(i) CrO_3 exists as equilibrium between $[HCrO_4]^-$ and $[HCr_2O_7]^-$ at pH 2 to 6[24, 25]*;
(ii) Oxidation of arsenic(III) to arsenic(V) is a two-electron process which may take place through oxygen exchange[26] between Cr^{VI} or Cr^{V} on one side and arsenic(III) on the other;
(iii) The conversion of Cr^{IV} to Cr^{V} may involve reaction with $Cr^{VI}{=}O$[27].

Application of the reported criterion, that a reaction of As^{III} with Cr^{VI} to give As^{V} and Cr^{III} takes place through Cr^{V} in acidic medium[24] and through Cr^{II} in basic medium[28], to the formation of complex *(6)* supports Scheme 1 rather than any other involving Cr^{II} since the pH of this reaction lies in the acidic range.

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* The pH of the solution was measured by applying a correction (not more than +0.85 pH units) as extended, to aqueous-acetone mixture, by Van Uitert and Haas, *J. Am. Chem., Soc., 75,* 451 (1953). The pH meter readings in acetone solutions were 6.15 (solvent); 1.5 (CrO_3); 2.5(1), M = H) and 3 on mixing solutions of CrO_3 and *(1)*. The hydrolysis of CrO_3 to $H_2CrO_4/H_2Cr_2O_7$ might have been due to adventitious moisture.

Kinetics of Reduction of Copper(II) by Sodium Tetrahydroborate

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Summary

The kinetics of reduction of copper(II) ion by sodium tetrahydroborate in buffered aqueous solution have been investigated. The rate of the reaction is first order in the concentrations of each of the reactants. The activation parameters were evaluated and a plausible mechanism for the reduction of copper(II) ion is proposed.

Introduction

The reactions of hydroborate ion with transition metal compounds usually result either in reduction of the metal to a lower oxidation state and possibly to the formation of a hydride compound, or the formation of a hydroborate or a diborane derivative[1, 2]. Sodium tetrahydroborate in water or methanol solution was found to be an effective reagent for the conversion of aldehydes or ketones into the corresponding alcohols[3]. The rate of reduction of ketones by sodium tetra-

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hydroborate in isopropanol solvent was found to follow second-order kinetics[4]. There have been some reports on the reduction of copper(II) complexes to a copper(I) species[5, 6]. Kinetic studies on the reduction of transition metal ions by sodium tetrahydroborate have not received much attention. Hence, it was thought worthwhile to investigate the kinetics of reduction of copper(II) ion by sodium tetrahydroborate, in buffered aqueous solution. The present investigation reports a novel method for the preparation of cuprous hydride.

Experimental

Materials, methods and stoichiometry

$NaBH_4$ (Loba Chemical Co.) was kept *in vacuo*. Copper(II) sulphate, NH_4OH, and $NaClO_4$ were from E. Merck.

Solutions of $NaClO_4$ (in 5 M NH_4OH) and $CuSO_4$ (in 5 M NH_4OH) was separately prepared. The pH of each solution was checked (Systronics pH meter, digital model). The two solutions were separately thermostated at 30 °C for 1 h, and then mixed in equal vols by syringing into the spectrophotometric cell. The progress of the reaction was monitored by following the disappearance of Cu^{II} using the decrease in optical density at 615 nm (Cary 2300 spectrophotometer) and up to 50% disappearance of Cu^{II}, the relation between log k_{obs} and t being linear in this range. The pH of the reaction mixtures was checked periodically and was found to remain constant.

The stoichiometry of the reaction was determined in the following manner: reaction mixtures containing $NaBH_4$ and an excess of Cu^{II} were allowed to react at 30 °C for 24 h, and then analyzed, spectrophotometrically, at 615 nm, for the Cu^{II} which was left. The results accord with the equation:

$$[BH_4]^- + 8\,Cu^{2+} + 3\,H_2O \rightarrow B(OH)_3 + 8\,Cu^+ + 7\,H^+$$

Product analysis

(a) $CuSO_4$ (0.5 M, taken in 50 cm^3 of 5 M NH_4OH), was mixed with $NaBH_4$ (0.5 M, taken in 50 cm^3 of 5 M NH_4OH), and 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 cm^3 of H_2O, and boiled for 1 h to dissolve any free boric acid or borate. The precipitate was filtered and washed with hot H_2O until the washings were free from boric acid or borate. The precipitate was dried. The filtrate was analyzed for the presence of borate, described in (c).

A known weight of the precipitate (0.1203 g) was mixed with H_2O (100 cm^3), and concentrated H_2SO_4 (5 cm^3) was added. The solution was heated till the precipitate dissolved. A light blue solution was obtained. 10 cm^3 of 5 M NH_4OH was added, the precipitate formed was redissolved in dilute A_{COH} (5 cm^3), and the mixture was titrated against standard sodium thiosulphate solution. It was found to contain 0.1160 g of copper, which corresponded to 96.48% of copper in the product (CuH). This value compares favourably, within the limits of experimental error, with the theoretical percentage of copper present in CuH (98.44%).

(b) Determination of the oxidation state of copper

The copper present in the coffee-coloured particles (Cu^I) was oxidized to the Cu^{II} state, by using an excess of $K_2Cr^2O_7$ solution, and the unreacted $K_2Cr_2O_7$ was titrated against ferric ammonium sulphate. The quantity of Cr^{VI} solution consumed due to the oxidation of Cu^I was thus determined, and compared with the standard value, in order to assign the oxidation state of copper.

0.0376 g of the precipitate was treated with 0.1 N $K_2Cr_2O_7$ solution (10 cm^3). Concentrated H_2SO_4 (5 cm^3) and syrupy H_3PO_4 (5 cm^3) were added. The mixture was allowed to stand until the particles were completely dissolved. 0.1 N Na_2CO_3 (5 cm^3) was added, and the quantity of Fe^{III} consumed for the oxidation of Cu^+ was found to be 0.0092 g of Cr^{VI}, which was equivalent to 0.0341 g of CuH (theoretical value). This confirmed that the oxidation state of copper in the particles was I.

Earlier work reported the formation of cuprous hydride by the reaction of copper(I) and lithium aluminium hydride[7, 8]. In the present investigation, we have been successful in preparing water-insoluble cuprous hydride by the reaction of cupric(II) sulphate in NH_4OH and $NaBH_4$ in NH_4OH.

The i.r. spectrum (Perkin Elmer IR 983 spectrometer) of the cuprous hydride (in KBr) has an intense peak at 521 cm^{-1}, which can be assigned to the presence of a ...Cu..H..Cu..H... bridge-type of structure. The absence of any peaks in the region between 2250 cm^{-1} and 1700 cm^{-1} indicated low covalent character, an observation which finds support from earlier reported work[9,10]. Cuprous hydride has been earlier used as a reducing agent[10], and its reducing properties are presently under further investigation in this laboratory.

(c) Analysis of the filtrate obtained in (a) and (b).

The filtrate was slowly evaporated in a porcelain dish to near dryness. It was then digested with concentrated HCl, and again evaporated to dryness to obtain the residue, which was recrystallized from hot H_2O. A small portion of the recrystallized product (0.2 g) was taken in a porcelain dish, and mixed with concentrated H_2SO_4 (2 cm^3) to make a paste. Methanol (3 cm^3) was added, the solution heated and the vapours ignited. A green-edged flame confirmed the presence of boric acid. The i.r. spectrum of the product is identical with that of boric acid.

Results and Discussion

Kinetic results

The rate of disappearance of copper(II) is first order in each of the reactants (Table 1). A plot of log k_{obs} *versus* a twenty-five fold range of concentration of $[BH_4]^-$ gave a straight line that

passed through the origin. At constant $[BH_4]^-$ concentration (large excess), the *pseudo*-first-order rate constant (k_{obs}) does not change with copper(II) concentrations (ten-fold range).

The rate of the reaction was found to vary as a function of pH (Table 1). The logarithm of the rate of disappearance of copper(II) divided by the tetrahydroborate ion concentration is linear with pH indicating a first-order dependence on hydrogen ion concentration.

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

$$\text{Rate} = -d[Cu^{II}]/dt = k_{obs}\,[Cu^{II}][BH_4]^-[H^+]$$

The reaction rate is influenced by temperature (Table 1), and the activation parameters were evaluated.

$E = 77 \pm 4$ kJ/mol, $A = 1 \times 10^{12}\,s^{-1}$, $\Delta H^{\neq} = 74 \pm 4$ kJ/mol, $\Delta S^{\neq} = -26 \pm 3$ J/K/mol.

Ionic strength of the medium using $NaClO_4$ (μ = 0.01 M to 0.075 M), does not affect the rate of the reaction.

Table 1. Rate data for the reduction of Cu^{II} by $Na[BH_4]$ at 30 °C[a].

$[BH_4]^-$ (10^3 M)	$[Cu^{II}]$ (10^4 M)	pH	$10^2\ k_{obs}$ (s^{-1})
1.0	1.0	12.0	4.4
5.0	1.0	12.0	22.0
10.0	1.0	12.0	45.0
25.0	1.0	12.0	112.0
1.0	0.75	12.0	4.6
1.0	0.50	12.0	4.5
1.0	0.25	12.0	4.4
1.0	0.10	12.0	4.5
1.0	1.0	12.5	3.9
1.0	1.0	11.0	7.0
1.0	1.0	10.0	10.0
1.0	1.0	9.0	14.0
1.0	1.0	8.0	22.0
1.0	1.0	12.0	7.0[b]
1.0	1.0	12.0	12.5[c]
1.0	1.0	12.0	18.0[d]
1.0	1.0	12.0	30.2[e]

[a] μ = 0.05 M; [b] 35 °C; [c] 40 °C; [d] 45 °C; [e] 50 °C, (all temperature corrections were ±0.1 °C). All values of rate constants were the average of three experiments; agreement, ±3%.

Mechanism

Since the rate of the reaction is dependent on the concentrations of both tetrahydroborate and hydrogen ions, the first step of the reaction can be written as below.

$$[BH_4]^- + H^+ \longrightarrow H^+[BH_4]^- \quad (1)$$

The steps following Equation 1 can be represented as follows:

$$H^+[BH_4]^- \longrightarrow \tfrac{1}{2}\,B_2H_6 + H_2$$

$$4H_2 + 8Cu^{2+} \longrightarrow 8Cu^+ + 8H^+$$

$$\tfrac{1}{2}\,B_2H_6 + 3H_2O \longrightarrow B(OH)_3 + 3H_2$$

The reduction of copper(II) by H_2, involving Cu–H species as intermediates, has been reported in detail[11].

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The Solvolysis of *trans*-$[Co(4\text{-Mepy})_4Cl_2]ClO_4$ in Water-Methanol Mixtures

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Summary

The solvolysis of the *trans*-$[Co(4\text{-Mepy})_4Cl_2]ClO_4$ complex was studied in 0 to 70% v/v H_2O : MeOH mixtures at 40, 45, 50 and 55 °C. The high negative ΔS^* values found for the complex cation under investigation, relative to that of *trans*-$[Co(py)_4Cl_2]^+$ reported in the literature, were attributed to the substituent methyl groups. The free energies of transfer of both the ground and the transition states were calculated from which the dominant effect of the solvent on the transition state is apparent.

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Introduction

It has been realized that the medium may have a tremendous effect on the reactivity of reacting species as manifested by the reaction rate. Therefore, it is imperative that the external structure surrounding the reacting species be clearly understood. A survey of reactions of coordination complexes shows that plots of log (rate constant) *versus* the reciprocal of the dielectric constant of the medium, D_s^{-1}, are often far from linear[1–3] although linearity has been observed for some reactions[4–7]. These observations confirm that the solvent plays an important role in the course of the reaction.

The present investigation describes the solvolysis of *trans*-$[Co(4\text{-Mepy})_4Cl_2]^+$ [where 4-Mepy = 4-methylpyridine (γ-picoline)] and determination of the solubility of the hexa-

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