The Oxidation of Iodide by the Tetrahydroxoargentate(III) Ion in Aqueous Alkaline Media

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Iodide is rapidly oxidized by $[Ag(OH)_4]^-$ in strongly alkaline media to give hypoiodite and Ag^I according to the stoicheiometric equation (i). Stoicheiometry measurements are consistent with

$$[Ag(OH)_4]^- + I^- \longrightarrow Ag^I + 2OH^- + IO^- + H_2O \qquad (i)$$

complementary two-electron redox both at excess of Ag^{III} and excess of I^-. The kinetics of the reaction are first order in the silver(III) and iodide concentrations. The second-order rate constant is 76 ± 1 $dm^3\ mol^{-1}\ s^{-1}$ (25 °C, I = 1.2 mol dm^{-3}) and the enthalpy and entropy of activation are 32.5 ± 0.6 kJ mol^{-1} and −100 ± 2 J $K^{-1}\ mol^{-1}$, respectively. While precipitation of AgI interferes with spectral measurements at lower (excess) iodide concentrations, the product formation has no effect on the kinetics of the system. The mechanism proposed involves a simultaneous two-electron transfer within an intermediate of composition $[Ag(OH)_4I]^{2-}$. The values of the activation parameters are similar to those of other silver(III) reactions.

The redox reactions of iodide ion have been intensively studied[1-17] since the discovery of 'clock' reactions by Landolt[18] a century ago. Indeed, two-component 'simple' oscillators such as ClO_2^-–I^- and BrO_3–I^- are just continuous oxidations of iodide to iodine.[7] Recent interest in aqueous iodine, chemistry has arisen because radioactive iodine, a highly toxic uranium fission product, is produced in water-cooled nuclear reactors.[19-22] The reduction of chloramines (NH_2Cl, $NHCl_2$, and NCl_3), hypobromite, and hypochlorite by iodide has recently been investigated.[8] The reactions of iodide with transition-metal complexes including $[Pt(CN)_4Br(H_2O)]^-$,[9] $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and $[Fe(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine),[10] $[Ni(cyclam)(H_2O)_2]^{3+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane),[11,12] $[Au(NH_3)_4]^{3+}$,[13] $[Os(bipy)_3]^{3+}$,[14] $[TiO_2]^{2+}$,[15] $[Cr(Et_2C_2O_3)_2O]^-$,[16] $Cu^{III}(H_{-n}L)$ (L = deprotonated peptide),[6] $[Fe(CN)_6]^{3-}$,[2] and $[MnO_4]^-$ [3,17] have been studied. Of particular interest among these reactions is the reduction of the hexacyanoferrate(III) ion by iodide.[2] Majid and Howlet[5] reported that the rate of the reaction is second order in iodide concentration and first order in $[Fe(CN)_6{}^{3-}]$ and insensitive to variation in ionic strength. Iodide-complexation reactions with various metal ions have also been studied.[23-26] For instance, kinetic studies of the anation of the copper(II) complex of the macrocyclic ligand tetb (tetb = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) by iodide to give copper(I) showed that the reaction goes by an associative interchange mechanism.[27] Wilmarth *et al.*[28] reported that substitution of co-ordinated H_2O by I^- in the complex *trans*-$[Co(CN)_4(SO_3)(OH_2)]^{3-}$[23] occurs without redox *via* a five-co-ordinate intermediate. Platinum and palladium concentrations in rocks and soils were recently determined as their iodo complexes, after extraction into isobutyl methyl ketone, by electrothermal atomic absorption spectrometry.[29]

In our laboratory, we have been investigating the reactions of the tetrahydroxoargentate(III) ion, $[Ag(OH)_4]^-$.[30-35] The complex ion is a square-planar d^8 system which has a half-life of about 90 min in 1.2 mol dm^{-3} base. Its absorbance maximum is at 267 nm ($\varepsilon = 1.17 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$). The redox reactions of $[Ag(OH)_4]^-$ are generally preceded by axial attack on the square-planar metal followed, in some cases, by replacement of a bound hydroxyl. Electron transfer can involve either one-or two-electron processes. In this paper, we report on the stoicheiometry and kinetics of the reaction of iodide with $[Ag(OH)_4]^-$.

Experimental

Reaction Solutions.—The preparation of the tetrahydroxoargentate(III) complex ion has been described elsewhere.[30,36] Solutions were prepared by placing 1.2 mol dm^{-3} NaOH (*ca.* 200 cm^3) in a polyethylene beaker (250 cm^3) containing a silver-foil anode and electrolysing at high current density. Nitrogen or argon gas was bubbled through the solution during electrolysis from a capillary placed near the anode, to exclude oxygen and CO_2 and to provide constant stirring of the solution. After electrolysis, solutions were filtered[37] to remove silver oxide.

All chemicals were reagent grade and used without further purification. For all experimental runs, sodium iodide solutions were freshly made in doubly distilled water, or in 1.2 mol dm^{-3} $NaClO_4$, by exact weighing of reagent-grade sodium iodide (Allied Chemical or Fisher). Sodium hydroxide solutions were prepared from 50% low-carbonate NaOH (Fisher). A 1.2 (or 6) mol dm^{-3} $NaClO_4$ solution was used for ionic strength adjustment when appropriate. Sodium perchlorate was prepared from 50% NaOH and $HClO_4$ (Fisher) adjusted to pH 7, followed by filtration.[30]

An Aminco-Morrow stopped-flow apparatus was used in the kinetic runs. Large excesses of iodide were used for all experiments. Due to the high absorbance of iodide in the vicinity of the $[Ag(OH)_4]^-$ peak (267 nm), the disappearance of $[Ag(OH)_4]^-$ was monitored at 300 nm at which iodide did not show any significant absorbance. The reaction was followed on a Tektronix 564B storage oscilloscope coupled to a Tandy TRS-80 computer.[31] Kinetic data were processed on a personal computer using the OLIS kinetic fitting (Kinfit) program.[38] All reported pseudo-first-order rate constants are reproducible to less than 5%. Because of interference from AgI at low iodide, experiments were done at I = 2.0 mol dm^{-3} (to allow $[I^-]$ up to 0.8 mol dm^{-3}) as well as in our traditional medium of I = 1.2 mol dm^{-3}. Because of ion pairing,[30,39] rate constants are essentially independent of ionic strength in this range. Spectral analyses were done on a Cary 210 or on an HP 8451 diode-array spectrophotometer.

Table 1. Stoicheiometry of the reaction $[Ag(OH)_4]^- + I^-$

$10^4[I^-]_0$/mol dm^{-3}	$10^4\Delta[Ag^{III}]$/mol dm^{-3}	$[I^-]_0/[Ag^{III}]_0$	Stoicheiometry
Excess of iodide			$\Delta[I_2]/\Delta[Ag(OH)_4^-]$ [a]
50	1.88	27	0.99
100	1.88	53	1.03
200	1.88	106	1.08
400	1.88	213	1.07
			Average 1.04 ± 0.04
Excess of Ag^{III}			$\Delta[I^-]/\Delta[Ag(OH)_4^-]$ [b]
0.833	0.83	0.09	1.0
1.43	1.32	0.2	1.1
1.9	1.8	0.3	1.1
2.22	1.9	0.4	1.2
2.5	2.1	0.45	1.2
			Average 1.12 ± 0.10
			$\Delta[I^-]/\Delta[I_2]$ [c]
0.35	9.62	0.036	1.1
0.83	8.32	0.10	1.1
1.3	7.34	0.18	1.1
1.4	6.9	0.2	1.2
1.5	8.03	0.2	0.93
			Average 1.1 ± 0.1

[a] Iodine determined by thiosulphate titration after acidification. [b] Silver(III) determined as the difference between Ag^{III} initially present and that complexed by periodate in base at the end of the reaction. [c] Iodine obtained spectrophotometrically as I_3^- after acidification in excess of I^-.

Product Analysis.—Known concentrations of $[Ag(OH)_4]^-$ and iodide were allowed to react to completion. Spectra of the product were immediately taken. The mixture was then acidified with $HClO_4$ (Fisher). The presence of I_3^- was confirmed by the spectrum of the acidified liquor[40] and by its reaction with a starch solution to give an intense blue colour which was absent from blank iodide solutions.[41]

Stoicheiometry.—Three different methods were used in determining the reaction stoicheiometry. (*i*) At excess of $[Ag(OH)_4]^-$, a solution of basic $NaIO_4$ (Allied Chemical) was used to complex Ag^{III} left over after completion of the reaction.[36] The change in absorbance of the $[Ag(H_2IO_6)_2]^{3-}$ complex ($\lambda_{max.}$ = 348 nm, $\varepsilon = 1.18 \times 10^4$ dm^3 mol^{-1} cm^{-1}) was used to determine the decrease in $[Ag(OH)_4^-]$. This value, $\Delta[Ag^{III}]$, was compared to the initial amount of iodide. (*ii*) Also at excess of silver(III), the I_2 produced after acidification was measured spectrophotometrically and compared to the initial iodide concentration. (*iii*) At excess of iodide, the stoicheiometry of the reaction was determined by iodimetric titration using standard thiosulphate.[41]

Results and Treatment of Data

Products and Stoicheiometry of the Reaction.—A spectrum of the product in alkaline medium showed a shoulder at 260 nm and a sharp increase in absorbance at wavelengths below 250 nm, features of the hypoiodite ion (ε = 400 dm^3 mol^{-1} cm^{-1}).[20,42] After acidification (and if appropriate, addition of excess of I^-), the u.v.–visible spectrum showed two peaks at 350 and 288 nm characteristic of the tri-iodide ion ($\varepsilon = 2.64 \times 10^4$ and 4.0×10^4 dm^3 mol^{-1} cm^{-1}, respectively).[40] Furthermore, when a starch solution was added to the acidified solution an intense blue colour developed. These features are absent for iodide blanks.

At excess of $[Ag(OH)_4]^-$, the ratios $\Delta[I^-]/\Delta[Ag^{III}]$ and $\Delta[I^-]/\Delta[I_2]$ were found to be 1:1 (Table 1). Furthermore, when excesses of iodide were used the ratio of the estimated I_2 formed to initial silver(III) concentration was also 1:1. Based on the 1:1 stoicheiometry and the spectral observations, the net reaction is as in equation (1). Upon acidification in the

$$[Ag(OH)_4]^- + I^- \longrightarrow Ag^I + 2OH^- + IO^- + H_2O \qquad (1)$$

presence of excess of I^- the protonated hypoiodous acid gives rise to I_2 *via* equilibrium (2)[43] accompanied by formation of I_3^- (K_{eq} = 708 dm^3 mol^{-1} at 25 °C).[44]

$$HIO + I^- + H^+ \rightleftharpoons I_2(aq) + H_2O \qquad K_{eq} = 5 \times 10^{12}\ dm^6\ mol^{-2} \qquad (2)$$

Kinetics.—The light yellow $[Ag(OH)_4]^-$ solution turns cloudy when mixed with excesses of iodide less than 0.05 mol dm^{-3}. This precipitation, which is due to the formation of yellow AgI ($K_{sp} = 8.3 \times 10^{-17}$ dm^6 mol^{-2}),[41] makes it difficult to obtain kinetic data at low iodide concentrations. At higher iodide concentrations, however, the mixture becomes progressively transparent due to the formation of anionic silver(I)–iodide complexes.[45] Therefore, data were collected at iodide concentrations ranging from 0.05 to 0.8 mol dm^{-3}. Under these conditions the reaction could be reliably monitored as a first-order absorbance decrease in the range 300—400 nm. The dependence of the reaction rate on iodide concentration was studied at 25 °C and I = 1.2 and 2.0 mol dm^{-3}, $0.12 \leqslant [OH^-] \leqslant 1.2$ mol dm^{-3}, with initial silver ranging from 1×10^{-5} to 1×10^{-4} mol dm^{-3}. The pseudo-first-order rate constants are independent of $[OH^-]$. The reaction shows a first-order dependence in excess of iodide and $[Ag(OH)_4]^-$ as given in equation (3).

$$\begin{aligned} -d[Ag(OH)_4^-]/dt &= k_{obs.}[Ag(OH)_4^-] \\ &= k[I^-][Ag(OH)_4^-] \qquad (3) \end{aligned}$$

A linear least-squares treatment of the data resulted in a value of r^2 better than 0.999 and a small intercept. However, the

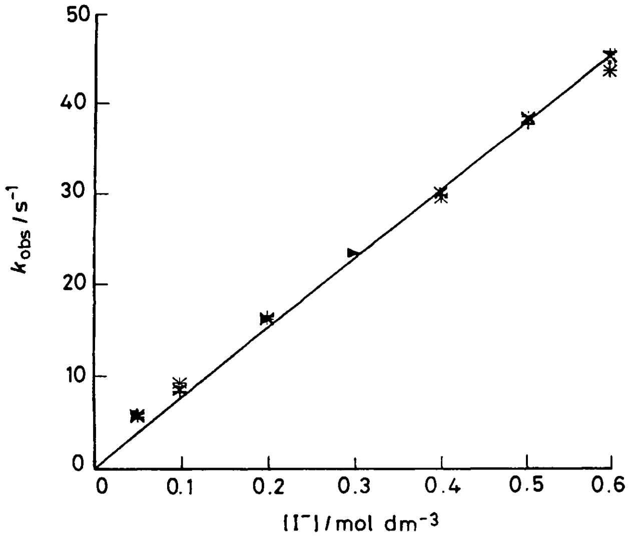

Figure 1. Dependence of the observed pseudo-first-order rate constants on iodide at different hydroxide concentrations: (+) 0.12, (✱) 0.3, (×) 0.48, (▶) 0.6, and (*) 0.9 mol dm^{-3}; I = 1.2 mol dm^{-3}; 25 °C. Experimental data were collected for all hydroxide concentrations listed above at all iodide concentrations, except at $[I^-]$ = 0.3 mol dm^{-3} where experiments were performed only for $[OH^-]$ = 0.6 mol dm^{-3}

Table 2. Pseudo-first-order rate constants for the oxidation of I^- by Ag^{III} at I = 1.2 mol dm^{-3}

$[OH^-]$/mol dm^{-3}	$[I^-]$/mol dm^{-3}	$k_{obs.}/s^{-1}$	$k_{calc.}/s^{-1}$
0.12	0.05	5.93	3.80
	0.1	8.26	7.60
	0.2	16.4	15.2
	0.3	29.5	30.3
	0.5	37.6	37.9
	0.6	45.5	45.5
0.3	0.05	5.5	3.80
	0.1	9.25	7.60
	0.2	16	15.2
	0.4	29.5	30.3
	0.5	38.4	37.5
	0.6	43.5	45.5
0.48	0.05	5.75	3.80
	0.1	8.5	7.60
	0.2	16.2	15.2
	0.4	30	30.3
	0.5	38.2	37.9
	0.6	45	45.5
0.6	0.05	6.1	3.80
	0.1	8.7	7.60
	0.2	16.2	15.2
	0.4	30.4	30.3
	0.5	37.8	37.9
	0.6	44.3	45.5
0.9	0.05	5.8	3.80
	0.2	16.1	15.2
	0.3	23.4	22.7
$[OH^-]$ = 1.2 mol dm^{-3}, I = 2.0 mol dm^{-3}			
	0.08	7.1	6.10
	0.1	8.9	7.60
	0.2	16.8	15.2
	0.4	30	30.3
	0.6	45	45.5
	0.8	60.4	60.8

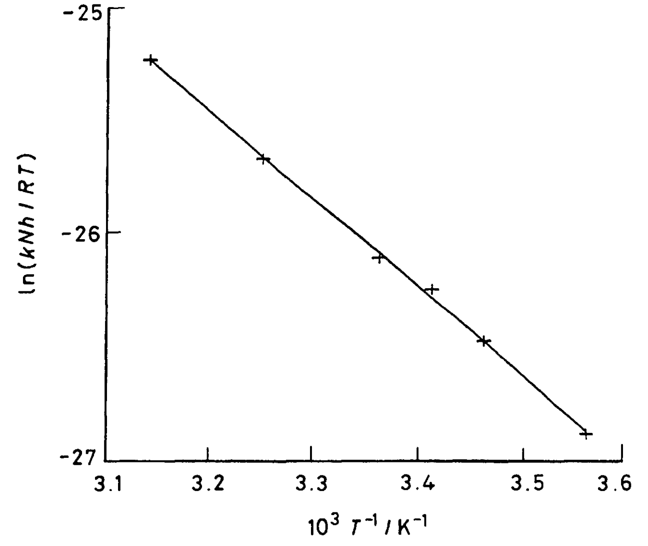

Figure 2. Temperature dependence for the reaction between $[Ag(OH)_4]^-$ and iodide ($[I^-]$ = 0.4, $[OH^-]$ = 0.6 mol dm^{-3}, I = 1.2 mol dm^{-3})

fit is not significantly different if the intercept is set to zero (Figure 1). The second-order rate constant obtained from the latter treatment is k = 76 ± 1 dm^3 mol^{-1} s^{-1}. There is generally good agreement between the observed and calculated pseudo-first-order rate constants (Table 2). Several silver(III) rate laws contain ligand-independent terms.[31,33] These have been explained by a path involving the formation of $Ag(OH)_3(H_2O)$ with a rate constant ≈ 1 s^{-1}. Although this path may be a minor contributor in the present system, we are unable to distinguish between a zero-order (in iodide) contribution and (see above) interference from solid products as the cause of deviation at the lowest $[I^-]$.

Temperature Dependence.—The reaction was carried out over the range 8—45 °C with 0.4 mol dm^{-3} iodide at $[OH^-]$ = 0.6 mol dm^{-3}, I = 1.2 mol dm^{-3}. An Eyring plot of the data using equation (4)[46] is linear (Figure 2). The enthalpy and entropy of activation calculated from the slope and

$$\ln(kNh/RT) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R \qquad (4)$$

intercept of the least-squares treatment of the data (r^2 = 0.999) are $\Delta H^{\ddagger}$ = 32.5 ± 0.6 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -100 ± 2 J K^{-1} mol^{-1}.

Discussion

The 1:1 stoicheiometry observed both at excess and limiting iodide concentrations is consistent with the iodine(I) product obtained as is also reported in the two-electron-transfer reactions of iodide with hypochlorite[12,20,47] under similar conditions (strong alkaline media). Although hypoiodite disproportionates in base to give iodide and iodate[43] [equation (5)], that reaction is sufficiently slow[47–50] to be unimportant

$$3IO^- \rightleftharpoons 2I^- + IO_3^- \qquad K_{eq} = 1 \times 10^{20}\ (\text{ref. } 38) \qquad (5)$$

under our conditions, the second-order rate being less than 7×10^{-2} dm^3 mol^{-1} s^{-1} in 1 mol dm^{-3} NaOH.[21,50]

Iodide ion being a good nucleophile,[11] the possibility of ligation in the intimate step of the reaction is high, and indeed complexation and reduction reactions of $[Ag(OH)_4]^-$ generally involve axial association.[35] However, formation of four-co-ordinate $[Ag(OH)_3I]^-$ in equilibrium with $[Ag(OH)_4]^-$ would be expected to give rise to an inverse hydroxide-ion dependence in the rate law [equation (3)]. The absence of such a term as well as of any rapid, initial spectral change indicate that $[Ag(OH)_3I]^-$ is either (*i*) not an intermediate or (*ii*) undergoes rapid redox in steady-state concentrations. If no four-co-ordinate complex is formed, then it is likely that electron transfer occurs in an axially co-ordinated intermediate. Several silver(III) redox reactions have been found to proceed *via* five-co-ordinate intermediates. For instance, the presence of third-order terms in the rate expressions of the reactions of Ag^{III} with ethylenediamine,[51] HO_2^-,[52] hypophosphite,[33] and thiourea[31] supplies evidence that redox occurs *via* OH^- assistance within a five-co-ordinate silver(III) species. Oxidation of thiosulphate involves reaction of $[Ag(OH)_4(S_2O_3)]^{3-}$ with a second thiosulphate ion.[35] Iodide–metal intermediate adducts have been reported for the redox reactions of iodide with complexes of Au^{III},[13] Cu^{III},[1] and Ni^{III}.[11,12]

The activation parameters obtained in this study are similar to those from other silver(III) reaction systems[24,51,52] where an inner-sphere mechanism was also postulated. In the reaction between $[Ag(OH)_4]^-$ and arsenite ions the temperature dependence was non-linear because of changing degrees of protonation among three reacting arsenic(III) species. Although ion pairing is expected at high ionic strength, the excellent linearity of the plot in Figure 2 confirms the absence of significant competing paths involving both I^- and Na^+I^- ion pairs.

We now consider the alternative modes of redox; *i.e.* whether the reaction goes by a one-step two-electron transfer or by a two-step two-electron pathway. The first involves direct attack of incoming I^- on the square-planar $[Ag(OH)_4]^-$ centre followed by simultaneous donation of two electrons to the empty *d* orbitals on the metal ion to give hypoiodite and Ag^I [equations (6) and (7)]. Assuming that formation of $[Ag(OH)_4I]^{2-}$ is not

$$[Ag(OH)_4]^- + I^- \xrightleftharpoons{K_I} [Ag(OH)_4I]^{2-} \qquad k_1, k_{-1} \tag{6}$$

$$[Ag(OH)_4I]^{2-} \xrightarrow{k'} Ag^I + 2OH^- + IO^- + H_2O \tag{7}$$

rapid and complete, the empirical second-order rate constant, *k*, corresponds either to rate-determining formation of the five-co-ordinate intermediate (k_1) or to a composite process involving pre-equilibrium formation of $[Ag(OH)_4I]^{2-}$ followed by redox. In that case, the rate constant would correspond to $k'K_I$.

An alternative path involves rapid complexation between iodide and the tetrahydroxoargentate(III) ion as in equation (6), followed by an intramolecular one-electron transfer in the rate-determining process [equation (8)] to give Ag^{II} and $I^•$. The

$$[Ag(OH)_4I]^{2-} \xrightarrow[slow]{k_2} Ag^{II} + I^• + 4OH^- \tag{8}$$

$$Ag^{II} + I^- \xrightarrow{fast} Ag^I + I^• \tag{9}$$

$$2I^• \xrightarrow{fast} I_2 \tag{10}$$

$$I_2 + 2OH^- \xrightarrow{fast} IO^- + I^- + H_2O \tag{11}$$

resulting Ag^{II} rapidly reacts with another I^- to give Ag^I and an iodine radical [equation (9)]. In a basic medium, rapid formation of I_2 would be followed by disproportionation [equations (10) and (11)]. The observed rate constant for this path would be $k_{obs.} = k_2K_I[I^-]$.

The following points argue against the mechanism given in equations (8)—(11). (*i*) If $I^•$ were formed, it would be expected to compete for unreacted Ag^{III} as in equation (12). This would

$$[Ag(OH)_4]^- + I^• \longrightarrow Ag^{II} + IO^- + 2H_2O \tag{12}$$

predict a change in stoicheiometry as $[I^-]/[Ag^{III}]$ decreases. Indeed, such a change is seen in the reaction of Ag^{III} with HO_2^-,[52] but not in the present system (Table 1). (*ii*) The redox potential of the I^-–$I^•$ couple is unfavourable by about 1.3 V,[14,53] which, when combined with our estimate of 0.74 V for the one-electron reduction of Ag^{III} to Ag^{II},[54] would predict a thermodynamic barrier to equation (8) which is inconsistent with the observed reaction rate. While this barrier would be lowered by formation of $I_2^{•-}$, the absence of a second order (in $[I^-]$) contribution to the rate law argues both against this possibility and against direct formation of molecular I_2. Other studies in which one-electron oxidation of I^- has been postulated do, indeed, involve second-order terms[14] or other evidence for participation of two iodide ions.[5,12] Therefore, we conclude that the one-step two-electron transfer [equations (6) and (7)] best describes the reaction.

Evidence for a simultaneous two-electron transfer reaction can be found in other iodide reactions with potential two-electron acceptors. The reduction of permanganate to Mn^{2+} by iodide, for example, yields HOI and $[MnO_4]^{3-}$ in the rate-determining step.[17] Westheimer[55] postulated that the reduction of Cr^{VI} (to give Cr^{III}) by iodide involves a concerted two-electron transfer I^- to Cr^V step. Similar behaviour was also reported for the reaction of hypobromite and hypochlorite with iodide.[8,47] A single-step two-electron exchange was inferred when bromite was allowed to react with iodide in alkaline media.[56]

It is of interest to contrast the oxidation of I^- by $[Ag(OH)_4]^-$ with the oxidation of azide ion to N_2.[57] Although the overall driving force for the latter reaction is much greater than in the present case, neither a two-electron oxidation product nor one-electron formation of $N_3^•$ occurs. Rather, high energy barriers to both one- and two-electron redox with a single N_3^- result in a two-stage reaction in which redox takes place only after formation of *cis*-$[Ag(OH)_2(N_3)_2]^-$.

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