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Kinetics and Mechanism of Reduction of Hexacyanoferrate(III) by Sodium Tetrahydroborate

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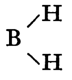
A kinetic investigation of the reduction of hexacyanoferrate(III) by sodium tetrahydroborate in buffered aqueous solution has been carried out. The rate of the reaction is proportional to the concentration of both, tetrahydroborate and hydrogen ions. The effect of the addition of some inorganic salts has been studied. The temperature has been varied, and the Arrhenius parameters have been evaluated. The rate of hydrolysis of tetrahydroborate has been separately studied. It has been observed that the activation energies for both the reactions—the reduction of hexacyanoferrate(III) and the hydrolysis of tetrahydroborate—are equal. A plausible mechanism for the reduction of hexacyanoferrate(III) has been proposed.

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.[1] The rate of reduction of ketones by sodium tetrahydroborate in isopropyl alcohol as solvent was found to follow second order kinetics.[2] It was though worthwhile to investigate the kinetics of reduction of hexacyanoferrate(III) ions by using this versatile reducing agent, $NaBH_4$, and to propose a mechanism consistent with the observed kinetic data. The decomposition of $NaBH_4$ as a function of time and temperature was separately studied with a view to support the mechanism proposed for this reaction.

Experimental

Materials. Sodium tetrahydroborate (Loba Chemical Co.) was kept under vacuum. The purity of $NaBH_4$ was checked by infrared analysis. Two sharp peaks were obtained at 2290 cm^{-1} and 1120 cm^{-1}, both being characteristic for $NaBH_4$. These have been assigned[3] as follows:

(i) 2290 cm^{-1}: $(B\text{–}H)_{asym}$ stretching

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

The $(B\text{–}H)_{asym}$ stretching mode 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.[4]

All other substances used were of BDH(AR) grade.

Methods. Sodium tetrahydroborate was weighed out accurately and the solution was prepared in sodium hydroxide, whose strength had been determined. Potassium hexacyanoferrate(III) was weighed out accurately and the solution was prepared in sodium hydroxide. The pH of each solution was checked using a pH meter (Toshniwal, digital model). The two solutions were separately thermostated at 25 °C for 3 h. The solutions were then mixed in equal volumes, and the reaction was followed by observing the disappearance of hexacyanoferrate(III). Readings were taken at regular intervals of time, by noting the decrease in optical density at 420 nm,[5] using a spectrophotometer (Systronics, Mk II model). At this wave length, the absorption due to hexacyanoferrate(II) was negligible.[6] The pH of the reaction mixture was checked periodically, during the course of the reaction.

All infrared measurements were carried out using an IR 297 (Perkin-Elmer) spectrophotometer.

Product Analysis. Sodium tetrahydroborate (5×10^{-2} M†) in NaOH (1×10^{-2} M), and potassium hexacyanoferrate(III) (5×10^{-4} M) in NaOH (1×10^{-2} M), were mixed in equal volumes. The mixture was allowed to stand at room temperature for 48 h to ensure the completion of the reaction. The reaction mixture 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. The residue was recrystallized from hot water.

A small portion of the recrystallized product was taken in a porcelain dish, mixed with a small amount of concentrated H_2SO_4 to make a paste. About 3 ml of absolute methanol was added. The solution was heated and the vapours ignited. A green-edged flame was obtained, confirming the presence of the borate radical in the residue.

An infrared spectrum of the product sample was taken and compared with the infrared spectrum of a pure boric acid sample. Both the samples were found to be identical. This confirmed that the residue was boric acid.

Results and Discussion

Stoichiometry. The stoichiometry of the reaction was confirmed from colorimetric measurements in the following manner: reaction mixtures containing an excess of hexacyanoferrate(III) were allowed to go to completion, and then analyzed, spectrophotometrically, for the hexacyanoferrate(III) which was left. The results gave a 1:8 ratio according to

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

Kinetic Results. The rate of disappearance of hexacyanoferrate(III) was first order in each, the tetrahydroborate and hydrogen ions.

Effect of Tetrahydroborate. The rate of the reaction was found to be directly proportional to the concentration of BH_4^- ions. A plot of log k_1 *versus* the concentration of BH_4^- ions was linear, confirming the first order dependence of the reaction on the concentration of BH_4^- ions (Fig. 1).

Effect of Hydrogen Ions. The reaction was studied at varying pH. The rate of the reaction was found to vary as a function of the hydrogen ion concentration. The logarithm of the rate of disappearance of hexacyanoferrate(III) divided by BH_4^- ion concentration was plotted against pH. The plot was

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† 1 M=1 mol dm^{-3}.

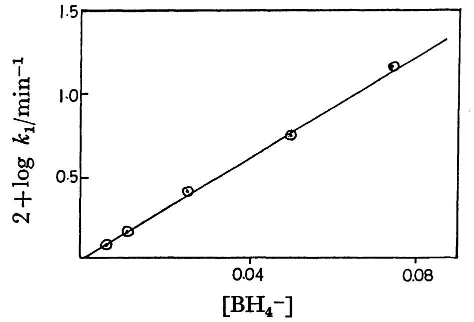

Fig. 1. Plot of logarithm of rate constant (k_1) *versus* the concentration of $[BH_4^-]$.

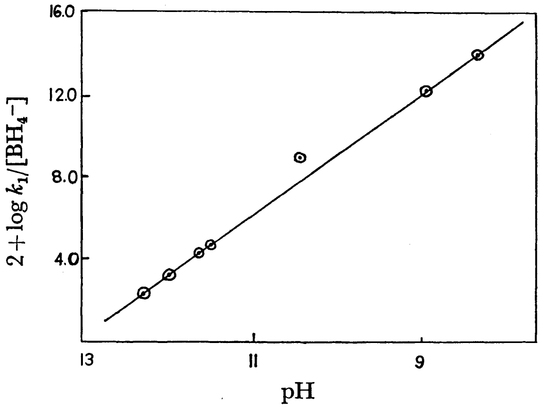

Fig. 2. Plot of logarithm of rate constant (k_1) divided by concentration of $[BH_4^-]$ *versus* pH.

TABLE 1. EFFECT OF HEXACYANOFERRATE(III)

[Hexacyanoferrate(III)] / 10^4 M	$10^2\, k_1/\text{min}^{-1}$
1.0	2.71
2.5	2.60
5.0	2.54
7.5	2.44
10.0	2.56
25.0	2.50
50.0	2.62

$[BH_4^-]=2.5\times10^{-2}$ M; NaOH$=1\times10^{-2}$ M; pH$=$ 11.50; Temp$=$25 °C.

linear, with a slope equal to unity (Fig. 2). This indicated a first order dependence of the reaction on the hydrogen ion concentration.

Effect of Hexacyanoferrate(III). The rate of the reaction was found to be independent of the concentration of hexacyanoferrate(III) ions in the range studied, from 1.0×10^{-4} M to 5.0×10^{-3} M (Table 1).

Effect of Hexacyanoferrate(II). The addition of hexacyanoferrate(II) ion to the reaction mixture resulted in a decrease in the rate of the reaction (Table 2). This decrease in the rate might suggest the possibility of an equilibrium being attained between the hexacyanoferrate(III) and the hexacyanoferrate(II). In the reaction of As(III) with hexacyanoferrate(III) in alkaline medium,⁽⁷⁾ added hexacyanoferrate(II) was found to retard the rate of the reaction. In the reaction of mercaptoacetic acid with hexacyanoferrate(III) in acid medium,⁽⁸⁾ a similar retardation was also observed when hexacyanoferrate(II) was added to the reaction mixture.

TABLE 2. EFFECT OF HEXACYANOFERRATE(II)

[Hexacyanoferrate(II)] / 10^4 M	$10^3\, k_1/\text{min}^{-1}$
0.0	9.50
1.0	4.86
2.5	2.29
4.0	0.84

Hexacyanoferrate(III)$=2.5\times10^{-4}$ M; $[BH_4^-]=8\times10^{-3}$ M; NaOH$=1\times10^{-2}$ M; pH$=$11.50; Temp$=$25 °C.

TABLE 3. EFFECT OF COPPER(I) IONS

[Copper(I) ion] / 10^5 M	$10^3\, k_1/\text{min}^{-1}$
0.0	9.50
2.5	7.50
5.0	4.36
7.5	3.05
10.0	1.84
12.5	1.07

Hexacyanoferrate(III)$=2.5\times10^{-4}$ M; $[BH_4^-]=8\times10^{-3}$ M; NaOH$=1\times10^{-2}$ M; pH$=$11.50; Temp$=$25 °C.

Effect of Copper(I) Ions. The addition of copper(I) ions to the reaction mixture resulted in a decrease in the rate of the reaction (Table 3).

The choice of copper(I) ions was appropriate, since under the present experimental conditions, there was no possibility of further reduction of the copper(I) ions by the BH_4^- ion. The retardation in the rate of the reaction thus observed may be due to the formation of copper(I) tetrahydroborate ($CuBH_4$), which is stable at −12 °C, but undergoes decomposition at higher temperatures. At 25 °C, the $CuBH_4$ formed would be unstable and would undergo decomposition.

Effect of Added Salts. Potassium, rubidium, and caesium are known to form simple tetrahydroborates, $M(BH_4)_n$, which are stable or decompose only very slowly. The stability of these tetrahydroborates is in the order K<Rb<Cs, and can be related to two factors: (a) the electronegativities of the metal atom of the salts added (K, Rb, Cs), which are much lower than that of boron; and (b) the percentage ionic character. The greater the ionic character, the more stable will be the metal tetrahydroborate.

It is to be expected that the rates would follow the order of stability of these metal tetrahydroborates. This has been observed (Table 4).

Effect of Temperature. The reaction has been studied over the temperature range 25 °C to 55 °C. The rate of the reaction was found to be directly dependent on the temperature, the rate showing an increase with an increase in temperature (Table 5). The plot of log k_1 *versus* the reciprocal of temperature was linear, and the slope was used to calculate the activation energy. The Arrhenius parameters have been calculated and are shown in Table 6. The

TABLE 4. EFFECT OF ADDED SALTS

Concentration of salt / 10^5 M	$10^3 k_1/\text{min}^{-1}$ for K⁺	Rb⁺	Cs⁺
1.0	0.88	13.20	16.03
2.5	0.97	14.50	18.80
5.0	1.62	15.40	23.67
7.5	6.29	18.40	25.20

Hexacyanoferrate(III) = 2.5×10^{-4} M; [BH_4^-] = 8×10^{-3} M; NaOH = 1×10^{-2} M; pH = 11.50; Temp = 25 °C.

TABLE 5. EFFECT OF TEMPERATURE

Temp/°C	$10^2 k_1/\text{min}^{-1}$
25	4.54
30	4.97
35	5.55
45	6.58
55	7.37

Hexacyanoferrate(III) = 2.5×10^{-4} M; [BH_4^-] = 8×10^{-3} M; NaOH = 1×10^{-2} M; pH = 11.50.

TABLE 6. ARRHENIUS PARAMETERS

Energy of activation (E_a) = 19.14 kJ mol^{-1}
Frequency factor (A) = 1.59 s^{-1}
Entropy of activation (ΔS) = −241.4 J K^{-1} mol^{-1}
Enthalpy of activation (ΔH) = 19.14 kJ mol^{-1}

reaction has a large negative entropy of activation. Qualitatively, this would imply a lowering of the potential energy of the transition state. This would enable the facile formation of the transition state. Moreover, a large negative entropy of activation would correspond to a very low frequency factor; this has been observed for the reaction.

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.

$NaBH_4$ (0.05 M) was prepared in water, and the solution was kept at 25 °C. At definite intervals of time, 5 ml aliquots of this solution were removed, and mixed with 5 ml of a solution of hexacyanoferrate(III) (5.0×10^{-4} M) in NaOH (2.0×10^{-2} M), also maintained at 25 °C. The reaction was followed by measuring the decrease in optical density at 420 nm. The rate constant (k_1) was determined, and the concentration of BH_4^- was calculated from the equation:

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_1[BH_4^-].$$

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 data are given in Table 7.

TABLE 7. DECOMPOSITION OF $NaBH_4$ AS A FUNCTION OF TIME AND TEMPERATURE

Temperature / °C	Time / min	$10^2 k_1/\text{min}^{-1}$	[BH_4^{-1}] / $10^4\times$M
25	30	22.20	5.55
	60	14.60	3.65
	90	9.55	2.39
30	30	25.36	6.34
	60	16.60	4.15
	90	10.96	2.74
40	30	31.80	7.95
	60	20.70	5.17
	90	13.60	3.40

Hexacyanoferrate(III) = 2.5×10^{-4} M; NaOH = 1×10^{-2} M.

A plot of log k_1 *versus* the reciprocal of temperature was linear, and the slope was used to calculate the activation energy. The activation energy for the hydrolysis of $NaBH_4$ was found to be 19.14 kJ mol^{-1}. For the reaction involving the reduction of hexacyanoferrate(III) by $NaBH_4$, the value of the activation energy was also found to be 19.14 kJ mol^{-1} (Table 6).

Mechanism

Since the rate of the reaction is proportional to the concentrations of both, tetrahydroborate and hydrogen ions, the chemical composition of the activated complex can be written as $H^+BH_4^-$.

The first step of the reaction is:

$$BH_4^- + H^+ \xrightarrow{k_1} H^+BH_4^-. \tag{1}$$

A kinetic scheme consisting of Eq. (1), 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:

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

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

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

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

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

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

The overall stoichiometric reaction would then be:

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

The rate law could be expressed as

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_1[BH_4^-][H^+].$$

It has been found that for this reaction, k_1 has the frequency factor of 1.59 s^{-1}, and an activation energy of 19.14 kJ mol^{-1}.

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 is 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:

(a) $BH_2OH + H_2O \longrightarrow BH(OH)_2 + H_2$,

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

(c) $BH(OH)_2 + H_2O \longrightarrow H_3BO_3 + H_2$.

This mechanism would predict

$$-\frac{d[BH_4^-]}{dt} = k_1[BH_4^-][H^+].$$

The rate of hydrolysis of $NaBH_4$ was measured and it was found that the rate constant, k_1, corresponds to an activation energy of 19.14 kJ mol^{-1}. This was in agreement with the value determined from the kinetic studies, in the presence of hexacyanoferrate(III).

Intermediate Boron Compounds. The intermediate boron compounds, described in the reaction sequence, could not be isolated. However, there is evidence for the existence of such intermediates from the reaction of diborane with ice and with the "bound water" in silica gel.[9]

These intermediates differ in reducing capacity, and the formulas of the boron intermediates used are primarily intended to show the reducing capacity of the intermediate.

Consider the following steps:

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

and

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

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:

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

and

(b) $BH_2OH + H_2O \longrightarrow BH(OH)_2 + H_2$.

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

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