2 PERKIN

Kinetics of oxidation of 3-aminopropan-1-ol and related compounds by silver(III) species

Anil Kumar,[*a] **Vaishali**[a] **and P. Ramamurthy**[b]

[a] *Department of Chemistry, University of Roorkee, Roorkee – 247 667, Uttranchal, India*
[b] *Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai – 600 025, India*

Received (in Cambridge, UK) 7th December 2000, Accepted 3rd May 2001

The oxidation of 3-aminopropan-1-ol (3-AP) and certain diamines by diperiodatoargentate(III) (DPA) has been studied by stopped-flow spectrophotometry at pH 8.0. The kinetics of the reaction of 3-AP consist of three steps—an induction period, then a fast decay, which is followed by a slower decay. The initial step involves the axial binding of the substrate to the silver(III) species; this rearranges during the induction period (0.2 s) and takes up another ligand in the following step with a second-order rate constant of 4×10^3 dm^3 mol^{-1} s^{-1} to yield [Ag^{III}(H$_2$IO$_6$)(3-AP)$_2$]. The silver(III) centre in this complex is reduced by 3-AP in the rate-determining step with a rate constant of 0.50×10^2 dm^3 mol^{-1} s^{-1}. Both of these processes show inverse dependence on [IO$_4^-$] and [OH$^-$]. The kinetics of the oxidation of diamines by silver(III) follow a different kinetic behaviour. The rates of their complexation and oxidation follow the order 1,2-diaminoethane > 1,3-diaminopropane > 1,4-diaminobutane. Separation of the two functional groups by an additional CH$_2$ in the studied substrates reduces the rates of both the steps. In case of the diamines, the formation of a cyclic complex involving silver(III) and the substrate prior to its oxidation is suggested. The mechanisms of these reactions are being analysed.

Introduction

Higher oxidation state species of transition metal ion(s) have often been found to be involved in redox reactions involving their respective stable ions.[1–4] Most of these species are fairly short lived and highly reactive. Copper in its 3+ oxidation state is thought to be involved in certain metalloenzyme systems.[1] Gold(III) species have shown antitumour activity and cytotoxicity.[5] The applications of cuprate(III) and argentate(III) in analytical chemistry have been reported by several workers.[6,7] Ag(III) is a strong two-electron acceptor and has a d^8 configuration similar to Cu(III) and Au(III); for this reason, its reactions with different organic and inorganic species have been examined. Efforts have been made to stabilize the unusual oxidation state species of silver(III) by using a variety of ligands.[8–11] Reactions of silver(III) have been performed using several of these complexes, such as [Ag(OH)$_4$]$^-$,[12,13] ethylenebis(biguanide)-silver(III),[14] diperiodatoargentate(III) (DPA)[15–17] among others. DPA has the advantage of being a relatively strong oxidant, and is fairly stable in mild as well as highly basic media. In the oxidation of 1,2-diaminoethane (1,2-DAE) by DPA, it has been observed that both the complexation and redox of silver(III) through the amino group are fairly fast, compared to other functional groups, such as OH or COOH.[16] In the present work we investigate the oxidation of 3-aminopropan-1-ol (3-AP), 1,3-diaminopropane (1,3-DAP) and other related compounds by DPA. The effect of the separation of the two functional groups on the kinetics of these reactions is examined. In the case of diamines, a cyclic silver(III) complex is suggested as an intermediate. Increased separation of these groups, however, disfavours the formation of such a complex. Although the involvement of silver(III) and the formation of cyclic silver(III) complexes with diols in the Ag$^+$-catalysed redox reactions of cyclic 1,2-diols by S$_2$O$_8^{2-}$ have been suggested, no experimental evidence has been found to support this.[1,18]

Results and discussion

The mixing of a solution of DPA (5×10^{-5} mol dm^{-3}) and 3-AP (1×10^{-3} mol dm^{-3}) at pH 8.0 results in the disappearance of the yellow color of DPA within about 50 s. The progress of this reaction could, therefore, be monitored by the stopped-flow technique. The representative kinetic traces for this reaction are shown in Fig. 1. This reaction consists of three steps, namely, an induction period, then a fast decrease in absorbance followed by a slower decrease. The first decay process attains a limiting value after about a 30% decrease in absorbance over less than a second and can be distinctively separated kinetically from the other decay process, which occurs over some tens of seconds. Both of these processes were found to follow pseudo-first-order kinetics as shown in the insets for the respective traces (Fig. 1). It should be mentioned that the observed change in kinetics does not arise due to a change in the pH, as this remains unchanged during the course of the reaction. Moreover, the pK_a of 3-AP is reported in the literature[19] to be 9.96, which is about 2 units away from the pH and would not be influenced by the kinetic behaviour. The kinetics of both of these processes were not affected by an increase in the ionic strength of the medium; this was established by adding the neutral salt KClO$_4$ up to 2×10^{-3} mol dm^{-3}. Therefore, the ionic strength of the medium was not maintained in these experiments.

Effect of [3-aminopropan-1-ol]

An increase in [3-AP] (5×10^{-4} to 1×10^{-3} mol dm^{-3}) enhances the rate of both of the decay processes without influencing the duration of the induction period. For the first step the variation of the pseudo-first-order rate constant as a function of [3-AP] is shown in Fig. 2. At low [3-AP] the rate constant increased linearly, whereas at higher concentrations (2.5×10^{-3} mol dm^{-3}) it attains its limiting value. From the linear part of this curve, the second-order rate constant for the process was determined to be 4.0×10^3 dm^3 mol^{-1} s^{-1}. However, a plot of $1/k_1$ *vs.* 1/[3-AP] was linear and depicted an intercept (Fig. 3a). It kinetically demonstrates the formation of an intermediate between DPA and 3-AP. For the second step a plot of pseudo-first-order rate constant (k_2) *vs.* [3-AP] varies linearly and passes

DOI: 10.1039/b009821n

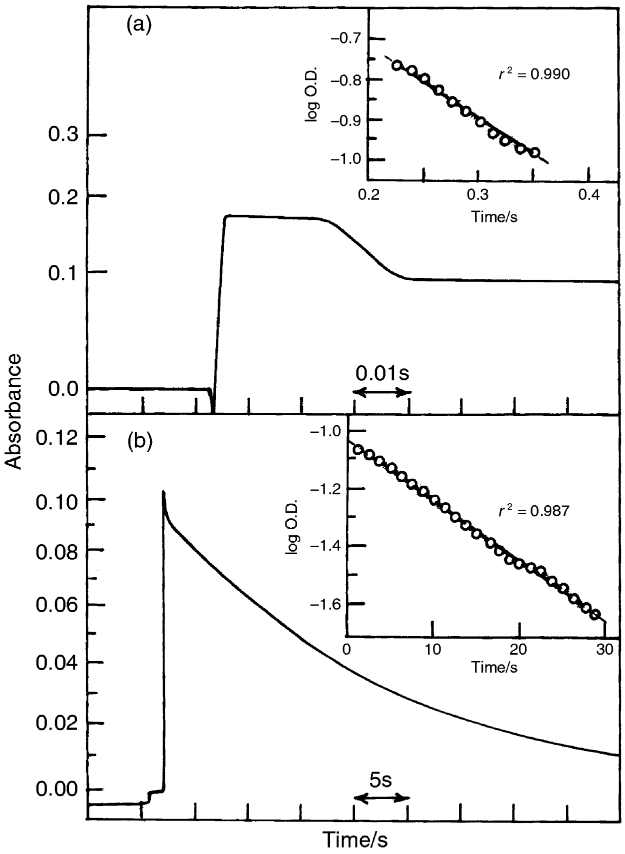

Fig. 1 Kinetic traces recorded in stopped-flow experiments at 360 nm upon mixing DPA (5×10^{-5} mol dm^{-3}) and 3-AP (1×10^{-3} mol dm^{-3}) at pH 8.0 on the time scales indicated in the respective traces. Inset: Pseudo-first-order kinetic plots.

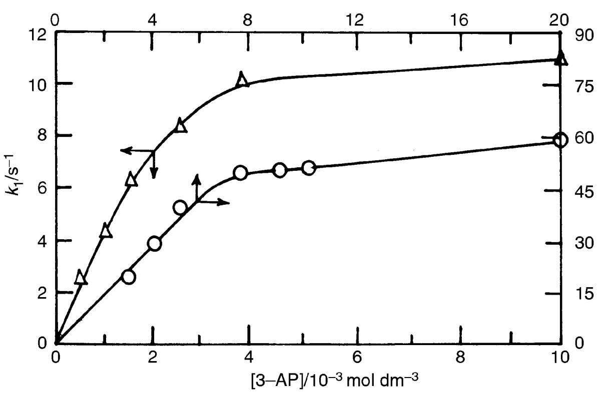

Fig. 2 Plots of pseudo-first-order rate constants for complexation (k_1) *vs.* [substrate] – 3-AP (Δ); 1,3-DAP (O).

through the origin (Fig. 3b). This gives a second-order rate constant of 0.5×10^2 dm^3 mol^{-1} s^{-1} for this process. At pH 8.0, the reactive silver(III) species in the reactions of DPA is known to be $[Ag^{III}(H_2IO_6)(H_2O)_2]$.[16]

$$[Ag^{III}(H_2IO_6)_2]^{3-} + 3H_2O \rightleftharpoons [Ag^{III}(H_2IO_6)(H_2O)_2] + H_3IO_6^{2-} + OH^- \quad (1)$$

The possibility of the formation of an intermediate(s) between DPA and 3-AP was checked by recording absorption spectra at different time intervals from the stopped-flow kinetic traces. These measurements were carried out at different wavelengths between 300–600 nm at pH 8.0 (Fig. 4). It should be noted that 3-AP does not possess any absorption in the recorded wavelength region. The spectrum obtained immediately after mixing the reactants differs from that of DPA and can be assigned to the complex formed between DPA and 3-AP, reaction (2).

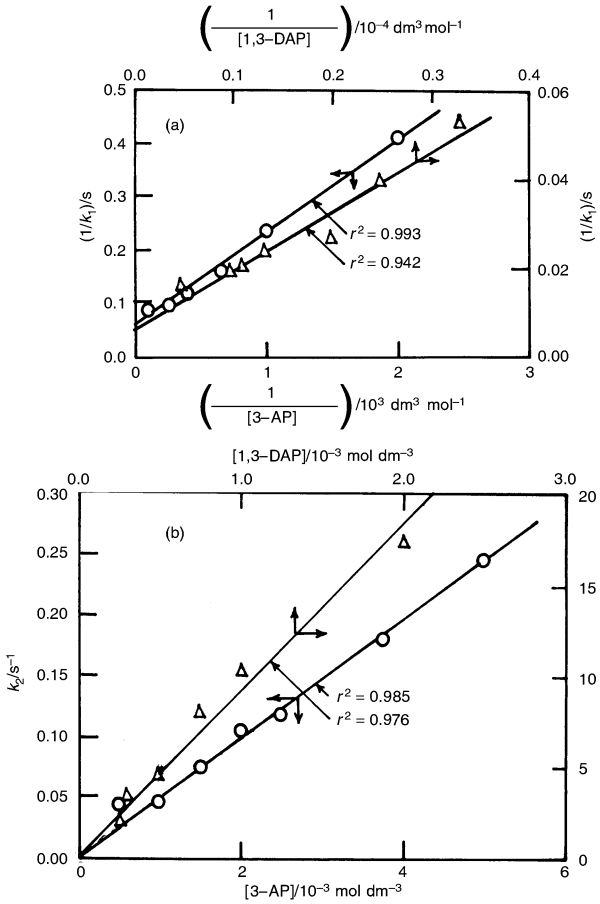

Fig. 3 (a) Plots of $1/k_1$ *vs.* 1/[substrate] – 3-AP (O); 1,3-DAP (Δ). (b) Plots of pseudo-first-order rate constants for oxidation (k_2) *vs.* [substrate] – 3-AP (O); 1,3-DAP (Δ).

$$[Ag^{III}(H_2IO_6)(H_2O)_2] + 3\text{-AP} \rightleftharpoons [Ag^{III}(H_2IO_6)(H_2O)(3\text{-AP})] + H_2O \quad (2)$$

The absorption due to this species remains unchanged during the induction period, but an increase in [3-AP] reduces the absorbance of the starting signal (Inset: Fig. 4). It suggests that 3-AP initially binds to the silver(III) species axially, rearranging during the induction period. This is the reason why a change in [3-AP] does not influence the length of the induction period. This spectrum decays in the fast process to produce another species in about 5 s. Since the rate of this process depends upon [3-AP], and its absorption does not completely decay to zero, it is, therefore, suggested that there is further uptake of 3-AP by $[Ag^{III}(H_2IO_6)(H_2O)(3\text{-AP})]$ in this step to yield the intermediate, $[Ag^{III}(H_2IO_6)(3\text{-AP})_2]$, reaction (3).

$$[Ag^{III}(H_2IO_6)(H_2O)(3\text{-AP})] + 3\text{-AP} \rightleftharpoons [Ag^{III}(H_2IO_6)(3\text{-AP})_2] + H_2O \quad (3)$$

This spectrum then decays in the 300–450 nm region, along with a simultaneous buildup of absorption from 450–600 nm. At longer times (after about 60 s) a bleaching of the absorption due to the $[Ag^{III}(H_2IO_6)(3\text{-AP})_2]$ species can be seen at wavelengths 340–370 nm, which results in an increase at longer wavelengths on the same time scale. The rates for the decay and buildup at these wavelengths are kinetically very similar. These spectral changes depicted an isosbestic point at 440 nm. The intermediate formed after 70 s of reaction (Fig. 4, curve -●-)

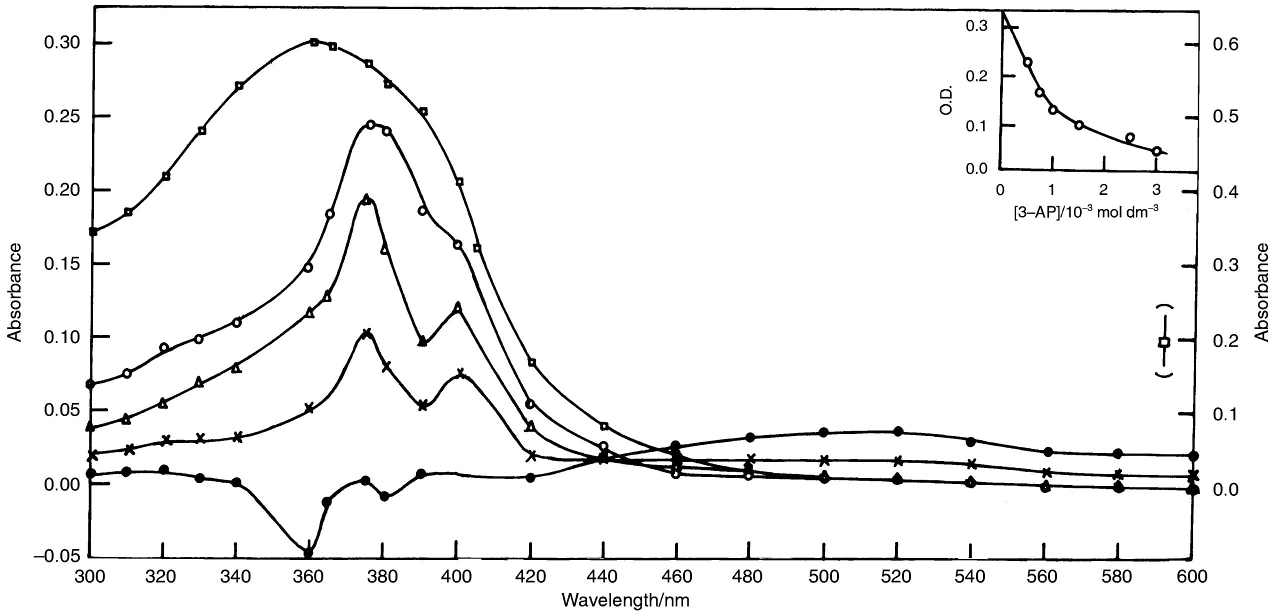

Fig. 4 Absorption spectra of DPA and intermediates formed upon mixing DPA (5×10^{-5} mol dm^{-3}) and 3-AP (2×10^{-3} mol dm^{-3}) at pH 8.0 – 0.25 s (○); 10 s (△); 30 s (×); 70 s (●); absorption spectrum of DPA (-□-). Inset: Plot of absorbance as a function of [3-AP] immediately after mixing of DPA and 3-AP.

can be attributed to $[Ag^{II}(H_2IO_6)(3\text{-}AP)_2]$, formed by the transfer of an electron from the free 3-AP to the silver(III) centre within the complex [reaction (4)]. This assignment is supported

$$[Ag^{III}(H_2IO_6)(3\text{-}AP)_2] + 3\text{-}AP \longrightarrow [Ag^{II}(H_2IO_6)(3\text{-}AP)_2] + 3\text{-}AP^{\bullet +} \quad (4)$$

by a pulse radiolysis experiment, in which the reduction of DPA was performed by e^-_{aq}.[20]

However, the amino radical cation shown in reaction (4) could not be identified, as it is expected to have little absorbance in the UV region below 250 nm.[21] The radical cation, $3\text{-}AP^{\bullet +}$ might undergo a series of reactions to form aldehyde and ammonia, reactions (5)–(7).

$$N^{\bullet +}H_2CH_2CH_2CH_2OH \longrightarrow N^{\bullet}HCH_2CH_2CH_2OH + H^+ \quad (5)$$

$$N^{\bullet}HCH_2CH_2CH_2OH + [Ag^{II}(H_2IO_6)(3\text{-}AP)_2] \longrightarrow NH{=}CH(CH_2)_2OH + Ag^I + H_2IO_6^{3-} + 2(3\text{-}AP) \quad (6)$$

$$NH{=}CH(CH_2)_2OH \xrightarrow{H_2O} NH_3 + OHCCH_2CH_2OH \quad (7)$$

Effect of [periodate]

Since DPA contains two periodate ligands coordinated to silver(III) and one of them is released into the aqueous media, reaction (1), the effect of [periodate] on the kinetics of this reaction was examined. The addition of periodate (5×10^{-4} mol dm^{-3}) reduces the rate of the initial decay process significantly from 4.2 (in the absence of periodate) to 1.1 s^{-1}. Moreover, the variation in the rate constant with $[IO_4^-]$ was nonlinear (Fig. 5). The plot of $1/k_1$ *vs.* $[KIO_4]$ is, however, linear with an intercept. This inverse rate dependence on KIO_4 verifies the dissociation pre-equilibrium shown in reaction (1). The rate of the reaction observed for the second step is also reduced in the presence of periodate. However, in contrast to the kinetics of the first step, the rate of this process varies linearly with $[IO_4^-]$. The addition of 5×10^{-4} mol dm^{-3} of IO_4^- reduced it from 0.05 to 0.013 s^{-1}. Thus in the mild basic pH range $[Ag^{III}(H_2IO_6)(H_2O)_2]$ will be the chief reactive species. Upon applying the steady state treatment to the intermediates $[Ag^{III}(H_2IO_6)(H_2O)_2]$, $[Ag^{III}(H_2IO_6)(H_2O)(3\text{-}AP)]$ and $[Ag^{III}(H_2IO_6)(3\text{-}AP)_2]$ in reactions (1)–(4), the rate law for the oxidation of 3-AP, assuming $k_{-3} <<< k_4$, is given by eqn. (8).

$$\text{Rate} = \frac{K_1K_2k_3[Ag^{III}(H_2IO_6)_2]^{3-}[3\text{-}AP]}{[H_3IO_6]^{2-}[OH^-]} \quad (8)$$

This rate law explains all the kinetic features observed above at pH 8.0.

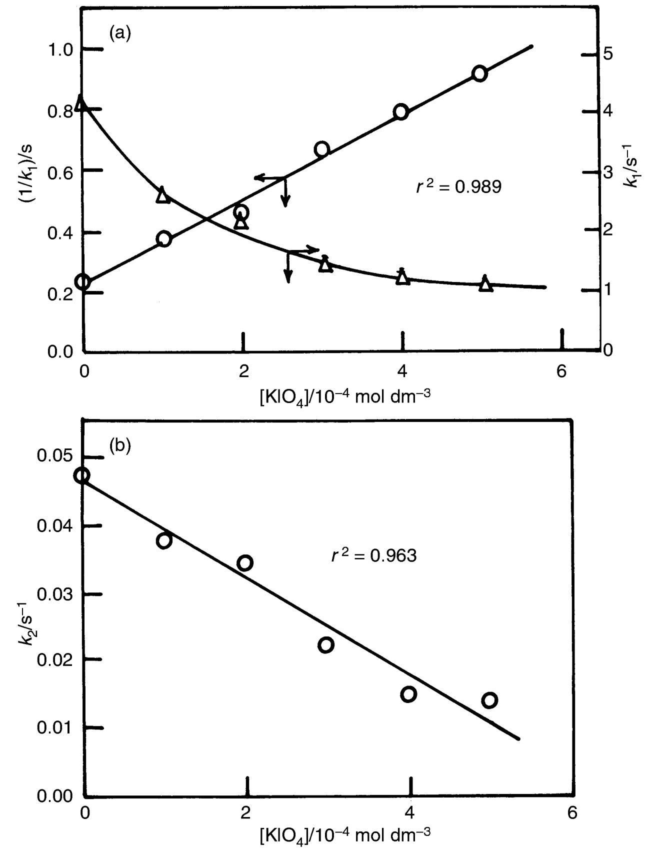

Fig. 5 (a) Effect of [periodate] on the pseudo-first-order rate constant (k_1) and a plot of $1/k_1$ *vs.* [periodate] at pH 8.0. (b) Effect of [periodate] on pseudo-first-order rate constant for oxidation (k_2). [DPA] = 5×10^{-5} mol dm^{-3}; [3-AP] = 1×10^{-3} mol dm^{-3}.

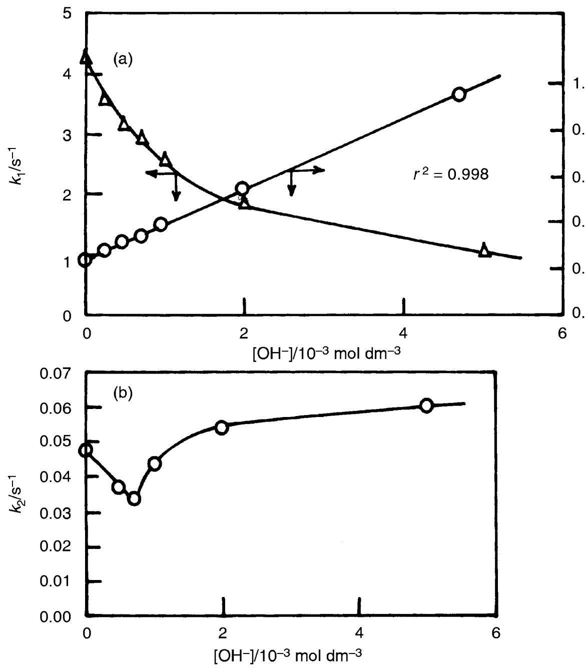

Fig. 6 (a) Effect of [OH$^-$] on pseudo-first-order rate constant (k_1) and a plot of 1/k_1 *vs.* [OH$^-$]. (b) Effect of [OH$^-$] on pseudo-first-order rate constant for oxidation (k_2). [DPA] = 5 × 10^{-5} mol dm^{-3}; [3-AP] = 1 × 10^{-3} mol dm^{-3}.

Effect of [OH$^-$]

The kinetics of both the processes, *i.e.* complexation and oxidation, are influenced by the addition of OH$^-$ (Fig. 6). The addition of 5 × 10^{-4} mol dm^{-3} OH$^-$ reduced the pseudo-first-order rate of complexation from 4.23 to 1.1 s^{-1}. This decrease in rate was non-linear with [OH$^-$]. In this case, the variation of 1/k_1 *vs.* [OH$^-$] was also linear. This behaviour at low pH is consistent with the rate law derived in eqn. (8). A further increase in [OH$^-$] affects the kinetics of the second step in a complex manner. Initially, the rate of this process decreases up to 7.5 × 10^{-4} mol dm^{-3} of OH$^-$ and, thereafter, it increases and starts attaining a limiting value at high [OH$^-$] (Fig. 6). At higher [OH$^-$] the reactive silver(III) species in the reaction system might change because of hydroxylation of DPA reaction (9).

$$[Ag^{III}(H_2IO_6)_2]^{3-} + OH^- + H_2O \rightleftharpoons [Ag^{III}(H_2IO_6)(OH)_2] + H_3IO_6^{3-} \quad (9)$$

Then, as per the above observation, the hydroxylated silver(III) species may release OH$^-$ into the solution, as shown in reactions (10) and (11).

$$[Ag^{III}(H_2IO_6)(OH)_2]^{2-} + 3\text{-AP} \longrightarrow [Ag^{III}(H_2IO_6)(OH)(3\text{-AP})]^- + OH^- \quad (10)$$

$$[Ag^{III}(H_2IO_6)(OH)(3\text{-AP})]^- + 3\text{-AP} \longrightarrow [Ag^{III}(H_2IO_6)(3\text{-AP})_2] + OH^- \quad (11)$$

A comparison of the kinetic data obtained from the DPA–3-AP system with that of DPA–2-aminoethanol (2-AE)[17] reveals that the rates of both complexation and oxidation are slightly less for 3-AP under similar experimental conditions, but are of the same magnitude. The difference between 3-AP and 2-AE is the increased separation in the former of the two functional groups, NH$_2$ and OH, by an additional CH$_2$.

Effect of replacement of OH by NH$_2$ in 3-AP on the kinetics

This was investigated by examining the kinetics of the reaction of DPA with 1,3-diaminopropane (1,3-DAP). This reaction was fairly fast and was over in less than a second. The kinetic traces depicting the different steps of this reaction are shown in Fig. 7. This reaction consists of three steps: a rapid decrease in absorbance, followed by a slow decrease, which is then followed by a relatively fast decay in absorbance. The first fast decay in absorption is completed in about 40 ms. The intermediate formed in this step decays slowly over 0.15 s and the resulting species then decays in the fast process. All three processes follow pseudo-first-order kinetics. The effect of [1,3-DAP] on the rate of the first two steps is shown in the inset of Fig. 7. The second-order rate constants for complexation and reduction of the silver(III) complex by 1,3-DAP have been computed to be 6.9 × 10^4 and 9.8 × 10^3 dm^3 mol^{-1} s^{-1}, respectively (Figs. 2 and 3). In contrast to the DPA–1,2-DAE system, where the complexation of silver(III) with 1,2-DAE was complete in about 10 ms, it would be possible to follow the rate of complexation of 1,3-DAP with silver(III).

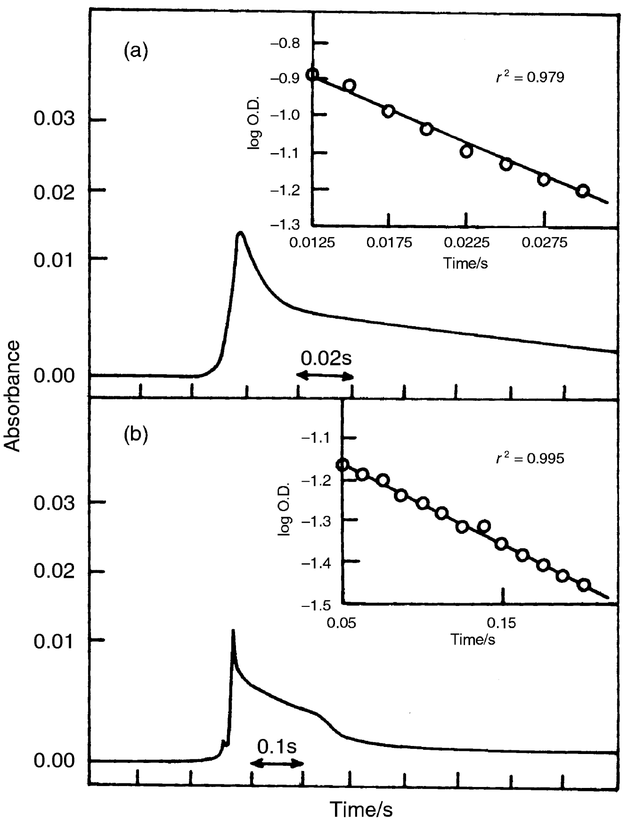

Fig. 7 Kinetic traces recorded in stopped-flow experiments at 360 nm upon mixing DPA (5 × 10^{-5} mol dm^{-3}) and 1,3-DAP (5 × 10^{-4} mol dm^{-3}) at pH 8.0 on the time scales indicated in the respective traces. Inset: Pseudo-first-order kinetic plots.

To further analyse the effect of the separation of the two amino groups on the kinetics, the next homologue of the diamine series, *i.e.* 1,4-diaminobutane (1,4-DAB) was examined. Its kinetic behaviour was quite different to that of the other diamines, *viz.* the DPA–1,3-DAP and DPA–1,2-DAE[17] systems.

In this case the reaction is attended by an induction period of about 0.2 s, and its kinetic behaviour is very similar to that of the DPA–3-AP system (Fig. 8). For this system the rate of complexation of 1,4-DAB with DPA is determined to be 0.6 × 10^4 dm^3 mol^{-1} s^{-1}. In the following step 1,4-DAB then transfers an electron to the silver(III) centre and this process occurs with a second-order rate constant of 4.3 × 10^2 dm^3 mol^{-1} s^{-1}. Interestingly, the rates of both of these processes are fairly slow compared to 1,3-DAP. Thus, both observations (a change in the kinetic behaviour and a reduction in the rates of complexation and oxidation) suggest the absence of the formation of a cyclic complex in this case. The initial complexation in this case apparently takes place through one amino group, in a similar

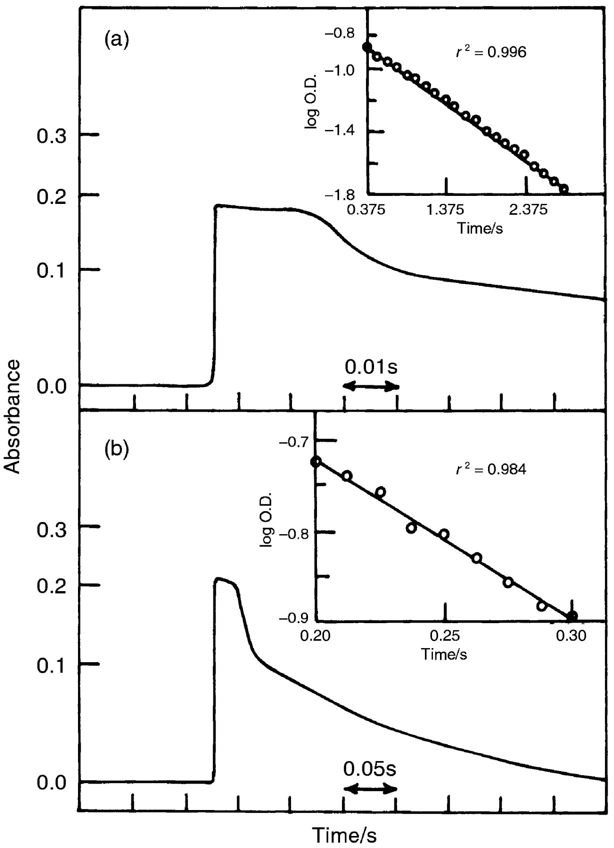

Fig. 8 Kinetic traces recorded in stopped-flow experiments at 360 nm upon mixing DPA (5×10^{-5} mol dm^{-3}) and 1,4-DAB (6×10^{-4} mol dm^{-3}) at pH 8.0 on the time scales indicated in the respective traces. Inset: Pseudo-first-order kinetic plots.

manner to the DPA–3-AP system, and there is an uptake of another ligand in the subsequent step.

Thus the above observed kinetic data with different substrates can be classified into two categories: (i) showing an induction period; (ii) not exhibiting any induction period. For the first category of reaction it appears that there is an axial binding of the substrate to the silver(III) centre. This complex then rearranges to give a more stable four-coordinate complex by substituting water or an OH$^-$ group in DPA. For this reason the length of the induction period remains unchanged with increasing [substrate] during the induction period. On the other hand, the reactions of the second category are completed in a fraction of a second. The difference in the two cases might be interpreted as the formation of a cyclic complex in the latter case. Thus, the highest rate of complexation of silver(III) has been observed with 1,2-DAE, in which it is very likely that the silver(III) forms a cyclic complex involving the two amino groups. Separation of these groups by an additional CH$_2$ in 1,3-DAP, increases their separation by 1.54 Å, which decreases both the rates of complexation and oxidation but still results in the formation of a cyclic complex. In the next homologue, 1,4-DAB, the separation of the amino groups is further increased to 3.08 Å, which does not allow complexation to occur involving both amino groups simultaneously. For this reason the kinetic behaviour of 1,4-DAB is very similar to that of the aminoalcohols, in which no such complexation has been observed.

To examine the above hypothesis, the kinetic study of Ag(III) was performed with propane-1,3-diol (1,3-PD), where no amino group is present. Indeed, the rates of both of the processes are reduced substantially (Table 1). Further, the electronic spectra of the intermediate assigned as the complex in this case show weak complexation (Fig. 9) compared to the substrates containing amino groups like 3-AP (Fig. 4), 2-AE and 1,2-DAE.[16] The possibility of complexation and oxidation through a single amino group was checked at pH 8.0 by performing the reaction of DPA with *N*-propylamine (*N*-PA), which does not contain another functional group. Its kinetic behaviour was similar to that of 3-AP and 1,4-DAB, and depicts an induction period of about 0.2 s. In this case the initial complexation is completed in <1 s and it undergoes oxidation with a second-order rate constant of 0.17×10^2 dm^3 mol^{-1} s^{-1}.

Table 1 Rates for complexation and oxidation at pH 8.0

Substrate	Rate of complexation/ dm^3 mol^{-1} s^{-1}	Rate of oxidation/ dm^3 mol^{-1} s^{-1}
3-Aminopropan-1-ol (3-AP)	0.4×10^4	0.5×10^2
2-Aminoethanol (2-AE)[a]	1.0×10^4	1.3×10^2
1,2-Diaminoethane (1,2-DAE)[a]	—	1.4×10^4
1,3-Diaminopropane (1,3-DAP)	6.9×10^4	9.8×10^3
1,4-Diaminobutane (1,4-DAB)	0.6×10^4	4.3×10^3
Propane-1,3-diol (1,3-PD)	0.0063	0.0011
N-Propylamine (*N*-PA)	—	0.17×10^2[b]

[a] Ref. 17. [b] Estimated value.

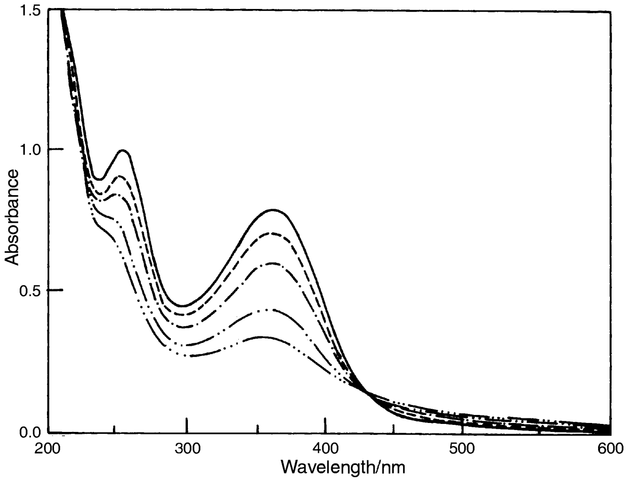

Fig. 9 Absorption spectra of DPA and intermediates formed upon mixing of DPA (5×10^{-5} mol dm^{-3}) and 1,3-PD (2×10^{-3} mol dm^{-3}) at pH 8.0 – 1.5 min (---); 9.0 min (-·-·-); 24 min (-··-··-); 56.5 min (-···-···-); absorption spectrum of DPA (——).

In summary, 3-AP forms a complex with silver(III) through axial binding of NH$_2$. This complex then rearranges prior to the uptake of another ligand. In contrast, diamines are complexed at a faster rate, without exhibiting an induction period. In this case, the formation of a cyclic complex involving two NH$_2$ groups is suggested. Increasing the separation of the two groups by inserting a CH$_2$ group prevents the formation of such an intermediate, which then behaves in a similar manner to substrates having a single amino group. In both cases the reduction of the silver(III) intermediate then takes place by transference of an electron from the uncomplexed substrate.

Experimental

Materials

All the used compounds, namely 3-aminopropan-1-ol (3-AP), propane-1,3-diol (1,3-PD) (Aldrich), *N*-propylamine (*N*-PA) (Thomas Baker), 1,3-diaminopropane (1,3-DAP), 1,4-diaminobutane (1,4-DAB), 2-aminoethanol (2-AE), silver nitrate, potassium metaperiodate, potassium peroxodisulfate, chromotropic acid (Merck), KOH (SRL), NaOH (BDH) were of analytical grade. The purity of the *N*-propylamine, 1,3-diaminopropane and 1,4-diaminobutane used was further ensured by distillation and recording their boiling points. Acrylonitrile and

$K_2S_2O_8$ were also purified by distillation and recrystallisation prior to their use.

Equipment

Slow kinetics and absorption spectra were measured on Shimadzu UV-2100/s and UV-1601 PC spectrophotometers. Fast kinetic measurements were made on an Applied Photophysics-1705-Stopped-flow apparatus equipped with an IP 28 nine stage photomultiplier. The transients signal was stored in a DL-905 datalab transient digitizer. The kinetic traces from the scopex were transferred with the help of a YT recorder. The dead-time of the apparatus was 1 ms. IR spectra were recorded on an M-1640 Perkin-Elmer FTIR.

Methodology

The synthesis of sodium diperiodatoargentate(III) was carried out by a literature method.[11,22,23] This complex was identified by its characteristic IR and electronic spectra. The absorption spectrum has three peaks at 214, 254 and 362 nm. Its molar absorptivity coefficient at 362 nm was found to be 1.4×10^4 dm^3 mol^{-1} cm^{-1} at pH 8.0, which was in agreement with the previous reports. The diamagnetism of the compound was checked by its magnetic moment, which was 0.4 μ_B.

The progress of the reaction was followed kinetically by monitoring the absorbance of the DPA–substrate complex at 360 nm. None of the used substrates possess any absorption at this wavelength. The electronic spectra of the intermediates were measured from 300–600 nm. All the kinetic experiments were carried out under pseudo-kinetic conditions, in which the concentration of the substrate was maintained about 10 times higher than that of DPA. The stopped-flow experiments were performed at (20 ± 0.5) °C whereas the slow kinetics were carried out at (35 ± 0.1) °C. The pH of the reactants was measured prior to their mixing and was found not to change after mixing within the duration of the experiment. First-order plots of kinetic data were linear through at least more than 75% of the completion of reaction. The correlation coefficient of the observed linear curve has been reported in the respective trace.

The oxidation products of the reactions of DPA with 3-AP and 1,3-DAP were identified as the respective aldehyde and NH_3, tested by Schiff's and Nessler's reagents, respectively. None of these substrates yielded the C–C bond cleavage product. This observation was in contrast to the reactions of DPA with 2-aminoethanol (2-AE), 1,2-diaminoethane (1,2-DAE) and ethane-1,2-diol, in which HCHO is formed as one of the products.

Acknowledgements

We gratefully acknowledge the financial assistance of CSIR, New Delhi, in the undertaking of this work. Thanks are also due to the Director, National Centre for Ultrafast Processes, Chennai, for providing us with stopped-flow apparatus facilities.

References

1 W. Levason and M. D. Spicer, *Coord. Chem. Rev.*, 1987, **76**, 45.
2 S. Bhattacharya, B. Saha, A. Dutta and P. Banerjee, *Coord. Chem. Rev.*, 1998, **170**, 47.
3 J. A. McMillan, *Chem. Rev.*, 1962, **62**, 65.
4 S. Mukhopadhyay, S. Kundu and R. Banerjee, *Proc. Indian Acad. Sci., Chem. Sci.*, 1995, **107**, 403.
5 C. F. Shaw III, *Chem. Rev.*, 1999, **99**, 2589.
6 Y. Deborah, H. D. Moya, R. L. Bonifacio and N. Coichev, *Spectrosc. Lett.*, 1998, **31**, 1495.
7 W. G. Movius, *Inorg. Chem.*, 1973, **12**, 31.
8 P. Ray, *Nature*, 1943, **151**, 643.
9 H. Furuta, T. Okawa, Y. Uwatoko and K. Araki, *Inorg. Chem.*, 1999, **38**, 2676.
10 G. L. Cohen and G. Atkinson, *J. Electrochem. Soc.*, 1968, **115**, 1236.
11 G. L. Cohen and G. Atkinson, *Inorg. Chem.*, 1964, **3**, 1741.
12 Y. Sun, L. J. Kirschenbaum and I. Kouadio, *J. Chem. Soc., Dalton Trans.*, 1991, 2311.
13 A. Kumar and A. Panwar, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1207.
14 R. Banerjee, R. Das and S. J. Mukhopadhyay, *J. Chem. Soc., Dalton Trans.*, 1992, 1317.
15 T.-S. Shi, *Sci. China, Ser. B*, 1990, **33**, 1436.
16 A. Kumar, P. Kumar and P. Ramamurthy, *Polyhedron*, 1999, **18**, 773.
17 A. Kumar, Vaishali and P. Ramamurthy, *Int. J. Chem. Kinet.*, 2000, **32**, 286.
18 E. S. Huyser and L. G. Rose, *J. Org. Chem.*, 1972, **37**, 851.
19 *Comprehensive Organic Chemistry*, ed. I. O. Southerland, Pergamon Press, Oxford, 1979, p. 104.
20 A. Kumar and E. Janata, personal communication. The reduction of DPA by e_{aq}^- produces an absorption spectrum very similar to that observed in the present experiment.
21 D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 2244.
22 A. Balikungeri, M. Pelletier and D. Monnier, *Inorg. Chim. Acta*, 1977, **22**, 7.
23 A. Balikungeri and M. Pelletier, *Inorg. Chim. Acta*, 1978, **29**, 141.