

Equilibria in Acidic Aqueous Pyridine N-Oxide Solutions of Chromium(III)^{1,2}

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Abstract: Chromium(III) species containing the ligands pyridine N-oxide and water, $\text{Cr}(\text{OH})_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$ ($n = 0-6$ inclusive, including isomeric species with $n = 2, 3,$ and 4), are formed in acidic aqueous solutions of pyridine N-oxide. Equilibrium in this system at 70° has been characterized on the basis of cation-exchange separation of the species (including isomers) present in equilibrated mixtures. For the reaction $\text{Cr}(\text{OH})_6^{3+} + \text{C}_5\text{H}_5\text{NO} = \text{Cr}(\text{OH})_5(\text{ONC}_5\text{H}_5)^{3+} + \text{H}_2\text{O}$, $Q = 3.9 \text{ l. mole}^{-1}$. Equilibrium quotients for formation of other species in the series have been evaluated, and, with appropriate statistical correction, they have been used in attempting to assign configuration of the isomeric species.

Pyridine N-oxide forms complex ions with a number of transition metal ions,^{3,4} but existing studies have not characterized the equilibria in solution. The present paper reports a study of equilibrium in acidic aqueous pyridine N-oxide solutions of chromium(III) at 70° . Ion-exchange techniques have proved useful in analyzing the equilibrium mixtures because of the inertness of chromium(III) ion toward ligand substitution in its first coordination shell. Species of different composition



have been separated by such methods, and the pairs of isomeric species with $n = 2-4$ also were separated. (Although species of different composition were separated in a study of chromium(III) in water-ethanol solutions, pairs of isomeric species were not separated.⁵) Equilibrium quotients for formation of the eight different species have been calculated.

Experimental Details

Reagents. Water was doubly distilled, with treatment by an ion-exchange demineralizer (Barnstead Bantum BD-1) employed before the second distillation (from a Pyrex still). Pyridine N-oxide (Matheson Coleman and Bell, purified grade) was crystallized from chloroform and then sublimed twice at $3-5 \text{ mm}$ at 100° . It was stored in a darkened nitrogen-filled desiccator over phosphorus pentoxide. Chromium(III) perchlorate was prepared from reagent grade chromium(VI) oxide by reaction with hydrogen peroxide in perchloric acid solution. Excess perchloric acid was present, and water was evaporated until the solution was concentrated enough to form crystalline hydrated chromium(III) perchlorate upon cooling to room temperature. The material was recrystallized from aqueous perchloric acid. The chromium(III) perchlorate prepared in this way was relatively free of polymeric hydroxy-chromium(III) species as judged from the ratio of absorbancies at 230 and $260 \text{ m}\mu$ $A_{230}/A_{260} \cong 0.2$.⁶ Reagent grade Dowex 50W-X2 cation-exchange resin (100-200 mesh) was subjected to additional purification before use. Initial purification and regeneration of

resin after use consisted of alternate treatment with 4 M hydrochloric acid and alkaline ($0.5-1.0 \text{ M}$ sodium hydroxide) peroxide solution at $\sim 90^\circ$; the resin was rinsed with distilled water between treatments with acid and alkali. This procedure was repeated until the alkaline solution was colorless and the absorbancy of the rinse after the acidic treatment was negligible at $254 \text{ m}\mu$ (<0.3 in 1-cm cell). The resin in the hydrogen ion form was used on the day of purification since it decolorized upon standing.

Analytical Methods. Chromium analysis involved conversion of chromium(III) species ($\text{Cr}(\text{OH})_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$, $n = 0, 1, \dots$) to chromate ion with alkaline peroxide for measurement of light absorption at $372 \text{ m}\mu$ ($a = 4.82 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$).⁷ This analysis was unaffected by the presence of pyridine N-oxide. Analysis for pyridine N-oxide involved measurement of light absorption at $254 \text{ m}\mu$ ($a = 1.21 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$, a value which agrees reasonably well with literature values⁸ 1.19×10^4 and⁹ $1.18 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$). Before analysis of pyridine N-oxide bound to chromium(III), the solution was made alkaline which caused rapid conversion of chromium(III)-pyridine N-oxide species to free pyridine N-oxide and hydroxychromium(III) species. Interference due to the latter species in the spectrophotometric analysis for pyridine N-oxide was negligible ($<1\%$ for solutions with $\bar{n} \cong 1$; \bar{n} is the average number of bound pyridine N-oxide molecules per chromium(III)).

Equilibration of Solutions. Solutions containing chromium(III) perchlorate, perchloric acid, pyridine N-oxide, and water were prepared from solid pyridine N-oxide and analyzed stock solutions. Before being sealed in Pyrex vials for equilibration, these solutions were deoxygenated by a stream of nitrogen. The equilibration was conducted in the absence of light, although this precaution was not proved to be necessary. The time required for establishment of equilibrium at 70° was studied by determination of \bar{n} as a function of time. The ion-exchange method used for separating all chromium(III) species from the solvent was similar to that employed in earlier studies.^{5,10} In a solution with the composition 0.16 M perchloric acid, 0.3 M pyridine N-oxide, and 0.01 M chromium(III) perchlorate, values of \bar{n} as a function of time are (given as t (hr), \bar{n}): 4, 0.40; 10, 0.66; 23, 0.91; 32, 0.89; 44, 0.89; and 72, 0.92. In a solution with the composition 0.36 M perchloric acid, 2.5 M pyridine N-oxide, and 0.01 M chromium(III) perchlorate, the data are (t (hr), \bar{n}): 0.5, 0.3; 1, 0.62; 3, 1.66; 7.5, 2.71; 13, 2.95; and 16.5, 2.94. Equilibration times were selected on the basis of these data and data from two other such experiments. The dependence of \bar{n} upon solvent composition was not interpreted in the present study since concentrations of individual species as a function of solvent composition are more informative. The value of \bar{n} was determined, however, for each solution upon which fractionation was performed.

Ion-Exchange Procedures. Column ion-exchange procedures were used for two purposes: the evaluation of \bar{n} and the separation of individual species. In both procedures, Dowex 50W X-2 (100-200 mesh) resin was used. (Chromium(III) species in a diluted

(1) Based upon the Ph.D. thesis of T. J. Weeks, Jr., University of Colorado, Dec 1966.

(2) This work was supported by the National Science Foundation (Grant GP-680).

(3) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(4) R. L. Carlin, *ibid.*, **83**, 3773 (1961).

(5) D. W. Kemp and E. L. King, *ibid.*, **89**, 3433 (1967).

(6) C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961).

(7) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(8) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

(9) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(10) J. C. Jayne and E. L. King, *ibid.*, **86**, 3989 (1964).

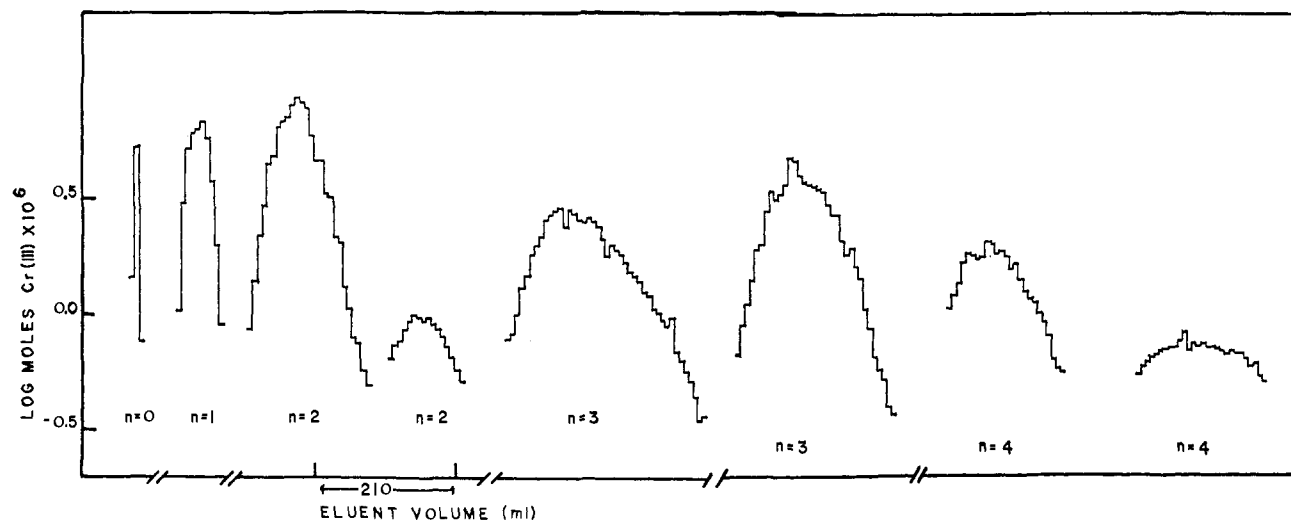


Figure 1. Elution of chromium(III) species in solution with the composition 1.56 *M* pyridine *N*-oxide, 0.32 *M* perchloric acid, and 1.1×10^{-2} *M* chromium(III) perchlorate (solution 7 of Table II). Elution procedure described in text.

solution with $\bar{n} \cong 3.6$ were incompletely absorbed into the resin phase by resin with cross-linking X-12 and X-8. Although resin with cross-linking X-4 absorbed the chromium(III) species completely, elution was slower than when the X-2 resin was used.) The fractionation experiments were carried out in a cold room at $\sim 5^\circ$ using a column of 1.2 cm i.d. with ~ 100 cm depth of resin. A 40-ml portion of chilled equilibrated solution was diluted with 150 ml of 0.01 *M* perchloric acid and stirred with an excess of resin at 0° until the chromium(III) species were absorbed completely (>99%) into the resin phase. This batch of resin was transferred to a sintered glass funnel and washed free of unbound pyridine *N*-oxide with cold ($0-5^\circ$) 0.01 *M* perchloric acid. For solutions of high \bar{n} , as much as 2 l. of the dilute acid was needed, with the rinsing extending over 2.5 hr. Rinsing was judged complete when the pyridine *N*-oxide concentration in the rinsing solution was 10^{-6} *M* or less. The chromium-containing resin was then transferred to the top of the resin bed in the column. The resin-containing column had been precooled in the cold room and had been pre-equilibrated with 3 *M* hydrochloric acid. Elution was carried out using aqueous hydrochloric acid. In most experiments elution was carried out slowly (0.05–0.1 drop sec^{-1}) with 3 *M* hydrochloric acid as the initial eluting agent. The concentration of hydrochloric acid was raised to 4.5 *M* after elution of $\text{Cr}(\text{OH}_2)_5(\text{ONC}_5\text{H}_5)_3^{3+}$ and to 5 *M* after elution of the more easily eluted isomer of $\text{Cr}(\text{OH}_2)_5(\text{ONC}_5\text{H}_5)_4^{3+}$. For solutions with the highest \bar{n} values studied, elution required as long as 9 days, and some difficulty arose from aqution of species on the column.

If appreciable amounts of chlorochromium(III) species formed during the elution with hydrochloric acid, well-defined elution peaks would not be expected since the chlorochromium(III) species with charge 2+ would move much more rapidly than the ions of charge 3+. An additional argument against formation of appreciable amounts of chlorochromium(III) species is the very low rate expected for the formation of pentaquo chlorochromium(III) ion at 5° in aqueous solution ($t_{1/2} \cong 300$ days at 4 *M* chloride ion¹¹). This calculation by itself would not be definitive since both the environment and reactant species are different, but it is consistent with the indirect experimental evidence against formation of chlorochromium(III) species during the ion-exchange procedure.

In some experiments the eluent was collected in 7-ml portions using a fraction collector; in others entire separated fractions were collected in volumetric flasks. The chromium content of eluent portions was determined in all cases, and the pyridine *N*-oxide content was determined for some eluent portions and for all separated fractions. Figure 1 gives an elution curve for an equilibrated solution with $\bar{n} \cong 2.8$. The figure shows clear evidence for separation of isomeric species. Two geometrical isomers are possible for species containing two and three pyridine *N*-oxide molecules, and two elution peaks are observed for each of these composi-

tions in all elutions performed. Two isomers are possible also for species containing four pyridine *N*-oxide molecules, but separation of these species was accomplished in only two of seven experiments in which there was an appreciable concentration of tetra(pyridine *N*-oxide)chromium(III) species. Until identification of each of the pairs of isomers is discussed, they will be identified as α (the more easily eluted isomer) and β (the less easily eluted isomer).

Since analysis of pyridine *N*-oxide was based upon light absorption in the ultraviolet region (254 $m\mu$), there was some difficulty in achieving a transparent blank on solutions which had passed through the ion-exchange column; in addition slow aqution on the column of less easily eluted species produces pyridine *N*-oxide. The pyridine *N*-oxide content of eluent portions containing species with one, two, and three bound pyridine *N*-oxide molecules was corrected for this low background (<10% of the measured light absorption) on the basis of the apparent pyridine *N*-oxide concentration in the eluent between the well-separated elution peaks due to species containing one, two, and three bound pyridine *N*-oxide molecules. All analyzed portions of eluent in the experiments summarized in Figure 1 had values of \bar{n} within 0.1 unit of integers.

The situation is less clear with eluent portions from experiments on solutions with high \bar{n} (experiments 10 and 11 in Table II). In these experiments identification of the elution peaks was marred by apparent nonintegral values of \bar{n} , but the discrepancies are consistent with appreciable aqution on the column of species containing four–six pyridine *N*-oxide molecules. For experiment 10, values of \bar{n} for the first and second peaks due to tri species (the α and β isomers) were 3.6 and 3.5, respectively. The identification of these peaks as due to species containing three bound pyridine *N*-oxide molecules is, however, unequivocal since they can be identified on the basis of elutibility and spectra with corresponding elution peaks in experiments in which no such difficulties exist. These eluent portions contain too much pyridine *N*-oxide, presumably because of the aqution of less easily eluted species present in the resin phase. Analysis of the next three elution peaks gave values of \bar{n} of 4.1, 4.4, and 4.5. These have been identified as being due to species containing four, four, and five bound pyridine *N*-oxide molecules, respectively. The eluent portions containing tetra species are assumed to have values of \bar{n} which are too high because of free pyridine *N*-oxide, and that containing penta species is assumed to have a value of \bar{n} which is too low because of partial aqution by the time it is finally eluted after 9 days on the column. No elution peak due to hexa(pyridine *N*-oxide) was observed in any of the elutions, although this species probably was present to a limited extent in the most concentrated solutions of pyridine *N*-oxide. (In some solutions, precipitation of a small amount of hexa(pyridine *N*-oxide)chromium(III) perchlorate occurred in the chilled, quenched solution. Such solutions were warmed to cause dissolution of the solid before a portion was taken for analysis.)

(11) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

Recovery of chromium was not quantitative, and the over-all value of \bar{n} calculated from the yield of individual species was lower than the value determined on a portion of equilibrated solution which was subjected to an ion-exchange procedure for separating unbound pyridine N-oxide from chromium species (*i.e.*, the conventional procedure for evaluation of \bar{n} ^{5,10}). This suggests greater loss of species with larger values of \bar{n} , which is not unexpected since tailing of elution peaks is common.

Distribution of Pyridine N-Oxide between Water and Carbon Tetrachloride. To learn the concentration range over which the activity of pyridine N-oxide in aqueous solution is proportional to its concentration, the distribution of pyridine N-oxide between water and carbon tetrachloride was studied at room temperature (23–26°). The concentration of pyridine N-oxide in the aqueous phase was determined, after appropriate dilution, by the spectrophotometric method already mentioned. The carbon tetrachloride phase was reextracted with water, and the resulting aqueous solution was then analyzed for pyridine N-oxide. Since the distribution greatly favors the aqueous phase, the single reextraction was sufficient for essentially complete recovery of the pyridine N-oxide present in the carbon tetrachloride phase.

Experimental Results

The Ideality of Aqueous Solutions of Pyridine N-Oxide. The results of studies of the distribution of pyridine N-oxide between carbon tetrachloride and water are presented in Table I. The distribution

Table I. The Distribution of Pyridine N-Oxide between Water and Carbon Tetrachloride^a

$[\text{C}_5\text{H}_5\text{-NO}]_{\text{aq}}, M$	D	$[\text{C}_5\text{H}_5\text{-NO}]_{\text{org}}, M$	D
0.12	1460 ± 120 (3)	0.72	1600 ± 5 (2)
0.32	1540 ± 10 (3)	2.8	1540 ± 5 (3)
0.42	1560 ± 50 (3)	4.4	1170 ± 20 (3)
0.46	1420 (1)		

^a $D = [\text{C}_5\text{H}_5\text{NO}]_{\text{aq}}/[\text{C}_5\text{H}_5\text{NO}]_{\text{org}}$ ($T = 23\text{--}26^\circ$). Values of D are given with the number of experiments in parentheses and the average difference between the individual values and the average value as the uncertainty.

coefficient is essentially constant up to a concentration of 2.8 M in the aqueous phase. Since the concentration of pyridine N-oxide in the carbon tetrachloride phase in equilibrium with this aqueous phase is $1.8 \times 10^{-3} M$, it seems reasonable to assume solution ideality (Henry's law) for this phase. The ideality of the aqueous phase to 2.8 M pyridine N-oxide is, therefore, indicated by the approximate constancy of the distribution coefficient. The maximum concentration of pyridine N-oxide studied in the equilibrium experiments was 2.94 M , and it will be assumed that, with the exception of effects due to protonation of pyridine N-oxide, the activity coefficients of both water and pyridine N-oxide are unity in the aqueous solutions studied at 70°.

The Composition of Equilibrated Solutions. On the basis of the elution procedures already described, amounts of the different chromium(III)-pyridine N-oxide species present at equilibrium in aqueous solutions with 0.338–2.94 M pyridine N-oxide have been determined. These data are summarized in Table II.

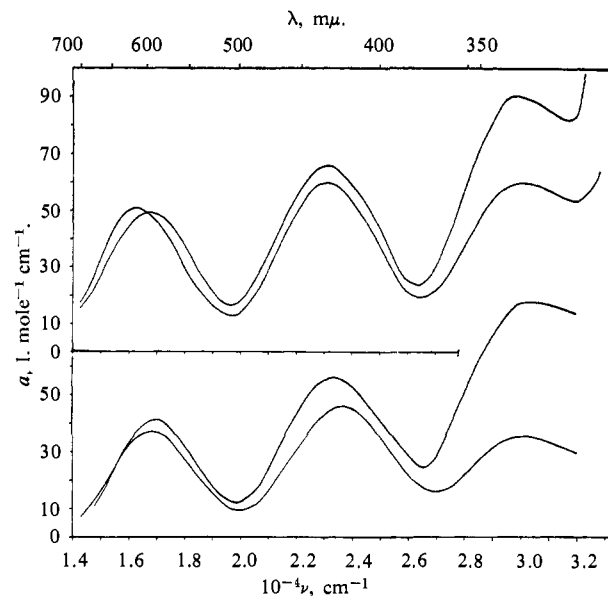
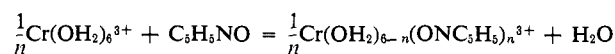


Figure 2. Spectra of species containing two and three pyridine N-oxide ligands: upper figure for $\text{Cr}(\text{OH}_2)_6(\text{ONC}_5\text{H}_5)_3^{3+}$ (upper curve, β isomer; lower curve α isomer); lower figure for $\text{Cr}(\text{OH}_2)_4(\text{ONC}_5\text{H}_5)_2^{3+}$ (upper curve, β isomer; lower curve, α isomer).

Spectra of the Species $\text{Cr}(\text{OH}_2)_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$. Spectra of the different species were measured on freshly eluted samples. The positions of the maxima in the visible region of the spectrum and the molar absorptancy indices are summarized in Table III. Values are not reported for species $n = 4$ (β isomer) or $n = 5$, the two least easily eluted species. When finally eluted, these species have aquated partially, and the measured spectra do not correspond to pure species. Because a direct comparison of spectra of isomeric species is of interest, the complete spectra for species $n = 2$, α and β isomers, and $n = 3$, α and β isomers, are presented in Figure 2. Spectra in the ultraviolet region are undoubtedly a function of the concentration of chloride ion (as is the case for hexaquochochromium(III) ion¹²).

Interpretation of Experimental Results

Equilibrium Distribution of $\text{Cr}(\text{OH}_2)_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$ Species. The ion-exchange procedure has allowed evaluation of the relative amounts of the individual species. From these data, summarized in Table II, equilibrium quotients for the reactions¹³



$$Q_n = \left\{ \frac{[\text{Cr}(\text{OH}_2)_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}]}{[\text{Cr}(\text{OH}_2)_6^{3+}]} \right\}^{1/n} \frac{Z_{\text{H}_2\text{O}}}{[\text{C}_5\text{H}_5\text{NO}]}$$

(12) H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

(13) There is a rational basis for considering this series of reactions rather than another possible set. The choice of which of the possible reactions converting one isomeric di species to an isomeric tri species is avoided with the set of reactions chosen. Each species (except hexaquochochromium(III) ion) is involved in only a single reaction. Direct comparisons of statistically corrected equilibrium quotients for these reactions are appropriate regardless of the value of n since (a) 1 mole of chromium(III)-ligand bonds is broken and made, and (b) the differences between the number of solute particles on the two sides of each chemical equation are the same, -1 .

Table II. Equilibrium Composition of Aqueous Pyridine N-Oxide Solutions of Chromium(III) at 70°

	$\text{Cr}(\text{OH}_2)_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$										
	Expt No.										
	1	2	3	4	5	6	7	8	9	10	11
$C_{\text{py-N-O}}$, mole/l.	0.338	0.338	0.290	0.868	0.868	1.04	1.56	1.56	2.94	2.94	2.94
$10^2 C_{\text{H}}$, mole/l.	5.75	15.9	8.8	11.8	25.9	18.2	32.0	12.0	26.1	29.1	69.1
$10^2 C_{\text{Cr}}$, mole/l.	1.16	1.18	0.983	1.20	1.20	3.23	1.11	1.11	1.07	1.61	1.61
\bar{n}^a	1.13	0.97	0.99			2.31	2.82	2.90	3.66	3.66	3.67
$Z_{\text{H}_2\text{O}}$, mole fraction	0.994	0.994	0.994	0.984	0.984	0.981	0.968	0.969	0.934	0.933	0.931
Cr recovery, %	92	92	100	91	91	96	86	86	45	97	90
Cr present as (moles $\times 10^3$)											
$n = 0$	143	174	178	31.9	38.6	84	7.5	6.9			
1	170	170	173	99.0	109	286	40.0	36.0	9.2	18.5	18.0
2 α	103	80	67	141	141	459	106	99.5	47.6	71.3	72.8
2 β			9.3	21.8	19.4	66.3	15.1	13.9	6.9	9.1	10.4
3 α			7	51.2	49.4	237	74.1	74.2	61.1	128	101
3 β			9	61.6	53.6	260	76.8	76.4	67.4	134	130
4 α				14.0 ^b	12.1 ^b	102 ^b	40.4 ^b	45.2 ^b		125	117
4 β										28	26
5						(28) ^c	(19.2) ^c	(20.8) ^c		87	85

^a \bar{n} determined on separate sample of equilibrated solution. ^b This is the sum of concentrations of isomeric tetra species; separation of isomers was not achieved in these experiments. ^c Uncertain.

Table III. Positions of Maxima in Visible Spectrum of $\text{Cr}(\text{OH})_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$

Species	Medium	λ , $m\mu$ (a , l. mole ⁻¹ cm ⁻¹)
$n = 0$	3 M HCl	574 (13.6); 404 (16.5)
$= 1$	2 M HCl	586 (26.0); 414 (30.8)
$= 2 \alpha$	3 M HCl	593 (37.1); 422 (46.0)
$= 2 \beta$	3 M HCl	586 (41.1); 429 (56.0)
$= 3 \alpha$	3 M HCl	617 (51.4); 432 (60.2)
$= 3 \beta$	3 M HCl	600 (49.4); 433 (66.2)
$= 4 \alpha$	4 M HCl	618 (63.4); 439 (78.9)
$= 6^a$	Acetone	650 (83.4); 444 (125.7)

^a From D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

will be calculated. (In the equation for Q_n , $Z_{\text{H}_2\text{O}}$ is the mole fraction of water, with only water and pyridine N-oxide being considered.)

Since pyridine N-oxide has appreciable basicity in dilute aqueous solution⁸ ($K_{\text{C}_5\text{H}_5\text{NOH}^+} = 0.16$ at 24°), its protonation must be taken into account if this occurs to a significant extent in the solutions studied. The concentration of hydrogen ion was varied in some series of experiments with approximately equal stoichiometric concentrations of pyridine N-oxide. If appreciable protonation of pyridine N-oxide occurs in such solutions, values of provisional equilibrium quotients (Q_n^{\oplus}) involving the total stoichiometric concentration of pyridine N-oxide would vary with hydrogen ion concentration, *i.e.*

$$Q_n^{\oplus} = Q_n \frac{K_{\text{HB}}}{K_{\text{HB}} + [\text{H}^+]}$$

in which Q_n is the equilibrium quotient for the reaction in which $(1/n)$ mole of $\text{Cr}(\text{OH}_2)_{6-n}(\text{ONC}_5\text{H}_5)_n^{3+}$ is formed from $(1/n)$ mole of $\text{Cr}(\text{OH}_2)_6^{3+}$, and K_{HB} is the acid dissociation quotient for pyridine N-oxonium

ion. The concentration of hydrogen ion is not equal to the stoichiometric concentration of acid, and values of Q_n and K_{HB} must be calculated simultaneously from the data. Since the equilibrium quotients Q_n and K_{HB} may show a medium dependence in the relatively concentrated solutions of pyridine N-oxide under consideration, only data taken at particular stoichiometric concentrations of pyridine N-oxide were considered in each calculation. Since each reaction being considered involves an ion of charge 3+ as reactant and product, it will be assumed that the equilibrium quotients do not depend upon ionic strength. The data are, however, only mildly sensitive to the value of K_{HB} , which increases with an increase in the stoichiometric concentration of pyridine N-oxide. Values which are appropriate for the solutions studied are: $C_{\text{C}_5\text{H}_5\text{NO}} = 0.34$ M, $K_{\text{HB}} = 0.15 \pm 0.03$; $C_{\text{C}_5\text{H}_5\text{NO}} = 0.87$ M, $K_{\text{HB}} = 0.6 \pm 0.2$; and $C_{\text{C}_5\text{H}_5\text{NO}} \geq 1.5$ M, $K_{\text{HB}} > 2$. A summary of Q_n values with estimated uncertainties derived from the data and these values of K_{HB} is (the dimensions of each Q is l. mole⁻¹)

$$\begin{aligned} Q_1 &= 3.9 \pm 0.1 \\ Q_{2\alpha} &= 2.6 \pm 0.2 & Q_{2\beta} &= 1.0 \pm 0.1 \\ Q_{3\alpha} &= 1.46 \pm 0.1 & Q_{3\beta} &= 1.52 \pm 0.1 \\ Q_{4\alpha} &= 1.0 \pm 0.1 & Q_{4\beta} &= 0.7 \pm 0.1 \\ Q_5 &= 0.74 \pm 0.1 \end{aligned}$$

(The medium dependence of these equilibrium quotients, for which provision was made in the calculations, was not larger than the experimental uncertainty.)

If there were no medium effects upon isomer distribution, the ratio of [α isomer]/[β isomer] for $n = 2-4$ would be the same in all solutions studied. This is observed within experimental error. For $n = 2$, the values of this ratio for the experiments summarized in Table II are: 7.2, 6.5, 7.3, 6.9, 7.0, 7.2, 6.9, 7.8, and 7.0. For $n = 3$, the values are 0.78, 0.83, 0.93, 0.91, 0.96, 0.97, 0.95, and 0.78. For $n = 4$, only two values are available; each is 4.5.

Discussion

Despite the ease of preparation of coordination compounds containing six pyridine N-oxide molecules bonded as ligands to a central transition metal ion,^{3,4} the stability of mono(pyridine N-oxide)chromium(III) in aqueous solution is not extraordinary. The value $Q_1 = 3.9$ (at 70°) is only slightly greater than the value for the corresponding equilibrium quotient for formation of monochlorochromium(III) ion.^{12,14} The electrostatic factor operating to decrease the relative stability of successive chlorochromium(III) species is, of course, absent in the series of pyridine N-oxide species, and the stabilities of successive pyridine N-oxide chromium(III) species are remarkably constant.

Before a sound comparison of the stabilities of the successive species can be made, however, the statistical contribution to the equilibrium quotients must be taken into account.¹⁵ This will be done by multiplication by the n th root of the ratio of the symmetry numbers of

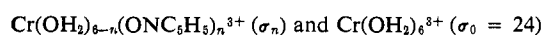
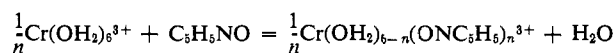


Table IV gives two sets of values, one for the assignment $\alpha = cis$, $\beta = trans$, and one for the assignment $\alpha = trans$, $\beta = cis$. Steric interactions of *cis*-pyridine N-

Table IV. Statistically Corrected Values of the Equilibrium Quotients for Alternate Assignment of Configuration to Isomeric Species



n	$Q_n(70^\circ)$, l. mole ⁻¹	$Q_n(\text{cor})$, l. mole ⁻¹	
		$\alpha = trans$	$\alpha = cis$
1	3.9	0.65	0.65
2 α	2.6	1.5	0.75
2 β	1.0	0.28	0.56
3 α	1.46	0.64	0.73
3 β	1.52	0.76	0.66
4 α	1.0	0.75	0.53
4 β	0.70	0.36	0.52
5	0.74	0.52	0.52
6	(0.5) ^a	(0.5) ^a	(0.5) ^a

^a Estimated from values of $Q_n(\text{cor})$ presented in this table.

oxide ligands might be expected to lower the stability of species in which such interactions are present. If such were the case the assignment of *cis* configuration to the species $n = 2$ (β isomer) would be consistent with the low value of $Q_{2\beta}(\text{cor})$. But if such steric effects are important, low corrected values for both $Q_{3\alpha}$ and $Q_{3\beta}$ would be expected. These are not observed.

On the basis of the relative stabilities of the mono-, di-, and tripyridine N-oxide species, therefore, it seems reasonable to assign tentatively the *cis* configuration to the more easily eluted isomer of bis(pyridine N-oxide)chromium(III) ion. This assignment is the opposite

(14) C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967), and earlier references cited therein.

(15) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

of that which would be based on the generally greater ease of elution of *trans* $\text{MA}_4\text{B}_2^{n+}$ ions compared to the corresponding *cis* species.¹⁶ In the present study, however, one of the ligands (pyridine N-oxide) is much bulkier than those present in species upon which this principle of easier elutibility of *trans* isomers is based. The observed greater efficiency of the cation-exchange resin with lower degree of cross-linking in separating species in the present study demonstrates a difference between (pyridine N-oxide)chromium(III) cations and simpler species. This assignment appears also to conflict with the simple rule that light absorption (in the spectral region of d-d transitions) is greater for *cis*- $\text{MA}_4\text{B}_2^{n+}$ isomers.¹⁷

The assignment of configuration of the isomeric tri species is not possible on the basis of corrected values of the equilibrium quotients since the two isomers have comparable stability and similar symmetries. Although experimental uncertainties make discussion of the isomeric tetra species rather speculative, the data presented in Table IV suggest that the assignment $\alpha = cis$ for $\text{Cr}(\text{OH}_2)_2(\text{ONC}_5\text{H}_5)_4^{3+}$ is more reasonable.

The corrected values of equilibrium quotients suggest that steric factors do not play an appreciable role in determining stability of any of the species. Since pyridine N-oxide is a large ligand, this conclusion might seem surprising. However, the bulkiness of the ligand is distant from the coordination side, and structure studies¹⁸ on di- μ -(pyridine N-oxide)-bis(dichlorocopper(II)) which give dimensions of the ligand suggest that with appropriate conformation of the ligands in the chromium species they will not come in contact, even in *cis* positions relative to one another.

Isolation of appreciable amounts of hexa(pyridine N-oxide)chromium(III) ion from the equilibrated solutions was not achieved. One can estimate $Q_6 \cong 0.5$, which would correspond to a ratio

$$[\text{Cr}(\text{ONC}_5\text{H}_5)_6^{3+}]/[\text{Cr}(\text{OH}_2)(\text{ONC}_5\text{H}_5)_5^{3+}]$$

of ~ 0.2 at the highest concentration of pyridine N-oxide studied, where the penta species accounts for only $\sim 15\%$ of the total chromium. This calculation, although approximate, suggests no inconsistency between the observed stabilities of the species with $n \leq 5$ and the absence of appreciable amounts of hexa species in the solutions studied.

The rule of average environment¹⁹ has been used in predicting the positions of band maxima for species in a series of complexes $\text{MA}_n\text{B}_{6-n}$ such as those in the present study. The rule cannot, of course, be considered a quantitative guide since it would predict the same positions for isomeric species. It is of some

(16) For a number of octahedral $\text{MA}_4\text{B}_2^{n+}$ species, it has been shown that the *trans* isomer (with no net polarity) is the more easily eluted isomer: E. L. King and R. R. Walters, *ibid.*, **74**, 4471 (1952), and later papers. However, it has been suggested that *cis*- $\text{Ru}(\text{NO})(\text{NO}_2)_2(\text{OH}_2)_3^{2+}$ is more easily eluted than the *trans* isomer: D. Scargill, C. E. Lyon, N. R. Large, and J. M. Fletcher, *J. Inorg. Nucl. Chem.*, **27**, 161 (1965). These species are not, of course, of the MA_4B_2 type.

(17) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(18) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965); R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

(19) Discussed by C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 109.

interest, however, to check the rule using the data of Table III, particularly since few series of complexes have been studied for which there are as many data as in the present one. On this basis the expected positions of band maxima would be $n = 1$, 585 and 410 $m\mu$; $n = 2$, 597 and 416 $m\mu$; $n = 3$, 610 and 423 $m\mu$;

and $n = 4$, 623 and 430 $m\mu$. The agreement is not quantitative, but it could be improved by use of an extrapolated value of 462 $m\mu$ for the position of the high-energy band in hexa(pyridine N-oxide)chromium-(III) ion in aqueous solution. (Perhaps the position of this band maximum is sensitive to solvent.)

The Preparation and Characterization of Some New Pentafluorosulfuroxyalkanes and -alkenes¹

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Abstract: By means of the addition reaction of pentafluorosulfur hypofluorite, SF_5OF , with alkenes, three new pentafluorosulfuroxyalkanes have been prepared: $SF_5OCHClCHClF$, $SF_5OCH_2CCl_2F$, and $SF_5OCHBrCHBrF$. A qualitative radical reaction mechanism is presented which is a possible explanation for all the experimental observations associated with these addition reaction systems. The new chloro-substituted alkenes were starting materials for dehydrohalogenation reactions which yielded four new pentafluorosulfoxyalkenes: $SF_5OCCl=CHF$ and $SF_5OCH=CClF$ in both their *cis* and *trans* isomers. One of these alkenes further reacted with SF_5OF to yield a bis(pentafluorosulfuroxy)alkane. Most of the new compounds are reasonably stable, noncorrosive liquids with moderate vapor pressures at room temperature. Molecular structures were established by nmr with other physical measurements supporting the assigned structures. Special attention is given to the complex nmr spectra of $SF_5OCHClCHClF$ which contains two magnetically distinguishable species resulting from the asymmetry associated with the two carbon atoms in this substituted alkane.

After considering the potential usefulness of alkenes that contain the elements of SF_5OF for subsequent studies on the stability of the SF_5O group and of its effect on double-bond reactivity, a convenient preparative route was proposed that would utilize either a dehalogenation or dehydrohalogenation reaction on the corresponding alkane. It had been previously observed that the alkanes could be produced by addition of SF_5OF to certain alkenes³ in which the SF_5O group and the F atom are the two adding groups to the carbon atoms of the double bond.

Zinc dust could not be used to remove chlorine from the alkanes since it reduced the SF_5O group, so a solid-liquid heterogeneous dehydrohalogenation reaction between KOH and the substituted alkane was used to give good yields of the substituted alkene.

The 1,1- and 1,2-dichloroethylenes were used as starting materials in this study.

Experimental Section

General Procedures. Since most of the compounds investigated in this research had conveniently high volatilities, a general-purpose Pyrex glass vacuum system with the usual stopcocks, joints, and manometer was satisfactory for compound manipulation. Reac-

tion vessels of Pyrex glass or metal were used depending on particular reaction conditions.

Reactions between SF_5OF and alkenes can be regarded as potentially dangerous. Therefore, these reactions were initially investigated in metal vessels that could withstand any possible explosion. A prefluorinated 5-cm o.d. copper tube sealed with copper plates (approximate volume, 200 ml) and fitted with a No. 327 Hoke valve was used for large-scale preparative reactions while a prefluorinated 1-cm o.d. closed-end nickel tube fitted with a No. 327 Hoke valve had particular value as a high-pressure reaction vessel. A 1-l. Pyrex glass vessel equipped with a cold finger was also used for addition reactions which were found to proceed slowly. Dehydrohalogenation reactions were carried out in a 50-ml flask equipped with a reflux condenser and mercury bubbler.

Low-boiling products were removed and purified by fractional codistillation⁴ while higher boiling compounds could be separated using a Perkin-Elmer vapor fractometer (Model 154-L) equipped with a detector by-pass and a standard 3-m preparative column of 1-in. aluminum tubing packed with Celite 545 support and Dow Corning silicone grease (0) liquid phase. Relative retention times provided an excellent means for identification of the reaction products.

The infrared spectra of gaseous samples were obtained on a Perkin-Elmer 421 grating spectrophotometer using a 9-cm path-length cell equipped with NaCl windows. Nuclear magnetic resonance spectra were measured on Varian Associates equipment. The A-60 and HA-100 instruments were used for proton spectra, and an A-56.4/60.0 instrument provided the fluorine spectra. Internal standards of trichlorofluoromethane and tetramethylsilane calibrated the spectra. Mass spectra were obtained on Consolidated Electrodynamics Corp. Model 21-103-C and Varian Associates Model M-66 instruments. All mass spectra were taken with ionizing potentials of 70 V.

By using an apparatus similar to that described by Kellogg and Cady,⁵ equilibrium boiling points could be determined for a liquid

(1) This report is taken from the Ph.D. thesis of R. D. Place and was presented in part at the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

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(3) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

(4) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

(5) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).