media, was used for the synthesis of the novel mononuclear 8-coordinate zirconium complex, which was subjected to characterization and single crystal X-ray diffraction studies (47). The chemistry of pentamethyl-cyclopentadienyl substituted Group IV fluorides has now been shown to be a fertile area of research with far-reaching results. A series of mono and di-substituted cyclopentadienyl Group IV fluorides were prepared, and the properties of the acetyl acetonato complexes of titanium and zirconium were determined (48).

PRESENT WORK

The present work is a detailed kinetic investigation of the reduction of titanium(IV) and zirconium(IV) by sodium tetrahydroborate, in aqueous acidic media.

Effect of metal ion (M^{IV}) and $NaBH_4$

The reactions between metal ions and tetrahydroborate were observed to be first order in each of the reactants (Tables 1-2).

Table 1: Effect of $[Ti^{4+}]$ and $[BH_4^-]$

$[BH_4^-]$ (10^2 x M)	$[Ti^{4+}]$ (10^3 x M)	10^3 x k_1 (s^{-1})
1.0	1.0	4.8
1.5	1.0	7.0
2.0	1.0	9.2
2.5	1.0	12.3
5.0	1.0	23.0
1.0	0.5	4.8
1.0	0.1	4.9

pH = 0.3 Temp=30°C

Table 2. Effect of [Zr^{4+}] and [BH_4^-]

[BH_4^-] (10^2 x M)	[Zr^{4+}] (10^3 x M)	10^3 x k_1 (s^{-1})
1.0	1.0	4.6
1.5	1.0	6.1
2.0	1.0	7.9
2.5	1.0	10.1
5.0	1.0	19.7
1.0	0.5	4.4
1.0	0.1	4.5

pH = 0.3 Temp = 30°C

Plots of k_1 against a five-fold range of concentration of BH_4^- ions gave straight lines passing through the origin, indicating that the rates of the reactions were dependent on the first power of the concentration of BH_4^- ions.

At constant BH_4^- concentrations (large excess) the pseudo-first-order rate constants (k_1) did not change with changing metal ion concentrations, indicating a first order dependence of the rate on the concentration of metal ions (Tables 1-2).

Effect of pH

The reactions were carried out at varying pH (Tables 3-4).

Table 3. Effect of pH on Ti^{4+} - BH_4^- system

pH	$10^3 \times k_1$ (s^{-1})
0.12	8.8
0.3	4.8
0.6	2.6
1.0	1.4
1.3	0.7

$[BH_4^-] = 1.0 \times 10^{-2}$ M, $[Ti^{4+}] = 1.0 \times 10^{-3}$ M, Temp = 30°C

Table 4. Effect of pH on Zr^{4+} - BH_4^- system

pH	$10^3 \times k_1$ (s^{-1})
0.12	8.2
0.3	4.6
0.6	2.2
1.0	1.0
1.3	0.4

$[BH_4^-] = 1.0 \times 10^{-2}$ M, $[Zr^{4+}] = 1.0 \times 10^{-3}$ M,

Temp = 30°C

The logarithm of the rate of disappearance of the metal ions divided by tetrahydroborate ion concentrations was plotted against the respective pH. The plots were linear, indicating a first-order dependence of the rates of the reactions on the hydrogen ion concentrations.

Rate Law

Under the present experimental conditions, the rate law could be expressed as :

$$\text{Rate} = -\frac{d[M^{IV}]}{dt} = k\,[M^{IV}]\,[BH_4^-]\,[H^+]$$

where M = Ti and Zr

Effect of temperature

The rates of the reactions were influenced by changes in temperature and an increase in temperature resulted in an increase in the rates of the reactions (Tables 5-6).

Table 5. Effect of temperature on Ti^{4+} - BH_4^- system

Temp. (±0.1°C)	$10^3 x k_1$ (s^{-1})
25	3.2
30	4.8
35	6.2
40	8.4
45	11.9

$[BH_4^-] = 1.0 x 10^{-2}$ M ; $[Ti^{4+}] = 1.0 x 10^{-3}$ M ;

pH = 0.3

Table 6. Effect of temperature on Zr^{4+} - BH_4^- system

Temp (±0.1°C)	$10^3 x k_1$ (s^{-1})
25	3.3
30	4.6
35	6.4
40	8.3
45	12.1

$[BH_4^-] = 1.0 \times 10^{-2}$ M; $[Zr^{4+}] = 1.0 \times 10^{-3}$ M;

pH = 0.3

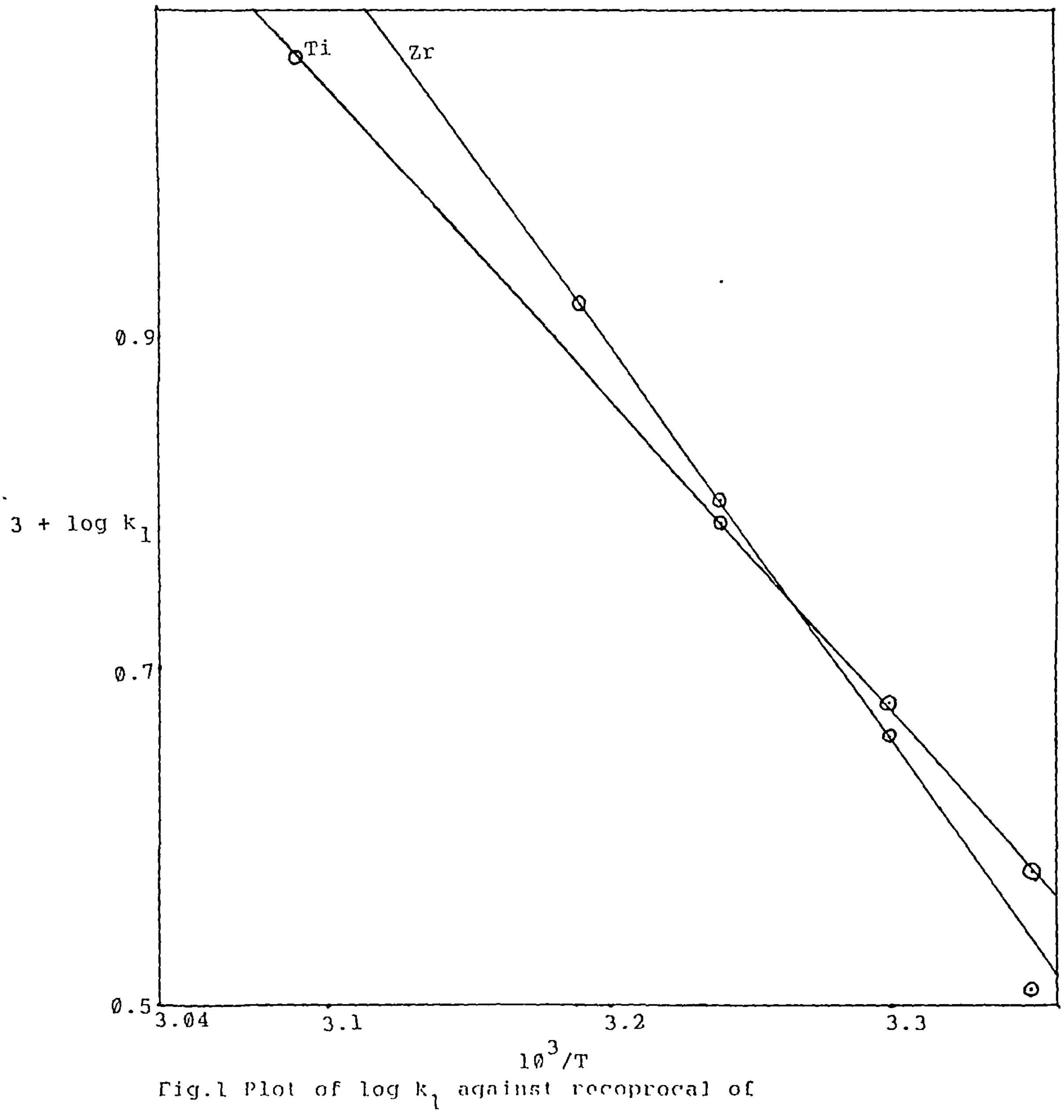


Fig.1 Plot of log k_1 against recoprocal of temperature [Substrate: Titanium(IV) and Zirconium(IV]

Plots of log k_1 against the reciprocal of temperature were linear (Fig.1), indicating the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the two systems.

The other activation parameters were calculated (vide 'Experimental' : Calculations) and have been shown in Table 7.

Table 7. Activation Parameters

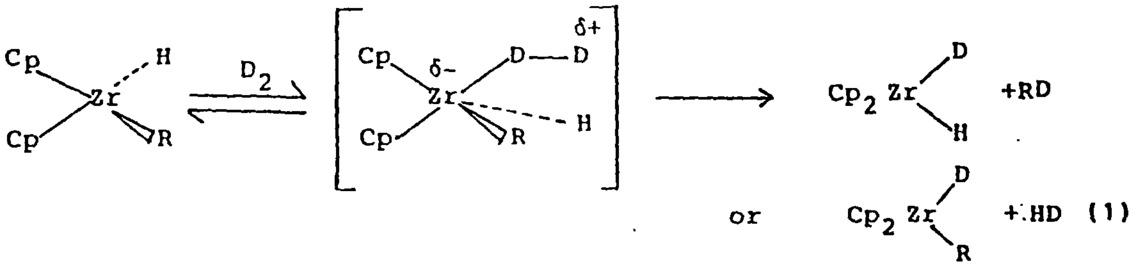
Parameters	Value ($Ti-BH_4^-$ system)	Value ($Zr-BH_4^-$ system)
E (kJ mol^{-1})	36±2	48±2
A (s^{-1})	7.5×10^4	8.2×10^4
$\Delta H^{\neq}$ (kJ mol^{-1})	33±2	45±2
$\Delta S^{\neq}$ ($JK^{-1} mol^{-1}$)	-315±3	-274±3
ΔG (kJ mol^{-1})	128±2	128±2

The negative entropies of activation would indicate that the process of electron transfer played a dominant role in both these reactions.

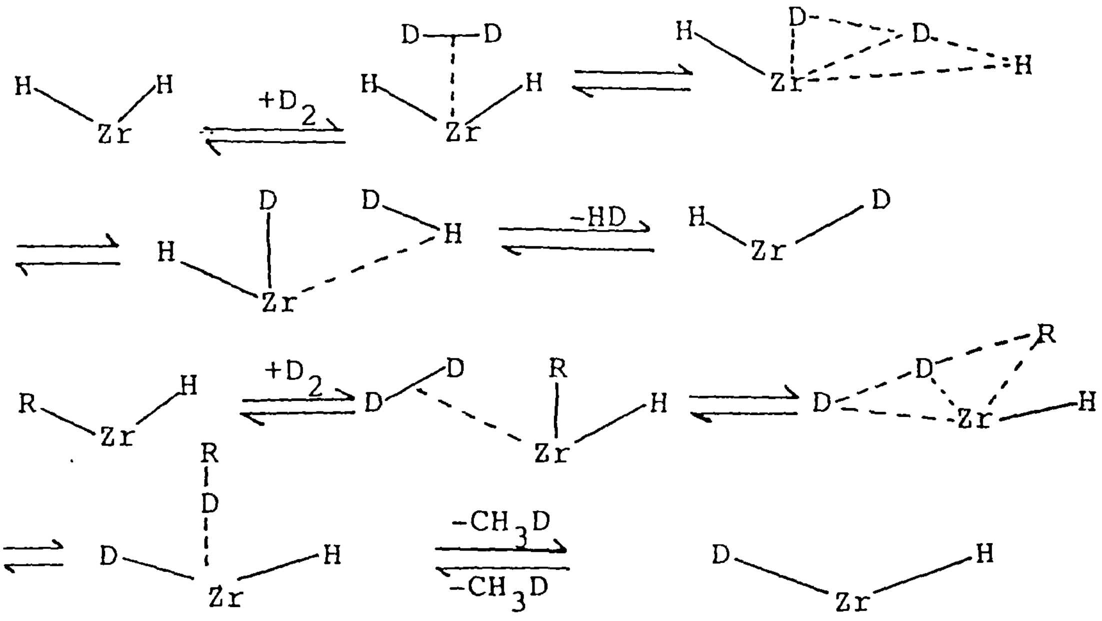
Mechanism

Titanium and zirconium in the +4 oxidation state are d^0 systems, and are known to activate hydrogen.

Olefin hydrogenation, catalysed by Cp_2ZrHR [R=(cyclohexyl)-methyl, $C_6H_{12}CH_2^-$], had indicated a hydride abstraction mechanism, where electrophilic attack by the H^+ (or D^+) moiety in the "five coordinate" intermediate gave either HD or the labelled alkane,



This mechanism was consistent with the observation that scrambling of the Zr-H with deuterium occurred faster than the production of RD (49). It was later proposed that a direct hydrogen transfer mechanism could be considered to be a limiting case of heterolytic activation of H_2, although the transition state contains no positively charged hydrogen species (50).



The reduction of $TiCl_4$ vapour with $LiBH_4$ (51) yielded tris (tetrahydroborato) titanium (III), Ti $(BH_4)_3$, wherein the parallel reduction of Ti(IV) to Ti(III) accompanied the substitution reaction, resulting in the formation of $Ti(BH_4)_3$. When titanium (IV) tetrabutoxide was treated with diborane in THF solution, the complex, $Ti(BH_4)_2.(OC_4H_9).(OC_4H_8)$, was formed, and substitution was accompanied by the corresponding reduction of metal to yield a titanium (III) complex (52).

The treatment of $Zr(BH_4)_4$ with tetra alkyl ammonium salts of $B_2H_7^-$ resulted in the formation of the complex anion, $[Zr(BH_4)_5^-]$,

$$(R_4N^+)\ (B_2H_7^-) + Zr(BH_4)_4 \longrightarrow [R_4N^+]\ [Zr(BH_4)_5^-] + \frac{1}{2}BH_3 \quad (2)$$

The significant aspect of this reaction was that Zr^{4+} could function as Lewis acid, with an acidity in excess of that exhibited by BH_3 (53).

The reaction of the organometallic complex, bis (cyclopentadienyl) titanium(IV) dichloride, with excess lithium tetrahydroborate yielded bis (cyclopentadienyl) titanium tetrahydroborate (54).

$$2(\eta^5\text{-}C_5H_5)_2TiCl_2 + LiBH_4 \longrightarrow 2(\eta^5\text{-}C_5H_5)_2Ti(BH_4) + 4LiCl + B_2H_6 + H_2 \quad (3)$$

The reaction of cyclopentadienyl titanium (IV) trichloride with three fold excess of $Li(BH_4)$ (55) gave cyclopentadienyl titanium (III) bis (tetrahydroborate),

$$2(\eta^5\text{-}C_5H_5)TiCl_3 + 6LiBH_4 \longrightarrow 2(\eta^5\text{-}C_5H_5)Ti(BH_4)_2 + 6LiCl + B_2H_6 + H_2 \quad (4)$$

The reduction of $(C_5H_5)_2TiBH_4$ or $(C_5H_5)_2ZrBH_4$ with CO and triphenylamine in benzene yielded $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_5)_2Zr(CO)_2$ respectively (56).

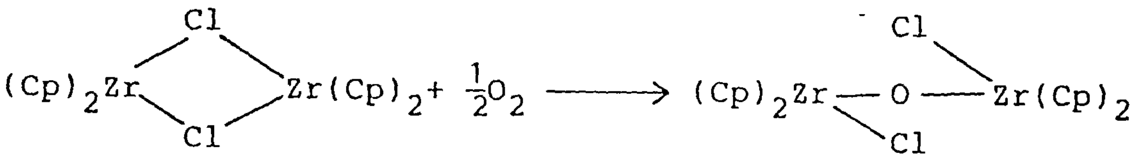
The reduction of zirconium(IV) to a lower oxidation state is difficult even when carried out in the presence of appropriate ligands like CO, phosphines and cyclopentadienyl. A few zirconium (II) model compounds have been reported (57-59), and these have been considered as highly reactive functional equivalents of monomeric 'Zirconocene'. It is known that zirconium tetrahydroborates are decomposed to hydrides by tertiary amines,

$$[Zr(Cp)_2(BH_4)_2]+NR_3 \longrightarrow NR_3.BH_3+[Zr(Cp)_2H(BH_4)] \qquad (5)$$

$$[Zr(Cp)_2(BH_4)_2]+2NR_3 \longrightarrow 2NR_3.BH_3+1/n[[Zr(Cp)_2H_2]_n] \qquad (6)$$

Zirconium(II) compounds have been used as starting materials for the facile synthesis of dimeric zirconium(III) complexes. Unlike the corresponding titanium compounds,these compounds, are diamagnetic (a consequence of a Zr-Zr bond). Whereas the final oxidation state is common for titanium and mild reducing agents can effect the $Ti^{IV} \longrightarrow Ti^{III}$ conversion, organo metallic complexes of zirconium(III) are not very common (60). Earlier attempts to synthesise bis-(cyclopentadienyl) zirconium(III) derivatives such as $[\{Zr(Cp)_2 X_n\}_n]$ by the conventional reduction of the corresponding zirconium (IV) complexes, $[Zr(Cp)_2 X_2]$, were not successful (61).

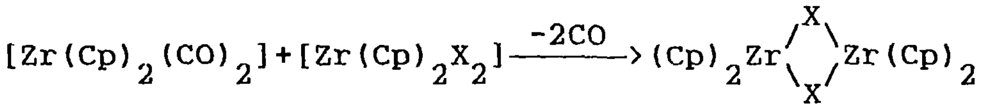
In the reactions leading to low-valent zirconium (III) complexes, there was some uncertainty regarding the cyclopentadienyl ligand. It was suggested that the absorption of oxygen would enable the conversion (62).



(7)

(I) (II)

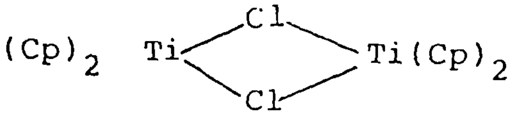
The compound(I) was observed to be diamagnetic. The diamagnetism of zirconium(III) dimers was explained by considering the $[Zr(Cp)_2]$ fragment orbitals to be greatly diffused, which would allow an efficient overlap between the two non-bonding orbitals with consequent Zr-Zr bond formation (63). There has been some evidence to show that zirconium could form metal-metal bonds, as characterized by several diamagnetic dimeric zirconium(III) complexes (64). It has also been observed (65) that zirconium(IV) compounds $[Zr(Cp)_2XY]$ (X=Cl ; Y=Cl, Me, OBu^t) could establish a metal-metal bond with the Ru (O) complex, $[Ru(Cp)(CO)_2]^-$, in a manner similar to that occurring between a basic and an acidic zirconium,



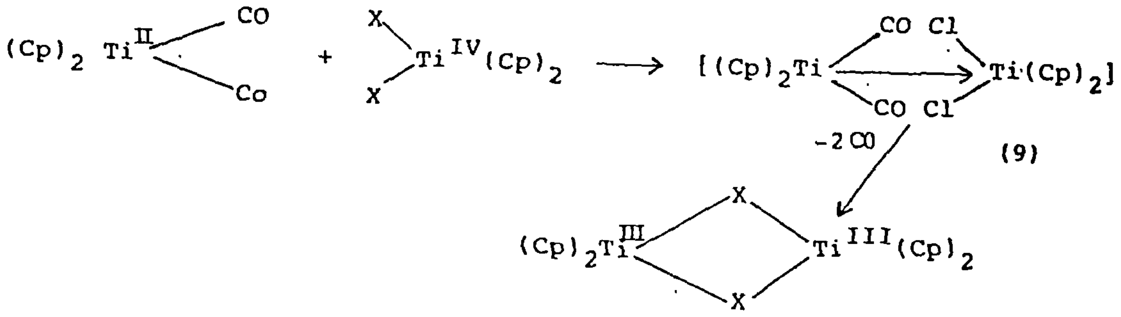
$$[Zr(Cp)_2(CO)_2]+[Zr(Cp)_2X_2]\xrightarrow{-2CO}(Cp)_2Zr\langle{}^{X}_{X}\rangle Zr(Cp)_2 \qquad (8)$$

(where X=Cl)

In the titanium analogues, magnetic moments are a little lower (1.4 - 1.5 BM) than the expected value of one unpaired electron per metal atom (1.73 BM). This was explained by suggesting a partial spin coupling through the bridging chlorine ligands(66) of the structure,



A general synthesis leading to bis-(cyclopentadienyl) titanium(III) complexes (67) can be extended to zirconium analogues. Such a reaction occurs between $[Ti(Cp)_2(CO)_2]$ and a titanium(IV) complex, $[Ti(Cp)_2X_2]$,



(9)

$(X = Cl,\ S\text{-}Ph\ \text{or}\ S\text{-}C_6H_4Me\text{-}p)$

The general reaction in which the Lewis base, Ti^{II}, attacks the Lewis-acid, Ti^{IV}, applies quite well to zirconium.

In the reaction of Ti^{III} with Fe^{III}, the rate was observed to be first order in both the reactants

$$-\frac{d[Ti^{III}]}{dt} = k_1[Ti^{III}][Fe^{III}],$$

where k_1 was dependent on both the chloride ion and hydrogen ion concentrations.

A similar first-order dependence on metal ion concentrations was observed in the reaction between Ti^{III} and Hg^{II},

$$Ti^{III} + Hg^{II} \xrightarrow{slow} Ti^{IV} + Hg^{I} \qquad (10)$$

$$Ti^{III} + Hg^{I} \xrightarrow{fast} Ti^{IV} + Hg^{o} \qquad (11)$$

$$Hg^{o} + Hg^{II} \xrightarrow{fast} (Hg^{I})_2 \qquad (12)$$

The slow step of the reaction was dependent on the hydrogen ion concentration. Chloride ions were shown to retard the reaction of titanium(III) and plutonium(IV).

$$Ti^{III} + Pu^{IV} \longrightarrow Ti^{IV} + Pu^{III} \qquad (13)$$

The rate equation was of the form,

$$- \frac{d[Ti^{III}]}{dt} = k\ [Ti^{III}]\ [Pu^{IV}]\ [H^{+}]^{-1} \qquad (14)$$

and chloride ions had little effect on the rate of the reaction (68).

The reaction between a strong oxidizing agent, perchlorate ions, and a strong reducing ion, $Ti^{III}(t_{2g}^{1})$, had indicated a one-equivalent oxidation of the metal ion (69).

$$8Ti^{III} + ClO_4^{-} + 8H^{+} \longrightarrow 8Ti^{IV} + Cl^{-} + 4H_2O \qquad (15)$$

with a rate law,

$$- \frac{d[Ti^{III}]}{dt} = k_1\ [Ti^{III}]\ [ClO_4^{-}]$$

There was a direct hydrogen ion dependence (69), but the addition of chloride ions retarded the reaction, apparently due to the formation of $TiCl^{2+}$. The mechanism involved an electron transfer from the metal ion to a d-orbital on the chlorine atom of the perchlorate ion.

In the present investigation, the rates of both the reduction reactions (the reduction of titanium(IV) and zirconium(IV)), respectively, by $NaBH_4$) were dependent on the concentration of tetrahydroborate and hydrogen ion. The composition of the activated complex could be written as $H^+BH_4^-$. The first step of the reaction would be

$$BH_4^- + H^+ \longrightarrow H^+BH_4^- \qquad (16)$$

Since the reduction of M^{4+} to M^{3+} involved a one-electron transfer, the mechanistic pathway for the reduction process of the metal ions by $NaBH_4$ could be rationalised. In the case of titanium, the peroxocomplex $[TiF_5O_2]^{3-}$ remained in the +4 state. On reduction by $NaBH_4$, a violet-coloured precipitate was obtained, which indicated that Ti^{4+} was reduced to the Ti^{3+} state. This precipitate, on keeping, was reoxidised to the Ti^{4+} state. The sequence of the steps could be represented as follows:

$$H^+BH_4^- + 2Ti^{4+} + H_2O \longrightarrow 2Ti^{3+} + [BH_3OH]^- + 3H^+ \qquad (17)$$

$$\underset{\text{(violet)}}{Ti^{3+}} \xrightarrow[-e]{[O]} \underset{\text{(white)}}{Ti^{4+}}$$

In the case of $ZrOCl_2$, zirconium exists in the +4 oxidation state. On reduction by $NaBH_4$, (ZrO^+) ion in solution was obtained. On keeping, zirconium was reoxidised to the +4 oxidation state, giving a white gelatinous precipitate of $ZrO_2.nH_2O$ (hydrated ZrO_2). The sequence of steps could be represented as follows:

$$H^+BH_4^- + 2Zr^{4+} + H_2O \longrightarrow 2Zr^{3+} + [BH_3OH]^- + 3H^+ \qquad (18)$$

$$Zr^{3+} \xrightarrow[-e^-]{[O]} Zr^{4+}$$

The Zr^{4+} was obtained as a white gelatinous precipitate of $ZrO_2.nH_2O$.

The reduction of M^{4+} to M^{3+} has been reported in earlier investigations (51-56). The formation of M^{3+} species in both the cases (Ti and Zr) have been observed, and evidence has been provided to confirm their presence (vide Experimental : 'Product Analysis'). The subsequent steps would involve the reactions of M^{4+} ions (titanium and zirconium) with tetrahydroborate species. There have been earlier reports regarding the formation of intermediate boron compounds (70, 71). In the present investigation, experimental evidence has been obtained for the formation of the intermediate boron compound, $Na[BH_3OH].H_2O$. This compound has been characterized, using chemical and spectral analyses (vide Experimental: `Analysis of the Boron Intermediate').

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CHAPTER 2

KINETICS OF REDUCTION OF IRON(III)

Iron(III) complexes have been used extensively for the oxidation of various organic and inorganic cpmpounds. Potassium hexacyanoferrate (III), in alkaline medium, has been used for the oxidation of diverse substrates such as cyclic alcohols (1,2), unsaturated alcohols (3), amino alcohols (4), phenothiazines (5), ethanolamines (6,7), benzylamines (8,9), arsenic(III) ions (10), sulphite ions (11), hydroxy acids (12), aldehydes(13), aliphatic and aromatic amines(14), inorganic sulphur compounds(15), phenols(16), and amino acids(17). In acid medium, potassium hexacyanoferrate(III) has been used for the oxidation of hydrazines (18), thioureas (19), organic sulphur compounds (20,21), hydrocarbons (22), arylalkanes (23), unsaturated compounds(24), and polynuclear hydrocarbons(25). Iron(III) complexes have been used for the oxidation of various substrates such as hydrazines(26-29), imidazoles(30), aromatic amines(31), phenols(32,33), peroxydisulphate catalysed by Ag(I) ions(34), cobalt(II) complexes(35,36), iodide ions(37), mercapto carboxylic ligands(38), iodine(39), molybdenum(IV) and molybdenum(V) complexes(40), and the cobalt(III) picolinate complexes(41). Electron transfer reactions have been studied in iron(II) and iron(III) systems(42,43). Chronovoltametric studies on the kinetics of electrode redox reactions involving the Fe(III)/Fe(II) system have been reported(44). Metal hydrides have been shown to be effective electron donors in the oxidative cleavage of iron(III)-tris-(phenanthroline) complexes(45). The kinetics of Fe^{2+} oxidation and Fe^{3+} reduction in MgO single crystals have been reported(46). The reactions of Fe^{III} and Fe^{II} thiocyanate with ammonia and their reductions with alkali metals in liquid ammonia solutions of alkali metal cyanides have been studied(47). The reduction of iron(III) complexes by haemoglobin has been reported(48). The kinetics of the intramolecular electron transfer from Ru^{II} to Fe^{III} in ruthenium-modified cytochrome has been studied(49).

Iron(II) ions have been used extensively for the reduction of cobalt(III) complexes(50-53), hydrogen peroxide(54), and cerium(IV) nitrate(55). The redox behaviour of the iron sulphur cluster, $[Fe_6(\mu\text{-}s)_8(PEt_3)_6]^{2+}$ has been reported(56).

The kinetics of oxidation of orthobenzoquinonedioxine by hexacyanoferrate(III) in buffered alkaline aqueous methanolic medium showed a first order dependence on the concentration of each of the reactants(57). The synthesis, structure, spectra and redox chemistry of iron(III) complexes of tridentate pyridyl and benzimidazolyl ligands have been reported. It was observed that iron(III) possessed rhombically distorted octahedral coordination, constituted by all the nitrogen atoms of the facial ligand the chloride ions(58).

PRESENT WORK

The present work is a detailed kinetic investigation of the reduction of Iron(III) in aqueous alkaline medium by sodium tetrahydroborate.

Effect of Fe^{3+} ions and $NaBH_4$

The reaction between Fe^{3+}, and tetrahydroborate ions was observed to be first order in each of the reactants (Table 1).

The plot of k_1 against a ten-fold range of concentration of BH_4^- ions gave a straight line passing through the origin, indicating that the rate of the reaction was dependent on the first power of the concentrations of BH_4^- ion (Table 1).

Table 1. Effect of [Fe^{III}] and [BH_4^-]

[BH_4^-] (10^2M)	[Fe^{III}] (10^4M)	$10^2 k_1$ (s^{-1})
2.5	2.5	2.6
5.0	2.5	5.1
7.5	2.5	7.9
10.0	2.5	10.6
12.5	2.5	13.2
2.5	1.0	2.7
2.5	5.0	2.5
2.5	7.5	2.5
2.5	10.0	2.6
2.5	25.0	2.5
2.5	50.0	2.6

pH = 11.5 Temp = 25°C

At constant BH_4^- concentration (large excess), the pseudo-first-order rate constant (k_1) did not change, with the changing metal ion concentration (ten-fold range), indicating a first order dependence of the rate on the concentration of the metal ion (Table 1).

Effect of pH

The reaction was studied at varying pH (Table 2).

Table 2. Effect of pH on Fe^{III}-BH_4^- system

pH	$10^2 k_1$ (s^{-1})
11.5	2.6
11.0	4.1
10.5	6.2
10.0	7.5
9.5	9.2
9.0	10.6

$[BH_4^-] = 2.5 \times 10^{-2}$M; $[Fe^{III}] = 2.5 \times 10^{-4}$M; Temp=25°C

The logarithm of the rate of disappearance of the Fe^{3+} ion, divided by the tetrahydroborate ion concentration, was plotted against the pH of the Fe-BH_4^- system. The plot was linear, indicating a first order dependence of the rate of the reaction on hydrogen ion concentration.

Rate law:

Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = -\frac{d[\text{Fe}^{3+}]}{dt} = k_1[\text{Fe}^{3+}][\text{BH}_4^-][\text{H}^+]$$

Effect of temperature

The rate of the reaction was influenced by changes in temperature, and an increase in temperature resulted in an increase in the rate of the reaction (Table 3).

Table 3. Effect of temperature on Fe^{III}-BH_4^- system.

Temp. $(\pm 0.1)\,^{o}\text{C}$	$10^2 k_1 (s^{-1})$
25.0	2.6
30.0	5.0
35.0	5.6
45.0	6.6
55.0	7.4

$[\text{BH}_4^-] = 2.5 \times 10^{-2}$M; $[\text{Fe}^{III}] = 2.5 \times 10^{-4}$M; pH=11.5

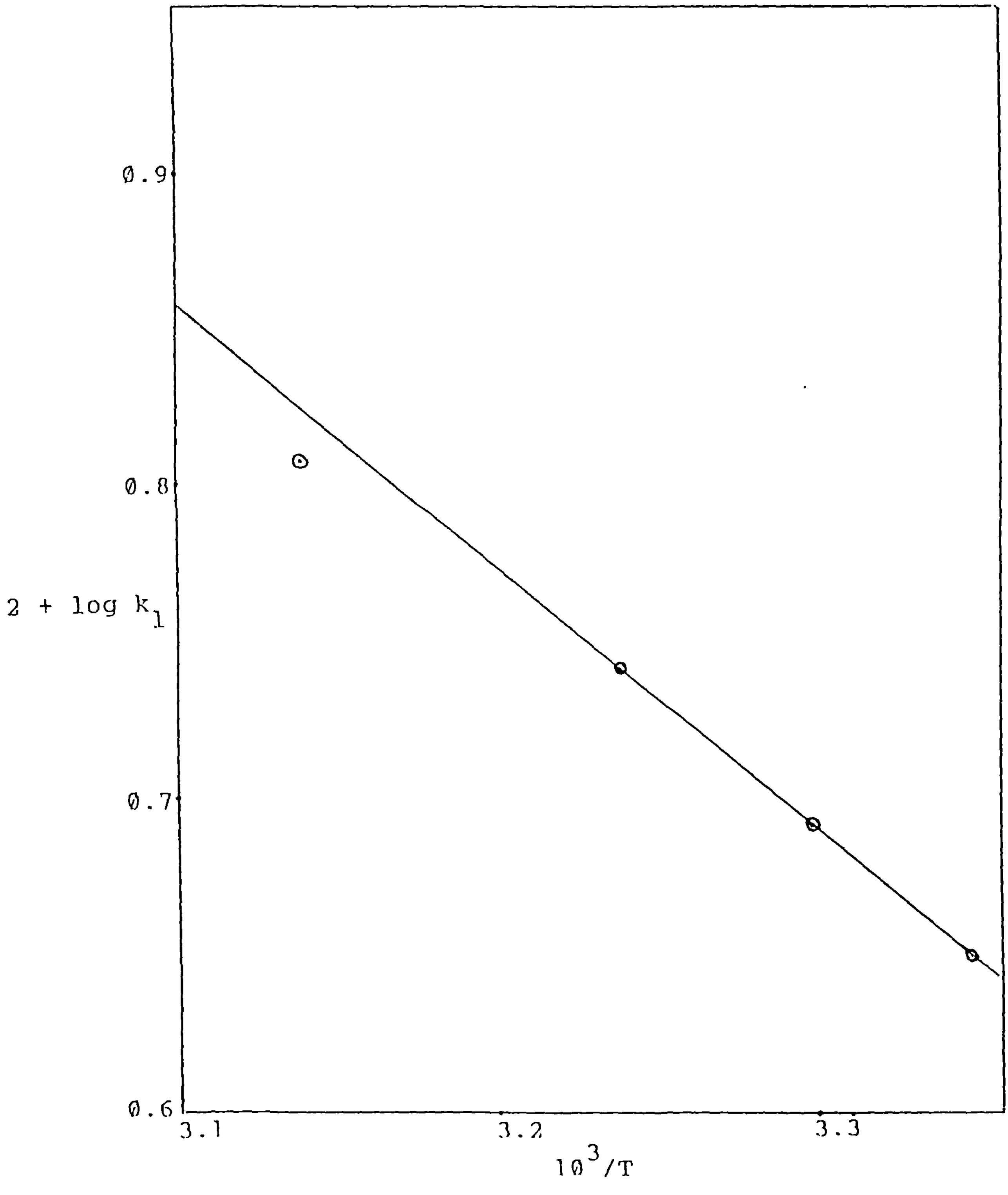


Fig.1 Plot of log k_1 against the reciprocal of temperature [substrate : Iron (III)]

The plot of log k_1 against the reciprocal of temperature was linear (Fig.1), indicating the validity of the Arrhenius equation. The slope of the plots was used to calculate the activation energy of the system. The other activation parameters were calculated (vide 'Experimental': Calculations) and have been shown in Table 4.

Table 4. Activation Parameters

Parameter	Value Fe - BH_4^- system
E (kJ mol^{-1})	19±2
A (s^{-1})	1.6
$\Delta H^{\neq}$ (kJ mol^{-1})	16±2
$\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	-241±3
$\Delta G^{\neq}$ ($kJmol^{-1}$)	72±2

The negative value of $\Delta S^{\neq}$ observed in the system (Table 4), indicated that the process of electron transfer played a dominant role in the system.

Mechanism

The tetrahydroborate ion in aqueous solution acts as a source of nucleophilic hydride ions, which reduces metal ions to a lower oxidation state. The reaction of the hydroborate ion with metal ions or compounds usually results *in either a reduction of the metal to a lower oxidation* state and the possible formation of a hydride compound, or the formation of a hydroborate or a borane derivative. Frequently, metal hydride complexes are formed (59,60).

The reaction of Cr^{2+}— Cl^- solution with Fe^{3+}(61) gave the rate equation

$$\text{Rate} = k_1[Cr^{2+}][Fe^{3+}]+k_2[Cr^{2+}][FeOH^{2+}]+k_3[Cr^{2+}][FeCl]^{2+}$$
$$+k_4[Cr^{2+}][Fe^{3+}][Cl^-],$$

consistent with the mechanism:

$$Cr(H_2O)^{2+} + Fe(H_2O)_6^{3+},\ Cl^- \longrightarrow$$
$$[(H_2O)_5Cr^{II}\text{-}Cl\text{-}H_2O\text{-}Fe^{III}(H_2O)_5]^{4+} \longrightarrow$$
$$Cr(H_2O)_5Cl^{2+} + Fe(H_2O)_6^{2+},$$

wherein the formation of $CrCl^{2+}$ would proceeded via an outer sphere activation complex in which Cl^- was bonded directly to the chromium.

In the reaction of Ti^{III} and Fe^{III}, the rate was first order in both the reactants. The rate law was expressed as

$$-\frac{d[Ti^{III}]}{dt} = k_{obs}\,[Ti^{III}][Fe^{III}] \qquad (1)$$

where k_{obs} was dependent on both, the Cl^- and H^+ ion concentrations,

$$k_{obs} = k_1 + k_2\,[H^+]^{-1} + k_3[Cl^-] \qquad (2)$$

The Fe^{III} oxidation of Np^{IV} to Np^V gave an overall reaction (62)

$$Np^{4+} + Fe^{3+} + 2H_2O \longrightarrow NpO_2^+ + Fe^{2+} + 4H^+,$$

where the rate law was

$$-\frac{d[Np^{IV}]}{dt} = k[Np^{IV}][Fe^{III}][H^+]^{-3} \qquad (3)$$

In the reaction between U^{IV} and Fe^{III}, the overall equation (63)

$$U^{4+} + 2Fe^{3+} + 2H_2O \longrightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+,$$

gave an acid dependence,

$$-\frac{d[U^{IV}]}{dt} = [U^{IV}][Fe^{III}](k_1[H^+]^{-1} + k_2[H^+]^{-2}) \qquad (4)$$

The reaction of V^{III} and Fe^{III} conforms to a stoichiometric equation

$$V^{III} + Fe^{III} \longrightarrow V^{IV} + Fe^{II}$$

The effect of V^{IV} was countered by adding Fe^{II} which was in agreement with the reaction sequence:

$$V^{III} + Fe^{III} \xrightarrow{k_1} V^{IV} + Fe^{II} \qquad (5)$$

$$V^{IV} + Fe^{III} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} V^{V} + Fe^{II} \qquad (6)$$

$$V^{V} + V^{III} \xrightarrow{k_3} 2V^{IV} \qquad (7)$$

This reaction was catalysed by Cu^{2+} ions (64), wherein the rate law was shown to be independent of Fe^{III}, that is,

$$\frac{d[V^{III}]}{dt} = k_{Cat}[V^{III}][Cu^{II}] \qquad (8)$$

This was in agreement with the reaction sequence

$$V^{III} + Cu^{II} \xrightarrow{k_{cat}} V^{IV} + Cu^{I} \qquad (9)$$

$$Cu^{I} + Fe^{III} \xrightarrow{fast} Cu^{II} + Fe^{II} \qquad (10)$$

For the reaction of V^{IV} and Fe^{III},

$$VO^{2+} + Fe^{3+} + H_2O \rightleftharpoons VO_2^{+} + Fe^{2+} + 2H^{+} \qquad (11)$$

the value of K was $10^{-6}\ l^{-2}\ mol^{-2}$ at $0^{o}C$.

When V^{IV} and Fe^{III} were mixed, there was no detectable reaction, since the above equilibrium was very much to the left, and the net conversion to V^{V} and Fe^{II} was negligible. The mechanism of the reaction of V^{III} with Co^{III}(65) was similar to that of the reaction of V^{III} with Fe^{III}. Thus,

$$V^{III} + Co^{III} \xrightarrow{k_1} V^{IV} + Co^{II} \qquad (12)$$

$$V^{IV} + Co^{III} \xrightarrow{k_2} V^{V} + Co^{II} \qquad (13)$$

$$V^{III} + V^{V} \xrightarrow{fast} 2V^{IV} \qquad (14)$$

with the rate law,

$$-\frac{d[Co^{III}]}{dt} = k_1[V^{III}][Co^{III}] + k_2[V^{IV}][Co^{III}] \qquad (15)$$

A comparison of the rate constants $[M^{-1}sec^{-1}]$ at $0^{o}C$ and in 1N perchloric acid for some Fe^{III} and Co^{III} oxidations of the vanadium ions are shown in Table 5.

Table 5. Comparison of rate data

Vanadium ion	Reaction with Fe^{III}	Reaction with Co^{III}
V^{II}	$>10^{5}$	>300
V^{III}	0.009	0.192
V^{IV}	~0.0025	0.260

The similarity of the relative rates for the Co^{III} and Fe^{III} reactions (Table 5), suggested that these reactions proceeded by the same electron transfer mechanism. For the reaction of V^{3+} with Co^{3+}, $\Delta S^{\neq} = 5$ e.u., and for the reactions of V^{3+} with Fe^{3+}, $\Delta S^{\neq} = -15$ e.u. Such values could be accounted for by considering partial hydrolysis, that is, loss of H^+ ions from a coordinated water within the transition complex.

The reaction between I^- ions and Fe^{3+} ions,

$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+} \qquad (16)$$

was studied in perchloric acid solution (66), giving a rate law

$$-\frac{d[Fe^{3+}]}{dt} = \frac{a[I^-]^2[Fe^{2+}]}{b[Fe^{2+}]/[Fe^{3+}]+1} \qquad (17)$$

which was consistent with the mechanism,

$$I^- + Fe^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeI^{2+} \qquad (18)$$

$$I^- + FeI^{2+} \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} Fe^{2+} + I_2^- \qquad (19)$$

$$I_2^- + Fe^{3+} \xrightarrow{K_3} I_2 + Fe^{2+} \qquad (20)$$

When aqueous solutions of hydazine were oxidised by Fe^{3+}, the products obtained were N_2 and NH_3 (67),

$$N_2H_4 \xrightarrow{-e} N_2H_3 \longrightarrow \frac{1}{2} N_4H_6 \longrightarrow \frac{1}{2} N_2 + NH_3 \qquad (21)$$

In the oxidation of sulphite solutions by Fe^{III}, the products obtained were dithionate and sulphate, with a stoichiometry of 1.2 (68).

$$SO_3^{2-} \xrightarrow{-1e} SO_3^- \longrightarrow \frac{1}{2} S_2O_6^{2-} \qquad (22)$$

The reaction between H_2SO_3 and Fe^{III} has been studied, and in the presence of Cu^{II} as catalyst, the mechanism suggested was :

$$H_2SO_3 + Fe^{III} \xrightleftharpoons{-H^+} HSO_3 + Fe^{II} \qquad (23)$$

$$2HSO_3 \longrightarrow H_2S_2O_6 \qquad (24)$$

$$HSO_3 + Fe^{II} \xrightarrow{-H^+} SO_3(H_2SO_4) + Fe^{II} \qquad (25)$$

$$HSO_3 + Cu^{II} \xrightleftharpoons{-H^+} SO_3(H_2SO_4) + Cu^{I} \qquad (26)$$

followed by

$$Cu^{I} + Fe^{III} \xrightarrow{fast} Cu^{II} + Fe^{II} \qquad (27)$$

The catalysis was dependent on reaction (26), which was faster than reaction (25).

For the one-equivalent reaction of Cr^{II} with Fe^{III}, a possible reaction sequence was

$$Cr^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{III} + e^{-}_{aq} \qquad (28)$$

$$Fe^{III} + e^{-}_{aq} \xrightarrow{k_2} Fe^{II} \qquad (29)$$

giving the rate equation

$$-\frac{d[Fe^{III}]}{dt} = \frac{k_1k_2[Fe^{III}][Cr^{II}]}{k_{-1}[Cr^{III}] + k_2[Fe^{III}]} \qquad (30)$$

The reaction of Fe^{II} with Fe^{III} has been studied using labelled Fe^{III}(69).

$$Fe^{II} + {}^{*}Fe^{III} \longrightarrow Fe^{III} + {}^{*}Fe^{II} \qquad (31)$$

The rate was found to have an inverse H^+ ion dependence, and with the addition of Cl^-, there was a direct Cl^- ion dependence.

Understanding the chemistry of the reduction of metal ions by tetrahydroborate ions has become of increasing importance, as this approach has been used to prepare "amorphous metals" (70-72), nanocrystalline magnetic materials (73-77), and catalysts (78,79). It has become clear that boron was incorporated into the solid products, but the metal/boron ratios varied widely. These variations were due to mixing procedures, solvent media, temperature, or other factors. As the need to find reproducible ways to produce ultrafine materials increased (for use in magnets, electronics and catalysts), it became necessary to gain a better understanding of this unique reduction chemistry.

The reduction of Fe^{2+} and Fe^{3+} in aqueous and non-aqueous (diglyme) media was reported, and it was found that the primary products formed depended on the reaction media (80). It was observed that

(i) Fe^{2+} yielded mainly noncrystalline nanoscale Fe(s) in aqueous solution. In dry diglyme, Fe^{2+} gave nanoscale Fe_2B as the product.

(ii) Fe^{3+} yielded Fe(s) in aqueous medium, whereas in diglyme, Fe^{3+} gave Fe_2B.

The interaction of iron(II) bromide and $NaBH_4$ in diglyme, at room temperature, yielded a pale yellow coordination compound **2**, according to :

$$FeBr_2 + 2NaBH_4 \xrightarrow{L=diglyme} \underset{\mathbf{2}}{(L)_nFe(BH_4)_2} + 2NaBr \qquad (32)$$

This compound was stable at room temperature. The formation of **2** and its thermal decomposition to Fe_2B were independent of both,the concentration of the reagents and the BH_4^-/Fe^{2+} ratio. The following reaction scheme was proposed:

$$2(L)_nFe^{2+} + 4BH_4^- \longrightarrow 2\underset{\mathbf{2}}{(L)_nFe(BH_4)_2}$$

$$2(L)_nFe(BH_4)_2 \xrightarrow{65\text{-}70^{o}C} \underset{\mathbf{3}}{[(L)_nFe_2(\mu - BH_4)]} + \frac{3}{2}H_2 + \frac{3}{2}B_2H_6 + nL$$

$$\mathbf{3} \longrightarrow Fe_2B(s) + 2H_2 + nL$$

$$\frac{3}{2}\ B_2H_6 \xrightarrow[Catalysis]{Fe_2B} 3B(s) + \frac{9}{2}\ H_2$$

$$2(L)_nFe^{2+} + 4BH_4^- \longrightarrow Fe_2B + 3B + 8H_2 + 2nL \qquad (33)$$

The effect of the addition of water to **2** was as follows:

$$\underset{(\mathbf{2})}{2(L)_nFe(BH_4)_2} + 9H_2O \longrightarrow \underset{(\mathbf{3})}{[(L)_nFe_2(\mu - BH_4)]} + [\frac{5}{2} H_2 + 3B(OH)_3]$$

$$\mathbf{3} \longrightarrow Fe_2B(s) + 2H_2 + nL$$

$$2(L)_nFe(BH_4)_2 + 9H_2O \longrightarrow Fe_2B(s) + \frac{25}{2} H_2 + 3B(OH)_3 \tag{34}$$

The addition of water caused the formation of intermediate **3**, which again decomposed to the observed products. This sequence of reactions was thermodynamically very favourable, since 3 mol of $B(OH)_3$ were formed.

In aqueous media (pure water and water-diglyme mixtures), the dissolution of $FeBr_2$ gave the $Fe(H_2O)_6^{2+}$ aqua complex, which then underwent reaction with BH_4^- to give Fe(s), as follows

$$Fe(H_2O)_6^{2+} + 2BH_4^- \longrightarrow Fe(s) + 7H_2 + 2B(OH)_3 \tag{35}$$

The addition of solutions of $FeBr_3$-diglyme to $NaBH_4$ - diglyme produced a bright red solution which was very stable under an inert atmosphere.

The reaction sequence suggested was:

$$(L)_nFe^{3+} + 3BH_4^- \longrightarrow \underset{(\underset{\sim}{4})}{(L)_nFe(BH_4)_3}$$

$$\underset{\sim}{4} \xrightarrow{95\text{-}100^{0}C} FeB + 3H_2 + B_2H_6$$

$$B_2H_6 \xrightarrow[\text{Catalysis}]{\text{FeB}} 2B(s) + 3H_2$$

$$(L)_nFe^{3+} + 3BH_4^- \longrightarrow FeB(s) + 2B(s) + 6H_2 + nL \qquad (36)$$

The addition of a small amount of water to the room-temperature diglyme solution of $(L)_nFe(BH_4)_3$, resulted in rapid gas evolution, with the precipitation of a black powder, confirmed by XRD and Mossbauer spectra to be Fe_2B.

Thus, the decomposition of $(L)_nFe(BH_4)_3$ could be achieved in two ways :

(a) $(L)_nFe(BH_4)_3 \xrightarrow{H_2O} Fe_2B + B(OH)_3$ (37)

(b) $(L)_nFe(BH_4)_3 \xrightarrow[95\text{-}100^{o}C]{\Delta} FeB$ (38)

In pure, deoxygenated water, the $Fe(H_2O)_6^{3+}$ aqua complex was formed. Addition of this solution to solid $NaBH_4$ resulted in an instantaneous reaction with gas evolution, and the major product was α - Fe.

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \longrightarrow Fe(s) + \frac{21}{2} H_2 + 3B(OH)_3 \quad (39)$$

In the present investigation, the mechanistic pathway for the reduction of Fe^{3+} to Fe^{2+} by sodium tetrahydroborate would involve a one-electron transfer. Kinetic studies have shown that the rate of the reaction involving the reduction of Fe^{3+} by $NaBH_4$ was proportional to the concentration of both, BH_4^- and H^+ ions. The chemical composition of the activated complex could be written as $H^+BH_4^-$. The first step of the reaction was:

$$BH_4^- + H^+ \longrightarrow H^+BH_4^- \quad (40)$$

Since the reduction of Fe^{3+} to Fe^{2+} involved a one-electron transfer, it would be reasonable to suggest that Fe^{3+} reacted with the tetrahydroborate species in the subsequent steps as follows :

$$H^+BH_4^- + 2[Fe(CN)_6]^{3-} + H_2O \longrightarrow 2[Fe(CN)_6]^{4-} + BH_3OH^- + 3H^+ \quad (41)$$

When the residue was digested with concentrated hydrochloric acid, there was the formation of a prussian blue complex.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow \text{Prussian blue complex} \qquad (42)$$

The final product of this reaction was isolated and characterized by chemical and spectral methods (vide Experimental : Product analysis).

Hydrolysis of $NaBH_4$ and evidence for intermediate boron compounds.

The tetrahydroborate ion is stable in alkaline solution to the extent of being capable of recrystallisation from such a medium (81). Hydrogen evolution becomes more rapid as the pH of the solution is decreased, and hence the pH plays a very important role in such reactions (82-86). The kinetics of the hydrolysis over the pH range 3.8 to 14.0 have shown that the rate would be expressed (87) by the equation :

$$-\frac{d[BH_4^-]}{dt} = k_1[H^+][BH_4^-] + k_2[BH_4^-] \qquad (43)$$

The isotope effect in the hydrolysis reaction, using D_2O, was measured and the most probable mechanism involved the formation of BH_5 in the rate-determining step (87),

$$BH_4^- + H^+ \xrightarrow{slow} BH_5 \longrightarrow BH_3 + H_2 \qquad (44)$$

rather than

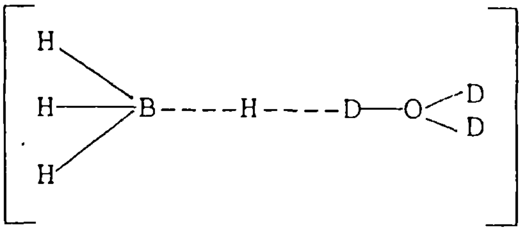
$$BH_4^- + H^+ \xrightarrow{slow} BH_3 + H_2 \qquad (45)$$

Following their isotope effect studies, Davis and coworkers (88) had suggested a different type of BH_5 intermediate,

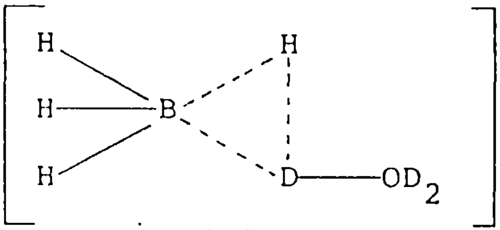
$$BH_4^- + H_3O^+ \underset{}{\overset{slow}{\rightleftharpoons}} \underset{H_2O}{[H^+BH_4^-]} \longrightarrow H_2 + BH_3(aq) + H_2O \qquad (46)$$

$$BH_3(aq) \xrightarrow[H_2O]{fast} H_3BO_3 + 3H_2 \qquad (47)$$

The transition state was suggested to be of the type shown in structure (1) and (2), and the existence of an aquated borane radical was supported by trapping it as $[(CH_3)_3NBH_3]$, with trimethylamine(89).



(1)



(2)

Other studies of the hydrolysis reactions were made using polarographic techniques (85,90,91).

A reaction scheme was proposed which involved the formation of intermediate boron species such as (BH_3OH^-) ion (90). The initial step in this reaction sequence was similar to the one proposed earlier (87,89), and the results further confirmed that the HA bond of the attacking acid was completely broken in the transition state,

$$BH_4^- + HA \xrightarrow{\text{slow}} \begin{bmatrix} H^+BH_4^- \\ A^- \end{bmatrix} \xrightarrow{\text{fast}} H_2 + BH_3 + A^- \qquad (48)$$

$$BH_3 + 2H_2O \xrightarrow{\text{fast}} BH_3OH^- + H_3O^+ \qquad (49)$$

$$BH_3OH^- + HA \xrightarrow{\text{slow}} \begin{bmatrix} H^+BH_3OH^- \\ A^- \end{bmatrix} \xrightarrow[2H_2O]{\text{fast}} H_3BO_3 + 3H_2 + A^- \qquad (50)$$

It was suggested that the electrode reaction probably arose from the oxidation (91),

$$BH(OH)_3^- + OH^- \longrightarrow BO_2^- + 2H_2O + \frac{1}{2} H_2 + e \qquad (51)$$

Independent support for the existence of an intermediate containing the BH_3 group came from a study of the anodic behaviour of the hydroborate ion in aqueous alkaline solution at a platinum electrode (92,93). The static potential was suggested to arise from a two-electron partial hydrogen ionization process which was observed to be independent of the concentrations of borate, hydroborate and hydrogen ion,

$$BH_4^- + Pt - 2e \longrightarrow Pt\ldots\ldots BH_3 + H^+ \qquad (52)$$

the borane intermediate being hydrolysed as

$$BH_3 + H_2O \longrightarrow BH_3OH^- + H^+ \qquad (53)$$

Infrared spectroscopy (94) and paper chromatography (95) techniques have been used to determine the type of intermediate involved in the hydrolysis of the borane intermediate. IR spectroscopy has led to the suggestion that BH_3OH^- is the only intermediate species in the hydrolysis of hydroborate ion (94). The reaction of potassium hydroborate with 8 M HCl at -70°C (96) gave strongly reducing solutions, and indicated the presence of a BH^{2+} cationic species,

$$BH_4^- + 2H^+ + 2H_2O \longrightarrow [(H_2O)_2BH_2]^+ + 2H_2 \qquad (54)$$

Above -20°C, the reaction was

$$[(H_2O]_2BH_2]^+ + H_2O \longrightarrow 2H_2 + B(OH)_3 + H^+ \qquad (55)$$

Although BH^{2+} ion could not be identified from the ^{11}B magnetic resonance spectrum, which consisted of a broad unresolved signal, similar signals were observed for other ions, such as $[(dioxane)_2BH_2]^+$ (97) and $[((CH_3)_2SO)_2BH_2]^+$ (98).

The reaction of the hydroborate ion and diborane, with KOH or an ethanol-water mixture, led to the suggestion that in the case of diborane, intermediate ions of the type $BH(OH_3)^-$ or $BH(OH)_2(OC_2H_5)^-$ were involved in the hydrolysis at low temperature, and these hydrolysed to boric acid as the solution was warmed (96). This suggested the possibility of ions of the type, $[(base)_2BH_2]^+$ and $BH(OH)_3^-$, being involved as short-lived intermediates in the hydrolysis of the hydroborate ion in acidic and basic conditions, respectively, at room temperature.

In the present investigation, since the rates of the reduction reactions were dependent on the concentrations of tetrahydroborate and hydrogen ions, the chemical composition of the activated complex could be written as $H^+BH_4^-$.

The first step of the reaction would be

$$BH_4^- + H^+ \longrightarrow H^+BH_4^- \qquad (56)$$

A kinetic equation consisting of equation (56), followed by consecutive steps involving hexacyanoferrate (III) could be used as a basis to explain the experimental results. Each boron intermediate could react with either a hexacyanoferrate (III) ion or with a hydrogen producing species such as water.

The reaction could be represented by the following sequence of steps :

$$BH_4^- + H^+ \longrightarrow H^+BH_4^-$$

$$H^+BH_4^- + 2Fe(CN)_6^{3-} + H_2O \longrightarrow BH_3OH^- + 2Fe(CN)_6^{4-} + 3H^+ \qquad (57)$$

$$BH_3OH^- + 2Fe(CN)_6^{3-} \longrightarrow BH_2OH + 2Fe(CN)_6^{4-} + H^+ \qquad (58)$$

$$BH_2OH + Fe(CN)_6^{3-} + H_2O \longrightarrow BH(OH)_2^- + Fe(CN)_6^{4-} + 2H^+ \qquad (59)$$

$$BH(OH)_2^- + Fe(CN)_6^{3-} \longrightarrow BH(OH)_2 + Fe(CN)_6^{4-} \qquad (60)$$

$$BH(OH)_2 + 2Fe(CN)_6^{3-} \longrightarrow BO_2^- + 2Fe(CN)_6^{4-} + 3H^+ \qquad (61)$$

The overall stoichiometric reaction would then be:

$$BH_4^- + 8Fe(CN)_6^{3-} + 2H_2O \longrightarrow BO_2^- + 8Fe(CN)_6^{4-} + 8H^+ \qquad (62)$$

The rate law would be expressed as

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}\ [BH_4^-][H^+] \qquad (63)$$

It has been found that for this reaction, k_{obs} has the frequency factor of $1.6s^{-1}$ and an activation energy of 19 kJ mol^{-1} (Table 4).

The essential feature of this mechanism is that any given intermediate reacts only with a hydrogen producing species, or else with hexacyanoferrate (III). There is thus no competition for a given intermediate.

Further support of this mechanism was found from the rate measurements of the hydrolysis of BH_4^- ion, in the absence of hexacyanoferrate (III). The mechanism for the hydrolysis may be represented by :

$$BH_4^- + H^+ \longrightarrow H^+BH_4^-$$

followed by hydrogen yielding steps of the type:

$$BH_2OH + H_2O \longrightarrow BH(OH)_2 + H_2 \qquad (64)$$

$$2BH_2OH + 2H_2O \longrightarrow 2BH(OH)_2^- + 2H^+ + H_2 \qquad (65)$$

$$BH(OH)_2 + H_2O \longrightarrow H_3BO_3 + H_2 \qquad (66)$$

This mechanism would predict

$$-\frac{d[BH_4^-]}{dt} = k_1[BH_4^-][H^+] \qquad (67)$$

The rate of hydrolysis of $NaBH_4$ was measured and it was found that the rate constant, k_1, corresponded to an activation energy of 19 kJ mol^{-1}. This was in agreement with the value determined from the kinetic studies, in the presence of hexacyanoferrate (III).

Intermediate boron compounds

There have been earlier reports regarding the existence of intermediate boron compounds (99). Experimental support for the existence of such intermediates was obtained from the reaction of diborane with ice and with the "bound water" in silica gel (100).

These intermediates differed in their reducing capacities, and the formulae of the boron intermediates used were primarily intended to show the reducing capacity of the intermediate.

Consider the following steps :

$$BH_2OH + Fe(CN)_6^{3-} + H_2O \longrightarrow BH(OH)_2^- + Fe(CN)_6^{4-} + 2H^+ \qquad (68)$$

and

$$2BH_2OH + 2H_2O \longrightarrow 2BH(OH)_2^- + 2H^+ + H_2 \qquad (69)$$

These steps describe a one-electron oxidation by hexacyanoferrate (III) and water respectively, to give the intermediate $BH(OH)_2^-$, which has three equivalents of reducing capacity. Again consider the following steps :

$$BH_2OH + 2Fe(CN)_6^{3-} + H_2O \longrightarrow BH(OH)_2 + 2Fe(CN)_6^{4-} + 2H^+ \quad (70)$$

$$BH_2OH + H_2O \longrightarrow BH(OH)_2 + H_2 \quad (71)$$

These steps involved a two-electron oxidation to give $BH(OH)_2$, which has a two-electron reducing capacity.

When hydroborates react with acidic species, diborane is generally formed in a molar amount equal to one-half the number of moles of hydroborate consumed, as for example in the reaction of sodium tetrahydroborate with concentrated sulphuric acid (101).

$$NaBH_4 + H_2SO_4 \longrightarrow \frac{1}{2} B_2H_6 + H_2 + NaHSO_4 \quad (72)$$

It could be postulated that the reaction of the tetrahydroborate ion with aqueous proton would be

$$BH_4^- + H^+ \xrightarrow{slow} BH_3 + H_2 \quad (73)$$

However, the other rate-determining steps could be considered, such as

$$BH_4^- + H^+ \rightleftharpoons BH_5 \xrightarrow{slow} BH_3 + H_2 \qquad (74)$$

$$H_3O^+ + BH_4^- \xrightarrow{slow} H_3OBH_3^+ + H^- \qquad (75)$$

$$BH_4^- + H^+ \xrightarrow{slow} BH_5 \longrightarrow BH_3 + H_2 \qquad (76)$$

Reactions of the type represented by Eq. (74) usually proceed faster in D_2O than in H_2O, because of the weaker basicity of D_2O with respect to H_2O (102). It has been observed that the hydrolysis of BH_4^- is faster in H_2O than in D_2O, thus ruling out the mechanism given in Eq. (74).

BD_4^- reacts faster than BH_4^-, and BH_4^- hydrolyzes faster in H_2O than in D_2O. This would indicate that, in the formation of the activated complex, a B-H bond is strengthened and an O-H bond is weakened. These observations would rule out the possibility of the mechanism given in Eq. (75).

When BH_4^- is hydrolysed in D_2O, about 4% of the evolved hydrogen is H_2 (103), whereas when BD_4^- is hydrolysed in water, about 1% of the hydrogen is D_2. It seems likely that, in a process such as that shown in Eq. (73), the reacting proton (which essentially plucks a hydride ion from the BH_4^- ion) would always end up in the molecular hydrogen. It would seem more consistent to visualise that intermediates of composition BH_4D or BD_4H would be formed. These would mainly decompose to give, respectively, HD and BH_3 (or BD_3). Hence, it would be justified to postulate that the mechanism shown in Eq.(76), would be quite favourable.

The methanolysis of sodium tetrahydroborate (104) was observed to follow the rate law

$$-\frac{d[BH_4^-]}{dt} = \frac{1}{4}\,\frac{d[H_2]}{dt} = k_1[BH_4^-] \qquad (77)$$

It has been shown (105-106) that the activated complex formed from the reaction of $NaBH_4$ and a general acid (HA_j) contains a protonic hydrogen and a hydridic tetrahydroborate,

$$HA_j + BH_4^- \rightleftharpoons \underset{A_j}{[H^+BH_4^-]^{\neq}} \longrightarrow H_2 + BH_3 + A_j \qquad (78)$$

It would be justified to postulate that the first step of the reaction would involve the reaction of H^+ with BH_4^- to give the intermediate, $H^+BH_4^-$. This finds support from the experimental observation that the kinetics of the reduction reaction of metal ions by sodium tetrahydroborate showed a first order dependence on the concentrations of both, tetrahydroborate and hydrogen ions. The first step of the reaction would be :

$$BH_4^- + H^+ \longrightarrow H^+BH_4^-$$

The stepwise hydrolysis of sodium tetrahydroborate has been reported, with the formation of BH_3OH^- ion as a probable intermediate (107-109). The formation of BH_3OH^- was suggested during the course of reduction of acetophenone by $NaBH_4$, and was shown to be $1.5X10^4$ times more reactive than the BH_4^- ions (110).

In the present investigation, there was evidence for the formation of $[BH_3OH]^-$ as the boron intermediate in the reduction of potassium hexacyanoferrate (III) by sodium tetrahydroborate in aqueous solution at 25°C. After work-up, shiny white crystals were obtained which were analysed and characterized as $Na[BH_3OH]$. The analysis and spectral characterisation of $Na[BH_3OH]$ have all been given (vide Experimental: `Analysis of the Intermediate Boron Compound'). Hence in the present investigation, the reaction of sodium tetrahydroborate with potassium hexacyanoferrate (III), in aqueous solution, may be explained by the overall stoichiometric reaction (Eq. 62). The boron intermediate, $(BH_3OH)^-$, would react with Na^+ ion to give $Na[BH_3OH]$. This compound could take up one molecule of water of crystallisation to form $Na[BH_3OH].H_2O$. The percentage of boron in this compound was determined to be 14.4%. This value compared favourably, within the limits of experimental error, with the theoretical percentage of boron (15.2%) present in the compound, $Na[BH_3OH].H_2O$ (vide Experimental: 'Analysis of the Boron Intermediate').

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CHAPTER 3

KINETICS OF REDUCTION OF COPPER (II)

The dipositive state is the most important one for copper. There is a well-defined aqueous chemistry of Cu^{2+}, and a large number of salts of various anions, many of which are water-soluble, exist in addition to a variety of complexes.

There have been several investigations of reactions between copper(II) and various organic substrates such as 2-mercapto succinic acid (1), tetramines(2), 3-5- ditertiary butylpyrocatechol(3), aldoses(4), ethylene diaminetetra-acetato-cobaltate(II) ion(5), and with substituted N, N' ethylene bis (p-R-benzoyl acetoneimines) (6). The kinetics and mechanism of the thermal decomposition of copper (II) succinate(7) and of copper (II) salonate (8) have been studied. The kinetics of the chemical and electrochemical reversible oxidation of bis(dithio-oxalato-5,5') cuprate (II) has been reported (9).

Copper(II) ions have been used as catalysts in the oxidation of malic acid by peroxodisulphate (10), and in the oxidation of lactic acid by chloramine-T in alkaline solution (11).

Electron Spin Resonance studies have been carried out on copper(II) alkyl porphyrins(12), copper(II) amino acid complexes(13,14), copper(II) chelates of 2-(2'-pyridylmethylene-hydrazono- methyl) phenol and related compounds(15), and on bis (tetrabutylammonium) bis (maleonitrile dithiolato) nickelate (II) doped with copper (II) (16).

Studies on copper (II) peptide complexes have focused attention on carbon-13 and proton relaxations in paramagnetic complexes of amino acids (17), on the complex formation between copper (II) and thioether groups of peptides (18), and on the influence of the proline residue on the coordination of copper (II) to peptides containing proline and proline-proline subunits (19).

The synthesis and properties of copper (II) complexes with Schiff bases have been reported (20-22). The preparation, crystal structure, properties and reactions of copper (II) complexes with pyridine bases have been studied (23-31). There have been reports of the synthesis and structure of copper (II) complexes with 1-allyl 3(o-,m-,p-carboxyphenyl) 2-thiourea (32), with picoline oxides (33), with s,s-bis(4 benzo-[15-crown-5] dithioglyoxime complexes (34), with phenanthrolines (35), with bis (dizirconiumennea-alkoxides) (36), and with phenoxy isobutyric acids (37). The synthesis, spectroscopic characterization and X-ray structures of aqua- (pyridoxal thiosemicarbazonato) copper (II) chloride monohydrate have highlighted the importance of thiosemicarbazones as coordinating agents (38).

The synthesis and characterization of binuclear copper (II) complexes of a heptadentate ligand have been used as Cu(II)- hemocyanin models (39). The synthesis and complexing properties of polyazacyclo alkanes with copper (II) have been reported (40). The synthesis, crystal structure, and properties of aqua (((2-carboxy ethyl) imino) diacetato) copper (II) complexes have shown the presence of an unusual 6-membered chelate ring involving the coordination of the carboxylic function to copper (II) ions (41). Ligand fields from misdirected valencies have indicated bent-bonding in copper (II) acetylacetonates (42). The crystal and molecular structures of copper (II) - (2 - chlorophenoxy) ethanoic acid complexes have indicated the presence of metal-phenoxyalkanoic acid interactions (43). The synthesis of copper (II) complexes of diastereoisomeric methionyl methionines in aqueous solution has shown the presence of the amide deprotonated complex in the L,L-dipeptide without sulphur coordination (44). Potentiometric investigations of the equilibrium between caffeic acid and copper (II) have been reported (45). Spectrophotometric and conductometric studies of copper (II) bromide - N,N, dimethyl formamide solutions have been studied (46).

The synthesis, structure and electrochemistry of a novel macrocyclic dicopper (II) complex revealed the presence of four one-electron transfer steps, producing binuclear copper (II) and copper (I) species and mixed valence-state species (47). The redox behaviour of copper(II) and copper (I) complexes with tetradentate bis (pyridyl) dithiaether and bis (pyridyl) - diaza ligands towards ruthenium-ammine and bipyridyl complexes has been reported (48). Pulse radiolysis studies have been carried out on the kinetics of the reaction of copper (I) and copper(II) ions with 2,5 - dioxacyclohexyl free radicals and homolysis of the aqua-copper (II)-2, 5-dioxacyclohexyl complex in aqueous solution (49). Structure-reactivity relationships in copper (II)/copper(I) electron transfer kinetics have been used to evaluate self exchange rate constants for copper polythiaether complexes (50).

The kinetics of oxidation of copper (I) complexes by oxygen have been studied by several groups (51-54). The kinetics of the electrochemical reduction of copper (I) oxide in redoxite has been reported (55). Various kinds of copper (I) complexes have been synthesised and their crystal structures and reactions have been characterized (56-64). The heats of solvation of copper(I) halide complexes in tetrahydrothiophene (65) and ESR studies of the copper(I)-9, 10-phenanthrene semiquinonate complexes has been reported

(66). The di-2-pyridyl ketone complexes of copper(I) have been shown to be efficient in the photocatalytic conversion of norbornadiene to quadricyclane (67).

There have been some reports on the kinetics of 1:1 electron transfer reactions involving blue copper proteins, pertaining to the reactivity pattern for stellacyamine (68), the effects of chromium (III) modifications on reactions of plastocyanin with cobalt(III) and iron (III) complexes (69), and the reactions of spinach plastocyanin with inorganic redox partners (70).

The reactivity of the organic acceptor 7,7,8,8-tetracyanoquino dimethane (TCNQ) in its neutral or anionic radical forms, with saturated di- and tri-aminoderivatives of copper was studied on the basis of the metal environment stability. The copper complexes exhibited a high tendency towards the reduction processes (71). Copper complexes of sterically demanding tris (pyrazolyl) hydroborate ligands have found application as synthetic analogues. The formation and reactivity of a peroxodicopper(II) adduct, and the structure of a dinuclear carbonate bridged complex has been studied (72). The thermodynamic stereoselectivity of Cu(II) complexes with respect to diastereoisomeric dipeptides has been explained (73). The coordination of copper was reported to be a distorted square pyramid, with the dipeptide occupying three basal positions. The presence of interactions between the copper(II) ion and the aromatic ring was evaluated by means of theoretical calculations (74).

PRESENT WORK

The present work is a detailed kinetic investigation of the reduction of copper (II) in aqueous alkaline medium, by sodium tetrahydroborate.

Effect of copper(II) and $NaBH_4$

The reaction between Cu^{II} and tetrahydroborate ion was observed to be first order in each of the reactants (Table 1).

Table 1. Effect of $[Cu^{II}]$ and $[BH_4^-]$

$[BH_4^-]$ (10^2xM)	$[Cu^{II}]$ (10^3xM)	$10^4 \times k_1$ (s^{-1})
1.0	1.0	4.2
1.5	1.0	6.2
2.0	1.0	7.5
2.5	1.0	9.5
5.0	1.0	19.6
1.0	0.5	4.0
1.0	0.1	4.1

pH = 11.0 Temp = 40°C

The plot of k_1 versus the concentration of BH_4^- ions gave a straight line passing through the origin, indicating that the rate of the reaction was dependent on the first power of the concentration of BH_4^- ions. At constant BH_4^- ion concentration (large excess), the pseudo-first-order rate constant, k_1 did not change with varying concentrations of copper ion (ten-fold range), indicating a first order dependence of the rate on the Cu^{II} ion concentration (Table 1).

Effect of pH

The reaction was carried out at varying pH (Table 2).

Table 2. Effect of pH on the Cu^{II} - BH_4^- system

pH	$10^4 \times k_1$ (s^{-1})
12	2.5
11	4.2
10	7.6
9.5	9.2
9	12.8
8	18.4

$[BH_4^-] = 1.0 \times 10^{-2}$ M ; $[Cu^{II}] = 1.0 \times 10^{-3}$ M ;

Temp = 40°C.

The logarithm of the rate of disappearance of Cu^{II} ions divided by the tetrahydroborate ion concentration, were plotted against the respective pH. The plot was linear, indicating a first order dependence of the rate of the reactions on hydrogen ion concentrations.

Rate Law

Under the present experimental conditions, the rate law of the system could be expressed as :

$$\text{Rate} = -\frac{d[\mathrm{Cu^{II}}]}{dt} = k\,[\mathrm{Cu^{II}}][\mathrm{BH_4^-}][\mathrm{H^+}],$$

Effect of temperature

The rate of the reaction was influenced by the change in temperature, and an increase in temperature resulted in an increase in the rate of the reaction (Table 3).

Table 3. Effect of temperature on $\mathrm{Cu^{II}}$ - $\mathrm{BH_4^-}$ system

Temp ($\pm 0.1^{o}$C)	$10^4 \times k_1$ (s^{-1})
30	1.8
35	2.8
40	4.2
45	6.1
50	8.3

$[\mathrm{BH_4^-}] = 1.0 \times 10^{-2}$ M; $[\mathrm{Cu^{II}}] = 1.0 \times 10^{-3}$ M; pH = 11.0

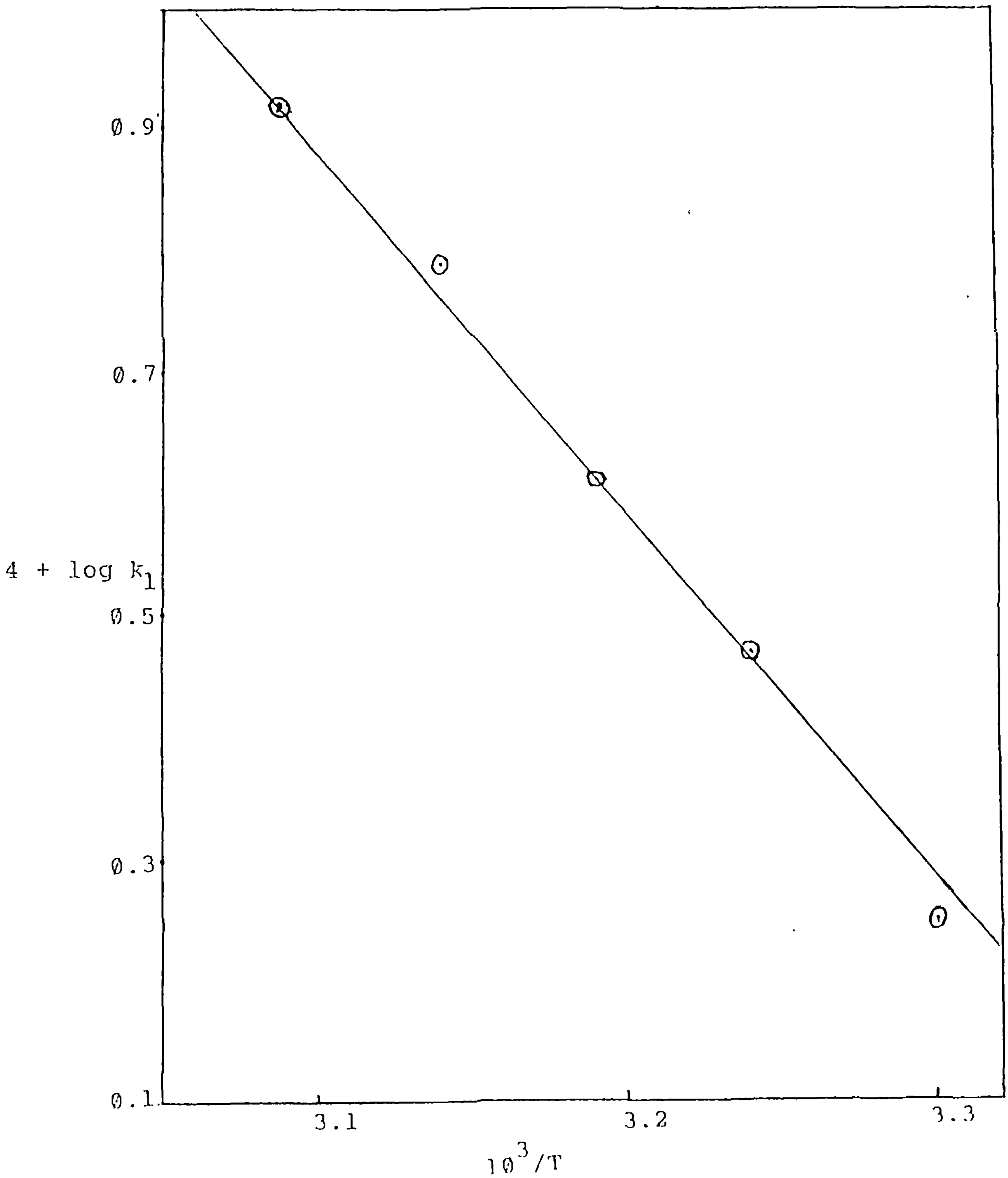

Fig.1 Plot of log k_1 against the reciprocal of temperature [substrate: Copper(II)]

The plot of log k_1 against the reciprocal of temperature was linear (Fig.1), indicating the validity of the Arrhenius equation. The slope of the plot was used to calculate the activation energy of the reaction. The other activation parameters were calculated (vide Experimental: Calculations) and have been shown in Table 4.

Table 4. Activation Parameters

Parameters	Value (Cu^{II} - BH_4^- system)
E ($kJ\ mol^{-1}$)	59±2
A (s^{-1})	2.6×10^6
$\Delta H^{\neq}$ ($kJmol^{-1}$)	56±2
$\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$)	-459±3
$\Delta G^{\neq}$ ($kJ\ mol^{-1}$)	87±2

Mechanism

The kinetics of reduction of copper(II) to copper(I) at 473 K in aqueous solution, in the presence of 2,2'- bipyridyl, has been reported (75). The kinetics and mechanism of the reduction of copper(II) by iron(II), in the presence of sodium fluoride in acidic medium, has been studied(76). The reduction of copper(II) complexes of the ligand 3,6 - bis (2-pyridyl thio) pyridazine and crystal structures of the aquocopper(II) diperchlorate trihydrate complexes with pyridyl thio and pyridazine ligands have been reported (77).

The most feasible mechanism for the formation of a copper hydride species from H_2 and Cu^{II} substrate appears to involve heterolytic cleavage. Earlier investigations on the catalytic reduction of cupric acetate in aqueous solution had shown bimolecular kinetics, which corresponded to a rate-determining hydrogen activation followed by a subsequent fast reaction with the substrate (78-80). The rate law was of the form:

$$-\frac{d[H_2]}{dt} = k[H_2][Cu(OAc)_2]$$

The cupric ion-catalysed reduction of dichromate in perchloric acid at high concentration showed an inhibition of the rate by acid, and the rate law proposed was:

$$-\frac{d[H_2]}{dt} = \frac{k_1k_2[Cu^{2+}][H_2]}{k_{-1}[H^+] + k_2[Cu^{2+}]} \qquad (1)$$

The mechanism involved the activation of H_2 by heterolytic cleavage (81),

$$Cu^{2+} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+ \qquad (2)$$

$$CuH^+ + Cu^{2+} \xrightarrow{k_2} 2Cu^+ + H^+ \qquad (3)$$

$$2Cu^+ + \text{Substrate} \xrightarrow{\text{fast}} 2Cu^{2+} + \text{Products} \qquad (4)$$

The Cu^{II} catalysed isotopic exchange of deuterium in perchloric acid solution provided evidence for heterolytic splitting (82),

$$Cu^{2+} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+$$

The absorption of hydrogen by a quinoline solution of cupric acetate indicated that the uptake of hydrogen corresponded to the reduction of Cu^{II} to Cu^{I}. The rate suggested that the cuprous salt was the catalytic species responsible for hydrogen activation. A first-order dependence on hydrogen, and a second-order dependence on cuprous ion concentration were observed. This indicated a termolecular rate determining step was involved (83), wherein a homolytic splitting of hydrogen was proposed, thus:

$$2\mathrm{Cu}^{I} + \mathrm{H}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Cu}^{II}\mathrm{H} \tag{5}$$

$$\mathrm{Cu}^{II}\mathrm{H} + \mathrm{Cu}^{II} \xrightarrow{k_2} 2\mathrm{Cu}^{I} + \mathrm{H}^{+} \tag{6}$$

In contrast to the reduction in quinoline solution, the hydrogenation of cupric acetate in pyridine or dodecyl amine solutions showed a first order dependence on the cuprous species. Both, heterolytic and homolytic cleavage of H_2 was thus suggested (84). The reduction of cupric heptanoate in heptanoic acid solution by hydrogen (85), and the reduction of cupric carboxylate salts in heptanoic acid, diphenyl, and octadecane by hydrogen (86) gave a rate law,

$$-\frac{d[\mathrm{H}_2]}{dt} = k_1[\mathrm{H}_2][\mathrm{Cu}^{II}] + k_2[\mathrm{H}_2][\mathrm{Cu}^{I}],$$

indicating heterolytic activation of hydrogen by both cuprous and cupric species.

The hydrogen reduction of Cu^{II} ions catalysed by Cu^{I} salts in quinoline and pyridine solutions gave a rate law (87) of the form,

$$-\frac{d[H_2]}{dt} = \frac{k[Cu^{II}][Cu^{I}][H_2]}{k' + k''[Cu^{II}]}$$

and the mechanism proposed for the reaction in both solvents (quinoline and pyridine) was as follows :

$$Cu^{I}X^{-} + H_2 \rightleftharpoons Cu^{I}X^{-}(H_2) \qquad (7)$$

$$Cu^{I}X^{-}(H_2) + Cu^{II} \longrightarrow Cu^{II}H + Cu^{I} + HX \qquad (8)$$

$$Cu^{I}X^{-}(H_2) + Cu^{I} \longrightarrow 2Cu^{II}H + X^{-} \qquad (9)$$

$$Cu^{II}H + Cu^{II} \longrightarrow 2Cu^{I} + H^{-} \qquad (10)$$

The hydrogen reduction of $CuSO_4$ in aqueous H_2SO_4 solution suggested a heterolytic activation of hydrogen by both, cupric and cuprous species (88,89), and the mechanism proposed was

$$Cu^{II} + H_2 \longrightarrow Cu^{II}H + H^{+} \qquad (11)$$

$$Cu^{II}H + Cu^{II} \longrightarrow 2Cu^{I} + H^{+} \qquad (12)$$

$$Cu^{I} + H_2 \longrightarrow Cu^{I}H + H^{+} \qquad (13)$$

$$Cu^{I}H + Cu^{II} \longrightarrow Cu^{II}H + Cu^{I} \qquad (14)$$

The rate was found to be inhibited by acids, which was taken as evidence in favour of a heterolytic mechanism.

The V^{III} - Fe^{III} reaction was catalysed by Cu^{II}(90). The rate law was given by

$$\frac{d[V^{III}]}{dt} = k_{cat}[V^{III}][Cu^{II}],$$

which was in agreement with the reaction sequence,

$$V^{III} + Cu^{II} \xrightarrow{k_{cat}} V^{IV} + Cu^{I} \qquad (15)$$

$$Cu^{I} + Fe^{III} \xrightarrow{fast} Cu^{II} + Fe^{II} \qquad (16)$$

The rate constant, k_{cat}, showed a dependence of H^+ ion. In the reduction of Cu^{2+} by H_2, the mechanism has been shown to be (91)

$$Cu^{2+} + H_2 \rightleftharpoons CuH^+ + H^+ \qquad (17)$$

$$CuH^+ + Cu^{2+} \xrightarrow{fast} 2Cu^+ + H^+ \qquad (18)$$

the intermediate CuH^+ being stabilised by covalent bonding.

The existence of the hydrated electron in solutions of alkali metals in aqueous ammonia, methylamine and ethyl amine, has been recognised for some time (92). Reactions of the hydrated electron were studied by having solutes present in the irradiated sample of water. In the presence of solute, the decay of the 700 nm hydrated electron peak is very rapid. With concentrations of metal ions in the 0.005-0.05 M region and small hydrogen ion concentrations, reactions which the hydrated electron would normally undergo in pure water,

$$e^-_{aq} + H_2O \longrightarrow H + OH^- \qquad (19)$$

and $$e^-_{aq} + H^+ \longrightarrow H \qquad (20)$$

were negligible. The rate constant obtained from the observed rate of decay (93,94) for the reaction of Cu^{2+} with e^-_{aq} at room temperature and pH 7, was = $2.9\times10^{10} M^{-1} s^{-1}$.

The X-ray structural characterization of a transition metal borohydride complex, boro-hydrido bis (triphenyl phosphine) Cu^I has been reported (95). A delocalised bonding scheme was proposed in which direct Cu-B overlap was significant. This required a greater fractional contribution of Cu 4s orbital to the bonding σ molecular orbitals (95). Cu(I) hydride was obtained when $LiAlH_4$ in ether solution was mixed with CuI in pyridine (96). The nature of soluble Cu(I) hydride was characterized by X-ray powder patterns, and cryoscopic measurements showed that CuH was a monomer in pyridine solution (97). Cu(I) hydride was prepared and its reactivity towards organocopper(I) compounds has been studied. It was observed that hydridic and σ organo metallic derivatives of Cu(I) readily reacted with one another and the mechanism of this reaction did not involve intermediate organic free redicals (98). The preparation and crystallographic characterization of the hydrido copper cluster $H_6Cu_6(PPh_3)_6$ has been reported (99). When cuprous chloride was reacted with an equimolecular quantity of $LiBH_4$ in THF at -45^oC, a thermally unstable solution was produced. Analytical data suggested that the copper borohydride which was formed was complexed with LiCl by - product (100). This intermediate represented by $(LiCl)_x(CuBH_4)$ underwent decomposition with the elimination of LiCl. Its copper borohydride component decomposed to CuH (and hence to Cu) and either B_2H_6 or elemental boron, according to the following sequence :

$$(LiCl)_xCuBH_4 \begin{array}{l} \nearrow xLiCl + CuH + B + 1.5H_2 \\ \searrow xLiCl + CuH + 0.5B_2H_6 + 0.5H_2 \end{array} \qquad (21)$$

$$CuH \longrightarrow Cu + 0.5H_2 \qquad (22)$$

In the present investigation, it was observed that the rate of the reduction reaction of Cu^{II} by $NaBH_4$ was proportional to the concentration of both, BH_4^- and H^+ ions. The chemical composition of the activated complex could be written as $H^+BH_4^-$. The first step of the reaction would be

$$BH_4^- + H^+ \longrightarrow H^+BH_4^- \qquad (23)$$

The redox steps following Eq. (23) would involve the reaction of Cu^{II} with the tetrahydroborate species. The reduction of Cu^{II} to Cu^{I} involved a one-electron transfer process. The sequence of steps could be represented as

$$H^+BH_4^- + 2Cu^{2+} + H_2O \longrightarrow 2Cu^+ + [BH_3OH]^- + 3H^+ \qquad (24)$$

The reduction of Cu^{II} by hydrogen involving CuH species as the intermediate has been reported (101).

Earlier work had shown that in the hydrolysis of diborane, intermediates of partially hydrolysed boron compounds were present, which differed in their reducing capacities. The reactions of diborane with ice and with the "bound water" in silica gel had suggested the existence of intermediate boron compounds (102).

In the present investigation, the intermediate boron species has been identified as $[BH_3OH]^-$, which has been characterized and confirmed to be $Na[BH_3OH].H_2O$ (vide Experimental : 'Analysis of the Boron Intermediate').

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CHAPTER 4

KINETICS OF REDUCTION OF BISMUTH (V)

Attempts have been made to study the solution chemistry of bismuth(V) and its redox kinetics. The inability to find bismuth(V) in solution from sodium bismuthate ($NaBiO_3$) was considered a handicap in the study of its solution properties. The first successful attempt reported was the preparation of fluoride complexes of bismuth(V) in a mixture of 1.0 mol dm^{-3} $HClO_4$ and 1.52 mol cm^{-3} HF(1).

Sodium bismuthate has been used as a strong oxidizing agent in analytical chemistry(2), synthetic organic chemistry(3-5), and in the selective oxidation of corticosteroids (6). The kinetics of oxidation of halides, thiocyanate, and Tl(I) hexachloroiridate with bismuth(V) had reported a rate which was independent of the reductant ; the mechanism suggested had involved the production of a peroxo-complex of Bi(III) in the rate determining step(7). The kinetics of electron transfer in aqueous acidic perchlorate-fluoride medium with respect to the oxidation of hypophosphorous acid(8), phosphorous acid(9), hexa aquo chromium(III) complex(10), and glutamic acid (11) with bismuth(V) have been reported.

The chemistry of bismuth compounds is now becoming important, both in terms of structural elucidation and redox reactions. The synthesis and X-ray crystal structure of $[\{(C_5H_4Me)Fe(CO_2)\}BiCl]_3$ have indicated the presence of a compound containing a planar 6-membered Bi_3Cl_3 ring(12). The importance of redox reactions was revealed in various transformations observed in the Bi-Fe-carbonyl cluster systems, and in the crystal structures of compounds such as $[Me_4N]_3[Bi_2Fe_2Co(CO)_{10}]$(13). Organometallic complexes of bismuth have been prepared, and the crystal and molecular structures of complexes such as $[(Co)_5M]_3Bi$(14) and bismuth diethyl dithio phosphinate benzene $Bi(S_2PEt_2)_3.C_6H_6$ have been reported(15).

The kinetics of reactions involving Bi(III) complexes have been reported(16,17). The synthesis and characterization of novel chalcogen and prictogen coordinated bismuth(III) complexes (the first Se, Se coordinated Bi metallocycle) have been reported(18).

The oxidation of lower oxidation states of bismuth namely Bi^{+}, $[Bi_5]^{3+}$ and $[Bi_8]^{2+}$ have been studied(19).

Bismuth gives a series of compounds which can formally be considered as bismuth(III) salts, but these do not give clear solutions in water, except in high acid concentrations, when complex species are present. On dilution, basic salts, which formally contain the bismuthyl ion BiO^{+}, precipitates. Usually, bismuth-oxygen framework(oxy cations) have anions interposed. The Bi^{V}-Bi^{III} couple is strongly oxidising, being able to oxidise water to oxygen. The formation of the species, BiX (X=Cl,Br, I), has been shown in the vapour state in equilibrium with Bi-BiX_3 mixtures and thermodynamic data have been obtained(20).

The diamagnetic "Bismuth monochloride" has a structure with bismuth clusters and two different complex anions(21, 22). Bismuth clusters have been observed in the compounds, $Bi_5[AlCl_4]_3$ and $Bi_8[AlCl_4]_2$, which were obtained by the reduction of a mixture of bismuth and aluminium trichlorides with bismuth in sodium tetrachloraluminate as solvent. Electronic spectra showed that the same bismuth clusters, Bi_5^{3+} and Bi_8^{2+} were present in various solvents. In very dilute solutions of bismuth in bismuth trichloride, Bi^+ (presumably solvated) and Bi^{3+} predominated. Species with bismuth in low oxidation states and their electronic spectra have been characterised(19,23).

The spectra of Bi^+ showed a similar pattern of absorption in various molten salt solvents. These were interpreted in terms of p-p transitions between various states of the p^2 configuration, modified by the crystal field of the anions. Thus Bi_8^{+2} was found with the compact ions $[AlCl_4]^-$ or $[Al_2Cl_7]^-$; but Bi_9^{5+}, with a higher charge density, required larger and more polarisable anions such as $[BiCl_5]^{2-}$ or $[Bi_2Cl_8]^{2-}$.

Bismuth hydroxide dissolved in acids giving solutions which contained Bi(III) ions. Such solutions remained clear only at high acid concentrations. As the hydrogen ion concentration was reduced, oxysalts were precipitated. Before precipitation occurred, a series of polymeric cations were detected in solution. The best characterized ion was $[Bi_6(OH)_{12}]^{6+}$, which had a structure with a Bi_6 octahedron joined by oxygen bridges. It was shown that the Raman band at 177 cm^{-1} was more intense than that at 450 cm^{-1}. If the intensity of the Raman bands were to be attributed only to Bi-O bonds, the mode would involve mainly bending. The intensity of the low energy absorption thus must be attributed to Bi-Bi interactions(23).

Chloride complexes of bismuth have been extensively studied in aqueous solutions and spectral information regarding individual species have been obtained(24,25). The ions $[BiCl_5]^{2-}$ and $[Bi_2Cl_8]^{2-}$ have been found with $BiCl_{1.167}$, and in both these ions, lone pairs occupied coordination positions(26).

Oxidising agents such as chlorine or peroxydisulphate give brown or black precipitates with alkaline solutions of bismuth(III) oxide, and these precipitates have been considered to be due to the formation of higher oxides. Bismuthates are useful oxidising agents, particularly in strong acid solutions(27). Glycols have been converted to compounds with carbonyl functions, and manganese has been quantitatively oxidised to permanganate.

The kinetics of oxidation of H_3PO_3 with Bi(V) fluoride complex was studied in $HClO_4$-HF mixtures. The mode of electron transfer from the substrate to the oxidant was indicated via a bridged outer-sphere mechanism(9). The kinetics of oxidation of hexa-aquo chromium(III) with bismuth(V) in perchloric acid-HF mixtures were studied, with a view to elucidate the mode of electron transfer from Cr(III) to Bi(V). An outer-sphere bridged activated complex was suggested(10). Bismuth(V), as $NaBiO_3$, was quantitatively reduced to Bi(III) in aqueous HF at the expense of water oxidation(28). The results of chemical analysis coupled with IR and Laser Raman studies on single crystals of Bi(III)-(2,2′-dimethyl propanoate pivalate), revealed that the structure consisted of isolated tetrameric units(29). Solution chemistry of Bi(V) in $HClO_4$-HF medium was studied, in order to examine the reactivity pattern for the oxidation of glutamic acid by fluorobismuthate species(11). The synthesis and molecular structure of the complex $Bi^{III}(NO_3)_3$

with tridentate ligands were reported(30). It was observed that the ligands were able to bind to Bi(III) in a tridentate manner, and the NO_3^- ions remained in the inner coordination sphere(30). Bi(III) chlorides with diphosphine and diarsine oxide ligands have been studied(31). The product isolated was characterized, by spectral and micro analytical data, as the 1:1 addition compounds of $BiCl_3$ with diphosphine and diarsine ligands(31). Two new water - soluble Bi(III) complexes with polyaminocarboxylate ligands have been prepared, and characterized by IR spectroscopy and crystal structure analysis(32).

Studies of the coordination chemistry of bismuth have been stimulated by several technologically important issues. In particular, Bi^{III} has been shown to be a component in a number of high T_c superconducting oxide compositions, and several of its coordination complexes have been found to be useful solution-processible chemical precursors for solid state materials(33). The coordination chemistry of Bi(III) is largely governed by its large charge-to-radius ratio (34). The ion is oxophilic, and it prefers to bind to anionic or neutral oxide donor ligands. In this regard, the ion has some similarities to the lanthanide(III) ions, and it is expected that chelating oxodonor ligands will form very stable complexes with Bi(III). The synthesis and molecular structures of complexes of $Bi(NO_3)_3$ with tridentate ligands (substituted pyridine N-Oxides) showed that the ligands were bound in a tridentate manner to Bi(III) and the nitrate ions remained in the inner coordination sphere (30).

Interest in bismuth chemistry was increased by the discovery of the high T_c superconductivity in the Bi-Ca-Sr-Cu-O system, promoting investigations on the use of bismuth-based compounds as potential precursors for the manufacture of bismuth containing ceramics(35). From a coordination point of view, interest in bismuth compounds was related to the potential stereochemical activity of the lone electron pair, giving rise to various structural peculiarities.

The discovery of oxide superconductors has favoured the synthesis and study of new volatile bismuth complexes with oxygen-donor ligands, which could be applied in superconducting film manufacture via chemical vapour deposition techniques. Along with alkoxides(36) and β - diketonates(36,37), Bi(III) carboxylates have also proved to be promising precursors. The crystal and molecular structure of bismuth(III) - 2, 2'-dimethyl propanoate (pivalate) was suggested, wherein it was shown that this complex, $Bi(O_2CCMe_3)_3$, vaporized quantitatively at low temperatures(29).

PRESENT WORK

The present work is a detailed kinetic investigation of the reduction of bismuth(V) by sodium tetrahydroborate in aqueous acidic medium.

Effect of Bismuth(V) and $NaBH_4$

The reaction between bismuth(V) and tetrahydroborate ions was observed to be first order in each of the reactants (Table 1).

Table 1. Effect of $[Bi^{5+}]$ and $[BH_4^-]$

$[BH_4^-]$ $(10^{-2}$ x M)	$[Bi^{5+}]$ $(10^{-3}$ x M)	10^4 x k_1 (s^{-1})
1.0	1.0	8.3
1.5	1.0	12.0
2.0	1.0	16.4
2.5	1.0	20.2
5.0	1.0	40.0
1.0	0.5	8.2
1.0	0.1	8.5

pH = 0.11 Temp = 40°C

A plot of k_1 against a five-fold range of concentration of BH_4^- ions gave a straight line passing through the origin, indicating that the rate of the reaction was dependent on the first power of the concentration of BH_4^- ions.

At constant BH_4^- concentration (large excess), the pseudo-first-order rate constant (k_1) did not change with changing bismuth ion concentration, indicating a first order dependence of the rate on the concentration of Bi^V ions (Table 1).

Effect of pH

The reaction was carried out at varying pH (Table 2).

Table 2. Effect of pH on Bi^{5+} - BH_4^- system

pH	$10^4 \times k_{obs}$ (s^{-1})
0.11	8.3
0.23	5.9
0.30	4.3
0.60	2.6

$[BH_4^-] = 1 \times 10^{-2}$ M ; $[Bi^{5+}] = 1 \times 10^{-3}$ M ; Temp = 40°C

The logarithm of the rate of disappearance of the bismuth ions divided by tetrahydroborate ion concentration was plotted against the respective pH. The plot was linear, indicating a first order dependence of the rate of the reaction on the hydrogen ion concentration.

Rate law

Under the present experimental conditions, the rate law could be expressed as :

$$\text{Rate} = -\frac{d[\mathrm{Bi}^{V}]}{dt} = k_1[\mathrm{Bi}^{V}][\mathrm{BH}_4^-][\mathrm{H}^+]$$

Effect of temperature

The rate of the reaction was influenced by the changes in temperature, and an increase in temperature resulted in an increase in the rate of the reaction (Table 3).

Table 3. Effect of temperature on Bi^{5+} - BH_4^- system

Temp. (±0.1°C)	$10^4 \times k_1$ (s^{-1})
30	4.6
35	6.5
40	8.3
45	10.6
50	12.2

$[BH_4^-] = 1.0 \times 10^{-2}$ M, $[Bi^{5+}] = 1.0 \times 10^{-3}$ M,
pH = 0.11

A plot of log k_1 against the reciprocal of temperature was linear (Fig.1), indicating the validity of

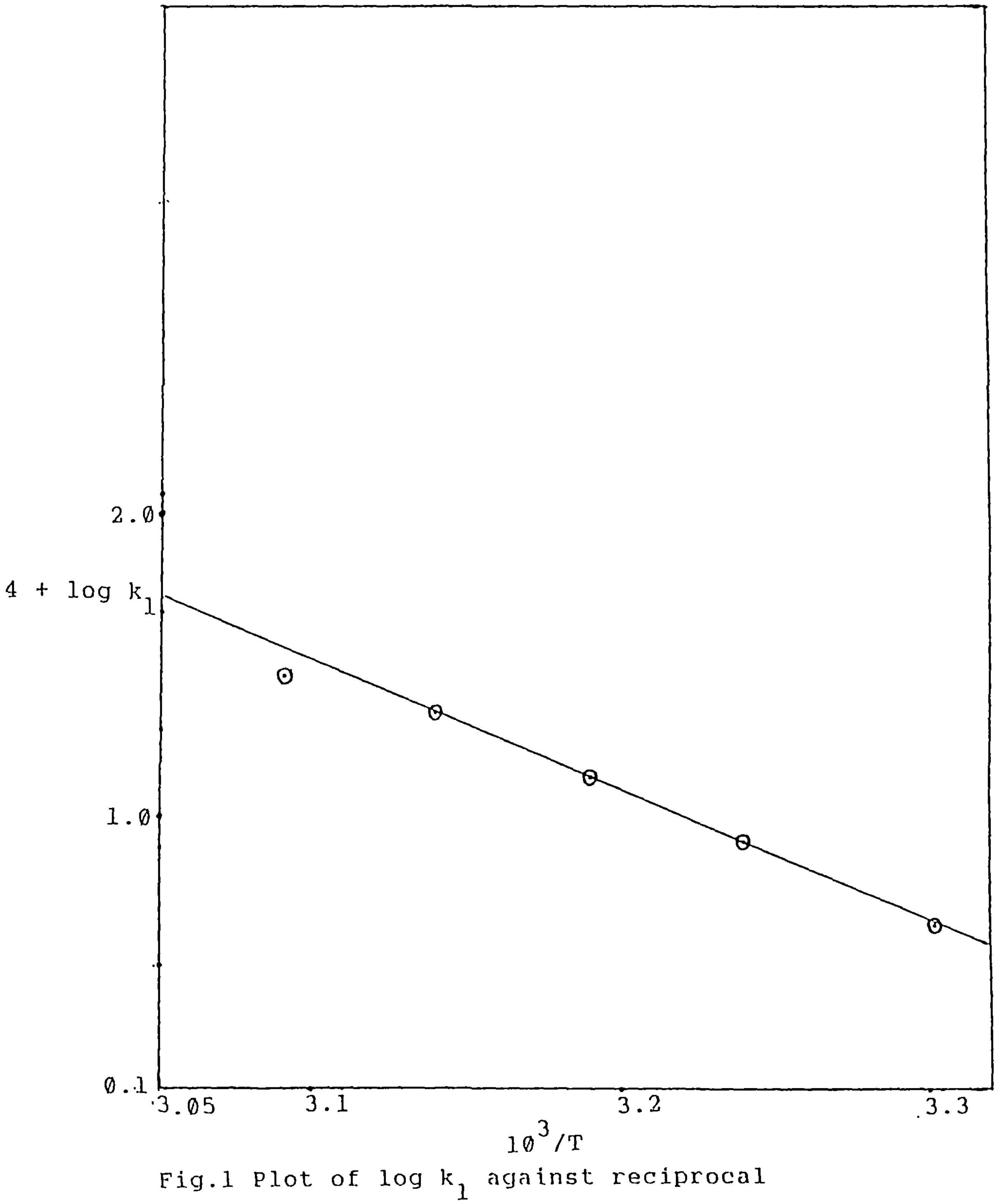

Fig.1 Plot of log k_1 against reciprocal of temperature[Substrate: Bismuth(V)]

the Arrhenius equation. The slope of the plot was used to calculate the activation energy of the system.

The other activation parameters were calculated (vide 'Expermiental' : Calculations), and have been shown in Table 4.

Table 4. Activation parameters

Parameter	Value (Bi^{5+} - BH_4^- system)
E ($kJ\ mol^{-1}$)	36±2
A (s^{-1})	8.8×10^2
$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	33±2
$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)	-333±3
$\Delta G^{\neq}$ ($kJ\ mol^{-1}$)	138±2

The negative entropy of activation would indicate that the process of electron transfer plays a dominant role in the system.

MECHANISM

Considerable chemistry for bismuth with oxidation states less than that of the familiar bismuth(III), appeared to be realized in, or via, melt reactions. On the basis of electrochemical experiments and phase diagram studies, it was proposed that Bi^+ (or $Bi^+.nBi^{3+}$ generally) was present in dilute solution; at higher concentrations, this was converted to a second species, $Bi_3^+.nBi^{3+}$ (38). A spectrophotometric study(39) of the same system confirmed the presence of just two species in the composition region, and demonstrated that the stoichiometric relationship between them was consistent with the products deduced in the earlier emf investigation(38). Very little was known about species in the more concentrated solution of metal in $BiCl_3$, although a complex solid phase was obtained. This was first thought to be stoichiometrically simple BiCl(40), which suggested that species such as Bi_n^{n+} might be formed in dilute solution as well. However, a structural study showed that the compound contained the unusual ion, Bi_9^{5+}, with approximately D_{3h} symmetry. Together with two types of chlorobismuth(III) anions, this had resulted in the stoichiometry $Bi_{12}Cl_{14}$(41). A molecular orbital treatment of the bonding in the cation was subsequently provided(42). Some experiments on BiCl suggested that $BiAlCl_4$ could be obtained by the acid-stabilization on bismuth (I) compounds, wherein the replacement of halide by the $AlCl_4^-$ ion yielded $BiAlCl_4$(43). Subsequently, a radial distribution analysis of the X-ray scattering by liquid and powdered samples of this composition were obtained(44). Further, its powder pattern data and the space group of a single crystal were reported(45). All were found to be consistent with the presence of triangular bismuth units (d_{Bi-Bi} = 3.04 Å), which were then formulated as Bi_3^{3+} ions, in accordance with the reported stoichiometry. The Bi_3^{3+} was observed to be compatible with the X-ray results, as well as with solution studies in $BiCl_3$(46). The trimeric species did not appear to exist as a solid tetrachloro aluminate. Instead two solid phases with the compositions, $Bi_5(AlCl_4)_3$ and $Bi_4(AlCl_4)$, were formed(47). These solids were also seen to show a considerable spectral resemblance to the ions, Bi_5^{3+} and

Bi_8^{3+}, which had been identified in dilute solution in $NaCl-AlCl_3$ and $KCl-ZnCl_2$ solvents (48-50).

The formation of lower oxidation states of bismuth, mainly Bi^+, Bi_5^{3+} and Bi_8^{2+} have been reported (49,50). Bi^+ has been prepared by the hydrogen reduction of a dilute solution of $BiCl_3$ in $AlCl_3$-NaCl eutectic at 310°C in a sealed optical cell(49). The uv spectrum of Bi^+ solution, prepared by the hydrogen reduction of $BiCl_3$ solution, showed very weak bands at 310 nm, 333 nm and 392 nm. The extremely weak band at 392 nm was due to the presence of Bi_5^{3+}, whereas the other two bands were due to Bi^+. In the reduction of $BiCl_3$ by hydrogen, the assumption that

$$Bi^{3+} + 2e^- \longrightarrow 3Bi^+$$

takes place, yielded a value of 309 lit/mol cm for the most intense band. In the Bi-$BiCl_3$ reduction, the assumption that $2Bi + Bi^{3+} \longrightarrow 3Bi^+$ takes place, yielded a value of 305 lit/mol cm for the same band. In the $AlCl_3$-NaCl eutectic at 130°C, $BiCl_3$ had a maxima at 297 and 210 nm ; similar bands were known for Bi^{3+} in various other chloride systems(49). Early investigations had shown that the uv-visible spectrum of Bi^+, in a molten salt medium, had principal absorptions at 585, 663, 800 and 900 nm, with a pronounced shoulder at 690 nm.

The band at 585 nm was highly skew-symmetric, so that there were broad unresolved bands on the high energy side of the sharp maximum (49). The absorption spectrum of Bi^+ was accounted for in terms of $6p^2 \longrightarrow 6p^2$ intra configurational transition with $6p^2$ states perturbed by ligand fields of less than cubic symmetry(48). The spectra of the reaction product formed in the reaction between bismuth metal and a dilute solution of $BiCl_3$ in the $ZnCl_2$-KCl eutectic, showed absorptions at 550 nm, 722 nm and 950 nm, with a shoulder at 850 nm. These bands were due to the presence of Bi^+ species (48,49). The ligand field theory of $p^{2,4} \longleftrightarrow p^{2,4}$ electric dipole transitions justified the presence of Bi(I) in the molten salt system, having a partially filled p-shell of electrons, even though the exact nature of Bi^+ - ligand bonding was not established (51).

It was shown that Bi^{5+} was quantitatively reduced to Bi^{3+} in aqueous HF to afford the fluoro-complex of Bi^{3+},

BiF_3-H_2O, which underwent dehydro-fluoridation(-2HF) at 350-400^oC, in the presence of air, to produce BiF(28).

In the reaction between phosphorous acid and Bi^{5+} - fluoride complex, in $HClO_4$-HF mixtures, it was shown that the mode of electron transfer occurred via a bridged outer-sphere mechanism. Hydrogen bonding assisted in bringing Bi^{5+} in close proximity of P(III), for the facile transport of the electron pair from phosphorus to Bi^V. The stoichiometry of the reaction showed that Bi^V was reduced to Bi^{III} species (9).

The oxidation of hexa aquo chromium(III) with bismuth(V), in $HClO_4$-HF mixtures indicated an outer-sphere bridged activated complex. The stoichiometry of the reaction corresponded to a sequence wherein bismuth(V) was reduced to bismuth(III) species (10).

In the oxidation of glutamic acid by Bi^V in aqueous $HClO_4$-HF medium, it was shown that the intermediate complex was formed through hydrogen bonding of the coordinated fluoride with the hydrogen of the α-carbonyl group. The reaction sequence and the stoichiometry established that bismuth(V) was reduced to bismuth(III) in this reaction(11). Bismuth(V) has been observed to be generally unstable in aqueous medium(52,53). The reaction between water and Bi(V) in acidic solution showed that water was slowly oxidised to oxygen(53).

It seemed apparent that the solution chemistry of Bi^V had not merited much attention. In the present investigation, it was thought pertinent to study the kinetics of the reaction between Bi^V and $NaBH_4$ in acid medium. It was felt that this study would serve two purposes:

(a) To determine the kinetic features of the reduction of bismuth(V) to its lower oxidation state ; and

(b) To isolate and characterize the bismuth species in its lower oxidation state.

When bismuth(V) in sodium bismuthate ($NaBiO_3$) 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 reduced form of bismuth in the +3 state (as BiOCl) was obtained as a white powder, and was characterized by IR analysis. The IR spectrum of BiOCl exhibited three sharp bands at 529, 340 and 285 cm^{-1}. The band at 529 cm^{-1} corresponded to the Bi-O stretching. It has been shown that metal - oxygen single bond stretching vibration occurred at 500 cm^{-1} (54,55). An earlier investigation had reported the IR spectrum of BiOF, wherein the broad band at 560 cm^{-1} had been assigned to ν(Bi-O) vibration (30). The other two bands observed at 285 and 340 cm^{-1} could be assigned to ν(Bi-Cl) vibration. It has been shown that for BiOF, the band at 365 cm^{-1} was assigned to ν(Bi-F) vibration (28). Therefore, spectral data confirmed that the final product obtained by the reduction of Bi^{V} by sodium tetrahydroborate ($NaBH_4$), in HCl medium, was BiOCl. The formation of this compound clearly established that bismuth(V) had been reduced to bismuth(III) in HCl medium.

For the reduction of Bi(V) by $NaBH_4$, in acid medium, the mechanistic pathway involved the formation of Bi(III) as the final oxidation state of bismuth.

Bismuth in sodium bismuthate ($NaBiO_3$) remains in the +5 oxidation state. Reduction by $NaBH_4$ gave Bi^{2+} in the first step, as follows:

$$Bi^{5+} \xrightarrow[-3e^-]{3[BH_4]^-} Bi^{2+}$$

The rate of the reaction was observed to be dependent on the first power of the concentrations of both, BH_4^- and H^+ ions. Hence, the activated complex could be written as $H^+BH_4^-$. The first step of the reaction is :

$$BH_4^- + H^+ \longrightarrow H^+BH_4^-$$

The bismuth(V) species would undergo a reaction, in the subsequent steps, to give bismuth(2+) as follows :

$$3[H^+BH_4^-] + 2Bi^{5+} + 3H_2O \longrightarrow 2Bi^{2+} + 3[BH_3OH]^- + 9H^+$$

It has been reported in the literature that the most stable oxidation state of bismuth is the +3 state. In the present investigation, Bi^{2+} was formed in solution. The Bi^{2+} had the tendency to attain its most stable oxidation state (+3 state). The isolation of BiOCl as the final product of the reduction reaction clearly indicated that, under the present experimental condition, Bi^{2+} was a transient state. The Bi^{2+} was finally converted to the +3 state. The analysis carried out for the reduction of Bi(V) by $NaBH_4$, in the present investigation, unequivocally established that Bi^{5+} was reduced to Bi^{3+} in the final step of the reduction reaction.

During the process of reduction of metal ions by $NaBH_4$, it has been suggested that intermediate boron compounds may be formed. Earlier work has shown the possibility of the formation of such intermediate boron compounds(56).

In the present investigation, the boron intermediate formed as the final product was the BH_3OH^- species. This was isolated and characterized as $Na[BH_3OH].H_2O$ (vide Experimental : `Analysis of the Boron Intermediate').

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SUMMARY

SUMMARY

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.