differs from the steric course of aquation of *trans*-$[Co(en)_2Cl_2]^+$ which gives 65% *trans*- and 35% *cis*-$[Co(en)_2ClOH_2]^{2+}$.[25] The respective activation energies for the two reactions are 26.0 and 26.7 kcal/mole[26] and the rate difference therefore resides substantially in the entropy term.

The relative rates of aquation of the α- and β-dichloro isomers might also be considered in conjunction with the rates for the series *cis*-$[Co(NH_3)_4Cl_2]^+$, *cis*-$[Co(en)(NH_3)_2Cl_2]^+$, *cis*-$[Co(en)_2Cl_2]^+$, and $[Co(trien)Cl_2]^+$.[8] For this series the rates decreased with increasing chelation and it was argued[8] that the increase in size of the ion decreased the stability of the transition state because it became less efficiently solvated. Clearly the rate for the β isomer does not fit this pattern and it would seem that this explanation is not valid. Possibly the explanation offered earlier for the difference in reactivity of the α- and β-dichloro ions also applies for the rest of the series quoted, but there are not sufficient data available to check this proposition.

A similar pattern was observed for the aquations of the α- and β-$[Co(trien)ClOH_2]^{2+}$ ions by both the chloroaquo and the chlorohydroxo paths; both aquations occur largely with retention of configuration by the two paths. Of the two β-chloroaquo geometrical isomers, substantial data have been obtained only for the "slow" isomer. When this is compared with the results for the α-chloroaquo ion, it is apparent that the β isomer reacts about 5 times faster than the α form. For the chlorohydroxo paths however, the β isomer is more reactive than the α form by approximately a factor of 20.

The *trans*-$[Co(trien)ClOH_2]^{2+}$ ion isomerized stereospecifically to the "slow" β-$[Co(trien)ClOH_2]^{2+}$ ion and it has been shown elsewhere[3] that $(+)_{589}$-*trans*-$[Co(trien)ClOH_2]^{2+}$ generated from optically pure $(+)_{589}$-*trans*-$[Co(trien)Cl_2]^+$ isomerized to optically pure $(+)_{589}$-β-$[Co(trien)ClOH_2]^{2+}$. This rearrangement has not been studied in detail yet, but it seems likely that the rearrangement is independent of $[H^+]$ like that for the *trans*-$[Co(en)_2ClOH_2]^{2+}$ ion, and there is some interest to see if it occurs with each act of water exchange. These factors along with the isomerization and racemization of the diaquo species and the degree of retention in the aquation of the chloroaquo ions will be considered in subsequent publications.

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[25] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

[26] S. C. Chan, *Australian J. Chem.*, **20**, 595 (1967).

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Ligand Redox Studies. I. The Oxidation of Isothiocyanatopentaamminecobalt(III) Ion by Aqueous Hydrogen Peroxide[1]

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The oxidation of isothiocyanatopentaamminecobalt(III) ion, $(H_3N)_5CoNCS^{2+}$, by H_2O_2 in acidic solution yields Co^{2+}, $Co(NH_3)_6^{3+}$, HCN, CO_2, and HSO_4^- with an acid-dependent stoichiometry for the cobalt, carbon, and nitrogen products. The rate law is of the form $d[(H_3N)_5CoNCS^{2+}]/dt = k_2[H_2O_2][(H_3N)_5CoNCS^{2+}]$ with k_2 dependent on acidity and on buffer concentration in bisulfate–sulfate buffers. The principal feature of the mechanism deduced from these results is the existence of a partially oxidized intermediate which can undergo either an *intramolecular* redox reaction with the Co(III) center or an acid-dependent hydrolysis. The oxidation rate is somewhat slower than for the free thiocyanate ion and the acid-dependent path relatively less important.

Introduction

Werner carried out oxidation reactions on many thiocyanate complexes of cobalt(III).[3] His observation that the complex containing five ammonia and one thiocyanate ligands could be oxidized in acidic solution to hexaamminecobalt(III) ion by oxidants containing no nitrogen (*e.g.*, Cl_2, H_2O_2) established the *isothiocyanate* (N-bonded) nature of these complexes. All of Werner's observations, including some in which aquation (or other substitution reaction) occurred at the thiocyanate site, were qualitative in nature, and no subsequent quantitative studies have appeared on the oxidation of inert thiocyanate complexes.

In this paper we report the results of detailed kinetic and stoichiometric studies on the hydrolytic oxidation of isothiocyanatopentaamminecobalt(III) ion by hydrogen peroxide. Despite the complexities encountered, it has been possible to establish the main features of the mechanism which include the participation of Co(III) in an intramolecular redox step.

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[1] (a) Based in part on a thesis submitted by M. D. G. in partial fulfillment of the requirements for the degree of Master of Science in chemistry, Jan 1966; (b) supported in part by National Science Foundation research participation grants and in part by NSF-GP2664; (c) preliminary results presented at the 7th International Conference on Coordination Chemistry, Stockholm, 1962.

[2] To whom inquiries should be addressed.

[3] A. Werner, *Z. Anorg. Chem.*, **22**, 91 (1900); *Chem. Ber.*, **44**, 876 (1911); *Ann. Chem.*, **386**, 1 (1919).

Experimental Section

$[(H_3N)_5CoNCS](ClO_4)_2$ was prepared by the aqueous reaction at elevated temperatures (60–70°) of $(H_3N)_5CoOH_2^{3+}$ (as the perchlorate salt) with a moderate excess of SCN^- (as the sodium salt).[4] The initial product was recrystallized from dilute perchloric acid. The purity was routinely checked by making a quantitative comparison of the absorption spectra with a reference spectrum obtained from an analyzed sample.[5]

Commercially available reagent grade chemicals were used throughout with the exception of CP sodium thiosufate used in the peroxide analyses

Rate Measurements.—The extreme inertness of $(H_3N)_5CoNCS^{2+}$ ion to (thermal) aquation has been observed in several previous studies[6,7] and was qualitatively confirmed by experiments under reaction conditions used in the present study. (Using the rate parameters reported in ref 6, a half-life of about 40 days has been calculated for 65°.) The aquation is strongly catalyzed by light and by hydroxide ion, features which demand that stock solutions be slightly acidified (perchloric acid) and stored in the dark.

The concentration of $(H_3N)_5CoNCS^{2+}$ ion in the kinetic runs was followed by measuring the absorbancy of the solution at the 305-mμ absorption maximum using either a Beckman Model DU or Cary Model 14R spectrophotometer. At this wavelength the molar absorbancy index of the thiocyanatopentaamminecobalt(III) ion is about 50 times higher than any other reactant or product. Aliquots were removed, quenched at 0°, and kept cold until read in the spectrophotometer. Auxiliary absorbancy measurements at the 495-mμ maximum (with lower precision because of the absorbancy decrease is only about 50% at this wavelength) were used to confirm the 305-mμ results. In some cases the concentrations of Co^{2+} and H_2O_2 were followed during the reaction, the former by the method described in the next section and the peroxide by a standard iodometric method.[8] Temperatures were maintained within 0.05° by a Sargent Thermonitor apparatus during the portion of the runs used for kinetic purposes.

Stoichiometric Measurements.—The following analytical methods were used in the stoichiometric studies: (a) Co_{aq}^{2+} by a spectrophotometric method involving extraction of $Co(SCN)_4^{2-}$ into an organic medium,[9] (b) $Co(NH_3)_6^{3+}$ by direct measurement of the absorption spectrum ($a = 56\ M^{-1}\ cm^{-1}$ at λ_{max} 475 mμ), (c) sulfate gravimetrically as $BaSO_4$ after removal of cobalt cations by Dowex 50W-X8 resin (50 mesh) in NH_4^+ form, (d) NH_4^+ by the Kjeldahl method, (e) CO_2 by absorption in standard $Ba(OH)_2$ solution and back-titration with standard HCl, and (f) HCN by absorption in $AgNO_3$ solution and back-titration with standard NaCN solution.[10] The HCN and CO_2 analyses were performed in runs in which a stream of N_2 gas passed through the reaction solution and then through $AgNO_3$ and $Ba(OH)_2$ solutions (in that order).

Miscellaneous Material.—Stock solutions containing $(H_3N)_5CoNCS^{2+}$ in 0.001 M $HClO_4$ were stored in the dark and all experiments were conducted in subdued light to prevent complications arising from photochemical decomposition of the thiocyanato complex. (Control experiments in the dark showed that there were no observable effects at the level of illumination normally used.)

Stoichiometric Results

The stoichiometry of the reaction has proven to be rather complex and certain details remain unresolved. The stoichiometric results will be discussed in two parts: (1) the fate of the cobalt and (2) the fate of the thiocyanate.

Cobalt Products.—One of the most interesting features of the reaction is the formation of aquocobaltous ion as one of the reaction products. The stoichiometric results are given in Table I. Since the only cobalt products observed were Co_{aq}^{2+} and $Co(NH_3)_6^{3+}$ ions, the results are expressed in terms of mole fractions based on total cobalt present. Cases of poor material balance are ascribed to analytical errors in the Co(II) determination and to failure to correct for loss of solvent by evaporation. As can be seen from Table I, the amount of cobaltous ion formed is a function of temperature, acidity, and (possibly) total cobalt concentration but is not dependent on the concentration of hydrogen peroxide. A plot of log ($[Co(NH_3)_6^{3+}]/[Co^{2+}]$) *vs.* log $[H^+]$ at constant temperature (65°) shows the experimental points scattered about a line with a slope of unity.

TABLE I

STOICHIOMETRIC YIELDS OF COBALT PRODUCTS FOR REACTION OF $(H_3N)_5CoNCS^{2+}$ WITH H_2O_2 (TOTAL COBALT 2–5 × 10^{-3} M, EXCEPT AS NOTED)

Reaction conditions				Products	
Temp, °C	$[H^+]_0$, M ($HClO_4$)	$[H_2O_2]_0$,[d] M	No. of expts	$X_{Co^{2+}}$	$X_{CoA_6^{3+}}$
				Fraction of total cobalt[a]	
25	0.095	0.14	2	0.11	0.88
32	0.50	0.25	1	Trace	1.00
	0.037	0.05, 0.50	2	0.16	0.84
50	0.20	0.16	1	0.10	0.87
65	1.40	0.964, 0.16	2	0.02	0.95
	0.72	0.064	1	Trace	0.96
	0.70	0.02	2	. . .	0.90
	0.50	0.02	2	. . .	0.90
	0.20	0.016–0.16	3	0.17	0.83
	0.10	0.08–0.16	3	0.25	0.76
	0.08	0.02	2	0.56[c]	. . .
	0.07	0.004–0.032	3	0.24	0.77
	0.06	0.02	6	0.57[c]	. . .
	0.05	0.006–0.16	2	0.27	0.72
	0.04	0.02	2	0.65[c]	. . .
	0.027–0.017[b]	0.02	2	0.80[c]	. . .
	0.003–0.001[b]	0.006	2	0.86[c]	. . .
	0.01[e]	0.10	1	0.11	0.82
	10^{-4} [e]	0.10	1	0.55	0.45
95	10^{-5} [f]	0.5 to 2.0	9	0.82[g]	0.18[h]
97	0.10		1	0.51	0.45

[a] Average of number of runs indicated in fourth column. [b] Initial and final acidities shown. [c] Total cobalt 5 × 10^{-4} M, too dilute for spectrophotometric determination of $Co(NH_3)_6^{3+}$. [d] No dependence of cobalt stoichiometry on initial peroxide concentration was observed. [e] HSO_4^-–SO_4^{2-} buffer. [f] Acetic acid–acetate buffer. [g] ±0.02. [h] ±0.05.

It can also be seen from Table I that the qualitative effect of increasing the temperature is to *increase* the

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[4] Following the procedure given in the first reference in footnote 3, except that perchlorate was used in place of sulfate.

[5] This was usually done by calculation of the ratio of absorbancies at the maxima which occur at 305 mμ ($a = 1550\ M^{-1}\ cm^{-1}$) and 497 mμ ($a = 177.4\ M^{-1}\ cm^{-1}$). These values were obtained by Birute Miniatas in this laboratory and are considered more reliable than several values which have appeared in the literature: Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, 29 (1956); M. Linhard, H. Sibert, and M. Weigel, *Z. Anorg. Allgem. Chem.*, **278**, 287 (1955); W. C. Waggener, J. A. Mattern and G. H. Cartledge, *J. Am. Chem. Soc.*, **81**, 2958 (1959); J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964). The a_{max} values in these references cover the ranges: ultraviolet peak, 1500–1583; visible peak, 138–192 M^{-1} cm^{-1}.

[6] D. L. Gay and G. C. Lalor, *J. Chem. Soc., Sect. A*, 1179 (1966).

[7] A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954).

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 600.

[9] R. S. Young and A. J. Hall, *Ind. Eng. Chem., Anal. Ed.*, **18**, 264 (1946).

[10] See ref 8, p 546.

fraction of the cobalt going to Co^{2+} and that the presence of sulfate–bisulfate buffer results in a marked *decrease* in the amount of Co^{2+} formed compared to unbuffered solutions of similar acidity. A similar effect is indicated by the results at 95° with acetate buffers, but the comparison is more difficult to make here.

Thiocyanate Products.—The stoichiometry with respect to the nitrogen, carbon, and sulfur of the thiocyanate ligand is more complex than that of the cobalt and has not been completely elucidated. These stoichiometric complications are not unexpected in view of the observation by Wilson and Harris[11] that sulfur dicyanide, $S(CN)_2$, is formed in the peroxide oxidation of thiocyanate ion. The experimental results are shown in Table II.

Table II

Stoichiometry of Thiocyanate: Carbon, Nitrogen, and Sulfate Products

Conditions[a]			Products[b]				Material balance	
Temp, °C	$[HClO_4]$, M	$[H_2O_2]$, M	SO_4^{2-}	$Co(NH_3)_6^{3+}$	HCN	CO_2	ΣC[d]	ΣN[d]
25	0.095	0.14	1.046[c]	0.88	...	...	...	...
32	0.037	0.50	...	0.852	0.061	0.950	1.011	0.913
32	0.037	0.05	...	0.837	0.087	0.937	1.024	0.924
65	0.07	0.032	1.022	0.763	...	...	...	...
65	0.07	0.004	...	0.775	0.108	0.851	0.959	0.883
65	0.05	0.032	0.012	0.725	...	...	...	...

[a] Initial $[(H_3N)_5CoNCS^{2+}] \sim 0.004\ M$. [b] Expressed as moles of product per mole of complex oxidized. [c] Used acid form of cation resin instead of NH_4^+ form. [d] Should be unity if all of the thiocyanate is accounted for.

The following statements are consistent with the experimental results obtained.

(a) All of the sulfur is converted into sulfate. (b) Thiocyanate nitrogen is converted into at least three products: (1) the sixth ammonia ligand of the hexaamminecobalt(III) ion, (2) HCN, and (3) some as yet unidentified product(s) as indicated by the low material balance for nitrogen. (c) Thiocyanate carbon appears to be nearly quantitatively converted into a mixture of CO_2 and HCN, although the 65° result suggests that an additional carbon-containing product may be formed.

Some rather indecisive experiments (95°, pH 5 with acetate buffer) involving Kjeldahl ammonia determinations of reaction solutions fractionated by cation resin chromatography suggest that the "unidentified nitrogen product" may indeed by NH_4^+ (or another substance which is converted to NH_3 under Kjeldahl conditions).

The stoichiometric results at high acidity and low temperature conform well to the equation

$$(H_3N)_5Co^{III}NCS^{2+} + 4H_2O_2 \longrightarrow (H_3N)_5Co^{III}NH_3^{3+} + HSO_4^- + CO_2 + 2H_2O \quad (1)$$

At low acidity and high temperature one or more additional reactions also participate; the simplest possibility consistent with the data is

$$(H_3N)_5Co^{III}NCS^{2+} + 3H_2O \longrightarrow Co^{2+} + SO_4^{2-} + {}^1/_2HCN + {}^1/_2CO_2 + {}^{11}/_2NH_4^+ + H_2O + {}^3/_2H^+ \quad (2)$$

Kinetic Results

$(H_3N)_5CoNCS^{2+}$ Dependence.—More than 50 experiments were performed in which the $(H_3N)_5CoNCS^{2+}$ concentration (0.00003–0.001 M) was followed in the presence of a large excess (40–500-fold) of oxidant; first-order behavior was observed over at least 2 half-lives in all cases. Some additional experiments were carried out with $[(H_3N)_5CoNCS^{2+}] = 0.01\ M$ and $[H_2O_2] = 0.02–0.12\ M$; second-order rate constants calculated by the method described by Benson[12] were in fair agreement with those obtained from experiments with a large excess of oxidant.

H_2O_2 Dependence.—Two sets of experiments (one at 0.05 M H^+ and one at 0.50 M H^+) were performed with varying amounts of H_2O_2 (ten and fourfold ranges, respectively). Figure 1 is a plot of log (A/A_0) *vs.* time for some typical experiments in 0.50 M $HClO_4$ ($A = A_t - A_\infty$ and $A_0 = A_{\text{initial}} - A_\infty$). The linearity of the points establishes the first-order dependence on complex and the slopes are seen to be proportional to the concentration of hydrogen peroxide. A plot of log $[H_2O_2]$ *vs.* log k_1 values (k_1 = pseudo-first-order rate constant) obtained from such data by a least-squares treatment gave a slope of 1.10 in each case.

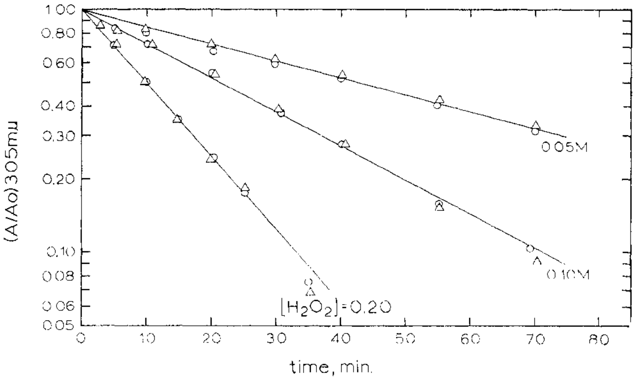

Figure 1.—First-order rate plots for the oxidation of $(H_3N)_5$-$CoNCS^{2+}$ ($5 \times 10^{-4}\ M$) by H_2O_2 at concentrations indicated. $[HClO_4] = 0.50\ M$; $\mu \cong 0.50$. Circles and triangles represent points from duplicate experiments. A and A_0 are defined in text.

Acid Dependence.—The results of twenty-two kinetic runs performed at $\mu = 0.50$ and initial $[(H_3N)_5$-$CoNCS^{2+}] = 0.0005\ M$ in unbuffered solutions over an acidity range of 0.01–0.50 M are shown in Table III. The results of several of these experiments are presented in Figure 2. Both the first-order dependence on complex and the nature of acid dependence are apparent. Calculated second-order rate constants (k_2) show a complicated dependence on acidity which suggests the presence of at least two terms in the rate law: an increase in rate as $[H^+]$ increases above 0.10 M and a possibly significant smaller increase at the lowest acidities used.

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(11) I. R. Wilson and G. M. Harris, *J. Am. Chem. Soc.*, **82**, 4515 (1960); **83**, 286 (1961).

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 17–20. A stoichiometric ratio of 3.5 H_2O_2 per Co(III) was assumed in the Benson procedure. This ratio is not known precisely and is a function of reaction conditions; however, trial calculations showed that the calculated value of k_2 is very insensitive to values of the stoichiometric ratio in the range 3.0–4.0.

TABLE III

SUMMARY OF KINETIC DATA IN UNBUFFERED SOLUTIONS[a]

No. of runs	$[H^+]$, M	$[H_2O_2]$, M	k_2, M^{-1} sec^{-1}
6	0.50	0.05–0.21	5.96 ± 0.50[b]
3	0.25	0.20	3.74 ± 0.25
2	0.10	0.20	2.38 ± 0.03
2	0.05	0.25	2.10 ± 0.08
2	0.025	0.25	2.03 ± 0.06
2	0.020	0.25	2.04 ± 0.03
2	0.015	0.25	2.10 ± 0.05
3	0.010	0.25	2.35 ± 0.13

[a] Unbuffered, $\mu = 0.50$; temperature 65°; $[(H_3N)_5CoNCS^{2+}]_0 \cong 5 \times 10^{-4}\ M$. [b] Average deviation from mean value.

TABLE IV

SUMMARY OF KINETIC DATA IN BUFFERED SOLUTIONS[a]

No. of runs	$[HSO_4^-]$, M	$[H^+]$, M	k_2, M^{-1} sec^{-1}
1	0.338	0.015	2.81
3	0.243–0.265	0.010	2.36 ± 0.10[b]
1	0.195	0.0075	2.06
1	0.180	0.0050	1.80
1	0.151	0.0050	1.93
2	0.131	0.004–0.010	1.80 ± 0.06
1	0.111	0.003	1.63
1	0.090	0.005	1.67

[a] Buffered, $\mu = 0.50$; temperature 65°; $[(H_3N)_5CoNCS^{2+}] \cong 5 \times 10^{-4}\ M$. [b] Average deviation from mean value.

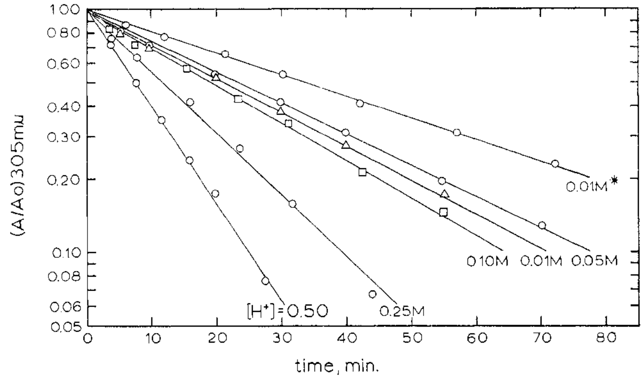

Figure 2.—First-order rate plots for the oxidation of $(H_3N)_5$-$CoNCS^{2+}$ ($5 \times 10^{-4}\ M$) at the acidities indicated. $[H_2O_2] = 0.25\ M$; $\mu = 0.50$ except for 0.01 M* for which $\mu = 0.012$. Data for three highest acidities have been recalculated from experiments in which $[H_2O_2] = 0.20\ M$ by assuming first-order dependence on H_2O_2. A and A_0 are defined in text.

Ionic Strength Dependence.—Information on the kinetic effects of the ionic strength of the medium can be obtained in two ways: from the rate variation with $[HClO_4]$ in the pH-independent region and from the effect of adding a large excess of $NaClO_4$. Each method is restricted to the low-acid region and each shows a relatively small dependence. *E.g.*, the first-order rate constant obtained from line 0.01 M ($\mu = 0.50$) in Figure 2 is only 60% greater than that obtained from line 0.01 M* ($\mu = 0.012$).

Buffer Dependence.—Results of several experiments similar to those described in the preceding paragraph but in solutions buffered with HSO_4^-–SO_4^{2-} are shown in Table IV. A graphical analysis of these results suggests a dependence on $[HSO_4^-]$ superimposed on an acid-independent path.

Rate Law.—The dependences on peroxide and complex concentrations are in good agreement with the rate law

$$-\frac{d[(H_3N)_5CoNCS^{2+}]}{dt} = k_2[H_2O_2][(H_3N)_5CoNCS^{2+}] \quad (3)$$

over a rather wide range of concentrations. The acid and buffer dependences are less definitely established.

Linear extrapolation of the k_2 values at higher acidity (0.05–0.50 M) to zero acidity and of the k_2 values from HSO_4^--containing solutions to $[HSO_4^-] = 0$ give nearly identical intercepts; this is taken to arise from a rate law term containing the first-power concentrations of H_2O_2 and complex only. The respective slopes can then be used to estimate rate constants for third-order terms containing H^+ and HSO_4^-. This approach leads to the rate law

$$-\frac{d[(H_3N)_5CoNCS^{2+}]}{dt} = (k + k'[H^+] + k''[HSO_4^-])[(H_3N)_5CoNCS^{2+}][H_2O_2] \quad (4)$$

At 65° and $\mu = 0.5$, $k = 1.3 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, $k' = 8.0 \times 10^{-3}\ M^{-2}\ \mathrm{sec}^{-1}$, and $k'' = 4.0 \times 10^{-3}\ M^{-2}\ \mathrm{sec}^{-1}$.

Rates calculated from eq 4 give good agreement with the experimental values except in the lower acidity unbuffered solutions, suggesting additional experimental or kinetic complications in this region. It is also observed that rates of reaction in the buffered solutions show no apparent dependence on SO_4^{2-} concentration; a dependence would have been expected if there were kinetic participation of an ion-pair species formed between SO_4^{2-} and $(H_3N)_5CoNCS^{2+}$. Additional evidence that ion pairing with sulfate is not kinetically significant is provided by the excellent first-order kinetic behavior despite the fact that sulfate is being produced during the reaction.

A few kinetic experiments have been carried out in the low-acidity region at 32 and 90° to obtain activation parameters; these data lead to the approximate values $\Delta H^* = 17.4$ kcal mole^{-1} and $\Delta S^* = -17$ cal mole^{-1} deg^{-1} for the acid-independent path (corresponding to the k term in eq 4).

Discussion

Comparison with Free SCN^-.—The oxidation of aqueous thiocyanate ion by hydrogen peroxide has been studied[11] from 20 to 50° in the range $1.3 > [H^+] > 10^{-12}\ M$. Table V summarizes the kinetic and stoichiometric results along with those of the present investigation.

For both free and captive thiocyanate, two-term rate laws are observed; the hydrogen ion dependent term is somewhat more important (by a factor of 5–10) for the free SCN^- ion. The autoinhibition effect seen with free thiocyanate (the k_a term) has not been observed in the oxidation of captive thiocyanate.

The qualitative effect of N coordination of the thiocyanate to cobalt(III) is seen to be a *decrease* in the rate by both reaction paths. The relatively small change in k suggests that the acid-independent paths may be rather similar for free and bound thiocyanate.

TABLE V

COMPARISON OF H_2O_2 OXIDATION OF SCN^- AND $(H_3N)_5CoNCS^{2+}$

	SCN^-	$(H_3N)_5CoNCS^{2+}$
Products		
High acid	HSO_4^-, HCN	HSO_4^-, $Co(NH_3)_6^{3+}$, CO_2
Low acid	SO_4^{2-}, HCO_3^-, NH_3	Above plus HCN and Co^{2+}
Rate Law		
Acid-dependent term	$k'(H_2O_2)^2(H^+)(SCN^-)/[(H_2O_2) + k_a(HCN)]$	$k'(H_2O_2)[(H_3N)_5CoNCS^{2+}](H^+)$
Acid-independent term	$k(H_2O_2)(SCN)^-$	$k(H_2O_2)[(H_3N)_5CoNCS^{2+}]$
Rate Parameters		
k', M^{-2} sec^{-1} (65°)	$(0.23)^a$	0.008
k, M^{-1} sec^{-1} (65°)	$(0.0062)^a$	0.0013
$\Delta H^{*\prime}$, kcal/mole	10.4	...
$\Delta S^{*\prime}$, eu	−32	...
ΔH^*, kcal/mole	14.9	17.4
ΔS^*, eu	−25	−17

[a] Extrapolated from the 20–50° range to 65°. The SCN^- results are from ref 11.

The much larger change in k', however, suggests the possibility of a significant change in mechanism for the acid-dependent path.

An interesting stoichiometric observation is the reversal in the nature of the carbon and nitrogen products in going from free to captive thiocyanate; this establishes the fact that the nature of the final products is controlled by reactions which occur *subsequent* to the rate-determining steps.

Kinetic Acid Dependence.—The acid-dependent term in the rate law could most reasonably arise from the rapid protonation of one of the reactants prior to the rate-determining step. The occurrence of an acid-dependent term in many oxidations by hydrogen peroxide has been considered in detail by Edwards,[13] who presents a convincing case for the view that the dependence arises from the participation of $H_3O_2^+$ in the rate-determining step. Although Wilson and Harris[11] did not suggest a mechanism for the acid dependence in the H_2O_2–SCN^- system, they did report that the rate of reaction was independent of the ionic strength (μ = 0.1–0.6). This latter observation is not consistent with a rate-determining reaction between charged species (*i.e.*, $H_3O_2^+$ and SCN^-). Support for participation of HSCN is provided by the recent report of Boughton and Keller[14] that HSCN has an acid dissociation constant of about 10^{-1}; if this value is correct, however, it is difficult to see why the kinetic data of Wilson and Harris (in the range 0.05–1.3 M H^+) would not have reflected the effect of a change in the predominant form of thiocyanate present. In any event, it seems improbable that thiocyanate bound to Co^{III} would retain sufficient proton affinity to merit giving serious consideration to $(H_3N)_5CoNCSH^{3+}$ as a participant in the oxidation of captive thiocyanate by hydrogen peroxide.

No simple explanation of the acid dependence appears possible which is consistent with all of the available data. Perhaps the best suggestion is that the acid dependence arises from different sources in the free and captive thiocyanate oxidations; namely, HSCN participates in the free ion case (but is a considerably stronger acid than reported[14]) and $H_3O_2^+$ in the captive thiocyanate oxidation. This explanation also readily accounts for the observation that the rate constant in the acid-dependent term (k') undergoes a much larger change than the acid-independent constant (k).

Cobalt(III) Participation.—A general scheme for the reaction of a ligand bound to cobalt(III) with an external oxidant, OX, is

$$Co^{III}L + OX \longrightarrow Co^{III}L' \tag{5}$$

$$Co^{III}L' + OX \longrightarrow Co^{III}\,L''(\text{or } Co^{III} + L'') \tag{6a}$$

$$Co^{III}L' \longrightarrow Co^{2+} + L'' \tag{6b}$$

$$Co^{III}L' \longrightarrow Co^{III}L_s' \tag{6c}$$

$$Co^{III}L' \longrightarrow Co^{III} + L' \tag{6d}$$

The primes indicate increasing extent of ligand oxidation. Reaction 5 represents the initial oxidation step(s) to produce a complex containing an oxidized form of the ligand (L′); if this complex is not a stable reaction product, it may undergo one or more additional reactions leading to the products in eq 6a–d. The reactions are: (6a), further reaction with OX; (6b), an intramolecular redox reaction involving participation of cobalt(III); (6c), a nonoxidative ligand change (*e.g.*, solvolysis) with retention of the Co^{III}–L bond and formation of a modified ligand L_s'; and (6d), a ligand-substitution process in which the Co–L bond is broken. Examples of several of these reaction types have been previously reported.[15–17]

The occurrence of an *intramolecular redox reaction* requires that reaction 6b compete favorably with the other possible reactions of the Co^{III}–L′ intermediate. In the present system, where Co^{III}–L is $(H_3N)_5Co$–NCS^{2+} and OX is H_2O_2, the stoichiometry is determined by the relative importance of reactions of the type represented by (6b) giving Co^{2+} and (6c) giving

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[13] J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience Publishers Inc., New York, N. Y., 1962, pp 67–106.

[14] J. H. Boughton and R. N. Keller, *J. Inorg. Nucl. Chem.*, **28**, 2851 (1966).

[15] For L = oxalate, reaction 6d or 6b depending on oxidant: P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

[16] L = formate, OX = MnO_4^-, reactions 6a and 6b concurrently: J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).

[17] L = I^-, OX = Ce^{IV}, *et al.*, reaction 6d followed by reaction of L′ with another Co^{III}L ion: A. Haim and H. Taube, *ibid.*, **85**, 495 (1963).

$Co(NH_3)_6^{3+}$, with no evidence for reactions 6a or 6d. The additional oxidation steps needed to obtain the final products are not involved in this competition as established by the lack of dependence of the stoichiometry on the concentration of added oxidant. One or both of these reactions involves an acidity dependence resulting in a net first-order dependence of the stoichiometry on acidity. In addition, there appears to be a stoichiometric (as well as kinetic) dependence on one or both of the buffer constituents. The stoichiometric observations allow one to calculate the ratio of the specific rate constants for reactions 6b and 6c if it is assumed that these reactions are both first order in the common intermediate Co^{III}–L′. This is possible because it is quite certain that neither Co^{2+} nor $Co(NH_3)_6^{3+}$ can undergo further reaction under the experimental conditions used. This approach leads to the relationship

$$(k_{6b}/k_{6c})_{65^\circ} = 25[H^+] \qquad (7)$$

Thus in 0.5 *M* acid, 92.5% of the original cobalt is converted to the Co^{III} hexaammine whereas at 0.01 *M* H^+ only 20% is. The increase in yield of Co^{2+} with increasing temperature indicates that the intramolecular redox reaction has a *larger* activation energy than the hydrolytic reaction.

It is not possible to draw any conclusions from the present results relevant to the electron equivalency of the redox steps, since there is no way to establish whether L′ in reaction 6b is an odd-electron or even-electron species.

Mechanism.—Wilson and Harris[11] have suggested a mechanism for the SCN^-–H_2O_2 reaction which combines electrophilic attack of H_2O_2 on sulfur (and carbon) with hydrolytic steps.

The present results support the suggestion that initial attack occurs at the sulfur atom.[18] The subsequent reactions are more rapid and therefore not susceptible to elucidation by the usual kinetic methods. The stoichiometric results, however, establish the presence of a competitive step somewhere in the reaction sequence as described in the previous section. This competitive step involves an acid dependence which is *not* related to that shown by the rate law.

Activation Parameters.—The activation parameters reported in Table III for the $(H_3N)_5CoNCS^{2+}$ oxidation are for the second-order path; they are rather similar to values reported previously for oxidation by hydrogen peroxide and other peroxo oxidants.[19,20]

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[18] Additional support is provided by unpublished observations of A. J. Sadowski of this laboratory that addition of Hg^{2+} ion to the reaction systems greatly reduces the rate of reaction. It is known that Hg^{2+} bonds strongly to the exposed sulfur of $(H_3N)_5CoNCS^{2+}$.

[19] Activation parameters for six second-order oxidations by hydrogen peroxide tabulated in ref 13 (p 92 ff) show the following ranges: $\Delta H = 12.8$–23.0 kcal/mole; $\Delta S^* = -25$ to -11 eu.

[20] NOTE ADDED IN PROOF.—We have just learned that the reaction of $(H_3N)_5CoNCS^{2+}$ with H_2O_2 has recently been studied by A. R. Norris and S. M. Caldwell (Queen's University, Kingston, Ontario). Working at 25° and in the range $[H^+] = 0.05$–0.50 they obtain a rate law in agreement with that reported here. They also have evidence that a significant fraction of the Co(III) product is in the form of a complex other than $Co(NH_3)_6^{3+}$.

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Nickel Complexes with 2-Diethylphosphinoethyl Ethyl Sulfide

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The new bidentate ligand diethylphosphinoethyl ethyl sulfide, DPES, has been synthesized, and a series of Ni(II) complexes characterized. Five-coordinate, diamagnetic complexes of general formula $[Ni(DPES)_2X]ClO_4$ (where X = Cl, Br, I) have been obtained, and spectral studies appear to be consistent with a square-pyramidal structure. The thiocyanate complex, $Ni(DPES)_2(NCS)_2$, exists in two isomeric forms, a diamagnetic, four-coordinate species in which DPES is believed to function as a monodentate ligand bonding only through phosphorus and a paramagnetic, octahedral adduct in which DPES is bidentate.

In recent years many nickel complexes with bidentate ligands containing phosphorus, arsenic, and sulfur have been reported. These include the complexes with *o*-phenylenebisdimethylarsine (DAS),[1] 1,2-bis(diethylphosphino)ethane,[2,3] 1,2-diethylthioethane,[4] and dimethyl-*o*-methylthiophenylarsine.[5] The physical properties of the bis-chelate adducts, $Ni(chelate)_2X_2$ (where X is a univalent anion), vary significantly with the nature of the bidentate ligand. For example, the diarsine and diphosphine complexes are diamagnetic and ionize in noncoordinating solvents as uni-univalent

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[1] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

[2] C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

[3] G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

[4] R. Backhouse, M. Foss, and R. S. Nyholm, *ibid.*, 1714 (1957).

[5] S. Livingstone, *ibid.*, 4222 (1958).