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SUBSTITUTION REACTIONS OF *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$. III. THE RATE OF SUBSTITUTION OF COORDINATED WATER BY 4-METHYLPYRIDINE, 4-ACETYLPYRIDINE, I^-, NO_2^-, CH_3NH_2, HSO_3^- AND $S_2O_3^{2-}$ *

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CONTENTS

A. INTRODUCTION

In the preceding paper [1] in this series we have presented kinetic studies of the substitution reactions of $Co(CN)_4(SO_3)OH_2^{3-}$ by various nucleophiles such as ammonia, pyridine, thiocyanate, azide, sulfite and cyanide ions [2].

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* Dedicated to the memory of Wayne Keith Wilmarth.

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The substitution reactions all occur by a limiting S_N1 mechanism with a reactive five-coordinate intermediate which is quite long-lived since it exhibits a remarkable discriminating ability in reactions with the above nucleophiles. Furthermore, the sulfito ligand in the *trans* position exhibits a strong kinetic *trans*-labilizing effect. The rate of displacement of ligand water under certain limiting conditions occurs remarkably fast with a half-life, for displacement at 25° and in unit ionic strength solution, of ~ 0.3 s.

In this third paper we report on an extension of the kinetic studies of the replacement of the coordinated water in *trans*-$Co(CN)_4(SO_3)OH_2^{3-}$ by several nucleophiles: 4-methylpyridine (4-mepy), 4-acetylpyridine (4-acpy), I^-, CH_3NH_2, HSO_3^-, $S_2O_3^{2-}$ and NO_2^-. These nucleophiles were selected in order to provide additional insight into the various factors that govern the relative reactivity pattern of the different nucleophiles with the reaction intermediate, $Co(CN)_4(SO_3)^{3-}$.

B. EXPERIMENTAL

(i) Reagents

All inorganic chemicals were reagent grade and used as purchased. The methylamine (40% aqueous solution), 4-methylpyridine (98%) and 4-acetylpyridine (98%) were obtained from the Aldrich Chemical Company and were also used without further purification. The preparation of $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ and its conversion to aqueous $Co(CN)_5(SO_3)OH_2^{3-}$ has been described earlier [1,2].

(ii) Apparatus

The recording spectrophotometer, stopped-flow apparatus, and pH meter were the same as those used in earlier work [1,2].

(iii) Formation constants

The equilibrium quotients, K_f, for the formation of $Co(CN)_4(SO_3)(S_2O_3)^{5-}$ and $Co(CN)_4(SO_3)I^{4-}$ were measured at 25°C and unit ionic strength by monitoring the absorbance changes accompanying the addition of aliquots of aqueous solutions of $Na_2S_2O_3$ and NaI to neutral solutions of $Co(CN)_4(SO_3)OH_2^{3-}$. Because of the rather large values of K_f for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with 4-methylpyridine and CH_3NH_2, it was necessary to study the equilibria in 0.5M OH^- where the predominant form of the Co(III) reactant is $Co(CN)_4(SO_3)OH^{4-}$. The symbol K_i is used to designate the equilibrium quotient determined under these conditions.

Values of the equilibrium quotients K_f for the reaction of I^- and $S_2O_3^{2-}$ with $Co(CN)_4(SO_3)OH_2^{3-}$ were obtained directly from the linear plots of $[Co(III)]/(A - A_0)$ vs. $1/[L^{n-}]$.

In the reactions of 4-methylpyridine with $Co(CN)_4(SO_3)OH^{4-}$ in alkaline solution, values of K_f were calculated using the expression $K_f = K_n K_1$, using the measured value of K_1 and the average value for K_n of 1050 [1,2].

(iv) Kinetic measurements

In general, the kinetic measurements involved use the procedure described earlier [1,2]. In all experiments carried out in which the OH^- concentrations were less than 10^{-3}M, pH control was achieved using dilute sodium borate buffers, with the ionic strength maintained at unity with added $NaClO_4$. In these experiments the pH of the solution was measured immediately after the completion of each reaction. Conversion to an OH^- concentration was effected using a calibration curve relating measured pH and OH^- concentration in a series of solutions of known concentration.

C. RESULTS

(i) Kinetic studies

The kinetic studies of the reaction

$$Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \rightleftharpoons Co(CN)_4SO_3L^{(3+n)-} + H_2O \qquad (1)$$

were carried out at 25° with the ionic strength adjusted to 1.0 or 0.10M with added $NaClO_4$ and/or NaOH. Pseudo-first-order conditions were employed with the nucleophile present in large excess. The values of the pseudo-first-order rate constants, k_{obs}, defined by eqn. 2 were evaluated from the slopes of linear plots of $\log(A - A_0)$ vs. time. In general, the plots were linear for two to three half-lives and reproducible in replicate experiments to ±5%.

$$\frac{-\mathrm{d}\ln\left([Co(CN)_4(SO_3)OH_2^{3-}] - [Co(CN)_4(SO_3)OH_2^{3-}]_{eq}\right)}{\mathrm{d}t} = k_{obs} \qquad (2)$$

In conformity with our earlier work, the results with $L^{n-} = S_2O_3^{2-}$, NO_2^-, I^-, HSO_3^-, 4-mepy, 4-acpy and CH_3NH_2 were all compatible with the following limiting S_N1 mechanism.

$$Co(CN)_4(SO_3)OH_2^{3-} + OH^- \overset{K_n}{\rightleftharpoons} Co(CN)_4(SO_3)OH^{4-} + H_2O \qquad (3)$$

$$Co(CN)_4(SO_3)OH_2^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_4(SO_3)^{3-} + H_2O \qquad (4)$$

$$Co(CN)_4(SO_3)^{3-} + L^{n-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Co(CN)_4(SO_3)L^{(3+n)-} \qquad (5)$$

In this mechanism, the complex $Co(CN)_4(SO_3)OH_2^{3-}$ loses a water molecule from its inner coordination sphere (k_1) to form the reactive intermediate $Co(CN)_4(SO_3)^{3-}$. This species then reacts with either the solvent, H_2O (k_2), or the added nucleophile, L^{n-} (k_3). The rate constant k_4 corresponds to the rate of loss of L^{n-} from the complex $Co(CN)_4(SO_3)L^{(3+n)-}$. The complex $Co(CN)_4(SO_3)OH_2^{3-}$ is in equilibrium with the substitution-inert complex $Co(CN)_4(SO_3)OH^{4-}$. Other pertinent equilibria are:

$$Co(CN)_4(SO_3)OH^{4-} + L^{n-} \overset{K_1}{\rightleftarrows} Co(CN)_4(SO_3)L^{(3+n)-} + OH^- \tag{6}$$

$$Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \overset{K_f}{\rightleftarrows} Co(CN)_4(SO_3)L^{(3+n)-} + H_2O \tag{7}$$

$$Co(CN)_4(SO_3)OH_2^{3-} + H_2O \overset{K_a}{\rightleftarrows} Co(CN)_4(SO_3)OH^{4-} + H_3O^+ \tag{8}$$

The reaction mechanism based on eqns. 3–5, when combined with the usual steady-state approximation, leads to the following relationship between k_{obs} and the kinetic parameters:

$$k_{obs} = \frac{\alpha k_1[L^{n-}]}{k_2/k_3 + [L^{n-}]} + \frac{k_4k_2/k_3}{k_2/k_3 + [L^{n-}]} \quad \text{where } \alpha = \frac{1}{1 + K_n[OH^-]} \tag{9}$$

In order to explain the kinetic results, it is necessary to assume that the reactive intermediate $Co(CN)_4SO_3^{3-}$ generated in reaction 4 has a lifetime long enough to exhibit a selective reactivity pattern towards the various nucleophiles in the system and that the ratio $55k_2/k_3$ is a measure of the relative rates of scavenging of H_2O and L^{n-} by $Co(CN)_4SO_3^{3-}$.

Before considering the experimental data it should be noted that there are several equations which provide relationships between the kinetic parameters and the various equilibrium quotients defined by eqns. 3–8. The ratio $k_1k_3/k_2k_4 = K_f$ can be used to test the internal consistency of the data by comparing this calculated value of K_f with an experimental value or with the value calculated using the expression $K_f = K_1K_n$.

Values of k_4 were obtained, in the manner previously described, by measuring k_{obs} in a solution in which aqueous OH^- at $\mu = 1.0$M was rapidly added to a dilute neutral solution of $Co(CN)_4(SO_3)L^{(3+n)-}$ containing a slight excess of L^{n-} at the same ionic strength. Microscopic reversibility restrictions require that the aquation reaction proceeds by the reverse of reaction 5, followed by the reverse of reaction 4, followed by the rapid conversion of $Co(CN)_4(SO_3)OH_2^{3-}$ to the kinetically inert $Co(CN)_4(SO_3)OH^{4-}$.

(ii) Ligation by iodide ion

The values of k_{obs} for the reaction

$$Co(CN)_4(SO_3)OH_2^{3-} + I^- \rightleftarrows Co(CN)_4(SO_3)I^{4-} + H_2O \tag{10}$$

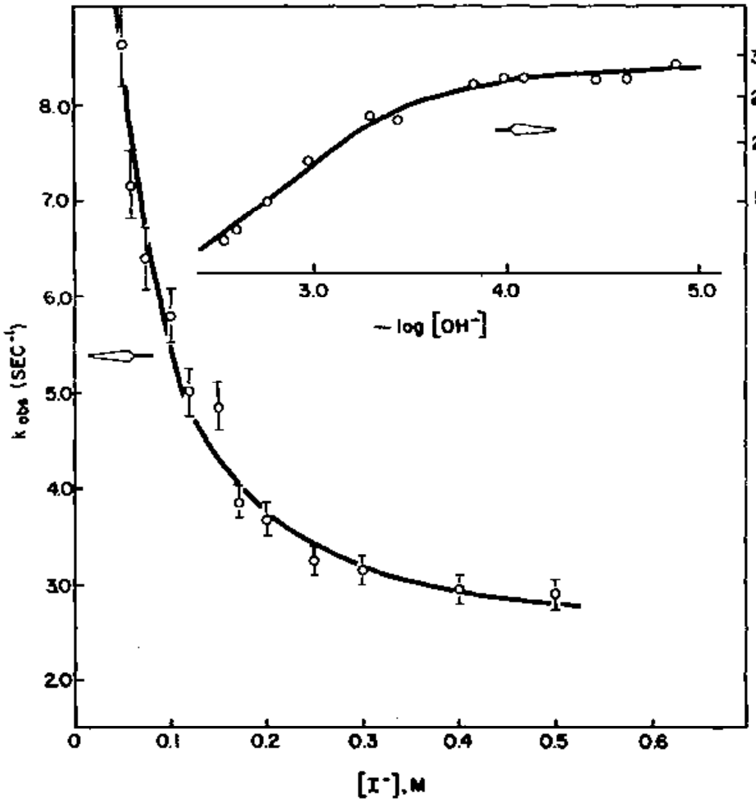

Fig. 1. Variation of k_{obs} with $[I^-]$ for the substitution of I^- on the complex $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C and unit ionic strength. $[OH^-] = 1.30 \times 10^{-5}M$. Variation of k_{obs} with $[OH^-]$ for the formation of $Co(CN)_4(SO_3)I^{4-}$ via reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with iodide ion. $T = 25.0°C$; $\mu = 1.00M$; $[I^-] = 0.50M$ (insert).

were measured over a range of I^- concentrations from 0.05 to 0.50M and OH^- concentrations ranging from 2.82×10^{-3} to $1.30 \times 10^{-5}M$. The results are depicted graphically in Fig. 1.

The appearance of Fig. 1, a plot of k_{obs} vs. $[I^-]$ at $[OH^-] = 1.30 \times 10^{-5}M$, is in sharp contrast with the corresponding results obtained with all other nucleophiles in that k_{obs} decreases with increasing I^- concentration. This unique and unusual kinetic behavior is readily explicable; it occurs in all limiting S_N1 mechanisms whenever $k_4 > k_1$. Consideration of eqn. 9 indicates that as $[I^-]$ approaches zero, the intercept approaches the value of $k_{obs} = k_4$. In the other limit, at $[I^-] \gg k_2/k_3$ and with $\alpha = 1.0$, the limiting value of k_{obs} is k_1. Thus, if $k_4 > k_1$, then k_{obs} must decrease on increasing $[I^-]$.

The results of the second series of experiments at a constant $[I^-]$ of 0.50M and variable alkalinity are presented as the upper curve in Fig. 1, a plot of k_{obs} vs. $-\log[OH^-]$.

A computer-assisted, non-linear least-squares fit of the experimental kinetic data to eqn. 9 yielded the values of k_1, k_2/k_3, k_4 and K_n which are listed in Table 1. These values were used, together with eqn. 9, to calculate the theoretical values of k_{obs} at various concentrations of iodide and hydroxide in Fig. 1 (solid line). It is clear from examination of this figure that the experimental results are in excellent agreement with the derived rate expression.

Comparison of the experimental values of k_{obs} for the I^- studies with those calculated using the least-squares parameters and eqn. 9 yielded an average relative deviation of 3.2% for 23 experiments. Because of the steepness of the plot of $[I^-]$ vs. k_{obs}, and the relatively large intercept at $[I^-] = 0.0M$ (k_4), the values of k_2/k_3 and k_4 cannot be determined with high precision. The values reported for the I^- ligation are probably accurate to within a factor of two.

(iii) Ligation by $S_2O_3^{2-}$, NO_2^-, 4-acpy and 4-mepy

The dependence of k_{obs} on $[L^{n-}]$ for the replacement of H_2O ligand in the inner coordination sphere of $Co(CN)_4(SO_3)OH_2^{3-}$ by $S_2O_3^{2-}$ and 4-acpy was studied at low hydroxide ion concentration ($[OH^-] < 2 \times 10^{-5}M$; borate buffer, 0.0179M), unit ionic strength, and at 25.0°. The results for the thiosulfate system are depicted in Fig. 2 together with the 4-acpy results. At very low hydroxide ion concentration, $K_n[OH^-] \ll 1$, k_{obs} should be virtually independent of $[OH^-]$ or K_n. Therefore, it should be possible to fit the experimental data to eqn. 9 using an approximate value of K_n. Seven earlier kinetic studies of related ligation reactions of $Co(CN)_4(SO_3)OH_2^{3-}$ yielded values of K_n which fall in the range 776–1114 M^{-1} [1,2]. A value of K_n of 1050 was used in the fitting of the experimental data to the theoretical rate expression (eqn. 9). At the hydroxide ion concentrations used in these studies an error of even 20% in the value of K_n would only result in an error in the value of the ratio $1/(1 + K_n[OH^-])$ of less than 0.35%. An error of this magnitude is insignificant relative to the scatter of the experimental kinetic data. The least-squares parameters obtained for these reactions are listed in Table 1. In Fig. 2 the solid lines represent the theoretical curves calculated using the least-squares parameters and eqn. 9. There is an average relative deviation from the least-squares line of 2.3% for the thiosulfate system (12 experiments), and 3.6% for the 4-acetylpyridine system (10 experiments).

The values of the pseudo-first-order rate constants, k_{obs}, for the ligations by NO_2^- and 4-mepy were measured at low hydroxide ion concentration

TABLE 1

Summary of rate and equilibrium constants for the reaction $Co(CN)_4(SO_3)OH_2^{3-} + L^{n-} \rightleftharpoons Co(CN)_4(SO_3)L^{(n+3)-} + H_2O$ [a]

L	k_l (s^{-1})	$10^3 k_2/k_3$ (M)	$55k_3/k_2$	$10^2 k_4$ (s^{-1})	K_n	K_f (calc.) (M^{-1})	K_f (measured) (M^{-1})
SO_3^{2-} [b]	2.5 ±0.3 [c]	380 ±50	1.5 ×10^2	(7.2 ± 0.4)×10^{-4}	1062± 30	9 ×10^5	—
$S_2O_3^{2-}$ [d]	2.7 ±0.1	95 ± 8	5.8 ×10^2	24.2 ± 0.6	—	116	122
HSO_3^- [d]	2.8 ±0.2	52 ± 6	1.06×10^3	—	776± 34	large	—
CN^- [e]	1.73±0.07	28.4± 1.0	1.9 ×10^3	0	—	1.6×10^3	—
NO_2^- [d]	2.00±0.15	14 ± 2	3.9 ×10^3	9.0 ± 0.5	—	4.3×10^5	6.5×10^5
CH_3NH_2 [d]	3.2 ±0.1	9.6± 0.6	5.8 ×10^3	0.072± 0.003	1000± 95	(2.6±0.4)×10^2	(2.5±0.3)×10^2
N_3^- [f]	2.2 ±0.1	7.5± 1.3	7.3 ×10^3	115 ±10	807± 54	(5.9±0.5)×10^4	(7.9±0.5)×10^4
NH_3 [b]	2.1 ±0.1	7.0± 0.4	7.9 ×10^3	0.51 ± 0.04	1093± 85	(5.1±0.8)×10^2	(5.0±0.3)×10^2
SCN^- [f]	2.3 ±0.1	5.9± 1.0	9.3 ×10^3	78 ± 8	—	(1.9±0.2)×10^4	—
4-acpy [d]	3.0 ±0.2	5.2± 0.6	1.06×10^4	2.9 ± 0.2	—	4.4×10^4	5.6×10^4
4-mepy	2.6 ±0.1	5.1± 0.4	1.08×10^4	1.17 ± 0.08	1114±58	(6.9±0.6)×10^4	(4.5±0.5)×10^4
py [f]	2.5 ±0.1	2.9± 0.4	1.9 ×10^4	1.25 ± 0.10	933±110	6.4	4.7
I^- [d]	2.15±0.08	2.3	2.4 ×10^4	14500			

[a] All data at unit ionic strength and 25°C. [b] Data from ref. 7. [c] Indicated uncertainties are computer-calculated standard deviation. [d] Data from this work. [e] Data from ref. 6. [f] Data from ref. 8.

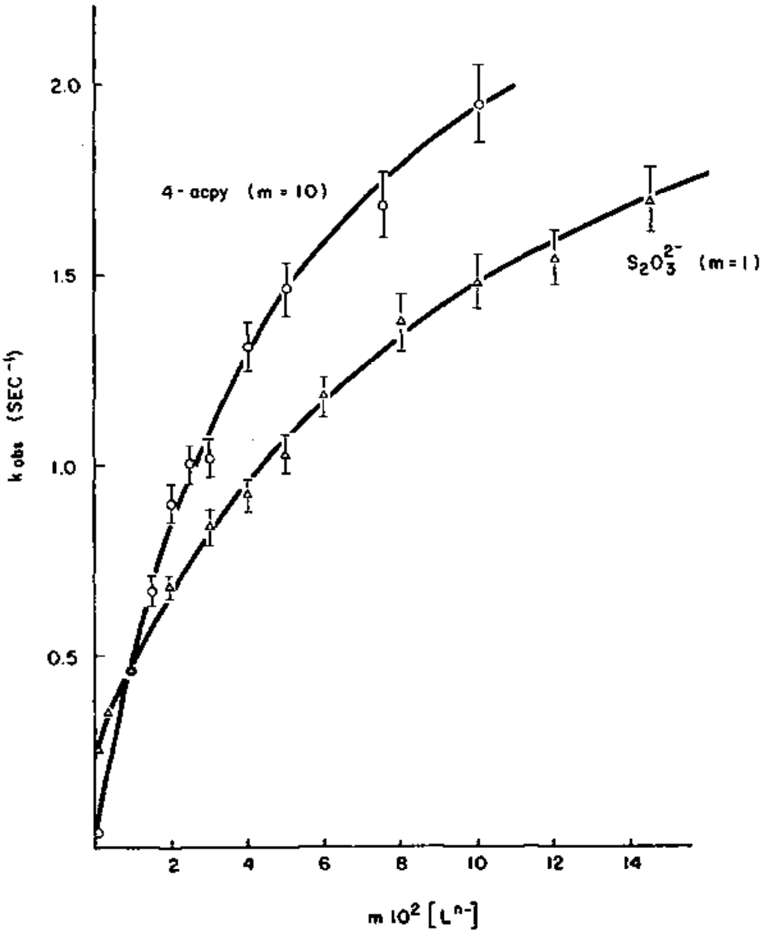

Fig. 2. Variation of k_{obs} with [4-acpy] (○) and [$S_2O_3^{2-}$] (△) for ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ by 4-acpy ([OH^-] = 1.66×10^{-5}M) and $S_2O_3^{2-}$ ([OH^-] = 1.82×10^{-5}M). T = 25.0°C; $\mu = 1.00$M.

(1.80×10^{-5}M) and over a wide range of nucleophile, L^{n-}, concentration (0.5–10^{-2}M). These reactions were studied in solutions of both 1.0 and 0.10M ionic strength. The kinetic data are depicted graphically in Figs. 3 and 4. The choice of the hydroxide ion concentration follows the same reasoning as in the $S_2O_3^{2-}$ and 4-acpy systems. A computer-assisted, least-squares fit of the experimental values of k_{obs} to eqn. 9 using a value of K_n of 1050 yielded the resulting parameters listed in Tables 1 and 2. Figures 3 and 4 show the excellent correspondence between the theoretical solid lines and the experimental points. The relative average deviations are 4.5% (15 experiments at $\mu = 1.0$M) and 4.0% (9 experiments at $\mu = 0.10$M) for the 4-mepy reaction,

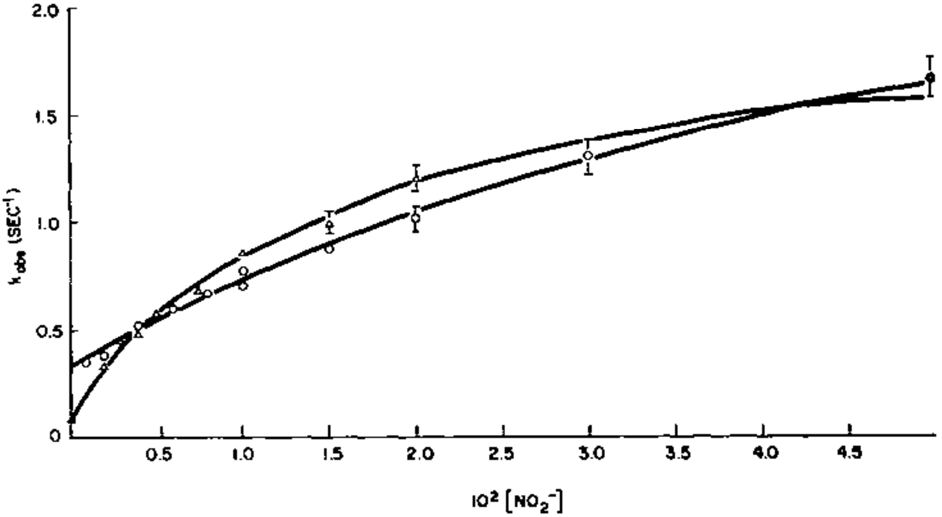

Fig. 3. Variation of k_{obs} with [NO_2^-] for the ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ by NO_2^- at 1.00M ionic strength (△) and 0.10M ionic strength (○). T = 25.0°C; [OH^-] = 1.80×10^{-5}M (0.018M borax buffer).

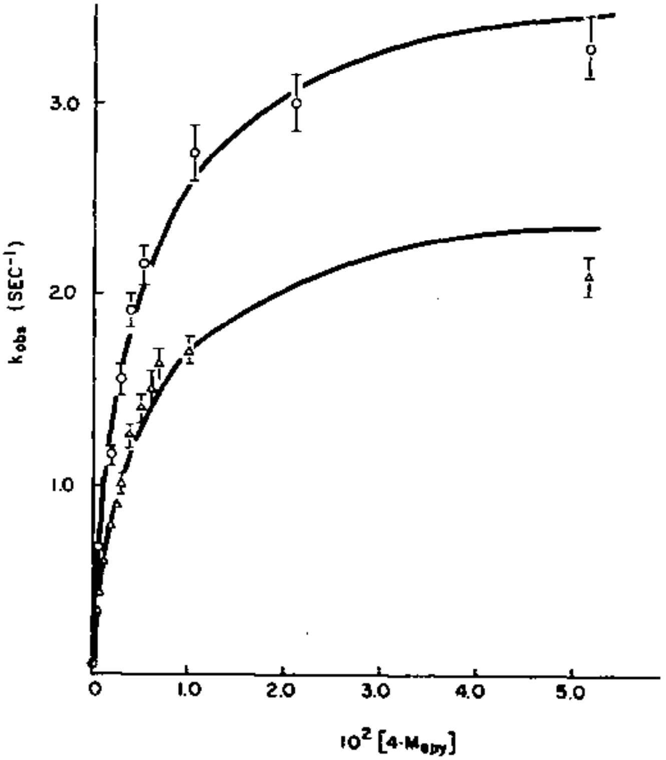

Fig. 4. Variation of k_{obs} with [4-mepy] for the ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ by 4-mepy at 1.00M ionic strength (△) and 0.10M ionic strength (○). T = 25.0°C; [OH^-] = 1.80×10^{-5}M (0.018M borax buffer).

TABLE 2

Summary of rate and equilibrium constants for the reaction *trans*-$Co(CN)_4(SO_3)L^{(3+n)-}$ + H_2O at 25°C and $\mu = 0.10M$

L	k_1 (s^{-1})	$10^3 k_2/k_3$ (M)	$10^2 k_4$ (s^{-1})	K_f (calc.) (M^{-1})
NO_2^-	3.6 ±0.6	70 ±18	33 ±1	1.6×10^3
4-mepy	3.85±0.15	4.6± 0.4	3.0±0.2	2.8×10^4

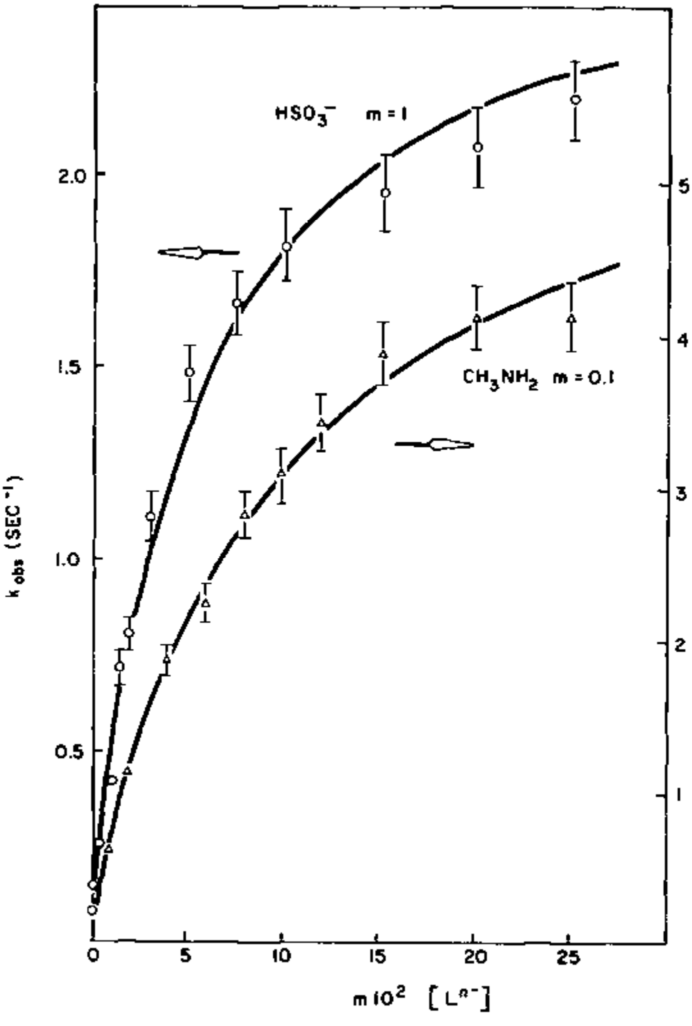

Fig. 5. Variation of k_{obs} with $[HSO_3^-]$ (○) and $[CH_3NH_2]$ (△) for the ligation of $Co(CN)_4(SO_3)OH_2^{3-}$ by HSO_3^- ($[H^+] = 0.11\text{–}5.3 \times 10^{-4}M$) and CH_3NH_2($[OH^-] = 0.50M$). T = 25.0°C; $\mu = 1.00M$.

and 4.5% (10 experiments at $\mu = 1.0M$) and 3.3% (11 experiments at $\mu = 0.10M$) for the NO_2^- reaction.

(iv) Ligation by CH_3NH_2

The kinetics of the ligation by methylamine were followed at unit ionic strength, 25.0°C, and with the $[OH^-]$ held at 0.050M. At this concentration of OH^-, the fraction of the total methylamine which is present as $CH_3NH_3^+$ is negligible.

No attempt was made to study the variation of k_{obs} with $[OH^-]$ since the experiments would have been limited to the narrow range of $[OH^-]$ from 0.050 to 1.0M. Under these conditions, determination of K_n is not possible and thus it is again necessary to use an approximate value of K_n in fitting the experimental data to the expression for k_{obs}. The kinetic results for the methylamine system are shown in Fig. 5. In making the computer fit of the experimental results to eqn. 9 a value of 1050 M^{-1} was assumed. In addition, our calculations show that the value of the kinetic parameter of primary interest here, k_2/k_3, is fortunately quite insensitive to the value chosen for K_n. If a value of K_n of 970 M^{-1} (± 98), the average of the seven values of K_n thus far determined, is used, the value of k_2/k_3 is the same. The overall fit of the data (11 experiments) to eqn. 9 is quite good with an average relative deviation of only 2.4%.

(v) Ligation by HSO_3^-

The kinetics of the replacement of H_2O by HSO_3^- in the complex $Co(CN)_4(SO_3)OH_2^{2-}$ was studied at unit ionic strength with the concentration of HSO_3^- varied from 1.0×10^{-3} to 0.25M. The results are shown as the upper curve in Fig. 5. In order to keep the free sulfite in the bisulfite form, the pH of the reactant solutions were kept between 3 and 5. Under these conditions, the equilibrium is shifted far to the right [3] and the rate constant

$$Co(CN)_4(SO_3)SO_3H^{4-} + H_2O \rightleftarrows Co(CN)_4(SO_3)_2^{5-} + H_3O^+ \tag{11}$$

for loss of H_2O from the complex $Co(CN)_4(SO_3)OH_2^{3-}$ (k_1) is independent of pH. Since the reaction being followed does not go to completion, the rate expression for the reaction must include the contribution from all of the paths which correspond to the reverse reactions, i.e., formation of $Co(CN)_4(SO_3)OH_2^{3-}$ or $Co(CN)_4(SO_3)OH^{4-}$. A previously reported study [3] of the kinetics of the acid-induced hydrolysis of $Co(CN)_4(SO_3)_2^{5-}$ suggests the following mechanism (eqns. 12–16):

$$Co(CN)_4(SO_3)_2^{5-} + H_2O \xrightarrow{k_5} Co(CN)_4(SO_3)OH_2^{3-} + SO_3^{2-} \tag{12}$$

$$HCo(CN)_4(SO_3)_2^{4-} \overset{K_4}{\rightleftarrows} H^+ + Co(CN)_4(SO_3)_2^{5-} \tag{13}$$

$$HCo(CN)_4(SO_3)_2^{4-} + H_2O \xrightarrow{k_6} Co(CN)_4(SO_3)OH_2^{3-} + HSO_3^- \tag{14}$$

$$H_2Co(CN)_4(SO_3)_2^{3-} \overset{K_5}{\rightleftarrows} H^+ + HCo(CN)_4(SO_3)_2^{4-} \tag{15}$$

$$H_2Co(CN)_4(SO_3)_2^{3-} \xrightarrow{k_7} Co(CN)_4(SO_3)OH_2^{3-} + SO_2 \tag{16}$$

The expression for the first-order rate constant derived for the above mechanism is shown below:

$$k_{obs} = \frac{k_5 K_4 K_5 + k_6 K_5[H^+] + k_7[H^+]^2}{K_4 K_5 + K_5[H^+] + [H^+]^2} \tag{17}$$

where $k_5 = (7.2 \pm 0.4) \times 10^{-6}\ s^{-1}$, $k_6 = (2.0 \pm 0.4) \times 10^{-1}\ M^{-1}\ s^{-1}$, $k_7 = (9.8 \pm 1.3) \times 10^{-1}\ s^{-1}$, $K_4 = (1.8 \pm 0.4) \times 10^{-1} M$ and $K_5 = (6.0 \pm 2.3) \times 10^{-2} M$. This expression thus corresponds to k_4 in eqn. 9. In order to simplify the treatment of the data for this system, the results were fitted to eqn. 9 as in the previous sections. The value of k_4, however, was calculated using eqn. 17 and the $[H^+]$, which was measured immediately following completion of the reaction. The values of k_{obs}, $[HSO_3^-]$, and the corresponding calculated values of k_4 were then used to determine the least-squares values of the parameters k_1 and k_2/k_3 by non-linear least-squares analysis. (In using eqn. 9, the factor $1/(1 + K_n[OH^-])$ was neglected since under the conditions of the experiments $K_n[OH^-] \ll 1$.) The resulting values of k_1 and k_2/k_3 are 2.8 ± 0.2 and $0.052 \pm 0.006\ s^{-1}$, respectively.

As for the previously studied nucleophiles, the values of k_1, k_2/k_3 and k_4 were then used to calculate k_{obs}. These calculated values are represented as the solid curve in Fig. 5. The average relative deviation between the calculated and experimental values of k_{obs} (14 experiments) is 7.8%.

(vi) Formation constants

The equilibrium constants for the formation of the complexes $Co(CN)_4(SO_3)(S_2O_3)^{5-}$, $Co(CN)_4(SO_3)I^{4-}$, $Co(CN)_4(SO_3)mepy^{3-}$ and $Co(CN)_4(SO_3)CH_3NH_2^{3-}$ were measured at 25.0°C and unit ionic strength. Using the experimental data depicted in Fig. 6, values of the formation constants, K_f, were calculated as described in Section B and are listed in Table 1. These values of K_f were then used to calculate the solid curves in Fig. 6 and thus illustrate graphically the excellent fit of the experimental points to the theoretical curves.

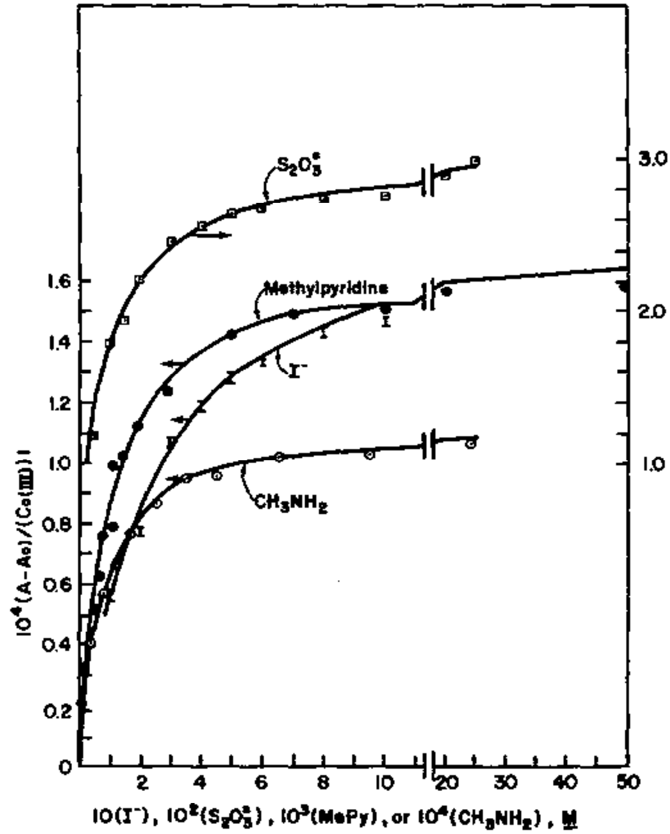

Fig. 6. Variation of absorbance with $[CH_3NH_2]$, $[I^-]$, [4-methylpyridine] and $[S_2O_3^{2-}]$ for ligation of the complex $Co(CN)_4(SO_3)OH_2^{3-}$ at 25.0°C and unit ionic strength.

D. DISCUSSION

(i) Reactivity towards the intermediate

The parameter k_2/k_3 is the ratio of rate constants for the reaction of the proposed reactive intermediate $Co(CN)_4(SO_3)^{3-}$ with water (k_2) and the nucleophile L^{n-} (k_3). In these studies the ratio has not been corrected for the concentration of water. Assuming medium effects are negligible, a comparison of the values of k_2/k_3 obtained for a series of nucleophiles will yield the order of reactivity of the various nucleophiles towards $Co(CN)_4(SO_3)^{3-}$.

It is usually assumed that differences in nucleophilicity of various nucleophiles arise from differences in charge, basicity in the Arrhenius sense, and polarizability. In the previous paper [1], we commented on the lack of correlation of the reactivity of the nucleophiles studied towards $Co(CN)_4(SO_3)^{3-}$, with the basicity of those nucleophiles. The results reported here reinforce our earlier conclusions. The kinetic and thermodynamic parameters for those nucleophiles studied thus far in solutions of unit ionic strength are summarized in Table 1. The reactivities of the various nucleophiles relative to H_2O can be calculated using the expression $55k_3/k_2$ and are also listed in Table 1. A comparison of this pattern with the order of the pK_a values of the conjugate acids of the nucleophiles (i.e., CH_3NH_2 [4] > NH_3 > CN^- ~ SO_3^{2-} > 4-mepy [4] > py > N_3^- > 4-acpy [5] > NO_2^- > $S_2O_3^{2-}$ > SCN^- > I^-) and with the order of the stability constants of the complexes of the various nucleophiles with the soft acid CH_3Hg^+ (i.e., CN^- > $S_2O_3^{2-}$ > NH_3 > SCN^- > py > NO_2^-) [6], indicates a lack of correlation. When similar comparisons are made for nucleophiles having identical charge there is still no parallel between the reactivity towards $Co(CN)_4(SO_3)^{3-}$ and the basicity towards the proton or the methylmercury ion or other accepted scales of nucleophilicity. Despite the fairly large range of pK_a values of the three pyridines, for example (4-acpy, 3.51 [5]; py, 5.30 [4]; 4-mepy, 6.03 [4]), there is little if any difference in reactivity between them. There has been a recent suggestion that the scavenging abilities of nucleophiles towards the five-coordinate intermediates in the ligation of $Rh(H_2O)_6^{3+}$ and $RhCl_5(H_2O)^{2-}$ by Cl^- and Br^- are primarily a result of coulombic interactions [7]. We have also commented on the apparent correlation of the reactivity of the various nucleophiles, L^{n-}, with charge type in ligation of $Co(CN)_4(SO_3)OH_2^{3-}$. With the extension of the kinetic studies to those reported here, this correlation is less apparent. There is considerable overlap of the values of $55k_3/k_2$ for the charged and uncharged nucleophiles. This overlap is a direct result of the relatively high ionic strength of the solutions in which the reactions were studied. For the uncharged species of L^{n-}, $55k_3/k_2$ corresponds to a ratio of rate constants for two reactions between uncharged nucleophiles (L and H_2O) and a charged substrate ($Co(CN)_4(SO_3)^{3-}$), therefore $55k_3/k_2$ should be independent of the ionic strength. On the other hand, the values of $55k_3/k_2$ obtained for reactions of negatively charged nucleophiles correspond to the ratio of rate constants for reaction of a charged complex with a negatively charged nucleophile (k_3) to the rate constant for reaction of a negatively charged complex with an uncharged species, i.e., H_2O (k_2), and therefore, the value of $55k_3/k_2$ should decrease as the ionic strength is reduced since the value of k_3 would decrease relative to k_2. This is based on a qualitative application of the Bronsted–Bjerrum equation [8]. These predictions are confirmed in the results of the kinetic studies at low (0.10M) ionic strength. The value of $55k_3/k_2$ is virtually unchanged for the 4-mepy reaction when the ionic strength is reduced from 1.0 to 0.10M, while it is decreased by a factor of approximately five for the NO_2^- reaction. The values of the corresponding ratios for the SO_3^{2-} reactions should be even more greatly affected by a reduction in ionic strength. However, kinetics of these reactions at low (0.10M) ionic strength were not studied since reliable values for the kinetic parameters could not be obtained because of the reduced curvature of the k_{obs} vs. $[L^{n-}]$ plots caused by both the increase in k_2/k_3 and the concentration limits on the nucleophile forced by the ionic strength. If one extrapolates the reactivity pattern, as measured by $55k_3/k_2$, to low ionic strength the order shows a clear separation into charge type, i.e., py > 4-mepy ~ 4-acpy > NH_3 > CH_3NH_2 > I^- > SCN^- > N_3^- > NO_2^- > CN^- > HSO_3^- > SO_3^{2-} Therefore, it seems likely that the major factor influencing the reactivity pattern is coulombic repulsion of the incoming nucleophile by the negatively charged reactive intermediate, $Co(CN)_4(SO_3)^{3-}$.

It is clear that H_2O does not fit into this scheme. It is far less reactive than its neutral nature would predict; for example, correcting k_2/k_3 for the solvent concentration (~ 55M), H_2O is approximately 9000 times less reactive than SCN^- and 150 times less reactive than SO_3^{2-} in solutions of unit ionic strength. It is possible that low reactivity of H_2O reflects its special position as solvent and its orientation about the reactive intermediate.

In the case of the $Co(NH_3)_4SO_3^+$ system, for which the following reactivity pattern has been reported [9]: OH^-, ~ 1×10^4; SO_3^{2-}, 2×10^2; NO_2^-, 58; CN^-, ~ 40; SCN^-, 30; NH_3, 1 ($\mu = 1.0M$; $T = 25°C$), a similar extrapolation to low ionic strength can be made. The above reactivity pattern is likely to remain unchanged since the reactivity of the charged nucleophiles would be expected to increase relative to NH_3, with that for SO_3^{2-} increasing more than the uninegative ions such as CN^-. This increased sensitivity of dinegative ions, relative to uninegative ions, to the ionic strength, would probably not be sufficient to make SO_3^{2-} a better nucleophile than OH^-. The very great reactivity of hydroxide ion toward the $Co(NH_3)_4SO_3^+$ intermediate may again be related to the special position of H_2O as solvent and the possibility of a Grotthus-type mechanism in the reaction of OH^- with $Co(NH_3)_4SO_3^+$. Therefore, the above nucleophiles, with the exception of OH^-, would also fall into a charge-type order at low ionic strength, with the more highly negatively charged nucleophiles being the most reactive toward the positively charged intermediate $Co(NH_3)_4SO_3^+$. This is reasonable if charge considerations are of primary importance.

The values of k_2/k_3 (uncorrected for $[H_2O]$) for reactions of $Co(CN)_5(OH_2)^{2-}$ are Br^-, 10; NH_3, 6.71; I^-, 5.15; SCN^-, 2.95; py, 2.33; and N_3^-, 1.90 ($\mu = 1.0M$; $T = 40°C$) [10]. Although the effect of ionic strength on these values of k_2/k_3 should be less than for the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ because of the smaller negative charge of the intermediate, $Co(CN)_5^{2-}$, an extrapolation to low ionic strength should yield a separation of nucleophiles into charge types as in the above systems. This is concluded on the basis of the small range of the reactivates in solutions of unit ionic strength.

REFERENCES

1 W.K. Wilmarth, J.E. Byrd, H.N. Po, H.K. Wilcox and P.H. Tewari, Coord. Chem. Rev., 51 (1983) 181 and references therein.
2 P.H. Tewari, R.W. Gaver, H.K. Wilcox and W.K. Wilmarth, Inorg. Chem., 6 (1967) 611.
3 H.H, Chen, M-S. Tsao, R.W. Gaver, P.H. Tewari and W.K. Wilmarth, Inorg. Chem., 5 (1966) 1913.
4 D.D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solution. IUPAC, Butterworths, London, 1965.
5 S. Cabani and G. Conti, Gazz. Chim. Ital., 95 (1965) 533.
6 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd edn. Wiley, New York, 1967, pp. 138–141.
7 R.J. Buchacek and G.M. Harris, Inorg. Chem., 15 (1976) 926.
8 A.A. Frost and R.G. Pearson, Kinetics and Mechanism, Wiley, New York, 1961, p. 150.
9 J.M. Pratt and R.G. Thorp, in H.J. Emelius and A.G. Sharp (Eds.), Advances in Inorganic Chemistry and Radiochemistry. Academic Press, New York, 1969, p. 406.
10 R. Barca, J. Ellis, M-S. Tsao and W.K. Wilmarth, Inorg. Chem., 6 (1967) 243.