

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

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ABSTRACT:

The kinetics of oxidation of L-arginine 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 arginine in excess over DPA. The reaction is first order in [DPA] ($k_{\text{obs}} = 0.52 \times 10^{-4} \text{ s}^{-1}$ at the standard conditions, independent of the initial [DPA]), shows fractional positive orders in arginine (0.53) and hydroxide ion (0.62), and a fractional negative order in periodate ion. A plot of $1/k_{\text{obs}}$ versus $1/[\text{arginine}]$ is linear with a non-zero intercept, consistent with a 1:1 complex between the active oxidant species and arginine formed before the rate-determining step. The rate increases marginally with ionic strength and decreases with increasing dielectric constant, and added Ag(I) has no significant effect. One mole of DPA is consumed per mole of arginine; the organic product, which gives a positive carbonyl test, is provisionally assigned as 4-guanidinobutanal, together with ammonia, carbon dioxide and Ag(I). The acrylonitrile polymerisation test was negative in three replicates, giving no evidence for polymerisable free-radical intermediates. Over 298–313 K the activation parameters are $E_a = 42.98 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 40.44 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -191.20 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger = 97.42 \text{ kJ mol}^{-1}$ at 298 K. A plausible mechanism involving the monoperioatoargentate(III) species is proposed and the rate law derived from it is shown to account for the observed dependences.

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

I. INTRODUCTION

The oxidation of amino acids by transition-metal oxidants continues to attract interest because these reactions provide well-defined models for the electron-transfer and oxidative-deamination processes that occur in biological systems [1–4]. Amino acids carry an amino and a carboxylic acid group on the α -carbon together with a side chain that varies in size, polarity and functionality. Their oxidation kinetics have been studied with many oxidants [5], but the mechanism differs from one reaction system to another, and the reactions may proceed by oxidative deamination [6] or by

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decarboxylation.

Arginine differs from most amino acids studied kinetically in that its side chain ends in a strongly basic guanidino group, -NH-C(=NH)-NH_2 ($\text{pK}_a \approx 12.5$) [7], in which the positive charge of the protonated group is delocalised over three nitrogen atoms. This structural feature bears on the sign and size of the salt and dielectric-constant effects, which are diagnostic of the charge on the species entering the rate-determining step. Arginine is also the metabolic precursor of nitric oxide, polyamines and creatine and a participant in the urea cycle [8, 9], so a chemical kinetic study of its oxidation complements the literature on smaller aliphatic and aromatic amino acids.

Diperiodatoargentate(III) (DPA) is a stable, water-soluble complex in which Ag(III) is chelated by two bidentate periodate ligands [10, 11]. Its use as an oxidising reagent was established by Jaiswal and Yadava [12], and it is a convenient two-electron oxidant in alkaline solution, where it decomposes only slowly [13]. In alkaline solution DPA is in equilibrium with a monoperiodato species (MPA), formed by displacement of one periodate ligand under the influence of hydroxide; depending on whether MPA or DPA is the more reactive towards a given substrate, this equilibrium can produce either positive or negative orders in $[\text{OH}^-]$ and $[\text{IO}_4^-]$ [14, 15]. DPA has been used to oxidise glycine, alanine, valine, leucine, isoleucine, phenylalanine, tyrosine, tryptophan, lysine and ornithine [16–21], and recent work has extended DPA kinetics to drugs [22, 23], nucleobases [24] and micellar systems [25]. The oxidation of arginine by DPA in alkaline medium has, however, not been reported.

The present paper reports a systematic kinetic and mechanistic study of this reaction. The objectives are (i) to establish the stoichiometry and the nature of the products, (ii) to determine the orders with respect to [DPA], [arginine], $[\text{OH}^-]$ and $[\text{IO}_4^-]$, (iii) to examine the effects of ionic strength, dielectric constant and added Ag(I), (iv) to determine the activation parameters, and (v) to propose a mechanism consistent with the kinetic evidence.

II. MATERIALS AND METHOD

L-Arginine (S.D. Fine Chemicals) was used without further purification. KOH and KIO_4 were of analytical-reagent grade, other reagents were of Analar or equivalent grade and were used as supplied, and doubly distilled water was used throughout. DPA was prepared by oxidising silver(I) nitrate with potassium persulphate in the presence of potassium periodate under alkaline conditions [1, 11, 12]: KOH (28 g) and KIO_4 (23 g) were dissolved in 100 cm^3 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 cm^3 of water at about 80°C , filtered and cooled to give orange DPA crystals. Working solutions were standardised spectrophotometrically at $\lambda_{\text{max}} = 360 \text{ nm}$ ($\epsilon \approx 1.30 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) immediately before use [26]. The ionic strength of all reaction mixtures was maintained with KNO_3 .

Kinetic runs were carried out under pseudo-first-order conditions with arginine in large excess

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over DPA. Solutions of KOH, KIO₄, KNO₃ and arginine were mixed and thermostatted at the desired temperature (298 K unless otherwise stated; control ± 0.1 K). The reaction was started by adding thermostatted, freshly standardised DPA, the mixture was transferred to a 1 cm quartz cell in a Systronics Model 166 UV-Visible spectrophotometer, and the decay of absorbance at 360 nm was recorded every 10 min up to 90 min. The standard conditions were [DPA] = 5.0×10^{-5} , [arginine] = 5.0×10^{-4} , [KOH] = 0.08 and [IO₄⁻] = 5.0×10^{-5} mol dm⁻³, $I = 0.10$ mol dm⁻³, $D = 72$ and $T = 298$ K. Pseudo-first-order rate constants were obtained from the slope of plots of $\ln(A_0/A_t)$ against time, since absorbance is proportional to [DPA]:

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

These plots were linear over at least 80% of the reaction, and each rate constant is the mean of triplicate runs, reproducible to within $\pm 5\%$. The dielectric constant was varied with *t*-butanol–water mixtures and the effect of the reduction product was tested by adding Ag(I) initially. Activation parameters were obtained from the Arrhenius and Eyring relationships [27–29], with $\Delta H^\ddagger = E_a - RT$ and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

For the stoichiometry, mixtures with DPA in excess over arginine, at constant ionic strength, alkalinity and temperature, were left at 298 K until the reaction was complete and the unreacted DPA was estimated spectrophotometrically. Ammonia was detected with Nessler's reagent [30] and carbon dioxide by passing the evolved gas through lime water, and the organic product was tested with 2,4-dinitrophenylhydrazine (2,4-DNPH) for a carbonyl group [31]. For the free-radical test, three independent mixtures containing DPA, arginine, KOH, IO₄⁻ and 10% (v/v) acrylonitrile were kept under nitrogen for 24 h at 298 K and then diluted with methanol [32].

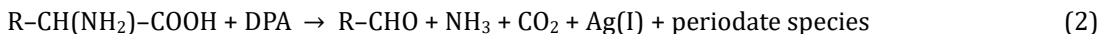
III. RESULTS AND DISCUSSION

Stoichiometry and product analysis

The results indicated that one mole of DPA is consumed per mole of arginine oxidised. Ammonia gave the characteristic yellow-brown colour with Nessler's reagent and carbon dioxide turned lime water turbid in all three runs. The positive 2,4-dinitrophenylhydrazine (2,4-DNPH) test²⁹ supports the presence of an aldehydic or ketonic carbonyl group [33, 34]. FT-IR characterisation of the isolated 2,4-dinitrophenylhydrazone derivative (the diagnostic bands expected being N–H stretches of the guanidino and hydrazone groups near 3150–3400 cm⁻¹, a C–H stretch near 2850–2950 cm⁻¹, C=N stretches of the hydrazone and guanidino groups near 1610–1660 cm⁻¹. On the basis of the oxidative deamination–decarboxylation pathway of the proposed mechanism, the organic product is provisionally assigned as 4-guanidinobutanal; definitive identification requires direct product characterisation. The reduction product of DPA is Ag(I). The overall reaction is represented by Eq. (2), where R = $-(\text{CH}_2)_3-\text{NH}-\text{C}(=\text{NH})-\text{NH}_2$:

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Effect of [DPA]

The initial [DPA] was varied from 2.0×10^{-5} to 8.0×10^{-5} mol dm⁻³ at fixed [arginine], [KOH], [IO₄⁻], *I*, *D* and *T*. The pseudo-first-order plots were linear over about 80% of the reaction and almost parallel (Fig. 1), and $k_{\text{obs}} = 0.52 \times 10^{-4}$ s⁻¹ at every [DPA] (Table 1). The order with respect to DPA is therefore unity.

Table 1 : Effect of DPA, Arginine, KOH and IO₄⁻ on the Oxidation of Arginine by DPA in Aqueous Alkaline Medium at 298 K.

10 ⁵ [DPA] M	10 ⁴ [Arg] M	[KOH] M	10 ⁵ [IO ₄ ⁻] M	10 ⁴ k _{obs} s ⁻¹
2.0	5.00	0.08	5.00	0.52
3.0	5.00	0.08	5.00	0.52
4.0	5.00	0.08	5.00	0.52
5.0	5.00	0.08	5.00	0.52
6.0	5.00	0.08	5.00	0.52
7.0	5.00	0.08	5.00	0.52
8.0	5.00	0.08	5.00	0.52
5.0	1.00	0.08	5.00	0.23
5.0	2.00	0.08	5.00	0.31
5.0	3.00	0.08	5.00	0.39
5.0	4.00	0.08	5.00	0.46
5.0	5.00	0.08	5.00	0.52
5.0	6.00	0.08	5.00	0.58
5.0	7.00	0.08	5.00	0.64
5.0	5.00	0.04	5.00	0.32
5.0	5.00	0.05	5.00	0.37
5.0	5.00	0.06	5.00	0.42
5.0	5.00	0.08	5.00	0.52

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$10^5[\text{DPA}] \text{ M}$	$10^4[\text{Arg}] \text{ M}$	$[\text{KOH}] \text{ M}$	$10^5[\text{IO}_4^-] \text{ M}$	$10^4 k_{\text{obs}} \text{ s}^{-1}$
5.0	5.00	0.10	5.00	0.61
5.0	5.00	0.12	5.00	0.66
5.0	5.00	0.16	5.00	0.73
5.0	5.00	0.08	2.00	0.67
5.0	5.00	0.08	3.00	0.61
5.00	5.00	0.08	4.00	0.56
5.00	5.00	0.08	5.00	0.52
5.00	5.00	0.08	6.00	0.48
5.00	5.00	0.08	7.00	0.45
5.00	5.00	0.08	8.00	0.43

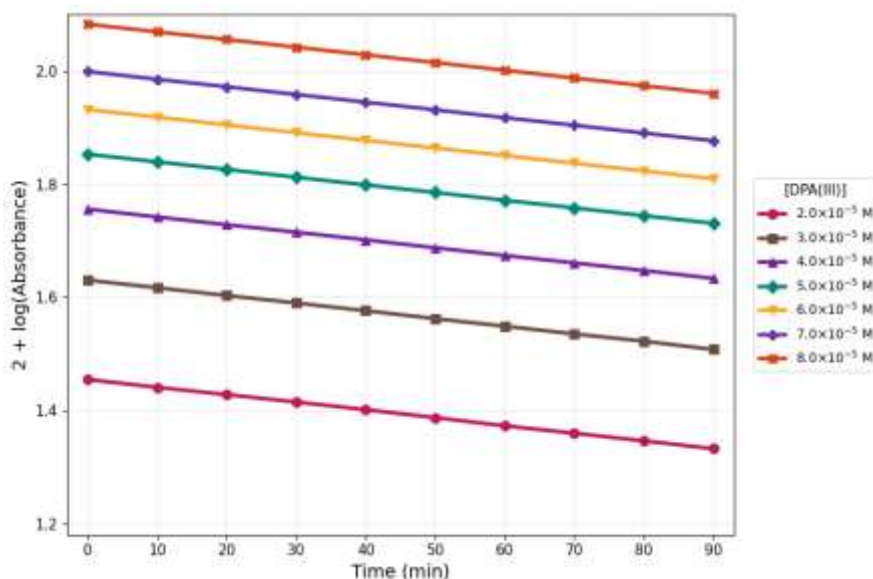


Fig. 1. Pseudo-first-order plots for the variation of $[\text{DPA}]$ (data of Table 1).

$[\text{Arginine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $D = 72$; $T = 298 \text{ K}$.

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Effect of [Arginine]

The arginine concentration was varied from 1.0×10^{-4} to 7.0×10^{-4} mol dm⁻³. The rate constant increased from 0.23×10^{-4} to 0.64×10^{-4} s⁻¹ (Table 1), and the plot of k_{obs} against [arginine] is approximately linear over this range ($R^2 = 0.9959$; Fig. 2a). The log-log plot has a slope of 0.53 ($R^2 = 0.9946$; Fig. 2b), i.e. a fractional order. The plot of $1/k_{\text{obs}}$ against $1/[\text{arginine}]$ is linear with a non-zero intercept ($R^2 = 0.9599$; Fig. 2c), consistent with the formation of a 1:1 pre-equilibrium complex between the active oxidant species and arginine before the rate-determining step [14, 16].

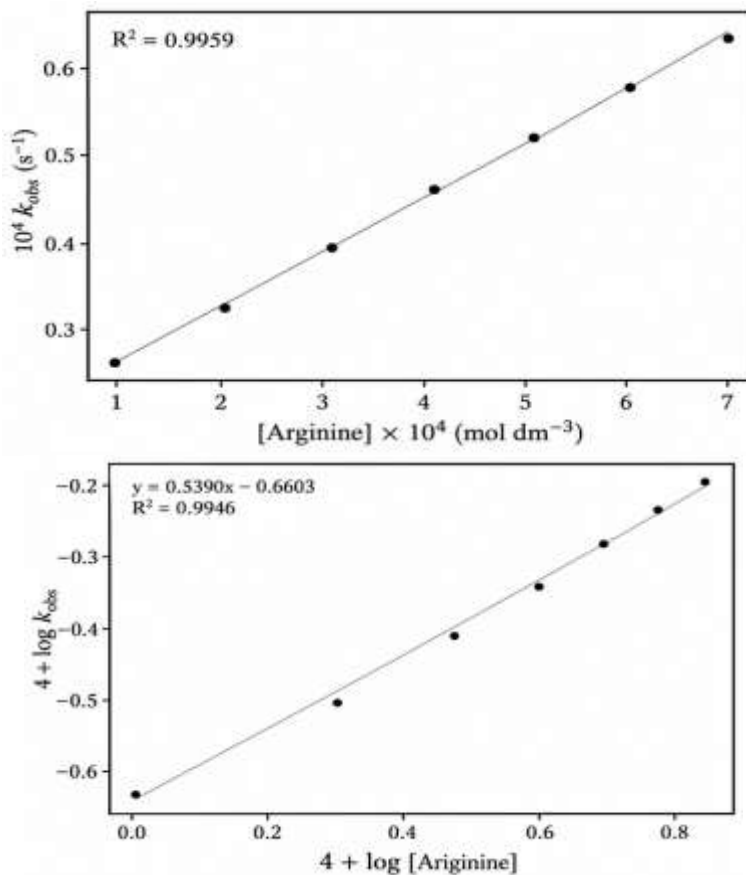


Fig. 2(a, b). Effect of [arginine]: (a) k_{obs} versus [arginine]; (b) $\log k_{\text{obs}}$ versus $\log$ [arginine].
[DPA] = 5.0×10^{-5} , [KOH] = 0.08, $[\text{IO}_4^-]$ = 5.0×10^{-5} mol dm⁻³; I = 0.10 mol dm⁻³; D = 72; T = 298 K.

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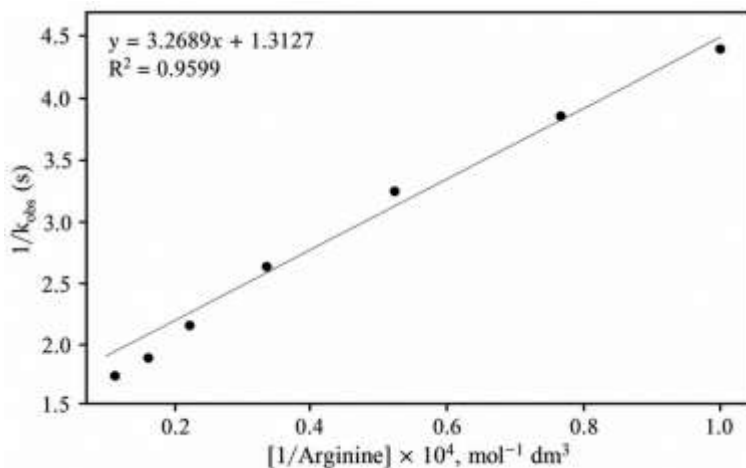
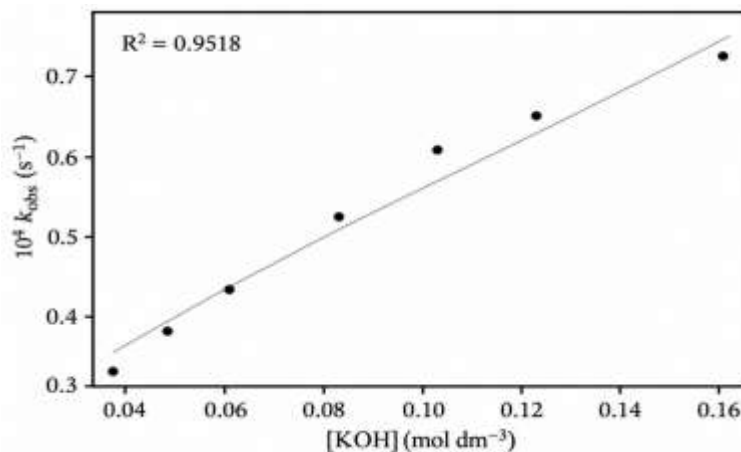


Fig. 2(c). Plot of $1/k_{\text{obs}}$ versus $1/[\text{arginine}]$ at 298 K

Effect of [KOH]

The hydroxide concentration was varied from 0.04 to 0.16 mol dm⁻³. The rate constant increased from $0.32 \times 10^{-4} \text{ s}^{-1}$ at 0.04 mol dm⁻³ to $0.73 \times 10^{-4} \text{ s}^{-1}$ at 0.16 mol dm⁻³ (Table 1, Fig. 3a). The plot of $\log k_{\text{obs}}$ against $\log [\text{KOH}]$ gives a fractional positive order of 0.62 ($R^2 = 0.9852$; Fig. 3b). The positive dependence supports the involvement of OH⁻ in the pre-equilibrium that generates the reactive monoperiodatoargentate(III) species.



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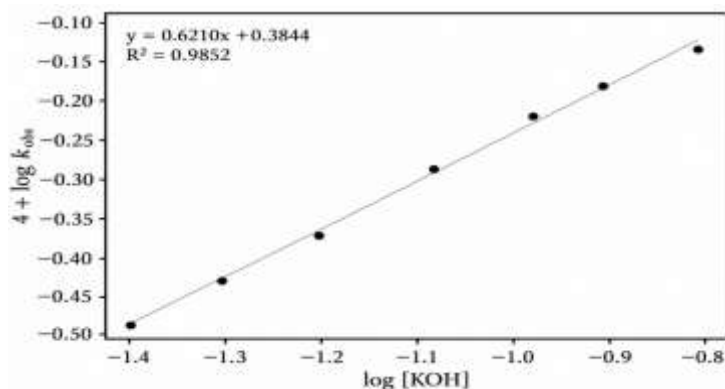
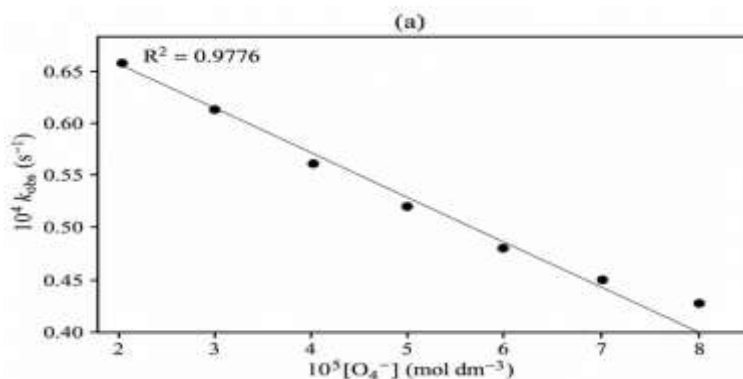


Fig. 3. Effect of [KOH]: (a) k_{obs} versus [KOH]; (b) $\log k_{\text{obs}}$ versus $\log [\text{KOH}]$

[DPA] = 5.0×10^{-5} , [arginine] = 5.0×10^{-4} , $[\text{IO}_4^-]$ = 5.0×10^{-5} mol dm⁻³; I = 0.10 mol dm⁻³; D = 72; 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 0.67×10^{-4} to 0.43×10^{-4} s⁻¹ (Table 1, Fig. 4a), a fractional negative order (the log-log slope of the tabulated values is about -0.33). The plot of $1/k_{\text{obs}}$ against $[\text{IO}_4^-]$ is linear with a positive intercept ($R^2 = 0.9983$; Fig. 4b), consistent with displacement of periodate from DPA to give the reactive MPA species. In the strongly alkaline medium used (pH 12–13), periodate is distributed between protonated forms, principally $\text{H}_3\text{IO}_6^{2-}$ and IO_4^- [35]; coupled with the DPA/MPA equilibrium, added periodate retards the reaction by mass action, suppressing the concentration of the kinetically active MPA.



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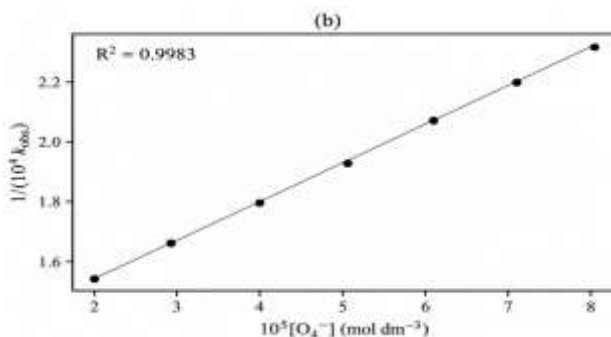


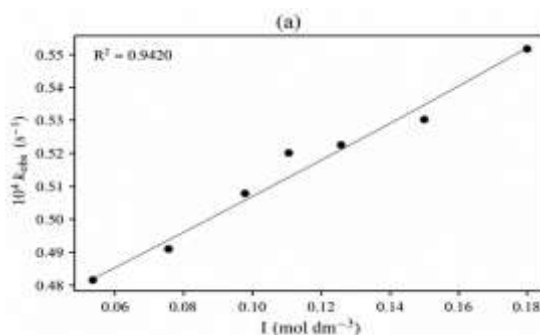
Fig. 4. Effect of $[\text{IO}_4^-]$: (a) k_{obs} versus $[\text{IO}_4^-]$; (b) $1/k_{\text{obs}}$ versus $[\text{IO}_4^-]$

$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{arginine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08 \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $D = 72$; $T = 298 \text{ K}$.

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 marginally, from 0.48×10^{-4} to $0.55 \times 10^{-4} \text{ s}^{-1}$ (Table 1, Fig. 5). Because this range extends beyond the limiting-law region, the Debye–Hückel interpretation [36] is used only qualitatively: a small positive salt effect is expected for a reaction between similarly charged species.

The dielectric constant was varied from 55 to 78 with *t*-butanol–water mixtures. The rate constant decreased from 0.60×10^{-4} at $D = 55$ to $0.50 \times 10^{-4} \text{ s}^{-1}$ at $D = 78$ (Table 6), and the plot of $\log k_{\text{obs}}$ against $1/D$ is linear with a positive slope ($R^2 = 0.9778$; Fig. 6a). According to the Amis theory [37], a decrease in rate with increasing D is characteristic of a reaction between species bearing charges of the same sign, in agreement with the proposed rate-determining interaction between like-charged species. Added Ag(I) (0.00 – 0.20 mol dm^{-3}) had no appreciable effect on the rate (Fig. 6b): k_{obs} stayed at $(0.51$ – $0.52) \times 10^{-4} \text{ s}^{-1}$, so there is no kinetically significant product inhibition.



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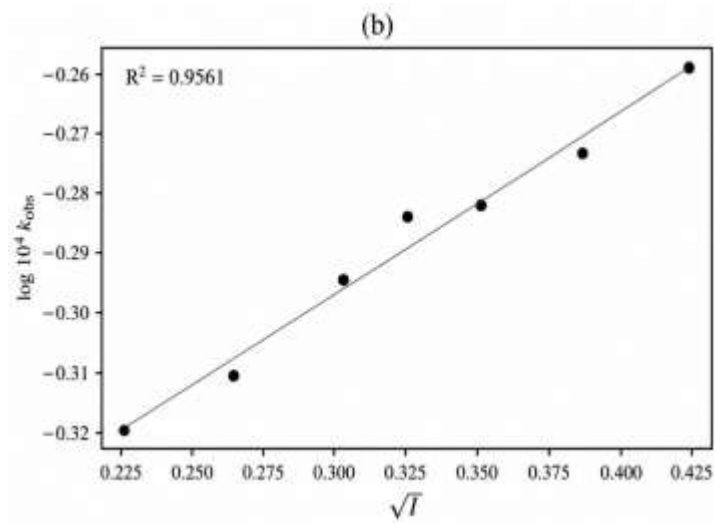
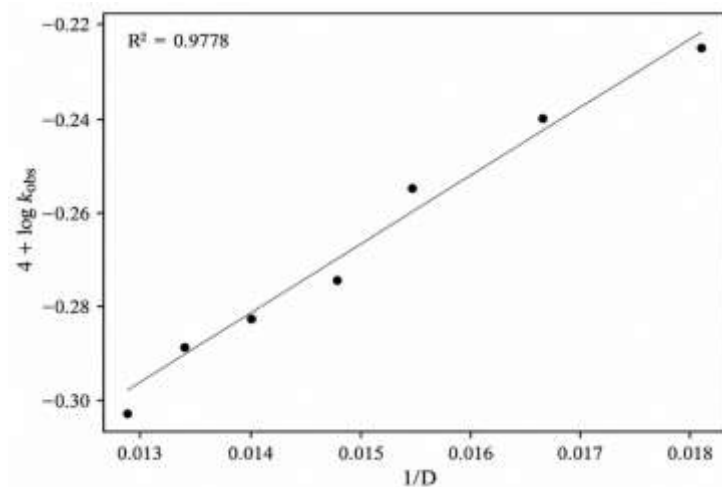


Fig. 5. Effect of ionic strength: (a) k_{obs} versus I ; (b) $\log k_{\text{obs}}$ versus $\sqrt{I}$

$[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{arginine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $D = 72$; $T = 298 \text{ K}$.



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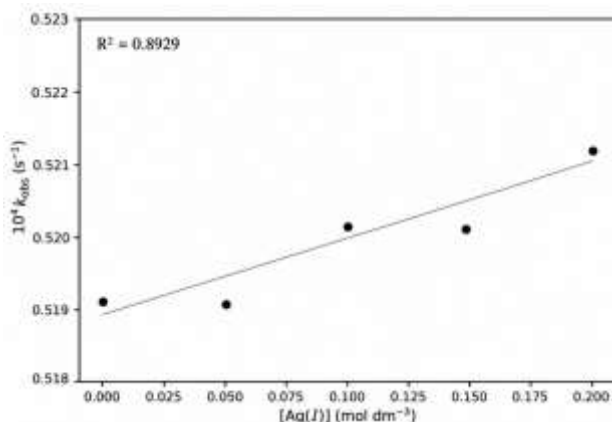


Fig. 6. (a) Plot of $\log k_{\text{obs}}$ versus $1/D$ (b) effect of added $[\text{Ag(I)}]$ on k_{obs}

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

(b) $[\text{DPA}] = 5.0 \times 10^{-5}$, $[\text{arginine}] = 5.0 \times 10^{-4}$, $[\text{KOH}] = 0.08$, $[\text{IO}_4^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$; $D = 72$; $T = 298 \text{ K}$.

Effect of temperature and activation parameters

The reaction was studied at 298, 303, 308 and 313 K. The rate constant increased from 0.52×10^{-4} to $1.19 \times 10^{-4} \text{ s}^{-1}$ (Table 2). The Arrhenius plot of $\ln k$ against $1/T$ and the Eyring plot of $\ln(k/T)$ against $1/T$ are both linear ($R^2 = 0.9998$; Fig. 7) and give the activation parameters in Table 3. E_a and $\Delta H^\ddagger$ are related by $E_a = \Delta H^\ddagger + RT$. The strongly negative $\Delta S^\ddagger$ ($-191.20 \text{ J mol}^{-1} \text{ K}^{-1}$) is consistent with increased ordering on forming the activated state and with an associative contribution to the rate-determining step; the parameters support an ordered activated state but do not by themselves prove a particular molecular mechanism.

Table 2. Effect of temperature on absorbance at 360 nm and on k_{obs}

Time (min) \ T (K)	298	303	308	313
$10^4 k_{\text{obs}} (\text{s}^{-1})$	0.52	0.70	0.92	1.19

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

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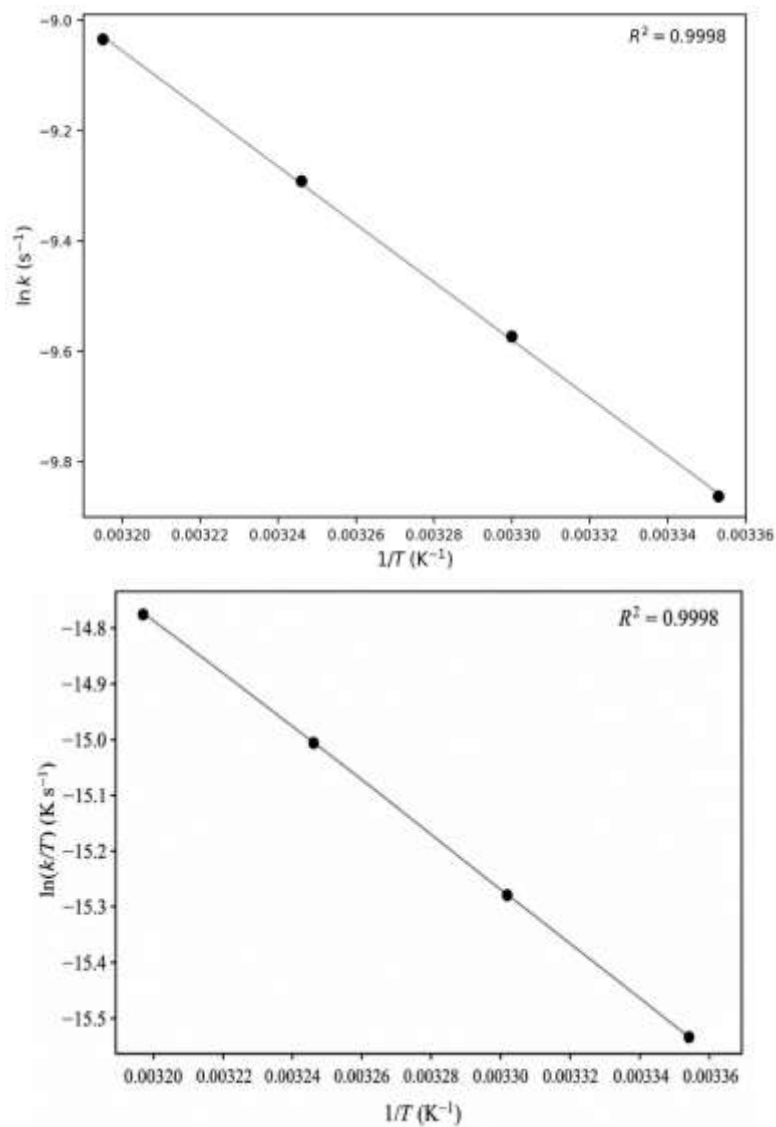


Fig. 7. (a) Arrhenius plot ($\ln k$ versus $1/T$); (b) Eyring plot ($\ln(k/T)$ versus $1/T$) (data of Table 8).

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

Parameter	Value	Unit
E_a	42.98	kJ mol^{-1}
$\log A$	3.250	$\log \text{s}^{-1}$
$\Delta H^\ddagger$	40.44	kJ mol^{-1}
$\Delta S^\ddagger$	-191.20	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta G^\ddagger$ (298 K)	97.42	kJ mol^{-1}
R^2 (Arrhenius / Eyring)	0.9998 / 0.9998	–

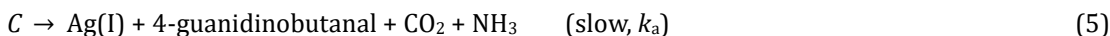
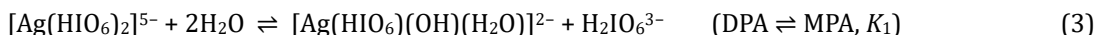
Test for free radicals

In none of the three replicate mixtures containing acrylonitrile was a polymeric precipitate seen on dilution with methanol. The uniformly negative result gives no evidence for polymerisable free-radical intermediates under these conditions and is consistent with a non-radical pathway; it supports, but does not independently prove, a concerted inner-sphere two-electron transfer within the pre-formed substrate–oxidant complex [38].

Mechanism and rate law

The kinetic results are: first order in DPA; fractional positive orders in arginine and hydroxide; a fractional negative order in periodate; a linear $1/k_{\text{obs}}-1/[\text{arginine}]$ plot with a non-zero intercept; a small positive salt effect and a negative dielectric effect; and no product inhibition. These are accommodated by Scheme 1: DPA is hydrolysed to the reactive MPA species with release of periodate (K_1); MPA forms a 1:1 complex C with the arginine anion (K_2); and the complex decomposes in two parallel slow steps, spontaneously (k_a) and by hydroxide-assisted attack (k_b) [14].

Scheme 1. Proposed mechanism for the oxidation of L-arginine by DPA ($R = -(\text{CH}_2)_3\text{-NH-C(=NH)-NH}_2$)



From the equilibrium constants, $[\text{MPA}] = K_1[\text{DPA}]/[\text{H}_2\text{IO}_6^{3-}]$ and $[C] = K_2[\text{MPA}][\text{arginine}] = K_1K_2[\text{DPA}][\text{arginine}]/[\text{H}_2\text{IO}_6^{3-}]$. The rate through the two slow steps is $\text{Rate} = (k_a + k_b[\text{OH}^-])[C]$, and the total DPA is $[\text{DPA}]_T = [\text{DPA}] + [\text{MPA}] + [C] = [\text{DPA}]\{1 + K_1/[\text{H}_2\text{IO}_6^{3-}] + K_1K_2[\text{arginine}]/[\text{H}_2\text{IO}_6^{3-}]\}$. Since $\text{Rate} = k_{\text{obs}}[\text{DPA}]_T$, the rate law is

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$$k_{\text{obs}} = \frac{(k_a + k_b[\text{OH}^-]) K_1 K_2 [\text{arginine}]}{[\text{H}_2\text{IO}_6^{3-}] + K_1 (1 + K_2 [\text{arginine}])} \quad (7)$$

The rate law accounts for each observed dependence. The unit order in DPA follows because both pre-equilibria consume one DPA-derived species per complex formed, so that Rate remains proportional to $[\text{DPA}]_T$. At low [arginine] the term $K_1 K_2 [\text{arginine}]$ is small compared with $[\text{H}_2\text{IO}_6^{3-}] + K_1$, and k_{obs} is nearly first order in arginine; as [arginine] increases this term becomes comparable to, and eventually dominates, the denominator, so that k_{obs} tends to the substrate-independent limit $(k_a + k_b[\text{OH}^-])/K_2$ and the apparent order is fractional. At fixed [arginine] and $[\text{OH}^-]$, k_{obs} decreases as $[\text{H}_2\text{IO}_6^{3-}]$ (i.e. $[\text{IO}_4^-]$) increases. The numerator contains the hydroxide-independent term k_a and the hydroxide-dependent term $k_b[\text{OH}^-]$, so the apparent order in hydroxide lies between zero and one, as observed (0.62). Inverting Eq. (7) gives the two linear forms that were tested experimentally:

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_2\text{IO}_6^{3-}] + K_1}{(k_a + k_b[\text{OH}^-]) K_1 K_2} \cdot \frac{1}{[\text{arginine}]} + \frac{1}{k_a + k_b[\text{OH}^-]} \quad (8)$$

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_2\text{IO}_6^{3-}]}{(k_a + k_b[\text{OH}^-]) K_1 K_2 [\text{arginine}]} + \frac{1 + K_2 [\text{arginine}]}{(k_a + k_b[\text{OH}^-]) K_2 [\text{arginine}]} \quad (9)$$

Eq. (8) predicts a linear $1/k_{\text{obs}}-1/[\text{arginine}]$ plot with a positive intercept (Fig. 2c), and Eq. (9) a linear $1/k_{\text{obs}}-[\text{H}_2\text{IO}_6^{3-}]$ plot with a positive intercept, i.e. linear in $[\text{IO}_4^-]$ (Fig. 4b). The strongly negative $\Delta S^\ddagger$ supports an ordered, associative activated state, the negative free-radical test is consistent with a non-radical two-electron pathway within the pre-formed complex, and the absence of product inhibition supports treating the decomposition of C as an irreversible forward step. The proposed mechanism and rate law should be regarded as a plausible model consistent with the observed kinetic trends rather than a uniquely demonstrated elementary pathway.

IV. CONCLUSION

The oxidation of L-arginine by diperiodatoargentate(III) in aqueous alkaline medium has been examined spectrophotometrically at 298 K. The reaction is first order in DPA, shows fractional positive orders in arginine (0.53) and hydroxide (0.62) and a fractional negative order in periodate, and gives a linear double-reciprocal plot with a non-zero intercept, consistent with a pre-equilibrium 1:1 complex of the monoperiodatoargentate(III) species with arginine. One mole of DPA is consumed per mole of arginine; the organic product is provisionally assigned as 4-guanidinobutanal, and its definitive identification requires direct characterisation. The rate increases modestly with ionic strength, decreases with increasing dielectric constant and is unaffected by added Ag(I). The acrylonitrile test was negative in three replicates, giving no evidence for polymerisable radical intermediates. The activation parameters ($E_a = 42.98 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 40.44 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -191.20 \text{ J}$

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$\text{mol}^{-1} \text{K}^{-1}$, $\Delta G^\ddagger = 97.42 \text{ kJ mol}^{-1}$ at 298 K) are internally consistent. The proposed mechanism and rate law are a plausible model of the observed kinetic trends.

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