Metal-ion Oxidations in Solution. Part X.[1] A Reinvestigation of the Reactions of Thiourea and its *N*-substituted Derivatives with Cobalt(III) Ions in Aqueous Perchlorate Media

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The oxidation of thiourea and its *N*-substituted derivatives by cobalt(III) ions has been reinvestigated, over the temperature range 8—25 °C at hydrogen-ion concentrations 0·17—1·44M, using a stopped-flow apparatus. There is no evidence for intermediate-complex formation and the observed rate constants, k_{obs}, may be expressed in the form $k_{obs} = k_1 + (k_2K_h/[H^+])$ where k_1 and k_2 refer to reactions involving $Co^{3+}(aq)$ and $[Co(OH)]^{2+}(aq)$ ions respectively. Thermodynamic parameters are compared with those for other oxidations of this type; the rate-determining steps are metal-ion substitution controlled with possible effects of the sulphur-containing ligand on the cobalt(III)-ion exchange rate.

THE nature and reactivity of the hexa-aquocobalt(III) ion in aqueous solution have been discussed in several recent studies,[2-6] although an exhaustive sequence of investigations is limited by the instability of the species in aqueous media. From the data available, it would appear that both the ions $Co^{3+}(aq)$ and $[Co(OH)]^{2+}(aq)$ are reactive and that the mechanism of oxidation of substrates may involve a dissociative-interchange type of inner-sphere process. In an earlier study of the reactions of *N*-substituted thioureas with this oxidant in this laboratory[7] a process of this type was postulated, but the data were obtained at varying ionic strengths over the hydrogen-ion concentration range 0·4—1·0M. Results at higher ionic strengths were included in order to extend the hydrogen-ion concentration range, but at that time the effects of ionic strength on these reactions were not completely identified and this may have contributed to uncertainties in the absolute rate constants and thermodynamic data, especially those involving the $Co^{3+}(aq)$ ion.[8] We have now repeated these measurements at a single ionic strength and extended the series to include the monosubstituted *N*-methyl species. Since this work was begun, a study of the corresponding manganese(III) reactions has been published[9] and it is of interest to compare the reactivities of these two oxidants.

EXPERIMENTAL

The preparation, standardisation, and storage of hexa-aquocobalt(III)-ion stock solutions and the preparation of the thioureas were carried out as described previously.[7] In the case of the *N*-methylthiourea, the overall stoicheiometry of the reaction was determined by spectrophotometric titration of the substrate by the oxidant at $\lambda = 400$ and 600 nm and was found to be $1{\cdot}00 \pm 0{\cdot}05$, in accord with that found for the previous reductants.

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Rate data were obtained using a stopped-flow apparatus modified from that described previously.[10] The drive syringes were of 2 cm^3 capacity and the observation cell, *together with* the mixing chamber and solution 'delivery lines,' were completely enclosed in a thermostatted metal block maintained to a temperature of $\pm 0{\cdot}1$ °C. Reactant solutions were left to thermostat for at least 30 min prior to measurements being made. Changes in transmission measured using an EMI 6256s photomultiplier tube were monitored using a storage oscilloscope, where voltage changes were referred to a known voltage such that absolute optical densities could be calculated at any point during a run. Transmission data were fed into a Nova 1200 computer and thus converted to optical-density changes. The disappearance of hexa-aquocobalt(III) in the presence of excess of thiourea was monitored at either 400 or 600 nm, plots of $\log(\mathrm{OD}_t - \mathrm{OD}_\infty)$ being linear to greater than 85% completion of reaction. In some cases second-order conditions were used, and in instances where comparisons were possible the data agreed to $\pm 6\%$ with those from first-order plots.

The ionic strength was maintained at a constant value of $1{\cdot}50\,\mathrm{M}$ using sodium perchlorate (Fluka puriss p.a.) and the hydrogen-ion concentration was varied from $0{\cdot}17$ to $1{\cdot}44\,\mathrm{M}$ using stock solutions made up from AnalaR material.

RESULTS AND DISCUSSION

The rate data were consistent with strict adherence to second-order kinetics, first order with respect to each reactant, over the concentration range studied. Optical densities of hexa-aquocobalt(III) obtained from extrapolation of rate plots to $t = 0$ were identical with those for similar concentrations of oxidant alone. No kinetic or spectroscopic evidence was found for the existence of transient intermediates which have been observed previously in reactions with chloride ions[11] and thiomalic acid.[12] The results of temperature and hydrogen-ion concentration variations on the rates are given in Table 1.

As observed in the previous studies,[5,7] the data may be represented by expression (1), where $[\mathrm{L}]_\mathrm{T}$ represents the

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = [\mathrm{L}]_\mathrm{T}[\mathrm{Co^{III}}]\{k_\mathrm{a} + (k_\mathrm{b}/[\mathrm{H^+}])\} \qquad (1)$$

total thiourea concentration. Because of differences in the experimental conditions, few direct comparisons with the previous study[7] are possible. In the case of *NN'*-ethylenethiourea, however, the value of the observed second-order rate constant, k_0, of 20 l mol^{-1} s^{-1} at $6{\cdot}7$ °C may be compared with an extrapolated value in the present study of 22 l mol^{-1} s^{-1}. For the reaction with thiourea, however, the previous values are a factor of 2—3 smaller than those currently derived and must be seen to be erroneous.

The predominant forms of cobalt(III) present under the experimental conditions used are $[\mathrm{Co(OH)}]^{2+}$(aq) and $\mathrm{Co^{3+}}$(aq),[2,3] where an upper limit of 5×10^{-3} mol l^{-1}

$$\mathrm{Co^{3+}(aq)} \overset{K_\mathrm{h}}{\rightleftharpoons} [\mathrm{Co(OH)}]^{2+}\mathrm{(aq)} + \mathrm{H^+} \qquad (2)$$

for K_h has been indicated.[5] Under the present $[\mathrm{H^+}]$ conditions, the thioureas are considered to exist predominantly as monoprotonated species,[13] although the dissociation constant K_a for reaction (3) (L = a thiourea)

$$\mathrm{HL^+} \rightleftharpoons \mathrm{H^+} + \mathrm{L},\ K_\mathrm{a}\ ca.\ 10^{-2}\ \mathrm{mol\ l^{-1}} \qquad (3)$$

has been derived only in the case of unsubstituted thiourea. The kinetic data are consistent with the reaction scheme (4)—(7), where $\mathrm{L_2'}$ represents the product

$$\mathrm{Co^{3+}(aq)} + \mathrm{HL^+} \xrightarrow{k_1} \mathrm{Co^{II}} + \mathrm{L'} + \mathrm{H^+} \qquad (4)$$

$$[\mathrm{Co(OH)}]^{2+}\mathrm{(aq)} + \mathrm{HL^+} \xrightarrow{k_2} \mathrm{Co^{II}} + \mathrm{L'} + \mathrm{H^+} \qquad (5)$$

$$\mathrm{Co^{3+}} + \mathrm{L} \xrightarrow{k_3} \mathrm{Co^{II}} + \mathrm{L'} \qquad (6)$$

$$2\mathrm{L'} \xrightarrow{\text{fast}} \mathrm{L_2'} \qquad (7)$$

thiourea which may be protonated. Reaction (6) has been included since this is kinetically indistinguishable from (5). Under the present experimental conditions, the observed second-order rate constant, k_0, may be written as in equation (8). At the lowest hydrogen-ion

$$k_0 = \frac{k_1 + (k_2K_\mathrm{h}/[\mathrm{H^+}]) + (k_3K_\mathrm{a}/[\mathrm{H^+}])}{\left(1 + \dfrac{K_\mathrm{h}}{[\mathrm{H^+}]}\right)\left(1 + \dfrac{K_\mathrm{a}}{[\mathrm{H^+}]}\right)} \qquad (8)$$

concentrations employed, using the values of K_a and K_h quoted above, $K_\mathrm{h}/[\mathrm{H^+}]$ and $K_\mathrm{a}/[\mathrm{H^+}]$ are *ca.* 2×10^{-2} and *ca.* 6×10^{-2} respectively so that equation (8) reduces to (9).

$$k_0 = k_1 + (k_2K_\mathrm{h}/[\mathrm{H^+}]) + (k_3K_\mathrm{a}/[\mathrm{H^+}]) \qquad (9)$$

It is of interest to note that no term in $[\mathrm{H^+}]^{-2}$ was observed over the $[\mathrm{H^+}]$ range studied, which would result from reaction of the ion $[\mathrm{Co(OH)}]^{2+}$ and the unprotonated form L. This circumstantial evidence supports the suggestion[7] that the thioureas are present principally as the protonated forms. The question of the contribution of reaction (6) to the observed rate may also be considered. If reactions involving $\mathrm{Co^{3+}}$(aq) are substitution controlled[5] then a rate constant similar to that for reaction (4) would be indicated, whereas the observed combined rate constant must be a factor of 10^2—10^3 (K_a and K_h terms) greater than this. It would appear, therefore, that $k_3K_\mathrm{a} \ll k_2K_\mathrm{h}$, an assumption which has been made previously in the hexa-aquocobalt(III) oxidation of oxalic acid[14] and in similar complex-formation reactions involving iron(III) species[1,15] where the hydroxo-ion reacts much more rapidly. Reactions (4) and (5) are thus considered to predominate, and rate and thermodynamic parameters for the systems under study are compared in Table 2 with other systems where, in some cases, protonation of the reductant may be neglected.

In the reactions with $\mathrm{H_2O_2}$,[5] $\mathrm{Br^-}$,[5] $\mathrm{HN_3}$,[8] $\mathrm{ClO_2}$,[16] and

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TABLE 1

Observed rate data and rate constants at various temperatures and hydrogen-ion concentrations: $I = 1{\cdot}50$; $[\mathrm{Co^{III}}]_T = 2{\cdot}8 \times 10^{-3}$—$4{\cdot}9 \times 10^{-3}$M; [L] = concentration of substrate

	$[\mathrm{H^+}]$/M	k_0/l mol^{-1} s^{-1}	k_a/l mol^{-1} s^{-1}	k_b/s^{-1}
Thiourea				
8·3 °C, [L] = $8{\cdot}59 \times 10^{-2}$M	$0{\cdot}17_8$	169 + 9	21·7 ± 3·7	26·3 ± 1·2
	$0{\cdot}35_5$	96 ± 2		
	0·50	71 ± 1		
	0·70	58 ± 1		
	1·00	54 ± 1		
13·9 °C, [L] = $8{\cdot}60 \times 10^{-2}$M	$0{\cdot}17_4$	398 ± 4	46·2 ± 3	60·9 ± 1·0
	$0{\cdot}34_7$	219 ± 7		
	0·50	167 ± 3		
	0·75	122 ± 5		
	1·00	109 ± 3		
	1·30	98 ± 3		
16·9 °C, [L] = $8{\cdot}58 \times 10^{-3}$M	$0{\cdot}16_5$	830 ± 30	69·5 ± 5·6	124·2 ± 2·2
	$0{\cdot}32_9$	430 ± 10		
	0·45	354 ± 6		
	0·75	233 ± 8		
	1·0	197 ± 3		
	1·44	158 ± 3		
20·0 °C, [L] = $9{\cdot}90 \times 10^{-3}$M	$0{\cdot}17_0$	1 180 ± 40	132 ± 12·4	179 ± 4
	0·50	510 ± 10		
	0·75	357 ± 10		
	1·00	296 ± 10		
	1·30	270 ± 4		
25 °C, [L] = $7{\cdot}93 \times 10^{-3}$M	0·50	920 ± 20	163 ± 21	382 ± 15
	0·70	719 ± 16		
	1·00	558 ± 15		
	1·44	415 ± 8		
NN′-Ethylenethiourea				
7·9 °C, [L] = $5{\cdot}97 \times 10^{-2}$M	$0{\cdot}26_3$	77 ± 4	14·6 ± 1·8	16·7 ± 0·7
	$0{\cdot}30_0$	67 ± 2		
	0·45	50 ± 1		
	1·00	31 ± 1		
14·2 °C, [L] = $4{\cdot}46 \times 10^{-2}$M	$0{\cdot}26_3$	190 ± 3	30 ± 4	44 ± 1·8
	0·30	176 ± 4		
	0·45	135 ± 3		
	0·75	90 ± 2		
	1·00	77 ± 1		
	1·10	73 ± 1		
	1·44	65 ± 1		
20° C, [L] = $4{\cdot}46 \times 10^{-2}$M	$0{\cdot}26_3$	490 ± 15	67 ± 10	116 ± 4·4
	$0{\cdot}34_4$	335 ± 10		
	0·45	301 ± 7		
	0·60	247 ± 10		
	0·75	218 ± 4		
	0·80	224 ± 10		
	1·10	145 ± 9		
	1·30	163 ± 4		
	1·44	135 ± 3		
24·85 °C, [L] = $7{\cdot}55 \times 10^{-3}$M	$0{\cdot}17_8$	1 423	130 ± 18	241 ± 8
	$0{\cdot}35_6$	912		
	0·50	565		
	0·60	500		
	0·75	474		
	0·80	412 ± 16		
	1·00	361 ± 7		
	1·10	347 ± 3		
	1·30	302 ± 6		
	1·44	320		
N-Methylthiourea				
7·9 °C, [L] = $6{\cdot}57 \times 10^{-2}$M	$0{\cdot}34_7$	125 ± 3	38 ± 2·9	29·4 ± 1·7
	0·60	78 ± 3		
	0·80	73 ± 2		
	1·00	69 ± 2		
	1·30	63 ± 1		
	1·44	61 ± 1		

TABLE 1 (*Continued*)

	[H$^+$]/M	k_0/l mol^{-1} s^{-1}	k_a/l mol^{-1} s^{-1}	k_b/s^{-1}
N-Methylthiourea				
14·3 °C, [L] = 6·57 × 10^{-2}M	0·34$_7$	307 ± 3	75·6 ± 4·8	79·6 ± 3·0
	0·60	206 ± 10		
	0·80	167 ± 3		
	1·00	160 ± 8		
	1·30	141 ± 1		
	1·44	130 ± 2		
16·9 °C, [L] = 5·52 × 10^{-3}M	0·17$_7$	917 ± 18	150 ± 11	136 ± 3
	0·35$_4$	544 ± 10		
	0·45	447 ± 9		
	0·75	331 ± 4		
18·3 °C, [L] = 6·50 × 10^{-3}M	0·48$_7$	504 ± 4	124 ± 12	183 ± 10
	0·72$_7$	366 ± 7		
	0·94	324 ± 20		
	1·09	275 ± 15		
	1·45	264 ± 10		
20 °C, [L] = 6·69 × 10^{-2}M	0·34$_7$	731 ± 17	169 ± 8	185 ± 14
	0·36$_1$	636 ± 4		
	0·50	556 ± 10		
	0·75	457		
	0·80	430 ± 10		
	1·00	347 ± 10		
	1·30	320 ± 4		
	1·44	283 ± 7		
25 °C, [L] = 7·74 × 10^{-3}M	0·35$_5$	1 370 ± 20	361 ± 38	367 ± 20
	0·50	1 140 ± 18		
	0·70	910 ± 20		
	1·00	753 ± 8		
	1·44	550 ± 50		
NN'-Diethylthiourea				
8·0 °C, [L] = 2·27 × 10^{-2}M	0·27	155 ± 6	61·8 ± 2·8	24·4 ± 1·3
	0·35$_6$	128 ± 3		
	0·50	107 ± 5		
	0·75	92 ± 2		
	1·00	84 ± 2		
	1·44	83 ± 3		
8·3 °C, [L] = 1·174 × 10^{-2}M	0·32$_9$	154 ± 1	55·9 ± 3·7	33·1 ± 2
	0·45	130 ± 5		
	0·75	108 ± 1		
	1·00	88 ± 2		
	1·44	73 ± 1		
14·3 °C, [L] = 2·294 × 10^{-2}M	0·26$_5$	336 ± 3	105 ± 7	63 ± 3
	0·50	248 ± 2		
	0·75	191 ± 4		
	1·00	167 ± 3		
	1·43	138 ± 2		
16·9 °C, [L] = 1·292 × 10^{-2}M	0·25$_6$	540 ± 7	148 ± 5	103 ± 2·6
	0·45	369 ± 4		
	0·75	300 ± 2		
	1·00	250 ± 2		
	1·44	215 ± 3		
20 °C, [L] = 6·69 × 10^{-2}M	0·36$_5$	625 ± 10	170 ± 16	160 ± 9
	0·50$_2$	445 ± 9		
	0·67	410 ± 8		
	0·99	331 ± 5		
	1·29$_6$	300 ± 6		
25·5 °C, [L] = 1·209 × 10^{-2}M	0·26$_9$	1 760 ± 80	348 ± 39	367 ± 17
	0·35$_4$	1 340 ± 70		
	0·45	1 130 ± 40		
	0·75	817 ± 27		
	1·00	730 ± 25		
	1·44	632 ± 5		

TABLE 1 (*Continued*)

NN′-Dimethylthiourea	$[H^+]$/M	k_0/l mol^{-1} s^{-1}	k_a/l mol^{-1} s^{-1}	k_b/s^{-1}
8·9 °C, [L] = $5{\cdot}63_8 \times 10^{-2}$M	$0{\cdot}16_6$	200 ± 3	42·7 ± 2·4	26·0 ± 0·7
	$0{\cdot}32_2$	116 ± 3		
	0·70	83 ± 1		
	0·90	70 ± 1		
	1·20	64 ± 4		
15·2 °C, [L] = $5{\cdot}64 \times 10^{-2}$M	$0{\cdot}16_6$	452 ± 8	96 ± 7	60 ± 1·8
	$0{\cdot}33_2$	293 ± 2		
	0·90	152 ± 4		
	1·20	142 ± 6		
	1·44	133 ± 4		
20 °C, [L] = $5{\cdot}05 \times 10^{-2}$M	$0{\cdot}17_8$	880 ± 15	184 ± 6	124 ± 2·3
	$0{\cdot}35_5$	523 ± 3		
	$0{\cdot}50_2$	445 ± 10		
	0·70	364 ± 8		
	0·99	319 ± 2		
	$1{\cdot}29_6$	270 ± 6		
24·9 °C, [L] = $8{\cdot}19 \times 10^{-3}$M	$0{\cdot}37_3$	1 105 ± 25	263 ± 19	318 ± 12
	0·60	805 ± 5		
	0·80	675 ± 13		
	0·91	592 ± 14		
	1·30	503 ± 3		

TABLE 2

Kinetic and thermodynamic parameters for oxidations by the ions Co^{3+}(aq) and $[Co(OH)]^{2+}$ at 25 °C and I = 1·50M

Reductant	k_1/l mol^{-1} s^{-1}	$\Delta H_1^‡$/kcal mol^{-1}	$\Delta S_1^‡$/cal K^{-1} mol^{-1}	k_2K_h/s^{-1}	$\Delta H_{2h}^‡$/kcal mol^{-1}	$\Delta S_{2h}^‡$/cal K^{-1} mol^{-1}	Ref.
$(NH_2)_2CSH^+$	163 ± 21	19·9 ± 1·7	20 ± 6	382 ± 16	26·3 ± 0·3	43 ± 2	*a*
$(MeNH)_2CSH^+$	270 ± 20	18·8 ± 1·2	18 ± 4	318 ± 12	25·3 ± 1·3	39 ± 5	*a*
$(MeNH)(NH_2){\cdot}CSH^+$	361 ± 40	21·2 ± 1·4	26 ± 5	367 ± 20	24·2 ± 0·9	36 ± 4	*a*
$(EtNH)_2CSH^+$	300 ± 30	15·6 ± 0·8	7 ± 3	320 ± 15	24·1 ± 0·9	35 ± 4	*a*
$(CH_2NH)_2CSH^+$	130 ± 18	21·7 ± 1·6	23 ± 5	241 ± 8	26·5 ± 0·3	41 ± 2	*a*
H_2O_2 [b]	⩽2			23·0	23·5	25	5
HNO_2 [b]	18	18·3	9	17·2	21·7	19	5
Br^- [b]	⩽5			30·4	26·1	37	5
HN_3 [c]	⩽2			35·2	23·1	15	8
ClO_2 [d]	⩽1			59·6	21·8	23	16
SCN^- [b]	86·5	20·6	20	79·6	25·6	37	5
$HO{\cdot}C_6H_4{\cdot}OH$ [b]	2 200	18·2	18	1 280	18·6	18	5
I^- [b]	8 000	19·4	25	2 860	21·5	30	5
$H_2C_2O_4$ [b]	2			10·6	24	28	14
$HC_2O_4^-$ [b]				81·5	25·9	39	14

[a] This work. [b] I = 3·0M. [c] I = 2·0M. [d] I = 2·1M.

Thermodynamic data for k_2K_h are uncorrected for enthalpies and entropies of dissociation of the aquated metal ion (see ref. 4).

$H_2C_2O_4$,[14] a small acid-independent term is observed but it has been suggested [5] that this may be due to changes in activity coefficients on replacement of H^+(aq) by Na^+(aq) or Li^+(aq). In reactions of Co^{3+}(aq), where it is possible to derive thermodynamic data, there appears to be surprisingly good consistency of $\Delta H^‡$ and $\Delta S^‡$ values, although some variation in the rates is observed. The small spread of values of k_1 and k_2K_h for the reaction of the substituted thioureas would tend to suggest a common mechanism with little stereochemical crowding. The similarity of value of both k_1 and k_2K_h with that for NCS^- may be important and comparison of these data with HN_3 (Table 2) suggests that the sulphur atom may be a potential site of attachment to the metal ion. These data contrast with those for Mn^{III} [9] in that whereas the reactions involving $[Mn(OH)]^{2+}$ show reasonable consistency, only that between Mn^{3+}(aq) and thiourea could be characterised.

In reactions involving an inner-sphere mechanism [17] it has been suggested that small differences in the forward rate constant may be due to ligand effects ($k_f = k_0K_0$) and are the result of variations in the outer-sphere equilibrium constant, K_0. Recent evidence [18] indicates that solvent structure may also be important. A mechanism of this type for cobalt(III) reactions can be postulated in that an increase in rate with increasing charge product of the reactants is observed.[14] In the present systems, however, the charge products are positive and yet the rate constants are greater than those observed previously, with the exception of iodide ion and hydroquinone [5] which cannot be interpreted in terms of a purely dissociative model. The situation is clearly more complex and the labilising influence of the co-ordinated hydroxide ion may also be important. The positive entropies are indicative of a high electronic-transition probability between the two reactant ions.[19]

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Thus, parts of the hydration spheres of these ions have to be rearranged to a greater extent leading to water molecules being ' unfrozen ' in the formation of each activated complex, From the data available (Table 2), especially those for k_2K_h ($\Delta H^\ddagger$ values are fairly similar), it can be seen that changes in $\Delta S^\ddagger$ are more marked and the rate increases in the present systems may be due to effects of the sulphur-containing ligand on the nature and rate of cobalt(III) exchange.

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