Kinetics and Mechanism of the Silver(I)-catalyzed Oxidations of Arsenic(III) and Antimony(III) with Peroxodiphosphate in Acetate Buffers

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A kinetic study of the silver(I)-catalyzed oxidations of As^{III} and Sb^{III} with peroxodiphosphate (pdp) was performed by estimating As^{III} and Sb^{III} with permanganate. The oxidation of As^{III} was found to conform to the rate law (i) in the range pH 2.10—4.52, where K_2 and K_3 are the acid-dissociation

$$-d[As^{III}]/dt = [pdp][As^{III}][Ag^{I}](k_1K_2^{-1}[H^+]^2 + k_2[H^+])/([H^+] + K_3) \quad (i)$$

constants of $H_3P_2O_8^-$ and $H_2P_2O_8^{2-}$; k_1/K_2 and k_2 were found to be (5.0 ± 0.2) × 10^4 dm^9 mol^{-3} s^{-1} and 38 ± 3 dm^6 mol^{-2} s^{-1} at 50 °C. The oxidation of Sb^{III} was first order in [Sb^{III}], [pdp], and [Ag^I], and independent of pH, [acetate], and [tartrate]; the third-order rate was found to be 18 ± 1 dm^6 mol^{-2} s^{-1} at 50 °C in the range pH 3.00—4.61. The silver(I) catalysis operates through complex formation of pdp and Ag^I rather than Ag^I/Ag^{III} redox cycling.

As a prelude to studying the kinetics of silver(I)-catalyzed oxidations with peroxodiphosphate (pdp), recently the silver(I)-catalyzed oxidation of water by pdp was reported.[1] The rate constant for the pdp–Ag^I reaction was found to be comparable to that of the corresponding reaction with peroxodisulphate (pds),[2] indicating that both reactions occur *via* the same mechanism. So far only one[3] silver(I)-catalyzed oxidation with pdp has been reported and hence studies with various reductants would seem to provide a proving ground for the verification of the mechanism already suggested. A comparison of the results with those from the silver(I)-catalyzed pds reactions also seemed to offer further insight.

Studies of oxidations with pdp in acidic solutions are complicated by the readily occurring hydrolysis of pdp to peroxomonophosphoric acid and in a large number of cases this hydrolytic step becomes rate controlling[4–6] since the rate was found to be independent of the reductant concentration. Thus, studies of the oxidations of arsenic(III)[5] and antimony(III)[6] which were carried out in acidic solutions are essentially studies of the hydrolysis of pdp. Oxidations with pdp in acetate buffers are quite slow, but are strongly catalyzed by silver(I). Thus, such studies can be made without any interference from hydrolysis and the oxidations can be ascribed to the various species of pdp.

Experimental

Arsenic(III) oxide and 'potassium antimonyl tartrate,' K(SbO)-$C_4H_4O_6$ were from May & Baker and BDH (AnalaR) respectively. All other chemicals including $K_4P_2O_8$, its standardization, and the maintenance and variation of pH using acetic acid–sodium acetate buffers were as described previously.[1]

The kinetics were followed by estimating arsenic(III) or antimony(III) with standard permanganate.[7] Aliquot portions were added to a titration flask containing concentrated HCl (2 cm^3), distilled water (10—15 cm^3), and a drop of 2.5 × 10^{-3} mol dm^{-3} KIO_3, and titrated against standard $KMnO_4$.

Solutions of arsenic(III) were prepared as described.[5] Antimonyl tartrate was employed for antimony(III), and this is readily soluble in water. A few preliminary experiments indicated that, under the conditions of the experiment, tartrate was not oxidized by pdp.

Initial rates were determined at different concentrations of As^{III} and Sb^{III} by the plane-mirror method.[8] A plot of initial rate *versus* [As^{III}] or [Sb^{III}] yielded a straight line with a slope of unity which passed through the origin. This established the first-order dependence of the rate on [As^{III}] and [Sb^{III}]. Subsequently, experiments were performed under pseudo-first-order conditions, the concentration of pdp being at least ten times greater than that of As^{III} or Sb^{III}. First-order plots were constructed and the results were reproducible to ±5%.

Results

Stoicheiometry.—Reaction mixtures (*ca.* 10^{-3} mol dm^{-3}) containing an excess of As^{III} or Sb^{III} were allowed to react for about 24 h and the excess of reagent was determined by the permanganate method. Arsenic(V) could also be determined iodometrically. One mol of pdp was found to oxidize 1 mol of As^{III} or Sb^{III}, yielding 1 mol of As^V or Sb^V. Phosphate was the reduction product of pdp.

Oxidation of Arsenic(III).—*Peroxodiphosphate, arsenic*(III), *and silver*(I) *dependences*. The concentrations of these three main reactants were varied as shown in Table 1 at pH 3.20, I = 1.0 mol dm^{-3}, and 50 °C. Pseudo-first-order rate constants (k_0) were obtained from the first-order plots. The results are in accord with the empirical rate law (1) where k was found to be

$$-d[As^{III}]/dt = k[pdp][As^{III}][Ag^{I}] \quad (1)$$

69 ± 4 dm^6 mol^{-2} s^{-1}. There is no effect of ionic strength on the rate.

Hydrogen-ion dependence. The effect of [H$^+$] was studied in acetate buffers in the range pH 2.10—4.52 by varying the concentration of CH_3CO_2H at a fixed total acetate concentration of 0.045 mol dm^{-3} and I = 1.0 mol dm^{-3} adjusted with $NaNO_3$. The pH was also varied by changing the ratio of the concentrations of acetate and acetic acid. The results were similar in both cases at identical pH, the rate decreasing with increasing pH (Figure 1). Hydrolysis at pH < 2 and the formation of a white turbidity in the reaction mixture at pH > 4.7 limited the pH range which could be employed.

Acetate-ion dependence. The concentration of acetate was varied from 0.15 × 10^{-2} to 1.2 × 10^{-2} mol dm^{-3} at fixed pH 3.20 by varying the concentrations of acetic acid and acetate ion at a fixed ratio of [CH_3CO_2H]:[$CH_3CO_2^-$].

Table 1. Rate constants for the silver(I)-catalyzed oxidation of As^{III} with peroxodiphosphate at 50 °C, $I = 1.0$ mol dm^{-3}, and pH 3.20

10^2[pdp]	$10^3[As^{III}]$	$10^4[Ag^I]$	$10^2[O_2CMe^-]$	10^4k_0	k
mol dm^{-3}				s^{-1}	$dm^6\ mol^{-2}\ s^{-1}$
2.55	3.70	2.0	0.12	3.5	69
3.40	3.70	2.0	0.12	4.5	66
4.25	3.70	2.0	0.12	5.8	68
5.10	3.70	2.0	0.12	7.3	71
5.95	3.70	2.0	0.12	8.8	74
6.80	3.70	2.0	0.12	10	74
7.65	3.70	2.0	0.12	11.5	75
4.25	3.70	1.0	0.12	3.2	75
4.25	3.70	1.5	0.12	4.2	66
4.25	3.70	2.0	0.12	5.8	68
4.25	3.70	3.0	0.12	7.5	60
4.25	3.70	4.0	0.12	11	67
4.25	3.70	5.0	0.12	13	63
4.25	3.70	6.0	0.12	16	62
5.10	3.70	2.0	0.12	7.3	71
5.10	5.25	2.0	0.12	7.3	71
5.10	7.80	2.0	0.12	7.3	71
5.10	8.75	2.0	0.12	7.3	71
5.10	9.90	2.0	0.12	7.3	71
					Av. 69 ± 4

There was no effect of the acetate-ion concentration on the rate (Table 2).

Oxidation of Antimony(III).—The concentrations of pdp, antimonyl tartrate complex, and silver(I) were varied as shown in Table 3. The third-order rate constant was found to be 18 ± 1 $dm^6\ mol^{-2}\ s^{-1}$ at 50 °C and $I = 1.0$ mol dm^{-3}. The rate of reaction was unaffected by variation of pH (3.34—4.61), [acetate], [tartrate], and the ionic strength (Tables 3 and 4). The empirical rate law (2) holds for these results.

$$-d[Sb^{III}]/dt = k[Sb^{III}][pdp][Ag^I] \qquad (2)$$

Discussion

The acid-dissociation constant of H_3AsO_3 is small[9] and hence this acid exists mainly in the form of undissociated molecules in the pH range investigated. Cationic species of As^{III} are not known and hence a protonated form of H_3AsO_3 is not likely. With regard to Sb^{III}, it is well known that the tartrate complex[10] has 1 mol of Sb^{III} to 1 mol of tartaric acid, but the exact structure is still a matter of speculation;[11] furthermore, both the hydroxyl groups of tartaric acid participate in complex formation.[12] The absence of any effect of pH and tartrate on the rate enables us to denote by Sb^{III} whatever species is present in the system.

It is known[13,14] that the protolytic equilibria (3)—(6) are

$$H_4P_2O_8 \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- + H^+ \qquad (3)$$

$$H_3P_2O_8^- \overset{K_2}{\rightleftharpoons} H_2P_2O_8^{2-} + H^+ \qquad (4)$$

$$H_2P_2O_8^{2-} \overset{K_3}{\rightleftharpoons} HP_2O_8^{3-} + H^+ \qquad (5)$$

$$HP_2O_8^{3-} \overset{K_4}{\rightleftharpoons} P_2O_8^{4-} + H^+ \qquad (6)$$

possible with pdp in acidic solutions. Only kinetically estimated values for K_1 and K_2 are available and hence the values reported are different.[4,13,15] In any case they are larger than 0.3 mol dm^{-3} and equilibria (3) and (4) will be insignificant for the pH range investigated. The values of K_3 and K_4 have been determined[13] to be (6.6 ± 0.3) × 10^{-6} and (2.1 ± 0.1) × 10^{-8} mol dm^{-3} respectively. Hence the only significant equilibrium for the predominant species of pdp is (5). However, this does not rule out the reactivity of other species, $H_3P_2O_8^-$ and $H_4P_2O_8$, which are present in small concentrations, since the rate increases with increasing $[H^+]$.

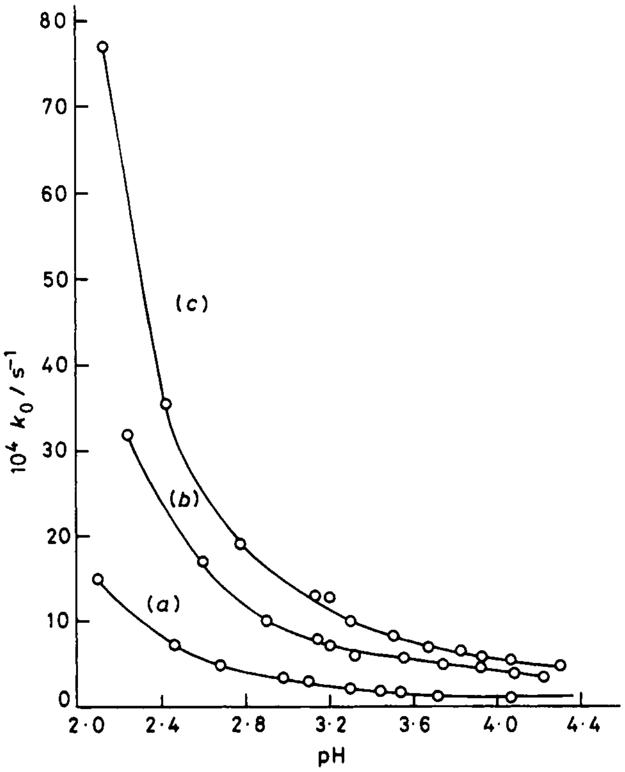

Figure 1. Variation of k_0 with pH in the pdp–As^{III} reaction at 40 (*a*), 50 (*b*), and 60 °C (*c*). [pdp] = 5.1 × 10^{-2}, $[As^{III}]$ = 3.7 × 10^{-3}, $[Ag^I]$ = 2 × 10^{-4}, and I = 1.0 mol dm^{-3}

There is no positive evidence for the operation of a Ag^I/Ag^{II} or Ag^I/Ag^0 cycle for the silver(I) catalysis since the rate is not independent of any of the reactants. A third possibility through which such catalysis may operate is by formation of a reactive complex with either pdp or As^{III}. Complexing between pdp and Ag^I may be possible since complexes of pdp with Na^+, Li^+, K^+, and Mg^{2+} have been reported.[13,14] Complexing has also been reported in the oxidation[3] of Cr^{III}. Complexing between Ag^I and As^{III} has not been reported so far and there is no evidence for it in the present investigation.

The rate of the present reaction is independent of the acetate-ion concentration, although Ag^I is likely to be present partially as a complex with acetate ions having a small equilibrium constant.[16] Silver(I) acetate complexes may be very unstable and less reactive than Ag^I. The mechanism in equations (7)—(12) may be proposed on the basis of the above

$$H_3P_2O_8^- + Ag^I \overset{K_5}{\rightleftharpoons} [H_3P_2O_8Ag^I] \qquad (7)$$

$$H_2P_2O_8^{2-} + Ag^I \overset{K_6}{\rightleftharpoons} [H_2P_2O_8Ag^I]^- \qquad (8)$$

$$HP_2O_8^{3-} + Ag^I \overset{K_7}{\rightleftharpoons} [HP_2O_8Ag^I]^{2-} \qquad (9)$$

$$[H_3P_2O_8Ag^I] + As^{III} \xrightarrow{k_1'} \text{products} \qquad (10)$$

$$[H_2P_2O_8Ag^I]^- + As^{III} \xrightarrow{k_2'} \text{products} \qquad (11)$$

$$[HP_2O_8Ag^I]^{2-} + As^{III} \xrightarrow{k_3'} \text{products} \qquad (12)$$

Table 2. Rate constants for the silver(I)-catalyzed oxidation of As^{III} with pdp at different acetate concentrations; [pdp] = 5 × 10^{-2}, [As^{III}] = 3.7 × 10^{-3}, [Ag^{I}] = 2.0 × 10^{-4}, I = 1.0 mol dm^{-3}, and 50 °C

$10^2[O_2CMe^-]$/mol dm^{-3}	0.04	0.08	0.12	0.60	1.2	1.8	2.4	3.0	3.6	4.2	4.8
pH	3.11	3.15	3.20	3.32	3.55	3.74	3.92	4.08	4.22	4.40	4.52
10^4k_0*/s^{-1}	8.4	8.1	7.3	6.9	6.1	5.0	4.6	4.2	3.8	3.4	3.0
	—	(8.1)	(7.3)	(6.9)	(6.1)	(5.0)	(4.6)	(4.2)	(3.8)	—	—
k/dm^6 mol^{-2} s^{-1}	82	79	72	68	60	49	45	41	37	33	29

* The figures in parentheses are the corresponding values at [O_2CMe^-] = 4.5 × 10^{-2} mol dm^{-3}.

Table 3. Rate constants (k) for the silver(I)-catalyzed oxidation of Sb^{III} with pdp at 50 °C, I = 1.0 mol dm^{-3}, pH 3.32, and [O_2CMe^-] = 0.003 mol dm^{-3}

10^2[pdp]	$10^3[Sb^{III}]$	$10^3[Ag^{I}]$	10^4k_0	k
mol dm^{-3}			s^{-1}	dm^6 mol^{-2} s^{-1}
2.55	3.55	1.0	3.8	16
3.40	3.55	1.0	5.8	17
4.25	3.55	1.0	6.9	16
5.10	3.55	1.0	9.0	18
5.95	3.55	1.0	9.9	17
6.80	3.55	1.0	11.5	17
7.65	3.55	1.0	12.7	17
5.10	3.55	0.3	2.9	18
5.10	3.55	0.4	3.9	19
5.10	3.55	0.5	5.0	20
5.10	3.55	0.6	5.8	19
5.10	3.55	0.7	6.8	18
5.10	3.55	0.8	7.6	19
5.10	3.55	0.9	8.4	19
5.10	3.55	0.95	8.9	18
5.10	3.55	1.0	9.2	18
5.10	1.50	1.0	9.2	18
5.10	2.52	1.0	9.2	18
5.10	3.55	1.0	9.2	18
5.10	5.25	1.0	9.2	18
5.10	6.25	1.0	9.2	18
5.10	7.25	1.0	9.0	17
				Av. 18 ± 1

Table 4. Rate constants k for the silver(I)-catalyzed oxidation of Sb^{III} with pdp at different pH and [O_2CMe^-]; 50 °C, [Sb^{III}] = 3.55 × 10^{-3}, [Ag^{I}] = 1.0 × 10^{-3}, and I = 1.0 mol dm^{-3}

10^2[pdp] / mol dm^{-3}	pH	$10^2[O_2CMe^-]$ / mol dm^{-3}	10^4k_0 / s^{-1}	k / dm^6 mol^{-2} s^{-1}
5.10	3.00	0.3	9.2	18
5.10	3.32	0.6	9.2	18
5.10	3.44	0.6	9.1	18
5.10	3.61	1.2	9.6	19
5.10	3.76	1.8	9.2	18
5.10	3.91	2.4	9.2	18
5.10	4.00	3.0	9.2	18
5.10	4.11	3.6	9.2	18
5.10	4.34	4.2	9.4	18
5.10	4.52	4.8	9.2	18
5.10	4.61	5.4	9.2	18
3.40	3.32	0.3	5.4	16
3.40	3.32	0.6	5.8	17
3.40	3.32	1.2	5.8	17
3.40	3.32	4.5	5.4	16
3.40	3.32	6.0	5.3	16
3.40 [a]	3.32	0.3	5.4	16
3.40 [b]	3.32	0.3	5.4	16
3.40 [c]	3.32	0.3	5.4	16
3.40 [d]	3.32	0.3	5.8	17

[Tartrate] = 4 × 10^{-3},[a] 6 × 10^{-3},[b] 8 × 10^{-3},[c] and 1 × 10^{-2} mol dm^{-3}.[d]

results. If the values of the equilibrium constants K_5, K_6, and K_7 are small, the rate law (13) can be derived, where $k_1 = K_5k_1'$, $k_2 = K_6k_2'$,and $k_3 = K_7k_3'$. Alternatively, equation (13) can be written as (14). The first term of the denominator,

$$\frac{-\mathrm{d}[As^{III}]}{\mathrm{d}t} = [As^{III}][pdp][Ag^{I}]\left\{\frac{k_1K^{-1}[H^+]^2 + k_2[H^+] + k_3K_3}{([H^+]^2/K_2) + [H^+] + K_3}\right\} \quad (13)$$

$$k = (k_1K^{-1}[H^+]^2 + k_2[H^+] + k_3K_3)/\{([H^+]^2/K_2) + [H^+] + K_3\} \quad (14)$$

$[H^+]^2/K_2$, can be neglected in comparison to ($[H^+] + K_3$) for reasons already stated. Several functions of k and $[H^+]$ were tried in attempts to obtain a linear plot and it was found that a plot of $k(K_3 + [H^+])/[H^+]$ *versus* $[H^+]$ was linear (Figure 2), using a value of K_3 = 6.6 × 10^{-6} mol dm^{-3}. This would be the case if $HP_2O_8^{3-}$ contributes negligibly to the total rate and the term k_3K_3 is also negligible compared to the other two terms. The values of k_1/K_2 (dm^9 mol^{-3} s^{-1}) and k_2 (dm^6 mol^{-2} s^{-1}) were found to be (8.3 ± 0.4) × 10^4 and 55 ± 5, (5.0 ± 0.2) × 10^4 and 38 ± 3, and (1.8 ± 0.1) × 10^4 and 13 ± 3 at 60, 50, and 40 °C respectively.

An alternative mechanism assuming a weak complexing between Ag^{I} and H_3AsO_3 and a subsequent redox reaction between this complex and pdp species can also be proposed and the same rate law would be obtained.

The oxidation of Sb^{III} is unique since its rate is independent of the concentrations of hydrogen, acetate, and tartrate ions, although the order in each of [pdp], [Sb^{III}] and [Ag^{I}] is unity. The aqueous chemistry of Sb^{III} has been studied much less than that of As^{III} and it may be difficult to give a unique mechanism for the oxidation of Sb^{III}. In general, the two systems are expected to behave similarly. However, the different hydrogen-ion dependences clearly show that the mechanisms in the two cases are different. The hydrogen-ion dependence in the arsenic(III) system cannot be connected with the arsenic itself since the pH of the system is several units larger than the pK of H_3AsO_3. We cannot make a distinction in the behaviours of pdp in the two systems. Another fact worth reporting is that there have been few kinetic studies with antimonyl tartrate. In oxidations [17,18] with pds, the rates are independent of $[H^+]$. However, in aqua-antimony(III) perchlorate systems [19,20] the rate is not independent of $[H^+]$. One is tempted to correlate the independence of rate on $[H^+]$ with the bulky nature of the complex of antimonyl tartrate. On this basis the following differences in the mechanisms for the two systems can be noted.

In the case of As^{III} it is the peroxide linkage which is attacked by As^{III}. The presence of protons on the phosphorus atoms can decrease the electron density at the site of attack and increase the rate. In the case of Sb^{III} there is no

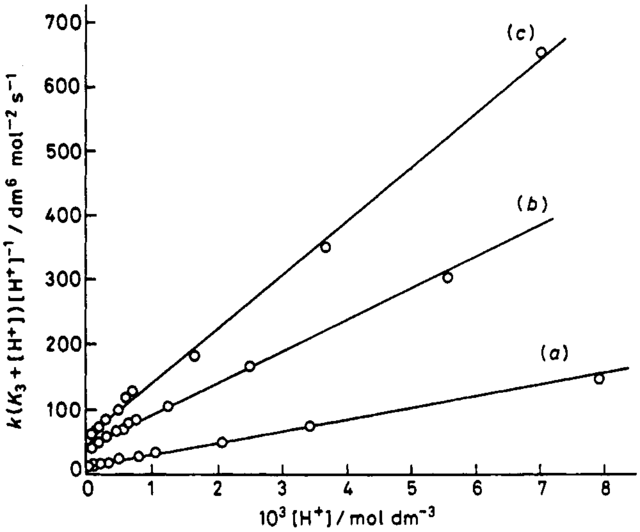

Figure 2. Plot of $k(K_3 + [H^+])/[H^+]$ *versus* $[H^+]$ at 40 (*a*), 50 (*b*), and 60 °C (*c*). [pdp] = 5.1×10^{-2}, $[As^{III}] = 3.7 \times 10^{-3}$, $[Ag^I] = 2.0 \times 10^{-4}$, and $I = 1.0$ mol dm^{-3}

attack on the peroxide linkage because the Sb^{III} is present in a bulky complex, and the electron transfer occurs through Ag^I. Since the site of attack is somewhat distant from the protons, the latter do not have a significant influence on the rate of reaction and thus all the pdp species are equally reactive. This suggestion is, however, incapable of any proof.

It is interesting to compare the results for the arsenic(III) system with those for the silver(I)-catalyzed oxidation of water [1] where formation of higher valent silver was assumed. There is no evidence for such an oxidation state in the present investigation. Assuming that the silver(I)-catalyzed oxidation of water occurred by a similar mechanism to the one given here for As^{III}, a comparison can be made if we divide k_3 for the first reaction [1] by the water concentration. We thus calculate the rate constant for $H_3P_2O_8^-$ to be 7.2×10^{-4} dm^6 mol^{-2} s^{-1} at 50 °C which is several orders of magnitude less than the rate constant for the oxidation of As^{III}. The latter oxidation is therefore much faster compared to the water oxidation. However, the order of reactivity of $H_3P_2O_8^-$, $H_2P_2O_8^{2-}$, and $HP_2O_8^{3-}$ is reversed in the oxidation of As^{III}. Since the uncatalyzed oxidations with pdp and its decomposition [21] are slow, attack on the peroxide linkage does not appear to be facile, but the presence of silver(I) makes it so, through complex formation. Considering a couple of oxidations [22,23] with peroxomonophosphate, it is seen that reactivity increases with increasing electrophilicity of the phosphate species. However, in the oxidation [24] of As^{III} by peroxomonophosphate this is true only up to pH 3 and the trend is reversed at higher pH. The latter behaviour implies a nucleophilic attack of the phosphate on As^{III}. If the same argument is extended to the silver(I)-catalyzed oxidation with pdp, it can be suggested that the water acts as an electrophile while attacking the peroxide linkage, whereas As^{III} acts as a nucleophile. This may explain the difference in the order of reactivities of the various pdp species towards water and As^{III}.

The rate of the corresponding pds reaction [25] is independent of the concentration of As^{III} and hence the formation of higher valent silver was proposed as the rate-determining step. In the present case, the order in $[As^{III}]$ is one and hence Ag^{III}, even if formed, would be in rapid equilibrium with pdp and Ag^I as shown in equation (15).

$$H_nP_2O_8^{n-4} + Ag^I \overset{\text{rapid}}{\rightleftharpoons} [Ag^{III}PO_4] + H_nPO_4^{n-3} \quad (15)$$

$$[Ag^{III}PO_4] + As^{III} \xrightarrow{\text{slow}} \text{products} \quad (16)$$

It has been reported [17] that the oxidation of antimonyl tartrate with pds is not catalyzed by Ag^I. Higher valent silver is said to be formed, which oxidizes water in preference to Sb^{III}. Since in the present (pdp) reaction the oxidation of Sb^{III} is catalyzed by Ag^I, one more difference should be noted. This probably arises on account of the different forms of Ag^{II} or Ag^{III} in the two cases, and is supported by the fact that one can obtain higher valent silver oxide in the solid state from the pds–Ag^I reaction but not from the pdp–Ag^I reaction.

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