The existence of a discrete 2:1 molecular complex, aside from the vapor pressure–composition study, is further supported by molecular weight measurements which gave a value consistent with the species $2C_7H_8 \cdot CuAlCl_4$ when $CuAlCl_4$ is dissolved in toluene. An infrared study carried out on the liquid 2:1 complex[23] indicates the presence of two chemically different toluene molecules complexed to the Cu(I) center.

Acknowledgments.—I wish to thank Drs. R. B. Long, J. J. Elliott, and M. T. Melchior for their many helpful suggestions during the course of this study. Special thanks are also extended to R. S. Matyas for experimental assistance and to H. T. Oakley for a least-mean-squares treatment of the data.

[23] J. J. Elliott, private communication. An article dealing with the infrared spectra of 1:1 and 2:1 toluene–$CuAlCl_4$ complexes is in preparation.

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Inner-Sphere Mechanisms of Oxidation. II.[1] Stoichiometry and Kinetics of the Manganese(III) Oxidation of Thiocyanate, Thiourea, and Some Alkylthioureas in Acid Perchlorate Solution

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The kinetics of the rapid manganese(III) oxidation of excess thiourea, *N,N'*-dimethylthiourea, *N,N'*-diethylthiourea, and *N,N'*-ethylenethiourea have been studied in a stopped-flow apparatus over a range of acidities and temperatures at ionic strength 4.0 *M*. Although the reaction with SCN^- was too fast to be followed by this method at 25° ($k_{obsd} \geq 3 \times 10^5$ M^{-1} sec^{-1} at $[H^+] = 1.00$ *M* and ionic strength 4 *M*), the stoichiometry of reaction with excess SCN^- was the same as that measured with the thioureas in the presence of excess manganese(III), *viz.*, $\Delta[Mn(III)]/\Delta[\text{reductant}] = 1$, corresponding to the formation of S–S bonded products in each case. Evidence is presented for changes in the state of protonation and possibly the extent of tautomerism of alkylthiourea molecules over the experimental acidity range. By using the rate parameters for reaction of $Mn^{3+}{}_{aq}$ and $MnOH^{2+}{}_{aq}$ with monoprotonated thiourea as a basis, the rate constants for reactions of $MnOH^{2+}{}_{aq}$ with the monoprotonated alkylthiourea species are derived. Comparison of these rate constants with those for other reductants suggests an inner-sphere mechanism, with substitution at the manganese(III) center as the rate-determining process.

Introduction

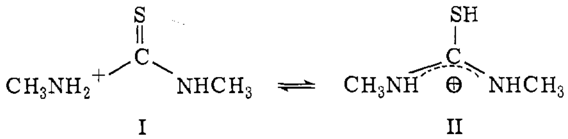
The rates of complexation and oxidation of thiocyanate and its derivatives may depend on whether or not attack takes place at the nitrogen or sulfur atoms of the molecule. For example, in this work it is shown that the rate of complexation of iron(III) by thiocyanate is considerably decreased by the presence of manganese(II), presumably because of the removal of free NCS^- in the form of an N-bonded $MnNCS^+$ complex under these conditions. In addition, the inner-sphere oxidations of free thiocyanate by iron(III)[2] (in acetonitrile) and cobalt(III)[3] (in acid perchlorate solution) produce S–S bonded $(SCN)_2$, whereas the much slower oxidations of the inert, N-bonded complex $Co(NH_3)_5NCS^{2+}$ by H_2O_2[4] and cerium(IV)[5] produce $Co(NH_3)_5CN^{2+}$ (*via* isomerization of $Co(NH_3)_5NC^{2+}$), $Co(NH_3)_6{}^{3+}$, and $SO_4{}^{2-}$, rather than S–S bonded products.

Thiourea and the symmetrical alkylthioureas are converted to the corresponding disulfides in analogous reactions with cerium(IV)[6] and cobalt(III),[7] which might thus be construed as evidence for attack at nitrogen atoms rather than sulfur in these molecules.

The aquomanganese(III) cation $Mn^{3+}{}_{aq}$ is a strong

$$Mn^{3+}{}_{aq} \rightleftharpoons MnOH^{2+}{}_{aq} + H^+{}_{aq} \quad K_h \qquad (1)$$

acid in aqueous perchlorate media, with $K_h = 0.93$ *M* at 25° and ionic strength 1–4 *M*,[8] and this factor is important in determining the acid dependence of oxidation reactions of the Mn(III)–Mn(II) couple. Although thiourea molecules are believed to be monoprotonated[9] under the strongly acidic conditions where manganese(III) species are stable, the predominant molecular forms in solution have been the subject of debate.[10] For example, the tautomeric forms of the monoprotonated *N,N'*-dimethylthiourea species might be written



$$CH_3NH_2{}^+\!-\!C(=S)\!-\!NHCH_3 \rightleftharpoons CH_3NH\!\overset{SH}{\overset{|}{C}}\!\overset{\ominus}{}NHCH_3 \qquad (2)$$

I II

The observation of a disulfide product does not necessarily distinguish between these two forms even if they yield different oxidation products, since they might be rapidly interconvertible with reactions to disulfide being the fastest oxidation processes. Very rapid oxidation of II might conceivably lead to a situa-

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[1] Part I: G. Davies and K. O. Watkins, *Inorg. Chem.*, **9**, 2735 (1970).

[2] B. Kratochvil and R. Long, *Anal. Chem.*, **42**, 43 (1970).

[3] G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).

[4] S. M. Caldwell and A. R. Norris, *Inorg. Chem.*, **7**, 1667 (1968).

[5] K. Schug, B. Miniatas, A. J. Sadowski, T. Yano, and K. Ueno, *ibid.*, **7**, 1669 (1968).

[6] (a) W. A. Alexander, C. J. Mash, and A. McAuley, *Analyst (London)*, **95**, 657 (1970); (b) U. D. Gomwalk and A. McAuley, *J. Chem. Soc. A*, 2948 (1968).

[7] A. McAuley and U. D. Gomwalk, *ibid.*, 977 (1969).

[8] G. Davies, *Coord. Chem. Rev.*, **4**, 199 (1969).

[9] T. J. Lane, J. A. Ryan, and L. J. Walter, *J. Amer. Chem. Soc.*, **78**, 5560 (1956).

[10] E. E. Reid, "Organic Chemistry of Divalent Sulfur," Vol. V, Chemical Publishing Co., New York, N. Y., 1963, p 17ff; see also D. R. Eaton and K. Zaw, *Can. J. Chem.*, **49**, 3315 (1971).

tion in which the establishment of equilibrium (2) was rate determining, and the observed rate would then be independent of [oxidant]. However, the rate of oxidation of several thiourea derivatives by the strongly oxidizing cobalt(III)–cobalt(II) couple appears to be limited only by the rate of substitution of the reductant into the inner-coordination sphere of the cobalt(III) center,[7] and it is of interest to investigate the analogous reactions with manganese(III), which also exhibits substitution control in some of its more rapid redox reactions.[8] In this paper the stoichiometry and kinetics of the manganese(III) oxidation of thiocyanate and four thiourea derivatives are reported, and it is concluded that a substitution-controlled mechanism probably operates in each case.

Experimental Section

Reagents.—The preparation and standardization of solutions of perchloric acid and the perchlorates of manganese(III), manganese(II), and sodium were as described previously.[8] Sodium thiocyanate was recrystallized once from water, and the thioureas were all recrystallized from suitable solvents.[7] Their purity was confirmed by elemental analysis (C, H, and N, University of Kent Analytical Services). All other reagents were of analytical grade and triply distilled water was used throughout. Solutions of the thioureas were prepared immediately before use to avoid complications due to slow decomposition reactions which occur in the presence of perchloric acid.

Stoichiometry Measurements.—The stoichiometry of the reaction with excess thiocyanate was determined iodometrically as described previously.[5] The concentrations used were [Mn(III)] = (1.78–5.44) × 10^{-8} *M*, [SCN^-] = 0.24–0.72 *M*, [I^-] = 1.0–2.5 *M*, and [H^+] = 2.0–3.0 *M*. Variation of the excess thiocyanate or iodide concentrations had no effect on the stoichiometric results.

The stoichiometries of reaction with the thioureas were determined by spectrophotometric measurement[8] of the excess of manganese(III) remaining immediately after reaction with a known concentration of the reductant. The reactant conditions used were [reductant] = (0.24–4.04) × 10^{-4} *M*, [Mn(III)] = (1.55–5.31) × 10^{-4} *M*, [Mn(II)] = 0.54 *M*, and [H^+] = 2.0 *M* at 25°.

Kinetic Measurements.—The disappearance of manganese(III) in the presence of excess thiourea was monitored in the wavelength range 260–550 nm using the thermostated stopped-flow apparatus described previously.[11] Most of the measurements were made at 470 nm, where the absorbance of manganese(III) is a maximum in the visible region.[8] A very small absorption increase which was detected in attempted measurements of the kinetics of the manganese(III)–SCN^- reaction at 25° can be ascribed to the formation of $FeNCS^{2+}$ due to the presence of trace iron(III) impurities in perchloric acid (see Results section). The temperature was varied between −1.3 and +25.3° in the reactions with thioureas in the presence of a sufficient excess of reductant to ensure pseudo-first-order conditions. The acidity range employed was 0.25–3.70 *M* at total ionic strength 4.0 *M*. Each kinetic run was repeated at least twice, with replicate measurements usually agreeing to within ±5%.

Results

Stoichiometry.—The stoichiometric measurements established that the reactions occurring are

$$2\mathrm{Mn(III)} + 2\mathrm{SCN^-} \longrightarrow 2\mathrm{Mn(II)} + (\mathrm{SCN})_2 \qquad (3)$$

$$2\mathrm{Mn(III)} + 2\mathrm{R_2N_2H_3CS^+} \longrightarrow 2\mathrm{Mn(II)} + \mathrm{R_4N_4H_4C_2S_2^{2+}} + 2\mathrm{H^+} \qquad (4)$$

$$(\mathrm{R} = \mathrm{H}, \mathrm{CH_3}, \text{ or } \mathrm{C_2H_5})$$

with an experimental uncertainty of ±5%. Although the oxidation product was not positively identified in this study, the stoichiometry of reaction 3 is the same as that observed in the analogous reactions with iron(III)[2] (in acetonitrile) and cobalt(III)[3] (in acid perchlorate) where thiocyanogen was isolated and fully characterized. Because of analytical difficulties connected with the low concentrations of manganese(III) available[8] and the small extinction coefficients of the thiourea reactants and disulfide products the stoichiometry of reactions 4 was measured with excess manganese(III), while for practical reasons[8] the kinetics were followed with excess thiourea. However, the stoichiometry Δ[Mn(III)]/Δ[reductant] = 1 was independent of the initial concentration ratio R = [Mn(III)]$_0$/[reductant]$_0$ in the range 1.31–16.8; this result, taken with the observations of a similar stoichiometry with excess thiourea in the reactions with cerium(IV)[6a] and cobalt(III)[7] and the isolation of the corresponding disulfide products,[6,7] makes the assumption of the stoichiometry of reaction 4 reasonable under the conditions of the kinetic measurements.

Kinetics. **(A) Thiocyanate.**—The concentrations of free thiocyanate in mixtures of manganese(II), perchloric acid, sodium thiocyanate, and sodium perchlorate at ionic strength 4.0 *M* and 25° were calculated from the equilibrium constant $K_1 = 5.4\ M^{-1}$ in the reaction[12]

$$\mathrm{Mn^{2+} + SCN^-} \rightleftarrows \mathrm{MnNCS^+} \quad K_1 \qquad (5)$$

At the lowest calculated concentration employed ([SCN^-] = 3.1 × 10^{-4} *M*) the disappearance of manganese(III) in 1.00 *M* acid occurred in less than the dead time of the apparatus[11] (*ca.* 10 msec). If it is assumed that the reaction is first order in both reactants a lower limit of $k_{\text{obsd}} \geq 3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ may be calculated at 25° and at [H^+] = 1.00 *M* and ionic strength 4.0 *M*.[13–15]

(B) Thioureas.—First-order plots of ln ($A_t - A_\infty$) *vs.* time, where A_t and A_∞ are measured absorbancies at times t and after several half-times, respectively, were linear for at least 85% reaction in the presence of a tenfold or greater excess of the thiourea, establishing a first-order dependence of the rate on [Mn(III)].

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[11] G. Davies, *Inorg. Chem.*, **10**, 1155 (1971).

[12] S. Tribalat and J. M. Caldero, *J. Electroanal. Chem.*, **5**, 176 (1963).

[13] As mentioned above, the only absorbance change which we observed was evidently related to the formation of $FeNCS^{2+}$ from iron(III) impurities (principally present in concentrated perchloric acid) *via* the reactions

$$\mathrm{Fe^{3+}} \rightleftarrows \mathrm{FeOH^{2+} + H^+} \quad K_h$$

$$\begin{tikzcd} \mathrm{Fe^{3+} + SCN^-} \arrow[r, shift left, "k_1"] & \mathrm{FeNCS^+} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "-\mathrm{H^+}\quad K_a"] \\ \mathrm{FeOH^{2+} + SCN^-} \arrow[r, shift left, "k_2"] & \mathrm{Fe(OH)NCS^+} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left, "\mathrm{H^+}"] \end{tikzcd} \qquad (A)$$

For future comparison we note that the data obtained at 25° and ionic strength 4 *M* (H^+, Na^+, Mn^{2+}, ClO_4^-) conform to the rate law d ln [$FeNCS^{2+}$]/dt = ($k_1 + k_2K_h$/[H^+])[SCN^-] + $k_{-1} + k_{-2}K_a$/[H^+], corresponding to scheme A in the range [H^+] = 0.25–3.00 *M*. The values of the parameters are k_1 = (1.18 ± 0.08) × $10^2\ M^{-1}\ \text{sec}^{-1}$, k_2K_h = (0.14 ± 0.04) sec^{-1}, k_{-1} = (0.66 ± 0.06) sec^{-1}, and $k_{-2}K_a$ = (0.19 ± 0.02) *M* sec^{-1}. These values compare favorably with previous data at ionic strength 3 *M*.[14] It is interesting to observe that the retardation in rate of complexation with increasing [Mn(II)] is evidently due to the rapid preequilibration of SCN^- as *inert* $MnNCS^+$ *via* eq 5. If $FeNCS^{2+}$ is principally formed by attack at the nitrogen atom of NCS^- [14] this would imply that the manganese(II) complex is correctly formulated in eq 5, *i.e.*, with an Mn–N bond, consistent with the conclusion that Mn^{2+}_{aq} is a hard center.[15]

[14] T. J. Conocchioli and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 282 (1967), and references therein.

[15] See, *e.g.*, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 25ff.

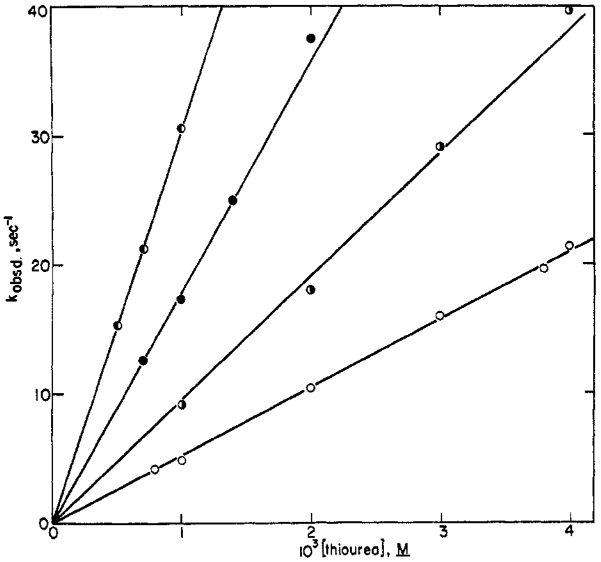

Figure 1.—Plots of k_{obsd} (sec^{-1}) *vs.* [thiourea] for the reaction with thiourea at $[H^+] = 1.85$ *M*, ionic strength 4.0 *M*, and the following temperatures: ○, 1.35; ◑, 8.25; ●, 16.4; ◐, 24.6°.

An example of linear plots of k_{obsd} (sec^{-1}) *vs.* [thiourea] at various temperatures is shown in Figure 1. Similar plots under all reaction conditions indicate a rate law of the form

$$\frac{-d[Mn(III)]}{dt} = k_{obsd}[Mn(III)][thiourea] \qquad (6)$$

for each reaction. The second-order rate constants k_{obsd} (M^{-1} sec^{-1}) were found to be independent of variations of [Mn(III)], [Mn(II)], [thiourea], [O_2], and wavelength of measurement at constant temperature and acidity at ionic strength 4.0 *M*. Extinction coefficients of manganese(III) obtained by extrapolation of plots to $t = 0$ were similar to those obtained in the absence of reductant.

Estimates of k_{obsd} for reaction with the four thiourea reductants at various acidities and temperatures are collected in Table I.

Mechanism

The following mechanism is consistent with the experimental observations.

$$Mn^{3+} \rightleftharpoons MnOH^{2+} + H^+ \quad K_h \qquad (7)$$

$$TH^+ \rightleftharpoons T + H^+ \quad K_a \qquad (8)$$

$$Mn^{3+} + TH^+ \xrightarrow{k_1} Mn^{2+} + X + 2H^+ \qquad (9)$$

$$MnOH^{2+} + TH^+ \xrightarrow{k_2} Mn^{2+} + X + H^+ \qquad (10)$$

$$Mn^{3+} + T \xrightarrow{k_3} Mn^{2+} + X + H^+ \qquad (11)$$

$$MnOH^{2+} + T \xrightarrow{k_4} Mn^{2+} + X \qquad (12)$$

$$2X \xrightarrow{\text{fast}} X_2 \qquad (13)$$

In these equations T and TH^+ are unprotonated and monoprotonated thiourea molecules, X is the radical produced by oxidation (state of protonation not known), and X_2 is the disulfide product formed in the rapid dimerization reaction 13. For this mechanism the empirical rate law (6) obtains, with

$$k_{obsd} = \frac{k_1[H^+] + k_2K_h + k_3K_a + k_4K_aK_h/[H^+]}{([H^+] + K_h)(1 + K_a/[H^+])} \qquad (14)$$

TABLE I

KINETIC DATA FOR REACTION WITH THIOUREAS IN PERCHLORATE MEDIA AT IONIC STRENGTH 4.0 $M^{a,b}$

$[H^+]$	Temp, °C	10^{-4} k_{obsd}^c	$[H^+]$	Temp, °C	10^{-4} k_{obsd}^c
		(a) Thiourea[d]			
0.250	0.4	0.675	1.85	1.35	0.620
	9.0	1.12		8.25	0.964
	15.7	1.95		16.4	1.80
	25.0	3.10		24.6	2.95
0.500	2.5	0.583	3.00	1.35	0.580
	9.8	1.18		8.25	0.870
	19.7	2.25		16.4	1.42
	25.3	3.20		25.0	2.33
1.00	1.1	0.570	3.70	0.3	0.131
	11.7	1.31		10.55	0.330
	19.6	2.01		23.9	0.645
1.50	1.1	0.600			
	11.7	1.28			
	16.4	1.76			
	25.3	3.10			
		(b) *N,N'*-Dimethylthiourea[e]			
0.250	−0.7	0.453	1.85	0.20	0.295
	9.2	0.840		9.25	0.370
	19.0	1.47		21.1	0.620
	25.0	2.05	3.00	−0.7	0.200
0.500	1.6	0.525		9.25	0.288
	9.6	0.770		19.2	0.405
	19.2	1.38		25.0	0.490
	25.0	1.82	3.70	1.95	0.091
1.00	−0.4	0.560		9.85	0.199
	10.05	0.710		21.6	0.430
	21.6	0.910		25.3	0.610
	25.0	0.97			
		(c) *N,N'*-Diethylthiourea[f]			
0.250	−0.3	0.535	2.50	−0.7	0.132
	9.25	0.930		9.7	0.283
	19.5	1.43		20.0	0.570
	25.0	1.97		25.0	0.790
0.500	2.1	0.450	3.00	2.1	0.125
	9.05	0.670		9.05	0.218
	19.3	1.24		19.3	0.485
	25.0	1.76		24.6	0.680
1.00	2.1	0.276	3.70	2.3	0.0605
	11.15	0.560		11.4	0.137
	19.3	0.951		24.0	0.328
1.85	−0.7	0.173			
	9.7	0.325			
	24.0	0.915			
		(d) *N,N'*-Ethylenethiourea[g]			
0.250	0.3	0.583	1.85	−0.4	0.468
	6.75	1.02		9.75	0.980
	11.8	1.84		21.6	2.02
	19.9	3.75	3.00	−1.3	0.330
0.500	−0.4	0.603		6.75	0.541
	10.0	1.69		18.0	1.14
	18.05	4.02		25.3	1.81
0.750	−1.3	0.538	3.70	1.6	0.328
	8.95	1.45		9.4	0.460
	20.6	3.16		21.6	0.825
1.00	0.2	0.81			
	9.5	1.28			
	20.6	2.73			
	25.0	3.50			

[a] All concentrations are molar; $[Mn(III)]_0 = (0.54\text{–}3.36) \times 10^{-4}$ *M*. [b] Ionic strength adjusted with $NaClO_4$ and/or Mn(II). [c] Units are M^{-1} sec^{-1}. [d] [Thiourea] in the range $(0.50-4.02) \times 10^{-3}$ *M*. [e] [Dimethylthiourea] in the range $(0.51\text{–}4.08) \times 10^{-3}$ *M*. [f] [Diethylthiourea] in the range $(0.48\text{–}3.84) \times 10^{-3}$ *M*. [g] [Ethylenethiourea] in the range $(0.48\text{–}3.84) \times 10^{-3}$ *M*.

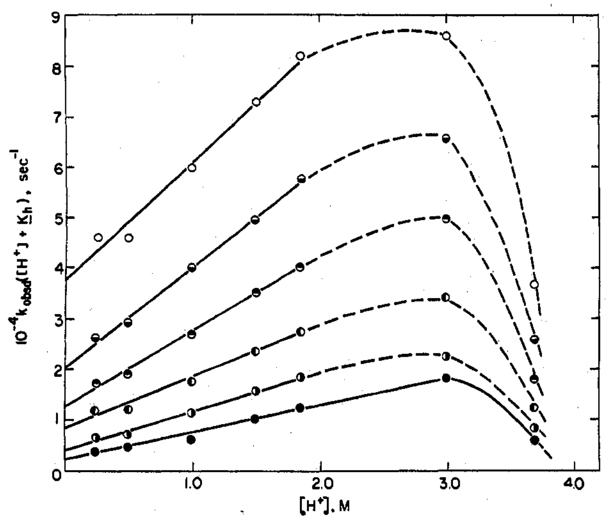

Figure 2.—Plots of $k_{obsd}([H^+] + K_h)$ *vs.* $[H^+]$ for reaction with thiourea at ionic strength 4.0 *M* and the following temperatures[16]: ●, 0; ◑, 5.0; ◐, 10.0; ◓, 15.0; ◒, 20.0°; ○, 25.0°.

Two limiting cases of this equation will be of interest, since they have also been observed in other reactions of manganese(III):[8] (a) if $K_a(k_3 + k_4K_h/[H^+]) << k_1 \cdot [H^+] + k_2K_h$ and $1 >> K_a/[H^+]$, then

$$k_{obsd} = \frac{k_1[H^+] + k_2K_h}{[H^+] + K_h} \qquad (14a)$$

and

$$k_{obsd}([H^+] + K_h) = k_1[H^+] + k_2K_h$$

(b) if $k_2K_h \gg k_1[H^+]$ in eq 14a, then

$$k_{obsd} = \frac{k_2K_h}{[H^+] + K_h} \qquad (14b)$$

and

$$1/k_{obsd} = [H^+]/k_2K_h + 1/k_2$$

The above assumptions will be tested as the kinetic data are analyzed. For this mechanism the establishment of limiting forms 14a and 14b at any particular temperature is seen to be largely dependent on the magnitude of K_a, which is only available for thiourea ($K_a \simeq 10^{-2}$ *M* at 25°).[9] However, with this order of magnitude for K_a, the implicit assumption is obviously that the rate constants k_3 and k_4 are not very much larger than k_1 and k_2, although, of course, they could be of similar magnitude or even smaller (see below). We now turn to the results obtained for the individual thioureas.

(A) **Thiourea.**—Plots of eq 14a are shown in Figure 2 at various (interpolated) temperatures[16] for reaction with thiourea, using values of K_h calculated from literature data.[8] Linear plots are obtained at all temperatures for acid concentrations less than about 2 *M*, but the rates at higher acidities are lower than anticipated. For example, the rate of reaction at 20° is a factor of about 3 lower at $[H^+] = 3.70$ *M* than that expected from the results at lower acidity. Since the decomposition of thioureas by perchloric acid is too slow to account for these deviations, and kinetic medium effects of this magnitude seem very unlikely, it is reasonable to suppose that further protonation of the thiourea occurs at high acidity, producing species which react at lower rates with manganese(III).

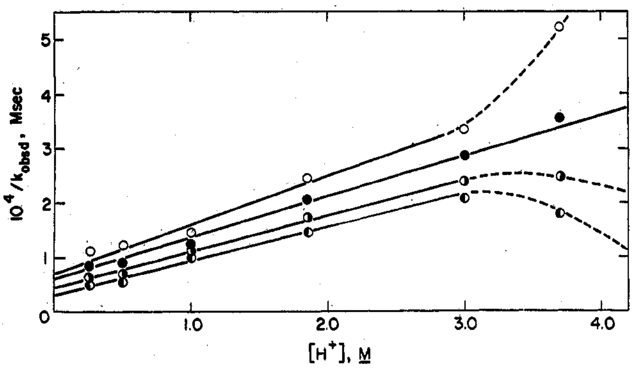

Figure 3.—Plots of $1/k_{obsd}$ *vs.* $[H^+]$ for reaction with *N,N'*-dimethylthiourea at ionic strength 4.0 *M* at the following temptures[16]: ○, 10.0; ●, 15.0; ◑, 20.0; ◐, 25.0°.

According to eq 14a the slopes and intercepts of the linear portions of Figure 2 give k_1 and k_2K_H, respectively, at the various temperatures.

The neglect of steps 11 and 12 in the mechanism and the corresponding assumptions in deriving eq 14a may now be critically examined. If we assume that

$$k_1[H^+] + k_2K_h \gtrsim 10k_4K_aK_h/[H^+] \qquad (15)$$

at the lowest experimental acid concentration ($[H^+] = 0.25$ *M*) in eq 14, then with $K_a = 10^{-2}$ *M* and $K_h \approx 1$ *M*, it follows that $k_4 \lesssim 4 \times 10^5$ M^{-1} sec^{-1} at 25°. It has been found in a number of faster reactions of manganese(III) that $k_3 \lesssim k_4$ in steps corresponding to (11) and (12) (Table II). Thus it is likely that $k_3 \lesssim 4 \times 10^5$ M^{-1} sec^{-1} at 25°, justifying the assumption that the intercepts of plots of eq 14a for the data for thiourea are essentially k_2K_h, as substantiated by linear Arrhenius plots for these parameters. The extension of this analysis to the results for the other thioureas also appears to be consistent with the above assumptions (see Discussion section). The kinetic parameters derived for thiourea on this basis are collected in Table II.

(B) ***N,N'*-Dimethylthiourea.**—The acid dependence of the kinetic data for oxidation of *N,N'*-dimethylthiourea is more complicated than are those for the other reductants. Since application of eq 14 requires a knowledge of K_a, which is not available, limiting forms 14a and 14b were first applied to the data. At temperatures above *ca.* 10° linear plots of $1/k_{obsd}$ *vs.* $[H^+]$ are obtained for $[H^+] \leq 3.0$ *M* (Figure 3). It is interesting to note opposite effects of high acidity on the rate at low (rate too low at 0°) and high temperatures. At each temperature values of k_2 and the product k_2K_h may be derived from the intercept and slope, respectively, of the linear portions of the plots and the ratio of intercept/slope may be compared with the value of K_h measured independently.[8] For example the ratio intercept/slope is (0.6 ± 0.2) *M* at 20°, close to a direct estimate[8] of $K_h = (0.81 \pm 0.03)$ *M* at this temperature. Values of k_2 and the activation parameters for reaction 10 with *N,N'*-dimethylthiourea are collected in Table II.

Although approximate linearity is observed in plots

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[16] For all the reductants the Arrhenius plots are sufficiently linear to allow accurate interpolation of data so that plots of eq 14a-14b may be made at constant temperature.[11]

TABLE II

KINETIC PARAMETERS FOR REACTIONS OF MANGANESE(III) IN PERCHLORATE MEDIA AT IONIC STRENGTH 4 M^a

Reductant	$10^{-4}k_1{}^b$	$10^{-4}k_2{}^b$	$\Delta H_1^{\ddagger c}$	$\Delta S_1^{\ddagger d}$	$\Delta H_2^{\ddagger c}$	$\Delta S_2^{\ddagger d}$
$NH_3NH_2^+$	$\lesssim 0.05$	1.03				
$CH_3NH_2NH_2^+$	$\lesssim 0.008$	0.30				
$(CH_3)_2NHNH_2^+$	$\lesssim 0.01$	0.40				
$(CH_3)NH_2NHCH_3^+$	$\lesssim 0.004$	0.073				
$(CH_3)_2NHNHCH_3^+$	$\lesssim 0.002$	0.053				
$(CH_3)_2NHN(CH_3)_2^+$	0.028	≈ 0.003				
NH_3OH^+	0.14	0.31				
$NH_3OCH_3^+$	0.00006	0.0006				
$(NH_2)_2CSH^+$	2.6 ± 0.13	3.6 ± 0.18	9.1 ± 0.2	−6 ± 2	10.9 ± 0.2	0.4 ± 2
$(CH_3NH)_2CSH^+$	$\lesssim 0.16$	3.25 ± 0.20			10.3 ± 0.2	−1.4 ± 1.1
$(EtNH)_2CSH^+$	$\lesssim 0.06$	2.3 ± 0.15			6.6 ± 0.3	−10.6 ± 1.3
$(CH_2NH)_2CSH^+$	$\lesssim 0.2$	8.3 ± 0.4			9.5 ± 0.3	2.3 ± 1.3
H_2O_2	7.3	3.2				
HNO_2	2.2	4.9				
p-$C_6H_4(OH)_2$	0.48	3.3				

[a] Data from this work and ref 8. [b] Units are M^{-1} sec^{-1} at 25.0°. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25.0°.

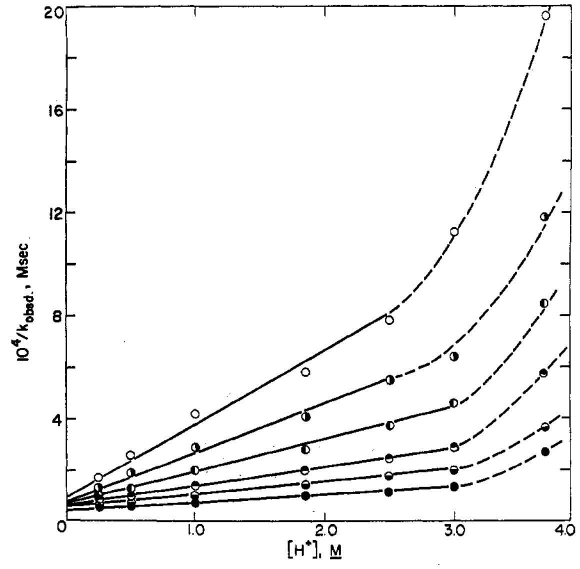


Figure 4.—Plots of $1/k_{obsd}$ *vs.* [H^+] for reaction with *N,N'*-diethylthiourea at ionic strength 4.0 *M* at the following temperatures[16]: ○, 0; ◑, 5.0; ◐, 10.0; ◓, 15.0; ◒, 20.0; ●, 25.0°.

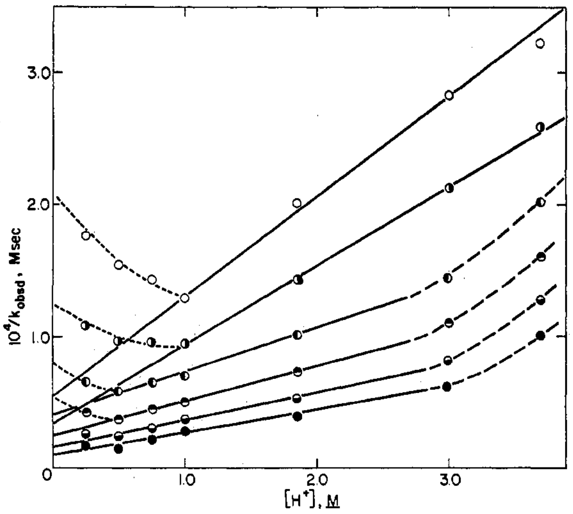


Figure 5.—Plots of $1/k_{obsd}$ *vs.* [H^+] for reaction with *N,N'*-ethylenethiourea at ionic strength 4.0 *M* and the following temperatures[16]: ○, 0.0; ◑, 5.0; ◐, 10.0; ◓, 15.0; ◒, 20.0; ●, 25.0°.

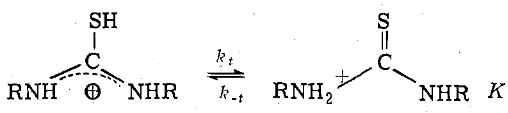
of eq 14a for [H^+] ≤ 1.0 *M* in the temperature range 0–10° deviations of even greater magnitude than that found for thiourea (Figure 2) are apparent in the reaction with *N,N'*-dimethylthiourea at higher acidities. For example, the rate of the reaction in 3.70 *M* acid at 0° is about ten times slower than that predicted from the data at lower acidity ([H^+] ≤ 1.0 *M*). This suggests that deprotonation of *N,N'*-dimethylthiourea occurs at low temperatures and acidities resulting in a large rate increase. The analysis of this data is not straightforward in the absence of values for K_a, however (*vide supra*), and no rate parameters for reactions like (11) and (12) can be unequivocally assigned. Rate parameters applicable to conditions with temperatures in excess of *ca.* 10° and [H^+] ≤ 3.0 *M* are collected in Table II.

(C) ***N,N'*-Diethylthiourea.**—The kinetic data for the manganese(III) oxidation of *N,N'*-diethylthiourea are consistent with eq 14b for [H^+] ≤ 3.0 *M* at temperatures in the range 0–25° (Figure 4). At [H^+] = 3.70 *M* the rates are lower than expected, with the rate at 25° being only about 70% of the rate anticipated from the results at the lower acidities; this retardation is similar in magnitude to that observed in the manganese(III) oxidation of *O*-methylhydroxylamine under comparable conditions,[8] and is likely due to increased protonation of the molecule at higher acidities. Plots of eq 14b give values of K_h = intercept/slope which compare favorably with those measured directly (*vide supra* and reference 8). Kinetic parameters at [H^+] ≤ 3.0 *M* are collected in Table II.

(D) ***N,N'*-Ethylenethiourea.**—Plots of $1/k_{obsd}$ *vs.* [H^+] (eq 14b) for the data obtained in the reaction with *N,N'*-ethylenethiourea are linear under certain conditions (Figure 5). Rates which are lower than anticipated are observed under conditions of low acidity and low temperature, and higher temperature and [H^+] ≥ 3.0 *M*, respectively. Although the latter effect could be due to increased protonation, as found for the dimethyl- and diethylthioureas, the retardation of rate at low acidity is opposite to that anticipated from deprotonation of the reductant (see Discussion section). The parameters derived from experiments under which eq 14b appears satisfactory are collected in Table II.

Discussion

The common second-order rate law observed in the manganese(III) oxidations of thiourea and its symmetrical dialkyl derivatives is of the same form as those for the corresponding reactions with cobalt(III)[7] and cerium(IV).[6] In each case, a first-order dependence of the rate on the concentrations of both oxidant and thiourea is consistent with negligible stoichiometric concentrations of complexes between the reactants and a lack of tautomeric kinetic control[17] such as that in the equilibria



III IV (16)

The data are thus consistent with the very rapid establishment of proton equilibria such as (7) and (8) and tautomeric equilibria like (16), if the thioureas actually exist in enol (III) and/or keto (IV) forms in solution.[10]

As pointed out earlier, the assignment of a complete mechanism through equations such as (14) requires a knowledge of K_a, which has only been estimated for the parent thiourea molecule. In any event, derived rate constants will refer to reactions of either or both tautomers in eq 16.

A knowledge of the magnitude of K_a for thiourea itself[9] and the observation that eq 14a accounts reasonably well for the kinetic data for reactions of this species (*vide supra*) suggest that the rate parameters for thiourea may be used as a basis for the discussion of the reactions of the alkyl derivatives.

The rate constants for reactions of $Mn^{3+}{}_{aq}$ and $MnOH^{2+}{}_{aq}$ with monoprotonated thiourea are similar to those of complexation of manganese(III) by *neutral* HF[18] and to the rate constants for their redox reactions with *neutral* H_2O_2, HNO_2, and hydroquinone (Table II). In addition, the upper limits of rate constants for reactions of $Mn^{3+}{}_{aq}$ and $MnOH^{2+}{}_{aq}$ with unprotonated thiourea molecules (and presumably the unprotonated alkylthioureas) are evidently not too different from those for the monoprotonated species. The small range of rate constants for reactions of $MnOH^{2+}{}_{aq}$ with the monoprotonated thioureas is analogous to that found in the corresponding substitution-controlled redox reactions of $CoOH^{2+}{}_{aq}$,[7,19] and contrasts sharply with the much larger range of rates with cerium(IV) as oxidant in 0.5 M sulfuric acid.[6] These observations indicate that the reactions of thioureas with manganese(III) are essentially controlled by substitution at the oxidant center in an overall inner-sphere process.[8,19] Thus if $k_{el} > k_{-o}$ in the scheme[19]

$$\mathrm{Mn(III)} + \mathrm{B} \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} (\mathrm{Mn(III),B}) \quad K_o \tag{17}$$

$$(\mathrm{Mn(III),B}) \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} (\mathrm{Mn(III)B}) + H_2O \tag{18}$$

$$\downarrow k_{el}$$

$$\text{products}$$

then $k_{obsd} = K_o k_o$ and the rate will be limited by the rate of conversion of the ion pair (Mn(III),B) into the inner-sphere complex (Mn(III)B). A substitution-controlled model extends to the observed activation parameters, *e.g.*

$$\Delta H^{\ddagger}{}_{obsd} = \Delta H_o{}^{\ddagger} + \Delta H_o \tag{19}$$

where $\Delta H_o{}^{\ddagger}$ and ΔH_o are the enthalpies of activation and ion-pair association, respectively.

Although the application of a simple electrostatic model[20] for estimation of the parameters of ion-pair association is certainly open to question at high ionic strengths, the results for substitution-controlled reactions of $CoOH^{2+}{}_{aq}$ at ionic strength 3 M are reasonably consistent with its predictions.[1] We note, however, that the similar rate constants at 25° for reactions of $MnOH^{2+}{}_{aq}$ with the thioureas are the result of small compensating enthalpic and entropic variations which are evidently related to the properties of the reductant in the overall complexation process. Solvational changes in an aqueous medium are likely to be cooperative in both ion pair formation and activation and these may be the source of the observed effects.[21] Inspection of the activation parameters of substitution-controlled $CoOH^{2+}{}_{aq}$ reactions[1,19] suggests that small or slightly negative entropies of activation might be expected in the analogous reactions of $MnOH^{2+}{}_{aq}$ with monoprotonated thiourea molecules, as observed.

Another indication that the rate parameters are sensitive to the formal charge on the reductant is provided by the observation of complicated acid dependences in the reactions with the thioureas. Increasing protonation evidently leads to a decrease in rate, except in the case of ethylenethiourea, where the rate of reaction with the unprotonated reductant species appears to be lower than that with the monoprotonated form. Both charge and steric effects are obviously important in determining rates of substitution at the manganese(III) center, and the fact that the terminal nitrogen atoms in ethylenethiourea are linked through an ethylene bridge may impose quite different steric or solvational restrictions as compared to the thioureas with "free" terminal nitrogen atoms if coordination through unprotonated nitrogen atoms is the rate-determining process.

Alkylation of the nitrogen atoms in thiourea has such a marked effect on the rates of reaction with $Mn^{3+}{}_{aq}$ that only upper limits for the rate constants may be derived. Coordination through nitrogen atoms is evidently important in both the thiourea series and in the corresponding reactions of monoprotonated hydrazines,[22] where the reaction with $MnOH^{2+}{}_{aq}$ is also the only detectable reaction pathway. The general sensitivity of the $Mn^{3+}{}_{aq}$ center to the nature of potential coordination sites in hydrazines,[22] hydroxylamines,[23] and thioureas suggests that H atom transfer provides an energetically favorable route in oxidation reactions of $MnOH^{2+}{}_{aq}$.[8] The smaller kinetic effects of blocking of the nitrogen atoms in thioureas as compared to the large general rate decrease observed with hydrazines may be due to preferred attachment of $MnOH^{2+}{}_{aq}$ at the sulfur atom of the enol form of the reductant.

An outer-sphere mechanism is possible for all these reactions but, as we have seen, the available evidence has many of the features expected of a substitution-controlled inner-sphere process. More extensive data for complexation reactions of manganese(III) would obviously be useful in testing this hypothesis further as

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(17) See, *e.g.*, M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, **93**, 2878 (1971).

(18) H. Diebler, *Z. Phys. Chem.*, **68**, 64 (1969).

(19) G. Davies and B. Warnqvist, *Coord. Chem. Rev.*, **5**, 349 (1970).

(20) M. Eigen, *Z. Phys. Chem.*, **1**, 176 (1954); R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(21) G. Davies, to be published.

(22) G. Davies and K. Kustin, *J. Phys. Chem.*, **73**, 2448 (1969).

(23) G. Davies and K. Kustin, *Inorg. Chem.*, **8**, 484 (1969).

would activation parameters for the other reactions with an apparent substitution-controlled mechanism.

It is possible that the rapid manganese(III) oxidation of thiocyanate is also substitution controlled, as found in the analogous reaction with cobalt(III).[5] If the trends observed in complexation reactions of Fe$^{3+}{}_{aq}$[14,15,24] and substitution-controlled redox reactions of Co$^{3+}{}_{aq}$[5,19] are maintained in the manganese(III) series then the rate of the Mn$^{3+}{}_{aq}$–SCN$^-$ reaction might be expected to be somewhat higher than those for complexation by Br$^-$ and Cl$^-$, the rate constants of which are presumably at least 10^6 M^{-1} sec^{-1} at 25°.[8]

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Kinetics and Mechanism of the Reaction between Vanadium(II) and Chromium(VI)

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The rate of oxidation of V(II) with Cr(VI) to form V(III) in perchloric acid solution was studied at 10°, primarily under second-order conditions and with V(II) in excess. The observed rate law for the reaction in 1.00 M NaClO$_4$ is $-d[\mathrm{Cr(VI)}]/dt = (k_1 + k_2[\mathrm{H}^+] + k_3[\mathrm{V(II)}])[\mathrm{HCrO_4}^-][\mathrm{V(II)}]$ where $k_1 = (1.02 \pm 0.01) \times 10^5$ M^{-1} sec^{-1}, $k_2 = (7.9 \pm 0.26) \times 10^4$ M^{-2} sec^{-1}, and $k_3 = (1.27 \pm 0.09) \times 10^7$ M^{-2} sec^{-1}. The first step in the reaction results in the direct formation of V(III) by means of a one-electron redox process. Evidence is presented for the absence of the direct formation of vanadium(IV) under the conditions of these experiments. A mechanism is proposed based on the observed rate law.

Introduction

The net reaction between chromium(VI) and vanadium(II) in acid solution when V(II) is in excess can be represented by the equation

$$3\mathrm{V}^{2+} + \mathrm{Cr(VI)} = 3\mathrm{V}^{3+} + \mathrm{Cr}^{3+} \qquad (1)$$

Since it is highly improbable that the mechanism involves a single three-electron transfer step, the reaction must occur in a sequence of steps involving either one-electron processes or a combination of one- and two-electron processes.

The vanadium(II)–chromium(VI) reaction appears to be particularly interesting because V(II) can undergo both one- and two-electron oxidation in aqueous acidic solutions. Previous studies[1] have indicated that whether one- or two-electron transfer occurs may be directly related to oxygen atom transfer. Since V(IV) is an oxo species, there exists the possibility of doing tracer studies[2] to show the origin of the oxygen in the complex when V(IV) is a product of the overall oxidation reaction.

Although Luther and Rutter[3] refer to the oxidation of V(II) by Cr(VI) and have established that the reaction induces the oxidation of iodide ion, no kinetic studies on this very rapid reaction have been published. The objectives of this research were the elucidation of those features of the Cr(VI)–V(II) reaction mechanism that were discernible from the stoichiometry and the form of the rate law and a direct comparison with the corresponding Cr(VI)–V(III) and Cr(VI)–V(IV) reactions.[4]

Experimental Section

Reagents.—Sodium chromate solutions were prepared from Baker's Analyzed reagent grade Na$_2$CrO$_4$·4H$_2$O without further purification. The Cr(VI) concentration was determined with standard Fe(II).

Oxovanadium(IV) perchlorate solutions were prepared by electrolytic reduction of V$_2$O$_5$ suspensions at platinum wire electrodes.[5] Certified reagent grade vanadium pentaoxide was purchased from Fischer Scientific Co. Failure to give an iodine test[6] when V(IV) was shaken with either KIO$_3$ or KI in CCl$_4$ was taken as evidence that the concentration of either V(III) or V(V), respectively, was less than 10^{-4} M.[7] Oxovanadium(IV) solutions were standardized by titration with KMnO$_4$. Vanadium(II) perchlorate solutions were prepared by reducing measured aliquots of standard V(IV) in HClO$_4$ on a Jones reductor. The reduced vanadium solution was delivered into a volumetric flask under a N$_2$ atmosphere. The N$_2$ was freed of O$_2$ by passing tank nitrogen through two columns of Cr(II) solution. Vanadium(II) solutions were prepared just prior to their use. Vanadium(III) perchlorate solutions were prepared by reacting equimolar amounts of V(II) and V(IV) in a volumetric flask. Syringes calibrated[8] to deliver volumes reproducible to better than ±0.5% were used to make certain that equimolar amounts were used. These solutions were allowed to stand under an atmosphere of deoxygenated N$_2$ for at least 30 min to ensure complete reaction.[9]

The acid concentration of the vanadium solutions was determined from the acid concentration of the original V(IV) stock solution. An aliquot of V(IV) was placed on a column of the acid form of Dowex 50W-X12 cation-exchange resin and the eluent was titrated with standard base. The difference between the total hydrogen ion concentration and the equivalent concentration of the VO^{2+} species was taken to be the hydrogen ion concentration.

Chromium(III) solutions were prepared from hexaaquochromium(III) perchlorate which had been recrystallized three times from dilute HClO$_4$ solution. When the ratio of the absorbance at 230 nm to the absorbance at 260 nm reached a minimum

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(1) (a) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962); (b) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966); (c) M. G. Ondrus and G. Gordon, *ibid.*, **10**, 474 (1971).

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