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Effects of SO_2, HSO_3^-, and SO_3^{2-} as Auxiliary Ligands on the Reactivity of Ammineruthenium(II)-Ligand Bonds

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The values of pK corresponding to the equilibria (trans forms) $[Ru(NH_3)_4SO_2H_2O]^{2+} + H_2O = [Ru(NH_3)_4(HSO_3)H_2O]^+ + H^+$ and $[Ru(NH_3)_4(HSO_3)H_2O]^+ = [Ru(NH_3)_4SO_3H_2O] + H^+$ at 25° and ionic strength *ca.* 0.10 have been measured as 2.15 ± 0.1 and 5.05 ± 0.1, respectively. These values have been applied in interpreting data on the rate of replacement of water in the trans tetraammine by pyrazine (pz) as a function of pH. The specific rates for substitution into the sulfito, the bisulfito, and sulfur dioxide complexes at 25° have been determined as 13.5 ± 0.1, 0.20 ± 0.01, and 0.033 ± 0.004 M^{-1} sec^{-1}, respectively. From data on the reverse reaction, the equilibrium constant for the reaction $[Ru(NH_3)_4SO_3H_2O] + pz = [Ru(NH_3)_4SO_3pz] + H_2O$ at 25° is calculated as 3×10^3. Data on rates as a function of temperature have been obtained and, as well, data with isonicotinamide as the entering group. In *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ the rate of substitution is independent of the concentration of the entering ligand over a wide range of concentration. Substitution, rather than occurring by replacing H_2O, waits on release of ammonia trans to SO_3^{2-}, and in the concentration range covered by our studies, this is the rate-determining step in the overall reaction.

Sulfite ion in recent times has attracted considerable attention because of the strong labilizing effect it has on ligands trans to it in cobalt(III) complexes.[1-5] Though sulfito and sulfur dioxide complexes of ruthenium ammines[6,7] have been known for almost four decades, the labilizing or delabilizing effects exerted by these ligands in this class of complexes have not heretofore been investigated systematically. The present study is part of an effort devoted to exploring the effect on the lability of the Ru(II)-OH_2 bonds and on the stability of the complexes of replacing NH_3 in $[(NH_3)_5Ru\text{-}OH_2]^{2+}$ by other ligands. Because of the important role which back-donation[8-10] plays in the binding of unsaturated ligands to Ru(II), the effects are not necessarily simple extensions of those observed for Co(III) or those expected for Ru(III).

The evidence for strong back-donation which is presented in the references cited is spectroscopic in nature or involves comparisons of reactivity. Back-bonding has been invoked also to explain the short Ru-SO_2 (2.07 Å) bond length in *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$.[11] The π component to the binding and the circumstance that the coordinated sulfite adopts the several forms SO_2, HSO_3^-, and SO_3^{2-} attracted us to the present study. It deals with the rate of substitution in *cis*- or *trans*-$[Ru^{II}(NH_3)_4L(OH_2)]$ (L = SO_2, HSO_3^-, or SO_3^{2-}) by various nitrogen heterocyclics, as well as with the rate of loss of the nitrogen heterocyclic from the complexes.

Experimental Section

A. Materials. Pyrazine,[12] Puriss grade 99+%, purchased from Aldrich Chemical Co., Inc., was used as supplied.

Isonicotinamide[12] (Aldrich) was twice recrystallized from water before use.

The methylpyrazinium tosylate was prepared by M. Clark. *Anal.* Calcd for $[C_5H_7N_2]C_7H_7SO_3$: C, 53.9; H, 5.24; N, 10.5. Found: C, 53.8; H, 5.33; N, 10.3.

Except for those preparations which are described below, all other chemicals used were reagent grade and were used as supplied.

B. Preparation of the Ruthenium Complexes. ***trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ and $[Ru(NH_3)_5SO_2]Cl_2$.** These compounds were prepared following literature methods.[6,7,11] Microanalysis gave the following results for $[Ru(NH_3)_4Cl(SO_2)]Cl$. *Anal.* Calcd: N, 18.42; H, 3.98; S, 10.53; Cl, 23.36; Ru, 33.22. Found: N, 18.47; H, 3.81; S, 10.79; Cl, 23.41; Ru, 33.15. Calcd for $[Ru(NH_3)_5SO_2]Cl_2$: N, 21.81; H, 4.71; S, 9.96; Ru, 31.5; Cl, 22.12. Found: N, 21.72; H, 4.50; S, 10.15; Ru, 31.1; Cl, 21.76.

***trans*-$[Ru(NH_3)_4(SO_2)isn](CF_3SO_3)_2$.** One-tenth gram of *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$ was added to 0.25 g of isonicotinamide in 7 ml water and stirred for 5 min at room temperature. An intense yellow-orange color developed immediately. The solution was then filtered and an equal volume of 3 M CF_3SO_3H was added to the filtrate. After the solution was cooled in the refrigerator, fine orange needles developed. These were filtered, washed with ethanol and ether, and then dried in a vacuum desiccator. Yields obtained were 80-85%. *Anal.* Calcd for $[Ru(NH_3)_4(SO_2)isn](CF_3SO_3)_2$:

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(7) K. Gleu, W. Breuel, and K. Rehm, *Z. Anorg. Allg. Chem.*, 235, 201, 211 (1938).
(8) P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968).
(9) P. C. Ford, *Coord. Chem. Rev.*, 5, 75 (1970).
(10) R. E. Shepherd and H. Taube, *Inorg. Chem.*, 12, 1392 (1973).
(11) L. Vogt, J. Katz, and S. Wiberley, *Inorg. Chem.*, 4, 1157 (1965).
(12) Pyrazine will often be denoted as pz, isonicotinamide as isn, and *p*-toluenesulfonate ion as tosylate.

C, 14.70; N, 12.86; S, 14.73; H, 2.76; Ru, 15.7. Found: C, 14.71; N, 12.54; S, 15.18; H, 2.76; Ru, 15.7.

trans-$[Ru(NH_3)_4(SO_2)pz](C_7H_7SO_3)_2$. For this compound the procedure just described was followed but the precipitating anion was tosylate, added as an equal volume of saturated sodium tosylate to the filtrate which has been acidified with 5 ml of 3 *M* CF_3SO_3H. In this case, long brown needles were obtained. *Anal.* Calcd for $[Ru(NH_3)_4(SO_2)pz](C_7H_7SO_3)_2$: C, 32.29; N, 12.43; H, 4.64; S, 14.81; Ru, 15.5. Found: C, 32.97; N, 12.82; H, 4.62; S, 14.67; Ru, 15.4.

cis-$[Ru(NH_3)_4(SO_2)H_2O](PF_6)_2$. Brief mention of this compound was made by Gleu,[13] but a detailed preparative method was not described. The method herewith recorded produces the compound in *ca.* 25% yield and is preferred to an alternative method which was tried, in which the entering ligand was predominantly in the SO_2 form.

The ion *cis*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ was generated by reducing *cis*-$[Ru(NH_3)_4Cl_2]Cl$ (180 mg in 10 ml of water) with zinc amalgam. An equimolar amount of $NaHSO_3$ was added and the solution was left at room temperature for 5 min. Thereupon it was acidified with HPF_6 (1 ml of concentrated acid) and concentrated to half its volume by rotary evaporation. On adding NH_4PF_6, a light brown solid formed. This was recovered by filtration, washed with ethanol and ether, and dried. *Anal.* Calcd for $[Ru(NH_3)_4(SO_2)H_2O](PF_6)_2$: C, 0.0; N, 10.35; S, 5.9; Ru, 18.7; H, 2.60. Found: C, 0.90; N, 11.37; S, 6.1; Ru, 19.7; H, 2.76. The alternative method produced a material giving a better analysis, but in very low yield (~5%).

C. Methods. 1. Titration of *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$. About 200 mg of *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ was dissolved in 10–20 ml of doubly distilled, deaerated water and transferred to a cell holding a combination electrode. The titrating solution, 1.00 *N* NaOH, measured by means of a glass micrometer calibrated to read 0.001 ml, was conducted through a stainless steel needle connected to a section of fine polyethylene tubing passing through a serum cap. The temperature was 25° ± 1, measured during the experiment. Standard NBS buffers at pH 4.01 and 6.86 (25.0°) were used to standardize the pH meter. In order to evaluate the dissociation constants at the low-pH range, the ruthenium salt had to be used at relatively high concentration (*ca.* 0.03 *M*). In one experiment, 0.1 *M* NaCl was also present; in this experiment, the ionic strength varied from 0.19 at low pH to 0.16 at high pH. Other experiments were done without added NaCl, but with [Ru(II)] at somewhat higher concentration. The p*K* values were not significantly different for the two sets of experiments.

It should be noted that the replacement of Cl^- by H_2O in $[Ru(NH_3)_4(SO_2)Cl]^+$ is essentially complete on the time scale of dissolution; as a result, the values of p*K* refer to the aquo rather than the chloro complex.

2. Rate Measurements. (a) Substitution in *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ and Derived Complexes. (i) Pyrazine as Entering Ligand. The rate of substitution for the reaction

$$trans\text{-}[Ru^{II}(NH_3)_4(L)H_2O] + pz = trans\text{-}[Ru^{II}(NH_3)_4(L)pz] + H_2O \quad (1)$$

(where L is SO_2, HSO_3^-, or SO_3^{2-}) was studied using a Cary 15 spectrophotometer. Acidity was controlled with buffers–Na_2CO_3–$NaHCO_3$ for the pH range 10.0–8.3 and NaOAc–HOAc for the pH range 5.5–3.5—or for the more acidic range with HCl. Ionic strength was maintained with sodium chloride. Concentrations of ligand and of Ru(II) were fixed by measuring the requisite volumes of the respective stock solutions. For pH 10–4.4, mixtures of 3.5–4.0 ml of buffer and 1.0–1.5 ml of 0.01 *M* pyrazine solution were degassed with argon in a 2.0-cm cell (covered tightly with a serum cap) for 15 min and then placed in a thermostated Cary 15 cell compartment and left there for 20–30 min. The ruthenium solution was also equilibrated in the same water bath. To initiate reaction, 0.25 ml of the ruthenium solution was syringed quickly into the cell and the reaction was followed at λ 400 nm. In all cases, reaction was followed to more than 95% completion. Ionic strength was maintained at 0.1 *M* for pH 10-4.4 and at 0.08 *M* for the runs at higher acidity.

With $[Ru(NH_3)_5OH_2]^{2+}$ [14,10] as reactant, complications arising from oxidation of Ru(II) by the ligand have been reported. No evidence for such side reactions was encountered with the more weakly reducing Ru(II) complexes used in our studies.

(ii) Isonicotinamide as Entering Ligand. This ligand was used only at high pH, ≥5. At lower pH rates become very slow owing to protonation of the ligand ($pK_a = 3.5$).[15] There is no evidence that the protonated form of the ligand reacts on the time scale of the experiments. The concentration of isonicotinamide was varied over the range 1.5×10^{-3} to 0.1 *M*. For the high ligand concentrations, a stopped-flow instrument was used.[16] Solutions of 0.02–0.2 *M* isonicotinamide in 0.1 *M* $NaHCO_3$ were mixed with 2×10^{-4} *M* Ru(II) solution in 0.1 *M* $NaHCO_3$ at 25°. The oscilloscope traces obtained (at λ 400 nm) were recorded on Polaroid 146-L film.

(iii) Methylpyrazinium Tosylate. In contrast to isonicotinamide, the free nitrogen on methylpyrazinium ion is very hard to protonate. This made it a useful ligand to study in acidic solutions (up to 2 *M* acid). Experiments were done using 0.08 *M* stock solution and were followed spectrophotometrically at λ 550 nm.

To cover the high-acid range, 60 mg of methylpyrazinium tosylate was dissolved in 2.0 ml of 2 *M* CF_3SO_3H; 0.5 ml of a 10^{-3} *M* Ru(II) solution was added and the reaction was monitored at λ 540 nm.

(b) Substitution in $Ru(NH_3)_5SO_3$ and in *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ Complexes. A series of experiments with variable amounts of pyrazine (0.1–1.0 ml of 1.0 *M* stock solution at an ionic strength (NaCl) of 0.1) were pipetted into a 2-cm cell containing 4.0 ml of 0.1 *M* $NaHCO_3$. The volume was made up to 5.0 ml with 0.1 *M* NaCl. From here on the procedure was the same as that used for *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$.

(c) Aquation of *trans*-$[Ru(NH_3)_4(SO_3)pz]$ and *trans*-$[Ru(NH_3)_4(SO_3)isn]$ and Derived Forms. About 1 mg of the desired analyzed solid was dissolved in 20 ml of degassed water and 1.0 ml of this solution was quickly syringed into 24 ml of 0.1 *M* $NaHCO_3$ in a 10-cm cell. The decrease in absorbance at 400 nm was monitored. At these concentrations, ~5×10^{-6} *M*, there is no interference from the forward reaction. The variation of rate with temperature was studied for the aquation of the pyrazine complex.

In all cases, the ruthenium salts were dissolved in 0.01 *M* HCl to minimize the aquation of the trans ammonia (see Results). Solids were weighed, dissolved, and used directly for each run.

3. Calculations. Pseudo-first-order rate constants were determined graphically from plots of log $(A_\infty - A_t)$ *vs.* time (where A_∞ and A_t are the final absorbance and that at time t, respectively) yielding values of k_{obsd}. The ligand concentration exceeded that of Ru(II) by at least a factor of 10. Good pseudo-first-order behavior was observed in all cases, proving that the reactions are first order in [Ru(II)]. By changing the initial concentration of ligand, the reaction order in ligand was determined, and specific rates were determined. As will presently appear, in some systems the reactions were first order and in others zero order in the ligand. In studying the rate of formation of the complex, under some conditions, namely at low ligand concentration the formation reactions were incomplete. Under these circumstances and with ligand in excess the specific rate k_{obsd} is given by $k_1(L) + k_{-1}$ where k_1 is the second-order specific rate for the formation reaction and k_{-1} the first-order specific rate for the reverse reaction. The values of k_{-1} can be found without complication by the $k_1(L)$ term because at the low concentration of complex used in measuring the rates of aquation, 5×10^{-6} *M*, this reaction is essentially complete.

With pyrazine as the nucleophile the formation reaction was studied over a wide range in pH where at one extreme Ru(II) is present as the sulfite and at the other predominantly as the sulfur dioxide complex. The specific rate corresponding to substitution in $[Ru(NH_3)_4(SO_3)H_2O]$ could readily be evaluated at high pH. At lower pH's, the sulfito complex contributes virtually nothing to the rate. Using the known values of p*K* and the rate constant recorded above for the substitution in $[Ru(NH_3)_4(SO_3)H_2O]$, the specific rate for the substitution in $[Ru(NH_3)_4(HSO_3)H_2O]^+$ and $[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ were computed using a least-squares computer program[17] to fit the variation of rate with pH (eq 4; *vide infra*).

For the reaction of pyrazine with $[Ru(NH_3)_4(SO_3)H_2O]$, the variation of rate with temperature was studied. These experiments were done at a pH sufficiently high (above *ca.* pH 8) so that conversion to the sulfito complex was virtually complete and as a result no complications by the equilibria involving formation of the bisulfito or sulfur dioxide complexes were introduced.

Equilibrium constants for the association of isonicotinamide and pyrazine were determined by a kinetic method, combining measurements of the rate of loss of ligand, k_{-1}, for a particular complex with the rate of formation of the complex, k_1.

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(17) The program NIHH23 LEASQR was used: R. I. Shrager, *J. Ass. Comput. Machinery*, 17, No. 3 (July 1970). The program was run by M. J. Clark, whose assistance is gratefully acknowledged.

Results

1. Band Maxima and Extinction Coefficients for the Complexes. The observations on the absorption characteristics of the complexes germane to this study are shown in Table I.

2. Titration of *trans*-$Ru(NH_3)_4(SO_2)(H_2O)^{2+}$ by Alkali. The results for the titration of the trans SO_2 complex (0.025 *M*, 0.10 *M* NaCl, 25°) are shown in Figure 1. From the graph, two p*K* values can be determined, one at 2.15 ± 0.1 and the other at 5.05 ± 0.1. The first of these is taken to correspond to the reaction

$$[Ru(NH_3)_4(SO_2)H_2O]^{2+} + H_2O \overset{K_1}{\rightleftharpoons} [Ru(NH_3)_4(HSO_3)H_2O]^{+} + H^{+} \quad (2)$$

and the second to

$$[Ru(NH_3)_4(HSO_3)H_2O]^{+} \overset{K_2}{\rightleftharpoons} [Ru(NH_3)_4(SO_3)H_2O] + H^{+} \quad (3)$$

It is unlikely that dissociation of coordinated H_2O comes into question in the pH range under consideration—note that for *trans*-$[Ru(NH_3)_4isnH_2O]^{2+}$ the pK_a at 25° has been determined as 11.7.[18] If the charge on the aquo complex is a dominant factor in determining pK_a for acid dissociation of the water, pK_a for $Ru(NH_3)_4(SO_3)H_2O$ would be expected to be even greater than 11.7.

It should be noted that $[Ru(NH_3)_5SO_2]^{2+}$ and *cis*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ cannot be titrated by the slow procedure available to us, owing to release of the ammonia molecule trans to S(IV).

3. Substitution in *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$. In Table II, the results for pyrazine as the entering group (and in Table VI those for the reverse reaction) are summarized. Using the appropriate values of k_{-1} the values of $k_{obsd}/[L]$ are corrected to yield those for k_1 (*cf.* column 5).

Since the form of the ruthenium complex changes with pH, the values of k_1 are also expected to change. From the known values of the equilibrium constants, K_1 and K_2, governing the interconversions of the sulfito, bisulfito, and sulfur dioxide forms (*cf.* reactions 2 and 3) and the measurements of k_1 as a function of pH, the specific rate coefficients for substitution of a ligand into the sulfite complex (k_{SO_3}), the bisulfite complex (k_{HSO_3}), and the sulfur dioxide complex (k_{SO_2}) can be calculated. If these specific rates are assumed to be independent of pH, k_1 as a function of $[H^+]$ is given by

$$k_1 = \frac{k_{SO_2}[H^+]^2 + k_{HSO_3}K_1[H^+] + k_{SO_3}K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (4)$$

At low values of $[H^+]$ this function reduces to k_{SO_3} and at high values to k_{SO_2}. When the data of Table II were treated by the method outlined in the Experimental Section, k_{SO_2}, k_{HSO_3}, and k_{SO_3} were calculated as 0.033 ± 0.004, 0.01, and 13.5 M^{-1} sec^{-1}, respectively. Figure 2 shows the theoretical curve calculated using these specific rates and the known values for K_1 and K_2. It appears from the agreement of the experimental points with the calculated curve that the data are fully accounted for by the simple assumption made.

At the lowest pH of Table II, 1.35, only 15% of the total pyrazine is in the form of pyrazinium ion. An experiment at 2 *M* acid using methylpyrazinium ion as the nucleophile yielded for k_{obsd} the value 0.050 sec^{-1} (*cf.* Table IV). When this is corrected for the reverse reaction—for this purpose k_{-1} was assumed to be the same as it is for pyrazine—k_1 is calculated as 0.034 M^{-1} sec^{-1}. Methylpyrazinium for present purposes is probably a good stand-in for pyrazinium ion, and thus it appears that a correction for the conversion of pyrazine to pyrazinium ion at pH 1.3 is too small to be significant.

It needs to be acknowledged that because of the difference in ionic strength between the titration and the rate studies, the values of K_1 and K_2 recorded are not strictly applicable to the rate experiments. Attention has already been drawn to the fact that K_1 and K_2 appear not to be very sensitive to ionic strength in the range covered. Moreover, the values of k_{SO_2}, k_{HSO_3}, and k_{SO_3} are not very sensitive to K_1 and K_2.

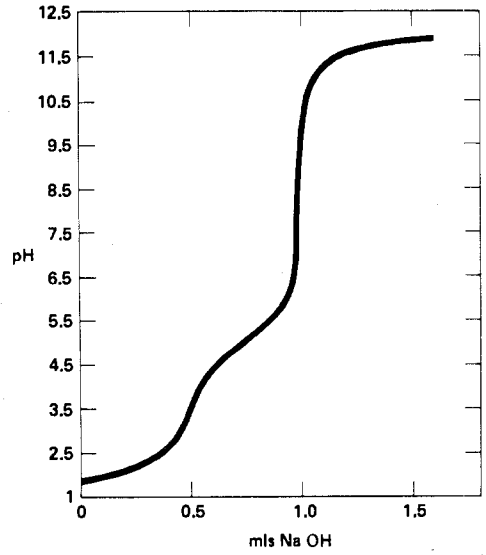

Figure 1. Titration curve for *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ (20 ml of 0.025 *M*) with NaOH (1.00 *M*) (25°).

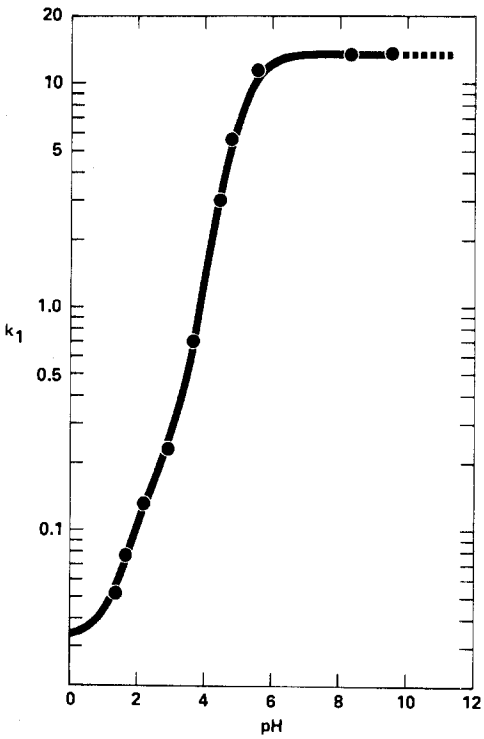

Figure 2. A semilog plot for the variation of k_1 with pH for eq 4. The black circles represent the experimental points. The solid line is the predicted variation when experimental values for K_1, K_2, and k_{SO_3} and calculated values for k_{HSO_3} and k_{SO_2} were substituted in eq 4.

(18) C. G. Kuehn, work in progress.

Table I. Uv-Vis Band Maxima (nm) and Extinction Coefficients (M^{-1} cm^{-1}) for the Sulfur Dioxide and Sulfite Complexes

Complex	Band maxima (extinction coefficients)		Conditions
$[Ru(NH_3)_5SO_2]^{2+}$	288 (4.0×10^3)	225 sh (1.1×10^3)	1 M CF_3SO_3H
trans-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$	281 (4.3×10^3)	220 sh (1.0×10^3)	1 M CF_3SO_3H
cis-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$	288	225 sh	1 M CF_3SO_3H
trans-$[Ru(NH_3)_4(SO_3)H_2O]$	343 (240)	250 sh (440)	0.1 M $NaHCO_3$
trans-$[Ru(NH_3)_4(SO_3)isn]$	417 (6.6×10^3)	*a*	0.1 M $NaHCO_3$
trans-$[Ru(NH_3)_4(SO_3)pz]$	433 (5.7×10^3)	*a*	0.15 M $NaHCO_3$
trans-$[Ru(NH_3)_4(SO_3)N$  $NCH_3]^+$	580	*a*	0.1 M $NaHCO_3$

[a] Experiments done by dissolving the solid complex in excess of ligand solution in $NaHCO_3$. The uv part of the spectrum is not seen due to free ligand absorption.

Table II. Substitution in *trans*-$Ru(NH_3)_4(SO_2)H_2O^{2+}$ and Derived Forms by Pyrazine[a]

T, °C	pH	[Pyrazine], M	k_{obsd}/[ligand], M^{-1} sec^{-1}	k_1, M^{-1} sec^{-1}	Ionic strength
25.0	9.50	2.86×10^{-3}	15.2	13.6	0.1 M (Na_2CO_3–$NaHCO_3$)
	9.50	2.86×10^{-3}	15.0	13.4	0.1 M (Na_2CO_3–$NaHCO_3$)
25.0	8.35	2.86×10^{-3}	15.2	13.6	0.1 M ($NaHCO_3$)
	8.35	2.86×10^{-3}	15.1	13.5	0.1 M ($NaHCO_3$)
25.0	5.55	2.86×10^{-3}	13.0	11.6	0.1 M (acetate buffer)[c]
	5.55	2.86×10^{-3}	13.1	11.7	0.1 M (acetate buffer)[c]
25.0	4.88	2.86×10^{-3}	6.82	5.65	0.1 M (acetate buffer)[c]
	4.88	2.86×10^{-3}	6.71	5.54	0.1 M (acetate buffer)[c]
25.0	4.45	2.86×10^{-3}	4.06	2.94	0.1 M (acetate buffer)[c]
	4.45	2.86×10^{-3}	4.22	3.10	0.1 M (acetate buffer)[c]
25.0	3.65	4.76×10^{-2}	0.76	0.735	0.08 M (acetate buffer)[c]
	3.65	4.76×10^{-2}	0.69	0.672	0.08 M (acetate buffer)[c]
25.0	2.90	4.76×10^{-2}	0.240	0.230	0.08 M (acetate buffer)[c]
	2.90	4.76×10^{-2}	0.235	0.230	0.08 M (acetate buffer)[c]
25.0	2.17	3.81×10^{-2}	0.151	0.134	0.08 M (NaCl–HCl)
	2.17	3.81×10^{-2}	0.145	0.128	0.08 M (NaCl–HCl)
25.0	1.63	5.71×10^{-2}	0.096	0.088	0.08 M (NaCl–HCl)
	1.63	5.71×10^{-2}	0.093	0.085	0.08 M (NaCl–HCl)
25.0	1.35	3.81×10^{-2}	0.070	0.053	0.08 M (NaCl–HCl)
	1.35	3.81×10^{-2}	0.070	0.053	0.08 M (NaCl–HCl)
24.8	8.35	1.91×10^{-3}	15.25	12.88	0.1 M ($NaHCO_3$)
	8.35	1.91×10^{-3}	15.55	13.19	0.1 M ($NaHCO_3$)
20.8	8.35[b]	1.91×10^{-3}	9.6	8.35	0.1 M ($NaHCO_3$)
	8.35	1.91×10^{-3}	9.3	8.09	0.1 M ($NaHCO_3$)
16.2	8.35[b]	1.91×10^{-3}	6.7	5.12	0.1 M ($NaHCO_3$)
	8.35	1.91×10^{-3}	6.04	5.43	0.1 M ($NaHCO_3$)
9.8	8.35[b]	1.91×10^{-3}	3.11	2.92	0.1 M ($NaHCO_3$)
	8.35	1.91×10^{-3}	3.34	3.16	0.1 M ($NaHCO_3$)
29.75	8.35[b]	1.91×10^{-3}	25.65	20.82	0.1 M ($NaHCO_3$)
	8.35	1.91×10^{-3}	26.1	21.24	0.1 M ($NaHCO_3$)

[a] $[Ru(II)] = 5 \times 10^{-5}$ M. [b] As measured at 25°. In this pH range, the complex is predominantly in the sulfito form and the reaction rates are insensitive to small changes in pH. [c] Ionic strength maintained with NaCl.

This is clearly the case for k_{SO_3}, because conditions can be found under which Ru(II) is virtually completely converted to the sulfito complex. This argument applies also to k_{SO_2} and k_{HSO_3}, but with decreasing force on this order.

In Table II are recorded, also, data for the rate of substitution by pyrazine at pH 8.35 for a variety of temperatures. Since at this pH the Ru(II) complex is essentially completely converted to the sulfito form, the data can be used to calculate the activation parameters for the process

trans-$[Ru(NH_3)_4(SO_3)H_2O]$ + pz =
trans-$[Ru(NH_3)_4(SO_3)pz]$ + H_2O (5)

The values of $\Delta H^{\ddagger}_{SO_3}$ and $\Delta S^{\ddagger}_{SO_3}$ obtained applying the Eyring equation to the data are 16.3 ± 0.8 kcal mol^{-1} and 0.8 ± cal mol^{-1} deg^{-1}.

In Table III, the results with methylpyrazinium as entering group are summarized. These measurements were undertaken mainly to assess how seriously the rate of substitution is affected by protonating the pyrazine. The specific rate at highest acidity, where $[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ is the dominant form of Ru(II), is ~0.034 M^{-1} sec^{-1}. The

Table III. Methylpyrazinium Ion as Nucleophile[a]

pH	$10^2 \cdot$ [L], M	k_{obsd}/[L],[b] M^{-1} sec^{-1}	pH	$10^2 \cdot$ [L], M	k_{obsd}/[L],[b] M^{-1} sec^{-1}
2.7	3.05	0.14	1.7	3.05	0.12
2.05	3.05	0.13	2.0 M CF_3SO_3H	9.5	0.05

[a] $[Ru(II)] = 5 \times 10^{-5}$ M; temperature 25.0°; ionic strength 0.10 M, except in last experiment where it was 2.0 M. [b] Each entry is an average of two experiments.

comparison to k_{SO_2} as recorded above, 0.033 M^{-1} sec^{-1}, indicates that protonation of pyrazine does not seriously affect the rate of substitution. This is a rather surprising result because the statistical factor of 2 operates to decrease the rate for methylpyrazinium ion relative to that for pyrazine. It should be noted the values of k_{obsd}/[ligand] for the two ligands agree rather well, also, at somewhat higher pH's.

In the experiments with pyrazine, the concentration of the ligand was not varied systematically. But throughout the series of experiments recorded in Table II, this variable did change significantly and the internal consistency of the

results as displayed in Figure 2 constitutes at least indirect evidence that the rate of reaction is first order in [ligand]. With isonicotinamide as the entering ligand, a large change in the concentration was covered. This was done for the dual purpose of determining the order with respect to [ligand] and also of learning if the rate becomes less than first order in ligand at the higher levels of concentration. "Rate saturation" with increasing ligand concentration sets in when an intermediate formed from the reactant is scavenged so efficiently by the nucleophile that the intermediate is depleted below its equilibrium concentration. In these circumstances, it is possible to estimate the specific rate for the formation of the intermediate. The results of Table IV show that the rate of complex formation is fairly strictly first order in [ligand] over a 60 range in concentration, and no evidence for "rate saturation" is observed even in the stopped flow range of rates.

4. Substitution in *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ and in $[Ru(NH_3)_5SO_3]$. The systems are closely related with respect to their kinetic behavior and on this account are reported together (Table V). The specific rate k_{obsd} in Table V is defined by the rate law $d[product]/dt = k_{obsd}[Ru(II)]$.

In contrast to *trans*-$[Ru^{II}(NH_3)_4(SO_3)H_2O]$, where the rate of substitution is first order in the entering ligand, when NH_3 is trans to the sulfite group, the rate of reaction proves to be independent of the concentration of the entering ligand. The fact that the rate is virtually identical for the two complexes dealt with in Table V shows that the systems have a rate-determining process in common. These observations are understood if it is assumed that for both *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ and $[Ru(NH_3)_5SO_3]$ the rate-determining step is replacement of NH_3 trans to SO_3^{2-} by H_2O. The spectrum of the product of the reaction of pz with $[Ru(NH_3)_5SO_3]$ (λ_{max} at 433 nm) was observed to be identical with that obtained with *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$ as reactant. When the cis complex is the reactant, λ_{max} for the product is at 432 nm, and from the similarity in the spectrum to those mentioned above, we conclude that the product is $[Ru(NH_3)_3pzSO_3H_2O]$ where pz is trans to SO_3^{2-}.

5. Aquation Rates for Isonicotinamide- and Pyrazine-Tetraamminesulfitoruthenium(II) Complexes. The data on the rate of replacement by water of the heterocyclic ligands pyrazine and isonicotinamide from their respecitve complexes are summarized in Tables VI and VII. Those for *trans*-$[Ru(NH_3)_4(SO_2)pz]$ cover a wide pH range. At the highest pH, 8.35, the data can safely be taken as referring to the sulfito complex as reactant and at the lowest pH, 1 *M* HCl, to the sulfur dioxide complex. These specific rates at 25.0° are 4.5×10^{-3} and 0.8×10^{-3} sec^{-1}, respectively (value extrapolated from 25.5° using the known temperature coefficient). The data at pH 8.35 serve to fix the activation parameters $\Delta H^{\ddagger}_{-1}$ and $\Delta S^{\ddagger}_{-1}$ for the loss of pyrazine from the sulfito complex. These are 25.8 ± 1.0 kcal mol^{-1} and 17.4 ± 3.3 cal mol^{-1} deg^{-1}.

It should be noted that at pH 5.5 the rate has almost reached the "saturation value," showing that at this pH the complex is almost completely in the sulfito form. Using the values of k_{-1} at intermediate pH's and choosing $k_{-1} = 0.7 \times 10^{-3}$ M^{-1} sec^{-1} as applying to the sulfito path, pK_2 for the reactant is calculated as 4.6 (the value at pH 4 was omitted as showing an extreme variance).

For the isonicotinamide complex, Table VII, the entries at pH 8.3 apply to the loss of the ligand from the sulfito form of the complex while at the lowest pH the complex is probably predominantly in the sulfur dioxide form.

6. Equilibrium Constants. Using the specific rates for the forward and reverse reactions, the equilibrium constants for reactions 6-8 at 25° are calculated as 2.9×10^3, 40, and 3.8×10^3. For reaction 6, using the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ applying to the forward and reverse processes, ΔH and ΔS are calculated as −9.5 ± 1.8 kcal mol^{-1} and −16.6 ± 4 cal mol^{-1} deg^{-1}.

Table IV. Isonicotinamide as Nucleophile[a]

pH	[Isonicotinamide], *M*	k_{-1}, M^{-1} sec^{-1}	pH	[Isonicotinamide], *M*	k_{-1}, M^{-1} sec^{-1}
8.35	1.5×10^{-3} [b]	24[c]	8.35	0.10[d]	23
8.35	0.01[d]	25	5.3	0.01[d]	21.5
8.35	0.01[d]	23			

[a] [Ru(II)] = 5×10^{-5} *M*; temperature 25.0°; ionic strength 0.10. [b] Using a Cary 15 spectrophotometer. [c] Rate has been corrected for k_{-1}(aquation); correction is not significant at 0.01 *M* ligand. [d] Using stopped-flow instrument.

Table V. Substitution by Pyrazine in *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ and $[Ru(NH_3)_5SO_3]$[a]

cis-$[Ru(NH_3)_4(SO_3)H_2O]$		$[Ru(NH_3)_5SO_3]$	
[Pyrazine], *M*	10^3k_{obsd}, sec^{-1}	[Pyrazine], *M*	10^3k_{obsd}, sec^{-1}
0.19	9.7	0.191	9.2
0.19	9.9	0.191	9.5
0.57	10.3	0.57	9.6
0.57	10.1	0.57	9.7
0.091	10.5	0.091	9.8
		0.091	9.6

[a] At 25.0°; [Ru(II)] = 5×10^{-5} *M*; μ = 0.1 *M* ($NaHCO_3$-NaCl).

Table VI. Aquation Rate of *trans*-$[Ru(NH_3)_4(SO_2)pz]^{2+}$ and Derived Forms[a]

T, °C	pH	10^3k_{-1}, sec^{-1}	*T*, °C	pH	10^3k_{-1}, sec^{-1}
25.0°	~1 *M* HCl	0.8	25.0	5.5	4.0
	1.25	0.7	25.5	8.35	4.9
	1.55	0.5		8.35	5.0
	2.20	0.7	30.4	8.35	9.53
	2.95	0.7		8.35	9.68
	3.65	1.1	36.9	8.35	26.6
	4.4	3.0	18.40	8.35	1.62
	4.8	3.35		8.35	1.52

[a] Ionic strength kept at 0.1 *M* ($NaHCO_3$, acetate buffer, NaCl). In the first experiment only, HCl was used. [Complex] = (0.4–0.6) × 10^{-5} *M*.

Table VII. Aquation Rates for *trans*-$[Ru(NH_3)_4(SO_3)isn]$[a]

pH	k_{-1}, sec^{-1}	Ionic strength
8.3	6.3×10^{-3}	0.1 *M* ($NaHCO_3$)
8.3	6.4×10^{-3}	0.1 *M* ($NaHCO_3$)
<1 (0.3 *M* HCl)	5.1×10^{-4}	0.3 *M* (HCl)

[a] At 25.0°; [Ru(II)] = 5×10^{-5} *M*.

trans-$[Ru(NH_3)_4(SO_3)H_2O]$ + pz = *trans*-$[Ru(NH_3)_4(SO_3)pz]$ + H_2O (6)

trans-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$ + pz = *trans*-$[Ru(NH_3)_4(SO_2)pz]^{2+}$ + H_2O (7)

trans-$[Ru(NH_3)_4(SO_3)H_2O]^{2-}$ + isn = *trans*-$[Ru(NH_3)_4(SO_3)isn]$ + H_2O (8)

Discussion

The X-ray diffraction work on salts containing SO_2 complexes of ruthenium(II) ammines show that S rather than O is linked to the metal. It is reasonable to assume that this structural feature is retained in solution. There is support of this assumption in the fact that the Ru(II)-S(IV) bond is very slow to dissociate, whichever of the three forms the

S(IV) ligand assumes. Without exception thus far, complexes with monodentate ligands oxygen-linked to Ru(II) are very labile[19] and usually also rather unstable. By contrast, the Ru-S bond in $[Ru(NH_3)_5(CH_3)_2S]^{2+}$ aquates very slowly.[20] The reasonable course of the titration of the SO_2 complex by alkali supports the view that Ru-S bonding is retained throughout the three forms which the ligand on Ru(II) can assume.

The values of pK_1 and pK_2 for coordinated SO_2 have been measured as 2.15 ± 0.1 and 5.05 ± 0.1; these values can be compared to 1.76 and 7.21 for the free acid. The purely inductive effect of the positive charge on the metal ion is expected to increase the acidity of coordinated S(IV) by a factor of at least 10^3 (HOAc coordinated to $[Ru(NH_3)_5]^{2+}$ is *ca.* fivefold more acidic than is free HOAc;[19] in the present system, the dispositive metal ion is one atom closer to the OH bond, and an enhancement of the effect of the ion by a factor of 600 might therefore be expected).[21] To explain the lower acidity of the coordinated compared to free SO_2, an opposing effect needs to be invoked. This can reasonably be assumed to be back-donation, which is expected to be greater for SO_2 than for HSO_3^-. A similar effect, but less marked, may also be in play for the second stage of association. The value of pK_2 for *trans*-$[Ru(NH_3)_4(SO_3)pz]$, 4.6, is only approximate, but it seems to be accurate enough to support the conclusion that the π acid ligand pz enhances the acidity of coordinated S(IV).

The rates of reaction of pz and isn with *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$ are increased *ca.* 250-300-fold over the rates reported for $[Ru(NH_3)_5H_2O]^{2+}$.[22] If the reactions are interpreted as involving pentacoordinated species as intermediates, and if the competition ratios for $[Ru(NH_3)_5]^{2+}$ and $[Ru(NH_3)_4SO_3]$ reacting with ligand *vs.* water are assumed to be the same, the 250-300-fold increase in rate can be interpreted as resulting from labilization of the Ru(II)-H_2O bond by SO_3^{2-}. Both of these assumptions appear to be reasonable and are tacit in some of the discussion which follows; none of the results, it should be added, constitute proof that a pentacoordinated intermediate is involved.

The labilizing effect of SO_3^{2-} on the Ru(II)-NH_3 bond trans to it can be calculated from the specific rate of conversion of $[Ru(NH_3)_5SO_3]$ to *trans*-$[Ru(NH_3)_4(SO_3)L]$ and the rate of spontaneous loss of NH_3 from $[Ru(NH_3)_6]^{2+}$. For the former process we have measured 9.6×10^{-3} sec^{-1}; for the latter, 9.3×10^{-6} sec^{-1} has been reported.[10] When the latter value is divided by the factor 6 to allow for the statistical factor, the rate enhancement in breaking a Ru(II)-NH_3 bond caused by replacing trans NH_3 by SO_3^{2-} is calculated as 6×10^3. This is considerably greater than for the Ru(II)-H_2O bond—an expected outcome because the latter bond is much more labile to begin with—and far short of the rate enhancement for a similar substitution on Co(III). The specific rate for replacement of NH_3 trans to NH_3 in $Co(NH_3)_5SO_3^+$ by rate-determining Co(III)-NH_3 bond rupture is reported as 1.2×10^{-2} sec^{-1}.[3] The exchange of ammonia with $Co(NH_3)_6^{3+}$ in aqueous solution at 35° has been measured, and $t_{1/2}$ for the approach of the coordinated NH_3 to isotopic equilibrium is reported as 363+ days.[23] In view of the much longer half-life for the exchange of NH_3 in $Co(NH_3)_6^{3+}$ compared to water in $Co(NH_3)_5H_2O^{3+}$,[24] the activation energy for the former reaction is expected to be higher. If the difference in half-life for the two processes at 35° is attributed solely to the difference in activation energy, that for the exchange of NH_3 with $Co(NH_3)_6^{3+}$ is estimated at 33 kcal. Using this value k for release of NH_3 from $Co(NH_3)_6^{3+}$ at 25° is calculated as 4×10^{-9} sec^{-1}. This is almost certainly a lower limit on the rate of interest to us—note that in the measurements the possiblity of catalysis by the surface or by OH^- was not investigated—but even using the lower limit, a greater sensitivity of the rate to replacing NH_3 by SO_3^{2-} at Co(III) compared to Ru(II) is demonstrated. The reason for the difference in sensitivity is not understood, nor is it known whether the great sensitivity of the Co(III) center to $NH_3SO_3^{2-}$ replacement is typical of tripositive ions.

At least two effects need to be taken into account in understanding the labilizing or delabilizing effects of the ligands on Ru(II). Those ligands which are strong π acids and relatively weak σ bases have uniformly been observed to decrease the rate at which water on Ru(II) is replaced by another ligand.[25] In the context of this kind of behavior, it is not surprising that the rate of substitution in *trans*-$[Ru^{II}(NH_3)_4L(H_2O)]$ decreases in the order SO_3^{2-}, HSO_3^-, and SO_2. But it is not at all clear what quality of SO_3^{2-} is responsible for the rate enhancement it causes. The capacity to engage in a strong σ interaction increases from SO_2 to SO_3^{2-} and this would seem to be a possible reason for the origin of the labilizing effect of SO_3^{2-} relative to, say, NH_3. But OH^- is expected to make a much stronger σ bond than does H_2O, yet the rate of conversion of $[Ru(NH_3)_5H_2O]^{2+}$ to the isn complex is only a factor of 5-6 less than for the corresponding *cis*- and *trans*-hydroxoaquo species.[26] Moreover, the labilizing effect is not limited to the trans position. On Co(III), OH^- labilizes slightly more strongly when cis than it does when trans to the leaving group. Thus the specific rates of aquation for *cis*- and *trans*-$[Co(en)_2(OH)Cl]^+$ are 1.2×10^2 and 0.16×10^2 sec^{-1}, respectively.[27] For $[Co(NH_3)_5Cl]^{2+}$, the specific rate is 1.7×10^{-6} sec^{-1}.[28]

Two additional points remain to be commented on in considering the labilizing effect of SO_3^{2-} in *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$. Both the enthalpy of activation (16.3 kcal mol^{-1}) and the entropy of activation (0.8 cal deg^{-1} mol^{-1}) are more favorable than for $[Ru(NH_3)_5H_2O]^{2+}$ where these quantities for the same ligand (pyrazine) are 17.5 kcal mol^{-1} and −6 cal deg^{-1} mol^{-1}, respectively.[10] The explanations for the labilizing effects which have been considered would appear to bear only on the enthalpy term, but the comparisons may be complicated because the difference in charge type between the two systems affects the values of the entropy changes. Finally, it should be noted that while SO_3^{2-} exerts a labilizing effect on the trans position, it has a delabilizing effect on the cis.

In the studies with *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$ no hint of a term second order in the concentration of ligand was detected. Consideration of the accuracy of the data places an upper limit of 10^{-3} M^{-1} sec^{-1} on a second-order rate term,

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(20) C. G. Kuehn, work in progress.
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(22) The specific rates for pz and isn reacting with $Ru(NH_3)_5H_2O^{2+}$ at 25° are reported as 0.11 and 0.056 M^{-1} sec^{-1}, respectively (*cf.* ref 10).
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(25) S. Isied, work in progress.
(26) The specific rates for the substitution of isn with *cis*- and *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ on 0.50 *M* NaOH at 25° are 0.60 and 0.53 M^{-1} sec^{-1}, respectively. Under these conditions the Ru(II) species are predominantly in the monohydroxo form.
(27) M. L. Tobe, *Sci. Progr.*, 48, 484 (1960).
(28) F. J. Garrick, *Trans. Faraday Soc.*, 33, 487 (1937).

which is to be compared to 0.05 M^{-1} sec^{-1} for the reaction of pyrazine with $[Ru(NH_3)_5H_2O]^{2+}$. The difference between SO_3^{2-}, which labilizes trans and delabilizes cis, and OH^-, which exerts approximately equal labilizing effects at the two positions, is noteworthy. If it is assumed that reaction proceeds through a pentacoordinated intermediate, say a tetragonal pyramid, the difference can be ascribed to a marked preference on the part of SO_3^{2-}, but not of OH^-, for a site at the apex rather than the base of the intermediate. This suggestion is obviously not an explanation and is offered only as suggesting a direction to pursue in looking for an explanation.

Attention has already been drawn to the magnitude of the labilizing effect on two saturated ligands when NH_3 in trans position is replaced by SO_3^{2-}. When the groups being replaced are π acids, an effect in addition to that operating with saturated ligands may come into play. This effect as it is manifested in affinities has already been recognized in other systems—note that though K_{eq} for the reaction of N_2 with $Ru(NH_3)_5H_2O^{2+}$ is *ca.* 10^4, replacement of a single NH_3 by pyridine so greatly reduces the affinity of N_2 for Ru(II) that no evidence of complex formation is observable with N_2 at 1 atm (this amounts to a reduction in K_{eq} by a factor of at least 10^2). Similar large effects on affinities are noted in the present system. The value of K_{eq} for the reaction of isn with $[Ru(NH_3)_5H_2O]^{2+}$ is $>10^8$, and for pz it is expected to be of the same order of magnitude.[10] The present work shows that with SO_3 trans to these ligands, the values of K_{eq} are 4×10^3 and 3×10^3, respectively. The effect of SO_3^{2-} can be attributed at least in part to its role as a π acid. To the extent that a ligand absorbs electron density from a πd orbital, back-bonding to another ligand using the same orbital will be weakened. It is not possible with present knowledge to factor the overall effect of SO_3^{2-} on the bonding, say of isn, into the component pertaining to saturated ligands and that arising from back-donation. Such factoring may not be possible in principle; the so-called synergistic effect is likely to be strong for SO_3^{2-}, with σ-bonding formation strongly promoting back-donation. Some insight into the matter would be provided by studies of the cis cases. The effects arising from back-donation would be only slightly affected but others would be strongly altered. Such studies have not yet been done and might prove to be difficult because they would undoubtedly be complicated by loss of NH_3 in the position trans to SO_3^{2-}.

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Registry No. *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$, 23346-07-8; *trans*-$[Ru(NH_3)_4(SO_2)isn](CF_3SO_3)_2$, 51175-00-9; *trans*-$[Ru(NH_3)_4(SO_2)pz](C_7H_7SO_3)_2$, 51271-76-2; *cis*-$[Ru(NH_3)_4(SO_2)H_2O](PF_6)_2$, 51175-02-1; *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$, 51175-03-2; *trans*-$[Ru(NH_3)_4(HSO_3)H_2O]^+$, 51202-30-3; *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$, 51175-04-3; $Ru(NH_3)_5SO_3$, 51174-85-7; *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$, 51174-86-8; $[Ru(NH_3)_5SO_2]Cl_2$, 13874-06-1; *trans*-$[Ru(NH_3)_4(SO_3)isn]$, 51174-87-9; *trans*-$[Ru(NH_3)_4(SO_3)pz]$, 51174-88-0; *trans*-$[Ru(NH_3)_4(SO_3)(pzMe)]^+$, 51174-89-1; $[Ru(NH_3)_3pzSO_3H_2O]$, 51174-90-4.

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Activation Parameter Separation through Stereochemical Observation. Inversion Reaction of Tris(o-phenanthroline)iron(II) with Cyanide[1]

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Observation of the product stereochemistry of the reaction between $Fe(phen)_3^{2+}$ and CN^- as a function of temperature and comparison with the rate of mutarotation under the same conditions has allowed the separation of the second-order term into retention (k_{ret}) and inversion (k_{inv}) paths possessing the following activation parameters: k_{inv}, $E_a = 23.2 \pm 0.8$ kcal/mol, $\ln A = 33.6 \pm 1.4$ (A in M^{-1} sec^{-1}), $\Delta H^{\ddagger} = 22.6 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 6.2 \pm 2.7$ eu; and for k_{ret} the respective values are 24.5 ± 0.3, 35.4 ± 0.5, 23.9 ± 0.3, and 9.8 ± 1.0. Logical mechanistic considerations, activation parameters, hydroxide ion independence, and linear correlations (>0.999) cause us to favor this mechanism over several other possibilities. The entropies of activation lend support to the optical inversions being true chemical inversions and to the validity of exciton theory for these species.

Introduction

Cyanide ion reacts with optically active tris(o-phenanthroline)iron(II) to give an optically inverted dicyanobis(o-phenanthroline)iron(II) product.[2] This Bailar inversion[3] reaction is of prime importance for several reasons including the following: (1) the reaction exhibits a temperature-dependent stereochemistry and should allow an intimate look at the activated complex *via* appropriate activation parameters; (2) the reaction extends the octahedral, Bailar inversion reactions to d^6 systems other than cobalt(III);[3] (3) the product, which is several orders of magnitude more stable than the reactant, has a racemization half-life of 2 months in water at room temperature[2] so that accurate isomer data[4] are possible; and (4) nucleophilic dependence for octahedral substitution reactions in water is uncommon for complexes

(1) Preliminary data presented at the Kinetics and Mechanisms of Substitution Reactions of Metal Complexes Symposium at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971. Abbreviations used: phen, o-phenanthroline; bipy, 2,2'-bipyridine; PBA, α-(2-pyridyl)benzylideneaniline.

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(3) (a) J. C. Bailar, Jr., and R. W. Auten, *J. Amer. Chem. Soc.*, 56, 774 (1934); (b) J. C. Bailar, Jr., *Rev. Pure Appl. Chem.*, 16, 91 (1966); (c) R. D. Archer, "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 18.

(4) Modification of the Cary 60 for MCD studies included the installation of an end-on photomultiplier detection system, which has improved the signal to noise ratio for low rotations by a factor of about 4.