Kinetics and Mechanism of the Oxidation of Some Carboxylates by a Nickel(III) Oxime-Imine Complex

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ABSTRACT: The kinetics of the oxidation of formate, oxalate, and malonate by $[Ni^{III}(L^1)]^{2+}$ (where HL¹ = 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime) were carried out over the regions pH 3.0–5.75, 2.80–5.50, and 2.50–7.58, respectively, at constant ionic strength and temperature 40°C. All the reactions are overall second-order with first-order on both the oxidant and reductant. A general rate law is given as $-d/dt[Ni^{III}(L^1)^{2+}] = k_{obs}[Ni^{III}(L^1)^{2+}] = (k_d + nk_s[R])[Ni^{III}(L^1)^{2+}]$, where k_d is the auto-decomposition rate constant of the complex, k_s is the electron transfer rate constant, n is the stoichiometric factor, and R is either formate, oxalate, or malonate. The reactivity of all the reacting species of the reductants in solution were evaluated choosing suitable pH regions. The reactivity orders are: $k_{HCOOH} > k_{HCOO-}; k_{H_{2OX}} > k_{HOX}^{-} > k_{OX}^{2-}$, and $k_{H_{2}mal} > k_{Hmal}^{-} < k_{mal}^{-2}$ for the oxidation of formate, oxalate, and malonate, respectively, and these trends were explained considering the effect of hydrogen bonded adduct formation and thermodynamic potential. © 1996 John Wiley & Sons, Inc. Int J Chem Kinet **29**: 225–230, 1997.

INTRODUCTION

The synthesis and characterization of oxime-imine ligand like HL¹(I) (15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-ene-2-one oxime) which can stabilize the oxidation state of nickel upto + 3 is well documented in the literature [1]. This $[Ni^{III}(L^1)]^{2+}$ complex shows interesting chemical features in the redox transformations [1,2]. Although a number of

redox studies including organic and pure inorganic reductants have been made involving this ion [2–7], a broad knowledge concerning the electron transfer in simple carboxylates is yet to be explored. Among the simple carboxylates, formate is of significant interest because of its relevance to plant metabolism leading to oxidative decarboxylation [8,9]. The importance of oxalate is due to its use as a quencher in solar photochemistry [10–13] and as a potential electron donor in other excited state electron transfer reactions. On the other hand, the reactions of malonic acid with a variety of oxidants also showed versatile mechanistic features [14–18]. The present investigation concerns the study of redox reactions of [Ni^{III}(L¹)]²⁺ complex with formate, oxalate, and malonate.

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EXPERIMENTAL

Materials and Reagents

(15-amino-3-methyl-4,7,10,13-tetraazapentadec-3ene-2-one oximato) nickel(III) perchlorate, [Ni^{III} (L^1)](ClO₄)₂ was prepared by the method reported by Chakravorty et al. [1]. Analytical data were satisfactory (found: C, 27.30; H, 5.10; N, 15.85%, required for C₁₂H₂₇Cl₂N₆NiO₉:C, 27.35; H, 5.30; N, 15.80%, respectively). The complex solutions were standardized spectrophotometrically using the literature absorption coefficient: $\lambda/nm(\epsilon/L mol^{-1} cm^{-1})$ $498[(2.7 \pm 0.20) \times 10^3]$. Sodium formate (E. Merck), sodium malonate (E. Merck) and oxalic acid were of reagent grade and recrystallized twice before use. Doubly recrystallized sodium perchlorate (Fluka AG) was used to maintain the ionic strength of the medium. Doubly recrystallized sodium acetate and sodium dihydrogen phosphate, and acetic acid, perchloric acid, and sodium hydroxide, all of reagent grade, were used to maintain the pH of the medium. All the solutions were prepared freshly prior to kinetic study using double distilled water.

Kinetic Measurements

Kinetics of the reactions were followed using a uv-vis spectrophotometer (uv-2100, Shimadzu, Japan) equipped with thermostated cell compartments by monitoring the decrease in optical density at 498 nm. pH measurements were carried out with a Systronics (model 335, India) digital pH-meter. Although measured pH is usually defined in terms of hydrogen ion activity, the hydrogen ion concentration for each solution was obtained by calibrating the pH electrode with analytically prepared solutions maintained to the desired ionic strength. The reaction temperature (\pm 0.1°C) was controlled by circulating water around the reservoir for the reaction solutions from a Haake F3 thermostat.

Stoichiometry and Reaction Products

The direct determination of the stoichiometry for the oxidation of formate, oxalate, and malonate with

 $[Ni^{III}(L^1)]^{2+}$ complex was not possible due to slowness of the reactions and time dependent decomposition of the complex. Their product analyses were carried out very carefully in order to throw some light on the stoichiometries. For the oxidation of formate and oxalate the product was carbon dioxide as tested by the usual standard method. Analysis of the oxidation product of malonic acid was performed by reacting equimolar concentrations of [Ni^{III}(L¹)]²⁺ complex and the reducing agent (0.05 mol L^{-1}) as reported earlier [18]. The product was condensed for an hour [19] with an equimolar quantity of o-phenylenediamine in a minimum volume of dry ethanol. The solid residue was obtained on concentrating and cooling overnight in a deep freeze. It was recrystallized from anhydrous ethanol and dried in a desiccator. The melting point of the compound determined was 265.8°C which is identical to that of 2-hydroxy-3-isoquinoxaline carboxylic acid [20] obtained from the condensation of mesoxalic acid with o-phenylenediamine. The product also showed a positive 2,4-dinitrophenyl hydrazine test. Mesoxalic acid has been identified as a product in many of the oxidation reactions of malonic acid where a 4:1 stoichiometry with respect to the oxidant prevails [21,22]. The stoichiometric equations for the oxidation of formate, oxalate, and malonate at pH 4.5 can be represented as:

$$2[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{HCOOH} \longrightarrow 2[\mathrm{Ni}^{\mathrm{II}}(\mathrm{HL}^{1})]^{2+} + \mathrm{CO}_{2}$$

$$2[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4} \longrightarrow 2[\mathrm{Ni}^{\mathrm{II}}(\mathrm{HL}^{1})]^{2+} + 2\mathrm{CO}_{2}$$

$$4[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{H}_{2}\mathrm{C} \longrightarrow + \mathrm{H}_{2}\mathrm{O} \longrightarrow$$

$$4[\mathrm{Ni}^{\mathrm{III}}(\mathrm{HL}^{1})]^{2+} + \mathrm{O} = \mathrm{C} \longrightarrow + \mathrm{COOH}$$

$$4[\mathrm{Ni}^{\mathrm{III}}(\mathrm{HL}^{1})]^{2+} + \mathrm{O} = \mathrm{C} \longrightarrow + \mathrm{COOH}$$

Polymerization Study

All the three reactions were tested for the generation of free radicals during the course of the reaction by the method reported earlier [23]. The precipitation of a white polymer of acrylonitrile indicates that all the reactions proceed through the generation of free radicals.

RESULTS AND DISCUSSION

The kinetics of the oxidation of formate, oxalate, and malonate by $[Ni^{III}(L^1)]^{2+}$ were carried out under pseudo-first-order conditions with excess of reductant (> 10 times) over the complex at a constant tempera-

Table I Pseudo-First-Order Rate Constants for the Reduction of $[Ni^{III}(L^1)]^{2+}$ by Formate, Oxalate, and Malonate at Different Reductant Concentrations with $[Ni^{III}(L^1)^{2+}] = 1.0 \times 10^{-4} \text{ mol } L^{-1} \text{ and } [OAc^-] = 0.02 \text{ mol } L^{-1} \text{ at } 40^{\circ}\text{C}$

Reductant	[Reductant], mol L^{-1}	$10^4 k_{\rm obs,}, {\rm s}^{-1}$
Formate ^a	0.10	0.38
	0.30	0.48
	0.50	0.64
	0.70	0.74
	1.00	0.91
Oxalate ^b	0.001	4.60
	0.003	10.20
	0.005	14.80
	0.007	20.10
	0.010	28.30
Malonate ^c	0.10	0.46
	0.30	0.86
	0.50	0.92
	0.70	1.35
	0.90	1.65

 $^{\rm a}$ I = 1.00 mol L $^{-1}$ and k_d = (3.50 \pm 0.50) \times 10 $^{-5}$ s $^{-1}$ at pH 5.0.

^b I = 0.20 mol L⁻¹ and $k_d = (2.80 \pm 0.20) \times 10^{-4} \text{ s}^{-1}$ at pH 3.0. ^c I = 1.00 mol L⁻¹ and $k_d = (4.00 \pm 0.20) \times 10^{-5} \text{ s}^{-1}$ at pH

 $k_d = (4.00 \pm 0.20) \times 10^{-5}$ s at p1 5.0.

ture 40°C. The plots of $-\log A_t$ vs. *t* (where A_t represents the absorbance at time *t*) are linear for more than 75% of the total reactions. The pseudo-first-order rate constants (k_{obs}) were evaluated from the slopes of the straight lines and vary within the error limit of \pm 3%. Again the plots of k_{obs} at different reductant concentrations yield straight lines with a nearly common intercept on the rate axis at a certain pH which may indicate the auto-decomposition of the complex at that particular pH. Corresponding data are displayed in Table I. A general rate law consistent to the oxidation of all these three carboxylates may be given as

$$-\frac{d}{dt} [\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})^{2+}] = k_{\mathrm{obs}} [\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})^{2+}]$$
$$= (k_{d} + nk_{\mathrm{s}} [\mathrm{R}]) [\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})^{2+}] \quad (1)$$

where k_d is the auto-decomposition rate constant of the complex, found to be pH-dependent and studied separately earlier [7], k_s is the electron transfer rate constant, R is either formate, oxalate or malonate, *n* is the stoichiometric factor which is 2 for both formate and oxalate oxidations, and 4 for malonate oxidation.



Figure 1 Variation of k_s as a function of $-\log[H^+]$ for the reduction of $[Ni^{III}(L^1)]^{2+}$ by (a) formate and (b) oxalate at 40°C with $[Ni^{III}(L^1)^{2+}] = 1.0 \times 10^{-4}$ mol L⁻¹, I = 1.0 mol L⁻¹ for formate and 0.20 mol L⁻¹ for oxalate, and [buffer] = 0.02 mol L⁻¹. The solid line represents calculated k_s values and the experimental values shown by points.

Oxidation of Formate

Oxidation of formate by $[Ni^{III}(L^1)]^{2+}$ was carried out in the range pH 3.0–5.75 with $[Ni^{III}(L^1)^{2+}] =$ 1.0×10^{-4} mol L⁻¹, [formate] = 0.1–1.0 mol L⁻¹, and I = 1.0 mol L⁻¹ (NaClO₄). A plot of $k_s(=k_{obs} - k_d/2$ [formate]) vs. $-\log[H^+]$ is a curve of decreasing slope (Fig. 1(a)). The complex $[Ni^{III}(L^1)]^{2+}$ is a strong acid (p $K_m < 1.0$) [2], the reacting species of the complex in our experimental pH region would be the deprotonated one. Electrochemical studies showed a quasi-reversible wave with $E^0 =$ 0.91 V (vs. NHE) and given as

$$[Ni^{III}(L^1)]^{2+} + e + H^+ \rightleftharpoons [Ni^{II}(HL^1)]^{2+} (2)$$

The pK_m of the $[Ni^{II}(HL^1)]^{2+}$ complex is represented as

$$[\mathrm{Ni}^{\mathrm{II}}(\mathrm{HL}^{1})]^{2+} \xleftarrow{K_{m}} [\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{1})]^{+} + \mathrm{H}^{+}; \, \mathrm{p}K_{m} = 6.8$$
(3)

The potential of the related couple (4) has been estimated to be 0.49 V by using the value of pK_m (eq. (3))

$$[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{e} \rightleftharpoons [\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{1})]^{+} \qquad (4)$$

Thus, the proton dependence of rate in the experimental range of pH can be unambiguously ascribed to the protic equilibrium of formic acid [24],

HCOOH
$$\stackrel{K_1}{\longrightarrow}$$
 HCOO⁻ + H⁺; pK₁ = 3.53 (5)

As the reaction rates (k_0) fall with $-\log[H^+]$, it is expected that HCOOH is more reactive compared to the deprotonated species, HCOO⁻. This is contrary to our previous observations for formate oxidations [18,25]. Assuming $[Ni^{III}(L^1)]^{2+}$ as the sole reacting species, a suitable reaction scheme compatible to the experimental findings could be framed as

$$[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{HCOOH} \xrightarrow{k_{6}} [\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{1})]^{+} + \mathrm{HCOO}^{\cdot} + \mathrm{H}^{+} \quad (6)$$
$$[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}^{1})]^{2+} + \mathrm{HCOO}^{-} \xrightarrow{k_{7}} [\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{1})]^{+}$$

$$[\operatorname{Ni}^{\operatorname{III}}(\operatorname{L}^{1})]^{2+} + \operatorname{radical} \xrightarrow{\operatorname{Iast}} [\operatorname{Ni}^{\operatorname{III}}(\operatorname{L}^{1})]^{+} + \operatorname{CO}_{2}$$
(8)

and corresponding rate law could be derived as

$$k_{\rm s} = \frac{k_6[{\rm H}^+] + k_7 K_1}{[{\rm H}^+] + K_1} \tag{9}$$

Since pK_m of the complex $[Ni^{II}(HL^1)]^{2+}$ is 6.8, the reduction product of the complex would be the protonated species, in the experimental pH range.

$$[\mathrm{Ni}^{\mathrm{II}}(\mathrm{L}^{1})]^{+} + \mathrm{H}^{+} \xrightarrow{\mathrm{rapid}} [\mathrm{Ni}^{\mathrm{II}}(\mathrm{HL}^{1})]^{2+} \qquad (10)$$

In the absence of any monomer, the free radicals would react in a fast step with another $[Ni^{III}(L^1)]^{2+}$ to yield CO₂ and Ni(II) products (eq. 8). Equation (9) was solved by means of a nonlinear least-squares program and the evaluated parameters are:

$$k_6 = (6.75 \pm 0.04) \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}, k_7$$

= (1.01 ± 0.14) × 10⁻⁵ L mol⁻¹ s⁻¹, and K_1
= (5.35 ± 0.06) × 10⁻⁴ mol L⁻¹ (p K_1 = 3.27)

It is seen that there is an excellent agreement between the experimental and calculated k_s values (Fig. 1(a)) at each [H⁺] but there is a shift in pK_1 value for HCOOH towards the lower side.

Oxidation of Oxalate

Oxidation of oxalic acid by $[Ni^{III}(L^1)]^{2+}$ was carried out in the range pH 2.80–5.50 at [ox] = (1.0-10.0) $\times 10^{-3}$ mol L⁻¹, $[Ni^{III}(L^1)]^{2+} = 1.0 \times 10^{-4}$ mol L⁻¹, and I = 0.2 mol L⁻¹(NaClO₄). A plot of $-\log[H^+]$ vs. k_s is also a curve of decreasing slope (Fig. 1(b)]. The pK's [26] of oxalic acid are designated as,

$$\begin{array}{c} \text{COOH} & \xrightarrow{K_1(-H^+)} & \text{COO}^- & \xrightarrow{K_2(-H^+)} & \text{COO}^- \\ \text{COOH} & \xrightarrow{K_2(-H^+)} & \text{COO}^- & (11) \\ \text{(H}_2\text{ox}) & (\text{Hox}^-) & (\text{ox}^{2^-}) \end{array}$$

with $pK_1 = 1.20$ and $pK_2 = 4.21$. The reactive species of oxalate are likely to be H_2ox , Hox^- , and ox^{2-} in the experimental pH range and a plausible reaction scheme could be framed as:

$$[\operatorname{Ni}^{\operatorname{III}}(L^{1})]^{2+} + \operatorname{H}_{2}\operatorname{ox} \xrightarrow{k_{12}} [\operatorname{Ni}^{\operatorname{II}}(L^{1})]^{+} + \operatorname{Hox}^{\cdot} + \operatorname{H}^{+}$$
(12)
$$[\operatorname{Ni}^{\operatorname{III}}(L^{1})]^{2+} + \operatorname{Hox}^{-} \xrightarrow{k_{13}} [\operatorname{Ni}^{\operatorname{II}}(L^{1})]^{+} + \operatorname{Hox}^{\cdot}$$

$$\operatorname{NI}^{\mathrm{m}}(\mathbb{L}^{*})]^{*} + \operatorname{Hox} \longrightarrow [\operatorname{NI}^{\mathrm{m}}(\mathbb{L}^{*})]^{*} + \operatorname{Hox}$$
(13)

$$[\operatorname{Ni}^{\operatorname{II}}(L^{1})]^{2+} + \operatorname{ox}^{2-} \xrightarrow{\kappa_{14}} [\operatorname{Ni}^{\operatorname{II}}(L^{1})]^{+} + \operatorname{ox}^{\cdot}$$
(14)

The rate of the free radicals would be the same as mentioned earlier and the rate law can be derived as:

$$k_{\rm s} = \frac{k_{12}[{\rm H}^+]^2 + k_{13}K_1[{\rm H}^+] + k_{14}K_1K_2}{[{\rm H}^+]^2 + K_1[{\rm H}^+] + K_1K_2} \quad (15)$$

Equation (15) has been solved by means of a simplex optimization program and the evaluated parameters are: $k_{12} = (6.00 \pm 0.18) \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{13} = (2.27 \pm 0.07) \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{14} = (2.21 \pm 0.09) \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$, $K_1 = (4.25 \pm 0.15) \times 10^{-3} \text{ mol} \text{ L}^{-1}$ (p $K_1 = 2.37$), and $K_2 = (4.35 \pm 0.15) \times 10^{-5} \text{ mol} \text{ L}^{-1}$ (p $K_2 = 4.36$).

Oxidation of Malonate

The kinetics of the oxidation of malonate was studied using variable concentrations of malonate (0.10–0.90 mol L⁻¹) in the range pH 2.50–7.58 using fixed concentration of the complex ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) at a constant ionic strength [1.0 mol L^{-1} (NaClO₄)]. A plot of $-\log[H^+]$ vs. k_s (Fig. 2) showed a decrease in rate with $-\log[H^+]$, attains a minimum at around pH 5.0-5.75 ($-\log[H^+] = 4.89-5.61$) and then rate increases steadily with $-\log[H^+]$. The pK's of malonic acid are, $pK_1 = 2.88$ and $pK_2 = 5.68$ [26] owing to the equilibria,





Figure 2 Variation of k_s as a function of $-\log[H^+]$ for the oxidation of malonate at 40°C with $[Ni^{III}(L^1)^{2+}] = 1.0 \times 10^{-4}$ mol L⁻¹, I = 1.0 mol L⁻¹, and [buffer] = 0.02 mol L⁻¹. The curve has been drawn through calculated k_s values, while circles denote experimental points.

In the range pH 2.50–7.58 the reacting species of malonate are expected to be H_2 mal, Hmal⁻, and mal²⁻, and their reactions towards the complex $[Ni^{III}(L^1)]^{2+}$, are portrayed as,

$$[\operatorname{Ni}^{\operatorname{III}}(\operatorname{L}^{1})]^{2+} + \operatorname{H}_{2}\operatorname{mal} \xrightarrow{k_{17}} [\operatorname{Ni}^{\operatorname{II}}(\operatorname{L}^{1})]^{+} + \operatorname{Hmal}^{\cdot} + \operatorname{H}^{+} \quad (17)$$

$$[\operatorname{Ni}^{\operatorname{III}}(\operatorname{L}^{1})]^{2+} + \operatorname{Hmal}^{-} \xrightarrow{k_{18}} [\operatorname{Ni}^{\operatorname{II}}(\operatorname{L}^{1})]^{+} + \operatorname{Hmal}^{\cdot} \quad (18)$$

$$[\operatorname{Ni}^{\operatorname{III}}(\operatorname{L}^{1})]^{2+} + \operatorname{mal}^{2-} \xrightarrow{k_{19}} [\operatorname{Ni}^{\operatorname{II}}(\operatorname{L}^{1})]^{+} + \operatorname{mal}^{\cdot} \quad (19)$$

The radicals thus produced react with another Ni^{III} complex to give Ni^{II} complex and mesoxalic acid as the final products. If it is assumed that the reaction stoichiometry (4:1) is valid under the reaction condition, the corresponding rate law could be written as,

$$k_{\rm s} = \frac{k_{\rm obs} - k_{\rm d}}{4[\text{mal}]} = \frac{k_{17}[\text{H}^+]^2 + k_{18}K_1[\text{H}^+] + k_{19}K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$
(20)

The kinetic and equilibrium parameters of eq. (20) could be evaluated by considering suitable pH ranges. Thus in the range pH 2.50–5.50, the reactions (17) and (18) are likely to occur and the rate law reduces to

$$k_{\rm s} = \frac{k_{17}[{\rm H}^+] + k_{18}K_1}{[{\rm H}^+] + K_1}$$
(21)

Equation (21) was solved by a nonlinear least-squares computer-fit program and the evaluated values are as:

$$k_{17} = (5.06 \pm 0.04) \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}, k_{18}$$

= (1.75 ± 0.10) × 10⁻⁵ L mol⁻¹ s⁻¹, and K_1
= (9.80 ± 0.15) × 10⁻⁴ mol L⁻¹ (p K_1 = 3.0).

Similar approach was made in the pH range 5.80–7.58 to evaluate the rate parameters (k_{18}, k_{19}) and K_2 and the rate law takes the form

$$k_{\rm s} = \frac{k_{18}[{\rm H}^+] + k_{19}K_2}{[{\rm H}^+] + K_2}$$
(22)

The evaluated parameters are: $k_{18} = (1.67 \pm 0.28) \times 10^{-5}$ L mol⁻¹ s⁻¹, $k_{19} = (1.05 \pm 0.1) \times 10^{-4}$ L mol⁻¹ s⁻¹, and $K_2 = (3.85 \pm 0.12) \times 10^{-7}$ mol L⁻¹ (p $K_2 = 6.41$). All these evaluated rate and equilibrium constants were incorporated in the general rate expression (eq. (20)) and the values of k_s were calculated at each pH. These match excellently with the experimentally determined values (Fig. 2).

Nickel(III) ion in $[Ni^{III}(L^1)]^{2+}$ is in a pseudo-octahedral geometry $(t_{2g}^{6}e_{g}^{1})$ with the odd electron in d_{z}^{2} orbital. This complex is assumed to have a very low substitution lability though there is no accurate estimate for it. Due to low substitution lability, it is expected that the electron transfer reactions of $[Ni^{III}(L^1)]^{2+}$ would occur via outer-sphere pathway. However, in most of the oxidations by $[Ni^{III}(L^1)]^{2+}$, e.g., of ascorbic acid [6], benzene diols [2], S(IV) and Se(IV) [4], the reactions were proposed to take place via the formation of hydrogen-bonded intermediate which is supported by the higher reactivity of protonated species over the less protonated or deprotonated one. This is particularly apparent for S(IV) and Se(IV) oxidations by $[Ni^{III}(L^1)]^{2+}$ [4], where the overall reactivity order was found to be SO2. x H2O > HSO₃⁻ < SO₃²⁻ and H₂SeO₃ > HSeO₃⁻, respectively, and the formation constant values follow the trend: $SO_2 \times H_2O > HSO_3^- > SO_3^{2-}$. In the present study too, the oxidation rates were found to decrease with increase in pH (except for the malonate oxidation which is comparable to S(IV) oxidation) resulting in the higher reactivity of the protonated species over the less protonated and completely deprotonated ones. In fact the reactivity orders are: $k_{\text{HCOOH}} > k_{\text{HCOO}^-}; k_{\text{H}_2\text{ox}} > k_{\text{Hox}^-} > k_{\text{ox}^{2-}}, \text{ and } k_{\text{H}_2\text{mal}} > k_{\text{Hmal}^-} < k_{\text{mal}^{2-}}.$ The order of reactivity of carboxylates is contrary to the previous results [25,27,18] where the reverse trend was noted and an explanation was furnished based on thermodynamic potential considerations. In the present study, the effect of H-bonded adduct formation seems to predominate over the thermodynamic potential considerations providing a lower energy pathway for electron transfer from the reductant to $[Ni^{III}(L^1)]^{2+}$. The formation of H-bonded adduct is expected to occur between the carboxylate hydrogen and oximato oxygen atom $(=N-O^{-})$ of the coordinating ligand. The estimates for the formation constant of the H-bonded adducts, however, is not possible as the reactions do not proceed through rate saturation in our experimental reductant concentration but a definite impact on the *pK* values of the reductants is noted in some cases.

Of interest is the comparison of the reactivity of mal²⁻ to those of Hmal⁻ and H₂mal leading one to believe that thermodynamic potential values may exert well predominance here over the hydrogen-bonding effect. Similar behavior to this was observed in the study of the S(IV) oxidation with $[Ni^{III}(L^1)]^{2+}$ [4] where SO₃²⁻ shows a higher reactivity compared to So₂⁻ x H₂O and HSO₃⁻ species.

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