Polish J. Chem., **77**, 1833–1840 (2003)

Kinetics and Mechanism of Oxidative Degradation of L-Proline by Alkaline Diperiodatonickelate(IV) – A Free Radical Intervention and Decarboxylation

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(Received May 19th, 2003; revised manuscript August 8th, 2003)

The kinetics of oxidation of L-proline by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 0.50 mol dm^{-3} was studied spectrophotometrically. The reaction is of first order in [DPN], zero order in [alkali] and less than unit order in [L-proline]. Addition of periodate has no effect on the rate of reaction. Effect of added products, ionic strength and dielectric constant of the reaction medium have been investigated. The main products were identified by spot test and IR spectra. A mechanism involving the diperiodatonickelate(IV) (DPN) as the reactive species of the oxidant has been proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated. The isokinetic temperature was determined and discussed.

Key words: kinetics, DPN, oxidation, L-proline, activation parameters

The use of diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium is new and restricted to a few cases [1–3], due to the fact of its limited solubility and stability in aqueous medium. Reduction of nickel(IV) complexes have been received a considerable attention in order to understand the nature of intermediate oxidation states of nickel, such as nickel(III). Indeed, stable nickel(III) complexes are known [4]. Moreover, when nickel(IV) periodate is oxidant, it needs to be known, which of the species is the active form of oxidant, since multiple equilibria between the different nickel(IV) species are involved.

Amino acids have been oxidized by a variety of oxidizing agents [5]. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [6,7].

In earlier reports [1–3] on DPN oxidation, periodate had a retarding effect in almost all the reactions and monoperiodatonickelate(IV) (MPN) is considered to be the active species. However, in the present study we have observed entirely different kinetic results and diperiodatonickelate(IV) (DPN) is found to be the active form of the

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oxidant. Literature survey reveals that there are no reports on the oxidative mechanism of L-proline by diperiodatonickelate(IV) (DPN) oxidant.

The present study deals with the title reaction to investigate the redox chemistry of nickel(IV) in such media and to arrive at a plausible mechanism of the reaction on the basis of kinetic and spectral results.

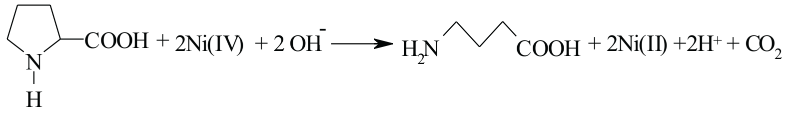
EXPERIMENTAL

Materials: All chemicals used were of reagent grade. Solution of L-proline (s.d. fine chem) was prepared by dissolving appropriate amount of recrystallized sample in double distilled water. The preparation of solutions, standardization and kinetics followed are as given earlier [8].

Regression analysis of experimental data to obtain the regression coefficient r and standard deviation S of points from the regression line was performed using a Pentium-III personal computer.

RESULTS AND DISCUSSION

Different reaction mixtures with different sets of concentrations of reactants, where [Ni(IV)] was in excess over [L-proline] at constant ionic strength and alkali were kept for about 6 hours at 25 ± 0.1°C in nitrogen atmosphere and in a closed vessel. The remaining [DPN] was assayed spectrophotometrically by measuring the absorbance at 410 nm. The product, nickel(II) was analyzed as the dimethyl glyoxime by gravimetrically [9]. The results indicated that two moles of DPN consumed one mole of L-proline as in equation (1).



(1)

The main reaction product was identified as 4-aminobutyricacid by spot test [10]. It was extracted with ether and recrystallized from aqueous alcohol and characterized by IR spectrum and m.p. 192°C. The presence of carboxylic acid was confirmed by IR spectroscopy which showed bands at 3444 cm^{-1} for NH stretching band at 1752 cm^{-1}, due to C=O stretching of carboxylic acid, and 2845 cm^{-1} for carboxylic acid OH stretching. The only organic product obtained in the oxidation is 4-aminobutyricacid, which is confirmed by single spot in TLC. It was observed that the 4-aminobutyricacid does not undergo further oxidation under the present kinetic conditions.

The order of the reactants was determined from the slope of log k_{obs} *versus* log concentration plots by varying the concentration of oxidant, reductant and alkali in turn; while keeping concentration of others constant. The non-variation in the pseudo-first order rate constants at various concentrations of DPN indicates the order in [DPN] as unity (Table 1). The k_{obs} values increased with increase in concentration of L-proline indicating an apparent less than unit order dependence on [L-proline] (Table 1). The k_{obs} values were not changed with increase in concentration of alkali indicating a zero order dependence on [alkali] (Table 1). It was found that the added periodate has no significant effect on the rate of reaction (Table 1). The effect of ionic strength and solvent polarity has negligible effect on the rate of the reaction.

Table 1. Effect of variation of [DPN], [L-proline], [OH⁻] and [IO_4^-] on oxidation of L-proline by DPN at 25℃, ($I = 0.5$ mol dm^{-3}).

[DPN] × 10^5 mol dm^{-3}	[L-proline] × 10^4 mol dm^{-3}	[OH^-] mol dm^{-3}	[IO_4^-]×10^5 mol dm^{-3}	k_{obs} × 10^3 s^{-1}	
				Exptl.	Calcd.
1.0	6.0	0.05	8.0	7.74	7.76
3.0	6.0	0.05	8.0	7.75	7.76
6.0	6.0	0.05	8.0	7.76	7.76
8.0	6.0	0.05	8.0	7.76	7.76
10	6.0	0.05	8.0	7.77	7.76
6.0	2.0	0.05	8.0	3.04	3.04
6.0	4.0	0.05	8.0	5.60	5.55
6.0	6.0	0.05	8.0	7.76	7.76
6.0	10	0.05	8.0	10.8	10.9
6.0	20	0.05	8.0	16.3	16.3
6.0	6.0	0.02	8.0	7.74	7.76
6.0	6.0	0.05	8.0	7.76	7.76
6.0	6.0	0.08	8.0	7.75	7.76
6.0	6.0	0.14	8.0	7.76	7.76
6.0	6.0	0.20	8.0	7.78	7.76
6.0	6.0	0.05	4.0	7.75	–
6.0	6.0	0.05	8.0	7.74	–
6.0	6.0	0.05	16	7.76	–
6.0	6.0	0.05	30	7.77	–
6.0	6.0	0.05	40	7.77	–

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of intervention of free radicals in the reaction.

The rate constants, k, of the slow step of the mechanism were obtained from the intercepts of the plots of $1/k_{obs}$ *versus* 1/[L-proline] at five different temperatures. The values of $k \times 10^2$ (s^{-1}) were obtained as 3.16, 3.69, 4.14, 4.69 and 5.31 at 25, 30, 35, 40 and 45℃ respectively. From the plot of log k *versus* 1/T ($r \geq 0.9956$, $S \leq 0.0213$) with least square analysis, the activation parameters, E_a, $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and logA are calculated as 20.1±1.0 k J mol^{-1}, 17.6±1.0 k J mol^{-1}, –214.2 ±10 J K^{-1} mol^{-1}, 83.6 ±4.1 k J mol^{-1} and 2.0±0.1. The initially added products such as Ni(II), in the form of $NiSO_4$ and 4-aminobutyricacid did not have any significant effect on the rate of the reaction.

The water soluble [4] Ni(IV) periodate complex is reported [8,11] to be $[Ni(HIO_6)_2(OH)_2]^{6-}$. Although, periodate is involved in multiple equilibria which prevail to varying extends depending on the pH employed, under condition of high pH 12.7 of the study the form which, predominates is understood to be the species, $H_3IO_6^{2-}$ (not as HIO_6^{4-} present in the Ni(IV) complex [3,11]).

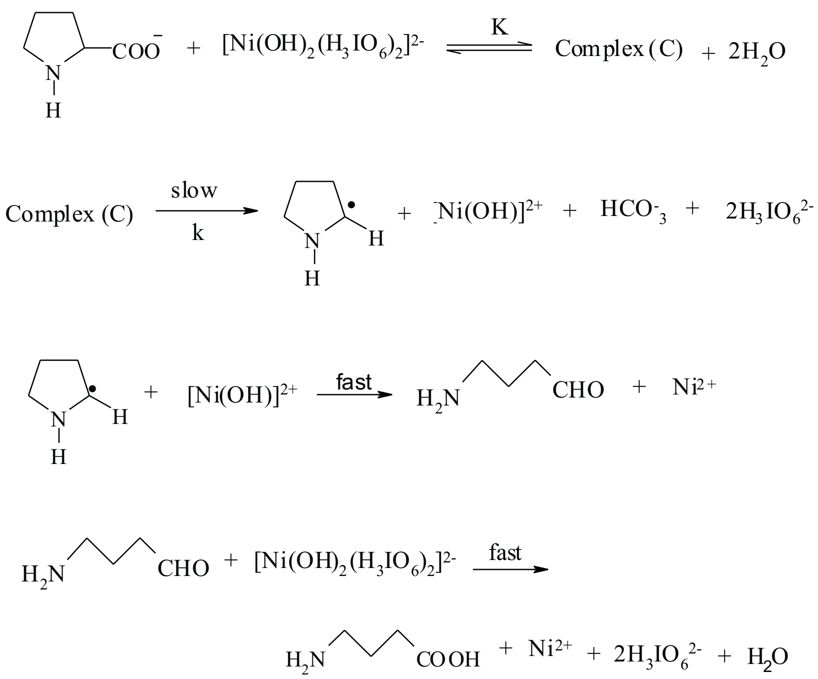
Periodic acid (H_5IO_6) exists in acid medium and also as $H_4IO_6^-$ around a pH of 7. Thus, under the conditions employed in the alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations periodate also tends to dimerise. Hence at the pH employed in the study, the Ni(IV) periodate complex exists as DPN, $[Ni(H_3IO_6)_2(OH)_2]^{2-}$, a conclusion also supported earlier [3,11].

It is known that L-proline exists in the form of Zwitter ion [12] in aqueous medium. In highly acidic medium it exists in the protonated form, whereas in highly basic medium it is in the fully deprotonated form [12].

In most of the reports [1–3] on DPN oxidation, periodate had a retarding effect and order in $[OH^-]$ was found to be less than unity and monoperiodatonickelate(IV) (MPN), is considered to be the active species. However, in the present kinetic study, different kinetic observations have been obtained. Periodate has totally no effect on the rate of reaction. The reaction shows zero order in $[OH^-]$ and it is interesting to note these effects, which is rarely observed. Accordingly, the DPN is considered to be the active species of the oxidant. The deprotonated form of L-proline reacts with DPN species $[Ni(OH)_2(H_3IO_6)_2]^{2-}$ to form a complex C. This complex C decomposes in a slow step to give a free radical derived from decarboxylated L-proline. This radical in turn reacts with Ni(III) species in a fast step to form intermediate aldehyde and finally, this intermediate aldehyde reacts with another molecule of DPN species in a fast step to yield the products (Scheme 1). The evidence of Ni(III) is in accordance with earlier work [13].

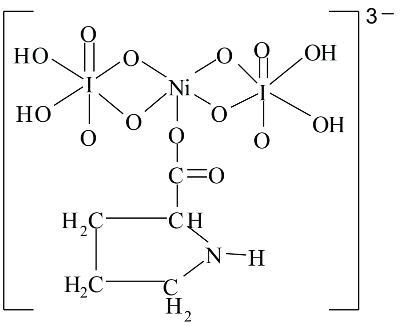
The thermodynamic quantities for the first equilibrium step in Scheme 1 can be evaluated as follows: The L-proline concentration, as in Table 1, were varied at four different temperatures and the K value was determined at each temperature. The values of $K \times 10^{-2}$ ($dm^3\ mol^{-1}$) were obtained as 5.33, 5.75, 6.17, 6.41 and 6.53 at 25, 30, 35, 40 and 45°C respectively. A van't Hoff's plot was made for the variation of K with temperature (*i.e*, log K *versus* 1/T) ($r \geq 0.9992$, $s \leq 0.0122$) and the values of the enthalpy of the reaction, ΔH, entropy of the reaction, ΔS, and free energy of reaction, ΔG, were calculated as 8.20 ± 0.41 k J mol^{-1}, 79.8 ± 3.9 J K^{-1} mol^{-1} and -16.3 ± 0.6 k J mol^{-1}, respectively. A comparison of the latter values with those obtained for the slow step of the reaction shows, that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step are fairly rapid and involves only a small activation energy [14].

Based on the observed kinetic results, a mechanism involving free radical has been proposed, which is shown in Scheme 1.



The probable structure of complex(C) is given as

Scheme 1



The less than unit order in [L-proline] presumably results from a complex formation between the oxidant and substrate prior to the formation of the products. Attempts to obtain spectral evidence for the complex formation between DPN and [L-proline] were not successful, since there is no change in UV-VIS spectra of DPN and mixture of DPN and [L-proline] at room temperature. However, at lower temperature (nearly 2°C), a bathochromic shift, λ_{max}, of *ca* 8nm from 269 to 278 nm of DPN and hyperchromicity at 278 nm was observed for the spectra of mixture of DPN and

[L-proline]. This indicates that complex formation is favored at low temperature. Indeed, it is to be noted that a plot of $1/k_{obs}$ *versus* 1/[L-proline] ($r \geq 0.9991$, $S \leq 0.0213$) shows a straight line with non-zero intercept (Fig. 1). Such a complex formation between the oxidant and substrate has been observed earlier [13]. All experimental results indicate a mechanism of the type as given in Scheme 1.

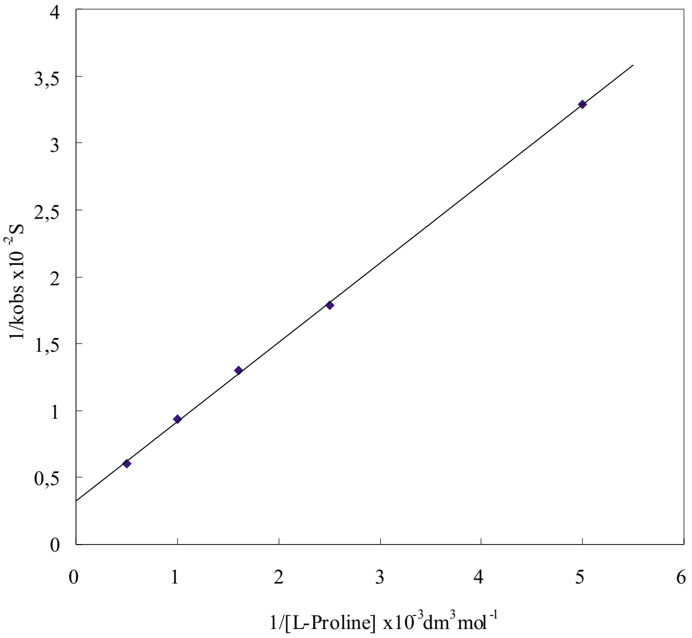


Figure 1. Verification of rate law (3) in the form of (4) (conditions as in Table 1).

Scheme 1 leads to the rate law equation (2)

$$\text{Rate} = \frac{-d[\text{Ni(IV)}}{dt} = \frac{kK[\text{Ni(IV)}[\text{L - Proline}]}{(1 + K[\text{L - Proline}])(1 + K[\text{Ni(IV)}])} \tag{2}$$

In view of the low concentration of [Ni(IV] used, the term $\{1 + K\ [\text{Ni(IV)}]\}$ in the denominator is approximated to unity.
Therefore,

$$k_{obs} = \frac{\text{Rate}}{[\text{Ni(IV)}]} = \frac{kK[\text{L - Proline}]}{1 + K[\text{L - Proline}]} \tag{3}$$

(3) can be rearranged to (4), which is suitable for verification

$$\frac{1}{k_{obs}} = \frac{1}{kK[\text{L - Proline}]} + \frac{1}{k} \qquad (4)$$

According to (4), other conditions being constant, the plots of $1/k_{obs}$ *versus* 1/[L-proline] ($r \geq 0.9991$, $S \leq 0.0213$) should be linear, as shown in Fig. 1. From the slopes and intercepts of K and k could be derived as $5.3 \pm 0.2 \times 10^2$ dm^3 mol^{-1} and $3.2 \pm 0.1 \times 10^{-2}$ s^{-1} respectively. Using these constants, the rate constants were calculated for different experimental conditions and there is a reasonable agreement between the calculated and experimental values (Table 1). A free radical scavenging experiments revealed such a possibility. The same type of radical intermediate has also been observed earlier in the context of alkaline nickel(IV) oxidation of various substrates [15].

The negligible effect of ionic strength and dielectric constant on the rate of reaction supports the mechanism proposed. The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron transfer processes. The value of $\Delta H^{\#}$ was due to a release of energy of solution changes in the transition state. The negative value of $\Delta S^{\#}$ within the range of radical reaction has been ascribed [16] to the nature of electron pairing and electron unpairing processes and indicates that the activation complex is more ordered than the reactants. The modest value of enthalpy of activation and the higher rate constant of the slow step of mechanism indicate that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion was supported earlier [17].

We have also calculated the isokinetic temperature (β) as 274.4 K. The value of β is lower than the experimental temperature (303 K). This indicates that the rate is governed by the enthalpy of activation [18]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar mechanism, as previously suggested.

CONCLUSIONS

Among various species of Ni(IV) in alkaline medium, in earlier reports the monoperiodatonickelate(IV) was the active species, whereas diperiodateonickelate(IV) itself is considered to be the active species for the title reaction. Rate constant of the slow step and other equilibrium constants involved in the mechanism are evaluated and the activation parameters with respect to the slow step of reaction were computed.

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