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Kinetics of Electron Transfer from Cyclic Ketones to Ni(IV) Periodate Complex in Aqueous Alkaline Medium

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The kinetics of electron transfer from cyclic ketones (represented by (S)) to Ni(IV) periodate complexes has been studied in aqueous alkaline medium. The kinetics exhibit a pseudo-first-order disappearance of Ni(IV) periodate complexes when the [substrate] is present in excess. The pseudo-first-order rate constants, k_{obs}, were linearly dependent on [S] and the order in [S] were found to be unity. The rate of the reaction increased with the increase in $[OH^-]$, however the rates were retarded with the increase in [periodate]. Salt and solvent effect studies indicate that the reaction is of ion-dipole type. A suitable mechanism involving slow adduct formation between enol and oxidant, and its decomposition in a fast step have been suggested. A rate law consistent with the proposed mechanism has also been derived. The products of oxidation were identified as corresponding decarboxylic acids.

The metal complexes containing nickel in the trivalent[1,2] and tetravalent[3-6] states have recently received considerable attention and significant progress has been made in understanding Ni(III) species. A few reports are also available on the preparation and characterization of Ni(IV) oxime complexes and their reactions with different organic and inorganic substrates.

In the kinetic studies of electron transfer reactions from ascorbate ion[5] and tris(1,10-phenanthroline)-cobalt(II),[6] it is reported that electron transfer at above pH 5 takes place by a two seperate one-electron reductive steps. In some cases electron transfer, such as from ascorbic acid[7] and hexacyanoferrate(II)[8] to tris (dimethylglyoximato)nickelate(IV), is assumed to proceed through a kinetically indistinguishable Ni(III) species. Kinetic studies on oxidation of organic compounds by dihydroxydiperiodatonickelate(IV) were reported earlier from our laboratory.[9-11] However, the present investigation is intended to study the mode of electron transfer from cyclic ketones to Ni(IV) periodate complexes and to suggest a suitable mechanism.

Material and Methods

All the solutions were prepared afresh in twice distilled water. Cyclic ketones viz. cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone were of Fluka (puriss) and were used as such. The other chemicals such as KOH, KIO_4, $NaClO_4$, *t*-butyl alcohol were of BDH AnalaR grade.

Preparation of Oxidant. The nickel(IV) periodate complex, $KNiIO_6\cdot 1/2\,H_2O$, was prepared by the method suggested by Ray[12] and standardized as given earlier.[9]

Kinetic Measurements. The kinetics of the reaction between the diperiodatonickelate(IV) ion and the substrate was followed in the temperature range 293—313 K by monitoring the disappearance of Ni(IV) at 410 nm employing a UV-vis double beam spectrophotometer model 140.02 (Shimadzu Corporation, Japan). A mixture containing requisite quantities of aqueous solution of cyclic ketone and potassium hydroxide and the solution of the Ni(IV) periodate complex were thermally equilibrated at desired temperature (±0.1 °C) separately for about 30 min and the known volume of aqueous solution of the Ni(IV) periodate complex was transferred to alkaline substrate solution. The supporting electrolyte for maintaining ionic strength was sodium perchlorate.

Pseudo-first-order rate constants, k_{obs}, were calculated from linear least square fit from Eq. 1, which was found to be valid well over three half-lives of disappearance of the Ni(IV) periodate complex

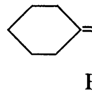
$$-\ln (A_t-A_\infty/A_0-A_\infty)=k_{obs}t \qquad (1)$$

where A_t, A_0, and A_∞, respectively, represent the absorbances at time *t*, before commencement of the reaction and at infinite time. Ni(II) periodate, a product of reduction of Ni(IV) periodate, was found to have negligible absorbance at 410 nm.

Results

Products of oxidation of cyclic ketones by the diperiodatonickelate(IV) ion were identified as corresponding dicarboxylic acids as determined by their characteristic tests.[13]

The stoichiometric experiments were conducted at different $[OH^-]$ range viz. 5.0×10^{-2} mol dm^{-3} to 10.0×10^{-2} mol dm^{-3}, $[Ni(IV)]=2.0\times10^{-4}$ mol dm^{-3} and $[S]_0=1.0\times10^{-5}$ mol dm^{-3}. Unreacted Ni(IV) was estimated spectrophotometrically at the end of the reaction. It was found that three moles of Ni(IV) reacted with one mole of cyclic ketone. The stoichiometric equation is



$$=O + 3[Ni(OH)_2(H_3IO_6)_2]^{2-} \longrightarrow$$
$$HOOC(CH_2)_4COOH + 3Ni(II) + 6H_3IO_6^{2-} + 3H_2O \qquad (2)$$

The kinetic results can be summarized as follows:

i) The rate of the reaction increased linearly with the increase in $[S]_0$. Under the conditions $[S]_0 \gg [Ni(IV)]$ the plot of $\log[(abs)_0/(abs)_t]$ versus time was linear passing through origin, showing first-order dependence on [Ni(IV)]. From the slope of such plots the pseudo-first-order rate constants, k_{obs}, were evaluated (Table 1). The plot of log k_{obs} versus log$[S]_0$ was linear and from the slope of such plots the order in [S] was found to be unity for all the cyclic ketones.

ii) The reactions were conducted at different $[OH^-]$. The rate of the reaction, at fixed $[S]_0$, [Ni(IV)], and [periodate] increased with the increase in $[OH^-]$ (Table 2).

iii) At fixed [Ni(IV)], [ketone], and $[OH^-]$ increase in [periodate] decreased the rate of the reaction. For example, under the conditions $[Ni(IV)]=1.0\times10^{-4}$ mol dm^{-3}, $[S]_0=5.0\times10^{-2}$ mol dm^{-3}, $[OH^-]=1.0\times10^{-2}$ mol dm^{-3}, increase in [periodate] from 1.0×10^{-5} mol dm^{-3} to 1.0×10^{-4} mol dm^{-3} decreased the $10^4\times k_{obs}$ values from 5.76 s^{-1} to 3.19 s^{-1} at 298 K.

iv) Effect of changing dielectric constant of the medium by using aqueous *t*-butyl alcohol as a solvent had negligible effect on the rate of the reaction. For example, under identical conditions as above and at $[\text{periodate}]=5.0\times10^{-5}$ mol dm^{-3} decreased negligibly the $10^4\times k_{obs}$ values from 4.35 s^{-1} to 4.16 s^{-1} at 298 K when the percentage of *t*-butyl alcohol was increased from 0—60% (v/v).

v) The rate of the reaction, at fixed $[S]_0$, $[OH^-]$, [Ni(IV)], and [periodate], was not altered by added sodium perchlorate.

vi) The reactions were carried out at different temperatures in the range of 293—313 K. Activation energy of the reaction and other thermodynamic parameters were evaluated (Table 3).

vii) The addition of acrylamide to deaerated reaction mixture did not alter the reaction rates nor there was any polymerization showing the absence of free radicals in the reaction.

viii) The observed order of the oxidation rate was found to be decreased in the order, cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone. Probably this may be due to enolic content of the above cyclic ketones decreasing in the same order.[14]

Table 1. Effect of [substrate] on the Rate of the Reaction

$10^2\times[S]$ / mol dm^{-3}	$10^4\times k_{obs}$ / s^{-1}
2.00	1.28
4.00	2.57
5.00	3.19
6.00	3.85
8.00	5.05
10.0	6.44

$[Ni(IV)])=1.0\times10^{-4}$ mol dm^{-3}, $[OH^-]=1.0\times10^{-2}$ mol dm^{-3}, $[\text{periodate}]=1.0\times10^{-4}$ mol dm^{-3}, T=298 K.

Table 2. Effect of $[OH^-]$ on the Rate of the Reaction

$10^2\times[OH^-]$ / mol dm^{-3}	$10^4\times k_{obs}$ / s^{-1}
0.500	2.27
1.00	3.19
2.00	4.63
5.00	6.08
8.00	7.93
10.0	8.51

$[Ni(IV)]=1.0\times10^{-4}$ mol dm^{-3}, $[S]=5.0\times10^{-2}$ mol dm^{-3}, $[\text{periodate}]=1.0\times10^{-4}$ mol dm^{-3}, T=298 K.

Discussion

Mukherjee et al.[15] reported the structre of the water-soluble Ni(IV) periodate complex as $[Ni(OH)_2(HIO)_6)_2]^{6-}$. The electronic spectrum of the water-soluble Ni(IV) periodate complex was reported to have a hump at 410 nm assignable to charge transfer from metal t_{2g} to ligand orbital and a strong band at 210 nm, due to IO_6 octahedron. The electronic spectrum of the complex prepared by us also showed similar spectral characteristics. However, in aqueous alkaline medium and in the pH range employed, the periodate cannot exist as HIO_6^{4-}.

Crouthamel and co-workers[16,17] suggested the following equilibria at different pH ranges

$$H_5IO_6 \xrightleftharpoons{K_1} H_4IO_6^- + H^+ \qquad (3)$$

$$H_4IO_6^- \xrightleftharpoons{K_2} H_3IO_6^{2-} + H^+ \qquad (4)$$

$$H_3IO_6^{2-} \xrightleftharpoons{K_3} H_2IO_6^{3-} + H^+ \qquad (5)$$

The dissociation constants K_1, K_2, and K_3 at 298 K are 2.3×10^{-2}, 4.35×10^{-9}, and 1.05×10^{-15} respectively. Among the above species periodic acid, H_5IO_6 exist in acidic media and $H_4IO_6^-$ near pH 7. Hence in the pH range employed in the present study, the main species can be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. The existence of $H_2IO_6^{3-}$ looks improbable owing to very low value of K_3 and

Table 3. Activation Parameters for the Oxidation of Cyclic Ketones with Diperiodatonickelate(IV) Ion in Aqueous Alkaline Medium

Substrate	$10^3\times k''$/dm^3 mol^{-1} s^{-1}					E_a	$\Delta H^{\#}$	$\Delta G^{\#}$	$-\Delta S^{\#}$
	293 K	298 K	303 K	308 K	313 K	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
Cyclopentanone	3.47	5.64	9.01	14.2	21.9	70.3	67.8	85.8	60.3
Cyclohexanone	8.00	12.6	19.6	30.0	45.3	66.1	63.6	83.8	67.8
Cycloheptanone	1.29	2.13	3.47	5.57	8.77	73.1	70.1	88.2	59.0
Cyclooctanone	3.96	6.40	10.2	15.9	24.7	69.9	67.4	85.5	60.8

$[NI(IV)]=1.0\times10^{-4}$ mol dm^{-3}, $[S]=5.0\times10^{-2}$ mol dm^{-3}, $[OH^-]=1.0\times10^{-2}$ mol dm^{-3}, $[\text{periodate}]=1.0\times10^{-4}$ mol dm^{-3}.

periodate exists in the dimerized form $I_2O_9^{4-}$ only when it is present in higher concentrations. Hence the soluble complex may be represented by the formula $[Ni(OH)_2(H_3IO_6)_2]^{2-}$.

The $[OH^-]$ depenednce of oxidation of cyclic ketones by the Ni(IV) periodate complex indicates the equilibrium between deprotonated reactive species **2** and deprotonated unreactive species **1**:

$$[Ni(OH)_2(H_3IO_6)_2]^{2-} + OH^- \rightleftharpoons [Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} + H_2O \quad (6)$$

The dependence of the rate of oxidation on the periodate complex indicates a dissociative equilibrium in which Ni(IV) moiety loses a periodate ligand from its coordination sphere forming the monoperiodatonickelate (IV) ion (**3**):

$$[Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} \rightleftharpoons [Ni(OH)_2(H_2IO_6)]^- + H_3IO_6^{2-} \quad (7)$$

The formation of species **3** directly from **1** is also possible:

$$[Ni(OH)_2(H_3IO_6)_2]^{2-} + OH^- \rightleftharpoons [Ni(OH)_2(H_2IO_6)]^- + H_3IO_6^{2-} + H_2O \quad (8)$$

A sequence of Eqs. 6 and 7 is preferred as the loss of the periodate ion occurs preferentially from a species having higher negetive charges. Hence deprotonated species **3** is assumed to be an active oxidant species. Such protonated and deprotonated forms in the inner sphere also exist for tris(dimethylglyoximato)nickelate(IV) complex[4] and the periodato and tellurato complexes of copper and the peptide complexes of silver in their trivalent states.[18-20] The assumption that **3** is the reactive species of oxidant is also in conformity with the earlier findings.[21] In the oxidation of the thiocyanate ion by the dihydroxydiperiodatonickelate(IV) complex the charge on the reactive species of oxidant was found to be unit negetive from the observed salt effect.

Oxidation of ketones may proceed by any one of the following stages:

(a) If the rate of oxidation>rate of enolization, the oxidation process can be represented as

$$\text{Ketone} + \text{Oxidant} \longrightarrow \text{Products} \quad (9)$$

with first-order dependence in oxidant.

(b) If the rate of enolization>rate of oxidation and the order in oxidant is unity, the oxidation can be represented as

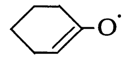
$$\text{Ketone} + OH^- \rightleftharpoons \text{Enol} \quad (10)$$

$$\text{Enol} + \text{Oxidant} \xrightarrow[\text{slow}]{} \text{Products} \quad (11)$$

(c) If the rate of enolization > rate of oxidation and the order in oxidant is zero, the oxidation can be represented as

$$\text{Ketone} + OH^- \overset{\text{slow}}{\rightleftharpoons} \text{Enol} \quad (12)$$

$$\text{Enol} + \text{Oxidant} \xrightarrow[\text{fast}]{} \text{Products} \quad (13)$$

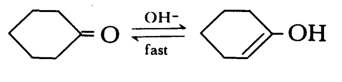
In the present study, the order in [oxidant] was found to be unity as the log (absorbance) versus time plot was perfectly straight line (correlation coefficient, r=0.9992) and the rate of oxidation of cyclic ketones was found to be in the order of ca. 10^{-8}. The rates of enolization of all cyclic ketones determined by iodination method were found to be in the order of ca. 10^{-6} to ca. 10^{-5} which are very much higher than the rate of oxidation of cyclic ketones with the diperiodatonickelate(IV) ion. Hence, it may be concluded that enol may be reacting with oxidant. One of the possibilities of an electron transfer may be due to the reaction between species **3** and enol giving an unstable adduct which decomposes subsequently to given an intermediate and Ni(II) in the fast step. The intermediate may react with two moles of Ni(IV) to give the final products. The other posibility of the electron transfer may be by two seperate one-electron reductive steps, the first step of which produces Ni(III) and enol free radical () which induces polymerization of acrylamide. However, no polymerization was observed by adding acrylamide to deaerated reaction mixture, showing the absence of one-electron reductive step. Hence in the absence of polymerization one could envisage that the adduct of 3-enol is formed in the slow step which dissociates with the electron transfer in the fast step.

A plausible mechanism, based on the above discussions for the electron transfer is shown in Scheme 1.

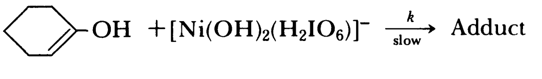
Though an adduct formation is envisaged no evidence could be given for its formation as it must be unstable and because of its low concentration it is difficult to detect it kinetically. A plot of $1/k_{obs}$ versus $1/[S]_0$ was linear yielding a straight line passing almost through origin. The observed stoichiometry

$$[DPN]^{a)} + OH^- \overset{K_1}{\rightleftharpoons} [Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} + H_2O \quad (14)$$

$$[Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} \overset{K_2}{\rightleftharpoons} [Ni(OH)_2(H_2IO_6)]^- + H_3IO_6^{2-} \quad (15)$$



(16)



(17)

$$\text{Adduct} \xrightarrow[\text{fast}]{} \text{Intermediate} + \text{Ni(II)} \quad (18)$$

$$\text{Intermediate} + 2[Ni(OH)_2(H_2IO_6)]^- \xrightarrow[\text{fast}]{} \text{Products} + 2\text{Ni(II)} \quad (19)$$

Scheme 1. a) Diperiodatonickelate(IV) ion, $[(Ni(OH)_2(H_3IO_6)_2]^{2-}$ is represented as [DPN] for simplicity.

i.e., 1 cyclic ketone : 3Ni(IV), salt and solvent effects also reinforce the above mechanism.

The rate of oxidation could be written as

$$\text{rate}=k[\text{enol}][\mathbf{3}]. \qquad (20)$$

As enol is consumed in product formation more and more ketone is converted into enol form. As [ketone] is far excess to [oxidant], [ketone] can be taken as equal to [enol]. The concentration of **3** can be calculated by taking into consideration the two equilibria, Eqs. 14 and 15, in terms of $[\text{DPN}]_{\text{total}}$.

$$[\text{DPN}]_t=[\mathbf{1}]+[\mathbf{2}]+[\mathbf{3}] \qquad (21)$$

As the disappearance of [DPN] is monitored, the rate of the reaction, Eq. 20 can be written as

$$\text{rate} = -\frac{d[\text{DPN}]}{dt} = \frac{kK_1K_2[\text{DPN}]_t[\text{ketone}][\text{OH}^-]}{K_1K_2[\text{OH}^-]+\{K_1[\text{OH}^-]+1\}[\text{H}_3\text{IO}_6^{2-}]}$$

$$\equiv k_{\text{obs}}[\text{DPN}]_t \qquad (22)$$

The above equation envisages a linear plot for $1/k_{\text{obs}}$ versus $1/[\text{OH}^-]$. In fact such a plot was obtained giving further support to the derived rate law. The above rate law also explains all experimental observations, such a first order in [DPN] and [ketone], fractional order in $[\text{OH}^-]$ and inverse fractional order in [periodate].

The equilibrium constants, K_1 and K_2 in Eqs. 14 and 15, were calculated kinetically from a kinetic study of oxidation of benzyl alcohol with diperiodatonickelate-(IV) ion.[22] The K_2 values were found to be 4.59×10^{-4}, 3.78×10^{-4}, and 3.39×10^{-4} at 300, 305, and 310 K respectively and K_1 values were found to be 33.1, 43.6, and 52.1 at 300, 305, and 310 K respectively. The K_1 and K_2 values were used to calculate k of the rate law and from this it follows that the concentration of **3** (monoperiodatonickelate(IV) ion, $[\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)]^-$) is around 10^{-7} mol dm^{-3}. Even if whole of the concentration of **3** is undergoing adduct formation with enol, the concentration of adduct of **3**-enol at any given time will not be more than 10^{-7} mol dm^{-3}. This may be the reason for non-detectability of adduct of **3**-enol.

The bimolecular rate constants, k'' obtained by dividing k_{obs} with [S], along with activation parameters are listed in Table 3. An examination of the data shows that the reactions are enthalpy controlled as the reaction with lowest enthalpy ($\Delta H^{\#}$) has highest rate. This is also confirmed from the fact that the plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ was found to be linear with isokinetic temperature, β=693 K (correlation coefficient, r= 0.9985) which is much higher than experimental temperature range (293—313 K). The consistency in $\Delta G^{\#}$ values indicates the similar mechanism to be operative in the present study.

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