Silver(I) Catalyzed Oxidation of Water with Cerium(IV) in Aqueous Perchloric Acid Solutions and the Reaction of Cerium(IV) with Silver(I) in the Presence of Bipyridyl

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The title reaction involves the equilibrium below and is made to go to completion by the reaction of Ag^{II} with water. An attempt to do this was also made by precipitating Ag^{II} with 2,2′-bipyridyl. Hydrogen-ion dependence shows

$$Ce^{IV} + Ag^{I} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ce^{III} + Ag^{II}$$

$$Ag^{II} + H_2O \xrightarrow{k_3} \text{products}$$

that $CeOH^{3+}$ is the reactive species and the complete rate law is given by equation (i), where K_1 and K_2 are the first and second hydrolysis constants for cerium(IV). With no added cerium(III) at constant $[H^+]$, the rate law reduces to equation (ii). k_1 and k_2/k_3 were found to be 4.0×10^{-3} dm³ mol⁻¹ s⁻¹ and 60 respectively at 30 °C

$$-d[Ce^{IV}]/dt = \frac{k_3 k''_1[H^+][Ce^{IV}][Ag^I]}{([H^+]^2 + K_1[H^+] + K_1K_2)(k_2[Ce^{III}] + k_3)} \quad \text{(i)}$$

$$-d[Ce^{IV}]/dt = k_1[Ce^{IV}][Ag^I] \quad \text{(ii)}$$

and $[HClO_4]$ = 0.5 mol dm⁻³. k''_1 was found to be 0.62 ± 0.25 dm³ mol⁻¹ s⁻¹ at 30 °C and I = 1.0 mol dm⁻³. In the presence of 2,2′-bipyridyl the complex of Ag^{II} with this ligand is precipitated and the rate is several times larger than the forward rate of the equilibrium, perhaps owing to the more reactive Ag^I–bipyridyl complex species

SILVER(I) catalysis in Ce^{IV} oxidations is now well known and some of the inorganic and organic compounds employed as reducing substances are isopropyl alcohol,[1] mercury(I),[2] thallium(I),[2] and hypophosphorous acid.[3] One way in which Ag^I catalysis occurs may be through the establishment of equilibrium (1) and the operation of

$$Ce^{IV} + Ag^{I} \rightleftharpoons Ce^{III} + Ag^{II} \quad (1)$$

an Ag^I/Ag^{II} cycle. Since the reaction[4] of Ag^{II} with H_3PO_2 is moderately fast, it appeared to us that equilibrium (1) and the operation of an Ag^I/Ag^{II} cycle may give an answer to the role of Ag^I as a catalyst in the Ce^{IV}–H_3PO_2 reaction.[3] It then becomes necessary to study the direct reaction of Ce^{IV} with Ag^I since so far nothing significant has been reported about the rate of this reaction or the equilibrium constant for equation (1). Some indirect details have been given by Higginson *et al.*,[2] and a mention has been made by Sutin and coworkers.[5]

The study of the forward reaction could be made in the presence of any reducing substance (R) capable of reacting with Ag^{II}. If the reactions ($Ag^{II} + Ce^{III}$) and (Ag^{II} + R) have comparable rates, then the rate constant for the forward reaction of (1) can be determined. It is precisely the latter method by which equilibrium (1) has been studied by Higginson *et al.*[2] There is an even simpler method to study this reaction. The reaction[6,7] of Ag^{II} with water is fast and a mixture of Ce^{IV} and Ag^I would show a decrease in concentration of Ce^{IV}. Since essentially cerium(IV) decreases in the presence of silver(I), the present reaction is appropriately regarded as silver(I) catalyzed oxidation of water with cerium(IV). Also an attempt was made to use 2,2′-bipyridyl[8] to complex and precipitate Ag^{II} obtained in the form of an orange coloured precipitate. This could thus be the most direct study of the forward reaction. However, the complexing reagent also forms a complex with Ag^I and thus the nature of the Ag^I species for reaction with cerium(IV) is changed and the rate of the forward reaction could not be determined by this method.

EXPERIMENTAL

Materials.—A stock solution of cerium(IV) perchlorate was prepared by dissolving cerium(IV) ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$ (E. Merck), in water, precipitating cerium(IV) hydroxide by the addition of ammonium hydroxide, allowing the precipitate to settle (48 h), leaching several times with water, and finally dissolving the precipitate in perchloric acid. The solution was filtered and standardised[9] against iron(II) ammonium sulphate using *N*-phenylanthranilic acid indicator.

Cerium(III) perchlorate, $Ce(ClO_4)_3$, was prepared by precipitating $Ce(OH)_3$ from a solution of $Ce_2(SO_4)_3$ (BDH) with ammonium hydroxide, washing the precipitate in a Buchner funnel, and dissolving the precipitate in perchloric acid. It was standardized by oxidizing[10] it with sodium peroxydisulphate in the presence of Ag^I and measuring the absorption of Ce^{IV} formed on Spectronic 20 Colorimeter at 350 nm.

Silver(I) perchlorate was prepared by precipitating Ag_2CO_3 from a solution of $AgNO_3$ (S. Merck G.R.) with Na_2CO_3 (BDH AnalaR), washing the precipitate and dissolving it in perchloric acid.

Perchloric acid was Riedel 60% and lithium perchlorate was prepared by the neutralization of lithium carbonate to pH *ca.* 7 with perchloric acid. Bipyridyl was of S. Merck quality.

All solutions were prepared in double-distilled water, the second distillation being from potassium permanganate. All vessels were made of Corning glass.

Stoicheiometry.—The amount of oxygen evolved cor responded to the equation below. A mixture of Ce^{IV} and

$$2\,Ce^{IV} + H_2O \xrightarrow{Ag^{I}} 2\,Ce^{III} + 2\,H^+ + \tfrac{1}{2}O_2$$

Ag^{I} does not show the absorption spectrum of Ag^{II}. An attempt to determine the stoicheiometry of the Ce^{IV} + Ag^{I} reaction was made by precipitating silver(II) as a bipyridyl perchlorate complex. The amount of Ce^{IV} consumed per mol of Ag^{I} varied from 1.2 to 1.7, increasing with the increase of initial concentration of Ce^{IV}. It appears that some Ag^{II} complex undergoes reaction with water and this was confirmed by the test for oxygen. One thing appears to be certain and it is that silver(III) is not formed directly, otherwise the amount of Ce^{IV} consumed per mol of Ag^{I} would have been larger than two equivalents. There is no independent significant reaction of cerium(IV) with 2,2'-bipyridyl, but nothing can be said about whether this reaction is catalyzed by Ag^{I}. However, the ratio of Ag^{I} : Ag^{II} produced in the form of bipyridyl perchlorate complex is always 1 : 1 after the reaction is over. The stoicheiometry with excess silver(I) could not be determined since 2,2'-bipyridyl interferes with the estimation of silver(I).[11]

Kinetic Procedure.—A known quantity of cerium(IV) solution was added to a temperature-equilibrated mixture of desired amounts of silver(I), HClO$_4$, and other reagents thermostatted at (30 ± 0.1) °C. Aliquots (5 cm^3) were withdrawn (5—10 min intervals) and determined for Ce^{IV} by quenching into a known excess iron(II) solution. Excess iron(II) was determined by titration against a standard solution of cerium(IV). Since no absorption corresponding to Ag^{II} was noted, the above method gives only the estimation of Ce^{IV}. The same procedure was adopted while carrying out the reactions in the presence of 2,2'-bipyridyl, but the reaction mixture was thoroughly shaken before withdrawing the aliquots, centrifuged, and then decanted into iron(II) solution. The data were processed for the initial rates by the 'plane mirror' method [12] with a precision of ±5%. The duplicate measurements were reproducible to ±6%.

RESULTS

Reaction in the Absence of 2,2'-*Bipyridyl.—Cerium*(IV) *and silver*(I) *dependences*. The concentration of the reactants was varied as shown in Table 1 and the plots of initial rates (v_0) *versus* concentration yielded straight lines passing through the origin. The second-order rate constant (k_1) at 30 °C and [HClO$_4$] = 0.5 mol dm^{-3} was found to be 4 × 10^{-3} dm^3 mol^{-1} s^{-1}.

TABLE 1

Initial rates (v_0) in the reaction of Ce^{IV} with Ag^{I}; [HClO$_4$] = 0.5 mol dm^{-3}, 30 °C, ionic strength adjusted with LiClO$_4$

10^3 [Ce^{IV}]/ mol dm^{-3}	10^3 [Ag^{I}]/ mol dm^{-3}	I/mol dm^{-3}	10^8v_0/ mol dm^{-3} s^{-1}
1.0	2.0	0.5	1.0
2.0	2.0	0.5	1.6
4.0	2.0	0.5	3.1
6.0	2.0	0.5	5.0
10.0	2.0	0.5	8.0
2.0	4.0	0.5	3.2
2.0	6.0	0.5	4.9
2.0	8.0	0.5	6.3
2.0	10.0	0.5	7.9
4.0	4.0	0.5	6.3
4.0	4.0	0.7	27.0
4.0	4.0	1.0	84.0
4.0	4.0	1.2	145.0
4.0	4.0	1.5	335.0

Effect of varying hydrogen-ion concentration. Hydrogen-ion concentration was varied with perchloric acid at constant ionic strength of 1.0 mol dm^{-3} adjusted with lithium perchlorate. The results at 30, 35, and 40 °C are shown in Table 2. The rate first increases and then decreases in each range of [H$^+$] studied. The maximum rate is found at [H$^+$] *ca*. 0.5 mol dm^{-3} at these three temperatures.

Effect of cerium(III). Since the reaction is involved in an equilibrium, investigation of the effect of concentration of the product on the rate seemed desirable. Cerium(III) in the form of Ce(ClO$_4$)$_3$ was varied in the range 0.001—0.01 mol dm^{-3}. The rates at 30, 35, and 40 °C are reported in Table 3. The rate decreases with the increase of [Ce^{III}]. This shows that there is an equilibrium step involved in the mechanism.

TABLE 2

Initial rates (v_0) at different hydrogen-ion concentrations and temperatures for the reaction of Ce^{IV} with Ag^{I}; [Ce^{IV}] = [Ag^{I}] = 4.0 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3}

[H$^+$]/ mol dm^{-3}	10^7v_0/mol dm^{-3} s^{-1}		
	30 °C	35 °C	40 °C
0.13	2.5	3.4	4.1
0.20	4.0	5.0	6.0
0.30	6.3	8.0	10.0
0.50	9.1	11.0	17.0
0.60	8.0	10.0	15.0
0.80	6.5	7.5	11.0
1.00	5.1	6.2	9.0

Effect of ionic strength. Ionic strength was varied with lithium perchlorate from *ca*. 0.5 to 1.5 mol dm^{-3} at fixed concentrations of other reactants. The results given in Table 1 show an increase in the rate with the increase of ionic strength.

Reactions in the Presence of 2,2'-*Bipyridyl*.—As stated earlier the reaction was studied also in the presence of bipyridyl by following the reaction stoicheiometry shown in the Experimental section. The results with different concentrations of cerium(IV), silver(I), bipyridyl, perchloric acid, and lithium perchlorate are given in Table 4. Plots of rate *versus* [Ce^{IV}], and rate *versus* [Ag^{I}] yield straight lines with intercepts. Although by and large the reaction appears to be first-order in both the reactants, the intercepts cannot be explained. A plot of rate *versus* [bipyridyl] also gives a straight line with an intercept which may represent the reaction in the absence of bipyridyl. The essential difference in the two reactions, one in the absence and the other in the presence of bipyridyl, is in the dependence on [H$^+$].

TABLE 3

Initial rates (v_0) at different concentrations of added Ce^{III} in the reaction of Ce^{IV} and Ag^{I}; [Ce^{IV}] = [Ag^{I}] = 4.0 × 10^{-3} mol dm^{-3}, [HClO$_4$] = 0.5 mol dm^{-3}

10^3 [Ce^{III}]/ mol dm^{-3}	10^8v_0/mol dm^{-3} s^{-1}		
	30 °C	35 °C	40 °C
1.0	6.2	—	—
2.0	3.5	10.0	16.0
4.0	5.1	8.5	12.0
6.0	4.5	7.2	11.0
8.0	4.3	6.6	9.0

DISCUSSION

The reaction is clearly first-order in both the main reactants and it is the hydrogen-ion dependence which is complex. The latter is discussed later. Since one of the products (Ce^{III}) decelerates the rate, the following mechanism [equations (1) and (2)] may be suggested. The rate law at fixed $[H^+]$ is given by equation (3). At

$$Ce^{IV} + Ag^{I} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ce^{III} + Ag^{II} \qquad (1)$$

$$Ag^{II} + H_2O \xrightarrow{k_3} \text{products} \qquad (2)$$

$$v_0 = \frac{-d[Ag^{II}]}{dt} = -\frac{d[Ce^{IV}]}{dt} = \frac{k_1k_3[Ce^{IV}][Ag^{I}]}{k_2[Ce^{III}] + k_3} \qquad (3)$$

the start of the reaction when the initial rates are determined, $k_3 \gg k_2[Ce^{III}]$ and the rate law reduces to equation (4).

$$-d[Ce^{IV}]/dt = k_1[Ce^{IV}][Ag^{I}] \qquad (4)$$

In the presence of cerium(III), the two terms of the denominator of the right-hand side of equation (3) are comparable and the plot of v_0^{-1} *versus* $[Ce^{III}]$ yields a straight line with an intercept. From the slope and intercept, the values of k_1 and k_2/k_3 were found to be $(3.9 \pm 0.2) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and 60 ± 4 at 30 °C, $(7.0 \pm 0.5) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and 80 ± 20 at 35 °C, and $(11 \pm 1) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and 100 ± 2.0 at 40 °C, respectively at $I = 0.5$ mol dm^{-3}.

TABLE 4

Oxidation of Ag^{I} with Ce^{IV} in the presence of 2,2′-bipyridyl in perchloric acid solutions at 30 °C

10^3 $[Ce^{IV}]$/ mol dm^{-3}	10^3 $[Ag^{I}]$/ mol dm^{-3}	$[HClO_4]$/ mol dm^{-3}	10^3 [bipy]/ mol dm^{-3}	I/mol dm^{-3}	10^6v_0/ mol dm^{-3} s^{-1}
1.0	2.0	0.5	5.0	0.5	3.0
2.0	2.0	0.5	5.0	0.5	3.9
3.0	2.0	0.5	5.0	0.5	5.1
5.0	2.0	0.5	5.0	0.5	8.1
8.0	2.0	0.5	5.0	0.5	11.0
10.0	2.0	0.5	5.0	0.5	13.0
2.0	1.0	0.5	5.0	0.5	2.6
2.0	2.0	0.5	5.0	0.5	4.0
2.0	3.0	0.5	5.0	0.5	5.2
2.0	5.0	0.5	5.0	0.5	8.0
2.0	8.0	0.5	5.0	0.5	11.0
2.0	2.0	0.1	5.0	1.0	9.0
2.0	2.0	0.2	5.0	1.0	6.0
2.0	2.0	0.4	5.0	1.0	3.7
2.0	2.0	0.6	5.0	1.0	3.4
2.0	2.0	1.0	5.0	1.0	2.3
2.0	2.0	0.5	1.0	0.5	1.6
2.0	2.0	0.5	2.0	0.5	2.5
2.0	2.0	0.5	3.0	0.5	3.0
2.0	2.0	0.5	5.0	0.5	4.0
2.0	2.0	0.5	10.0	0.5	7.3
2.0	2.0	0.5	15.0	0.5	10.0
2.0	2.0	0.5	20.0	0.5	13.0
2.0	2.0	0.5	25.0	0.5	16.0
2.0	2.0	0.5	30.0	0.5	23.0

The mechanism and the rate law become complicated by the hydrogen-ion dependence. There are at least two more cases of cerium(IV) oxidations where such complex behaviour has been found and they are oxidations of iron(II)[13] and antimony(III).[14] The results of hydrogen-ion dependence can be explained by considering the hydrolytic equilibria (5) and (6). The hydrolysis

$$Ce^{4+} + H_2O \overset{K_1}{\rightleftharpoons} CeOH^{3+} + H^+ \qquad (5)$$

$$CeOH^{3+} + H_2O \overset{K_2}{\rightleftharpoons} Ce(OH)_2^{2+} + H^+ \qquad (6)$$

of Ag^{2+} has also been considered previously by other workers.[15] The earlier values of the hydrolysis constant of Ag^{2+} have been reported[16] to be in the range 0.1—0.7, but the latest value[17] of pK has been reported to be 5.35. Hence in the acid solutions employed in the present investigation, Ag^{III} would be wholly in the form of Ag^{2+} and thus hydrogen-ion dependence is probably not related to this hydrolysis. Hydrogen-ion dependence would be involved, if $AgOH^+$ was considered as the reactive species, but then the results cannot be explained on this basis. Thus considering the reaction of Ag^{I} with all the three species of cerium(IV), the complete rate law for no added cerium(III) is given by equation (7), where

$$-d[Ce^{IV}]/dt = \frac{[Ce^{IV}][Ag^{I}](k'_1[H^+]^2 + k''_1K_1[H^+] + k'''_1K_1K_2)}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (7)$$

k'_1, k''_1, and k'''_1 are the rate constants for the species Ce^{4+}, $CeOH^{3+}$, and $Ce(OH)_2^{2+}$ respectively. The values of K_1 and K_2 are variously reported and they depend much on the ionic strength. The enthalpy change is[18] 5.2 kcal mol^{-1}.* The value (mol dm^{-3}) of K_1 is reported to vary[19] from 0.2 to 20 and that[20] of K_2 from 0.09 to 0.6. All these values of K_1 and K_2 are indirectly kinetically determined except those of Hardwick and Robertson,[21] determined spectrophotometrically; and those of Baker *et al.*[22] and Sherrill *et al.*[23] determined potentiometrically. The latest reported

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* Throughout this paper: 1 cal = 4.184 J.

value[24] of K_1 is 0.24 at 30 °C in the oxidation of malonic acid. Our results show that the species $CeOH^{3+}$ is much more reactive than other species. Hence the general rate law for hydrogen-ion dependence becomes equation (8). The first step of the mechanism

$$-d[Ce^{IV}]/dt = \frac{k''_1K_1[H^+][Ce^{IV}][Ag^I]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (8)$$

can now be rewritten as $CeOH^{3+} + Ag^+ \rightleftharpoons Ce^{3+} + AgOH^+$, or $CeOH^{3+} + Ag^+ \rightleftharpoons CeOH^{2+} + Ag^{2+}$, consistent with the above rate law. Equation (8) reduces to (9) in the lower range of $[H^+]$. A plot of $(\text{rate})^{-1}$

$$-d[Ce^{IV}]/dt = \frac{k''_1[Ce^{IV}][Ag^I][H^+]}{[H^+] + K_2} \qquad (9)$$

versus $[H^+]^{-1}$ in the lower concentration range (Table 2) yields a straight line with an intercept. From the intercepts and slopes the values of k''_1 (dm^3 mol^{-1} s^{-1}) and K_2 (mol dm^{-3}) were found to be 0.62 ± 0.25 and 5.0 ± 1.0 at 30 °C, 0.83 ± 0.2 and 5.0 ± 1.0 at 35 °C, and 1.2 ± 0.3 and 6.2 ± 1.0 at 40 °C, respectively.

In the higher range (Table 2), the rate law (8) may be approximated to (10). A plot of $(v_0)^{-1}$ *versus* $[H^+]$ yields

$$-d[Ce^{IV}]/dt = \frac{k''_1K_1[Ce^{IV}][Ag^I]}{[H^+] + K_1} \qquad (10)$$

a straight line with an intercept. From the slopes and intercepts, k''_1 (dm^3 mol^{-1} s^{-1}) and K_1 (mol dm^{-3}) were found to be 0.62 ± 0.25 and 0.053 ± 0.01 at 30 °C, 0.83 ± 0.1 and 0.065 ± 0.005 at 35 °C, and 1.2 ± 0.2 and 0.048 ± 0.002 at 40 °C, respectively, at $I = 1.0$ mol dm^{-3}. K_1 and K_2 by and large appear to be independent of temperature and are within the range reported by other workers. However, it must be realised that these are indirectly determined values.

The results in the presence of 2,2′-bipyridyl, though different, support the mechanism of the reaction in the absence of bipy. Bipyridyl, apart from forming and precipitating a complex of Ag^{II}, forms a complex with Ag^I also and this species appears to be highly reactive towards Ce^{IV}. The complex formation constant (dm^3 mol^{-1}) is reported[25] to be about 6.9 × 10^3 at 20 °C and 4.1 × 10^3 at 30 °C. Bipyridyl is protonated also and the protonation constant (dm^3 mol^{-1})[26] is about 2.16 × 10^4 at 25 °C and 3.09 × 10^4 at 20 °C. Thus bipy will be almost completely protonated and the concentration of free bipyridyl is expected to be small. The concentration of the complex of Ag^I would also be small and Ag^I would be present almost exclusively as Ag^+. Considering all these facts and assuming $CeOH^{3+}$ to be the reactive and also predominant species of Ce^{IV}, the following mechanism [equations (11)—(13)] would be tenable (bipy = 2,2′-bipyridyl). Thus the rate of the reaction in the presence of bipy is given by equation (14), where $[\text{bipy}]_T$ is the total concentration of 2,2′-bipyridyl.

$$\text{bipy} + H^+ \xrightleftharpoons{K_p} \text{Hbipy}^+ \qquad (11)$$

$$Ag^+ + \text{bipy} \xrightleftharpoons{K} Ag(\text{bipy})^+ \qquad (12)$$

$$CeOH^{3+} + Ag(\text{bipy})^+ \xrightarrow{k_c} CeOH^{2+} + Ag(\text{bipy})^{2+}\ (\text{precipitate}) \qquad (13)$$

$$-d[Ce^{IV}]/dt = \frac{k_cK_pK[CeOH^{3+}][Ag^+][\text{bipy}]_T}{[H^+]} \qquad (14)$$

Combining this with the rate of reaction in the absence of bipy, the total rate would be given by equation

$$-d[Ce^{IV}]/dt = \frac{k_1k_3[CeOH^{3+}][Ag^+]}{k_2[Ce^{III}] + k_3} + \frac{k_cK_pK[CeOH^{3+}][Ag^+][\text{bipy}]_T}{[H^+]} \qquad (15)$$

(15). If the concentration of $CeOH^{3+}$ in terms of total $[Ce^{IV}]$ was substituted in the above equations, the whole rate law would be very complicated and the limited data of the bipyridyl reaction are insufficient to prove this. However, if this rate law is considered at $[H^+] = 0.5$ mol dm^{-3}, where most of the reactions have been carried out and where (approximately) the rate maximum is obtained in the hydrogen-ion dependence in the absence of bipyridyl, $CeOH^{3+}$ would be predominant and $CeOH^{3+}$ can be replaced by Ce^{IV} [equation (16)]. A plot of rate

$$\frac{-d[Ce^{IV}]}{dt} = [Ce^{IV}][Ag^+]\left(\frac{k_1k_3}{k_2[Ce^{III}] + k_3} + \frac{k_cK_pK[\text{bipy}]_T}{[H^+]}\right) \qquad (16)$$

versus $[\text{bipy}]_T$ would yield a straight line with an intercept equal to 0.40 dm^3 mol^{-1} s^{-1} at 30 °C which is of the same order of magnitude as that found (0.62 ± 0.25 dm^3 mol^{-1} s^{-1}) in the absence of bipy. A similar plot of rate *versus* $[H^+]^{-1}$ cannot be made since $[CeOH^{3+}]$ would cease to be equal to $[Ce^{IV}]$ at other hydrogen-ion concentrations.

A complex of Ag^I and bipyridyl is more reactive than Ag^+ because the product, Ag^{2+}, is stabilized by bipyridyl and the latter may form part of the activated complex. The reaction probably occurs by an outer-sphere mechanism.

A comparison of the present reaction with the silver(I) catalyzed oxidations[2] of Tl^I and Hg^I with cerium(IV) may be worthwhile. If an Ag^I/Ag^{II} cycle were to operate and the reaction of Ag^{II} with Tl^I or Hg^I is fast, the rate of these two reactions should be similar to that of the present reaction. The rate constant for the oxidation of Tl^I was found to be 0.1 dm^3 mol^{-1} s^{-1} at 25 °C and $I = 4.5$ mol dm^{-3}, which is not very different from our value of 0.24 at 30 °C and $I = 1.0$ mol dm^{-3}. A comparison of the value of k_2/k_3 of the three reactions can give us some idea about the relative speeds of the reactions ($Ag^{2+} + Tl^I$), ($Ag^{2+} + Hg^I$), and ($Ag^{2+} + H_2O$). The value[2] of v_0 (mol dm^{-3} s^{-1}) for Tl^I is 35.7 at 25 °C with $[H^+] = 1.5$ mol dm^{-3} and at $I = 4.5$ mol dm^{-3}, 0.198 for Hg^I with $[H^+] = 1.5$ mol dm^{-3} at 20 °C and $I = 3.0$ mol dm^{-3}. In our case the value is 60 with $[H^+] = 0.5$ mol dm^{-3} at 30 °C and $I = 0.5$ mol dm^{-3}. Even with disregard to temperature, hydrogen-ion concentration, and ionic strength, it appears that the oxidations of Tl^I and H_2O have comparable rates and that the oxidation of Hg^I is faster.

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