can be calculated from appearance potential measurements, provided the ion source reaction is known or can be reasonably assumed and appropriate supporting thermochemical values are available. The pertinent equations are (for a hypothetical ion source reaction, $R_1R_2 \rightarrow R_1^+ + R_2$)

$$AP \geq \Delta H_f°(R_1^+) + \Delta H_f°(R_2) - \Delta H_f°(R_1R_2)$$

and

$$AP \geq I(R_1) + D(R_1\text{-}R_2)$$

where AP is appearance potential, I is ionization potential, $\Delta H_f°$ is standard heat of formation, and D is bond dissociation energy. The inequality holds when any of the products contain excess energy. The ancillary values employed in these calculations were (in kcal/mol): $\Delta H_f°(Co^+) = 287,$[14] $\Delta H_f°(CO) = -26.4,$[14] $\Delta H_f°(SiF_3) = -253,$[15] $\Delta H_f°(SiF_3^+) = 54,$[15] $\Delta H_f°(SiF_2) = -139,$[12] $I(SiF_3) = 307,$[15] $\Delta H_f°(Co(CO)_4) = -132,$[12] $\Delta H_f°(Co(CO)^+) = 203,$[12] and $\Delta H_f°(Co(CO)_2^+) = 138.$[12]

In Table II it is noted that the appearance potential of SiF_3^+ is 16.3 ± 0.3 V. Dibeler and Mohler have reported[16] the appearance potential of SiF_3^+ from SiF_4 as 16.1 ± 0.2 V. Since SiF_4 is one of the decomposition products of $SiF_3Co(CO)_4$ and in view of the agreement between the appearance potentials, it appears that the SiF_3^+ ion arises from SiF_4 and not the carbonyl. At least the AP of SiF_3^+ from SiF_4 is lower than the AP of SiF_3^+ from $SiF_3Co(CO)_4$.

The differences between the sum of the heats of formation of $Co(CO)_4$ and SiF_3 and the heat of formation of $SiF_3Co(CO)_4$ is the bond dissociation energy of the Si–Co bond in this compound. The heat of formation of $SiF_3Co(CO)_4$ (-490 ± 10 kcal/mol) is 53 kcal/mol more negative than $\Delta H_f°(CH_3SiF_2Co(CO)_4)$ (-437 ± 12 kcal/mol).[10] However, the bond dissociation energy $D(F_3Si\text{-}Co(CO)_4)$ (105 ± 12 kcal/mol) is 22 kcal/mol less than $D(CH_3SiF_2\text{-}Co(CO)_4)$ (127 ± 15 kcal/mol).[10] The relative difference in Si–Co bond dissociation energy is believed to be significant because the factors which give rise to the errors in the absolute values of the bond energy are essentially the same in both compounds. This difference suggests that there may be a greater degree of $(d \rightarrow d)\pi$ bonding between silicon and cobalt in $CH_3SiF_2Co(CO)_4$ than in $SiF_3Co(CO)_4$. The reason for this result can qualitatively be ascribed to the greater electron density in the silicon 3d orbital of $SiF_3Co(CO)_4$ arising from greater $(p \rightarrow d)\pi$ bonding between silicon and fluorine. The reduction in the π-electron density of the silicon when a fluorine atom is replaced by a methyl moiety might be expected to increase the amount of $(d \rightarrow d)\pi$ bonding between cobalt and silicon. It is interesting to note that greater (d

$\rightarrow$ d)π bonding between cobalt and silicon in CH_3SiF_2-$Co(CO)_4$, compared to $SiF_3Co(CO)_4$, is also suggested by the values reported[3] for $(k_e - k_a)$ of these compounds where k_e and k_a are the force constants for the equatorial and axial carbonyl ligands, respectively.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEEN'S UNIVERSITY, KINGSTON, ONTARIO, CANADA

Reactions of Coordinated Ligands. The Reaction of Isothiocyanatopentaamminecobalt(III) Ion with Hydrogen Peroxide in Acid Solution

BY S. M. CALDWELL AND A. R. NORRIS

The kinetics and stoichiometry of the reaction of $Co(NH_3)_5NCS^{2+}$ with H_2O_2 at temperatures between 25 and 97° has recently been reported.[1] In the course of our studies on the oxidation, reduction, and addition reactions of the coordinated thiocyanate ion in complexes primarily of the type *cis*- and *trans*-$Co(en)_2XN$-CS^{n+}, where $X = Cl, Br, NO_2, NH_3,$ and NCS, we have also investigated the behavior of $Co(NH_3)_5NCS^{2+}$ with H_2O_2 and here report some of our observations.

Experimental Section

Reagents and Preparations.—Except as indicated "Analar" reagents were used throughout without further purification. $[Co(NH_3)_5NCS](ClO_4)_2$ was prepared as described by Werner and Muller.[2] The crude perchlorate was recrystallized from water containing $NaClO_4$ until pure. *Anal.* Calcd for $[Co(NH_3)_5$-$NCS](ClO_4)_2$: Co, 14.70. Found: Co, 14.64. The compounds $[Co(NH_3)_6]Cl_3,$[3] $[Co(NH_3)_5H_2O]_2(C_2O_4)_3,$[4] and $[Co(NH_3)_5$-$CN]Cl_2$[5] were obtained by the methods described in the references cited. The salts were recrystallized from a minimum of water at room temperature and analyzed spectrophotometrically. Molar extinction coefficients (ϵ) of the pure complexes were measured on a Unicam SP800 or a Cary 14 spectrophotometer employing solutions of approximately 10^{-3} M concentration and matched cells of path lengths 1.0, 2.0, and 5.0 cm. The cell compartment was thermostated at 25.0° in all cases. Values of λ_{max} (ϵ) for each complex used in these studies are as follows (Å, M^{-1} cm^{-1}): $[Co(NH_3)_5NCS]^{2+}$, 4960 (208), 3050 (1770); $[Co(NH_3)_6]^{3+}$, 4740 (53.3), 3390 (47.8); $[Co(NH_3)_5H_2O]^{3+}$, 4890 (48.4), 3420 (53.5); $[Co(NH_3)_5CN]^{2+}$, 4410 (53.4), 3270 (51.5).

Stock solutions of hydrogen peroxide were prepared from Baker hydrogen peroxide (30%) containing 0.05% $Na_4P_2O_7 \cdot 10H_2O$ as preservative and the peroxide content was determined iodimetrically following Vogel's[6] procedure. Stock solutions of hydrogen peroxide ($\sim$9.0 M) were stored in the refrigerator when not in use and restandardized periodically.

(14) F. D. Rossini, D. D. Wayman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, Washington, D. C., 1952.

(15) J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O173.

(16) V. H. Dibeler and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **A40**, 25 (1948).

(1) K. Schug, M. D. Gilmore, and L. A. Olson, *Inorg. Chem.*, **6**, 2180 (1967).

(2) A. Werner and H. Muller, *Z. Anorg. Allgem. Chem.*, **22**, 91 (1900).

(3) D. M. Adams and J. B. Raynor in "Advanced Practical Inorganic Chemistry," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1965, p 161.

(4) W. G. Palmer in "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p 536.

(5) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

(6) A. Vogel in "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., London, 1962, p 363.

Kinetic Studies.—Stock solutions containing $Co(NH_3)_5NCS^{2+}$ were always prepared immediately before use and all experiments were carried out in subdued light to prevent complications arising from photochemical decomposition of the isothiocyanato complex.

All reaction mixtures were maintained at a fixed ionic strength of 0.50 using stock solutions of $NaClO_4$ (2.00 M) and $HClO_4$ (2.00 M). Solutions containing known amounts of the isothiocyanato complex, perchloric acid, and sodium perchlorate were prepared in volumetric flasks and the flasks and contents were allowed to equilibrate in a water bath at 25.0°. A known amount of hydrogen peroxide stock solution also at 25.0° was added to the volumetric flask, the contents were thoroughly mixed, and a portion of the solution was transferred to a clean, dry spectrophotometric cell of 4.0-cm path length previously equilibrated at 25.0° in the cell compartment of the spectrophotometer. The optical density of the solution at 496 mμ was recorded at approximately 100-sec intervals until the reaction was more than 80% complete. The solution was then removed and stored in the dark for approximately 8 hr at which time the optical density at 496 mμ and the visible and ultraviolet absorption spectra of the solution were recorded. Pseudo-first-order rate constants (k_{obsd}) were determined from the "least-squares" slopes of the $\ln[(OD)_t - (OD)_\infty]$ vs. time plots where $(OD)_t$ and $(OD)_\infty$ refer to the optical densities of the solutions at 496 mμ at times t and infinity, respectively. Graphical plots of $\ln[(OD)_t - (OD)_\infty]$ vs. time were linear to 80–90% completion of the reaction, and in duplicate runs k_{obsd} could be reproduced to within ±5%. Separate experiments showed that neither of the two major reaction products, $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5$-CN^{2+}, underwent further reaction, even at the highest concentrations of hydrogen peroxide and hydrogen ion used in these experiments.

Product Studies.—The reaction mixture (100 ml) containing approximately 1.2×10^{-4} mol of $Co(NH_3)_5NCS^{2+}$ and the required amounts of H_2O_2, $HClO_4$, and $NaClO_4$ was allowed to stand in the dark until the reaction went to completion (>10 half-lives). The visible and ultraviolet spectra of the solution was recorded and the solution was absorbed on an ion-exchange column (Dowex (H^+) 50W-X2, 200–400 mesh, 15 × 400 mm). The column was eluted first with 1 M KCl to remove the +1 and +2 charged complex ions and then with 3 M HCl to remove the hexaammine complex.[7] Optical densities of the solutions were measured immediately after recovery from the column. Chromatography of test solutions containing varying amounts of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5CN^{2+}$ always led to greater than 98% recovery of $Co(NH_3)_6^{3+}$ and a recovery of $Co(NH_3)_5CN^{2+}$ of between 90 and 95%.

Sulfate was determined gravimetrically as $BaSO_4$ following Vogel's procedure.[6]

Results

Kinetics.—The pseudo-first-order rate constants k_{obsd} for the disappearance of $Co(NH_3)_5NCS^{2+}$ under a variety of H_2O_2 and H^+ concentrations are listed in Table I. It is apparent that k_{obsd} is a function of both the H_2O_2 and the H^+ concentration in the solution. For a fixed concentration of H_2O_2, a plot of k_{obsd} vs. $[H^+]$ is linear with a positive slope and nonzero intercept indicating that both hydrogen-ion-dependent and hydrogen-ion-independent terms are present in the rate law. The slopes and intercepts are in turn directly proportional to the concentration of H_2O_2 to the power 1 as indicated in Table II. The kinetic data are thus consistent with a rate law of the form

$$\frac{-d[Co(NH_3)_5NCS^{2+}]}{dt} = [Co(NH_3)_5NCS^{2+}][H_2O_2]\{k_0 + k_1[H^+]\}$$

(7) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).

where at 25.0° and $\mu = 0.50$, $k_0 = (5.26 \pm 0.15) \times 10^{-5}$ M^{-1} sec^{-1} and $k_1 = (0.99 \pm 0.03) \times 10^{-3}$ M^{-2} sec^{-1} (mean values from all runs).

The form of the rate law agrees with that reported by Schug, Gilmore, and Olson.[1] Employing our value of k_0 at 25.0° and $k_0 = 1.30 \times 10^{-3}$ M^{-1} sec^{-1} at 65°,[1] we calculate that ΔH^* for the acid-independent path is 15.3 ± 0.2 kcal mol.$^{-1}$ This compares to an approximate ΔH^* of 17.4 kcal mol^{-1} previously reported.[1]

Products.—Under the reaction conditions employed in the kinetic runs 1 mol of $BaSO_4$ was produced per mol of $Co(NH_3)_5NCS^{2+}$ ion initially present in the system.

At infinite time, all of the reaction mixtures listed in Table II showed absorption maxima at wavelengths less than 474 mμ indicating that species other than $Co(NH_3)_6^{3+}$ were present in the reaction mixture. Preliminary investigations in which the reaction mixtures were slowly evaporated to dryness at room temperature showed two major species were present: the expected hexaammine which precipitated first as the perchlorate salt and a second product whose absorption maximum was near 440 mμ. This second species was recrystallized as the chloride salt from aqueous solution contain-

TABLE I

KINETICS OF THE $Co(NH_3)_5NCS^{2+}$–H_2O_2 REACTION AT 25.0°, $\mu = 0.50$, AND $[COMPLEX] = 1.0 \times 10^{-3}$ M

$[H^+]$, M	$10^4 k_{obsd}$,[a] sec^{-1}	$[H^+]$, M	$10^4 k_{obsd}$, sec^{-1}
2.05 M H_2O_2		1.03 M H_2O_2	
0.50	12.16 ± 0.20	0.50	5.71 ± 0.04
0.40	10.07 ± 0.10	0.40	4.71 ± 0.03
0.30	7.93 ± 0.06	0.30	3.48 ± 0.02
0.20	5.52 ± 0.02	0.20	2.55 ± 0.02
0.10	3.33 ± 0.01	0.10	1.59 ± 0.02
1.79 M H_2O_2		0.77 M H_2O_2	
0.50	10.87 ± 0.06	0.50	3.89 ± 0.02
0.40	8.22 ± 0.15	0.40	3.11 ± 0.01
0.30	6.34 ± 0.05	0.30	2.45 ± 0.09
0.20	4.29 ± 0.03	0.20	1.85 ± 0.02
0.10	2.76 ± 0.02		
1.56 M H_2O_2			
0.50	8.22 ± 0.11		
0.40	6.91 ± 0.06		
0.30	5.48 ± 0.04		
0.20	3.96 ± 0.01		
0.10	2.18 ± 0.01		

[a] k_{obsd} from the slope of the $\ln[(OD)_t - (OD)_\infty]$ vs. time plot. The slope was determined using a "least-squares" program. The error in k_{obsd} is based on the error in the slope.

TABLE II

KINETIC DATA FOR THE $Co(NH_3)_5NCS^{2+}$–H_2O_2 REACTION AT 25.0°, $\mu = 0.50$, AND $[COMPLEX] = 1.0 \times 10^{-3}$ M

$[H_2O_2]$, M	Slope[a] $\times 10^3$, sec^{-1} M^{-1}	Intercept[a] $\times 10^3$, sec^{-1}	$10^5 k_0$,[b] sec^{-1} M^{-1}	$10^3 k_1$,[c] sec^{-1} M^{-2}
2.05	2.20	11.42	5.58	1.08
1.79	1.80	9.80	5.47	1.00
1.56	1.50	8.37	5.35	0.97
1.03	1.04	4.83	4.72	1.01
0.77	0.68	4.00	5.20	0.88

[a] Slope and intercept of the k_{obsd} vs. $[H^+]$ plot determined by a "least-squares" program. [b] Intercept divided by $[H_2O_2]$. [c] Slope divided by $[H_2O_2]$.

ing sodium chloride and shown to have visible, ultraviolet, and infrared spectra identical with those of an authentic sample of $[Co(NH_3)_5CN]Cl_2$. The ion-exchange technique permitted a quantitative evaluation of the amounts of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5CN^{2+}$ formed in the reaction as indicated in Table III. Small amounts ($<2\%$) of other products were formed as well, including $Co(NH_3)_5H_2O^{3+}$ (eluted with 3 M HCl) and a light yellow species which was not eluted from the column with 4.8 M HCl and presumably has a charge greater than $+3$.

TABLE III

PRODUCTS OF REACTION RECOVERED
FROM ION-EXCHANGE COLUMN

$[H_2O_2]$, M	$[H^+]$, M	Initial $[Co(NH_3)_5-NCS^{2+}]$, mol $\times 10^4$	λ_{max} of reaction mixture	$[Co(NH_3)_5-CN^{2+}]$, mol $\times 10^4$	$[Co(NH_3)_6^{3+}]$, mol $\times 10^4$	% conversion to $Co(NH_3)_6^{3+}$
2.05	0.50	1.22	453	0.77	0.40	32.7
	0.10	1.24	464	0.28	0.69	55.6
1.79	0.50	1.27	456	0.71	0.44	34.6
1.56	0.50	1.27	455	0.77	0.44	34.6
1.03	0.50	1.27	456	...	0.43	35.6
0.77	0.50	1.22	459	0.35	0.51	41.8
	0.20	1.22	469	...	0.96	78.6
	0.10	1.24	469	0.14	1.10	88.9

The data in Table III suggest that at a fixed $[H^+]$ the conversion of starting material to $Co(NH_3)_6^{3+}$ is independent of or only slightly dependent on the hydrogen peroxide concentration over this range while, at a fixed concentration of hydrogen peroxide, the per cent conversion to hexaammine is markedly dependent on the H^+ concentration. The mechanistic implications of these observations and the process by which the cobalt–carbon bond in $Co(NH_3)_5CN^{2+}$ is generated from the original cobalt–nitrogen bond in $Co(NH_3)_5NCS^{2+}$ are under investigation.

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Ligand Redox Studies. II. Formation of Cyano Complexes by Oxidation of Captive Thiocyanate[1a]

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Several examples have been found of the formation of inert cyanide complexes on oxidation of the corresponding thiocyanate species: the oxidation of $(H_3N)_5CoNCS^{2+}$ by either Ce(IV) in H_2SO_4 or $S_2O_8^{2-}$ at low acidity and the oxidation of either $(C_2H_5)_4$dien-

PdNCS$^+$ or $(C_2H_5)_4$dienPdSCN$^+$ by hydrogen peroxide.

Experimental Section

Materials.—Isothiocyanatopentaamminecobalt(III) perchlorate, $[(H_3N)_5CoNCS](ClO_4)_2$, was prepared as described previously.[2] Thiocyanatotetraethyldiethylenetriaminepalladium(II) hexafluorophosphate, $[((C_2H_5)_4dien)PdSCN]PF_6$, was prepared as described by Basolo, Baddley, and Weidenbaum.[3] Isothiocyanatotetraethyldiethylenetriaminepalladium(II) perchlorate, $[((C_2H_5)_4dien)PdNCS]ClO_4$, was prepared[4] by recrystallizing the thiocyanate salt[3] from aqueous sodium perchlorate. Reagent grade chemicals were used elsewhere.

Ce(IV)–$(H_3N)_5CoNCS^{2+}$.—Solutions containing isothiocyanatopentaamminecobalt(III) perchlorate (0.0005–0.0015 M), sulfuric acid (0.25 M), and cerium(IV) sulfate (8–25 molar excess of cerium) were allowed to react for several weeks at room temperature to ensure complete reaction. The final solutions were treated with hydrogen peroxide to reduce Ce(IV) to Ce^{3+} and passed through anion resin columns (Amberlite IRA-410 in hydroxide form) to remove sulfate and cerium (the cerium(III) hydroxide precipitating on the column). The eluent was slightly acidified with perchloric acid and evaporated to a small volume by warming (60–70°) under reduced pressure. On slow cooling, two solid phases separated out—a powdery amorphous material (A) and a crystalline material (B). These solid phases were separated mechanically and each was recrystallized from perchloric acid. The resultant solids were identified as the cyanopentaammine (A) and the hexaammine (B) cobalt(III) perchlorates on the basis of elemental analyses, infrared spectra, and uv–visible absorption spectra of their aqueous solutions; results for solid A were as follows. *Anal.* Calcd: C, 3.25; H, 4.07; N, 22.77; NH$_3$, 23.0. Found: C, 3.31; H, 4.08; N, 22.64; NH$_3$, 22.7. Infrared spectrum: Reported:[5] sharp peak at 2145 cm^{-1} (identified as CN stretch). Found: sharp peak at 2150 cm^{-1}. Uv–visible spectra: absorption maxima and molar absorbancy indices calculated from spectra obtained with a Hitachi recording spectrophotometer are given in Table I.

TABLE I

VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA

	ν_{max}, cm^{-1}	Log a^d	ν_{max}, cm^{-1}	Log a
$[(H_3N)_5CoCN](ClO_4)_2 \cdot 0.5H_2O^a$	22,620	1.69	30,580	1.66
$[CoCN(NH_3)_5]Cl_2^b$	22,725	1.77	30,680	1.82
$Co(NH_3)_5CN^{2+c}$	22,700	1.75	30,560	1.72
Reaction products				
Ce(IV) oxidation	22,570	1.74	30,400	1.73
$S_2O_8^{2-}$ oxidation	22,830	(1.75)	30,770	1.72

^{a} Sample supplied by J. Espenson, Iowa State University. ^{b} M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964). ^{c} H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964). ^{d} a is the molar absorbancy index $(M^{-1}\text{cm}^{-1})$.

$S_2O_8^{2-}$–$(H_3N)_5CoNCS^{2+}$.—Oxidation of aqueous isothiocyanatopentaamminecobalt(III) perchlorate ($\sim 10^{-4}$ M) with excess sodium peroxodisulfate in acidic solution ($[H^+]$ = 0.1 M) produces hexaamminecobalt(III) ion quantitatively. At lower acidities, however, the visible absorption spectrum of the final solution establishes the presence of additional species. Quantitative spectral analyses and cation-exchange studies have been carried out

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(1) (a) Supported in part by National Science Foundation Grants GP-2664 and GP 6646 and in part by a grant from the Japanese Ministry of Education. (b) To whom reprint requests may be sent. (c) Illinois Institute of Technology. (d) Kyushu University.

(2) K. Schug, M. D. Gilmore, and L. A. Olson, *Inorg. Chem.*, **6**, 2180 (1967).

(3) F. Basolo, W. H. Baddley, amd K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

(4) A. J. Sadowski, Doctoral Thesis, Illinois Institute of Technology, 1967.

(5) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).