

Oxidation of Thiourea and its *N*-Substituted Derivatives by a Nickel(IV) Oxime–Imine Complex in Aqueous Perchlorate Medium

Santanu Bhattacharya, Amitava Dutta and Pradyot Banerjee*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

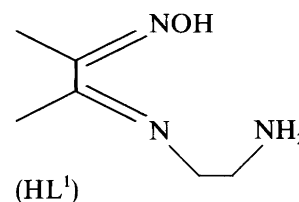
Bhattacharya, S., Dutta, A. and Banerjee, P., 1997. Oxidation of Thiourea and its *N*-Substituted Derivatives by a Nickel(IV) Oxime–Imine Complex in Aqueous Perchlorate Medium. – Acta Chem. Scand. 51: 676–682. © Acta Chemica Scandinavica 1997.

Thiourea and its *N*-substituted derivatives are oxidised by $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$, where $\text{HL}^1 = 6\text{-amino-3-methyl-4-azahex-3-en-2-one oxime}$ in the pH range 2.0–8.0 at 30 °C. Reactions conducted at $2.0 \leq \text{pH} \leq 5.0$ do not correspond to a pseudo-first-order monophasic $2e^-$ transfer path as observed with other reductants. A distinct biphasic $1e^-$ transfer reduction of the Ni^{IV} complex is observed at $\text{pH} \geq 6.0$, of which the $\text{Ni}^{\text{IV}} \rightarrow \text{Ni}^{\text{III}}$ reduction step is faster followed by a slower reduction for the $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ step. From these kinetic experiments, in combination with previously determined 'outside' protonation constant of the $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ complex, the rate parameters have been computed. The experimental findings are best explained by considering an inner-sphere electron-transfer process.

Thiourea derivatives are well known corrosion inhibitors,¹ and thus may show interesting electron-transfer properties. The kinetics and mechanism of oxidation of thiourea and its *N*-substituted derivatives by different aq complexes of metal ions^{2–7} such as Ce^{IV} , Co^{III} , V^{V} , Mn^{III} , OsO_4 , Cu^{II} , EDTA and HEDTA complexes of Cu^{II} (Refs. 8 and 9) have been reported. These studies show an electron transfer preceded by the formation of significant thermodynamically stable intermediate species, and this is also found to be the case for the oxidation of thioureas with hydrogen peroxide¹⁰ and IrCl_6^{2-} (Ref. 11). In an attempt to explore the kinetic behaviour of tetravalent nickel towards some sulfur-containing molecules, kinetic studies have been made of the redox interaction of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ (where $\text{HL}^1 = 6\text{-amino-3-methyl-4-azahex-3-en-2-one oxime}$) with thiourea (tu), *N*-methyl thiourea (mtu) and *N*-allyl thiourea (atu). These reagents are particularly useful for identifying pH effects on the complex, since there is no evidence for the protonation of thioureas^{12,13} over a wide pH range (1–10), and the relative reactivities of the complex ions may be explored.

Results

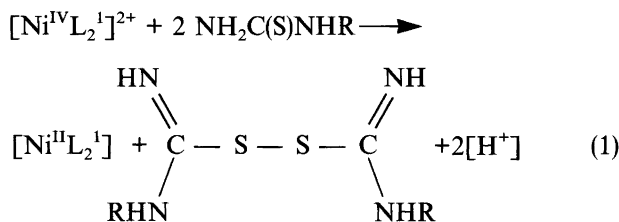
Kinetic studies were followed spectrophotometrically, with the thioureas in at least ten-fold excess over



the oxidant. The disappearance of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ was monitored at 505 nm (λ_{max} of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$, $\epsilon = 6100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

The stoichiometries of the reactions of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ with thioureas were also determined at this wavelength by reacting known concentrations of thioureas with a measured excess of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ at a constant ionic strength $I = 0.2 \text{ M}$ (NaClO_4), pH 6.0, and finally measuring the concentration of unreacted $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ after the reaction. The results from the spectral studies revealed a 1:2 ($[\text{Ni}^{\text{IV}}\text{L}_2]^{2+} : [\text{thioureas}]$) stoichiometry for the oxidation of all the thioureas. The products of oxidation were the respective disulfides of thioureas and the Ni^{II} complex under investigation. Generation of free radicals during the course of the reaction and characterisation of disulfide products were confirmed by methods reported earlier.^{3,14–17} The stoichiometric equation is thereby given by eqn. (1), where $\text{R} = \text{H}$, $-\text{CH}_3$ and $-\text{CH}_2-\text{CH}=\text{CH}_2$ for tu, mtu and atu, respectively.

* To whom correspondence should be addressed.



Kinetic studies in the range $2.0 \leq \text{pH} \leq 5.0$ showed that plots of $-\log A_t$ vs. t (where A_t is the absorbance at time t) do not correspond to a pseudo-first-order monophasic $2e^-$ transfer path. Rather, the plots indicated an autocatalytic phenomenon showing an induction phase (slowing down during this period) and then picks up speed (a rapid change in absorbance with time). The salient features of the reaction are as follows.

(i) With an increase in pH (>2.0), the induction period gradually diminishes and the rate of autocatalysis increases, attaining a maximum at pH 4.5 (Fig. 1). Although at pH 5.0 the plot of $-\log A_t$ vs. t shows a greater change in absorbance than that at pH 4.5, the more curved nature of the latter indicates a higher rate of autocatalysis.

(ii) Beyond pH 4.5, the autocatalytic process is retarded with increasing pH, and the reaction traces gradually assume a single-step $2e^-$ transfer reduction of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ up to pH 5.5, as has been observed in previous studies with this oxidant^{18,19} (Fig. 2). The lines drawn in Figs. 1 and 2 only indicate trends, and are not a computer fit, since no quantitative treatment is

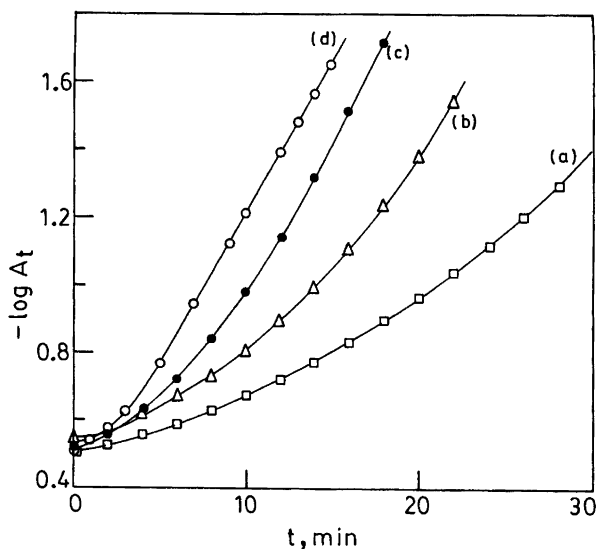


Fig. 1. Plot of $-\log A_t$ vs. t for the oxidation of thiourea by $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$. The conditions are: $[\text{Ni}^{\text{IV}}] = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{tu}] = 0.01 \text{ mol dm}^{-3}$, $I = 0.20 \text{ mol dm}^{-3}$ (NaClO_4) and $T = 30^\circ\text{C}$. (a) pH 2.0, (b) pH 3.0, (c) pH 4.50 (0.02 mol dm^{-3} sodium acetate used and pH adjusted by addition of perchloric acid), (d) pH 5.0 (0.02 mol dm^{-3} sodium acetate used and pH adjusted by addition of perchloric acid).

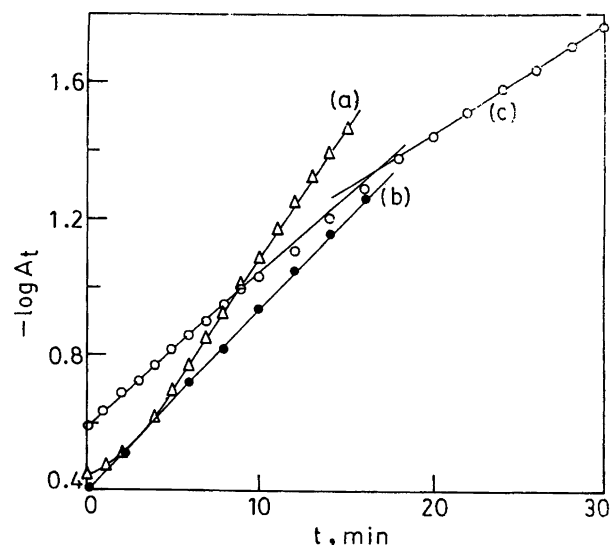


Fig. 2. Plot of $-\log A_t$ vs. t for the oxidation of thiourea by $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$. (a) pH 5.25 (0.02 mol dm^{-3} , acetate buffer), (b) pH 5.50 (0.02 mol dm^{-3} acetate buffer), (c) pH 6.0 (0.02 mol dm^{-3} Na_3PO_4 and pH adjusted by addition of perchloric acid). Other details are same as Fig. 1.

given. Also, no attempt has been made to verify the stoichiometry of the reaction during autocatalysis.

(iii) A plot of $-\log A_t$ vs. t is linear at pH 5.50 up to ca. 80% of the total reaction, indicating a first-order dependence of reaction rate on $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$. This is further verified by conducting some experiments with different concentrations of $[\text{Ni}^{\text{IV}}] = 5.0 \times 10^{-5} - 5.0 \times 10^{-4} \text{ M}$, $T = 30^\circ\text{C}$, pH 5.50, $I = 0.2 \text{ M}$ and $[\text{tu}] = 5.0 \times 10^{-3} \text{ M}$, where k_{obs} values remain unchanged.

(iv) At $\text{pH} \geq 6.0$, a distinct biphasic $1e^-$ transfer reduction of $[\text{Ni}^{\text{IV}}]$ is encountered (Fig. 2), showing a faster reduction step for $\text{Ni}^{\text{IV}} \rightarrow \text{Ni}^{\text{III}}$ followed by a slower reduction for the $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ step. From the slopes of the semilog plots, the pseudo-first-order rate constants (k_{obs}) for each step were evaluated.

Thiourea dependence. The variations in rate constants with thioureas were conducted by adopting the following condi-

Table 1. Dependence of pseudo-first-order rate constant ($k_{\text{obs}}/\text{s}^{-1}$) on reductant concentrations for the reduction of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ by thiourea and its *N*-substituted derivatives at pH 5.50.^a

[Reductant] /mol dm ⁻³	$k_{\text{obs}}/10^{-3} \text{ s}^{-1}$		
	tu	atu	mtu
0.001	0.30	0.35	0.32
0.003	0.80	0.82	0.76
0.005	1.30	1.56	1.28
0.008	1.86	2.24	2.06
0.01	2.25	2.72	2.44

^aOther conditions are: $[\text{Ni}^{\text{IV}}] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $I = 0.20 \text{ mol dm}^{-3}$ (NaClO_4), $[\text{acetate}]_{\text{total}} = 0.02 \text{ mol dm}^{-3}$ and pH maintained by addition of perchloric acid, and $T = 30^\circ\text{C}$.

tions, (a) for a clean monophasic $2e^-$ transfer step $[\text{Ni}^{\text{IV}}] = 5.0 \times 10^{-5} \text{ M}$, $I = 0.2 \text{ M}$ (NaClO_4), $T = 30^\circ\text{C}$, $\text{pH } 5.5$; (b) for clean biphasic $1e^-$ transfer steps $[\text{Ni}^{\text{IV}}] = 5.0 \times 10^{-5} \text{ M}$, $I = 0.2 \text{ M}$ (NaClO_4), $T = 30^\circ\text{C}$, $\text{pH } 6.5$. The concentration of the three thioureas was varied from 1.0×10^{-3} – $1.0 \times 10^{-2} \text{ M}$. Plots of k_{obs} under these conditions are given in Tables 1 and 2. Plots of k_{obs} at different reductant concentrations yield straight lines with almost the same intercept on the rate axis at a certain pH, indicating the auto-decomposition of the complex at that particular pH. The observed rate law for the reduction of Ni^{IV} by the thiourea species can, therefore, be expressed as

$$-\frac{d}{dt}[\text{Ni}^{\text{IV}}(\text{L}^1)_2^{2+}] = k_{\text{obs}}[\text{Ni}^{\text{IV}}] \\ = (k_d + 2mk_{\text{ox}}[\text{R}])[\text{Ni}^{\text{IV}}] \quad (2)$$

where k_d is the auto-decomposition rate constant of the oxidant at 30°C , $I = 0.2 \text{ M}$ and found to be pH-dependent. k_{ox} is the second-order electron-transfer rate constant and R is tu, mtu or atu. m is the stoichiometric factor due to oxidant and assumes the value 0.5 for $2e^-$ transfer and 1 for $1e^-$ transfer step.

pH dependence. Within the limits imposed by the need to retain clean $1e^-$ (biphasic) reaction profiles, it has been possible to determine the pseudo-first-order rate constants (k_{obs}) for the reactions of $\text{Ni}^{\text{IV}}/\text{Ni}^{\text{III}}$ with the thioureas in the range $\text{pH } 6.0$ – 8.0 . The corresponding $k_{\text{ox}} = \{(k_{\text{obs}} - k_d)/2m[\text{R}]\}$ values for the $\text{Ni}^{\text{IV}} \rightarrow \text{Ni}^{\text{III}}$ and

Table 2. Dependence of pseudo-first-order rate constant ($k_{\text{obs}}/\text{s}^{-1}$) on reductant concentrations for the reduction of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ by thioureas at $\text{pH } 6.50$ ($0.02 \text{ mol dm}^{-3} \text{ Na}_3\text{PO}_4$ and pH adjusted by adding HClO_4).^a

Reductant	[Reductant] / mol dm^{-3}	$k_{\text{obs}}^{\text{I}}/10^{-3} \text{ s}^{-1}$	$k_{\text{obs}}^{\text{II}}/10^{-3} \text{ s}^{-1}$
tu	0.001	0.70	0.375
	0.003	1.52	0.51
	0.005	2.30	0.62
	0.006	2.80	0.70
	0.008	3.55	0.84
	0.01	4.51	0.992
atu	0.001	0.80	0.48
	0.003	1.70	0.80
	0.005	2.51	1.14
	0.006	3.00	1.32
	0.008	3.75	1.60
	0.01	4.60	1.96
mtu	0.001	0.62	0.46
	0.003	1.40	0.84
	0.005	2.11	1.21
	0.006	2.42	1.36
	0.008	3.20	1.76
	0.01	3.84	2.10

^a $k_{\text{obs}}^{\text{I}}$ corresponds to the rate constant for $[\text{Ni}^{\text{IV}}] \rightarrow [\text{Ni}^{\text{III}}]$, whereas $k_{\text{obs}}^{\text{II}}$ is the rate constant for $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ conversion. Other details are same as Table 1.

$\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ indicate that the second-order rate constant for $\text{Ni}^{\text{IV}} \rightarrow \text{Ni}^{\text{III}}$ conversion increases with $-\log[\text{H}^+]$ (Fig. 3), whereas that for $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ decreases with increasing $-\log[\text{H}^+]$ (Fig. 4).

Discussion

Preliminary spectral scanning shows no indication for the formation of an appreciable amount of thermodynamically stable intermediate species in the oxidation of thioureas by $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ (Fig. 5). The interesting feature of this study is the autocatalytic oxidation of thioureas as indicated in the Figs. 1 and 2 in the $\text{pH } 2.0 \leq \text{pH} \leq 5.0$. The effect of metal ions (Cu^{2+} , Fe^{2+} etc.) on the reaction rate was verified by adding phenanthroline externally to the reaction mixture at a particular pH.

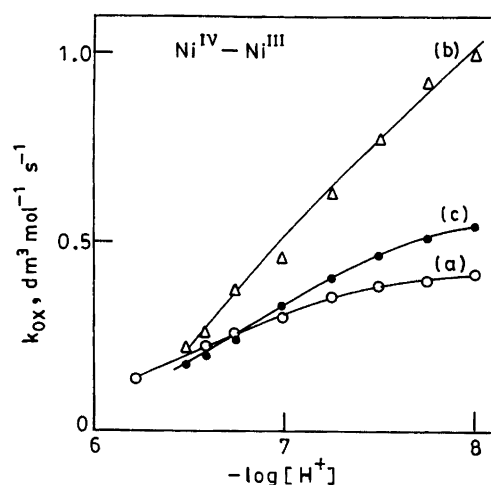


Fig. 3. Variation of $k_{\text{ox}} = (k_{\text{obs}} - k_d)/2m[\text{R}]$ as a function of $-\log[\text{H}^+]$ for the reduction of nickel(IV) to nickel(III) by (a) thiourea ($[\text{tu}] = 0.01 \text{ mol dm}^{-3}$), (b) *N*-allylthiourea ($[\text{atu}] = 0.005 \text{ mol dm}^{-3}$), (c) *N*-methylthiourea ($[\text{mtu}] = 0.005 \text{ mol dm}^{-3}$). $[\text{buffer}] = 0.02 \text{ mol dm}^{-3}$ (phosphate as in Fig. 2). Other conditions are the same as Fig. 1.

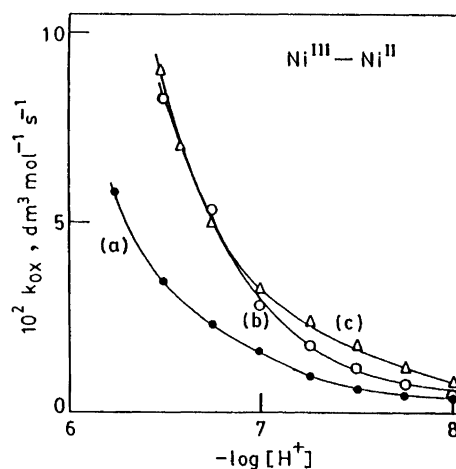


Fig. 4. Plot of k_{ox} vs. $-\log[\text{H}^+]$ for the reduction of $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ by (a) tu, (b) atu and (c) mtu. Other details are the same as Fig. 3.

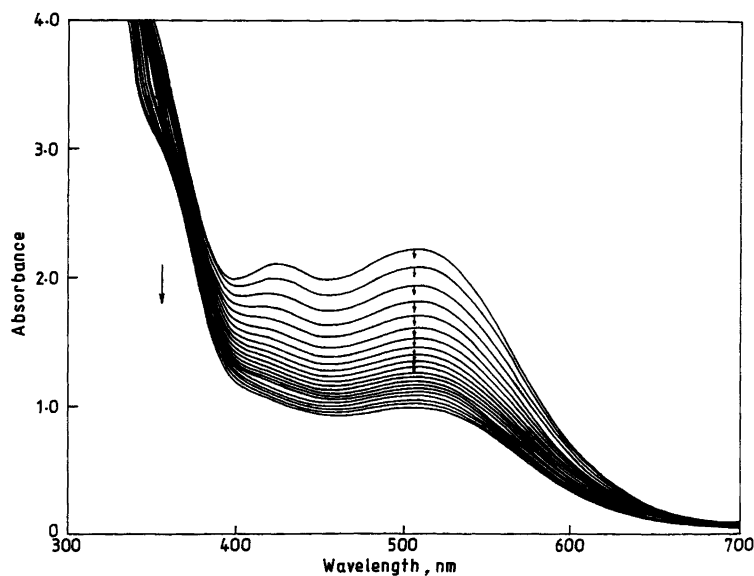
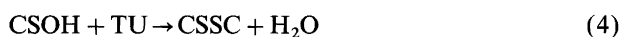
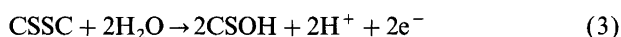


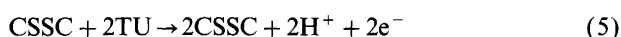
Fig. 5. Spectral scanning for the reduction of $[\text{Ni}^{\text{IV}}\text{L}_2^1]^{2+}$ with thiourea. The conditions are $[\text{Ni}^{\text{IV}}] = 3.60 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{tu}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.20 \text{ mol dm}^{-3}$ (NaClO_4), pH 5.50 (0.02 mol dm^{-3} acetate buffer as in Fig. 1) and $T = 30^\circ \text{C}$.

This showed no change on observed rate constant, suggesting the absence of any metal ion catalysis. Several explanations could be offered for the autocatalytic process: (a) involvement of the Ni^{III} intermediate to reduce Ni^{IV} in a competitive way; (b) products from the decomposition of $[\text{Ni}^{\text{II}}\text{L}_2^1]$ at low pH, i.e. aqueous Ni^{II} and biacetyl monoxime can impart reducing property on the Ni^{IV} complex; (c) radical intermediates generated from thioureas during the course of reaction can also interact with Ni^{IV} at low pH. The observations that all the reactions so far studied with this Ni^{IV} complex are free from these types of complications would point to a special feature of the thiourea reagents.

The (acidic) autocatalytic oxidation of thiourea by chlorite (ClO_2^-) ions has recently been studied both in an open reactor (CSTR) and under batch conditions.^{20,21} In the chlorite–thiourea system the autocatalytic species is assumed to be the disulfide compound $\text{NH}=\text{C}(\text{NH}_2)\text{--S--S--}(\text{NH}_2)\text{C}=\text{NH}$. Thus, by analogy, one may consider the following two-component processes (3) and (4) to explain autocatalysis in the thiourea oxidation:



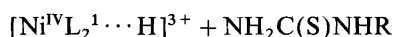
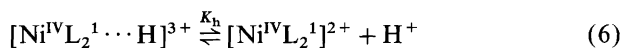
where CSSC is $\text{NH}=\text{C}(\text{NH}_2)\text{--S--S--}(\text{NH}_2)\text{C}=\text{NH}$, CSOH is $\text{NH}=\text{C}(\text{NH}_2)\text{--S--OH}$, and TU is thiourea. Making the combination (3) and (4) the overall process (5) is now autocatalytic in CSSC:

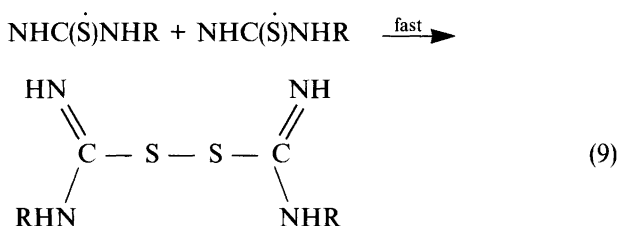


Of course the important intermediate in this scheme is CSOH, which is yet to be identified in the Ni^{IV} –thiourea reaction. Such a study could be addressed in a subsequent paper, dealing in more detail with the autocatalysis of

this interesting reaction. However, it is very difficult to determine the actual cause of autocatalysis owing to different factors operating simultaneously.

Reduction of nickel(IV) to nickel(III) at $\text{pH} \geq 6.0$. The reduction of nickel(IV) to nickel(III) by thioureas was studied in the range $6.0 \leq \text{pH} \leq 8.0$. Plots of k_{ox} vs. $-\log[\text{H}^+]$ show an ascending curve for all the three thioureas. The $\text{p}K_{\text{a}}$ of thiourea and its *N*-substituted derivatives are reported^{12,19} to be in the region $-1.5 \geq \text{p}K_{\text{a}} \geq -2.0$. Thus in the experimental range of pH the molecular form of all the thioureas are expected to exist. Hence such dependence of rate on pH can only be explained if there is any protic equilibrium involving the Ni^{IV} complexes. The $\text{p}K$ -value of $[\text{Ni}^{\text{IV}}\text{L}_2^1]^{2+}$ was pH-metrically determined as 6.1 ± 0.2 for outside protonation, giving rise to protonated Ni^{IV} species ($[\text{Ni}^{\text{IV}}\text{L}_2^1 \cdots \text{H}]^{3+}$). Thus the expected reactive species of nickel(IV) would be $[\text{Ni}^{\text{IV}}\text{L}_2^1 \cdots \text{H}]^{3+}$ and $[\text{Ni}^{\text{IV}}\text{L}_2^1]^{2+}$ under the reaction conditions, and a reasonable scheme consistent with the experimental observations could be framed as





The $\text{p}K$ value of $[\text{Ni}^{\text{III}}\text{L}^1(\text{HL}^1)]^{2+}$ is kinetically determined to be 4.43.^{18,22} In the experimental pH range (6.0–8.0) the generated nickel(III) species would apparently be a deprotonated one, and the rate law can be derived as

$$k_{\text{ox}} = \frac{k_1[\text{H}^+] + k_2K_h}{[\text{H}^+] + K_h} \quad (10)$$

Fitting of the experimental k_{ox} -values to eqn. (10) by means of a non-linear least-squares program of three variables yields the value of the parameters as follows. For tu, $k_1 = (2.60 \pm 0.78) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = (4.3 \pm 0.04) \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_h = (2.48 \pm 0.03) \times 10^{-7} \text{ mol dm}^{-3}$, ($\text{p}K_h = 6.60$); for atu, $k_1 = (5.55 \pm 1.07) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = (1.19 \pm 0.01) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_h = (5.37 \pm 0.08) \times 10^{-8} \text{ mol dm}^{-3}$, ($\text{p}K_h = 7.27$); for mtu, $k_1 = (3.23 \pm 0.34) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_2 = (6.5 \pm 0.20) \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $K_h = (1.11 \pm 0.06) \times 10^{-7} \text{ mol dm}^{-3}$, ($\text{p}K_h = 6.99$).

There is a good agreement between the experimental and calculated k_{ox} values (Fig. 3).

Reduction of nickel(III) to nickel(II) at $\text{pH} \geq 6.0$. The slower pH-dependent reactions at $\text{pH} \geq 6.0$ for $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ with tu, atu and mtu were identified with the reduction of nickel(III) species and confirmed by the electrochemically generated $[\text{Ni}^{\text{III}}\text{L}_2]^{1+}$ at $\text{pH} > 6.50$ as oxidant. Plots of k_{ox} vs. $[\text{H}^+]$ (Fig. 6) for the oxidation of all the three thioureas are straight lines with a positive intercept on the rate axis, thus confirming eqn. (11):

$$k_{\text{ox}} = a + b[\text{H}^+] \quad (11)$$

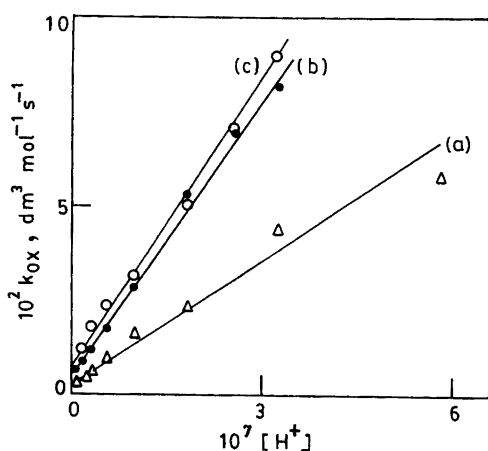
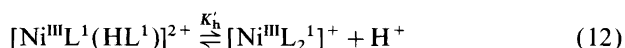
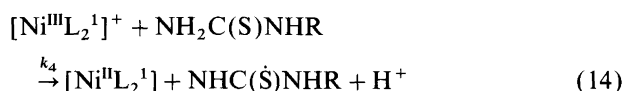
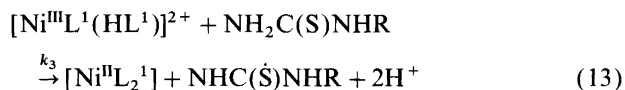


Fig. 6. Plot of k_{ox} vs. $[\text{H}^+]$ for the reduction of $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ by (a) tu, (b) atu and (c) mtu. Other details are the same as Fig. 3.

The $[\text{Ni}^{\text{III}}\text{L}_2]^{1+}$ complex is expected to exist in a protic equilibrium [eqn. (12)] with $\text{p}K_h' = 4.43$:



Thus a reasonable reaction scheme consistent with eqn. (11) could be framed as



The free radicals thus generated undergo dimerisation to give the disulfide product as in reactions (6)–(9). The nickel(II) species will abstract proton(s) from the medium in a very fast step to give the protonated species ($[\text{Ni}^{\text{II}}(\text{HL}^1)(\text{L}^1)]^+$ and $[\text{Ni}^{\text{II}}(\text{HL}^1)_2]^{2+}$), but the extent of protonation depends on the pH of the medium and the $\text{p}K$ values of the nickel(II) complex ($\text{p}K_1 = 7.80$ and $\text{p}K_2 = 10.00$). The above scheme of reactions, along with eqn. (12), would result in the rate law

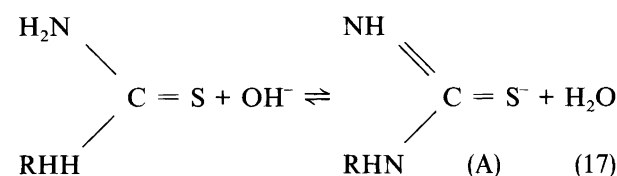
$$k_{\text{ox}} = \frac{k_3[\text{H}^+] + k_4K_h'}{[\text{H}^+] + K_h'} \quad (15)$$

In the experimental condition $[\text{H}^+] \ll K_h'$, ($[\text{H}^+]$, 10^{-6} – $10^{-8} \text{ mol dm}^{-3}$, K_h' , $3.71 \times 10^{-5} \text{ mol dm}^{-3}$), eqn. (15) becomes

$$k_{\text{ox}} = \frac{k_3}{K_h'}[\text{H}^+] + k_4 \quad (16)$$

and this is identical to eqn. (11) with $a = k_4$ and $b = k_3/K_h'$. A linear least-squares computer-fit program yields the value of the parameters as: $k_3/K_h' = (9.25 \pm 0.33) \times 10^4$, $(2.48 \pm 0.07) \times 10^5$ and $(2.45 \pm 0.07) \times 10^5 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$, and $k_4 = (4.17 \pm 0.82) \times 10^{-3}$, $(3.97 \pm 1.06) \times 10^{-3}$ and $(7.88 \pm 1.13) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for tu, atu and mtu, respectively.

In the present investigation, the reduction of $[\text{Ni}^{\text{IV}}\text{L}_2]^{2+}$ by the thioureas, there is a shift in $\text{p}K$ values of $[\text{Ni}^{\text{IV}}\text{L}_2 \cdots \text{H}]^{3+}$ to the higher side 6.60–7.27 from that obtained by potentiometric pH-titration of this oxidant (6.1). Although there are no $\text{p}K$ -values reported for the dissociation equilibrium of the thioureas, claims for the involvement of the anion (A)^{11,23} in the reaction at $\text{pH} \geq 3.0$ have been made.



This anion of thioureas may in turn react with oxidants, yielding disulfide products. The involvement of this anion

would further give rise to refinement in the calculation of p*K*-values of Ni^{IV} species.

A comparison of reactivity of the three thioureas with nickel(IV) and nickel(III) oxidants showed almost the same trend, which follows the order *atu* > *mtu* > *tu* for [Ni^{IV}L₂¹⋯H]³⁺, [Ni^{IV}L₂¹]²⁺ and [Ni^{III}L¹(HL¹)]²⁺ only differing in the case of [Ni^{III}L₂¹]⁺, where the order is found to be *mtu* > *tu* > *atu* (Table 3). We can reasonably put forward a sequence in which the reactions proceed through the formation of intermediates which then unimolecularly transfer an electron from the sulfur ligand to the metal centre:



Here *k* corresponds to the second-order rate constant of the oxidation of thioureas. Since the value of *Kk* is presumably very small, double-reciprocal plots (1/*k*_{obs} vs. 1/[S]₀) do not show any linearity. However, the observed reactivity order is dominated by the value of *K*, which is expected to follow the order *atu* > *mtu* > *tu* for [Ni^{IV}L₂¹⋯H]³⁺, [Ni^{IV}L₂¹]²⁺ and [Ni^{III}L¹(HL¹)]²⁺. This can be explained by consideration of the coordination of the sulfur ligand to the metal centre through the rupture of a M–L bond or due to the formation of sulfur–oxygen adduct through the participation of a d-orbital of the sulfur atom (in thioureas) with the oximate oxygen along, with the simultaneous operation of the inductive effect of the substituent (R = allyl for *atu*, methyl for *mtu* and hydrogen for *tu*). The order of reactivity of the thioureas toward [Ni^{III}L₂¹]²⁺ is at variance. It is a much more difficult matter, however, to decide which are controlling factors, since steric crowding, inductive effects, electrostatic effects etc. come into play. As there is no experimental evidence to support the inner-sphere route for these reactions, the transient [eqn. (18)] may be of the outer-sphere type. However, the experimental findings are best explained by consideration of an inner-sphere process. The proposition of an inner-sphere process, especially for Ni^{III} species, may be supported by a comparison of the electron-transfer rate and the lability of the metal centre (≈ 10² s⁻¹)^{12,18} of Ni^{III} complexes.

Experimental

The complex [Ni^{IV}L₂¹](ClO₄)₂ was prepared, characterised and standardised by the reported method.²⁴ All

the thioureas were of reagent grade and recrystallised twice before use. The solutions were prepared by dissolving required amounts of the reagents in doubly distilled water. The solutions were deaerated by bubbling dinitrogen through them. The pH of the solutions was measured in a Systronics digital pH meter (μ-pH system 361, India). High-purity perchloric acid, reagent-grade (recrystallised) sodium acetate and sodium dihydrogen phosphate (Na₂HPO₄) buffers were used to adjust the pH of the reaction solutions. The buffer species do not show any interaction with the nickel complexes. The measured pH is usually defined in terms of the activity of the hydrogen ion, and the hydrogen ion concentration was calculated by using the following relationship²⁵

$$[\text{H}^+] = 10^{-[(\text{pH} - 0.131)/0.982]}$$

where 0.131 is the factor due to the liquid junction potential between the glass electrode and the solution, and 0.982 denotes the activity coefficient in the reaction medium. Kinetic measurements were monitored using a Shimadzu (Japan) UV–VIS 2100 spectrophotometer. The reaction temperature was maintained within the limit ± 0.1 °C by a Haake F-3 thermostat.

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Table 3. Reactivity of thioureas towards different oxidising species.

Oxidant	<i>k</i> _{ox} /dm ³ mol ⁻¹ s ⁻¹		
	<i>tu</i>	<i>atu</i>	<i>mtu</i>
[Ni ^{IV} L ₂ ¹ ⋯H] ³⁺	(2.60 ± 0.78) × 10 ⁻²	(5.55 ± 1.07) × 10 ⁻²	(3.23 ± 0.34) × 10 ⁻²
[Ni ^{IV} L ₂ ¹] ²⁺	(4.3 ± 0.04) × 10 ⁻¹	(1.19 ± 0.01)	(6.5 ± 0.2) × 10 ⁻¹
[Ni ^{III} L ¹ (HL ¹)] ²⁺	(3.44 ± 0.12) ^a	(9.21 ± 0.26) ^a	(9.10 ± 0.26) ^a
[Ni ^{III} L ₂ ¹] ⁺	(4.17 ± 0.82) × 10 ⁻³	(3.97 ± 1.06) × 10 ⁻³	(7.88 ± 1.13) × 10 ⁻³

^a*k*_{ox} were calculated by utilising the reported p*K*_h for [Ni^{III}L¹(HL¹)]²⁺ as 4.43, i.e. *K*_h = 3.715 × 10⁻⁵.

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