

Kinetics and mechanism of oxidation of L-arginine by diperiodato-nickelate(IV) in aqueous alkaline medium

M. R. Kembhavi, A. L. Harihar and S. T. Nandibewoor*

P. G. Department of Studies in Chemistry, Karnatak University, Dharwad-580 003, India

Manuscript received 31 March 1998, revised 9 July 1998, accepted 20 July 1998

Oxidation of L-arginine by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium is first order in [DPN], but fractional order each in [L-Arg] and [OH⁻]. The rate of reaction decreases with the decrease in the dielectric constant of the medium. Added products and variation of ionic strength have no significant effect on the rate of the reaction. A mechanism involving the formation of an intermediate complex between oxidant and substrate has been proposed. The rate and equilibrium constants involved in the mechanism and the activation parameters for the slow step have been determined.

Studies of oxidation using diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium are limited^{1,2} due to its limited solubility and stability in aqueous media. Mechanistically, oxidation with nickel(IV) may involve the intervention of nickel(III). Indeed, stable nickel(III) complexes are known³. Since multiple equilibria involving different nickel(IV) periodate complexes prevail in an alkaline solution², it needs to know the active form of the oxidant in the reaction. L-Arginine is one of the essential amino acids. Amino acids have been oxidized by a variety of oxidants⁴ but not by DPN. In view of the biological importance of L-arginine and to explore the mechanistic aspects of DPN in alkaline medium, we have selected L-arginine for our kinetic study.

Results and Discussion

The reaction mixtures containing different quantities of [DPN] and [L-Arg] in the presence of 0.2 mol dm⁻³ KOH at 25.0 ± 0.1° and I = 0.80 mol dm⁻³ (Table 1) were kept for 2 h in closed vessels. The remaining Ni^{IV} was analyzed

Table 1 Stoichiometry of alkaline DPN oxidation of L-arginine
[OH⁻] = 0.20, [IO₄⁻] = 3.0 × 10⁻³, I = 0.80 mol dm⁻³

Taken		Found
10 ⁴ × [DPN] mol dm ⁻³	10 ⁴ × [L-Arg] mol dm ⁻³	10 ⁴ × [DPN] mol dm ⁻³
1.0	1.0	0.05
2.0	1.0	1.02
4.0	2.0	1.99
6.0	4.0	2.03

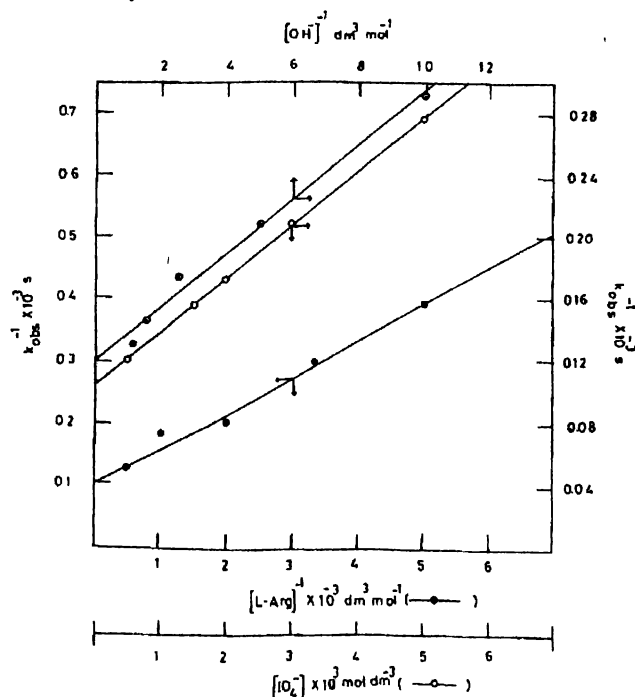
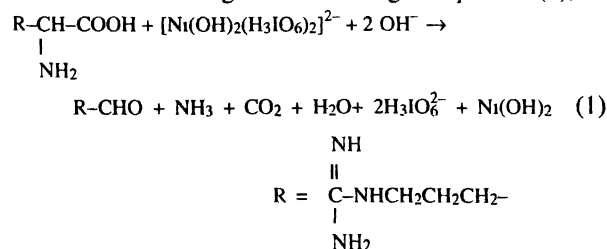


Fig. 1. Verification of rate law (11) (conditions as in Table 2)

spectrophotometrically at 410 nm ($\epsilon = 7500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). In the reaction products, Ni^{II} was detected and estimated as its dimethylglyoximate complex gravimetrically⁵, aldehyde⁶, by spot test, ammonia by Nessler's reagent⁵ test, and carbon dioxide was qualitatively detected by bubbling N₂ gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water. The results indicated that one mole of DPN consumes one mole of L-arginine according to equation (1),



It was further observed that the aldehyde undergoes no further oxidation under the present kinetic conditions. Test for the corresponding acid⁵ was negative.

Reaction order: The order of the reactants were determined from the k_{obs} vs concentration plots by varying the

concentration of reductant, alkali and periodate in turn while keeping others constant.

The [diperiodatonickelate(IV)] was varied in the range $(2.0-20.0) \times 10^{-5} \text{ mol dm}^{-3}$. The linearity of plots of $\log [\text{DPN}]$ vs time upto 70% of the reaction, indicated the order in [DPN] as unity. This was also confirmed by constant values of k_{obs} at varying [DPN] (Table 2). The [L-Arg] was varied in the range $(2.0-20.0) \times 10^{-4} \text{ mol dm}^{-3}$ at 25° keeping all other reactants concentration constant. The order in [L-Arg] was found to be less than unity (Table 2). The effect of $[\text{OH}^-]$ was studied from 0.1 to 0.8 mol dm^{-3} keeping all other reactants concentration constant. The rate increases with increase in $[\text{OH}^-]$ with order less than unity (≈ 0.4). The effect of $[\text{IO}_4^-]$ on the reaction was also studied as in Table 2 and it was found that added IO_4^- retards the rate of the reaction. Ionic strength effect on the reaction was studied by varying $[\text{KNO}_3]$, which had no influence on the rate. The effect of dielectric constant on the reaction was studied by changing the t-butanol-water content in the reaction medium keeping all other reactants concentration constant. Earlier, the inertness of the solvent, t-butanol with DPN was checked under the present experimental conditions. It was observed that the decrease in dielectric constant decreases the reaction rate. The plot of $\log k_{\text{obs}}$ vs $1/D$ gave a straight-line with negative slope. Added products such as aldehyde, ammonia and Ni^{II} did not affect the rate. Added acrylonitrile induces no polymerization and suggests the absence of free radical intervention in the reaction.

Table 2. Effect of variation of [DPN], [L-arg], $[\text{OH}^-]$ and $[\text{IO}_4^-]$ on the oxidation of L-arginine by DPN

Temp. = 25°, $I = 0.80 \text{ mol dm}^{-3}$					
$10^5 \times [\text{DPN}]$ mol dm^{-3}	$10^4 \times [\text{L-Arg}]$ mol dm^{-3}	$10 \times [\text{OH}^-]$ mol dm^{-3}	$10^3 \times [\text{IO}_4^-]$ mol dm^{-3}	$10^3 \times k_{\text{obs}}$ s^{-1}	
				Exptl.	Calcd.
2.0	5.0	2.0	3.0	4.70	4.78
3.0	5.0	2.0	3.0	4.73	4.78
5.0	5.0	2.0	3.0	4.79	4.78
10.0	5.0	2.0	3.0	4.75	4.78
20.0	5.0	2.0	3.0	4.75	4.78
5.0	2.0	2.0	3.0	2.55	2.68
5.0	3.0	2.0	3.0	3.32	3.54
5.0	5.0	2.0	3.0	4.79	4.78
5.0	10.0	2.0	3.0	6.30	6.47
5.0	20.0	2.0	3.0	7.67	7.86
5.0	5.0	1.0	3.0	3.41	3.40
5.0	5.0	2.0	3.0	4.79	4.78
5.0	5.0	4.0	3.0	5.75	6.01
5.0	5.0	6.0	3.0	6.90	6.57
5.0	5.0	8.0	3.0	7.69	6.89
5.0	5.0	2.0	0.5	8.19	8.23
5.0	5.0	2.0	1.5	6.41	6.39
5.0	5.0	2.0	2.0	5.81	5.74
5.0	5.0	2.0	3.0	4.79	4.78
5.0	5.0	2.0	5.0	3.62	3.58

Effect of temperature : The rate constants (k) of the slow step of the mechanism were obtained from the intercepts of the plots of $1/k_{\text{obs}}$ vs $1/[\text{L-Arg}]$ at four different temperatures and were used for the calculation of activation parameters (Table 3).

Table 3. Activation parameters for the oxidation of L-arginine by DPN in aqueous alkaline medium

$[\text{Ni}^{\text{IV}}] = 5.0 \times 10^{-5}$, $[\text{L-Arg}] = 5.0 \times 10^{-4}$, $[\text{OH}^-] = 0.20$, $[\text{IO}_4^-] = 3.0 \times 10^{-3}$, $I = 0.80 \text{ mol dm}^{-3}$

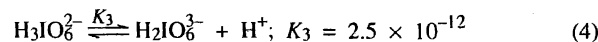
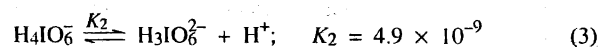
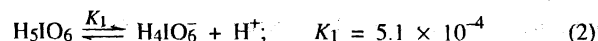
(a) Effect of temperature :

Temp. °C	$k \times 10^2 \text{ s}^{-1}$
25	1.0
30	1.4
35	1.9
40	2.3

(b) Activation parameters with respect to slow step of Scheme 1 :

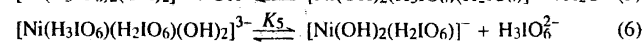
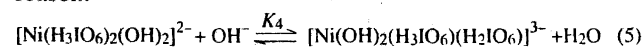
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	45 ± 2
$\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$	-36 ± 4
$\Delta G^\ddagger (\text{kJ mol}^{-1})$	56 ± 4

Mechanism : The water soluble Ni^{IV} periodate complex is reported⁷ to be $[\text{Ni}(\text{HIO}_6)_2(\text{OH})_2]^{6-}$. However, in an aqueous alkaline medium and in high pH range employed in this study, periodate is unlikely to exist as HIO_6^{2-} (as present in the complex) as is evident from its involvement in the multiple equilibria⁸ (2) to (4) depending on the pH of the solution,



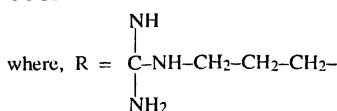
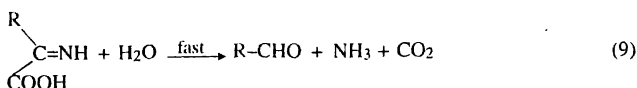
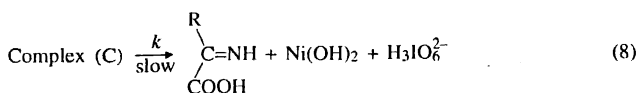
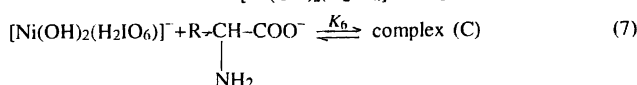
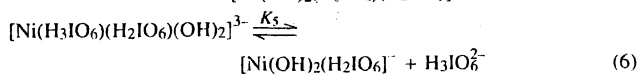
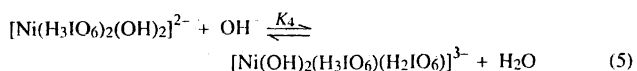
Periodic acid (H_5IO_6) exists as H_4IO_6^- around pH 7. Thus, under the alkaline conditions, the main species are expected to be $\text{H}_3\text{IO}_6^{2-}$ and $\text{H}_2\text{IO}_6^{3-}$. At higher concentrations, periodate also tends to dimerise. Hence, the soluble nickel(IV) periodate complex exists as $[\text{Ni}(\text{H}_3\text{IO}_6)_2(\text{OH})_2]^{2-}$ in aqueous alkaline medium, a conclusion also supported by earlier works².

The results of rate increase with alkalinity and the rate decrease with increasing periodate concentration, suggest that equilibria of different nickel(IV) periodate complexes as given in eqns. (5) and (6) matter. Such type of equilibria are well documented in literature⁷. It may be expected that a lower nickel(IV) periodate complex such as a mono-periodatonickelate(IV) (MPN) is more important in the reaction than the diperiodatonickelate(IV) (DPN). The inverse fractional order in $[\text{IO}_4^-]$ might also be due to this reason.



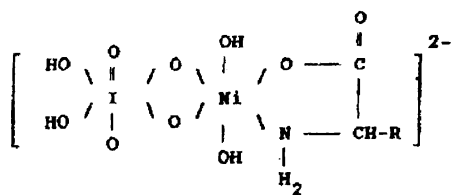
Therefore, MPN might be the main reactive form of the oxidant. Added acrylonitrile monomer did not undergo

polymerization under inert atmosphere indicating the absence of free radical formation in the reaction mixture. L-Arginine is known⁹ to exist as zwitterionic form (R-CH(NH₃)⁺-COO⁻) in aqueous medium. The same in highly basic media exists in the deprotonated form (R-CH(NH₂)-COO⁻). The fractional order in the substrate, L-arginine, presumably results from a complex formation between the oxidant and the substrate prior to the formation of products. Indeed it is to be noted that the Michaelis-Menten plot of $1/k_{\text{obs}}$ vs $1/[\text{L-Arg}]$ shows an intercept in agreement with such a complex formation. These results indicate a mechanism of the type presented in Scheme 1.



Scheme 1

Scheme 1 leads to eqn. (10), K_4 , K_5 and K_6 being the constants of the different equilibria and k is the rate constant of the decomposition of the complex, C. The probable structure of the complex (C) is



$k_{\text{obs}} =$

$$\frac{kK_4K_5K_6[\text{L-Arg}][\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_4[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_4K_5[\text{OH}^-] + K_4K_5K_6[\text{L-Arg}][\text{OH}^-]} \quad (10)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_4K_5K_6[\text{OH}^-]\text{L-Arg}} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_5K_6[\text{L-Arg}]} + \frac{1}{kK_6[\text{L-Arg}]} + \frac{1}{k} \quad (11)$$

According to equation (11), other conditions being constant, the plot of $1/k_{\text{obs}}$ vs $1/[\text{L-Arg}]$, $1/[\text{OH}^-]$ and $[\text{H}_3\text{IO}_6^{2-}]$ should be linear (Fig. 1.) From the slopes and intercepts the values of K_4 , K_5 , K_6 and k could be derived as $1.16 \pm 0.06 \text{ dm}^3 \text{ mol}^{-1}$, $6.1 \pm 0.3 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1}$, $5.0 \pm 0.2 \times 10^4 \text{ dm}^3$

mol^{-1} and $1.0 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$ respectively. The values of K_4 , K_5 and k are in good agreement with the earlier report¹⁰. Using these constants, the k_{obs} values were calculated over different experimental conditions, and there is reasonable agreement between the calculated and experimental values (Table 2).

The plot of $\log k_{\text{obs}}$ vs $1/D$ gives a straight line with a negative slope for reaction between negative ion and dipole or between two dipoles or between two negative ions whereas a positive slope, for a positive ion and dipole interaction¹¹. In the present study, it has been observed that the plot of $\log k_{\text{obs}}$ vs $1/D$ is a straight line with a negative slope which agrees with the proposed Scheme 1. However, the effect of ionic strength on the reaction is contrary to the expectation which might be due to the high ionic strength used in the reaction medium. The mechanism is also supported by moderate values of thermodynamic activation parameters (Table 3). A small negative value of ΔS^\ddagger suggests that the complex is less ordered than the reactants¹² while the moderate values of ΔG^\ddagger and ΔH^\ddagger indicate that the activated complex is highly solvated.

Experimental

All chemicals used were of reagent grade. Double-distilled water was used throughout. Stock solution of L-arginine (s.d. fine-chem) was prepared in double-distilled water. Solutions of nickel(IV) periodate complex¹³ were prepared in aqueous alkaline medium, and standardized by the reported method⁵. All other solutions were prepared by dissolving appropriate amounts of the samples in double-distilled water. KOH and KNO₃ were used to maintain required alkalinity and ionic strength respectively.

Kinetic runs : Runs were performed under pseudo-first order conditions where [L-Arg] was excess over that of [DPN] which also contained required amounts of KOH and KNO₃. The progress of the reaction was monitored by measuring the decrease in absorbance of DPN in a 1 cm quartz cell using a Hitachi 150-20 spectrophotometer at 410 nm, where other constituents did not absorb significantly. Beer's law for DPN in the medium employed was verified at 410 nm, giving $\epsilon = 7500 \pm 375 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed.

References

1. D. H. Macartney and A. McAuley, *Inorg. Chem.*, 1983, 22, 2062; M. A. Siddiqui, C. S. Kumar, U. Chandiraiah and S. Kandlikar, *Indian J. Chem., Sect. A*, 1991, 30, 849; S. A. Acharya, B. Neogi, R. K. Panda and D. Ramaswamy, *Int. J. Chem. Kinet.*, 1982, 14, 1253; A. G. Bappin, Laranjeira and O. L. Youdi, *J. Chem. Soc., Dalton Trans.*, 1981, 721.

2. G. H. Hugar and S. T. Nandibewoor, *Indian J. Chem., Sect. A*, 1993, **32**, 1056; S. T. Nandibewoor and G. H. Hugar, *Pol. J. Chem.*, 1997, **71**, 1572; S. M. Tuwar, S. T. Nandibewoor and J. R. Raju, *J. Indian Chem. Soc.*, 1992, **69**, 651; C. E. Crouthamel, A. M. Hayes and D. S. Martin, *J. Am. Chem. Soc.*, 1951, **73**, 82; U. Chandraiah, J. A. Khan, C. P. Murthy and S. Kandlikar, *Indian J. Chem., Sect. A*, 1987, **26**, 481.
3. R. T. Haines and A. Mcauley, *Coord. Chem. Rev.*, 1981, **39**, 77; K. Nag and A. Chakravarthy, *Coord. Chem. Rev.*, 1980, **33**, 87.
4. R. G. R. Bacon, W. J. W. Hanna and D. Stewart, *J. Chem. Soc. (C)*, 1966, 1388; R. G. Panari, R. B. Chougale and S. T. Nandibewoor, *Pol. J. Chem.*, 1998, **72**, 99; D. G. Lambert and M. M. Jones, *J. Am. Chem. Soc.*, 1966, **88**, 4615; R. B. Chougale, G. A. Hiremath and S. T. Nandibewoor, *Pol. J. Chem.*, 1997, **71**, 1471; D. S. Mahadevappa, S. Ananda, A. S. A. Murthy and K. S. Rangappa, *Indian J. Chem., Sect. A*, 1984, **23**, 17.
5. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS, London, 1978.
6. F. Feigl, "Spot Tests in Organic Analysis", Elsevier, New York, 1975.
7. H. G. Mukherjee, M. Bhansidhar and S. De, *Indian J. Chem., Sect. A*, 1984, **23**, 426.
8. J. C. Bailar, H. J. Emeleus, S. R. Nyholm and A. F. Trotman-Dickeman, "Comprehensive Inorganic Chemistry", Pergamon, Oxford, 1975, Vol. 2, p. 1456.
9. R. Chang, "Physical Chemistry with Applications to Biological Systems", McMillan, New York, 1981.
10. S. M. Tuwar, S. T. Nandibewoor and J. R. Raju, *J. Indian Chem. Soc.*, 1992, **69**, 651.
11. E. S. Amis, "Solvent Effects on Reaction Rates and Mechanism", Academic, New York, 1966.
12. D. S. Mahadevappa, K. S. Rangappa, N. M. M. Gowda and B. T. Gowda, *Int. J. Chem. Kinet.*, 1982, **14**, 1183.
13. P. Ray, *Inorg. Synth.*, 1957, **5**, 201.