Kinetic Studies on the Oxidation of Sulfur(IV) by Nickel(IV) Oxime–Imine Complexes†

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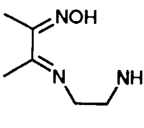
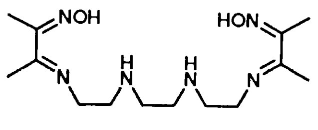
The oxidation of sulfite by the two nickel(IV) oxime–imine complexes $[Ni^{IV}L^1_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ (HL^1 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime and H_2L^2 = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) has been investigated in aqueous medium at 30 °C over the range pH 2.0–8.0. Single-step two-electron transfer reactions were encountered in the regions $2.0 \leqslant pH \leqslant 5.50$ for $[Ni^{IV}L^1_2]^{2+}$ and $2.0 \leqslant pH \leqslant 4.25$ for $[Ni^{IV}L^2]^{2+}$ reductions. A distinct biphasic process with faster initial one-electron reduction of Ni^{IV} to Ni^{III} followed by a slower conversion of Ni^{III} into Ni^{II} was observed above pH 5.75 and 4.50 for the respective complexes. Attempts were made to evaluate the reactivity of all the reacting species of the complexes as well as of sulfur(IV) by considering suitable pH regions. The stoichiometries of the reactions ($[S^{IV}]:[Ni^{IV}]$) were found to vary within the region ≈2.0–1.0 depending upon the mole ratios of the reactants. At pH 4.50 with an excess of complex over the reductant the ratio $[S^{IV}]:[Ni^{IV}]$ is less than 2:1 for both complexes giving a mixture of dithionate and sulfate as the oxidation products of sulfite. However, with an excess of sulfite over the complex this ratio reaches a limiting value of ≈2:1 at $[S^{IV}]:[Ni^{IV}] > 8$ giving dithionate as the major oxidation product. The observed stoichiometric ratios for both complexes are in accord with the distribution of the sulfate and dithionate products. Attempts were made to correlate the experimentally observed rate constants with those obtained from Marcus cross-relation calculations. Calculated rate constants for the oxidation of SO_3^{2-} by various nickel-(IV) and -(III) species were found to be one to two orders of magnitude lower than the corresponding experimental values. The oxidation of $SO_2{\cdot}H_2O$ and HSO_3^- is proposed to proceed through the formation of a hydrogen-bonded adduct.

The reactions of complexes of nickel in its higher oxidation states have attracted considerable interest. Chakravorty and co-workers[1–3] have synthesised and characterised oxime–imine complexes of nickel(IV) which undergo concerted electron and proton transfer and show interesting chemical features. Several kinetic investigations have also appeared on the reduction of $[Ni^{IV}L^1_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ having pseudo-octahedral NiN_6 co-ordination spheres (HL^1 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime and H_2L^2 = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) by organic molecules, metal ions and complexes.[4–14] However, there is no report on the reduction of these oxidants by non-metallic inorganic reagents.

We have reported earlier in detail the reaction chemistry of sulfite with an established outer-sphere oxidant, dodecatungstocobaltate(III), $[CoW_{12}O_{40}]^{5-}$.[15] This study and other reactions of sulfite with metal ions and complexes reveal unusual features involving both one- and two-electron transfer reactions.[16] The oxidation product of sulfur(IV) is dithionate or sulfate, or more often a mixture of the two depending upon the nature of the oxidants, with consumption ratios $[\text{oxidant}]:[S^{IV}]$ between 1 and 2:1 for one-electron oxidants. Any deviation from 2:1 manifests the production of dithionate with a diminishing yield of sulfate. The stoichiometry of these reactions is often correlated to the substitution lability of the complexes: a substitution-inert complex gives sulfate as the exclusive product, while a labile complex reacts forming a mixture of sulfate and dithionate, with a few exceptions.[15,17] Thus for a labile complex a non-integral stoichiometry between 1 and 2:1 is obtained. From these observations it has been inferred that a substitution-inert oxidant is effective to oxidise SO_3^{-}, an intermediate oxidation product of sulfur(IV).[18,19]


HL^1


H_2L^2

From the above discussion it is of interest to investigate the oxidation of sulfur(IV) by the above-mentioned nickel(IV) complexes which have moderate reduction potentials. These are also useful outer-sphere oxidants having moderate stability in aqueous solution. The present study aims at exploring the mechanism and testing the validity of the above proposition leading to the discrimination of outer- and inner-sphere processes.

Experimental

Reagents.—The nickel(IV) oxime–imine complexes $[Ni^{IV}L^1_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ (hereafter designated in general as Ni^{IV} or $[Ni^{IV}L_x]^{2+}$ with $x = 2$ for HL^1 and 1 for H_2L^2 unless mentioned otherwise) were prepared and analysed as their perchlorate salts by the literature methods.[3] Solutions were standardised spectrophotometrically using literature absorption coefficients: λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 505 (6.10×10^3) and 419 (4.90×10^3) for $[Ni^{IV}L^1_2]^{2+}$ and 500 (6.30×10^3) and 430 (5.96×10^3) for $[Ni^{IV}L^2]^{2+}$. Sodium sulfite of

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† *Supplementary data available* (No. SUP 57039, 5 pp.): stoichiometric results and product distribution at various mole ratios. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

analytical reagent grade was obtained from Fluka and used without further purification. Solutions were prepared in nitrogen-purged doubly distilled water prior to use, standardised by using an excess of standard iodine solution followed by back-titration with standard sodium thiosulfate solution and stored under a nitrogen atmosphere. Sodium dithionate of reagent grade was recrystallised twice before use. Doubly recrystallised sodium perchlorate (Fluka) was used to maintain the ionic strength of the reaction medium. Acetic acid–sodium acetate buffer was used to maintain the lower pH (3.50–5.90) and phosphate buffer to maintain the higher pH (6.0–8.0).

Analytical Methods.—The consumption of the oxidants under various conditions was monitored spectrophotometrically by the stopped-flow technique. A Union RA-401 stopped-flow spectrophotometer (Otsuka Electronics, Japan) interfaced with a data processor RA-451 (Otsuka Electronics, Japan) was used. The observed rate constants were evaluated by treating the kinetic curves of an average of at least five runs by a least-squares curve-fit method. The pseudo-first-order rate constants thus obtained varied within the error limit ± 3%. pH Measurements were done with a Systronics (model 335, India) digital pH meter. Although the 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 at the desired ionic strength. The reaction temperature was controlled (± 0.1 °C) by circulating water from a Haake F3 thermostat around the reservoir of the reaction solutions. All the solutions were prepared immediately prior to use and were bubbled with oxygen-free dinitrogen for at least 15 min to suppress aerial oxidation of sulfite.

Polymerisation and EPR Studies.—All the oxidations of sulfur(IV) by nickel(IV) complexes are believed to proceed through the generation of free radicals as confirmed by the polymerisation of acrylonitrile reported earlier.[15]

The EPR spectra were recorded in aqueous solution at pH 3.50 and 7.50 under conditions of (*i*) an excess of Ni^{IV} over S^{IV} and (*ii*) an excess of S^{IV} over Ni^{IV}. Under condition (*i*) a singlet was observed with a *g* value of 2.05 at both pH values, but no such EPR signal was encountered under condition (*ii*). Again, on generating Ni^{III}–L^2 by electrochemical oxidation of the corresponding nickel(II) complex at pH 7.50, the EPR spectrum showed the same *g* value as in (*i*). On addition of sulfite to this solution the signal disappeared. All these results point to the existence of a nickel(III) intermediate rather than a SO_3^- radical, as on the time-scale of this study the sulfite radical escapes detection.

Stoichiometry.—Stoichiometries of the oxidation of sulfite by the two nickel(IV) complexes, $[Ni^{IV}L^1{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ were determined separately at various mole ratios over a range of concentrations at pH 4.50. With an excess of S^{IV} over the nickel(IV) complex the stoichiometry was determined by treating the unreacted sulfite with an excess of standard dichromate and then measuring the analytical concentration of dichromate spectrophotometrically immediately after the reaction. Practically, there is no reaction between $[Cr_2O_7]^{2-}$ and $[Ni^{II}H_2(L_x)]^{2+}$ complexes within the time of measurement (1–1.5 min) and this affords an accurate determination of unreacted sulfite. With an excess of nickel(IV) the stoichiometry was determined by estimating the unreacted complexes spectrophotometrically. Since the complexes undergo some autodecomposition under this condition, respective blank solutions without S^{IV} were prepared simultaneously to evaluate the amount of complexes undergoing self-decomposition, and this was subtracted in each case to get the actual amount of the complex consumed.

The products of oxidation of sulfite by $[Ni^{IV}L^1{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ were examined by the following methods. Initially sulfur(IV) (0.05 mol dm^{-3}) was oxidised completely with an excess of nickel(IV) complex (0.06 mol dm^{-3}). Addition of $BaCl_2$ to this mixture yielded a white precipitate which was filtered off, dried, and then fused on charcoal with Na_2CO_3 and extracted with water. This on addition of $Na_2[Fe(CN)_5(NO)]$ solution yielded a violet colouration, indicating the presence of sulfate. The filtrate on concentrating and cooling to ≈10 °C yielded a white precipitate which was filtered off, washed with the minimum volume of cold water and pumped as dry as possible. This mass was treated with dichromate solution to known strength in 5 mol dm^{-3} $HClO_4$ and heated on a water-bath for ≈2 h. The change in the dichromate concentration determined spectrophotometrically at 348 nm indicated the presence of dithionate ion. The content of dithionate and sulfate was found to be dependent upon the mole ratio of the reactants in the reaction mixture. Assuming that sulfate and dithionate are the only oxidation products of sulfur(IV) their contents were determined for different $S^{IV}:Ni^{IV}$ mole ratios by the method reported earlier[15] (see SUP 57039). With an excess of S^{IV} ($[S^{IV}]:[Ni^{IV}] > 8.0:1$) dithionate is the major product of S^{IV} leading to a ≈ 2:1 stoichiometry. However, when $[S^{IV}]:[Ni^{IV}] < 0.125:1$ sulfate is the major oxidation product of sulfite. In the intermediate range, *i.e.*, $0.125 < [S^{IV}]:[Ni^{IV}] < 8$ both sulfate and dithionate are obtained. Similar observations were made for the oxidation of sulfite by $[Fe(CN)_6]^{3-}$[20] and $[CoW_{12}O_{40}]^{5-}$.[15]

Results and Discussion

Preliminary kinetic traces at pH 2.50, 5.0 and 7.0 showed that the oxidation of sulfite by both the nickel(IV) complexes proceeds with an initial slight increase in optical density within ≈20 ms followed by a slower decay. Controlled experiments showed that the first step arises only in the presence of S^{IV} along with the complexes and is independent of the added acetate or phosphate buffer. To determine whether it was an artifact, the stopped-flow gain of the RA-controller was set to a higher value (0.5 absorption units) simultaneously while adjusting the response knob; this eliminated the initial rise in optical density and provided reproducible kinetic traces.

Kinetic studies were conducted under pseudo-first-order conditions with $[S^{IV}] \gg [Ni^{IV}]$ and semilog plots were linear for over four half-lives or more indicating a first-order dependence of the rate on $[Ni^{IV}]$. Pseudo-first-order rate constants, k_{obs}, defined by equation (1) were obtained from

$$-d[Ni^{IV}]/dt = k_{obs}[Ni^{IV}] \qquad (1)$$

exponential fits of the kinetic curves. Externally added nickel(II) complexes, one of the reaction products, have no effect on the reaction rate, but the reactions were found to be highly sensitive to the presence of atmospheric dioxygen.

Electrochemical studies on $[Ni^{IV}L^1{}_2]^{2+}$ reveal pH-dependent redox equilibria.[1,4] Below pH 6.0, a single, two-electron transfer process is observed. Above pH 6.0 this couple is replaced by two separate one-electron reductions. The nickel(IV)–nickel(III) step [equation (2)] is independent of $[H^+]$

$$[Ni^{IV}L^1{}_2]^{2+} + e^- \rightleftharpoons [Ni^{III}L^1{}_2]^+; E^\circ = 0.63 \text{ V} \qquad (2)$$

($pK_h < 1.0$), whereas the reduction of nickel(III) is pH dependent, arising from the proton equilibrium (3) of

$$[Ni^{III}L^1(HL^1)]^{2+} \overset{K_h}{\rightleftharpoons} [Ni^{III}L^1{}_2]^+ + H^+; pK_h = 4.43 \qquad (3)$$

Table 1 Pseudo-first-order rate constants for the oxidation of sulfur(IV) by $[Ni^{IV}L^1{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ at different pH at 30 °C, $I = 0.20$ mol dm^{-3} ($NaClO_4$), $[Ni^{IV}] = 5.0 \times 10^{-5}$ mol dm^{-3}, [buffer] = 0.02 mol dm^{-3} (phosphate or acetate)

		10 k_{obs}/s^{-1}		
Oxidant	10[S^{IV}]/mol dm^{-3}	pH 2.25	4.0	7.0*
$[Ni^{IV}L^1{}_2]^{2+}$	0.02	0.60	7.52	300, 1.18
	0.04	1.15	15.2	608, 2.37
	0.05	1.53	21.1	688, 2.75
	0.06	1.90	24.9	885, 3.45
	0.08	2.40	34.6	114, 4.64
		pH 3.0	4.0	5.25*
$[Ni^{IV}L^2]^{2+}$	0.05	0.26	2.28	25.3, 0.40
	0.10	0.58	3.94	73.9, 0.89
	0.20	1.16	9.78	149, 2.06
	0.30	1.66	14.7	175, 2.54
	0.50	2.92	24.5	343, 4.17

* Value for $Ni^{IV} \longrightarrow Ni^{III}$ conversion followed by that for $Ni^{III} \longrightarrow Ni^{II}$ conversion.

$[Ni^{III}L^1(HL^1)]^{2+}$ (refs. 1 and 4), and is explained by equations (4) and (5). Similarly, $[Ni^{IV}L^2]^{2+}$ also undergoes a

$$[Ni^{III}L^1(HL^1)]^{2+} + e^- \rightleftharpoons [Ni^{II}L^1(HL^1)]^+;\ E^\circ = 0.63\ V \quad (4)$$

$$[Ni^{III}L^1{}_2]^+ + e^- \rightleftharpoons [Ni^{II}L^1{}_2];\ E^\circ = 0.30\ V \quad (5)$$

one-step two-electron transfer process at pH 5.0,[3,6] and above pH 5.0 two distinct one-electron transfer processes were noted in accord with equations (6)–(9).

$$[Ni^{IV}L^2]^{2+} + e^- \rightleftharpoons [Ni^{III}L^2]^+;\ E^\circ = 0.654\ V \quad (6)$$

$$[Ni^{III}L^2]^+ + e^- \rightleftharpoons [Ni^{II}L^2];\ E^\circ = 0.42\ V \quad (7)$$

$$[Ni^{III}(HL^2)]^{2+} \overset{K'_h}{\rightleftharpoons} [Ni^{III}L^2]^+ + H^+ \quad (8)$$

$$[Ni^{III}(HL^2)]^{2+} + e^- \rightleftharpoons [Ni^{II}(HL^2)]^+;\ E^\circ = 0.64\ V \quad (9)$$

These potentials have been used for kinetic analysis of rate constants in the subsequent sections.

Oxidation of Sulfite by $[Ni^{IV}L^1{}_2]^{2+}$ *and* $[Ni^{IV}L^2]^{2+}$.—Oxidation of sulfite by $[Ni^{IV}L^1{}_2]^{2+}$ and $[Ni^{IV}L^2]^{2+}$ is overall second order, first order in both [Ni^{IV}] and [S^{IV}] following the general rate law (10) where the factor of $\frac{1}{2}$ arises from the

$$-\frac{d}{dt}[Ni^{IV}L] = \tfrac{1}{2}k_{ox}[S^{IV}][Ni^{IV}] \quad (10)$$

stoichiometry under the actual reaction conditions. The dependence of k_{obs} on [S^{IV}] is listed in Table 1. The effect of acidity on the reaction rate was studied in the range pH 2.0–8.0. A distinct biphasic electron-transfer reaction trace appeared at pH $\geqslant$ 6.0 for $[Ni^{IV}L^1{}_2]^{2+}$ and pH $\geqslant$ 4.50 for $[Ni^{IV}L^2]^{2+}$, the initial faster step corresponding to the conversion of Ni^{IV} into Ni^{III} and the relatively slower decay to $Ni^{III} \longrightarrow Ni^{II}$. At lower pH $E^\circ(Ni^{IV}\text{–}Ni^{III}) \ll E^\circ(Ni^{III}\text{–}Ni^{II})$ and the reduction $Ni^{IV} \longrightarrow Ni^{III}$ is the rate-determining step followed by the very rapid reduction $Ni^{III} \longrightarrow Ni^{II}$. However, at higher pH, $E^\circ(Ni^{IV}\text{–}Ni^{III}) > E^\circ(Ni^{III}\text{–}Ni^{II})$ for the non-protonated nickel(III) complexes, but the protonated nickel(III) complexes $[Ni^{III}(HL_x)]^{2+}$ have comparable reduction potentials to those of the $[NiL_x]^{2+/+}$ couples. Since the pK_h values are ≈4.43 and 4.03 for $[Ni^{III}L^1(HL^1)]^{2+}$ and $[Ni^{III}(HL^2)]^{2+}$ complexes, $[Ni^{III}L_x]^+$ mainly exists in the higher pH region leading to a net lowering in reduction potential and thus phase separation.[1,3,4,6]

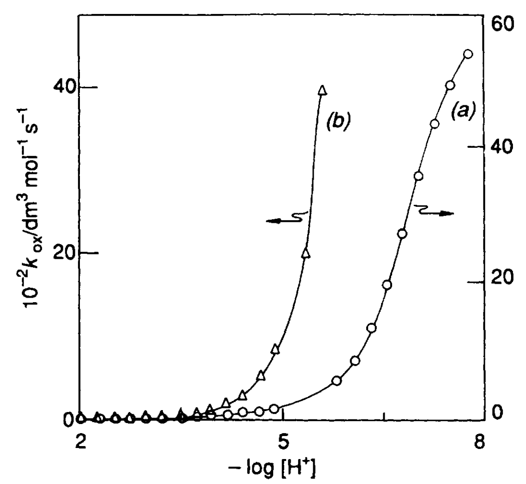

Fig. 1 Variation of k_{ox} (= $2k_{obs}/[S^{IV}]_T$) as a function of $-\log[H^+]$ for the reduction of nickel(IV) to nickel(III) by sulfur(IV) at $I = 0.2$ mol dm^{-3}, [nickel(IV)] = 5.0×10^{-5} mol dm^{-3}, 30 °C: (*a*) $[Ni^{IV}L^1{}_2]^{2+}$, (*b*) $[Ni^{IV}L^2]^{2+}$. The solid lines represent calculated values

The nickel(IV) complexes are expected to have $pK_h < 1.0$, hence in the experimental pH region (2.0–8.0) no protic equilibrium would be associated with $[Ni^{IV}L_x]^{2+}$. Plots of k_{ox} *vs.* $-\log[H^+]$ ($k_{ox} = 2k_{obs}/[S^{IV}]_T$) [Fig. 1(*a*) and 1(*b*)] show an increase in rate with $-\log[H^+]$ which doubtlessly reflects the involvement of protic equilibria of sulfurous acid [equations (11) and (12)], reported values[21] being

$$SO_2{\cdot}H_2O \overset{K_1}{\rightleftharpoons} H^+ + HSO_3^- \quad (11)$$

$$HSO_3^- \overset{K_2}{\rightleftharpoons} H^+ + SO_3^{2-} \quad (12)$$

$pK_1 = 1.78$ and $pK_2 = 6.99$. In the range pH 2.0–8.0 the reactive sulfur(IV) species are as $SO_2{\cdot}H_2O$, HSO_3^- and SO_3^{2-} and the suggested reaction sequence with $[Ni^{IV}L_x]^{2+}$ is represented by equations (13)–(15). The free radicals generated

$$[Ni^{IV}L_x]^{2+} + SO_2{\cdot}H_2O \xrightarrow{k_0} [Ni^{III}L_x]^+ + HSO_3 + H^+ \quad (13)$$

$$[Ni^{IV}L_x]^{2+} + HSO_3^- \xrightarrow{k_1} [Ni^{III}L_x]^+ + HSO_3 \quad (14)$$

$$[Ni^{IV}L_x]^{2+} + SO_3^{2-} \xrightarrow{k_2} [Ni^{III}L_x]^+ + SO_3^- \quad (15)$$

likely react in a fast step with another nickel-(IV) or -(III) complex depending upon the pH of the medium to give the sulfate product. These may otherwise undergo dimerisation yielding a dithionate product.

The above reactions are in accord with the rate equation (16).

$$k_{ox} = \frac{k_0[H^+]^2 + k_1K_1[H^+] + k_2K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (16)$$

This can be solved by means of a Simplex optimisation program by allowing the equilibrium constants to vary and thus the best-fit data were fitted by a non-linear least-squares computer-fit program involving six variables to evaluate the standard deviations. The evaluated parameters are: $k_0 = 5.01 \pm 2.89$, $k_1 = (11.1 \pm 0.30) \times 10^2$, $k_2 = (6.24 \pm 0.20) \times 10^4$ dm^3

$mol^{-1}\ s^{-1}$, $K_1 = (2.93 \pm 0.10) \times 10^{-4}$ ($pK_1 = 3.53$) and $K_2 = (1.23 \pm 0.04) \times 10^{-7}\ mol\ dm^{-3}$ ($pK_2 = 6.91$) for $[Ni^{IV}L^1{}_2]^{2+}$ reduction; and $k_0 = 1.52 \pm 0.50$, $k_1 = 2.49 \pm 0.10$, $k_2 = (2.86 \pm 0.10) \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$, $K_1 = (7.94 \pm 0.60) \times 10^{-3}$ ($pK_1 = 2.10$) and $K_2 = (3.89 \pm 0.10) \times 10^{-7}\ mol\ dm^{-3}$ ($pK_2 = 6.41$) for $[Ni^{IV}L^2]^{2+}$ reduction. The disproportionation of nickel(III) at pH < 5.0 is discounted since the disproportionation of $[Ni^{III}L^1{}_2]^+$ is very slow and the removal of such species is likely to take place in very rapid proton-associated steps [equation (17), $n = 1$ or 2].

$$[Ni^{III}L_x]^+ + e^- + nH^+ \rightleftharpoons [Ni^{II}H_n \cdots L_x]^{n+} \quad (17)$$

The second slower phase is well separated from the first especially at higher pH (≥6.0 for $[Ni^{IV}L^1{}_2]^{2+}$ and ≥4.75 for $[Ni^{IV}L^2]^{2+}$) allowing separate treatment of the reaction traces. Plots of k_{ox} *vs.* $-\log[H^+]$ for these steps [Fig. 2(*a*) and 2(*b*)] show a descending trend and these are identified as the reduction of Ni^{III}. This can be explained by considering the protic equilibria (3) and (8) involving the nickel(III) complexes.

Based on the redox potentials of $[Ni^{III}(HL_x)]^{2+}$ and $[Ni^{III}L_x]^+$ and the reaction conditions, a reaction scheme involving (18)–(21) can be proposed. The fate of the free radical

$$[Ni^{III}(HL_x)]^{2+} + HSO_3^- \xrightarrow{k_3} [Ni^{II}(HL_x)]^+ + HSO_3 \quad (18)$$

$$[Ni^{III}(HL_x)]^{2+} + SO_3^{2-} \xrightarrow{k_4} [Ni^{II}(HL_x)]^+ + SO_3^- \quad (19)$$

$$[Ni^{III}L_x]^+ + HSO_3^- \xrightarrow{k_5} [Ni^{II}L_x] + HSO_3 \quad (20)$$

$$[Ni^{III}L_x]^+ + SO_3^{2-} \xrightarrow{k_6} [Ni^{II}L_x] + SO_3^- \quad (21)$$

would be as stated earlier. The protonation of nickel(III) complexes enhances their reactivity, primarily due to the increased reduction potential of $[Ni^{III}L^1(HL^1)]^{2+}$ [equation (4)] with a value of 0.63 V *vis-à-vis* 0.30 V for $[Ni^{III}L^1{}_2]^+$ [equation (5)]. The rate equation (22) can be derived from the above scheme.

$$k_{ox} = \frac{k_3[H^+]^2 + (k_4K_2 + k_5K_h)[H^+] + k_6K_2K_h}{(K_2 + [H^+])(K_h + [H^+])} \quad (22)$$

Experimental data were fitted by equation (22) using a Simplex optimisation program and the evaluated parameters along with the experimental data were similarly fitted by means of a non-linear least-squares program involving six variables. The resulting parameters from the best-fit experimental data, with standard deviations, are: $k_3 = (3.05 \pm 0.10) \times 10^4$, $k_4 = (11.6 \pm 0.30) \times 10^3$, $k_5 = 22.2 \pm 0.70$, $k_6 = 19.2 \pm 0.60\ dm^3\ mol^{-1}\ s^{-1}$; $K_2 = (2.26 \pm 0.07) \times 10^{-7}$ ($pK_2 = 6.65$) and $K_h = (3.49 \pm 0.10) \times 10^{-5}\ mol\ dm^{-3}$ ($pK_h = 4.46$).

Attempts to fit the experimental k_{ox} values at different $[H^+]$ by use of equation (22) for the oxidation of sulfite by Ni^{III}–L^2 complexes gave poor results. This may arise from the reverse reactivity order of sulfur(IV) species: $HSO_3^- > SO_3^{2-}$ for $[Ni^{III}L^1(HL^1)]^{2+}$ and $[Ni^{III}L^1{}_2]^+$ and $SO_3^{2-} > HSO_3^-$ for corresponding protonated and deprotonated nickel(III) complexes of H_2L^2. Fitting of experimental data by equation (22) requires setting the k_5 term to zero, *i.e.* protonated S^{IV} is unreactive for this complex, and the evaluated parameters are: $k_3 = 137 \pm 4.0$, $k_4 = (4.43 \pm 0.10) \times 10^3$ and $k_6 = 4.68 \pm 0.10\ dm^3\ mol^{-1}\ s^{-1}$; $K_2 = (1.60 \pm 0.05) \times 10^{-7}$ ($pK_2 = 6.80$) and $K'_h = (9.81 \pm 0.30) \times 10^{-5}\ mol\ dm^{-3}$ ($pK'_h = 4.01$).

It is noteworthy that in each evaluation of the parameters the calculated and experimental k_{ox} values at different pH are in excellent agreement, as illustrated in Figs. 1 and 2. There is also good agreement between the calculated and reported p*K* values for sulfurous acid (kinetically determined pK_2 values fall in the range 6.41–6.91) and nickel(III) complexes with the only exception being pK_1 determined from the oxidation of sulfite by $[Ni^{IV}L^1{}_2]^{2+}$. The evaluated pK_1 (3.53) is higher than the reported value (1.78).[21] This difference is unexpected and may be explained by considering the hydrogen bonding between $SO_2 \cdot H_2O$ and the oximato oxygen of the ligand which results in the proton of $SO_2 \cdot H_2O$ being held strongly and difficult to release.

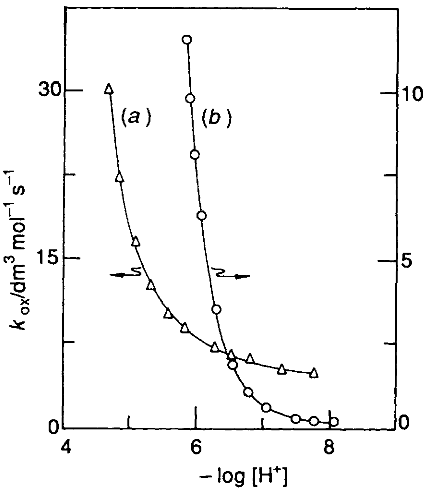

Fig. 2 Variation of k_{ox} as a function of $-\log[H^+]$ for the reduction of (*a*) Ni^{III}–L^1 and (*b*) Ni^{III}–L^2 by sulfur(IV); other details as in Fig. 1

The sequence of reaction steps outlined above seems to explain our experimental results. The nickel(IV) complexes studied are kinetically inert. Hence ligand substitution in the inner core of the metal centre is likely to be slow. In the nickel(III) complexes the axial positions are relatively labile, though the extent of this is yet to be reported. However, the substitution rates are generally less than $10^2\ s^{-1}$ for Ni^{III}–L^2 and on the basis of these considerations an outer-sphere process is likely for the reactions studied here.

From a comparison of the reactivity of the different sulfur(IV) species towards particular nickel-(IV) and -(III) complexes, some interesting trends are apparent. For the $Ni^{IV}L_x \longrightarrow Ni^{III}L_x$ reduction, the reactivity order follows the general trend,[22–24] $SO_2 \cdot H_2O < HSO_3^- < SO_3^{2-}$, and this is also valid for $[Ni^{III}L^2]^+ \longrightarrow [Ni^{II}L^2]$ and $[Ni^{III}(HL^2)]^{2+} \longrightarrow [Ni^{II}(HL^2)]^+$. However, the trend $HSO_3^- > SO_3^{2-}$ is at variance with the general picture of reactivity in the case of $[Ni^{III}L^1{}_2]^+$ and $[Ni^{III}L^1(HL^1)]^{2+}$ (Table 2). A logical interpretation, and one that agrees favourably with observations reported earlier,[17] is that the reactions proceed through the initial formation of a hydrogen-bonded adduct [equation (23)]. The intermediate **II** [equation (24)] may be of the outer-sphere type formed through

$$[Ni^{III}L^1{}_2]^+ + HSO_3^- \underset{}{\overset{K'_1}{\rightleftharpoons}} \mathbf{I} \xrightarrow{k'_1} \text{product} \quad (23)$$

$$[Ni^{III}L^1{}_2]^+ + SO_3^{2-} \underset{}{\overset{K'_2}{\rightleftharpoons}} \mathbf{II} \xrightarrow{k'_2} \text{product} \quad (24)$$

strong electrostatic attraction between the two oppositely charged species, as there is no possibility of hydrogen bonding. The greater reactivity of HSO_3^- can be attributed to the relatively higher value of K'_1 compared with K'_2 contributing to the overall electron-transfer rate constant (k_{et} =) $k'_1K'_1 > k'_2K'_2$. The higher value for K'_1 can be anticipated by the easier

Table 2 Reactivity of different sulfur(IV) species

			k/dm^3 mol^{-1} s^{-1}		
Couple	$E°$/V	k_{22}*/dm^3 mol^{-1} s^{-1}	$SO_2{\cdot}H_2O$	HSO_3^-	SO_3^{2-}
$[Ni^{IV}L^1{}_2]^{2+}$–$[Ni^{III}L^1{}_2]^+$	0.63	8.0×10^4	5.01 ± 2.89	$(11.1 \pm 0.30) \times 10^2$	$(6.24 \pm 0.20) \times 10^4$ (6.40×10^2)
$[Ni^{III}L^1{}_2]^+$–$[Ni^{II}L^1{}_2]$	0.30	8.0×10^3	—	22.2 ± 0.70	19.2 ± 0.60 (6.50×10^{-2})
$[Ni^{III}L^1(HL^1)]^{2+}$–$[Ni^{II}L^1(HL^1)]^+$	0.63	5.0×10^2	—	$(3.05 \pm 0.10) \times 10^4$	$(11.6 \pm 0.30) \times 10^3$ (50.0)
$[Ni^{IV}L^2]^{2+}$–$[Ni^{III}L^2]^+$	0.654	1.0×10^5	1.52 ± 0.50	2.49 ± 0.10	$(2.86 \pm 0.10) \times 10^4$ (11.0×10^2)
$[Ni^{III}L^2]^+$–$[N^{II}L^2]$	0.42	2.0×10^3	—	—	4.68 ± 0.10 (0.50)
$[Ni^{III}(HL^2)]^{2+}$–$[Ni^{II}(HL^2)]^+$	0.64	1.0×10^3	—	137 ± 4.0	$(4.43 \pm 0.10) \times 10^3$ (83.0)

Values in parentheses represent the rate constants calculated using Marcus relationships; $E°(SO_3^-–SO_3^{2-}) = 0.72$ V.* Refs. 4 and 5.

formation of the intermediate from HSO_3^- owing to hydrogen bonding between HSO_3^- and oximate oxygen. From the electrostatic point of view the reverse effect can be expected. Since the reduction to nickel(II) species requires additional protonation, the effect of hydrogen bonding would offset the electrostatic interaction. The results for the other nickel species, *e.g.* $[Ni^{IV}L^2]^{2+}$, $[Ni^{III}L^2]^+$ and $[Ni^{III}(HL^2)]^{2+}$, seem to be in keeping with the simplified reactivity pattern with respect to sulfur(IV) species, and an outer-sphere path cannot be ruled out.

Further insight into the outer-sphere interaction can be obtained by correlating the experimental electron-transfer rate constants with those obtained from the Marcus cross-reaction relationships.[25] The cross-relations employed are given by equations (25)–(28) where k_{12} represents the rate constants for

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}w_{12} \qquad (25)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \qquad (26)$$

$$w_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \qquad (27)$$

$$w_{ij} = 4.23 \times 10^{-8}Z_iZ_j/[a(1 + 3.28 \times 10^7\, aI^{\frac{1}{2}})] \qquad (28)$$

the electron transfer from SO_3^{2-} to the oxidant, k_{11} is the self-exchange rate constant for the couple SO_3^-–SO_3^{2-}, k_{22} is the self-exchange rate constant for the oxidising nickel complex and K_{12} is the equilibrium constant for the electron-transfer reaction, calculated by equation (29) at 30 °C; Z in equation

$$\log K_{12} = n\Delta E°/0.060\,23 \qquad (29)$$

(26) is the collision frequency, for which the value 1.0×10^{11} dm^3 mol^{-1} s^{-1} has been used, Z_i and Z_j are the ionic charges of the respective species, R is the universal gas constant (kcal mol^{-1}), and a is the centre-to-centre distance (cm) when the reacting species are in contact. It is necessary to include the work terms and factor f_{12} in the present calculations owing to the wide range of driving forces. The densities of the nickel-(IV) and -(II) complexes of the ligands HL^1 and H_2L^2 are known[26,27] and the radius (r) of the corresponding complex was calculated using the density relation.[28] We have used the average value of the radius $r = 5.1$ Å for all the complexes in order to evaluate the work terms. The radius of SO_3^{2-}/SO_3^- is reported to be 3.0 Å and the corresponding self-exchange rate constant (k_{11}) is 4.0 dm^3 mol^{-1} s^{-1}.[18] With the help of these parameters and reported $E°$ values, the self-exchange rate constants and the electron-transfer rate constants were calculated using equations (25)–(29) (Table 2). The experimental rate constants were found always to be greater than the calculated ones by a factor of 10–10^2. One would expect the two oxidation states (III and IV) and two types of ligands (tri- and hexa-dentate) to have inner-sphere rearrangement rates which depend on lability and steric factors. In case of Ni–L^1 complexes there are wider differences (10^2 times) between the experimental and calculated rate constants for the oxidation of SO_3^{2-} compared to those for Ni–L^2 complexes (Table 2). This reflects the ease of rearrangement of tridentate bis(oxime) ligands having no continuity of the 'backbone' compared to the single-chain hexadentate (continuous) systems where all sites may be affected equally, although in both cases there is a change in electronic structure from a low-spin $t_{2g}{}^6$ to a $t_{2g}{}^6\, e_g$ configuration. Differences of an order of magnitude (or more) between the experimental and observed rate constants are not unusual for the simplified cross-relation adopted here. Thus it is difficult to judge whether the oxidation of SO_3^{2-} proceeds through an outer-or inner-sphere process as there is no direct evidence for it. The reactions involving the other two species ($SO_2{\cdot}H_2O$ and HSO_3^-) would be expected to proceed through the formation of a transient hydrogen-bonded adduct and this is supported by the comparable reactivity of HSO_3^- and $SO_2{\cdot}H_2O$ towards $[Ni^{IV}L^2]^{2+}$ and by a shift in pK_1 of $SO_2{\cdot}H_2O$ with both nickel complexes. The observation of non-integral stoichiometries leading to both sulfate and dithionate may provide some evidence for an inner-sphere route.

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