ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2007, Vol. 81, No. 7, pp. 1046–1053. © Pleiades Publishing, Ltd., 2007.

CHEMICAL KINETICS AND CATALYSIS

A Study of the Kinetics and Mechanism of Oxidation of L-Tryptophan by Diperiodatonickelate(IV) in Aqueous Alkaline Medium[1]

S. A. Chimatadar, T. Basavaraj, and S. T. Nandibewoor

P.G. Department of Studies in Chemistry, Karnatak University, Dharwad–580 003, India
e-mail: stnandibewoor@yahoo.com

Abstract—The kinetics of oxidation of L-tryptophan by diperiodatonickelate(IV) (DPN) in an aqueous alkaline medium at a constant ionic strength of 0.30 mol dm^{-3} was studied spectrophotometrically. The reaction was first order in diperiodatonickelate(IV) and less than first order in tryptophan and the OH^- ion. The addition of periodate had no effect on the reaction, and nickel(II) produced did not influence the reaction rate significantly. An increase in ionic strength and decrease in medium permittivity did not affect the reaction rate. A mechanism involving the formation of a complex between L-tryptophan and reactive DPN species was proposed. The constants characterizing the mechanism were evaluated. The activation parameters for the slow reaction step were computed and discussed.

DOI: 10.1134/S0036024407070072

Kinetic studies of reactions with nickel(IV) complexes such as nickel(IV) oxime or nickel(IV) periodate as oxidants are few [1] because of their low stability and solubility in aqueous media. The intervention of nickel(III) as an intermediate can occur in reactions with nickel(IV). Indeed, stable nickel(III) complexes are also known [2]. Moreover, when nickel(IV) periodate is the oxidant, we observe multiple equilibria between different nickel(IV) species [1]. We must therefore know which species is the active oxidant.

Amino acids not only act as building blocks in protein syntheses but also play a significant role in metabolism and are oxidized by a variety of oxidizing agents [3]. Studies of the oxidation of amino acids are of interest because of their biological significance and selectivity toward oxidants and because their oxidation yields different products [4].

L-tryptophan is an essential amino acid, and it is needed to maintain optimum health. It is particularly abundant in bananas, dried dates, milk, cottage cheese, meat, fish, turkey, and peanuts. This amino acid is required for the production of niacin (vitamin B_3), which is a precursor of serotonin, a neurotransmitter important for normal nervous and mental activity. Serotonin is a useful chemical for stabilizing emotional moods, pain control, inflammation, intestinal peristalsis, etc. It is also important for controlling hyperactivity in children, assists in alleviating stress, and helps with weight loss and reducing appetite. Shortage of L-tryptophan may contribute to heart artery spasms.

[1] The text was submitted by the authors in English.

In earlier reports [5, 6] on oxidation with diperiodatonickelate(IV), periodate had retarding action on almost all reactions, and monoperiodatonickelate(IV) (MPN) was considered the active species. However, in the present study, we observed an entirely different kinetics, and deprotonated diperiodatonickelate(IV) (DPN) was found to be the active oxidant form. A survey of the literature shows that there are no reports on the oxidation of L-tryptophan (TRP) with diperiodatonickelate(IV). The present study is concerned with this reaction. Its purpose was to investigate the redox chemistry of nickel(IV) in alkaline media and determine a possible mechanism of its reaction.

EXPERIMENTAL

The chemicals used were reagent grade. The solvent was doubly distilled water in all experiments. The nickel(IV) periodate complex was prepared, purified, and characterized by the known procedure [7]. The concentration of nickel(IV) periodate in solution was determined gravimetrically [8] after reducing nickel(IV) to nickel(II), in the form of the nickel(II) dimethylglyoxime complex. A solution of periodate (s. d. fine–chem.) was prepared by dissolving the required amount of the substance in hot water. The solution was stored for 24 h before use. Its concentration was determined iodometrically [9] at neutral pH created by a phosphate buffer. A solution of nickel(II) was prepared by dissolving an appropriate amount of nickel sulfate (Thomas Baker) in water.

Because nickel(IV) periodate was present in excess in solutions of the diperiodatonickelate(IV) complex, the possibility of L-tryptophan oxidation by Ni perio-

date in aqueous alkaline media was checked. The results indicated that the reaction between Ni periodate and L-tryptophan was negligibly slow in comparison with the reaction between diperiodatonickelate(IV) and L-tryptophan under the experimental conditions. Potassium hydroxide (BDH) and potassium nitrate (BDH) were used to maintain the required pH and ionic strength, respectively, in reaction solutions.

The reaction was too fast to be monitored by usual methods, and kinetic measurements were performed on a Hitachi 150–20 spectrophotometer (Tokyo, Japan) connected to a rapid kinetic accessory (HITECH SFA–12 unit). The oxidation of L-tryptophan by diperiodatonickelate(IV) was studied under pseudofirst-order conditions, when L-tryptophan was present in excess with respect to diperiodatonickelate(IV) at 30 ± 0.1°C unless otherwise stated. The reaction was initiated by mixing previously thermostated solutions of diperiodatonickelate(IV) and L-tryptophan of the required concentrations. The reaction solution also contained the required amounts of potassium hydroxide, potassium nitrate, and potassium metaperiodate.

The total concentration of potassium hydroxide was calculated taking into account potassium hydroxide present in diperiodatonickelate(IV) and potassium hydroxide additionally introduced. Similarly, the total metaperiodate concentration was calculated taking into account metaperiodate present in the solution of diperiodatonickelate(IV) and metaperiodate additionally introduced. The reaction was monitored by measuring the absorbance of unreacted diperiodatonickelate(IV) in a reaction mixture in a 1 cm quartz cell in the temperature-controlled compartment of Hitachi 150–20 spectrophotometer at 410 nm, where other reaction constituents did not absorb significantly. The first-order rate constants, k_{obs}, were determined from the plots of log[DPN] versus time (Fig. 1). The plots were linear up to 85% conversions, and runs repeated three times were reproducible within ±5%.

The effect of dissolved oxygen on the reaction mixture was checked by preparing the reaction mixture and performing the reaction in an atmosphere of nitrogen. No significant difference in the results was observed in the presence and absence of nitrogen. Added carbonate had no effect on the reaction rate. However, fresh solutions were always used in experiments.

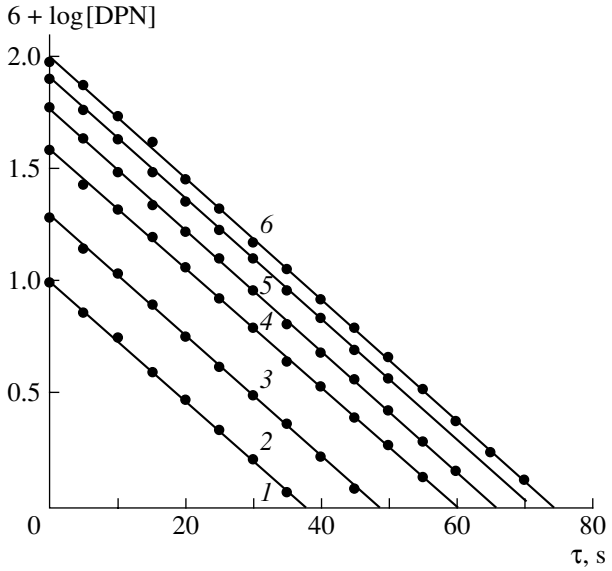
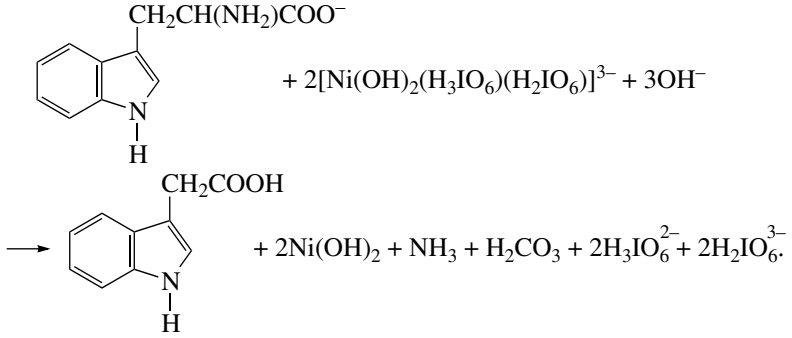


Fig. 1. Oxidation of L-tryptophan by diperiodatonickelate(IV) in aqueous alkaline medium at 25°C and [DPN] × 10^4 = (*1*) 0.1, (*2*) 0.2, (*3*) 0.4, (*4*) 0.6, (*5*) 0.8, and (*6*) 1.0/mol dm^{-3}.

In view of the moderate alkali concentrations in the reaction media, attention was also given to the effect of the surface of reaction vessels on kinetics. The use of polythene / acrylic equipment and a quartz or polyacrylate cell gave the same results as with glass vessels and cells.

RESULTS AND DISCUSSION

Different reaction mixtures with different concentrations of diperiodatonickelate(IV) and L-tryptophan at constant ionic strength and alkali concentration were kept for 2 h at 30°C in a nitrogen atmosphere. When diperiodatonickelate(IV) concentration was greater than that of L-tryptophan, unreacted diperiodatonickelate(IV) was determined by measuring its absorbance at 410 nm spectrophotometrically. The product, nickel(II), was determined gravimetrically as the dimethylglyoxime complex [8]. The results showed that one mole of L-tryptophan consumed two moles of diperiodatonickelate(IV) according to the equation



(1)

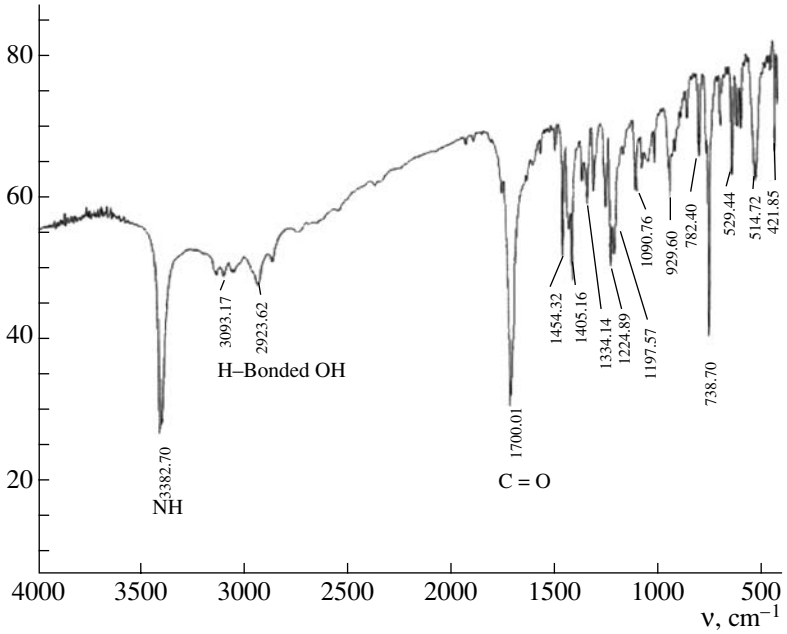


Fig. 2. IR spectra of indol-3-acetic acid in KBr.

The product, indole-3-acetic acid[1] was separated [10] by TLC using 45 : 35 : 20 (v/v) mixtures of methyl acetate, isopropanol and 25% ammonium hydroxide. It was characterized by its melting point (163°C) and IR spectra (Fig. 2). The IR spectra of tryptophan contained broad bands in the region between 3086 and 3310 cm^{-1}, which were assigned as stretching vibrations of carboxylic –OH, free –NH or $–NH_2$, and indole –NH groups. Two intense sharp bands at 1747 and 1716 cm^{-1} probably corresponded to free C=O and hydrogen-bonded C=O bonds of the carboxyl group, respectively.

The spectrum of the product (Fig. 2) had a sharp band at 3382 cm^{-1} assigned to the indole –NH group and a series of bands in the region of from 2650 to 3200 cm^{-1} corresponding to hydrogen-bonded –OH stretching frequencies. An intense sharp band at 1705 cm^{-1} was caused by C=O stretching vibrations of the carboxyl group. The absence of broad bands in the region between 3086 and 3310 cm^{-1} and the presence of only an intense sharp band at 3382 cm^{-1} confirms the absence of free $–NH_2$ groups and the presence of the indole –NH group. The bands of the product accurately reproduce the literature spectrum of the indole-3-acetic acid. The product indole-3-acetic acid was confirmed by its ^1H NMR (Fig. 3) and ^{13}C NMR (Fig. 4) spectra. The ^1H NMR spectrum contained peaks at 12.14, 0.89, 7.50, 7.36, 7.22, 7.09, 6.98, and 3.64 ppm, which were assigned to the protons positioned a, b, c, d, e, f, g, and i, respectively. The ^{13}C NMR peaks at 123.94, 107.75, 118.49, 121.07, 118.61, 111.41, 127.30, 36.19, 31.05, and 173.24 ppm were assigned to the 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 carbons atoms, respectively. The reaction orders were determined from the slopes of $\log k_{obs}$ versus $\log c$ plots by varying the concentrations of the reducing agent, periodate, and alkali in turn while keeping all other concentrations and conditions constant.

The concentration of diperiodatonickelate(IV) was varied over the range 1.0×10^{-5}–1.0×10^{-4} mol dm^{-3} at fixed concentrations of L-tryptophan and alkali and a constant ionic strength. The pseudofirst-order rate constants did not change as the concentration of diperiodatonickelate(IV) was varied, which was evidence that the reaction was first-order in diperiodatonickelate(IV) (table). This was also confirmed by parallel and linear plots of log[DPN] versus time (Fig. 1).

The concentration of the substrate, L-tryptophan, was varied from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}, the other reactant concentrations and ionic strength being fixed (table). The reaction order with respect to L-tryptophan was determined from the slope of the plot of $\log k_{obs}$ versus log[L-tryptophan] and was found to be less than one, ca. 0.54.

The effect of alkali concentration on the rate of the reaction was studied over the range 0.05–0.50 mol dm^{-3} at constant reagent concentrations and ionic strength. The reaction order with respect to alkali was obtained from the $\log k_{obs}$ versus $\log[OH^-]$ plot and was found to be less than one (0.49) (table).

The effect of periodate concentration was studied by varying the concentration from 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}, all the other reactant concentrations being constant. It was found that the periodate added

[1] SDBS No.: 2551, CAS Registry No.: 87-51-4 issued by National Institute of Advanced Industrial Science and Technology (AIST).

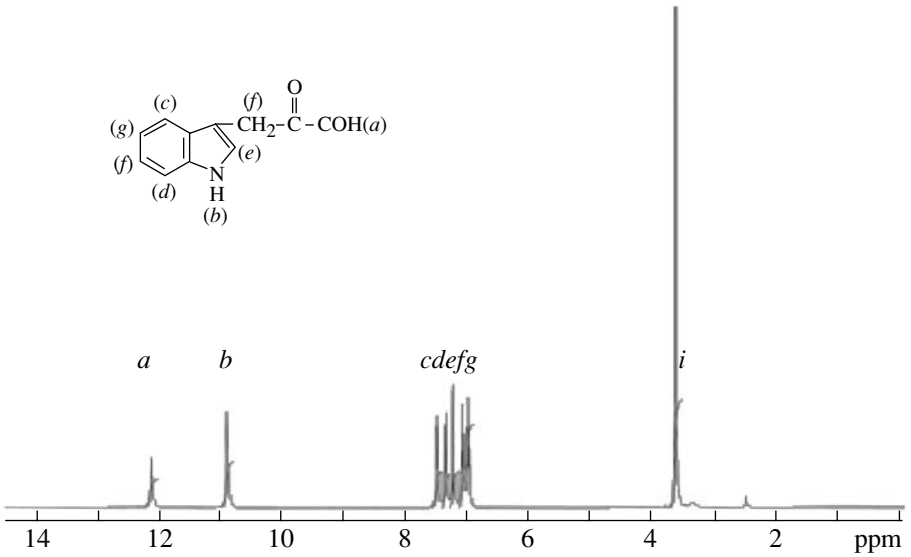


Fig. 3. PMR spectra of indol-3-acetic acid in DMSO d_6.

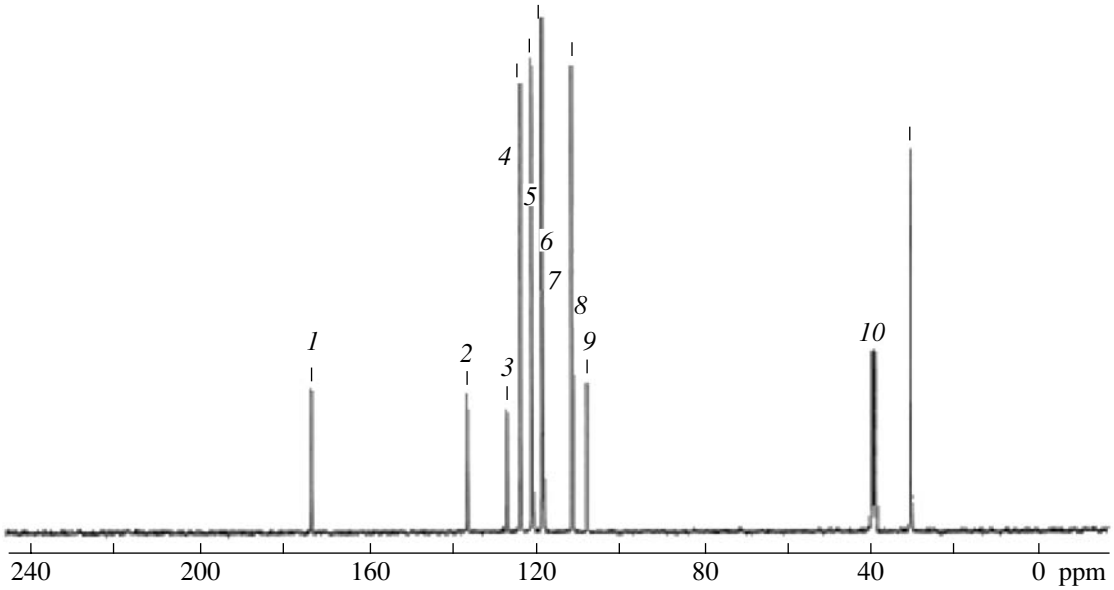


Fig. 4. ^{13}C NMR spectra of indol-3-acetic acid in DMSO d_6.

had no significant effect on the rate of the reaction (table).

The effect of initially added compounds such as Ni(II) in the form of $NiSO_4$ and indole-3-acetic acid was studied over the concentration ranges 1.0×10^{-5}–1.0×10^{-4} and 1.0×10^{-4}– 1.0×10^{-3} mol dm^{-3}, respectively, at constant concentrations of the other reagents. It was found that these compounds influenced the rate of the reaction insignificantly.

When the content of *tert*-butanol in the reaction medium was increased (up to 20% only), the reactant concentrations and other conditions remaining constant, it was found that a change in solution permittivity did not have any significant effect on the rate of the reaction. Similarly, ionic strength variations from 0.1 to 1.0 mol dm^{-3} with potassium nitrate as the background electrolyte had a negligible effect on the reaction rate.

The influence of free radicals was studied by mixing the reaction solution with acrylonitrile and holding it for 24 h under nitrogen. After dilution with methanol, a white precipitate of a polymer was formed, which indicated the intervention of free radicals in the reaction. Blank experiments of holding either diperiodatonicke-

Effect of diperiodatonickelate(IV), L-tryptophan, alkali, and periodate concentrations on the oxidation of L-tryptophan by diperiodatonickelate(IV) in alkaline media at $I = 0.30$ mol dm^{-3} and 30°C

$[DPN] \times 10^5$, mol dm^{-3}	$[TRP] \times 10^4$, mol dm^{-3}	$[OH^-]$, mol dm^{-3}	$[IO_4^-] \times 10^3$, mol dm^{-3}	$k_{obs} \times 10^2$, s^{-1}
1.0	6.0	0.2	5.0	6.02
2.0	6.0	0.2	5.0	6.37
4.0	6.0	0.2	5.0	6.41
6.0	6.0	0.2	5.0	6.14
8.0	6.0	0.2	5.0	6.10
10.0	6.0	0.2	5.0	6.31
6.0	1.0	0.2	5.0	2.34
6.0	2.0	0.2	5.0	3.43
6.0	4.0	0.2	5.0	5.14
6.0	8.0	0.2	5.0	7.61
6.0	10.0	0.2	5.0	8.32
6.0	6.0	0.05*	2.0	3.16
6.0	6.0	0.10	2.0	4.37
6.0	6.0	0.30	2.0	7.50
6.0	6.0	0.40	2.0	8.71
6.0	6.0	0.50	2.0	9.67
6.0	6.0	0.2	1.0	6.20
6.0	6.0	0.2	3.0	6.11
6.0	6.0	0.2	5.0	6.14
6.0	6.0	0.2	8.0	6.05
6.0	6.0	0.2	10.0	6.22

* When $[OH^-]$ was varied, ionic strength was maintained constant, $I = 0.6$ mol dm^{-3}.

late(IV) or L-tryptophan with acrylonitrile alone did not induce polymerization under the same conditions. Initially added acrylonitrile decreases the rate of the reaction, which also indicates the intervention of free radicals [11].The rate of the reaction was measured at different temperatures and various L-tryptophan concentrations, the other conditions being constant. The rate constant k for the slow step of Scheme 1 was obtained from the intersections of the dependences of $1/k_{obs}$ on 1/[TRP] at four different temperatures. The effect of temperature variations on the oxidation of L-tryptophan by diperiodatonickelate (IV) in an aqueous alkaline medium with respect to the slow step of the mechanism at [DPN] = 6.0×10^{-5}, [L-tryptophan] = 6.0×10^{-4}, $[OH^-] = 0.20$, $[IO_4^-] = 5.0 \times 10^{-3}$ mol dm^{-3}, and $I = 0.30$ mol dm^{-3} was

T, K	293	298	303	308
$k \times 10^{-2}$, s^{-1}	6.25	8.33	11.10	16.70

Activation parameters were $E_a = 46 \pm 1$ kJ mol^{-1}, $\Delta H^{\#} = 43 \pm 1$ kJ mol^{-1}, $\Delta S^{\#} = -120 \pm 10$ J K^{-1} mol^{-1}, $\Delta G^{\#} = 80 \pm 6$ kJ mol^{-1}, and $\log A = 6.9 \pm 0.4$. The activation energy was evaluated from the plot of $\log k$ versus $1/T$, from which the activation parameters were calculated.

The water-soluble [5, 6] nickel(IV) periodate complex, $[Ni(HIO_6)_2(OH)_2]^{6-}$, was reported in [4, 12]. However, in an aqueous alkaline medium and at high pH used in our study, periodate is unlikely to exist as $H_4IO_6^-$ (as in the complex). This follows from its involvement in the equilibria [13]

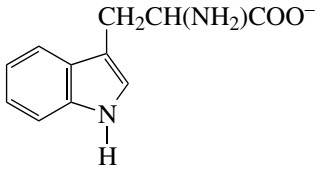
$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, \quad K_1 = 5.1 \times 10^{-4}, \qquad (2)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \quad K_2 = 4.9 \times 10^{-9}, \qquad (3)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+, \quad K_3 = 2.5 \times 10^{-12}. \qquad (4)$$

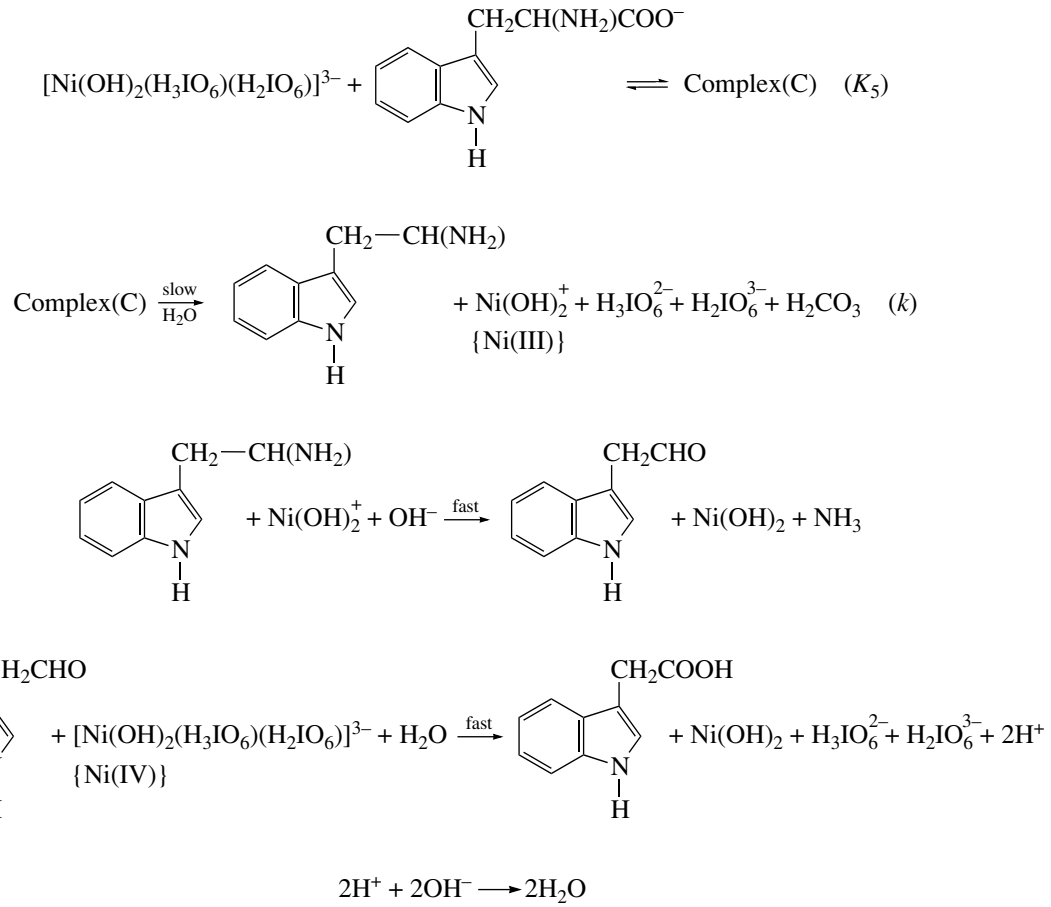
depending on pH of the solution.

Periodic acid (H_5IO_6) exists in acid media as $H_4IO_6^-$ at pH of about 7. Under the conditions used in alkaline media, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate tends to dimerize. Therefore, at pH of our solutions, the Ni(IV) periodate complex exists as diperiodatonickelate(IV), $[Ni(H_3IO_6)_2(OH)_2]^{2-}$. This conclusion finds support in the literature [4]. It is known that L-tryptophan exists in the form of the zwitterion [14] in aqueous media. In acid media, it exists in the protonated form, whereas in basic media it is fully deprotonated,



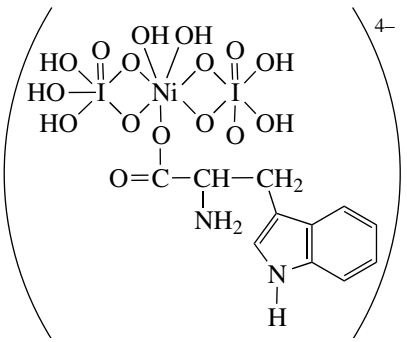
The reaction between diperiodatonickelate(IV) and L-tryptophan has a 2 : 1 oxidant : reducing agent stoichiometry. It is first-order in diperiodatonickelate(IV) and less than first-order in both L-tryptophan and alkali. In most of the oxidation reactions with diperiodatonickelate(IV) [4, 5], periodate had decelerating action and monoperiodatonickelate(III) (MPN) was considered the active species. However, in the present kinetic study, different kinetic observations were made. Periodate had no effect at all on the rate of the reaction. Accordingly, deprotonated diperiodatonickelate(IV) is considered to be the active oxidant form. The fractional order in the substrate, L-tryptophan, is presumably a consequence of complex formation between the oxidant and substrate. The complex decomposes at the slow reaction stage to produce free radicals from L-tryptophan and intermediate nickel(III) compounds. Free radicals react with nickel(III) com-

pounds at the fast stage to give an intermediate aldehyde of L-tryptophan with a nickel(II) compound. This intermediate aldehyde then reacts with another mole of diperiodatonickelate(IV) (a fast reaction) to give the product. Evidence for the formation of a nickel(III) intermediate is in agreement with the earlier data [15]. Indeed, the Michaelis–Menten plot $1/k_{obs}$ versus 1/[TRP] has a nonzero intercept, which indicates complex formation. Similar complex formation between substrates and oxidants was reported in [16]. The experimental results can be rationalized in terms of Scheme,



Scheme.

The probable structure of the complex is



Scheme, which includes the observed reaction orders in L-tryptophan, diperiodatonickelate(IV), alkali and periodate, leads to the rate law

$$\text{Rate} = -\frac{d[\text{DPN}]}{dt} = \frac{kK_4K_5[\text{DPN}][\text{OH}^-][\text{TRP}]}{1 + K_4[\text{OH}^-] + K_4K_5[\text{OH}^-][\text{TRP}]}. \quad (5)$$

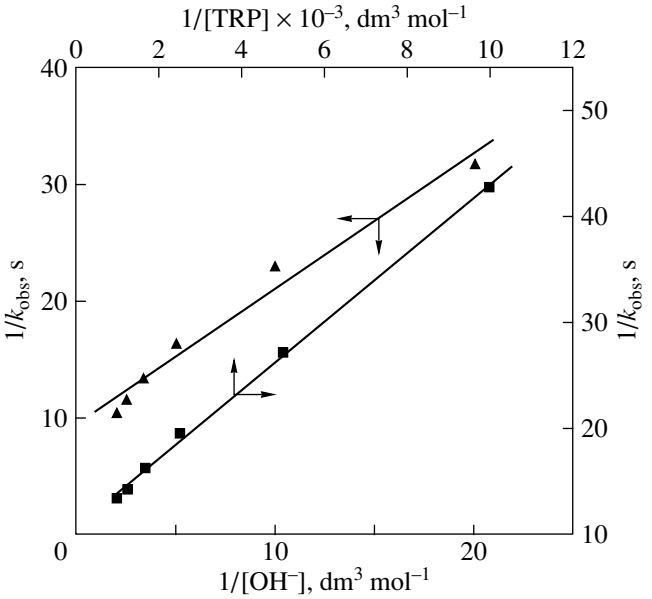


Fig. 5. Verification of rate law (5) in the form of Eq. (6).

Rate law (5) can be rearranged to the equation

$$\frac{1}{k_{obs}} = \frac{1}{kK_4K_5[TRP][OH^-]} + \frac{1}{kK_5[TRP]} + \frac{1}{k}, \quad (6)$$

which can conveniently be used for verification.

According to Eq. (6), the plots of $1/k_{obs}$ versus 1/[TRP] and $1/k_{obs}$ versus $1/[OH^-]$, other conditions being constant, should be linear and are found to be so (Fig. 5). The slopes and intercepts of these plots were used to determine K_4 K_5, and k, (0.31 ± 0.02) dm^3 mol^{-1}, $(4.47 \pm 0.22) \times 10^4$ dm^3 mol^{-1}, and $(11.1 \pm 0.3) \times 10^{-2}$ s^{-1}, respectively. The effect of ionic strength and permittivity could not be explained because of the involvement of various ionic species in the reaction. The suggested mechanism is supported by the moderate values of the thermodynamic activation parameters. The high negative $\Delta S^{\#}$ value suggests that the complex is more ordered than the reactants. The observed moderate enthalpy of activation and a higher rate constant for the slow step indicate that oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [17].

CONCLUSIONS

Among various Ni(IV) forms in alkaline media, the active Ni(IV) form is found to be $[Ni(OH)_2(H_3IO_6)(H_2IO)_6]^{3-}$ for the reaction studied. Medium pH plays a crucial role. The rate constants for the slow step involved in the mechanism were evaluated and the activation parameters with respect to the slow reaction step were computed. The overall mechanistic sequence described here is consistent with the reaction product and mechanistic and kinetic studies.

REFERENCES

1. D. H. Macartney and A. McAuley, Inorg. Chem. **22**, 2062 (1983); M. A. Siddiqui, C. S. Kumar, U. Chandraiah, and S. Kandlikar, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **30**, 849 (1991); S. Acharya, G. Neogi, R. K. Panda, and D. Ramaswamy, Int. J. Chem. Kinet. **14**, 1253 (1982); A. G. Lappin, M. C. Laranjeira, and O. L. Youdi, J. Chem. Soc., Dalton Trans., p. 721 (1981); Dutta, S. Bhattacharaya, and P. Banerjee, Polyhedron **17**, 2313 (1998); G. H. Hugar and S. T. Nandiberwoor, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **32**, 1056 (1993).
2. R. I. Haines and A. McAuley, Coord. Chem. Rev. **39**, 77 (1981); K. Nag and A. Chakravarty, Coord. Chem. Rev. **33**, 87 (1980); B. C. Verma, S. B. Kalia, and B. S. Manhas, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **36**, 160 (1997); S. Bhattacharya, B. Saha, A. Datta, and P. Banerjee, Coord. Chem. Rev. **170**, 47 (1998).
3. D. S. Mahadevappa, K. S. Rangappa, N. M. Gouda, and B. Thimmegowda, Int. J. Chem. Kinet. **14**, 1183 (1982).
4. M. K. Mahanti and D. Laloo, J. Chem. Soc., Dalton Trans., p. 311 (1990); R. M. Kulkarni, D. C. Bilehal, and S. T. Nandibewoor, Transition Met. Chem. **28**, 199 (2003); K. Nag and A. Chakravarthy, Coord. Chem. Rev. **33**, 77 (1980).
5. P. D. Pol, C. P. Kathari, and S. T. Nandibewooor, Transition Met. Chem. **28**, 209 (2003); D. C. Bilehal, R. M. Kulkarni, and S. T. Nandibewoor, Inorg. React. Mech. **4**, 103 (2002).
6. S. Bhattacharya, B. Saha, A. Datta and P. Banerjee, Coord. Chem. Rev. **47**, 170 (1998); R. I. Haines and A. McAuley, Coord. Chem. Rev. **39**, 77 (1981).
7. P. Ray, in *Inorganic Synthesis*, 5th ed., Ed. by T. Moellar (McGraw-Hill, New York, 1957), p. 201.
8. G. H. Jaffery, J. Bassett, J. Mendham and R. C. Denney, in *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed. (ELBS, Longman, Essex, U.K., 1996), p. 462.
9. G. P. Panigrahi and P. K. Misro, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **16**, 201 (1978).
10. K. Randrerath, *Thin Layer Chromatgraphy* (Academic, New York, 1968), p. 101.
11. I. M. Kolthoff, E. J. Meehan, and E. M. Carr, J. Am. Chem. Soc. **75**, 1439 (1953); A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (Wiley Eastern, New Delhi, 1970), p. 367.
12. U. Chandraiah, C. P. Murthy and S. Kandlikar, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **28**, 248 (1989); R. M. Kulkarni, D. C. Bilehal, and S. T. Nandibewoor, J. Chem. Res. **147**, 401 (2002).

13. J. C. Bailar, Jr., H. J. Emeleus, S. R. Nyholm, and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry* (Pergamon, Oxford, 1975), Vol. 2, p. 1456.

14. R. Chang, *Physical Chemistry with Application to Biological Systems* (MacMillo, New York, 1981) p. 326.

15. S. Bhattacharya, M. Ali, S. Gangopadhaya, and P. J. Banerjee, J. Chem. Soc., Dalton Trans., p. 2645 (1996); *Inorganic Reactions and Methods*, Ed. by J. J. Zuckermann (VCH, Deerfield Beach, FL, 1986), Vol. 15, p. 13.

16. J. Devi, S. Kothari, and K. K. Banerji, Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem. **29**, 241 (1995); S. A. Chimatadar, T. Basavaraj, and S. T. Nandibewoor, Oxid. Commun. **26**, 88 (2003).

17. M. Martinez, M. A. Pitarque, and R. V. Eldik, J. Chem. Soc., Dalton Trans., p. 2665 (1996); S. A. Farokhi and S. T. Nandibewoor, Tetrahedron **59**, 7595 (2003).