Kinetics of Reduction of Silver(II) by Sodium Tetrahydroborate

Manash DASGUPTA and Mahendra K. MAHANTI*
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

(Received September 28, 1987)

The kinetics of reduction of silver(II) by sodium tetrahydroborate in aqueous acidic solution has been investigated. The reaction was observed to proceed in two steps, namely, (a) the formation of the intermediate Ag^I and (b) the subsequent conversion of Ag^I to Ag^0. The activation parameters for the two steps have been separately calculated. The intermediate Ag^I species, and the final products, were characterized by chemical and spectral methods. A plausible mechanism for the reduction of Ag^{II} ions has been proposed.

The mechanism of oxidation by Ag^{II} has been the subject of several investigations in which organic[1] and inorganic[2] substrates have been used. The Ag^{II}/Ag^I couple has a high reduction potential of $+2.00$ V in 1.0 M $HClO_4$ (1 M=1 mol dm^{-3}).[3] Silver(II) reacts rapidly even with substrates that exhibit sluggish behavior towards other commonly employed reagents. The kinetics of oxidation of Fe^{2+}, Mn^{2+}, Co^{2+}, Ce^{3+}, and V^{4+} by Ag^{II} revealed a wide range of reduction potentials and self-exchange rates.[4] Many oxidation reactions such as the oxidation of Hg^I by Ce^{4+} ions,[5] the peroxydisulfate oxidations of Ce^{III}, Cr^{III}, V^{IV}, and N_2H_4,[6] and of oxalate,[7] are all catalyzed by Ag^+ ions, and the kinetics have been visualized as proceeding via the initial oxidation of Ag^I to Ag^{II}, which then undergoes reduction by the substrate. The reactions of the tetrahydroborate ion with transition metal compounds usually result either in a reduction of metal to a lower oxidation state and possibly the formation of a hydride compound, or the formation of a tetrahydroborate or a diborane derivative.[8,9] Sodium tetrahydroborate in water or methanol solution was found to be an effective reducing agent for the conversion of aldehydes and ketones to the corresponding alcohols.[10,11] In an earlier paper, we had reported our results on the kinetics of reduction of hexacyanoferrate(III) by sodium tetrahydroborate.[12] In continuation of our work on the kinetics of reduction of transition metal ions by sodium tetrahydroborate, we report here the kinetic features of the reduction of silver(II) by sodium tetrahydroborate in aqueous acidic medium, at constant ionic strength, under a nitrogen atmosphere. A plausible mechanistic pathway for the reduction reaction has been suggested.

Experimental

Materials, Methods, and Stoichiometry. Sodium tetrahydroborate (Loba Chemical Co.) was kept under vacuum. Tetrakis(pyridine)silver(II) peroxodisulfate, $[Ag(py)_4]S_2O_8$, was prepared by the standard procedure,[13] and was used as the source of Ag(II). Perchloric acid and sodium perchlorate were of E. Merck products. All solutions were prepared in dark-colored flasks in order to prevent exposure of Ag^{II} solutions to light.

Solutions of sodium tetrahydroborate were prepared in water. Since sodium tetrahydroborate undergoes hydrolysis in aqueous medium,[12] all the solutions used for the kinetic runs were prepared by dissolving 2.5 times more of $NaBH_4$ than what was theoretically necessary. Solutions of Ag^{II} were prepared in $HClO_4$ and $NaClO_4$ to maintain a constant ionic strength. It has been shown that Ag(II) can undergo disproportionation according to:[14,15]

$$2\,Ag^{II} \rightleftharpoons Ag^I + Ag^{III}$$

Hence, an excess of Ag^I solution (0.10 M) was added to prevent disproportionation of Ag^{II}. The two solutions were separately thermostated at 15 °C for 1 h under nitrogen, and then mixed in equal volumes by syringing into the spectrophotometric cell (UV-26, Beckman). The progress of the reaction was monitored at 375 nm by observing:

(i) An increase in the optical density due to the reduction of the Ag^{II} to the Ag^I species. This solution does not contain any Ag^{II} ion at the end of this reaction.

(ii) The subsequent decrease in the optical density at 375 nm (due to the reduction of the Ag^I to the Ag^0 species).

The pH of the reaction mixture was checked periodically during the course of the reaction (Control Dynamics, digital model), and found to remain constant. Since the grey-colored Ag^0 species was formed as the final reaction product, care was taken to ensure that the reaction mixture remained homogeneous for the duration of the kinetic runs. It was observed that there was no precipitation during the course of the kinetic runs.

The stoichiometry of the reaction was determined in the following manner: reaction mixtures containing $NaBH_4$ and an excess of Ag^{II} were allowed to react at 15 °C for 24 h under nitrogen, and then analyzed, spectrophotometrically at 375 nm for the Ag^{II} which was left. The results gave a ratio of substrate to reductant according to the equation:

$$2\,BH_4^- + 8\,Ag^{2+} + 6\,H_2O \longrightarrow 8\,Ag^0 + 2\,B(OH)_3 + 14\,H^+.$$

Analysis of the Ag(I) Intermediate. Two milliliters of the reaction mixture were withdrawn within 1 min of the initiation of the reaction, and spectrally analyzed over a range of wavelengths from 300 nm to 900 nm. The dark colored species[16] was found to absorb at 375 nm, which was due to the presence of the Ag^I intermediate species. In an earlier investigation, it was shown that Ag^{II} was reduced to an Ag^I species.[17]

Product Analysis. A solution of $NaBH_4$ (2×10^{-5} M) in 100 ml of water, was mixed with a solution containing the

Ag^{II} complex (2×10^{-5} M) in $HClO_4$, and excess of Ag^I solution (ionic strength adjusted to 0.05 M by the addition of $NaClO_4$), and the reaction mixture allowed to stand at 15 °C for 24 h under nitrogen. Greyish colored particles were precipitated along with a thin layer of shining silver mirror formed on the walls of the reaction vessel. The reaction mixture was filtered. The precipitate was washed with distilled water, tested for the complete removal of Ag^+ ions, and then dried. The filtrate was analyzed for the presence of borate, as described earlier.[12)]

The precipitate (0.5187 g) was taken, and converted to AgCl by the standard method,[18)] and gravimetrically estimated as AgCl. The weight of AgCl was 0.6682 g, which corresponded to 0.5029 g of silver. This value compared favorably, within the limits of experimental error, with the theoretical percentage of silver present in the final product (theoretically, 100%; experimentally obtained by this method, 96.9%). This confirmed that the silver was present in the final product as Ag^0.

Results and Discussion

Kinetics Results. The rates of the reactions (the formation of Ag^I from Ag^{II} and the subsequent conversion of Ag^I to Ag^0 species) were dependent on the first powers of the concentrations of each of the reactants (Table 1). The two rate constants have been separated, and individually calculated as k_1 (conversion of the Ag^{II} to the Ag^I species) and k_2 (conversion of the Ag^I to the Ag^0 species). Plots of k_1 and k_2, respectively, versus a twenty-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 first-order rate constants (k_1 and k_2, respectively) did not change with changing Ag^{2+} ion concentrations (twenty-fold range), which indicated a first order dependence on the Ag^{2+} ion concentration (Table 1).

The reaction was studied at varying pH (Table 1). The logarithm of the rate of disappearance of Ag^{2+} ion divided by the tetrahydroborate ion concentration, was plotted against pH. The plot was linear, indicating a first order dependence of the rate of the reaction on the hydrogen ion concentration.

The reaction was influenced by changes in the temperature (Table 1), and the activation parameters have been evaluated and shown in Table 2. It has been suggested[14)] that in the exchange of Ag^I with Ag^{II}, the

Table 1. Rate Data for the Reduction of Ag^{II} by $NaBH_4$ at 15 °C (μ=0.05 M)

$\frac{[\mathrm{BH_4^-}]}{10^3\,\mathrm{M}}$	$\frac{[\mathrm{Ag^{II}}]}{10^4\,\mathrm{M}}$	pH	$10^3 k_1/\mathrm{s^{-1}}$ $Ag^{II} \longrightarrow Ag^I$	$10^3 k_2/\mathrm{s^{-1}}$ $Ag^I \longrightarrow Ag^0$
1.0	1.0	2.0	14.2	6.2
5.0	1.0	2.0	72.5	31.5
10.0	1.0	2.0	145.0	61.2
25.0	1.0	2.0	360.0	156.0
1.0	0.75	2.0	14.0	5.8
1.0	0.50	2.0	14.8	6.0
1.0	0.25	2.0	14.5	6.5
1.0	0.10	2.0	14.0	6.0
1.0	0.05	2.0	14.5	6.5
1.0	1.0	2.5	12.6	5.5
1.0	1.0	3.0	11.0	4.8
1.0	1.0	3.5	9.8	4.3
1.0	1.0	4.0	8.5	3.7
1.0	1.0	5.0	6.6	2.9
1.0	1.0	6.0	5.1	2.2
1.0	1.0	2.0	18.0[a)]	7.4[a)]
1.0	1.0	2.0	20.9[b)]	10.5[b)]
1.0	1.0	2.0	25.2[c)]	13.5[c)]
1.0	1.0	2.0	29.5[d)]	17.6[b)]

a) 20 °C; b) 25 °C; c) 30 °C; d) 35 °C (all temperature corrections were ±0.1 °C). All values of rate constants were the average of three experiments, agreement being ±3%.

Table 2. Activation Parameters

Parameter	$Ag^{II} \longrightarrow Ag^I$	$Ag^I \longrightarrow Ag^0$
E	$28\pm2\,\mathrm{kJ\,mol^{-1}}$	$43\pm2\,\mathrm{kJ\,mol^{-1}}$
A	$2\times10^2\,\mathrm{s^{-1}}$	$5\times10^4\,\mathrm{s^{-1}}$
$\Delta H^{\neq}$	$25\pm2\,\mathrm{kJ\,mol^{-1}}$	$40\pm2\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^{\neq}$	$-208\pm4\,\mathrm{J\,K^{-1}\,mol^{-1}}$	$-166\pm4\,\mathrm{J\,K^{-1}\,mol^{-1}}$

rate law was consistent with a disproportionation mechanism

$$2\,Ag^{II} \rightleftharpoons Ag^{I} + Ag^{III}$$

the rate of exchange being equal to the rate of the disproportionation reaction at equilibrium. This would necessarily imply that the rate constant for the reverse reaction (the reaction between the Ag^{I} and the Ag^{III} species) must be quite large. In the present investigation, since excess Ag^{I} has been added to the initial Ag^{II} solution, one might envisage the suppression of the disproportionation reaction involving the formation of the Ag^{III} species. This would enable the facile conversion of Ag^{II} to Ag^{I} which has been reflected in the activation parameters (Table 2) for the first step of the reaction. The conversion of Ag^{I} to Ag^{0} has been observed in this investigation.

Variations in the ionic strength of the medium using $NaClO_4$ (range of ionic strength 0.01 to 0.075 mol l^{-1}), did not affect the rate of the reaction.

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

$$\text{Rate} = -\frac{d[Ag(II)]}{dt} = k_{obs}[Ag(II)][BH_4^-][H^+]$$

where k_{obs} corresponds to the composite rate constant for the reaction, which has been separated into the individual rate constants, k_1 and k_2 (Table 1).

Mechanism. Since the rate of the reaction was dependent on the concentrations of each of the reactants, the first step of the reaction could be represented as:

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

The redox steps following Eq. 1 would involve the reaction of Ag^{II} with the tetrahydroborate species. There is evidence from the hydrolysis of diborane[19] that intermediates of partially hydrolyzed boron hydride compounds do exist, and that these intermediates differ in their reducing capacities. In the present investigation, the intermediate boron compounds could not be isolated, although the reactions of diborane with ice and with the "bound water" in silica gel do indeed suggest the existence of intermediate boron compounds.[19]

Molecular hydrogen reacts homogeneously with a number of metal ions in solution, reducing them to a lower oxidation state. For example, the mechanism of reduction of Cu^{2+} to Cu^{+} has been shown to be [20,21]

$$Cu^{2+} + H_2 \rightleftharpoons CuH^+ + H^+$$

$$CuH^+ + Cu^{2+} \longrightarrow 2Cu^+ + H^+,$$

the intermediate CuH^+ being stabilized by covalent bonding.

The reactions of Hg^{2+}, Hg_2^{2+}, and MnO_4^- with molecular hydrogen had indicated that hydrogen behaved as a two-equivalent reductant. Thus, the mechanism for the reduction of Hg^{2+} to Hg_2^{2+} was suggested to be:[22]

$$Hg^{2+} + H_2 \longrightarrow Hg^0 + 2H^+$$

$$Hg^0 + Hg^{2+} \xrightarrow{\text{fast}} Hg_2^{2+}.$$

In the reactions with Hg_2^{2+} and MnO_4^-, the rate-determining step appeared to be a two-equivalent reduction, leading to the formation of Hg_2^0 and Mn^{V}, respectively, as intermediates.

It has been earlier reported that acidic solutions of Ag^{2+} ions have been reduced to metallic silver by a variety of reducing agents.[23–28] Aqueous solutions of $AgClO_4$ were reduced by hydrogen to the metal,[29] a homolytic cleavage of hydrogen being suggested as follows:

$$2\,Ag^+ + H_2 \longrightarrow 2\,AgH^+$$

$$2\,AgH^+ + \text{Substrate} \longrightarrow \text{Products} + 2\,Ag^+.$$

At lower concentrations of Ag^+, a heterolytic splitting of H_2 was proposed:[30]

$$Ag^+ + H_2 \longrightarrow AgH + H^+$$

$$AgH + Ag^+ \longrightarrow \text{Intermediate} \xrightarrow{\text{Substrate}} \text{Products.}$$

The effect of complex formation with ligands other than water was studied by following the reduction of silver complexes by hydrogen to the metal,[31] and the rate data indicated a heterolytic cleavage of hydrogen. The reduction of silver-amine complexes to metallic silver by hydrogen was investigated in an attempt to correlate reactivity with ligand properties,[32] thus:

$$[Ag(NR_3)_2]^+ + H_2 \longrightarrow Ag + 2R_3NH^+.$$

The kinetic results of the present investigation would suggest a stepwise reduction of Ag^{2+} ions by sodium tetrahydroborate. In the first instance, the Ag^{2+} ion would be reduced to Ag^{I}, which in turn, is converted to Ag^{0}.

In the present investigation, the reaction sequence could be represented as follows:

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

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

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

$$8\,Ag^+ + BH_4^- + 3\,H_2O \longrightarrow 8\,Ag^0 + B(OH)_3 + 7\,H^+$$

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

The overall stoichiometric reaction is:

$$2\,BH_4^- + 8\,Ag^{2+} + 6\,H_2O \longrightarrow 8\,Ag^0 + 2\,B(OH)_3 + 14\,H^+$$

The intermediate formation of the Ag(I) species, and also the formation of Ag^0 as the final product, have been confirmed by spectral and chemical methods, in the present investigation.

References

1) C. Baiocchi, G. Bovio, and E. Mentasti, *Int. J. Chem. Kinet.*, **14**, 1017 (1982); E. Mentasti and E. Palizzetti, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 77.

2) A. K. Indrayan, B. K. Mishra, and P. K. Gupta, *Inorg. Chem.*, **20**, 450 (1981); D. S. Honig, K. Kustin, and J. E. Martin, *Inorg. Chem.*, **11**, 1895 (1972).

3) G. Biederman, F. Maggio, V. Romano, and R. Zingales, *Acta Chem. Scand., Ser. A*, **35**, 287 (1981).

4) P. Arsalli, C. Baiocchi, E. Mentasti, and J. S. Coe, *J. Chem. Soc., Dalton Trans.*, **1984**, 475.

5) W. C. E. Higginson, D. R. Rosseinsky, B. Stead, and A. G. Sykes, *Disc. Faraday Soc.*, **29**, 49 (1960).

6) W. M. Cone, *J. Am. Chem. Soc.*, **67**, 78 (1945).

7) J. M. Anderson and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 1651 (1970); *J. Org. Chem.*, **35**, 986 (1970).

8) A. G. Ginsberg, *Adv. Trans. Metal Chem.*, **1**, 111 (1965).

9) M. L. H. Green and D. J. Jones, *Adv. Inorg. Radiochem.*, **7**, 215 (1965).

10) S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).

11) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

12) M. Bhattacharjee, A. K. Bhattacharjee, and M. K. Mahanti, *Bull. Chem. Soc. Jpn.*, **54**, 3566 (1981).

13) G. Pass and H. Sutcliffe, "Practical Inorganic Chemistry," Chapman and Hall, London (1974), p. 79.

14) B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958).

15) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, *J. Phys. Chem.*, **67**, 1617 (1963).

16) E. T. Borish, L. J. Kirchenbaum, and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, **1985**, 1789.

17) L. J. Kirschenbaum, E. T. Borish, and J. D. Rush, *Isr. J. Chem.*, **25**, 159 (1985).

18) A. I. Vogel, "A Text Book of Quantitative Analysis," ELBS (1985), p. 479.

19) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

20) E. Peters and J. Halpern, *J. Phys. Chem.*, **59**, 793 (1955).

21) J. Halpern, E. R. Macgregor, and E. Peters, *J. Phys. Chem.*, **60**, 1455 (1956).

22) G. J. Korinek and J. Halpern, *J. Phys. Chem.*, **60**, 285 (1956).

23) J. Kleinberg, *Chem. Rev.*, **40**, 381 (1947).

24) C. Wagner, *J. Metals*, **4**, 214 (1952).

25) L. Andrussow, *Z. Phys., Chem.*, **208**, 78 (1958).

26) M. A. Bernard and B. Nocher, *Compt. Rend.*, **258**, 3309 (1964).

27) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 713 (1964); **12**, 479 (1965).

28) R. J. Kline and C. J. Kershner, *Inorg. Chem.*, **5**, 932 (1966).

29) A. H. Webster and J. Halpern, *J. Phys. Chem.*, **60**, 280 (1956).

30) A. H. Webster and J. Halpern, *J. Phys. Chem.*, **61**, 1239 (1957).

31) A. H. Webster and J. Halpern, *J. Phys. Chem.*, **61**, 1245 (1957).

32) J. Halpern and J. B. Milne, Proc. 2nd Intl. Cong. Catal., Paris (1961), p. 445.