Kinetic and mechanistic study of oxidative degradation of isonicotinate ion by diperiodatonickelate(IV) in aqueous alkaline medium

R T Mahesh, M B Bellaki & S T Nandibewoor
P.G. Department of Studies in Chemistry, Karnataka University, Dharwad 580 003, India
Email: stnandibewoor@yahoo.com

Received 31 May 2004; revised 23 January 2006

The kinetics of oxidation of isonicotinate ion by alkaline diperiodatonickelate(IV) has been studied spectrophotometrically. The reaction is first order with respect to DPN and is apparently less than unit order each in [isonicotinate ion] and [alkali] under the experimental conditions. However, the order in [isonicotinate ion] and [alkali] changes from first order to zero order as their concentrations increase. Reaction rate increases with increase in ionic strength and decrease in solvent polarity of the medium. Addition of periodate has no effect on the reaction rate. A mechanism involving the deprotonated diperiodatonickelate(IV) (DPN) as the reactive oxidant species has been proposed. There is a good agreement between the observed and calculated rate constants under varying experimental conditions. The activation parameters with respect to the slow step of scheme have been discussed.

IPC Code: Int. Cl. C07B33/00

The use of diperiodatonickelate (IV)(DPN) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. Reduction of nickel(IV) complexes has received 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. Moreover, when nickel(IV) periodate is the oxidant, it is necessary to know which of the species is the active form of oxidant, since multiple equilibria between the different nickel(IV) species are involved.

In earlier studies on DPN oxidation, it is reported that peridate had a retarding effect and order in [OH] was found to be less than unity in almost all the reactions, while monoperiodatonickelate(IV) (MPN), was considered to be the active species. However, in the present study we have observed entirely different kinetic observations and deprotonated diperiodatonickelate(IV) (DPN) is found to be active form of the oxidant. The literature survey reveals that there are no reports on mechanistic study of isonicotinate ion oxidation by DPN. Thus, in order to explore the mechanism of oxidation by DPN in alkaline medium and to check the reactivity of amino acids towards DPN, we have selected isonicotinate ion as a substrate. The title reaction is studied to investigate the redox chemistry of the nickel (IV) in such media and to arrive at plausible mechanism.

Material and Methods

All chemicals used were of reagent grade. Doubly distilled water was used throughout the work. Isonicotinate solution (Fluka) was prepared by dissolving appropriate amount of recrystallised sample in alkali. The solid complex, nickel(IV) periodate, was prepared by known method. The purity of the complex was checked by its UV/Vis spectrum which showed a broad absorption band at 410 nm. Aqueous solution of DPN was obtained by dissolving the solid complex in 1.0 mol dm$^{-3}$ KOH solution. The Ni(IV) in alkaline solution was estimated gravimetrically after reducing it to Ni(II) and precipitating Ni(II) as its dimethylglyoxime complex. Potassium hydroxide and potassium nitrate were employed to maintain required alkalinity and ionic strength respectively.

Hitachi spectrophotometer (model 150-20), FTIR-spectrometer (Thernonickelate impact-410) and NMR spectrometer (Brooker-F 300MHz) were used in the study.

Since periodate was present in excess in the DPN complex, the possibility of isonicotinate ion oxidation by periodate in aqueous alkaline medium was tested. The results indicated that the reaction between IO$_3^-$ and isonicotinate ion is negligibly slow compared to the rate of reaction between DPN and isonicotinate ion under the experimental conditions.
Kinetic studies

Kinetic measurements were performed on Hitachi 150-20 spectrophotometer. All kinetic runs were followed under pseudo-first order conditions with the isonicotinate ion concentration in excess over that of the oxidant at 25 ± 0.1°C unless otherwise stated. The reaction was initiated by mixing thermally equilibrated solutions of DPN and isonicotinate ion, which also contained a definite quantity of KOH, KNO₃, and IO₄⁻. Here, the total concentration of hydroxide ion was calculated considering the KOH in DPN as well as the KOH additionally added. Similarly, the total metaperiodate concentration was calculated by considering the amount present in the DPN solution and also that additionally added. The course of reaction was followed by measuring the absorbance of unreacted DPN in the reaction mixture as a function of time in a 1 cm quartz cell located in the thermostated compartment of a Hitachi 150-20 spectrophotometer at λ_max 410 nm. Earlier it was verified that there is negligible interference from other species present in the reaction mixture at this wavelength. The obedience of Beer’s law by DPN at 410 nm was verified earlier, and the molar absorbance coefficient, ε, was found to be 7500 ± 375 dm³ mol⁻¹ cm⁻¹ at this wavelength. The reaction was followed to more than 80% completion. The first-order rate constants, k₁, were calculated from the slopes of log[DPN] versus time plots. The rate constants were reproducible to within ±5%.

In view of the modest concentration of alkali used in the reaction medium, the effect of the reaction vessel surface on the kinetics was also studied. Use of polyethylene/acrylic wares and quartz or polycrylate cells gave the same results, indicating that the surface does not have any significant effect on reaction rates.

Kinetic runs were also carried out in an N₂ atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N₂ atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. However, fresh solutions were nevertheless used while carrying out the kinetic study.

Regression analysis of experimental data was carried out to obtain regression coefficient r, and S, the standard deviations of points from the regression line.

Results and discussion

Different reaction mixtures with different sets of concentrations of reactants, where [Ni(IV)] was in excess over [isonicotinate ion] at constant ionic strength and alkali, were kept for about 6 h 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 results indicate that one mole of DPN consumed one mole of isonicotinate ion as in Eq. (1).

\[
\text{COO}^- + \text{Ni(IV)} + 2\text{OH}^- \rightarrow \text{(a)} + \text{Ni(II)} + \text{H}_2\text{O} \tag{1}
\]

The main reaction products were eluted with ether and Ni(II) was identified by its dimethyglyoxime complex by its visible spectra and N-O bond attached to isonicotinate ion tested by its spot test (Libermann test). The presence of nitroso group is also confirmed by IR spectra, which shows a band at 1225 cm⁻¹ due to N→O stretching and characterized by NMR spectra (DMSO) (doublet at 8.7 ppm due to aromatic protons (aa) and doublet at 7.8 ppm due to aromatic protons (bb)

The reaction orders were determined from the slopes of log kₐobs versus log concentration plots by varying the concentration of reductant and alkali in each, while keeping others constant. The oxidant, diperoxonickelate (IV) concentration was varied in the range of 5.0x10⁻⁵ to 5.0x10⁻³ mol dm⁻³ as shown in Table 1. All kinetic runs exhibited an identical characteristic. The linearity of plots of log (Abs) versus time, for different initial concentrations of (DPN) indicates the order in DPN as unity. This was also confirmed by varying [DPN], which did not show any change in pseudo-first order constants, k₁obs (Table 1).

The substrate, isonicotinate ion, was varied in the range of 5.0x10⁻⁴ to 5.0x10⁻³ mol dm⁻³ at 25°C, keeping all other reactant concentrations and conditions constant (Table 1). The kobs values increased with increase in concentration of isonicotinate ion indicating an apparent less than unit order dependence on substrate concentration. However, at lower concentration of isonicotinate ion the reaction was first order in [isonicotinate ion] and at high concentration of isonicotinate ion, the reaction
was independent of [isonicotinate ion]. The order in [isonicotinate ion] changes from first order to zero order as the [isonicotinate ion] varies.

The effect of alkali on the reaction was studied at constant concentrations of isonicotinate ion and diperiodatonicelicate (IV) and at a constant ionic strength of 0.80 mol dm$^{-3}$ at 25°C. The rate constant increased with increase in [alkali], indicating an apparent less than unit order dependence on [alkali] as given in Table 1. Similar to as in the case of isonicotinate ion, the order in alkali changes from first order to zero order as [alkali] increases. The effect of [IO$_4^-$] was observed by varying the concentration from 2.0x10$^{-5}$ to 6.0x10$^{-4}$ mol dm$^{-3}$ keeping all other reactants concentrations constant. It was found that the added periodate has no effect on the rate of reaction.

The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.5 to 1.2 mol dm$^{-3}$ at constant concentrations of diperiodatonicelicate(IV), isonicotinate ion and alkali. It was found that the rate constant increased with increase in concentration of KNO$_3$ and the plot of log$k_{obs}$ versus $1/\gamma$ was linear ($r >0.9258$, $S \leq 0.009$) with positive slope.

The effect of dielectric constant($\varepsilon_\gamma$) was studied by varying the $t$-butanol-water content in the reaction mixture with all other conditions being maintained constant. The solvent did not react with the oxidant under the experimental conditions. The rate constants, $k_{obs}$ increased with decrease in the dielectric constant of the medium. The plot of log $k_{obs}$ versus $1/\varepsilon_\gamma$ was linear($r=0.9273$, $S \leq 0.004$) with positive slope. The externally added product such as the nickel sulphate did not have any significant effect on the rate of the reaction.

The reaction mixture was mixed with acrylonitrile monomer and kept for 3 h in nitrogen atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed indicating the intervention of free radicals in the reaction. The blank experiments of either DPN or isonicotinate ion with acrylonitrile alone did not induce polymerization under the same conditions as those induced with reaction mixtures. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier studies$^{15}$.

The rate of the reaction was measured at four different temperatures with varying [isonicotinate ion], keeping other conditions constant. The rate was found

![Table 1—Effect of variation of [DPN], [ISNA], [IO$_4^-$] and [OH] on oxidation of isonicotinate ion by DPN at 25°C. ($I=0.8$ mol dm$^{-3}$)](table.png)
to increase with increase in temperature. The rate constant, \( k \), of the slow step of the reaction was obtained from the intercept of the plots of \( 1/\kappa_{obs} \) versus \( 1/[\text{isonicotinate ion}] \) \((r > 0.9769, S < 0.005)\) for different temperatures. The values of \( k \) (s\(^{-1}\)) \((4.87 \pm 0.20 \times 10^{-5}, 1.57 \pm 0.05 \times 10^{-5}, 2.18 \pm 0.10 \times 10^{-5}\) and \(2.88 \pm 0.10 \times 10^{-5}\)) and \(3.91 \pm 0.20 \times 10^{-5}\) at \(25, 30, 35\), \(40\), and \(45^\circ C\), respectively. The energy of activation corresponding to these constants was evaluated from the Eyring plot and other activation parameters of the reaction were calculated as \( E_a = 40 \pm 2 \) (kJ mol\(^{-1}\)), \( \Delta H^o = 38 \pm 2 \) (kJ mol\(^{-1}\)), \( \Delta S^o = -88 \pm 4 \) (J K\(^{-1}\) mol\(^{-1}\)), \( \Delta G^o = 65 \pm 3 \) (kJ mol\(^{-1}\)).

Nickel(IV) is a good oxidant in an aqueous alkaline medium. The water soluble nickel(IV) periodate complex is reported\(^{5,6,11,16-17}\) to be \( \text{[Ni(HIO}_6\text{)}_2\text{(OH)}_2]^{6-} \). Although periodate is involved in multiple equilibria depending on the pH employed, under the conditions of high pH as maintained in this study, periodate is likely to exist^{45} as \(\text{H}_2\text{IO}_6^-\). Hence, the species of Ni(IV) in alkali can be expected to be \(\text{[Ni(H}_2\text{IO}_6\text{)}_2\text{(OH)}_2]^{5-}\) (DPN), a conclusion that is also supported by earlier work\(^{2,1}\). The reaction between DPN and isonicotinate ion in alkaline medium has 1:1 stoichiometry of oxidant:reductant with first order dependence each in [DPN] and the apparent order of less than unity in [isonicotinate ion] and [OH\(^-\)]. In most of the reports on DPN oxidation\(^{4,7}\), periodate had a retarding effect and order in the [OH\(^-\)] was found to be less than unity and monoperiodatonicelate(IV) (MPN), is considered to be the active species. However, in the present kinetic study, different kinetic observations have been obtained, i.e., periodate has totally no effect on the rate of reaction. Accordingly, the deprotonated DPN is considered to be the active species of the oxidant. The fractional order in [isonicotinate ion] presumably results from a complex formation between the oxidant and substrate prior to the formation of the products.

The complex decomposes in a slow step to a free radical derived from isonicotinate ion, and intermediate of nickel(IV) species, i.e., nickel(III). This radical reacts with nickel(III) species in a fast step to yield the products as given in Scheme 1.

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of the isonicotinate ion, DPN and a mixture of both. A bathochromic shift of about 4.4 nm from 341.2 to 345.6 nm in the spectra of isonicotinate ion was also observed and hypochromicity was observed at 345.6 nm. Indeed, it is to be noted that a plot of \(1/\kappa_{obs}\) versus \(1/[\text{isonicotinate ion}]\) \((r > 0.896, S < 0.0047)\) shows a straight line with non-zero intercept (Fig. 1). Such complex formation between substrate and oxidant has been observed earlier\(^{13}\).

The probable structure of the complex (C) may be given as below (I):
The thermodynamic quantities for the first equilibrium step in Scheme 1 can be evaluated as follows: The hydroxyl ion concentration and isonicotinate ion concentration as in Table 1 were varied at four different temperatures and the \( K_f \) value was determined at each temperature. The values of \( K_f \) (dm\(^{-3}\) mol\(^{-1}\)) were obtained as 1.10, 1.40, 1.70, 2.0 and 2.74 at 25, 30, 35, 40 and 45°C, respectively. A van't Hoff's plot was made for the variation of \( K_f \) with temperature (i.e., \( \log K_f \) versus \( 1/T \) (\( \geq 0.971 \), \( S \leq 0.0112 \)) and the values of the enthalpy of the reaction, \( \Delta H \), entropy of the reaction, \( \Delta S \), and free energy of reaction, \( \Delta G \) were calculated as 34.6 ± 0.8 kJ mol\(^{-1}\), 117 ± 2 J K\(^{-1}\) mol\(^{-1}\) and -8.3 ± 0.6 kJ 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 determining step, supporting the fact that the reaction before the rate determining step are fairly rapid and involves only less activation energy. The reaction between substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work. Scheme 1 leads to the rate law as given in Eq. (2):

\[
\text{Rate} = \frac{d[\text{Ni(IV)}]}{dt} = \frac{kK_1K_2[DPN][\text{ISNA}][OH^-]}{1 + K_1[OH^-] + K_1K_2[\text{ISNA}][OH^-]}
\]

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

\[
k_{obs} = \frac{1}{K_1K_2[\text{ISNA}][OH^-]} + \frac{1}{kK_2}
\]

According to Eq. (4), other conditions being constant, the plots of \( 1/k_{obs} \) versus \( 1/[OH^-] \) \((r \geq 0.986, S \leq 0.0058)\), \( 1/[\text{ISNA}] \) \((r \geq 0.972, S \leq 0.0081)\) should be linear as shown in Fig. 1. From the slopes and intercepts, the values of \( K_1, K_2 \) and \( k \) could be derived as 1.14 ± 0.05 dm\(^3\) mol\(^{-1}\), (2.08 ± 0.10) × 10\(^{-2}\) dm\(^3\) mol\(^{-1}\), and (4.87 ± 0.20) × 10\(^{-2}\) s\(^{-1}\), respectively. The value of \( k \) is in agreement with earlier literature values.

The effects of ionic strength and dielectric constant of the medium on rate constant of the reaction are in accordance with involvement of two negatively charged species of reactants as given in Scheme 1. The values of \( \Delta H^0 \) and \( \Delta S^0 \) were both favourable for electron transfer processes. The values of \( \Delta S^0 \), within the range of radical reactions, have been ascribed to the nature of electron pairing and electron unpairing processes and to the loss of a degree of freedom, formerly available to the reactions on the formation of rigid transition state. The observed modest enthalpy of activation and a relatively low value of the entropy of activation indicate that the ISNA oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.

References