# Kinetics of the Silver(I)-catalysed Oxidation of $H_3PO_2$ with [Ethylenebis(biguanide)]silver(III) Cation in Aqueous Perchloric Acid Solution

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The silver(I)-catalysed oxidation of $H_3PO_2$ by [ethylenebis(biguanide)]silver(III) produces phosphite, $Ag^+$ and the free ligand quantitatively. A coloured intermediate **III** is formed within the time of mixing which is probably composed of the silver(III) complex, $Ag^+$ and hypophosphite in its active form. The first-order rate constant for the oxidation is $k_0 = kK_1K_2[Ag^+][P^I]/([H^+] + K_d)$, where $K_1K_2$ is the formation constant of **III** and $K_d$ is the acid dissociation constant of $H_3PO_2$. Phosphorous acid does not affect the kinetics and no free radicals could be detected during the course of the reaction. The second-order rate constant $kK_1K_2$ = 6.73 dm$^3$ mol$^{-1}$ s$^{-1}$ at 30 °C and $I$ = 1.0 mol dm$^{-3}$ is very much larger than the second-order rate constant reported for the oxidation of hypophosphite by silver(I). A plausible mechanism involves a two-step electron transfer from $P^I$ to $Ag^{III}$ *via* $Ag^I$ within **III**. The reaction has been utilised in developing a kinetic method for the estimation and detection of millimolar concentrations of hypophosphite; other oxoacids of phosphorus do not interfere.

There have been reports on the kinetics of $Ag^+$-catalysed oxidation[1] of $H_3PO_2$ by cerium(IV) and on the uncatalysed oxidation[2,3] of $H_3PO_2$ by $Ag^+$, and by silver(II) in acidic media. No such studies have, however, been made on the oxidation of $H_3PO_2$ by silver(III) species in acidic media despite the recent interest in the kinetics of reactions of higher-valent metal ions in solution stabilised by complexation with various ligands.[4–8]

[Ethylenebis(biguanide)]silver(III) perchlorate, $[Ag(H_2L)][ClO_4]_3$ (Fig. 1), is a rare example of an authentic cationic complex of silver(III) extensively stabilised[9] (log $K \approx 52$) by a square-planar acyclic tetraaza ligand. In acidic solution it is highly resistant to aquation and decomposition.[10] It is a milder oxidising agent than $Ag^+$ (ref. 11) and very slowly oxidises $N_2H_5^+$,[12] $HCO_2H$[13] and $H_3PO_2$ despite the considerable thermodynamic reducing strength of these reductants in acidic media.[14] All these reactions are, however, strongly catalysed by $Ag^+$ and a $Ag^+$–$Ag^0$ catalytic cycle operates for $N_2H_5^+$ (ref. 12) and $HCO_2H$.[13] It is interesting whether the same cycle operates in the oxidation of $H_3PO_2$.

Furthermore, $H_3PO_2$ can exist in two tautomeric forms,[15,16] *viz.* the predominant 'normal' form which is tetrahedral and the 'active' three-co-ordinated form: $H_2P(O)OH \rightleftharpoons H\ddot{P}(OH)_2$ ($K_{eq} \approx 10^{-12}$). Tautomerism is the slow rate-determining step in several redox reactions of $H_3PO_2$, but higher-valent metal ions like $Ce^{IV}$, $Ag^{II}$, $Cr^V$, $Cr^{IV}$, $Tl^{III}$, $Co^{III}$, $Au^{III}$ and $V^V$ and their complexes appear to facilitate the tautomeric shift and oxidation of $H_3PO_2$ occurs at a relatively high rate.[1,3,17–21] Such a situation may be attributed[17] to preliminary co-ordination of $P^I$ to the acidic metal centre thus mobilising the P-bound protons.

The electron affinity of $Ag^{III}$ in the present complex is high[22] and it is known from structural[23–25] and kinetic[26,27] studies that the complex undergoes axial co-ordination with alcohols, $H_2O_2$, $SO_4^{2-}$, $NO_3^-$ or even with $ClO_4^-$. Whether it can bind $H_3PO_2$ and to what effect was probed through the present kinetic investigation.

## Experimental

*Materials.*—Sodium hypophosphite hydrate (Aldrich) was quantitatively analysed for $P^I$ and $P^{III}$ by the method of Jones and Swift.[28] The sample contained 0.43% $P^{III}$ and 82.0% $P^I$. The reaction between $Ag^{III}$ and $P^{III}$ is undetectably slow even in the presence of $Ag^+$ and a large excess of $P^{III}$, and hence the presence of small amounts of $P^{III}$ in the phosphorus(I) sample had no effect on the kinetic results.

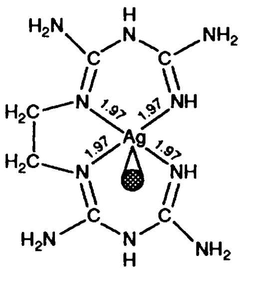


Fig. 1 Structure of $[Ag(H_2L)][ClO_4]_3$. Bond lengths in Å

All other materials including the silver(III) complex have been described earlier.[12,13]

*Test for Free Radical.*—Acrylonitrile (6% v/v) was added to the reaction mixture. A parallel blank experiment was carried out in the absence of $Ag^+$.

*Stoichiometry.*—Several acidic solutions having known concentrations of silver(III) were mixed with an excess of hypophosphite and $Ag^+$ to a total volume of 100 cm$^3$. There is a rapid rise in absorbance on mixing the reagents and the formation of a coloured intermediate is thus indicated. Therefore, the amount of unchanged $Ag^{III}$ was estimated as follows. An aliquot (5 cm$^3$) of the reaction mixture was mixed with a slight excess of cerium(IV) solution in $HClO_4$. The $Ce^{IV}$ quickly oxidised all the $P^I$ and thus quenched the reaction and decomposed the intermediate. The total volume was made up to 10 cm$^3$ and the unchanged $[Ag^{III}]$ was estimated from the solution absorbance at 450 nm where, after the addition of $Ce^{IV}$, only the silver(III) complex absorbs. The complex has an

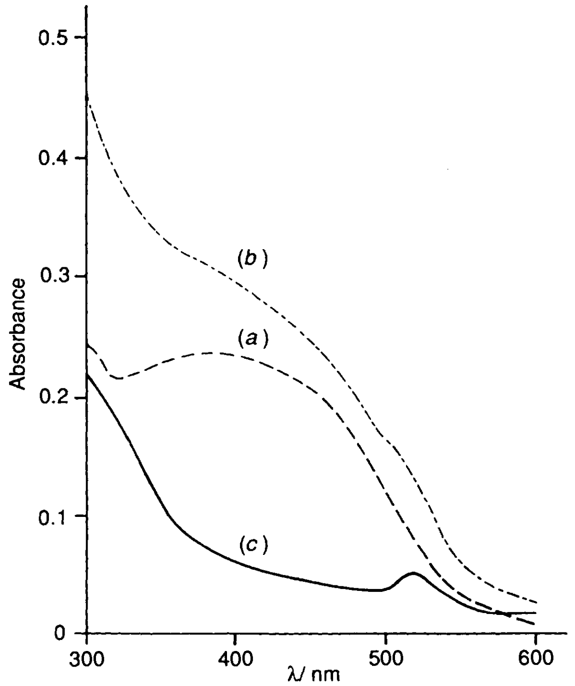


**Fig. 2** Spectrum of (*a*) 0.2 mmol dm$^{-3}$ silver(III) complex in 0.25 mol dm$^{-3}$ $HClO_4$, (*b*) a fresh mixture of the complex (0.2 mmol dm$^{-3}$), $[NaH_2PO_2]$ = 0.001 mol dm$^{-3}$, $[AgClO_4]$ = 0.008 mol dm$^{-3}$ in 0.25 mol dm$^{-3}$ $HClO_4$ at 25 °C. (*c*) The difference between (*a*) and (*b*)

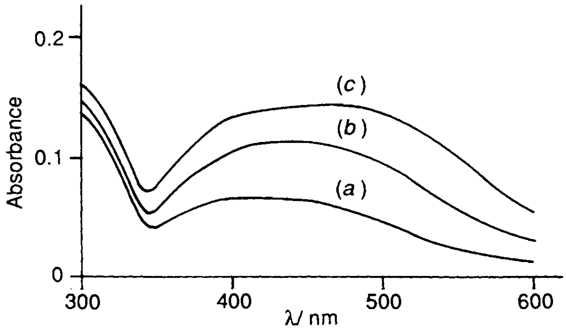


**Fig. 3** Spectra of a silver hydrosol at 25 °C, $[P^I]$ = 0.001 mol dm$^{-3}$, $[HClO_4]$ = 0.25 mol dm$^{-3}$, $[AgClO_4]$ = 0.008 mol dm$^{-3}$; (*a*) immediately after mixing, (*b*) after 225 s and (*c*) after 450 s. Very similar spectra are obtained by mixing $AgClO_4$ (0.003 mol dm$^{-3}$) and $[N_2H_6][SO_4]$ (0.001 mol dm$^{-3}$) at pH 5.1, but the changes are very much slower

absorption coefficient of 1030 dm$^3$ mol$^{-1}$ cm$^{-1}$ (0.01 < $[H^+]$ < 1.0 mol dm$^{-3}$) at 450 nm. Cerium(IV) does not consume the silver(III) complex under these conditions. The remaining 95 cm$^3$ of the reaction mixture was simultaneously quenched by the addition of a slight excess of NaCl to precipitate and remove the catalyst $Ag^+$ as AgCl. The amount of phosphite produced was estimated by the method of Jones and Swift[28] as follows.

The solution was largely neutralised with NaOH and phosphate buffer (pH ≈ 7.3) was added. The silver(III) complex was precipitated quantitatively and removed by filtration. The precipitate was washed with phosphate buffer until free from chloride. A known solution of iodine in phosphate buffer was added and the mixture was kept in the dark for about an hour and thereafter acidified with *ca.* 6 mol dm$^{-3}$ acetic acid solution. The excess of iodine was immediately titrated against standard thiosulfate to the starch–iodine end point. In these measurements aliquots were quenched before $[Ag^{III}]$ fell below *ca.* 0.06 mmol dm$^{-3}$, thus avoiding the direct reaction between $Ag^I$ and $H_3PO_2$. This practice was adopted in kinetic measurements also.

*Kinetic Measurements.*—The absorbance of the reaction mixture at different time intervals was generally measured at 380 nm with a Shimadzu Graphicord (UV-240) spectrophotometer using a 1 cm quartz cell. The reactions were initiated by rapid addition of $AgClO_4$ solution to a thermostatted mixture containing the other reactants.

In some kinetic runs the absorbance at different times was measured at 450 nm after the addition of 0.001 mol dm$^{-3}$ $Ce^{IV}$ in $HClO_4$ to aliquot portions in order to decompose the coloured intermediate and thus avoid its interference, if any, in the determination of rate.

*Estimation of Hypophosphorous Acid by Kinetic Method.*—A calibration curve was constructed using the fixed-time procedure[29] as follows. Several reaction mixtures were prepared. They contained fixed amounts of $Ag^{III}$, $HClO_4$ and $AgNO_3$ but $[NaH_2PO_2]$ was varied in the range 0.5–5.0 mmol dm$^{-3}$ at 45 °C. The absorbance of the reaction mixtures at 380 nm was measured at 5 and 45 min intervals. The difference in absorbance, $\Delta A$ at these two times, was plotted against $[NaH_2PO_2]$.

## Results and Discussion

*General Observations and Stoichiometry.*—No immediate colour change was observed upon addition of $Ag^+$ or $H_3PO_2$ separately to the silver(III) complex. However, when the three are mixed together, a coloured intermediate is formed within the time of mixing (60–120 s). The UV–VIS spectral studies suggest that this intermediate is not due to the formation of a coloured hydrosol of silver.

Spectra of the silver(III) complex alone and that of a mixture containing $Ag^+$, $H_3PO_2$ and $Ag^{III}$ in $HClO_4$ media immediately after mixing are shown in Fig. 2(*a*) and 2(*b*) respectively. The difference spectrum is shown in Fig 2(*c*), which should be that of the coloured intermediate assuming that a negligibly small amount of $Ag^{III}$ is consumed in its formation. However, the spectrum in Fig. 2(*c*) is clearly different from those[30–33] of silver hydrosols obtained by us (Fig. 3) and reported by other workers.[31–33] Therefore, it may be concluded that the coloured intermediate found in the present reaction is not the silver sol which is formed in the absence of $Ag^{III}$.

In stoichiometric experiments either $Ag^{III}$ or $H_3PO_2$ was present in excess. The mean of several such estimations (Table 1) may be represented by equation (1).

$$Ag^{III} + H_3PO_2 + H_2O \longrightarrow Ag^I + H_3PO_3 + 2H^+ \quad (1)$$

*Kinetics.*—In all the kinetic experiments the initial concentrations of $P^I$ and $Ag^+$ were much higher than that of the silver(III) complex and are thus considered to remain constant within each run. Under such conditions the kinetic profile in the presence of the coloured intermediate at 380 nm and in its absence at 450 nm (intermediate decomposed by the addition of $Ce^{IV}$ in $HClO_4$) indicated first-order processes. The two sets of absorbance–time data yielded comparable (within 7%) first-order rate constants $k_0$ obtained from the usual first-order plots and/or Guggenheim[34] plots which were good straight lines for 60–90% completion of reaction. The higher the $[Ag^{III}]_0$ the greater is the percentage of the reaction which follows linearity. Most of the kinetic runs were done with $[Ag^{III}]_0$ = 0.2 mmol dm$^{-3}$, when the linearity was obtained for at least 60–70% completion of reaction. Deviation from linearity in the later stages of reaction is due to the reaction between $Ag^+$ and $H_3PO_2$. This side reaction becomes appreciable when $[Ag^{III}]$ is very low. The first-order nature of the process is also indicated by the independence of $k_0$ on [complex] in the range 0.1–1.0 mmol dm$^{-3}$. Kinetic data are summarised in Table 2, from which it is seen that $k_0$ depends on $[H^+]$, $[P^I]$ and $[Ag^+]$ as indicated by equation (2), where the terms in square brackets

**Table 1** Stoichiometric results[a] for the $Ag^+$-catalysed oxidation of $P^I$ by the silver(III) complex

| $10^4[Ag^{III}]$/ mol $dm^{-3}$ | $10^3[P^I]$/ mol $dm^{-3}$ | $10^4[Ag^{III}]$ unchanged/ mol $dm^{-3}$ | $10^4[P^{III}]$ produced/ mol $dm^{-3}$ | $\frac{\lvert\Delta[P^{III}]\rvert}{\lvert\Delta[Ag^{III}]\rvert}$ |
|---|---|---|---|---|
| 1.0 | 3.0 | 0.50 | 0.45 | 0.90 |
| 2.0 | 5.0 | 0.98 | 1.16 | 1.14 |
| 5.0 | 10.0 | 1.42 | 3.85 | 1.08 |
| 5.0 | 10.0 | 1.46 | 3.97 | 1.12[b] |
| 10.0 | 10.0 | 3.95 | 5.88 | 0.97[c] |
| 10.0 | 10.0 | 2.12 | 8.62 | 1.09[c] |
| 10.0 | 6.0 | 5.05 | 4.81 | 0.97 |
| 20.0 | 1.0 | 10.05 | 10.92 | 1.09[d] |
| | | | | Average 1.05 ± 0.15 |

[a] $[Ag^+]$ = 0.03 mol $dm^{-3}$, $[H^+]$ = 0.50 mol $dm^{-3}$, 30 °C. [b] Reaction media purged with purified dinitrogen. [c] In the two sets the quenching times are different but all other conditions identical. [d] After completion of the reaction.

**Table 2** Some representative first-order rate constants for $Ag^+$-catalysed oxidation of hypophosphorous acid with $[Ag(H_2L)]^{3+}$ under different conditions[a]

| $[H^+]$/ mol $dm^{-3}$ | $10^2[Ag^+]$/ mol $dm^{-3}$ | $10^3[P^I]$/ mol $dm^{-3}$ | $10^4k_0/s^{-1}$ 20 | 30 | 40 °C |
|---|---|---|---|---|---|
| 0.10 | 3.0 | 2.0 | 15.6 | 17.7 | 20.9 (20.0) |
| 0.30 | 3.0 | 2.0 | 7.5 (7.2) | 9.4 | 11.2 |
| 0.50 | 3.0 | 2.0 | 5.8 | 6.5 | 7.5 |
| 0.70 | 3.0 | 2.0 | 4.4 | 4.9 | 5.8 |
| 1.0 | 3.0 | 2.0 | 3.1 (3.3) | 3.6 | 4.1 |
| 0.10 | 0.50 | 1.0 | 1.3 | 1.4 (1.4) | 1.7 (1.6) |
| 0.10 | 1.0 | 1.0 | 2.6 | 2.8 | 3.3 |
| 0.10 | 3.0 | 1.0 | 7.5 | 8.8 | 10.2 |
| 0.10 | 5.0 | 1.0 | 13.1 | 14.3 | 16.4 |
| 0.50 | 3.0 | 1.5 | 3.9 | 4.7 | 5.4 |
| 0.50 | 3.0 | 4.0 | 10.3 | 12.4 | 13.8[b] |
| 0.50 | 3.0 | 6.0 | 16.2 | 19.0[c] | 22.5 (24.0) |
| 0.50 | 3.0 | 10.0 | 26.4 | 31.0 | 35.1[d] |

[a] [complex] = 0.2 mmol $dm^{-3}$, $I$ = 1.0 mol $dm^{-3}$ ($NaClO_4$); values in parentheses were obtained by quenching with $Ce^{IV}$. [b] $k_0 = (13.5\text{–}14.3) \times 10^{-4}$ $s^{-1}$ for $[Ag^{III}]_0$ = 0.1–1.0 mmol $dm^{-3}$. [c] $k_0 = (18.9 \pm 0.6) \times 10^{-4}$ $s^{-1}$ when 0.01–0.1 mol $dm^{-3}$ $P^{III}$ was added. [d] Kinetics shows positive deviation from first-order plots when $[Ag^{III}] = [Ag^+]$ = 0.001 mol $dm^{-3}$.

**Table 3** Values of $A$ and $B$ [see equation (2)] at different temperatures

| | $T$/°C 20 | 30 | 40 |
|---|---|---|---|
| $A(=kK_1K_2)^a$/$dm^3$ $mol^{-1}$ $s^{-1}$ | 6.02 ± 0.17 | 6.73 ± 0.26 | 7.52 ± 0.36 |
| $B(=K_d)^a$/mol $dm^{-3}$ | 0.146 ± 0.016<br>(0.139)[b] | 0.134 ± 0.006<br>(0.130)[b] | 0.120 ± 0.011<br>(0.119)[b] |

[a] [complex] = 0.2 mmol $dm^{-3}$, $[H^+]$ = (0.10–1.0) mol $dm^{-3}$, $[P^I]$ = 0.001–0.01 mol $dm^{-3}$, $[Ag^+]$ = 0.005–0.05 mol $dm^{-3}$, and $I$ = 1.0 mol $dm^{-3}$ ($NaClO_4$). [b] Literature value[35] of $K_d$.

$$k_0 = \frac{A[P^I][Ag^+]}{B + [H^+]} \qquad (2)$$

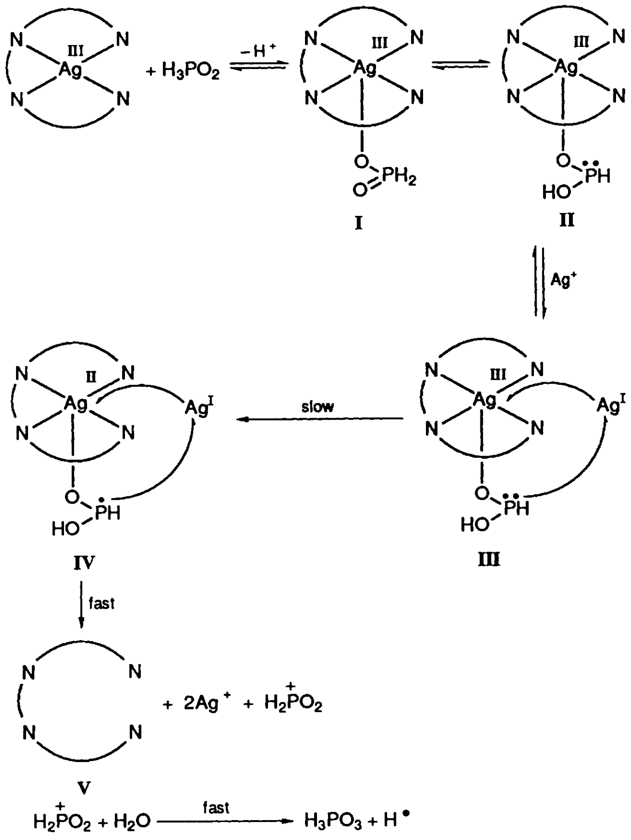
represent the analytical concentrations of $NaH_2PO_2$, $AgClO_4$ and $HClO_4$; $k_0$ was found to be independent of $[H_3PO_3]$ up to 0.1 mol $dm^{-3}$. Stray light, dissolved oxygen and occasional shaking of the spectrophotometric cell had no detectable influence on the kinetics. No polymerisation was detected in the course of the reaction in the presence of acrylonitrile. Duplicate runs reproduced individual $k_0$ values within 5% which were well fitted (within 8%) by the empirical equation (2). The least-squares values of $A$ and $B$ in Table 3 were obtained from the slope and intercept of plots of $1/k_0$ against $[H^+]$ which are good straight lines (regression coefficient, $r > 0.98$).

*Mechanism.*—It is noted that the values of $B$ are very close to the known[35] proton dissociation constant, $K_d$, of $H_3PO_2$ which suggests that the proton dissociation equilibrium has some role in the reaction. However the silver(III) complex is a weak acid ($pK_{a_1}$ = 3.8)[13] and suffers no proton dissociation in the range 0.1–1.0 mol $dm^{-3}$ $HClO_4$ used in the present study. It is also noted that $A$, the second-order rate constant for the oxidation of $H_3PO_2$, is very much larger than the second-order rate constant ($5.2 \times 10^{-2}$ $dm^3$ $mol^{-1}$ $s^{-1}$) reported[2] for the oxidation of $H_3PO_2$ by $Ag^+$. This and the first-order dependence of the present reaction on $[Ag^{III}]$ strongly suggests that direct oxidation of $Ag^+$ by $H_3PO_2$ is not the rate-determining step. This is in contrast to the observed mechanism for the $Ag^+$-catalysed oxidation of $N_2H_5^+$ (ref. 12) and $HCO_2H$[13] by this silver(III) complex. In the present reaction the sequence (3)–(7) correlates

$$H_3PO_2 \xrightleftharpoons{k_d} H^+ + H_2PO_2^- \qquad (3)$$

$$Ag^{III} + H_2P(O)OH \xrightleftharpoons{K_1} [Ag^{III}\{OPH(OH)\}]^{2+} + H^+ \qquad (4)$$

$$[Ag^{III}\{O\ddot{P}H(OH)\}]^{2+} + Ag^+ \xrightleftharpoons{K_2} [Ag^{III}\{OPH(OH)\}Ag^I]^{3+} \qquad (5)$$



Scheme 1

$$[\mathrm{Ag^{III}\{O\dot{P}H(OH)\}Ag^{I}}]^{3+} \xrightarrow[\text{slow}]{k} [\mathrm{Ag^{II}\{O\dot{P}H(OH)\}Ag^{I}}]^{2+} \quad (6)$$

$$[\mathrm{Ag^{II}\{O\dot{P}H(OH)\}Ag^{I}}]^{2+} \xrightarrow{\text{fast}} 2\mathrm{Ag}^{+} + \mathrm{H_2\overset{+}{P}O_2} \quad (7)$$

$$\mathrm{H_2\overset{+}{P}O_2} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{H_3PO_3} + \mathrm{H}^{+} \quad (8)$$

our data satisfactorily. This sequence leads to expression (9) if it

$$k_0 = \frac{kK_1K_2[\mathrm{P^I}][\mathrm{Ag}^+]}{[\mathrm{H}^+] + K_\mathrm{d}} \quad (9)$$

is assumed that ($[\mathrm{H}^+] + K_\mathrm{d}) \gg K_1[\mathrm{Ag^{III}}](1 + K_2[\mathrm{Ag}^+])$, and that $[\mathrm{H}^+]$, $[\mathrm{Ag}^+]$ and $[\mathrm{P^I}]$ are equal to the initial concentrations of $HClO_4$, $AgClO_4$ and $NaH_2PO_2$ respectively.

Equation (9) when compared with the empirical rate equation (2) gives $A = kK_1K_2$ and $B = K_\mathrm{d}$. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ corresponding to $kK_1K_2$ are $5 \pm 1$ kJ mol$^{-1}$ and $-212 \pm 15$ J K$^{-1}$ mol$^{-1}$ respectively. Since $kK_1K_2$ is a composite quantity, these activation parameters are the sum of the individual values for the activation step and the two equilibria. The large negative value of $\Delta S^\ddagger$ may be indicative of a compact transition state.

Our findings are consistent with Scheme 1, in which hypophosphorous acid co-ordinates axially to the square-planar $[\mathrm{Ag(H_2L)}]^{3+}$ complex ion and is thus deprotonated. The function of intermediate **I** is simply to hold the silver(III) and phosphorus(I) centres in proximity; the bridging oxygen is not transferred. The tautomeric shift **I** ⟶ **II** is then facilitated by the nearby $\mathrm{Ag^{III}}$. This leaves an exposed electron pair on phosphorus and precedes the act of stepwise electron transfer (**III** ⟶ **IV**, slow; and **IV** to **V**, rapid) through $\mathrm{Ag}^+$ attached to **III** and **IV**. Reduction of $\mathrm{AuCl_4}^-$ to $\mathrm{Au^I}$ is also brought about by $\mathrm{HP(OH)_2}$ through similar one-electron steps.[20] The strongly co-ordinated $d^8$ silver(III) complex is a weaker oxidant than $\mathrm{Ag^I}$ (ref. 11) and hence the electron transfer *via* $\mathrm{Ag}^+$ is preferred. Detachment of $\mathrm{H_2\overset{+}{P}O_2}$ from $\mathrm{Ag^{II}}$ has not been considered in the absence of any evidence for a free radical. It is possible that the act of electron transfer produces $\mathrm{Ag^0}$ transiently and that this is quickly reoxidised by $\mathrm{Ag^{II}}$ in the vicinity, so $\mathrm{Ag^0}$ does not escape into the bulk solution. This is a likely proposition because such 'nascent' $\mathrm{Ag^0}$ should be a very strong reducing agent since it is known that $\mathrm{Ag_2}^0$, $\mathrm{Ag_4}^0$ and other small clusters of $\mathrm{Ag^0}$ are powerful reducing agents.[36]

**Table 4** Fixed-time procedure for the estimation of $NaH_2PO_2$ *

| $10^3[\mathrm{NaH_2PO_2}]$/mol dm$^{-3}$ | Absorbance at 5 min | at 45 min | $\Delta A$ |
|---|---|---|---|
| 0.50 | 0.285 | 0.265 | 0.020 |
| 1.0 | 0.279 | 0.240 | 0.039 |
| 1.5 | 0.275 | 0.222 | 0.053 |
| 2.0 | 0.268 | 0.192 | 0.076 |
| 3.0 | 0.265 | 0.159 | 0.106 |
| 4.0 | 0.258 | 0.114 | 0.144 |
| 5.0 | 0.255 | 0.075 | 0.180 |

* [complex] = 0.2 mmol dm$^{-3}$, $[\mathrm{AgNO_3}]$ = 0.01 mol dm$^{-3}$, $[\mathrm{HClO_4}]$ = 0.50 mol dm$^{-3}$; 45 °C; $\lambda$ = 380 nm, path length 1 cm.

Spectral evidence suggests the coloured intermediate contains $\mathrm{Ag^I}$, $\mathrm{Ag^{III}}$ and $\mathrm{P^I}$ together. Thus **III** in Scheme 1 appears to be the coloured intermediate. Its colour may be very tentatively ascribed to some kind of $\mathrm{Ag^I} \longrightarrow \mathrm{Ag^{III}}$ charge transfer.

The proposed mechanism predicts autocatalysis in $\mathrm{Ag}^+$. Reaction at $[\mathrm{Ag}^+]_0$ = 1.0 mmol dm$^{-3}$ shows a detectable positive deviation (increase in rate) from apparent first-order kinetics (see footnote *d* in Table 2).

*Estimation of* $\mathrm{P^I}$ *by a Kinetic Method.*—The $\Delta A$ values for different $[\mathrm{NaH_2PO_2}]$ are shown in Table 4. They obey an excellent straight line relation ($r > 0.99$) with an intercept very close to zero. Linearity was obtained up to at least 0.005 mol dm$^{-3}$ $NaH_2PO_2$. Phosphite, phosphate or pyrophosphate do not interfere up to 0.1 mol dm$^{-3}$ and at least up to 70 °C. It might be mentioned here that, in the estimation of hypophosphite with $\mathrm{Ce^{IV}}$, phosphite interferes[37] above 60 °C. The present method is rapid, selective and may be utilised for the determination of hypophosphite down to 0.5 mmol dm$^{-3}$. The results are reproducible; the standard deviation is 1% for six estimations on one sample.

In order to compare this kinetic procedure with other standard non-kinetic techniques, we analysed a sample of $NaH_2PO_2$ (LOBA, G.R.) by use of $\mathrm{Ce^{IV}}$,[37] of $KMnO_4$ as catalysed by $\mathrm{Br}^-$,[38] by iodimetry in phosphate buffer[28] and by this kinetic method. The amount of hypophosphite in the sample as measured by these methods is 79.8, 78.0, 80.2 and 80.1% respectively. The somewhat low value obtained by permanganometry is typical of the method. The kinetic method is usable in sulfuric acid media. However, hydrohalogenic acids must be absent: $HNO_3$ in concentration greater than 1.0 mol dm$^{-3}$ interferes and hydrazine strongly inhibits the reaction.

## Acknowledgements

The awards of a senior research fellowship to R. D. by the University Grants Commission (New Delhi) and of a junior research fellowship to S. M. by Council of Scientific and Industrial Research (New Delhi) are gratefully acknowledged.

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*Received* 18*th November* 1991; *Paper* 1/05814B