Monatshefte für Chemie 134, 1341–1352 (2003)
DOI 10.1007/s00706-003-0608-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Kinetics and Mechanism of Oxidation of *L*-Leucine by Alkaline Diperiodatonickelate(IV) – A Free Radical Intervention, Deamination, and Decarboxylation

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Received September 19, 2002; accepted (revised) January 1, 2003

Summary. The kinetics of oxidation of *L*-leucine by alkaline diperiodatonickelate(IV) was studied spectrophotometrically using a rapid kinetic accessory. The reaction is first order with respect to [*DPN*] and apparently less than unit order, each in [*L*-leucine] and [alkali] under the experimental conditions. However, the order in [*L*-leucine] and [alkali] changes from first order to zero order as the concentrations change from lower to higher values. Addition of periodate has no effect on the reaction rate. A mechanism involving the deprotonated diperiodatonickelate(IV) (*DPN*) as the reactive oxidant is proposed. The reaction constants involved in the mechanism were evaluated. There is a good agreement between the observed and calculated rate constants under varying experimental conditions. The isokinetic temperature was determined and the activation parameters with respect to the slow step of the reaction scheme were evaluated and discussed.

Keywords. *L*-Leucine; Alkaline diperiodatonickelate(IV); Oxidation; Kinetics.

Introduction

The use of diperiodatonickelate(IV) (*DPN*) as an oxidant in alkaline medium is new and restricted to a few cases [1–6] due to the fact of its limited solubility and stability in aqueous medium. The reduction of nickel(IV) complexes has received considerable attention in order to understand the nature of intermediate oxidation states such as nickel(III). Indeed, stable nickel(III) complexes are known [7–9]. Moreover, when nickel(IV) periodate is the oxidant, it needs to be known which of the species is the active form, since multiple equilibria between different nickel(IV)

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species are involved. Amino Acids act not only as the building blocks in protein synthesis but they also play a significant role in metabolism. Amino Acids can undergo many types of reaction depending on whether a particular amino acid contains non-polar groups or polar substituents. *L*-Leucine is an essential amino acid. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So, oxidation of *L*-leucine may help in understanding some aspects of enzyme kinetics. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants [10–12]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant.

In earlier reports [4–7] on *DPN* oxidation, periodate had a retarding effect and the order in [OH^-] was found to be less than unity in almost all the reactions and monoperiodatonickelate(IV) (*MPN*) is considered to be the active species. However, in the present study entirely different kinetic observations have been made and deprotonated diperiodatonickelate(IV) (*DPN*) is found to be the active form of the oxidant. The literature survey reveals that there are no reports on mechanistic studies of *L*-leucine oxidation by *DPN*. Thus, *L*-leucine has been selected as a substrate in order to explore the mechanism of oxidation by *DPN* in alkaline medium and to check the reactivity of amino acids towards *DPN*. The title reaction is studied to investigate the redox chemistry of the nickel(IV) in such media and to arrive at a plausible mechanism.

Results and Discussion

Reaction Order

The orders with respect to [*L*-leucine], [periodate] and [alkali] were found by $\log k_{obs}$ *versus* log [concentration] plots; these orders were obtained by varying the concentration of reductant, periodate, and alkali in turn while keeping the respective others constant.

The concentration of diperiodatonickelate(IV) was varied in the range, 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed [*L*-leucine], [OH^-], and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of *DPN* indicates the order in [*DPN*] to be unity (Table 1). This was also confirmed by the linearity of plots of log [*DPN*] *versus* time up to 85% completion of the reaction. The substrate *L*-leucine was varied in the range of 4.0×10^{-4} to 4.0×10^{-3} mol dm^{-3} at 25°C keeping all other reactants concentrations and conditions constant (Table 1). The k_{obs} values increased with the concentration of *L*-leucine and indicated an apparent order in [*L*-leucine] less than unity (Table 1). However, at lower concentration of *L*-leucine the reaction was first order in [*L*-leucine] and at higher concentration of *L*-leucine the reaction was independent of [*L*-leucine]. The order in [*L*-leucine] changes from first to zero order as the [*L*-leucine] decreases. The effect of [alkali] on the rate of reaction was studied at constant concentrations of *L*-leucine and *DPN* at an ionic strength of 0.6 mol dm^{-3}. The rate constants increased with [alkali] indicating a less than unit order of this reactant (Table 1). Similar as in the *L*-leucine case the order changes from first to zero order as [alkali] decreases. The effect of [IO_4^-] was observed by

Table 1. Effect of variation of [*DPN*], [*L*-leucine], [IO_4^-], and [OH^-] on oxidation of *L*-leucine by *DPN* at 25°C, $I = 1.0\,\mathrm{mol\,dm^{-3}}$

[*DPN*] $\times 10^4$/ $\mathrm{mol\,dm^{-3}}$	[*L*-leucine] $\times 10^3$/ $\mathrm{mol\,dm^{-3}}$	[IO_4^-] $\times 10^4$/ $\mathrm{mol\,dm^{-3}}$	[OH^-]/ $\mathrm{mol\,dm^{-3}}$	$k_{obs} \times 10^2/\mathrm{s^{-1}}$	
				exptl.	calcd.
1.0	0.8	2.0	0.2	2.4	2.5
2.0	0.8	2.0	0.2	2.4	2.5
4.0	0.8	2.0	0.2	2.5	2.5
6.0	0.8	2.0	0.2	2.5	2.5
10	0.8	2.0	0.2	2.4	2.5
6.0	0.4	2.0	0.2	1.6	1.7
6.0	0.6	2.0	0.2	2.0	2.1
6.0	0.8	2.0	0.2	2.5	2.5
6.0	2.0	2.0	0.2	3.4	3.5
6.0	4.0	2.0	0.2	4.0	4.0
6.0	0.8	2.0	0.2	2.30	2.5
6.0	0.8	4.0	0.2	2.35	2.5
6.0	0.8	8.0	0.2	2.40	2.5
6.0	0.8	15.0	0.2	2.45	2.5
6.0	0.8	20.0	0.2	2.50	2.5
6.0	0.8	2.0	0.1	1.4	1.6
6.0	0.8	2.0	0.2	2.0	2.1
6.0	0.8	2.0	0.5	2.5	2.5
6.0	0.8	2.0	0.8	2.7	2.7
6.0	0.8	2.0	1.0	3.0	2.9

error ±4%

varying the concentration from 0.2×10^{-4} to $2.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ keeping all other concentrations of reactants constant. It was found that the added periodate has no effect on the rate of reaction.

Effect of Ionic Strength and Solvent Polarity

The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.2 to $1.0\,\mathrm{mol\,dm^{-3}}$ at constant concentrations of *DPN*, *L*-leucine, and alkali. It was found that the rate of reaction increases with increasing ionic strength of the medium. The plot of log k_{obs} *versus* $I^{1/2}$ was linear with positive slope (Fig. 1) ($r \geq 0.969$, $s \leq 0.0548$).

The relative permittivity (D) effect was studied by varying the *t*-butyl alcohol: water ratio in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of the pure liquids [13]. There was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constants, k_{obs}, decreased with the decrease in the dielectric constant of the medium. The plot of log k_{obs} *versus* $1/D$ was linear ($r \geq 0.976$, $s \leq 0.055$) (Fig. 1) with a negative slope.

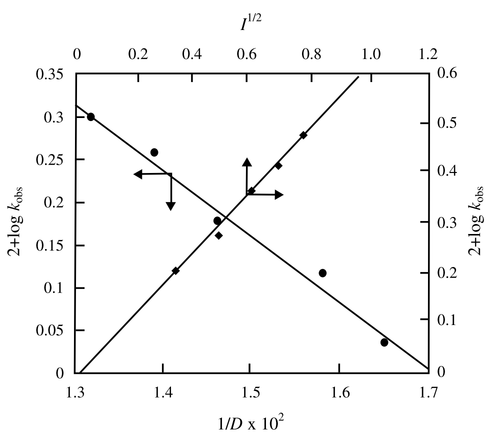


Fig. 1. Plot of $\log k_{obs}$ *versus* $I^{1/2}$ and $\log k_{obs}$ *versus* $1/D$

Effect of Initially Added Products

The initially added products, such as Ni(II) in the form of $NiSO_4$ did not have any significant effect on the rate of the reaction.

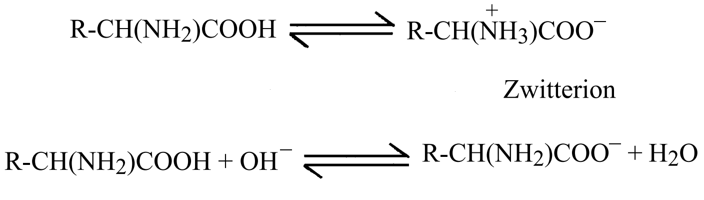
Test for Free Radicals

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

The water soluble Ni(IV) periodate complex is reported [5, 6, 14–16] to be $[Ni(HIO_6)_2(OH)_2]^{6-}$, 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 [4, 5] as $H_3IO_6{}^{2-}$. Hence, the species of Ni(IV) in alkali can be expected to be $[Ni(H_3IO_6)(H_2IO_6)(OH)_2]^{3-}$ (*DPN*). This conclusion is also supported by earlier work [2, 3].

It is known that in aqueous solution, amino acid exists as Zwitterionic [17] whereas in aqueous alkaline medium they exists as the anionic form according to the following equilibria (Scheme 1).

The reaction between *DPN* and *L*-leucine in alkaline medium has 2:1 stoichiometry of oxidant to reductant with first order dependence in [*DPN*] and the appar-



$$\text{R-CH(NH}_2\text{)COOH} \rightleftharpoons \text{R-CH(}\overset{+}{\text{N}}\text{H}_3\text{)COO}^-$$

Zwitterion

$$\text{R-CH(NH}_2\text{)COOH} + \text{OH}^- \rightleftharpoons \text{R-CH(NH}_2\text{)COO}^- + \text{H}_2\text{O}$$

Scheme 1

ent order of less than unity in [*L*-leucine] and [OH^-]. In most of the reports [4–7] on *DPN* oxidation, periodate had a retarding effect and the 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, *i.e.*, periodate has no effect whatsoever on the rate of reaction. Accordingly, the deprotonated *DPN* is considered to be the active species of the oxidant. The fractional order in [*L*-leucine] presumably results from a complex formation between the oxidant and substrate prior to the formation of the products. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from Uv-Vis spectra of the *L*-leucine, *DPN*, and mixture of both. A bathochromic shift of about 7 nm from 459 to 463 nm in the spectra of *L*-leucine was observed and hyperchromicity was observed at 463 nm. The Uv-Vis spectral changes occurring in the oxidation of *L*-leucine by *DPN* show the absence of isosbestic points, which supports the complex formation [18]. Indeed, it is to be noted that a plot of $1/k_{\mathrm{obs}}$ *versus* 1/[*L*-leucine] ($r \geq 0.986$, $s \leq 0.0058$) shows a straight line with non-zero intercept (Fig. 2). Such complex formation between substrate and oxidant has been observed earlier [19]. Based on the observed kinetic results a mechanism involving complex formation between oxidant and substrate has been proposed which is shown in Scheme 2.

The thermodynamic quantities for the first equilibrium step in Scheme 2 can be evaluated as follows: The hydroxyl ion and the *L*-leucine concentration as in Table 1 were varied at four different temperatures and the K_1 value was determined at each temperature. The values of K_1 ($\mathrm{dm^3\,mol^{-1}}$) were obtained as 7.5, 8.1, 8.9, and 9.3 at 25, 30, 35, and 40°C, respectively. A *Van't Hoff*'s plot was made for the variation of K_1 with temperature ($r \geq 0.9992$, $s \leq 0.0122$) and the values of the enthalpy of the reaction, $\Delta H°$, the entropy of the reaction, $\Delta S°$, and the free energy of the reaction, $\Delta G°$, were calculated as $11.4 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$, $17.7 \pm 1.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and $-54.5 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$, respectively. A comparison of the latter values with those obtained for the slow step of the reaction shows that

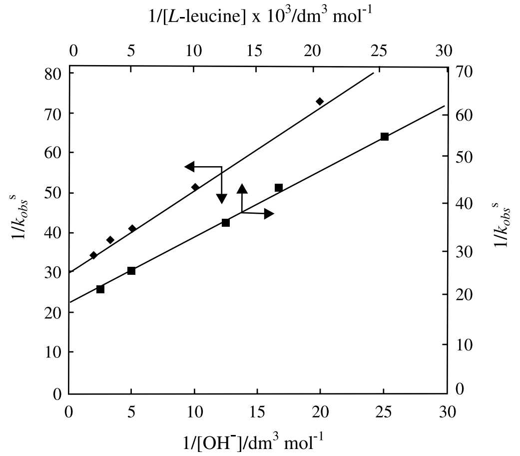
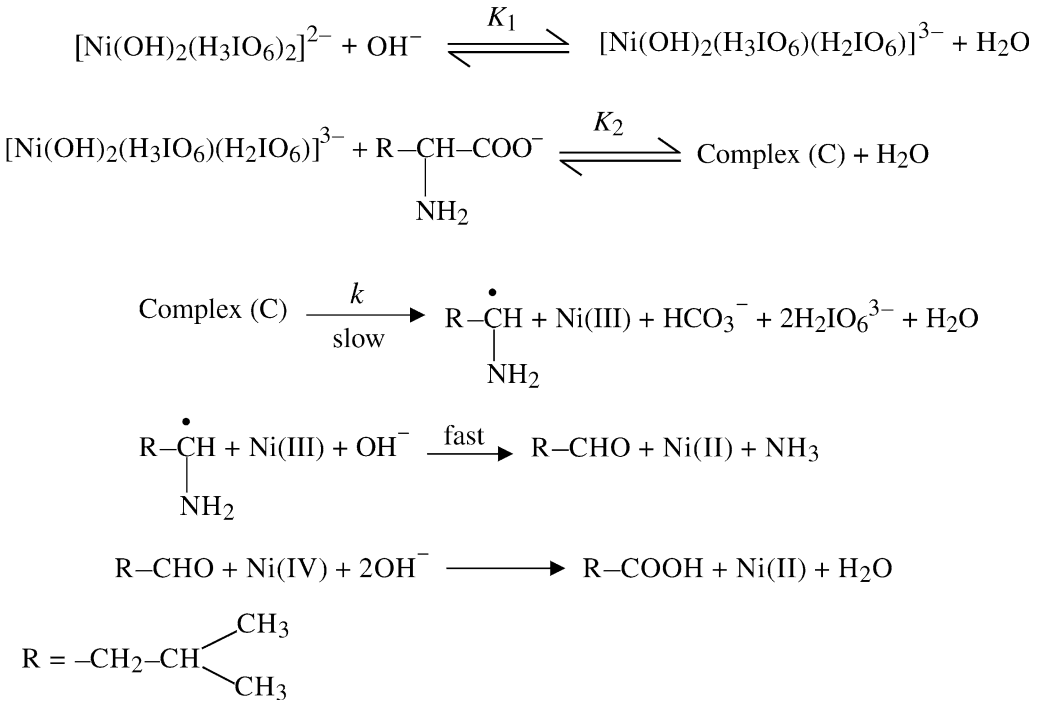


Fig. 2. Verification of rate law described by Eq. (2); plot of $1/k_{\mathrm{obs}}$ *versus* $1/[OH^-]$ and $1/k_{\mathrm{obs}}$ *versus* 1/[*L*-leucine] (conditions as given in Table 1)



Scheme 2

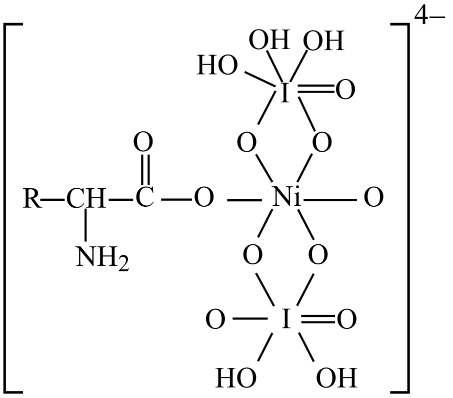


Fig. 3. Probable structure of complex C

these values mainly refer to the rate limiting step, supporting the fact that the reactions before the rate determining step are fairly rapid and involve only little activation energy [20].

Scheme 2 leads to the rate law given by Eq. (1).

$$\text{Rate} = -\frac{\mathrm{d}[\text{Ni(IV)}]}{\mathrm{d}t} = \frac{kK_1K_2[\text{Ni(IV)}][\text{OH}^-][L\text{-leucine}]}{1 + K_1[\text{OH}^-] + K_1K_2[L\text{-leucine}][\text{OH}^-]} \tag{1}$$

The terms $[1+K_1K_2[[\mathrm{Ni(OH)_2(H_3IO_6)_2}]^{2-}][\mathrm{OH^-}]]$ and $[1+K_1[[\mathrm{Ni(OH)_2}$ $\mathrm{(H_3IO_6)_2}]^{2-}]+K_1K_2[[\mathrm{Ni(OH)_2(H_3IO_6)_2}]^{2-}]$ [*L*-leucine]] should also be in the denominator of Eq. (1), but in view of the low concentration of [Ni(IV)] used they approximate to unity.

Therefore, Eq. (2) is obtained.

$$k_{\mathrm{obs}} = \frac{\text{Rate}}{[\mathrm{Ni(IV)}]} = \frac{kK_1K_2[\mathrm{OH^-}][L\text{-leucine}]}{1+K_1[\mathrm{OH^-}]+K_1K_2[L\text{-leucine}][\mathrm{OH^-}]} \tag{2}$$

Equation (2) can be rearranged to Eq. (3), which is suitable for verification

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{kK_1K_2[L\text{-leucine}][\mathrm{OH^-}]} + \frac{1}{kK_2[L\text{-leucine}]} + \frac{1}{k} \tag{3}$$

According to Eq. (3), other conditions being constant, the plots of $1/k_{\mathrm{obs}}$ *versus* $1/[\mathrm{OH^-}]$ ($r \geq 0.986$, $s \leq 0.0058$) and $1/[L\text{-leucine}]$ ($r \geq 0.972$, $s \leq 0.0081$) should be linear as shown in Fig. 2. From the slopes and intercepts, the values of K_1, K_2, and k could be derived as $7.5 \pm 0.1\,\mathrm{dm^3\,mol^{-1}}$, $23.8 \pm 0.4 \times 10^2\,\mathrm{dm^3\,mol^{-1}}$, and $4.7 \pm 0.2 \times 10^{-2}\,\mathrm{s^{-1}}$, respectively. The value of K_1 is in agreement with earlier values [21]. Using these constants, the rate constants were calculated over different experimental conditions and there is a reasonable agreement between the calculated and experimental values (Table 1) which fortifies the proposed mechanism. The increase in the rate with increasing ionic strength qualitatively explains the reaction between two negatively charged species of reactants (Scheme 2). The effect of solvent on the reaction rate was already described previously [22]. The plot of log k_{obs} *versus* $1/D$ gives a straight line with a negative slope for a reaction between negative ions and a neutral molecule, whereas a positive slope results for a positive ion and a neutral molecule. In our present study, a plot of log k_{obs} *versus* $1/D$ ($r \geq 0.984$, $s \leq 0.0053$) is linear with a negative slope (Fig. 1) which is in accordance with the involvement of negative ions as given in Scheme 2.

The activation parameters for the oxidation of some amino acids by *DPN* are summarized in Table 2. The entropy of the activation for the title reaction falls within the observed range. Variation in the rate within a reaction series may be caused by change in the enthalpy and/or entropy of activation. Changes in the rate

Table 2. Activation parameters for some amino acids (for isokinetic temperature)

Amino acid	$k \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}s^{-1}}$ at 298 K	$k \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ at 303 K	$\Delta S^{\neq}/\mathrm{JK^{-1}\,mol^{-1}}$	$\Delta H^{\neq}/\mathrm{kJ\,mol^{-1}}$	$\Delta G^{\neq}/\mathrm{kJ\,mol^{-1}}$	Refs.
L-arginine	1.0	1.4	-36 ± 4	45.0 ± 2	56 ± 4	[30]
L-aspartic Acid	2.0	2.8	-11.5 ± 1	51.0 ± 3	55 ± 3	[31]
L-valine	1.8	2.2	-45.3 ± 2.4	26.2 ± 1.3	40.0 ± 2	[32]
L-leucine	4.7	5.6	-49.9 ± 2.5	18.0 ± 1	33.3 ± 1.8	present work

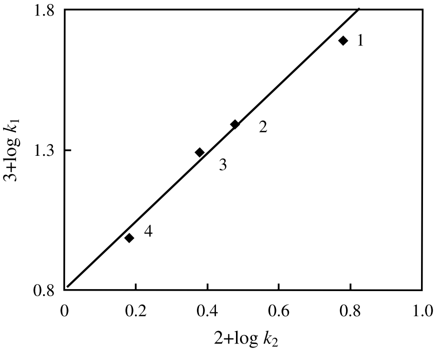


Fig. 4. Plot of log k_1 at 298 K *versus* log k_2 at 303 K (conditions as given in Table 2); 1. *L*-leucine; 2. *L*-aspartic acid; 3. *L*-valine; 4. *L*-arginine

are caused by changes in both $\Delta H^{\neq}$ and $\Delta S^{\neq}$, but the latter quantities are highly correlated. A plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ is linear according to Eq. (4).

$$\Delta H^{\neq} = \beta \Delta S^{\neq} + \text{constant} \tag{4}$$

β is called the isokinetic temperature. It has been asserted that apparently linear correlations of $\Delta H^{\neq}$ with $\Delta S^{\neq}$ are sometimes misleading and the evaluation of β by means of the above equation lacks statistical validity [23]. Exner [24] advocates an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and log k_2 (at T_2) is linearly related to log k_1 (at T_1), *i.e.* $\log k_2 = \mathrm{a} + \mathrm{b} \log k_1$, he proposes that β can be evaluated from Eq. (5).

$$\beta = T_1 T_2(\mathrm{b} - 1)/T_2\mathrm{b} - T_1 \tag{5}$$

We have calculated the isokinetic temperature as 342.2 K by plotting log k_1 at 298 K *versus* log k_2 at 303 K (Fig. 4) ($r \geq 0.979$, $s \leq 0.0051$). The value of β (342.2 K) is higher than the experimental temperature (303 K). This indicates that the rate is governed by the enthalpy of activation [25]. The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow a similar mechanism, as previously suggested.

Effect of Temperature

The kinetics were studied at four different temperatures under varying *L*-leucine concentrations. The rate constants k of the slow step were obtained from the intercept of $1/k_{\mathrm{obs}}$ *versus* 1/[*L*-leucine] ($r \geq 0.998$, $s \leq 0.0054$) plot at four different temperatures and were used to calculate the activation parameters. The values of $k \times 10^2$ were 4.76 ± 0.10, 5.60 ± 0.10, 6.45 ± 0.10, and $7.40 \pm 0.15\,\mathrm{s}^{-1}$ at 25, 30, 35, and 40°C, respectively. The energy of activation corresponding to these constants was evaluated from the *Arrhenius* plot of log k *versus* $1/T$, and other activation parameters were obtained and are listed in Table 3.

The mechanism is also supported by moderate values of activation parameters (Table 2). A high negative value of $\Delta S^{\neq}$ suggests that the intermediate complex is

Table 3. Thermodynamic activation parameters for the *L*-leucine oxidation by alkaline diperiodatonickelate(IV) complex with respect to slow step of Scheme 2

Activation parameters	Values
Ea (kJ mol^{-1})	20.6 ± 0.3
$\Delta H^{\neq}$ (kJ mol^{-1})	18.1 ± 0.2
$\Delta G^{\neq}$ (kJ mol^{-1})	33.3 ± 1.1
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-50 ± 2

more ordered than the reactants. The modest value of enthalpy of activation and the higher rate constant of the slow step of the mechanism indicated that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion was supported by earlier studies [26].

Conclusions

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

Experimental

Materials

All chemicals used were of reagent grade. Doubly distilled water was used throughout the work. The solution of *L*-leucine was prepared by dissolving an appropriate amount of a recrystallised sample in distilled water. The solid complex nickel(IV) periodate was prepared by a known method [27]. The purity of the complex was checked by its UV/Vis spectrum which shows a broad absorption band at 410 nm [14]. Aqueous solutions of *DPN* were obtained by dissolving the solid complex in 1.0 mol dm^{-3} KOH solution. The Ni(IV) in alkaline solution was estimated gravimetrically [28] after reducing it to Ni(II) and precipitating Ni(II) as its dimethyl glyoxime complex. Potassium hydroxide and potassium nitrate were employed to maintain the required alkalinity and ionic strength respectively.

Since periodate is present in excess in the *DPN* complex, the possibility of *L*-leucine oxidation by periodate in aqueous alkaline medium has been tested. The results indicated that the reaction between IO_4^- and *L*-leucine is negligibly slow compared to the rate of reaction between *DPN* and *L*-leucine under the experimental conditions.

Kinetic Measurements

Since the reaction was too fast to be monitored by the usual methods, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12). Kinetic runs were followed under pseudo-first order conditions with the *L*-leucine 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 *L*-leucine, which also contained a definite quantity of KOH, KNO_3, and IO_4^-. 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 additionally added one. The course of reaction was followed by measuring the absorbance of unreacted *DPN* in the reaction mixture in a 1 cm quartz cell located in the thermostated compartment of a Hitachi 150-20 spectrophotometer, at its maximum absorption wavelength of 410 nm as a function of time. 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 $7500 \pm 375\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ at this wavelength. The reaction was followed up to more than 80% completion. The first-order rate constants, k_{obs}, 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, attention was also directed to the effect of the reaction vessel surface on the kinetics. Use of polythene/acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on reaction rates.

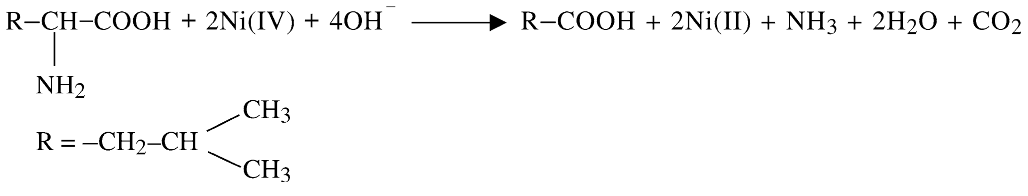
Kinetic runs were also carried out in an N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates, however, fresh solutions were nevertheless used for carrying out each kinetic study.

Regression analysis of experimental data to obtain regression coefficients *r* and *s*, the standard deviations of points from the regression line, was performed with a Pentium-III personnel computer.

Stoichiometry and Product Analysis

Different reaction mixtures with different sets of concentrations of reactants where [Ni(IV)] was in excess over [*L*-leucine] at constant ionic strength and alkali concentration were kept for about 6 h at 25 ± 0.1°C in a nitrogen atmosphere in a closed vessel. The remaining [*DPN*] was assayed spectrophotometrically by measuring the absorbance at 410 nm. The results indicated that two moles of *DPN* consumed one mole of *L*-leucine as shown in Scheme 3.

The main oxidation products were identified as pentanoic acid by spot test [29], Ni(II) was confirmed by its dimethyl glyoxime complex, and ammonia by *Nessler*'s reagent. CO_2 was qualitatively detected by bubbling N_2 gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water. The nature of the carboxylic acid was confirmed by the IR spectrum which showed a carbonyl (C=O) stretch at 1708 $\mathrm{cm^{-1}}$ and a signal of 3042 $\mathrm{cm^{-1}}$ due to O–H stretching of the acid.



$$\mathrm{R{-}\underset{\displaystyle NH_2}{CH}{-}COOH + 2Ni(IV) + 4OH^- \longrightarrow R{-}COOH + 2Ni(II) + NH_3 + 2H_2O + CO_2}$$

$$\mathrm{R = {-}CH_2{-}CH(CH_3)_2}$$

Scheme 3

Appendix

According to Scheme 2 the reaction rate is given by Eq. (I).

$$\text{Rate} = k[\text{C}] = kK_1K_2[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2}]_\text{f}[\text{OH}^-]_\text{f}[L\text{-leucine}]_\text{f} \qquad \text{(I)}$$

The total [Ni(IV)], $[\text{Ni(IV)}]_\text{t}$, is given as in Eq. (II) where the subscripts t and f stand for total and free, respectively.

$$\begin{aligned}
[\text{Ni(IV)}]_\text{t} &= [[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f} + [[\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)(\text{H}_3\text{IO}_6)]^{3-}] + [\text{C}]\\
&= [[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f} + K_1[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f}[\text{OH}^-]\\
&\quad + K_1K_2[\text{OH}^-][L\text{-leucine}][[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f}\\
&= [[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f}[1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][L\text{-leucine}]]
\end{aligned}$$

$$[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{f} = \frac{[\text{Ni(IV)}]_\text{t}}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][L\text{-leucine}]} \qquad \text{(II)}$$

Similarly, $[\text{OH}^-]_\text{f}$ and $[L\text{-leucine}]_\text{f}$ are obtained as described by Eqs. (III, IV).

$$[\text{OH}^-]_\text{f} = \frac{[\text{OH}^-]_\text{t}}{1 + K_1[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}] + K_1[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}][L\text{-leucine}]} \qquad \text{(III)}$$

$$[L\text{-leucine}]_\text{f} = \frac{[L\text{-leucine}]_\text{t}}{1 + K_1K_2[\text{OH}^-][[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]} \qquad \text{(IV)}$$

After substituting the values of (II), (III), and (IV) in Eq. (I), we get Eq. (V).

$$\text{Rate} = \frac{kK_1K_2[\text{Ni(IV)}]_\text{t}[L\text{-leucine}]_\text{t}[\text{OH}^-]_\text{t}}{\begin{array}{l}{[1 + K_1[\text{OH}^-]_\text{t} + K_1K_2[\text{OH}^-]_\text{t}[L\text{-leucine}]_\text{t}][1 + K_1K_2[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}][\text{OH}^-]_\text{t}]}\\ {[1 + K_1[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{t} + K_1K_2[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}]_\text{t}[L\text{-leucine}]_\text{t}]}\end{array}} \qquad \text{(V)}$$

The terms $[1 + K_1K_2[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}][\text{OH}^-]]$, $[1 + K_1[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}] + K_1K_2[[\text{Ni(OH)}_2(\text{H}_3\text{IO}_6)_2]^{2-}][L\text{-leucine}]]$ in the denominator of Eq. (V) approximate to unity in view of they low concentration of [Ni(IV)] used. Therefore, Eq. (V) becomes Eq. (VI) (omitting the subscript t and f).

$$k_\text{obs} = \frac{\text{Rate}}{[\text{Ni(IV)}]} = \frac{kK_1K_2[L\text{-leucine}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][L\text{-leucine}]} \qquad \text{(VI)}$$

References

[1] Macartney DH, McAuley A (1983) Inorg Chem **22**: 2062
[2] Acharya S, Neogi G, Panda RK, Ramaswamy D (1982) Int J Chem Kinet **14**: 1253
[3] Lappin AG, Laranjeira MC, Youdi OL (1981) J Chem Soc Dalton Trans 721
[4] Siddiqui MA, Kumar CS, Chandraiah U, Kandlikar S (1991) Indian J Chem **30A**: 489
[5] Tuwar SM, Nandibewoor ST, Raju JR (1992) J Indian Chem Soc **69**: 651
[6] Nandibewoor ST, Hugar GH (1997) Polish J Chem **71**: 1572
[7] Bhattacharya S, Saha B, Datta A, Banerjee P (1970) Coord Chem Rev **47**: 170
[8] Haines RI, McAuley A (1981) Coord Chem Rev **39**: 77
[9] Nag K, Chakravarty A (1980) Coord Chem Rev **33**: 87
[10] Lalo D, Mahanti MK (1990) J Chem Soc Dalton Trans 311

[11] Bal Reddy K, Sethuram B, Navaneeth Rao T (1981) Indian J Chem **20A**: 395; Chougale RB, Hiremath GA, Nandibewoor ST (1997) Polish J Chem **71**: 1471

[12] Hogale MB, Pawar PK, Nikam BP (1986) Acta Ciencia Indica **1**: 228

[13] Linde DR (1993) CRC Hand Book of Chemistry and Physics, 73rd ed, CRC press, London, p 8

[14] Chandraiah U, Khan JA, Murthy CP, Kandlikar S (1987) Indian J Chem **26A**: 481; Chandraiah U, Murthy CP, Kandlikar S (1989) Indian J Chem **28A**: 248; Chandraiah U, Kandlikar S (1989) Indian J Chem **28A**: 162

[15] Halligudi NN, Desai SM, Nandibewoor ST (1999) Int J Chem Kinet **31**: 789

[16] Kembhavi MR, Harihar AL, Nandibewoor ST (1999) J Indian Chem Soc **76**: 79

[17] Chang R (1981) Physical chemistry with Application to Biological system, MacMillan, New York, p 326

[18] Weissberger A (1974) In: Lewis ES (ed) Investigations of Rates and mechanism of Reactions in Techniques of Chemistry, vol. 4 Wiley Interscience publication, New York, p 176

[19] Harihar AL, Kembhavi, Nandibewoor ST (2000) Monatsh Chem **131**: 1129; Chandraiah U, Murthy CP, Kandlikar S (1989) Indian J Chem **28A**: 162

[20] Rangappa KS, Raghavendra MP, Mahadevappa DS, Channegowda D (1998) J Org Chem **63**: 531

[21] Harihar AL, Kembhavi MR, Nandibewoor ST (1999) Inorg React Mech **1**: 145

[22] Amis ES (1966) Solvent effects on reaction rates and mechanism, Academic press, New York; Entelis SG, Tiger RP (1976) In Reaction kinetics in the liquid. Wiley, New York

[23] Lewis ES (1995) Investigation of rates and mechanisms of reactions, 3rd ed, Wiley, New York, p 415

[24] Exner O (1964) Coll Czech Chem Commun **29**: 1094; Exner O (1972) Coll Czech Chem Commun **37**: 1425

[25] John E Leffler (1955) J Org Chem **20**: 1202

[26] Sutin N (1966) Ann Rev Phys Chem **17**: 119; Lancaster M, Murray RS (1971) J Chem Soc 2755; Martinez M, Pitarque M, Eldik RV (1996) J Chem Soc Dalton Trans 2665

[27] Ray P (1957) In: Moellar T (ed) Inorganic Synthesis, vol. 5 McGraw-Hill, New York, p 201

[28] Jeffery GH, Bassett J, Mendham J, Denney RC (1996) Vogel's Text Book of Quantitative Chemical Analysis 5th edn, ELBS Longman, Essex, UK, p 181

[29] Feigl F (1975) Spot Tests in Organic Analysis, Elsevier, Oxford, p 212

[30] Kembhavi MR, Harihar AL, Nandibewoor ST (1999) J Indian Chem Soc **76**: 79

[31] Kembhavi MR, Panari RG, Nandibewoor ST (1999) J Saudi Chem Soc **3**: 121

[32] Pol PD, Kulkarni RM, Nandibewoor ST (2002) Can J Chem (submitted)