

Kinetics and mechanism of oxidation of nitrilotriacetic acid by diperiodatoargentate(III)

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ABSTRACT: Diperiodatoargentate(III) oxidizes nitrilotriacetic acid in a mildly basic medium to produce formaldehyde and ammonia. This reaction follows a complex kinetic behaviour. The axial binding of NTA to silver(III) complex takes place on the millisecond time-scale with a second-order rate constant of $(4.8 \pm 0.5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Two electrons are transferred from bound NTA to the silver(III) centre sequentially. At low [NTA] ($< 1 \times 10^{-3} \text{ mol dm}^{-3}$), the rate law follows first-order kinetics with respect to NTA but at high [NTA] it becomes independent of its concentration. The first electron is transferred to the silver(III) centre with a second-order rate constant of $(7.2 \pm 0.5) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The second electron is transferred subsequently in the fast step from NTA radical to the silver(II) species. The latter stages of reaction consists of a composite process involving the oxidation of NTA and its products in parallel reactions. Kinetic experiments suggest that $[\text{Ag}^{\text{III}}(\text{H}_3\text{IO}_6)(\text{H}_2\text{O})_2]^+$ is the reactive silver(III) species involved. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: nitrilotriacetic acid oxidation kinetics; silver(III) oxidation; diperiodatoargentate(III) oxidation; reaction mechanism

INTRODUCTION

The chemistry of the unusual oxidation state species of silver has attracted considerable attention in the recent past because of their high redox potentials and their involvement in Ag^+ -catalysed redox reactions.^{1–7} Reactions of silver(III) species have generated further interest mechanistically, being a two-electron oxidant. The reduction of Ag(III) to Ag(I) may occur either by simultaneous two-electron transfer in a single step or in two successive one-electron steps. Various oxidants containing a silver(III) centre,^{5–8} e.g. $[\text{Ag}(\text{OH})_4]^{5,6}$ and [ethylenebis(biguanide)]silver(III),⁷ have been employed. Reactions of $[\text{Ag}(\text{OH})_4]^-$ are in general fairly fast and have to be monitored using the stopped-flow technique. In contrast, reactions of other silver(III) complexes are fairly slow.^{7,8} $[\text{Ag}(\text{OH})_4]^-$ is stable in highly alkaline medium^{5,6} whereas [ethylenebis(biguanide)]silver(III) cation is stable in highly acidic solutions.⁷ Moreover, in the investigations cited, mechanistic observations of the interaction of redox species and the mode of electron transfer were at variance. Hence further extensive studies of these reactions are required to establish a general conclusion. In the present work, we

examined the reaction of nitrilotriacetic acid (NTA) with the diperiodatoargentate(III) (DPA) complex in a moderately basic medium. DPA is known to be a relatively strong oxidant.¹ These investigations demonstrate step-wise electron transfer from axial bound NTA to the silver(III) centre.

EXPERIMENTAL

Reagents. NTA (Aldrich), KOH, AgNO_3 , sodium metabisulphite (BDH), 35% HCHO solution, $\text{K}_2\text{S}_2\text{O}_8$ (Merck), KClO_4 (Reidel de Haën), KIO_4 (Qualigen), acrylonitrile (SRL) and chromotropic acid (CDH) were of analytical grade. All chemicals except acrylonitrile and $\text{K}_2\text{S}_2\text{O}_8$ were used as received. Acrylonitrile and $\text{K}_2\text{S}_2\text{O}_8$ were purified by distillation and recrystallization to remove any traces of impurities. $\text{K}_2\text{S}_2\text{O}_8$ is known to decompose thermally and photochemically into SO_4^{2-} .^{9,10}

Equipment. The electronic spectra and slow kinetics were recorded on Shimadzu UV-2100/s and Beckman DU-6 spectrophotometers. Fast kinetic experiments were performed on an Applied Photophysics Model 1705 stopped-flow apparatus equipped with a DL-905 datalab transient digitizer.

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Synthesis. Sodium diperiodatoargentate(III) complex was prepared by following the reported method¹¹ by oxidation of Ag(I) with $S_2O_8^{2-}$ in the presence of KIO_4 . Its sodium salt was precipitated by the addition of NaOH, which produced a thick, reddish orange, crystalline product which was recovered by filtration through a G-3 frit and washed with cold water. The crystals thus obtained were recrystallized from water and recovered after washing with cold water. The product was stored in a dark bottle under vacuum. The formation of DPA was confirmed by its characteristic electronic spectrum, having three peaks at 213, 255 and 362 nm and a molar absorptivity of $1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 362 nm, in agreement with the earlier reports.¹¹ This complex had a magnetic moment value of 0.4 BM, which suggests it to be diamagnetic. Its oxidizing power was checked by liberating I_2 from KI.

Schiff's¹² and Nessler's¹³ reagents were prepared by following the literature methods.

Methodology. Chromotropic acid (10%) was used as a specific reagent for the detection of formaldehyde.¹⁴ It produces a violet colour which exhibits λ_{\max} at 570 nm. The amount of formaldehyde in unknown samples was estimated spectrophotometrically by preparing a calibration graph with an authentic sample at 570 nm. Nessler's reagent was used to test the formation of ammonia, which produces an orange-brown colour with this reagent. Its concentration in an unknown sample was measured spectrophotometrically at 415 nm¹³ by plotting a calibration graph with known concentrations of ammonia solutions.

The kinetics of the reaction were monitored by following the disappearance of absorption due to silver(III) species at 360 nm, where NTA has no absorption. Most of the kinetic experiments were designed under pseudo-kinetic conditions with NTA about 50 times in excess over DPA. Reactions were followed up to about 70% of their completion. The stoichiometry of the reaction was determined by measuring the amount of unreacted DPA spectrophotometrically at 360 nm.

RESULTS AND DISCUSSION

Product analysis

Upon mixing DPA ($4 \times 10^{-4} \text{ mol dm}^{-3}$) with NTA ($5 \times 10^{-3} \text{ mol dm}^{-3}$) at pH 10.5, the yellow colour of DPA disappeared within a few minutes. The product of this reaction was identified to be an aldehyde with Schiff's reagent. The production of a violet colour with chromotropic acid confirmed it to be formaldehyde.¹⁴ The amount of HCHO formed was estimated as a function of [NTA] (Fig. 1). In the low concentration range of NTA ($< 4 \times 10^{-3} \text{ mol dm}^{-3}$), the amount of

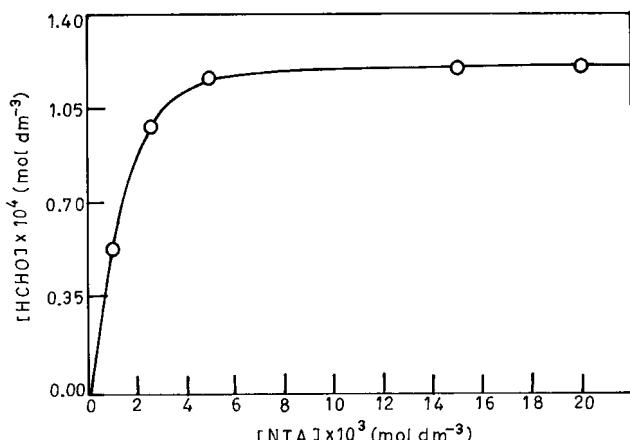
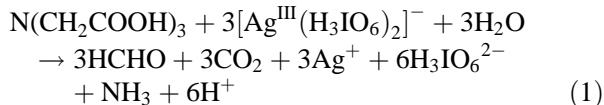


Figure 1. Amount of formaldehyde formed as a function of [NTA]

HCHO increased with increase in [NTA] but it attained a limiting value at high [NTA]. This suggested that at high [NTA], the HCHO formed undergoes further oxidation which restricts its amount. This could be verified by performing the oxidation of HCHO by DPA, which occurs efficiently under the experimental conditions used. HCHO formation does not take place in the reaction of NTA with periodate and NTA does not interfere with this test. The formation of free Ag^+ during the reaction course was tested by adding KCl, which produced a white precipitate of $AgCl$. The formation of ammonia was detected with Nessler's reagent, which produced an orange-brown colour with the above reaction mixture. For typical concentrations of DPA ($1.5 \times 10^{-5} \text{ mol dm}^{-3}$) and NTA ($3.0 \times 10^{-4} \text{ mol dm}^{-3}$), the concentration of NH_3 was estimated to be $0.25 \times 10^{-5} \text{ mol dm}^{-3}$. Hence the reaction involved may be



Stoichiometry

The reaction mixture containing NTA ($1 \times 10^{-4} \text{ mol dm}^{-3}$) and DPA ($1.1 \times 10^{-3} \text{ mol dm}^{-3}$) was left overnight for completion of the reaction. By estimating the amount of unreacted DPA at 360 nm, the stoichiometry of the reaction was determined to be about 1:5.7 (NTA:DPA). In view of reaction (1), the reaction obviously involves partial oxidation of products of oxidation also by silver(III) species. Had silver(III) alone participated in the oxidation process, the stoichiometry of the reaction would have been 1:6 (NTA:DPA). Apparently, the free periodate ion released in the solution by the decomposition of DPA might be contributing to a small extent to the oxidation of reactant and product. In blank

Table 1. Pseudo-first-order rate constants^a at different [NTA] and $[\text{OH}^-]$ for two-stage reaction^b

$[\text{OH}^-] \times 10^3$ (mol dm ⁻³)	$[\text{NTA}] \times 10^3$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	$k_2 \times 10^3$ (s ⁻¹)
0.32	0.50	3.8	5.5
0.32	0.75	5.3	8.9
0.32	1.00	6.7	10.3
0.32	1.50	9.0	10.7
0.32	2.00	9.4	11.0
0.32	2.50	10.3	11.4
0.32	3.00	10.6	14.0
0.57	2.50	8.1	10.0
0.82	2.50	7.3	9.0
1.07	2.50	6.4	7.7
1.32	2.50	5.5	6.7
1.57	2.50	4.6	5.7

^a k_1 and k_2 are pseudo-first-order rate constants for the initial and latter stages of reaction respectively. k_2 denotes the composite rate constant comprising k_1 , k' and k'' (k' and k'' are depicted in Scheme 1).

^b $I = 1.57 \times 10^{-3}$ mol dm⁻³ (KClO₄); [DPA] = 5×10^{-5} mol dm⁻³.

experiments, reactions of periodate (1×10^{-4} mol dm⁻³) were carried out with NTA (2×10^{-3} mol dm⁻³) and HCHO (2.5×10^{-3} mol dm⁻³) separately by monitoring periodate at 275 nm. Periodate reacted slowly with both of these substrates. In about 6 h, only 40% and 15% of periodate was consumed with NTA and HCHO, respectively.

Kinetic Studies

Complexation. To analyse the nature of the interaction between DPA and NTA, electronic spectra of the reactants and their reaction mixture were recorded. The absorption spectrum of the reaction mixture did not show any additional peak other than those of the reactants, except that a slight red shift was noted in the 362 nm peak of DPA. This is possibly due to complexation of NTA with DPA. The resulting absorption then simply decayed with time over the entire recorded wavelength range (280–500 nm) without producing any new peak. On the basis of the observed magnetic moment of 0.4 BM and comparison with other silver(III) systems,^{1,5,6,15} the geometry of DPA has been considered to be square planar, analogous to the diperiodatocuprate(III) complex.¹⁶ Hence only an axial position is available for nucleophilic attack by NTA which might be occurring in the fast step. A typical kinetic trace recorded in a stopped-flow experiment at 360 nm is shown in Fig. 2. Mixing of the two reactants exhibited a fast decay of DPA absorption in the millisecond time range, which recovered slightly to the seconds range. The recovery of absorption is possibly due to the rearrangement of the NTA-bound silver(III) complex before electron transfer

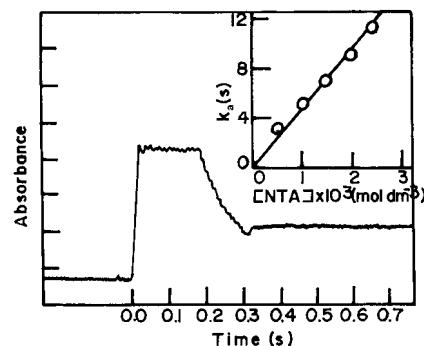


Figure 2. Kinetic trace for the uptake of NTA by DPA. Inset: dependence of the pseudo-first-order rate constant (k_a) on [NTA]. [DPA] = 5×10^{-5} mol dm⁻³; [NTA] = 2×10^{-3} mol dm⁻³

takes place. The initial decrease in absorbance showed a dependence on [NTA] (Fig. 2, inset) from which a second-order rate constant (k_a) of $(4.8 \pm 0.5) \times 10^3$ dm³ mol⁻¹ s⁻¹ is calculated for the uptake of NTA by DPA.

Effect of [NTA] on redox kinetics. Under pseudo-kinetic conditions, the decrease in absorbance of silver(III) species followed a complex kinetic behaviour. For the reaction mixtures containing DPA (5×10^{-5} mol dm⁻³) and various [NTA] (5×10^{-4} to 3×10^{-3} mol dm⁻³), the occurrence of two consecutive processes was recorded. Both processes followed pseudo-first-order kinetics. The pseudo-first-order rate constants for these processes are given in Table 1. A representative first-order plot is depicted in Fig. 3(a). The data in Table 1 [Inset: Fig. 3(a)] reveal that an increase in [NTA] up to 1.0×10^{-3} mol dm⁻³ enhanced the rate of reaction linearly but it became independent of [NTA] at higher concentrations. At low [NTA], the plot of $\log k_1$ vs $\log[\text{NTA}]$ gives a straight line with a slope of unity, which suggested that the order with respect to NTA is unity in this concentration range but becomes zero at high [NTA]. A plot of $1/k_1$ vs $1/[\text{NTA}]$ is, however, linear with an intercept [Fig. 3(b)]. This manifests kinetically the formation of an intermediate complex between DPA and

Table 2. Effect of [KIO₄] on pseudo-first-order rate constants^a

$[\text{KIO}_4] \times 10^4$ (mol dm ⁻³)	$k_1 \times 10^3$ (s ⁻¹)	$k_2 \times 10^3$ (s ⁻¹)
0.0	10.3	11.4
0.2	8.5	11.1
0.4	7.1	10.8
0.6	5.1	10.0
0.8	4.7	8.8
1.0	4.0	7.2

^a [DPA] = 5×10^{-5} mol dm⁻³; [NTA] = 2.5×10^{-3} mol dm⁻³; $[\text{OH}^-] = 0.32 \times 10^{-3}$ mol dm⁻³; $I = 1 \times 10^{-3}$ mol dm⁻³ (KClO₄).

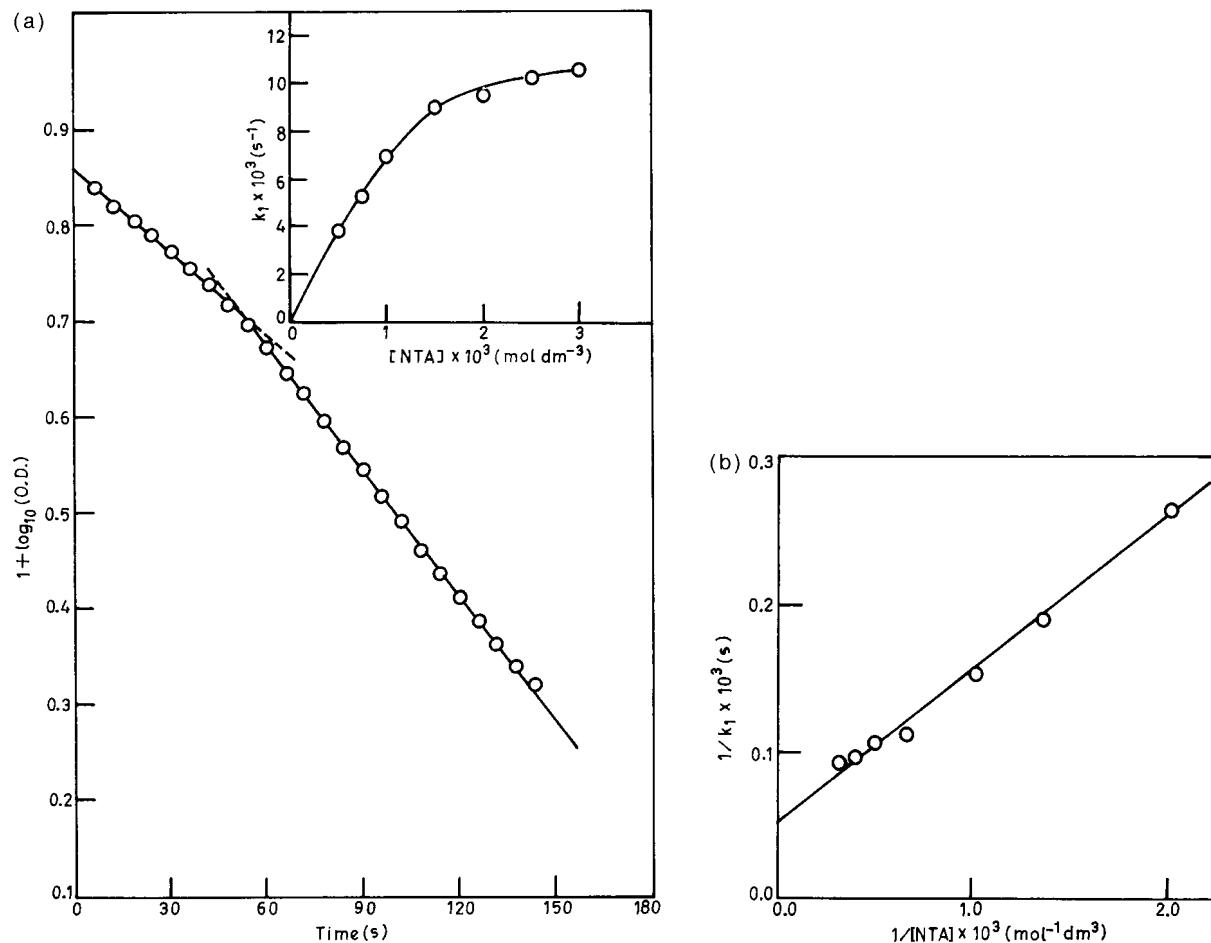


Figure 3. (a) Pseudo-first-order kinetic plots with $[\text{DPA}] = 5 \times 10^{-5}$ mol dm⁻³, $[\text{NTA}] = 1.0 \times 10^{-3}$ mol dm⁻³ and $[\text{OH}^-] = 3.2 \times 10^{-4}$ mol dm⁻³. Inset: dependence of pseudo-first-order rate constant (k_1) on [NTA]. (b) Plot of $1/k_1$ vs $1/[\text{NTA}]$

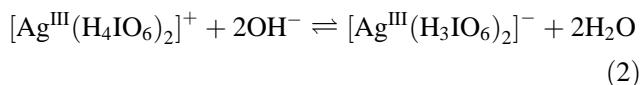
NTA. From the slope and intercept of this plot, the rate constants $k_{a'}$ and k_b (see below, Scheme 1) were calculated to be 10.06 and 0.02 s⁻¹, respectively.

The higher values of k_2 in Table 1 suggest that the second process might involve a composite reaction comprising simultaneous oxidation of NTA and its oxidation products. This was checked in an independent experiment by performing the oxidation of one of the products, HCHO, under identical pseudo-kinetic conditions with DPA. This reaction occurred efficiently with a second-order rate constant of 0.5 dm³ mol⁻¹ s⁻¹.

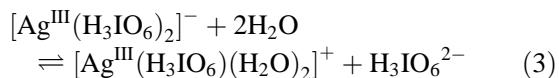
Effect of ionic strength. An increase in the ionic strength of the medium by adding a solution of neutral salt, KClO_4 , up to 0.01 mol dm⁻³, did not result in any change in the rate of reaction. This suggests that one of the reactive species in the reaction is neutral. It is therefore likely that uncharged NTA participates in the reaction.

Effect of [Periodate] and $[\text{OH}^-]$. In view of the periodate being the ligand in DPA, it was necessary to investigate the effect of [periodate] on the reaction

kinetics. At $\text{pH} < 8.0$, the predominant periodate species in solution will be H_4IO_6^- .¹⁷ Hence at low pH, DPA in solution can be represented as $[\text{Ag}^{\text{III}}(\text{H}_4\text{IO}_6)_2]^+$. Since the second $\text{p}K$ of the periodate monoanion in water is 8.36, in the basic medium used the important ligand species will be $\text{H}_3\text{IO}_6^{2-}$. The protonated and deprotonated DPA can be represented by the following equilibrium:



An increase in [periodate] reduced the rate of the DPA-NTA reaction drastically, as shown by the data in Table 2. The inverse rate dependence on [periodate] indicates a dissociation pre-equilibrium in which $[\text{Ag}^{\text{III}}(\text{H}_3\text{IO}_6)_2]^-$ loses a periodate ligand:



The above equilibrium clearly suggests that the monoperiodatosilver(III) complex is the reactive species in the reaction since an increase in [periodate] will shift

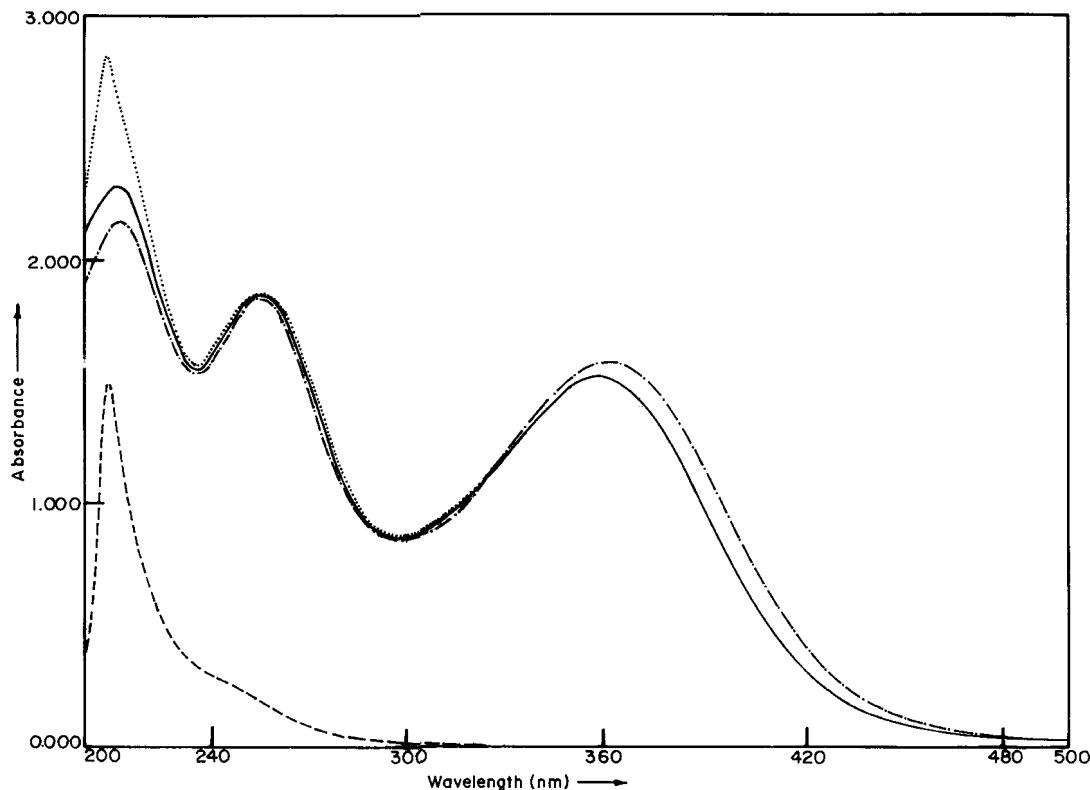
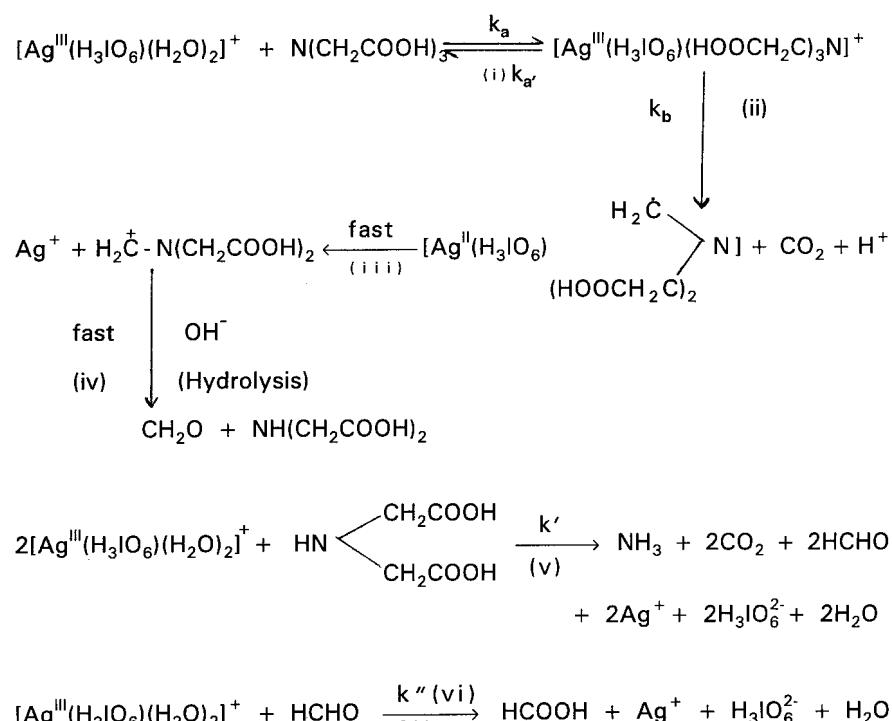


Figure 4. Electronic spectra of DPA (1.1×10^{-4} mol dm $^{-3}$) at pH (—) 9.5, (—) 10.7 and (· · ·) 11.3. Dashed line (— —), absorption spectrum of periodate (5×10^{-5} mol dm $^{-3}$) at pH 11.3



Scheme 1

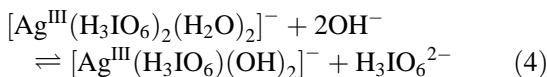
Table 3. Effect of [acrylonitrile] on pseudo-first-order rate constants^a

[Acrylonitrile] $\times 10^3$ (mol dm $^{-3}$)	$k_1 \times 10^3$ (s $^{-1}$)	$k_2 \times 10^3$ (s $^{-1}$)
0.0	10.3	11.4
1.5	9.6	11.0
3.0	9.0	10.7
5.0	8.8	10.4
7.5	8.4	9.8
10.0	8.3	9.7
15.0	8.2	9.6

^a[DPA] = 5×10^{-5} mol dm $^{-3}$; [NTA] = 2.5×10^{-3} mol dm $^{-3}$; [OH $^-$] = 0.32×10^{-3} mol dm $^{-3}$.

the equilibrium to the left to produce a diperiodato complex, which in turn reduces the rate of reaction.

A change in pH modifies the electronic spectrum of DPA. The absorption spectra of DPA in the pH range 9.5–11.3 are depicted in Fig. 4. The results show that an initial increase in pH causes a decrease in absorption at 362 nm with a slight blue shift along with a simultaneous increase in absorption around 210 nm. These changes exhibit an isosbestic point at 325 nm. Periodate shows absorption in 200–300 nm range (Fig. 4; dashed curve). This is exactly the wavelength range in which the increase in absorption is observed in Fig. 4 upon addition of OH $^-$ to DPA solution. Obviously, more of periodate is produced by adding OH $^-$ to the DPA solution:



The hydroxylation of silver(III)¹⁸ and Cu(III)¹⁹ species has also been proposed earlier.

The rate of the DPA–NTA reaction decreases with increase in [OH $^-$] (Table 1). In terms of the equilibrium shown in Eqn 4, the observed decrease in rate can be understood as being due to the formation of hydroxylated silver(III) species and free periodate ion. Apparently, the hydroxylated silver(III) species should be less reactive than the aquated silver(III) species and the periodate ions cause an inhibitory effect (see above).

Effect of [acrylonitrile]. The nature of the reaction was examined by following the reaction in the presence of a radical scavenger, acrylonitrile. The addition of acrylonitrile retarded the rate of reaction (Table 3). In the presence of 2×10^{-2} mol dm $^{-3}$ of acrylonitrile, the yield of ammonia was reduced by 40%. In a blank experiment it was observed that DPA did not react with acrylonitrile in the concentration range studied. These observations suggest the operation of a free radical mechanism.

In the light of the above results, the sequence of reaction steps can be outlined as shown in Scheme 1.

The observed kinetic features are consistent with the proposed Scheme 1. In the NTA–DPA reaction, mono-

periodatosilver(III) is the reactive species. NTA binds to this species axially in a bimolecular step to produce an intermediate complex. Initial electron transfer from NTA to the silver(III) centre occurs in the slow step to produce NTA radical, which is then oxidized by silver(II) in the fast step to yield HCHO and Ag $^{+}$. Silver(II) is known to oxidize NTA with a rate constant of $(2 \pm 0.5) \times 10^3$ s $^{-1}$.^{4a} The observed stoichiometry is in accordance with the involvement of silver(III) species in the oxidation of HCHO as shown in reaction (vi). It is also indicated by the higher value of rate constant (k_2) (Table 1) for the second stage of the reaction. Acrylonitrile possibly binds the NTA radical formed within the silver complex which inhibits its decomposition. It thus retards the rate of the reaction and eventually reduces the yield of products. The proposed reaction scheme parallels the Michaelis–Menten type of mechanism observed in enzyme-catalysed reactions.

The important outcomes of this work are that the reduction of silver(III) species occurs stepwise through sequential electron transfer from NTA and this reaction could be performed in a moderately basic medium. Although different silver(III) species are known to form in different pH conditions,¹⁸ their reactions could not be investigated owing to the strong reactivity of their precursors, Ag(II) intermediates, with the substrates⁴ in the pH range 4–10.

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