

Kinetic and Mechanistic Study of the Oxidation of L-Serine by Diperioatoargentate(III) in Aqueous Alkaline Medium

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ABSTRACT:

The kinetics of oxidation of L-serine by diperioatoargentate(III) (DPA) has been studied spectrophotometrically in aqueous alkaline (KOH) medium at 298 K and a constant ionic strength of 0.10 mol dm^{-3} . The reaction was followed at 360 nm under pseudo-first-order conditions with serine in excess over DPA. The disappearance of DPA is first order, and the pseudo-first-order rate constant at the standard conditions is $k_{\text{obs}} = 0.43 \times 10^{-4} \text{ s}^{-1}$, independent of the initial [DPA]. The reaction shows fractional positive-order dependence on serine ($n = 0.68$, $R^2 = 0.9990$) and hydroxide ion ($n = 0.62$, $R^2 = 0.9540$), and fractional negative-order dependence on periodate ion ($n = -0.34$, $R^2 = 0.9908$). The rate increases slightly with ionic strength and decreases with increasing dielectric constant of the medium; added Ag(I), a reaction product, has no systematic effect. The stoichiometry is 1:1 (mean DPA/serine consumption ratio 0.975 ± 0.028). The rate constant increases from 0.43×10^{-4} to $1.02 \times 10^{-4} \text{ s}^{-1}$ between 298 and 313 K, giving $E_a = 45.20 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 42.66 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -185.32 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger = 97.89 \text{ kJ mol}^{-1}$ at 298 K. A mechanism involving a pre-equilibrium hydrolysis of DPA to the reactive monoperioatoargentate(III) (MPA) species, formation of a 1:1 serine-MPA complex and its slow decomposition is proposed, and the rate law derived from it accounts for the observed orders.

KEYWORDS: Kinetics, Oxidation, Mechanism, L-Serine, Diperioatoargentate(III), Alkaline medium, Activation parameters.

I. INTRODUCTION

Oxidation reactions are of fundamental importance in organic synthesis, industrial processes and biological systems [1, 2]. The kinetics and mechanism of oxidation of amino acids are of particular interest because amino acids are the building blocks of proteins and take part in numerous metabolic pathways [3–5]. Amino acids have been oxidised by a wide range of oxidants in acidic and alkaline media [6–10], and recent work has extended such studies to micellar and catalysed systems [11–16]. The mechanism, however, differs considerably with the oxidant and the medium, and the reactions may proceed by oxidative deamination, oxidative decarboxylation or a combined deamination–

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decarboxylation pathway [8, 9].

Silver(III) complexes stabilised by periodate ligands have attracted attention as two-electron oxidants with well-defined redox chemistry [17–20]. Diperiodatoargentate(III) (DPA) is stable in alkaline solution, gives a kinetically inert Ag(I) product, and has a characteristic absorption near 360 nm that allows convenient spectrophotometric monitoring [21, 22]. In alkaline medium DPA is in equilibrium with the monoperiodatoargentate(III) species (MPA) and free periodate, which accounts for the positive hydroxide and negative periodate dependences that characterise DPA oxidations [21–23]. Oxidations of L-valine, L-tryptophan and L-lysine by DPA have been reported [21–23].

L-Serine (2-amino-3-hydroxypropanoic acid) is a non-essential α -amino acid with a hydroxymethyl side chain. It is the biosynthetic precursor of glycine, cysteine and phospholipids and plays important roles in cellular metabolism, neurotransmission and neuroprotection [24–29]. The oxidation of serine has been examined with oxidants such as cerium(IV) [7] and in auto-catalysed systems [30], but to the best of our knowledge the oxidation of serine by DPA in alkaline medium has not been reported. The present work therefore examines the kinetics of this reaction, evaluates the activation parameters, establishes the stoichiometry and the nature of the products, and proposes a mechanism with a rate law consistent with the experimental orders.

II. MATERIALS AND METHOD

Analytical-reagent grade chemicals and doubly distilled water were used throughout. Stock solutions of L-serine, KOH, KIO_4 , KNO_3 and AgNO_3 were prepared by weighing and diluting with doubly distilled water. DPA was prepared by oxidising silver(I) nitrate with potassium persulphate in the presence of excess potassium periodate in alkaline medium, following the established procedure [31, 32]: KOH (28 g) and KIO_4 (23 g) were dissolved in 100 cm³ of water, AgNO_3 (8.5 g) was added, the mixture was heated to boiling, and $\text{K}_2\text{S}_2\text{O}_8$ (20 g) was added in portions with stirring. After cooling and filtration through a fritted-glass filter, the filtrate was treated with NaOH (40 g) to precipitate the orange complex, which was washed with cold water, redissolved in 50 cm³ of water at about 80 °C, filtered and cooled to give orange DPA crystals. Working solutions were prepared by dissolving the crystals in alkaline solution, and their concentration was standardised spectrophotometrically from the absorption maximum at 360 nm ($\epsilon \approx 1.26 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [33].

Kinetic runs were carried out under pseudo-first-order conditions with serine in excess over DPA. The reaction was initiated by adding thermostatted DPA solution to the mixture of serine, KOH, KIO_4 and KNO_3 (used to adjust the ionic strength) that had been equilibrated at the desired temperature, and the decay of absorbance at 360 nm was recorded at 10 min intervals up to 90 min in a 1 cm quartz cell using a Systronics Model 166 UV-Visible spectrophotometer. The temperature was controlled to ± 0.1 K with a thermostatted water bath. The standard conditions were $[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{serine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$ and $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.10 \text{ mol dm}^{-3}$ and $T = 298 \text{ K}$. Since absorbance is proportional to $[\text{DPA}]$, the pseudo-first-order rate constant k_{obs} was obtained from the slope of the linear plot of $\ln(A_0/A_t)$ against time:

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$$\ln \left(\frac{A_0}{A_t} \right) = k_{\text{obs}} t \quad (1)$$

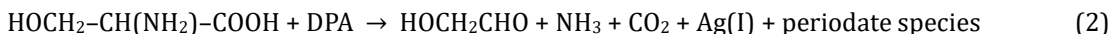
The effect of each reactant was studied by varying its concentration while keeping the others constant. The dielectric constant was varied with *t*-butanol–water mixtures, and the ionic strength with KNO₃. The effect of the reduction product was examined by adding Ag(I) initially. Activation parameters were obtained from the Arrhenius and Eyring relationships [34–36], with $\Delta H^\ddagger = E_a - RT$ and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

For the stoichiometry, mixtures containing different initial amounts of DPA and serine were allowed to react to completion at 298 K and the amounts consumed were determined from the residual reactants. Ammonia was detected with Nessler's reagent and carbon dioxide with lime water [37]; the organic product was tested with 2,4-dinitrophenylhydrazine (2,4-DNPH) for a carbonyl group [38]. The acrylonitrile polymerisation test for free-radical intermediates [39] was carried out on three independent reaction mixtures kept under nitrogen for 24 h at 298 K.

III. RESULTS AND DISCUSSION

Stoichiometry and product analysis

Reaction mixtures with different initial amounts of DPA and serine gave DPA-to-serine consumption ratios of 0.975, 1.000, 0.933, 0.967 and 1.000 (Table 1), a mean of 0.975 ± 0.028 . The plot of serine consumed against DPA consumed is linear (slope ≈ 1.01 , $R^2 = 0.9889$; Fig. 1), supporting a 1:1 stoichiometry [21]. Nessler's test for ammonia and the lime-water test for carbon dioxide were positive, and the organic product gave a positive 2,4-DNPH test for a carbonyl compound. The FT-IR spectrum of the 2,4-DNPH derivative shows the broad absorption around 3330 cm^{-1} is assigned to N–H stretching, whereas the band at 2930 cm^{-1} corresponds to aliphatic C–H stretching. The absorption near 1620 cm^{-1} is attributed to the C=N stretching vibration of the hydrazone group formed during derivatization with 2,4-DNPH. On this basis, and by analogy with the oxidative deamination–decarboxylation of amino acids by Ag(III) and other oxidants [7, 31], the organic product is assigned as glycolaldehyde. The reduction product of DPA is Ag(I). The overall reaction is represented by Eq. (2):

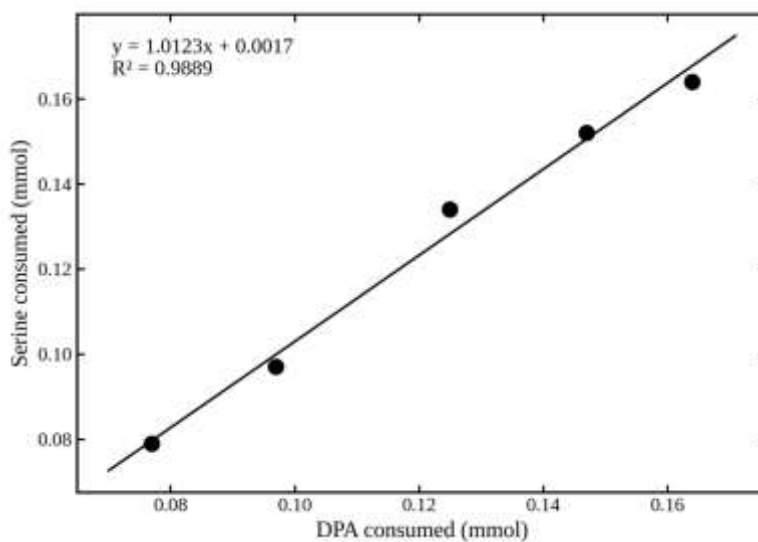


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Table 1. Stoichiometric analysis of the oxidation of L-serine by DPA at 298 K

Run	DPA initial (mmol)	Serine initial (mmol)	DPA consumed (mmol)	Serine consumed (mmol)	DPA/serine ratio
1	0.100	0.120	0.077	0.079	0.975
2	0.120	0.150	0.097	0.097	1.000
3	0.150	0.180	0.125	0.134	0.933
4	0.180	0.220	0.147	0.152	0.967
5	0.200	0.250	0.164	0.164	1.000

Fig. 1. Plot of serine consumed versus DPA consumed (slope ≈ 1.01 , $R^2 = 0.9889$; data of Table 1).

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Effect of [DPA]

The initial concentration of DPA was varied from 2.0×10^{-5} to 8.0×10^{-5} mol dm⁻³ at fixed [serine], [KOH], [IO₄⁻], *I* and *T*. The absorbance fell steadily at each concentration, and the plots of $\ln(A_0/A_t)$ versus time were linear and parallel (Fig. 2), showing first-order disappearance of DPA. The values of k_{obs} lay between 0.42×10^{-4} and 0.45×10^{-4} s⁻¹ (mean 0.43×10^{-4} s⁻¹, Table 2), i.e. k_{obs} is independent of the initial [DPA] and the order with respect to DPA is unity.

Table 2 : Effect of DPA, Serine, KOH, IO₄⁻ on the oxidation of Serine by DPA in alkaline Medium at 298 K.

10^5 [DPA] M	10^4 [Serine] M	[KOH] M	10^5 [IO ₄ ⁻] M	10^4 k_{obs} s ⁻¹
2.0	5.0	0.08	5.0	0.43
3.0	5.0	0.08	5.0	0.43
4.0	5.0	0.08	5.0	0.43
5.0	5.0	0.08	5.0	0.43
6.0	5.0	0.08	5.0	0.43
7.0	5.0	0.08	5.0	0.43
8.0	5.0	0.08	5.0	0.43
5.0	1.0	0.08	5.0	0.14
5.0	2.0	0.08	5.0	0.23
5.0	3.0	0.08	5.0	0.30
5.0	4.0	0.08	5.0	0.37
5.0	5.0	0.08	5.0	0.43
5.0	6.0	0.08	5.0	0.48
5.0	7.0	0.08	5.0	0.52
5.0	5.0	0.04	5.0	0.32
5.0	5.0	0.05	5.0	0.37
5.0	5.0	0.06	5.0	0.42
5.0	5.0	0.08	5.0	0.43
5.0	5.0	0.10	5.0	0.61

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10^5 [DPA] M	10^4 [Serine] M	[KOH] M	10^5 [IO ₄ ⁻] M	10^4 k _{obs} s ⁻¹
5.0	5.0	0.12	5.0	0.66
5.0	5.0	0.16	5.0	0.73
5.0	5.0	0.08	2.0	0.58
5.0	5.0	0.08	3.0	0.50
5.0	5.0	0.08	4.0	0.46
5.0	5.0	0.08	5.0	0.43
5.0	5.0	0.08	6.0	0.41
5.0	5.0	0.08	7.0	0.37
5.0	5.0	0.08	8.0	0.36

[serine] = 5.0×10^{-4} , [KOH] = 0.08, [IO₄⁻] = 5.0×10^{-5} mol dm⁻³; *I* = 0.10 mol dm⁻³; *T* = 298 K.

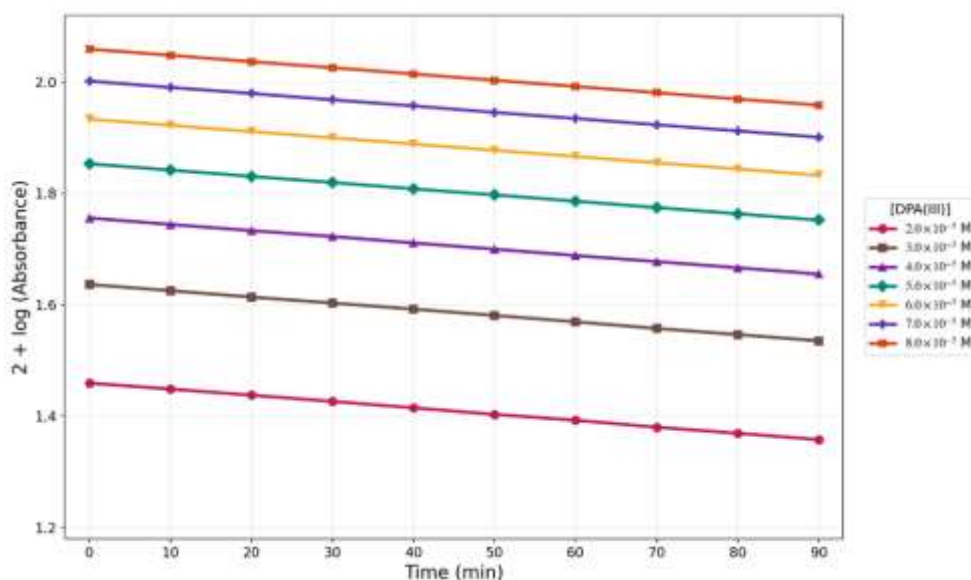


Fig. 2. Pseudo-first-order plots for the variation of [DPA] (data of Table 2).

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Effect of [Serine]

The serine concentration was varied from 1.0×10^{-4} to 7.0×10^{-4} mol dm⁻³. The rate constant increased from 0.14×10^{-4} to 0.52×10^{-4} s⁻¹ (Fig. 3a). The plot of $\log k_{\text{obs}}$ against $\log [\text{serine}]$ is linear ($R^2 = 0.9990$) with a slope of 0.68 (Fig. 3b), i.e. a fractional positive order. The plot of $1/k_{\text{obs}}$ against $1/[\text{serine}]$ is linear with a positive intercept ($R^2 = 0.9963$; Fig. 3c), which is characteristic of the formation of a substrate-oxidant complex in a pre-equilibrium step before the rate-determining step [9, 23]. The fractional order shows that the rate tends towards saturation as the substrate concentration increases.

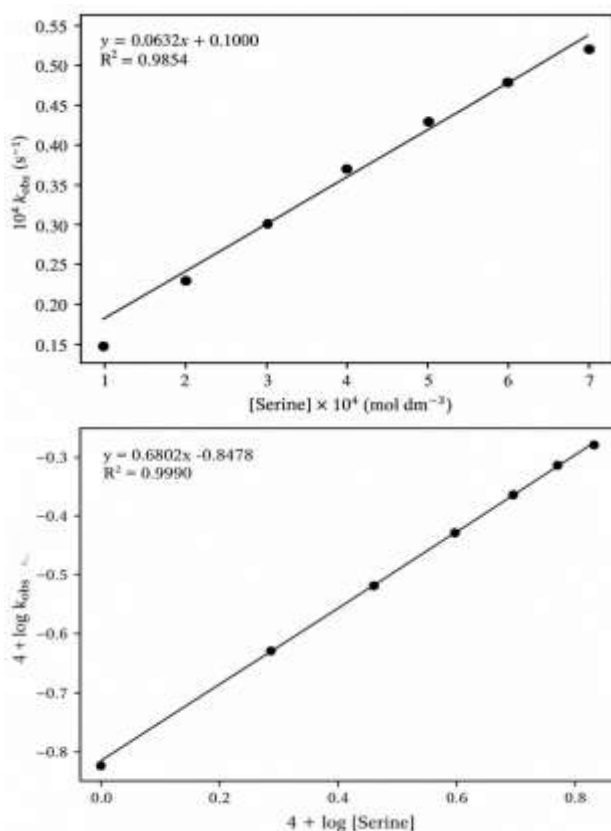


Fig. 3 (a, b). Effect of [serine]: (a) k_{obs} versus [serine]; (b) $\log k_{\text{obs}}$ versus $\log [\text{serine}]$
 [DPA] = 5.0×10^{-5} , [KOH] = 0.08, $[\text{IO}_4^-]$ = 5.0×10^{-5} mol dm⁻³; I = 0.10 mol dm⁻³; T = 298 K.

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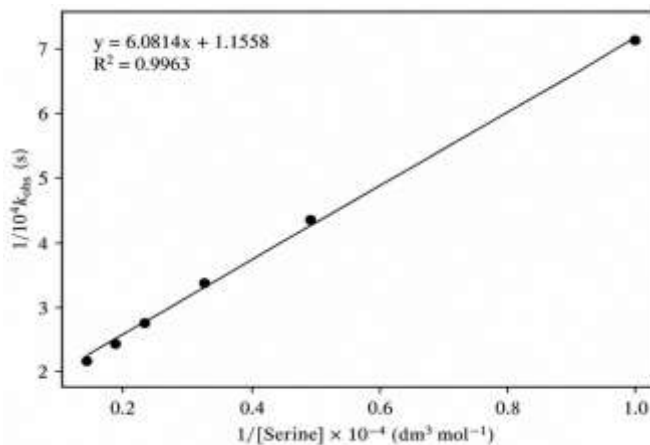
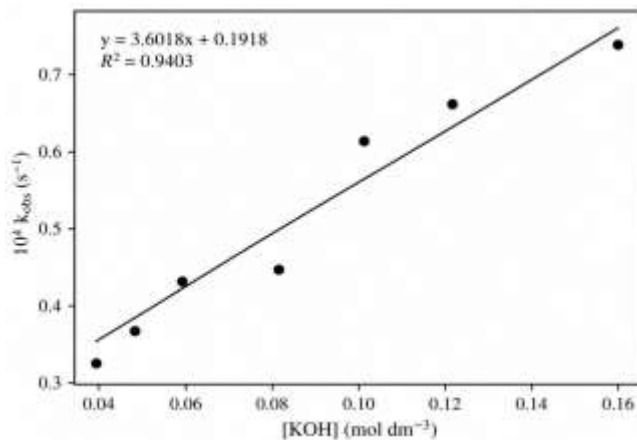


Fig. 3(c). Plot of $1/k_{\text{obs}}$ versus $1/[\text{serine}]$

$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $T = 298 \text{ K}$.

Effect of $[\text{KOH}]$

The hydroxide concentration was varied from 0.04 to 0.16 mol dm^{-3} at constant ionic strength. The rate constant increased from 0.32×10^{-4} to $0.73 \times 10^{-4} \text{ s}^{-1}$ (Fig. 4a). The plot of $\log k_{\text{obs}}$ versus $\log [\text{KOH}]$ gave a positive fractional order of 0.62 ($R^2 = 0.9540$; Fig. 4b). This indicates that hydroxide takes part in a pre-equilibrium rather than as a simple reactant in the rate-determining step, consistent with the hydroxide-assisted formation of the reactive MPA species [22, 23].



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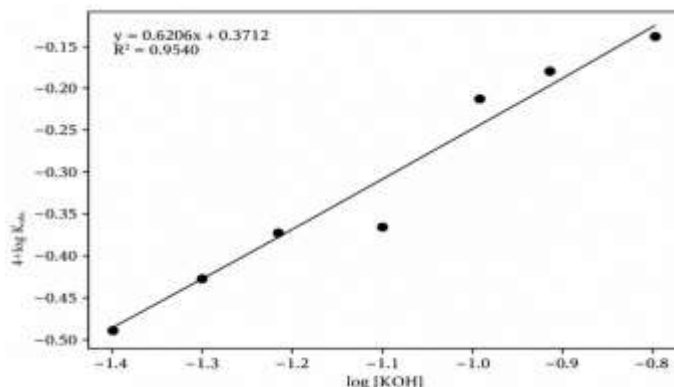


Fig. 4. Effect of [KOH]: (a) k_{obs} versus [KOH]; (b) $\log k_{\text{obs}}$ versus $\log [\text{KOH}]$ (data of Table 4).

[DPA] = 5.0×10^{-5} , [serine] = 5.0×10^{-4} , $[\text{IO}_4^-]$ = 5.0×10^{-5} mol dm $^{-3}$; I = 0.10 mol dm $^{-3}$; T = 298 K.

Effect of $[\text{IO}_4^-]$

The periodate concentration was varied from 2.0×10^{-5} to 8.0×10^{-5} mol dm $^{-3}$. The rate constant decreased from 0.58×10^{-4} to 0.36×10^{-4} s $^{-1}$ (Fig. 5a). The log-log plot gave a fractional negative order of -0.34 ($R^2 = 0.9908$), and the plot of $1/k_{\text{obs}}$ against $[\text{IO}_4^-]$ is linear with a positive intercept ($R^2 = 0.9835$; Fig. 5b). The retarding effect of periodate is consistent with the displacement of one periodate ligand from DPA in a pre-equilibrium, which is suppressed by free periodate and so lowers the concentration of the reactive MPA species [21, 22].

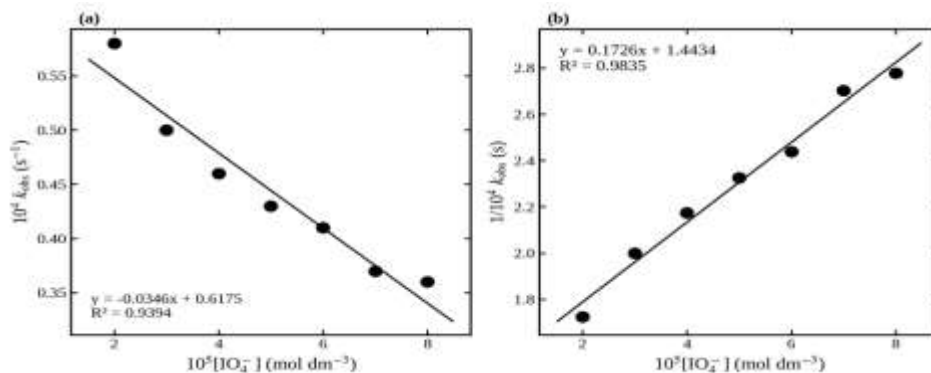


Fig. 5. Effect of $[\text{IO}_4^-]$: (a) k_{obs} versus $[\text{IO}_4^-]$; (b) $1/k_{\text{obs}}$ versus $[\text{IO}_4^-]$

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[DPA] = 5.0×10^{-5} , [serine] = 5.0×10^{-4} , [KOH] = 0.08 mol dm^{-3} ; $I = 0.10 \text{ mol dm}^{-3}$; $T = 298 \text{ K}$.

Effect of ionic strength, dielectric constant and added Ag(I)

The ionic strength was varied from 0.05 to 0.18 mol dm^{-3} with KNO_3 . The rate constant increased slightly, from 0.40×10^{-4} to $0.47 \times 10^{-4} \text{ s}^{-1}$ (Fig. 6), and the plot of $\log k_{\text{obs}}$ versus $\sqrt{I}$ has a small positive slope of about 0.368 ($R^2 = 0.9899$). Because the ionic strengths used lie beyond the limiting-law region, the Debye-Hückel treatment [40] is used only qualitatively: the small positive salt effect indicates that charged species are involved in the activated state, consistent with a reaction between like-charged ions (the anionic MPA species and the serine anion).

The dielectric constant was varied from 55 to 78 with *t*-butanol-water mixtures. The rate constant decreased from 0.47×10^{-4} to $0.41 \times 10^{-4} \text{ s}^{-1}$ as D increased, and the plot of $\log k_{\text{obs}}$ versus $1/D$ is linear with a positive slope of about 10.86 ($R^2 = 0.9685$; Fig. 7a). A decrease in rate with increasing D is the behaviour predicted for a reaction between ions of like charge [30, 41], in line with the salt effect.

Ag(I), the reduction product of DPA, was added initially from 0.00 to 0.20 mol dm^{-3} . The values of k_{obs} remained in the narrow range $(0.41\text{--}0.43) \times 10^{-4} \text{ s}^{-1}$ with no systematic trend (Fig. 7b), so there is no measurable product inhibition and Ag(I) does not take part in a kinetically significant pre-equilibrium or in the slow step.

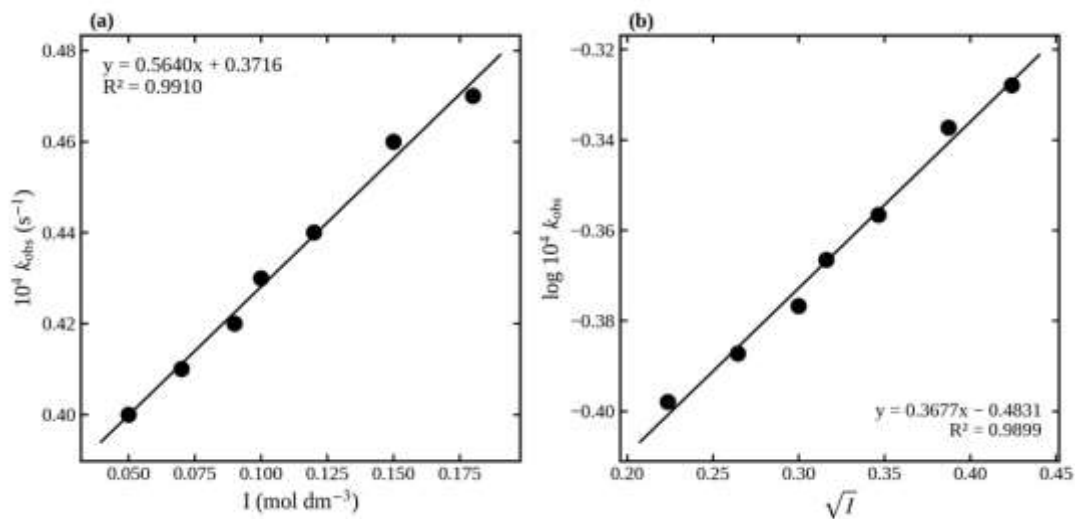


Fig. 6. Effect of ionic strength: (a) k_{obs} versus I ; (b) $\log k_{\text{obs}}$ versus $\sqrt{I}$

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$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{serine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $T = 298 \text{ K}$.

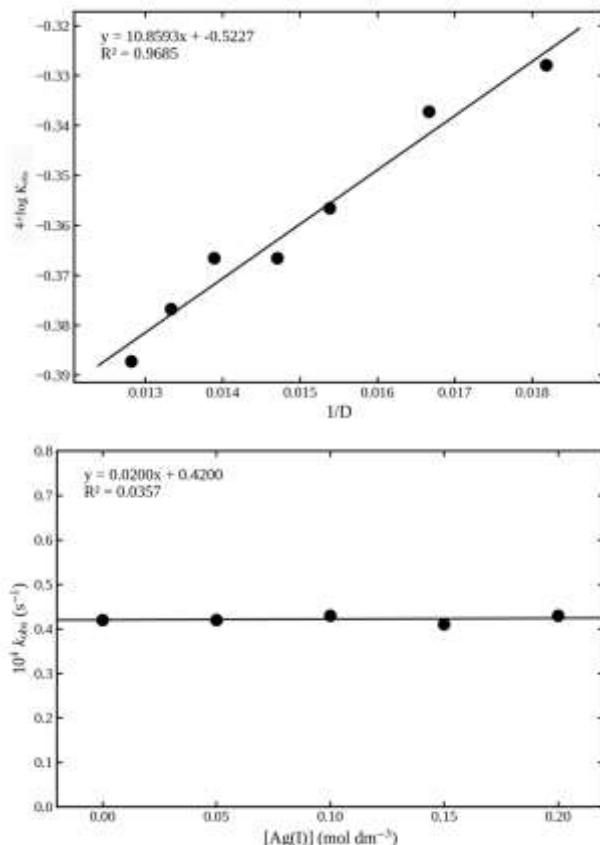


Fig. 7. (a) Plot of $\log k_{\text{obs}}$ versus $1/D$; (b) effect of added $[\text{Ag(I)}]$ on k_{obs}

$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{serine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $T = 298 \text{ K}$

Effect of temperature and activation parameters

The reaction was studied at 298, 303, 308 and 313 K under otherwise standard conditions. The rate constant increased from 0.43×10^{-4} to $1.02 \times 10^{-4} \text{ s}^{-1}$. The Arrhenius plot of $\ln k$ versus $1/T$ ($R^2 = 0.9980$) and the Eyring plot of $\ln(k/T)$ versus $1/T$ ($R^2 = 0.9977$) are linear (Fig. 8) and give the parameters in Table 3. The moderate activation energy and the large negative entropy of activation

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($-185.32 \text{ J mol}^{-1} \text{ K}^{-1}$) indicate an ordered, associative activated complex formed by close association of the substrate with the reactive Ag(III) species before electron transfer [9, 10].

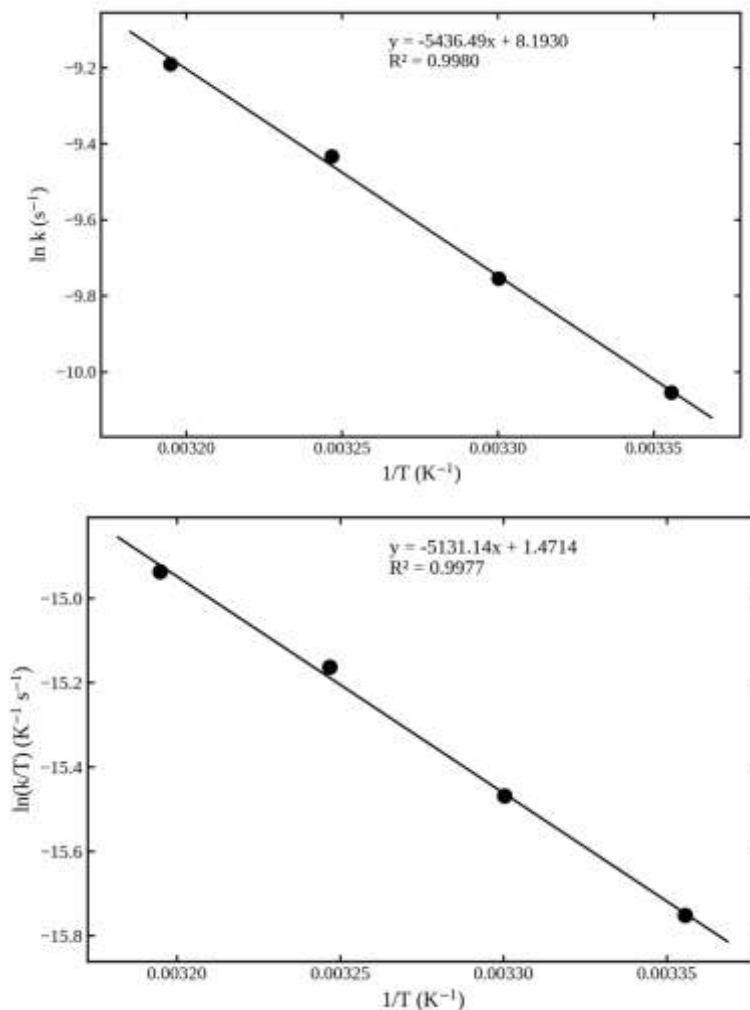


Fig. 8. (a) Arrhenius plot ($\ln k$ versus $1/T$); (b) Eyring plot ($\ln(k/T)$ versus $1/T$)

$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{serine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $D = 72$.

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Table 3: Activation parameters for the oxidation of L-serine by DPA (298–313 K)

Parameter	Value	Unit
E_a	45.20	kJ mol^{-1}
$\ln A$ ($\log A$)	8.193 (3.558)	$\ln \text{s}^{-1}$ ($\log \text{s}^{-1}$)
$\Delta H^\ddagger$	42.66	kJ mol^{-1}
$\Delta S^\ddagger$	-185.32	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta G^\ddagger$ (298 K)	97.89	kJ mol^{-1}
R^2 (Arrhenius / Eyring)	0.9980 / 0.9977	–

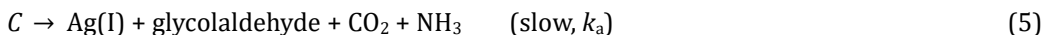
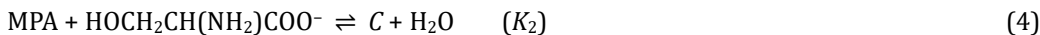
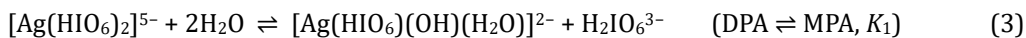
Test for free radicals

Three independent mixtures of DPA, serine, KOH and IO_4^- containing acrylonitrile were kept under nitrogen for 24 h at 298 K. No turbidity, precipitate or gel was observed in any replicate, so there is no evidence for polymerisable free-radical intermediates [39]. Because the test is qualitative, this supports a non-radical pathway but does not by itself prove a concerted two-electron transfer within the pre-formed substrate–oxidant complex [42].

Mechanism and rate law

The kinetic results are: first order in DPA; fractional positive orders in serine and hydroxide; a fractional negative order in periodate; a linear $1/k_{\text{obs}} - 1/[\text{serine}]$ plot with a positive intercept; a small positive salt effect and a negative dielectric effect; and no product inhibition. These are accommodated by Scheme 1, in which DPA is first hydrolysed to the reactive MPA species with release of periodate (K_1); MPA then forms a 1:1 complex C with the serine anion (K_2); and the complex decomposes in two parallel slow steps, spontaneously (k_a) and by hydroxide-assisted attack (k_b), to the products [21–23, 43].

Scheme 1. Proposed mechanism for the oxidation of L-serine by DPA



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From the equilibrium constants, $[MPA] = K_1[DPA]/[H_2IO_6^{3-}]$ and $[C] = K_2[MPA][\text{serine}] = K_1K_2[DPA][\text{serine}]/[H_2IO_6^{3-}]$. The rate through the two slow steps is $\text{Rate} = (k_a + k_b[OH^-])[C]$, and the total DPA is $[DPA]_T = [DPA] + [MPA] + [C] = [DPA]\{1 + K_1/[H_2IO_6^{3-}] + K_1K_2[\text{serine}]/[H_2IO_6^{3-}]\}$. Since $\text{Rate} = k_{\text{obs}}[DPA]_T$, the rate law is

$$k_{\text{obs}} = \frac{(k_a + k_b[OH^-]) K_1 K_2 [\text{serine}]}{[H_2IO_6^{3-}] + K_1 (1 + K_2 [\text{serine}])} \quad (7)$$

The rate law reproduces every observed dependence. The unit order in DPA follows because both pre-equilibria are written for DPA-derived species, so Rate is proportional to $[DPA]_T$. At low $[\text{serine}]$ the term $K_1K_2[\text{serine}]$ in the denominator is small and the rate is nearly first order in serine, whereas at higher $[\text{serine}]$ this term becomes comparable to $[H_2IO_6^{3-}] + K_1$, giving the fractional order and saturation. Since $[H_2IO_6^{3-}]$ increases with added periodate, k_{obs} falls as $[IO_4^-]$ rises, and the numerator term $k_b[OH^-]$, together with the hydroxide-promoted conversion of DPA to MPA, accounts for the positive fractional order in hydroxide. Inverting Eq. (7) gives the two linear forms that were tested experimentally:

$$\frac{1}{k_{\text{obs}}} = \frac{[H_2IO_6^{3-}] + K_1}{(k_a + k_b[OH^-]) K_1 K_2} \cdot \frac{1}{[\text{serine}]} + \frac{1}{k_a + k_b[OH^-]} \quad (8)$$

$$\frac{1}{k_{\text{obs}}} = \frac{[H_2IO_6^{3-}]}{(k_a + k_b[OH^-]) K_1 K_2 [\text{serine}]} + \frac{1 + K_2 [\text{serine}]}{(k_a + k_b[OH^-]) K_2 [\text{serine}]} \quad (9)$$

Eq. (8) predicts a linear $1/k_{\text{obs}}-1/[\text{serine}]$ plot with a positive intercept (Fig. 3c), and Eq. (9) a linear $1/k_{\text{obs}}-[H_2IO_6^{3-}]$ plot with a positive intercept, i.e. linear in $[IO_4^-]$ (Fig. 5b). The large negative $\Delta S^\ddagger$ agrees with an ordered activated complex formed from the substrate-MPA complex, the small positive salt effect and negative dielectric effect with charged species of like sign in the rate-determining step, and the absence of $Ag(I)$ inhibition with treating the decomposition of C as an effectively irreversible forward step. The proposed mechanism should be regarded as a plausible model consistent with the kinetic trends rather than a uniquely demonstrated elementary pathway.

IV. CONCLUSION

The oxidation of L-serine by diperiodatoargentate(III) in aqueous alkaline medium is first order in DPA and shows fractional positive orders in serine (0.68) and hydroxide (0.62) and a fractional negative order in periodate (-0.34). The stoichiometry is 1:1 (mean ratio 0.975 ± 0.028), with $Ag(I)$, ammonia, carbon dioxide and a carbonyl compound, assigned as glycolaldehyde, as the products. The rate increases slightly with ionic strength, decreases with increasing dielectric constant, and is

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unaffected by added Ag(I). The activation parameters are $E_a = 45.20 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 42.66 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -185.32 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger = 97.89 \text{ kJ mol}^{-1}$. The results are explained by a mechanism in which DPA is hydrolysed to the reactive monoperiodatoargentate(III) species, which forms a 1:1 complex with serine that decomposes in the slow step; the derived rate law accounts for the observed orders and the linear double-reciprocal plots. The negative acrylonitrile test gives no evidence for polymerisable free-radical intermediates.

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