

ground states with one unpaired electron per iron, $S = 1/2$. X-Ray powder patterns have shown that the compounds $[\text{FeClNO}(\text{das})_2][\text{ClO}_4]$ are essentially isomorphous with the *trans*- $[\text{CoCl}_2(\text{das})_2][\text{ClO}_4]$ compound. Recently, a single crystal of this compound has been examined by X-ray diffraction techniques.²⁴ Although the chloride and nitrosyl groups disorder as they must to be isomorphous with *trans*- $[\text{CoCl}_2(\text{das})_2][\text{ClO}_4]$, the *trans* arrangement of the chloride and nitrosyl ligands has been confirmed. In addition, although the measurements are not accurate due to the disorder problem, the Fe-N-O bond angle is approximately 148° . While many other transition metal complexes with an M-N-O angle of less than 180° also have structures plagued with disorder problems, Ibers⁵ has reported a structure in which the M-N-O bond angle is 120° and the NO group is ordered in the crystal.

Regarding the NO group as a strong-field ligand, we see that there is an important difference, however, between $[\text{FeCl}_2(\text{das})_2]^+$ and $[\text{FeCl}(\text{NO})(\text{das})_2]^+$. The nitrosyl group dominates the bonding with the metal in most of its transition metal complexes and is usually placed near the cyanide ligand in the spectrochemical series. Consequently the axial field will be stronger than the field of the four arsenic ligand atoms in the xy plane. Thus the splitting of the ${}^2T_{2g}$ state will be of opposite sign to that for $[\text{FeCl}_2(\text{das})_2]^+$. In a strong tetragonal field, the electron configuration for $[\text{FeCl}(\text{NO})(\text{das})_2]^+$ should be $d_{xy}^2(d_{xz}, d_{yz})^3$ which would give rise to a 2E ground state.

However, all attempts to fit the temperature-dependent magnetic moments (Table I) of *trans*- $[\text{FeCl}(\text{NO})(\text{das})_2]^+$ and *trans*- $[\text{FeBr}(\text{NO})(\text{das})_2]^+$ to a tetragonal model failed to provide any successful assignment of the ground state. Because the observed g tensor is rhombic

(24) R. W. Perry, Ph.D. Dissertation, University of Wisconsin, 1968.

($g_x \neq g_y \neq g_z$),²⁵ a rhombic (D_{2h}) model was used to calculate theoretical moments as a function of field distortion, spin-orbit coupling, and electron delocalization.²⁶ Although complete computer fitting was not performed, the nearly spin-only behavior is compatible with only a rhombically distorted 2E ground term. More importantly, the quadrupole splitting in the Mössbauer spectrum for spin-paired, tetragonally distorted iron(III), 2B_2 , should be 1.5 times the quadrupole splitting for the rhombically distorted iron(III), 2E . Rhombic distortion of the 2B ground term produces a system with no quadrupole splitting.²⁶ The data in Table II show the quadrupole splitting in *trans*- $[\text{FeBr}_2(\text{das})_2]^+$ to be approximately 2.4 times that found for *trans*- $[\text{FeBr}(\text{NO})(\text{das})_2]^+$.

Conclusions

These studies have shown that both *trans*- $[\text{FeX}_2(\text{das})_2]^+$ and *trans*- $[\text{FeX}(\text{NO})(\text{das})_2]^+$ can be treated as complexes of Fe(III). This implies that the NO group has two electrons more than are present in the $\text{N}\equiv\text{O}^+$ group, leaving the nitrosyl group with one negative charge. This point of view is consistent with the low NO stretching frequencies and the small bond angles of these iron nitrosyl complexes. The magnetic susceptibility indicates that there is a tetragonal splitting of the ${}^2T_{2g}$ ground state of *trans*- $[\text{FeX}_2(\text{das})_2]^+$ and a rhombic splitting in the nitrosyl complexes. The Mössbauer spectra show that the field is of opposite sign in the nitrosyl and the dihalides as is predicted by a simple ligand field model.

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(25) H. Crain and R. D. Feltham, unpublished results.

(26) W. Wesolowski, Ph.D. Dissertation, University of Arizona, 1971.

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Kinetics of Ruthenium(II) Substitution Reactions. Reaction of Aquopentaammineruthenium(II) with Various Pyridines and Organonitriles¹

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Substitution rates for the complex ion $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ are reported for replacement of the labile coordinated water by various substituted pyridines and by several organonitriles (acetonitrile, benzonitrile, perfluorobenzonitrile, and 3- and 4-cyanopyridine). Over considerable ligand concentration ranges, the reactions obey the second-order rate law $d[\text{Ru}(\text{NH}_3)_5\text{L}^{2+}]/dt = k_L[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}][\text{L}]$ with rate constant k_L ranging from 0.048 to $0.32 \text{ M}^{-1} \text{ sec}^{-1}$ (25°) depending on the nature of L and certain media conditions. The 3- and 4-substituted pyridines follow a reactivity order parallel to their basicities, electron-withdrawing substituents decreasing the rate and electron-donating substituents increasing the rate; however, the rate differences are small, a fact which is interpreted as implying an $\text{S}_{\text{N}}1$ (dissociative) substitution mechanism. The organonitriles generally react more rapidly than do the pyridines. The rates and activation parameters for all these reactions are compared with similar data previously reported for the reactions of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with N_2 , N_2O , and $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ and interpreted in terms of two transition state features: steric effects and the nature of the developing metal-ligand bond.

Introduction

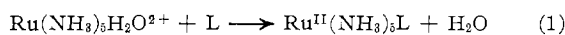
During the past several years, a number of new pentaammineruthenium(II) complexes of π -unsaturated

(1) Presented in part at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, Calif., Oct 1970.

ligands, $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$, have been described. These ligands (L) include aromatic nitrogen heterocycles such as pyridine,² organonitriles, such as benzonitrile,

(2) P. C. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

acetonitrile, and acrylonitrile,³ carbon monoxide,⁴ and, most dramatically, molecular nitrogen.⁵ The stability and relative inertness (to substitution reaction in aqueous solution) of these complexes as well as a number of physical and chemical properties have been interpreted as indicating π back-bonding from the ruthenium(II) into the unfilled π -symmetry ligand orbitals to a degree previously unseen for other cationic metal-amine complexes.⁶ The Ru(II) complexes can each be made by the simple displacement of the labile water molecule from aquopentaammineruthenium(II) (eq 1), the reaction which is the focus of this work.



Analogous substitution reactions of octahedral complexes, especially those of pentaamminecobalt(III) and -rhodium(III), have been studied extensively.⁷ However, the significance of the Ru(II)-to-ligand π back-bonding in the $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ product lends particular interest to a mechanistic elucidation of reaction 1. Recently rates for the reaction of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with N_2 ,^{8,9} with N_2O ,¹⁰ and with $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ ⁸ have been reported. Here, we report similar rate studies for the reaction with various substituted pyridines and with various organonitriles. Investigation of a series of analogous nucleophiles L, such as the 3- and 4-substituted pyridines, allows one to determine the rate effects of relatively subtle changes in the electronic character of the nucleophile coordination site without perturbation of its stereochemical characteristics. Such substituent effect studies, though common to the study of organic reaction mechanisms, have received scant attention in the study of octahedral substitution mechanisms. Similar information derives from comparison of the reactivities of the various organonitriles, where an additional feature is the analogy which can be drawn³ between the metal-ligand coordination of $\text{Ru}^{\text{II}}\text{N}\equiv\text{CR}$ and of $\text{Ru}^{\text{I}}\text{N}\equiv\text{N}$.

Experimental Section

Materials.—Chloropentaammineruthenium(III) dichloride was prepared from ruthenium trichloride (Engelhard Industries) by the method of Allen, *et al.*,⁵ and recrystallized several times to ensure purity. Pyridine and benzonitrile (Matheson Coleman and Bell), perfluorobenzonitrile (Peninsular Chemresearch Inc.), and all other pyridines and organonitriles (Aldrich Chemical Co.) were purchased from commercial sources. Each ligand used in the rate studies was purified either by distillation from barium oxide or by recrystallization and subsequent sublimation. Water used to prepare the kinetic solutions was redistilled from alkaline permanganate. The aqueous methanol kinetics solutions were prepared volume to volume with redistilled water and with anhydrous methanol (Mallinckrodt analytical reagent, stored over Linde Type 3A Molecular Sieve). The sodium perchlorate and sodium *p*-toluenesulfonate employed to maintain solution ionic strength were recrystallized prior to use. Argon used to entrain reaction solutions was deoxygenated by passage through Cr(II) solution in gas-scrubbing bottles.

(3) (a) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970); (b) *ibid.*, **9**, 495 (1970); (c) P. C. Ford, R. D. Foust, and R. E. Clarke, *ibid.*, **9**, 1933 (1970).

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(6) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 124-246.

(8) C. M. Elson, I. J. Itzkovitch, and J. A. Page, *Can. J. Chem.*, **48**, 1639 (1970).

(9) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 6170 (1970).

(10) J. N. Armor and H. Taube, *ibid.*, **91**, 6874 (1969).

Rate Studies.—The rate measurements were carried out by observing the formation of the $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ product with a Cary 14 recording spectrophotometer equipped with a thermostated cell compartment. Example wavelengths are 408, 376, and 229 nm for L = pyridine, benzonitrile, and acetonitrile, respectively. Prior to a kinetic run all component solutions were deaerated by entraining with argon and were thermostated in a constant-temperature bath. A run was started by transferring the solutions *via* syringe techniques to a thermostated, deoxygenated cell (capped with a rubber septum), shaking the cell thoroughly, and placing it in the spectrophotometer cell compartment.

Two methods were used to generate $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ for the rate studies. The method employed for a majority of the rate studies used *p*-toluenesulfonic acid to adjust solution pH and sodium *p*-toluenesulfonate to maintain the ionic strength ($\mu = 0.20$ for most runs). The reactant $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ was generated by Zn(Hg) reduction of a deaerated stock $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ solution. Page and coworkers⁸ have used a similar technique to generate this reactant. A run was initiated by transferring the ruthenium(II) solution *via* syringe techniques to a thermostated, deaerated ligand solution in the capped reaction cell. The other method was less useful owing to complication of the known redox reaction between Ru(II) and ClO_4^- under certain experimental conditions.⁶ To initiate a reaction, excess chromium(II) solution (prepared by Zn(Hg) reduction of standardized $\text{Cr}(\text{ClO}_4)_3$ solution) was added *via* syringe to a deaerated solution of $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ and the appropriate ligand in the reaction cell. Reduction of $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ by Cr(II) to generate $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ under these conditions is essentially instantaneous relative to the subsequent reaction between $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and L. The Cr(II)-initiated reactions were all carried out in perchlorate solution using sodium perchlorate to maintain the ionic strength ($\mu = 0.53$) and perchloric acid to adjust solution pH. The reactions with various pyridines were carried out in the buffer region (pH) of the individual ligand (see Results).

For both techniques, the ligand (L) concentrations in the reaction solutions always greatly exceeded the initial $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ concentration ($\sim 10^{-4}$ M for each run). Under these conditions, formation of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ was essentially quantitative as determined spectrophotometrically. Consequently, good pseudo-first-order rate constants (k') could be obtained by plotting $-\ln(A_\infty - A)$ vs. time for the λ_{max} of the developing $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ product. Second-order rate constants (k_L) reported in the Results were each obtained from a plot of k' vs. four or more ligand concentrations which in most cases ranged from less than 0.01 M to greater than 0.1 M.

Temperature dependences of the rate constants k_L were determined for the reactions of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with pyridine, benzonitrile, acetonitrile, 4-picoline, and 3-chloropyridine. With the more volatile pyridine and acetonitrile, the ligand solutions were deaerated prior to thermostating at the higher temperatures used. The first method of generating Ru(II) was employed in each case and sodium *p*-toluenesulfonate was used to maintain the ionic strength ($\mu = 0.20$), except for the reactions with acetonitrile. The reactions with acetonitrile were carried out at essentially zero ionic strength (the only contribution being from the $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ plus the Zn^{2+} generated by the Zn(Hg) reduction of the $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ stock solution ($\sim 10^{-4}$ M)) since the observation wavelength, 229 nm, would be obscured by the *p*-toluenesulfonate absorption bands. The temperature range studied was 18-45°.

Solution pH measurements were made at room temperature on a Sargent-Welch Model NX digital pH meter calibrated against commercial buffer solutions (pH 2.00, 4.00, and 7.00).

Results

Rate Studies in Aqueous Solution.—Each rate run was carried out by spectrophotometrically monitoring the product formation of the reaction between $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and a large excess of ligand L. The different methods of generating $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ did not influence the rate behavior significantly. In each case, the reaction displayed first-order dependence on the aquo complex concentration giving the rate law

$$\frac{d[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}]}{dt} = k'[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}] \quad (2)$$

For each pyridine or organonitrile investigated under a particular set of conditions, k' proved to be a linear function of ligand concentration (Figure 1) giving a zero intercept, therefore obeying the rate law

$$\frac{d[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}]}{dt} = k_L[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}][\text{L}] \quad (3)$$

The majority of the rate data were taken in aqueous solution at pH's sufficiently basic (pH 7.5–8.5, unbuffered) that the various pyridine ligands were in

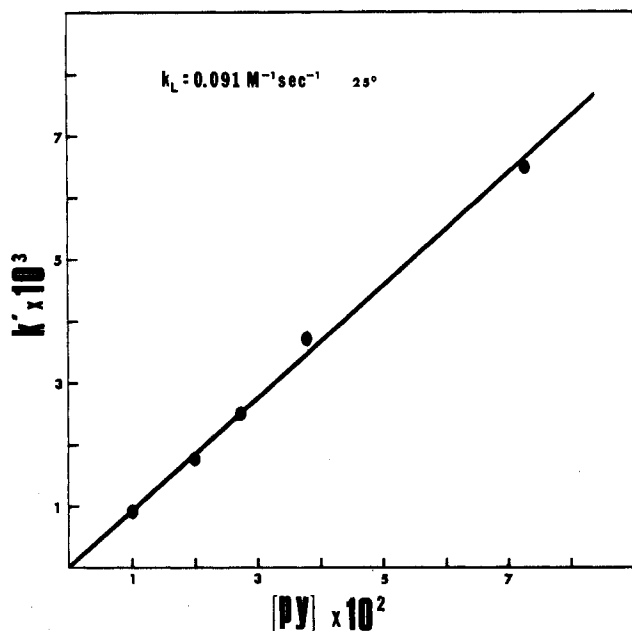


Figure 1.—Plot of pseudo-first-order rate constant $k'(25^\circ)$ vs. the concentration of pyridine for the reaction $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} + \text{py} = \text{Ru}(\text{NH}_3)_5\text{py}^{2+} + \text{H}_2\text{O}$. The slope gives the second-order rate constant k_L .

their free base forms. The various k_L 's obtained at 25° for different substituted pyridines and those organonitriles sufficiently soluble in water are reported with the respective activation parameters in Table I. In general, the reactivity order for the pyridines follows ligand basicity. The nitriles, however, are somewhat faster than the most basic pyridine. The pyridine reactivity order appears to be reflected in the enthalpies of activation, although the ΔH^\ddagger differences are smaller than the experimental uncertainty. The activation parameters for the organonitriles show larger activation enthalpies but a more favorable ΔS^\ddagger term than for the pyridines.

The rate data obtained using chromous ion reduction of $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ to generate the $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ gave k_L values (Table II) similar to the runs in *p*-toluenesulfonate media. Since this method necessitated addition of some acid with the Cr(II) solution, the reactions with the pyridines were carried out at the different buffer regions characteristic of the individual pyridines. The rate constants k_L were then based on the concentration of free ligand (not protonated) as calculated from the measured solution pH and the published pK_a for that ligand (Table I). That these k_L rate constants (Table II) were not particularly sensitive to the solution pH is demonstrated by the pH independence of k_L for pyridine obtained at three different pH's (Table II). Some differences between

TABLE I
SECOND-ORDER RATE CONSTANTS (k_L) AND ACTIVATION
PARAMETERS FOR THE REACTION

$$\text{L} + \text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} \xrightarrow{k_L} \text{Ru}(\text{NH}_3)_5\text{L}^{2+} + \text{H}_2\text{O}$$

| Ligand | Temp, °C | $10^3 k_L^a$, $M^{-1} \text{sec}^{-1}$ | pK_a^b (free ligand) | ΔH^\ddagger , kcal/mol | ΔS^\ddagger , eu |
|----------------------|----------|---|------------------------|--------------------------------|--------------------------|
| 3-Chloropyridine | 18.0 | 3.8 ± 0.2 | 2.83 | 15.4 ± 0.6 | -13 ± 2 |
| | 25.0 | 6.4 ± 0.7 | | | |
| | 35 | 16.7 ± 0.4 | | | |
| | 43.6 | 30 ± 2 | | | |
| Pyridine | 18.0 | 5.0 ± 0.2 | 5.30 | 15.3 ± 0.2 | -13 ± 1 |
| | 25.0 | 9.1 ± 0.2 | | | |
| | 33.9 | 21.4 ± 1.4 | | | |
| | 43.5 | 43.5 ± 2.0 | | | |
| 3-Methylpyridine | 25.0 | 10.1 ± 0.9 | 5.68 | ... | ... |
| 4-Methylpyridine | 25.0 | 11.0 ± 0.8 | 6.11 | 15.1 ± 0.6 | -13 ± 2 |
| | 33.9 | 24.9 ± 1.5 | | | |
| | 43.6 | 49.3 ± 3.8 | | | |
| 3,5-Dimethylpyridine | 25.0 | 11.7 ± 0.4 | 6.23 | ... | ... |
| | 18.0 | 13.4 ± 0.6 | | | |
| Benzonitrile | 25.0 | 26.8 ± 1.8 | ... | 15.8 ± 0.6 | -8 ± 2 |
| | 33.9 | 54 ± 1 | | | |
| | 38.8 | 85 ± 2 | | | |
| | 18.0 | 15.0 ± 0.9 | | | |
| Acetonitrile | 25.0 | 26.2 ± 0.8 | ... | 16.2 ± 0.6 | -7 ± 2 |
| | 35.0 | 73.0 ± 0.8 | | | |

^a $\mu = 0.20 M$ (*p*-toluenesulfonate) for all reactions except where L = acetonitrile. In this case $\mu \cong 10^{-4} M$. pH of all solutions is 8.0 ± 0.3 except for acetonitrile at pH 5; solvent is H_2O . ^b K. Schofield, "Hetero Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967.

TABLE II
VALUES^a FOR k_L DETERMINED USING Cr(II) REDUCTION AS
THE METHOD TO GENERATE $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$

| Ligand | Solution pH | $10^3 k_L^b$, $M^{-1} \text{sec}^{-1}$ |
|------------------|-------------|---|
| 3-Chloropyridine | 2.83 | 5.8 ± 0.3 |
| | 4.30 | 12.3 ± 0.5 |
| | 5.30 | 11.7 ± 0.6 |
| Pyridine | 6.30 | 11.8 |
| | 5.40 | 19.5 ± 1.0 |

^a At 25° ; $\mu = 0.53 M$ (ClO_4^-). ^b Based on the concentration of the free base form of ligand as calculated from the solution pH and the ligand pK_a (see Table I).

the rate data for the *p*-toluenesulfonate medium system and the chromous perchlorate medium system are apparent (see Tables I and II); however, the reactivity patterns are quite similar with the more basic pyridines showing greater reactivity. Nonetheless, the *p*-toluenesulfonate media data must be considered the more reliable, as those second-order rate constants do not depend upon the accuracy either of the solution pH measurement or of the reported ligand pK_a values which were determined under conditions somewhat different from the rate studies.

Effect of Ionic Strength and Solution pH.—A probe into the substitution mechanism of reaction 1 is the effect of the medium ionic strength on k_L . This potential effect was tested by doing a series of rate studies at $\mu = 0.20 M$ and at $\mu = 1.0 M$ sodium *p*-toluenesulfonate. The k_L 's determined at $\mu = 1.0 M$ (pH ~ 8.0) are summarized in Table III. Comparison of these data with the k_L 's determined for $\mu = 0.20 M$ (Table I) shows that there is a slight but not dramatic increase (15–40%) in the reaction rate for each ligand L resulting from the increased ionic strength. The reactivity order of the various L's remains the same. In addition, the activation parameters for reaction 1 (L = pyridine) are essentially unperturbed by the ionic strength change. The modest rate difference again appears to be reflected in the

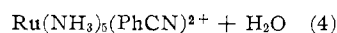
TABLE III
 VALUES OF k_L AT IONIC STRENGTH 1.00 M^a

| Ligand | Temp, °C | $10^3 k_L$, $M^{-1} \text{sec}^{-1}$ | ΔH^\ddagger , kcal/mol | ΔS^\ddagger , eu |
|------------------|----------|---------------------------------------|--------------------------------|--------------------------|
| 3-Chloropyridine | 25.0 | 9.4 ± 0.7 | | |
| Pyridine | 18.0 | 6.4 ± 0.3 | | |
| | 25.0 | 11.8 ± 0.6 | 15.2 ± 0.2 | -12 ± 1 |
| | 33.9 | 26.5 ± 2.6 | | |
| | 43.6 | 58.7 ± 1.8 | | |
| 4-Methylpyridine | 25.0 | 13.1 ± 0.4 | | |
| Benzonitrile | 25.0 | 32.0 ± 1.6 | | |

^a Solvent is H_2O ; $\mu = 1.0 M$ (*p*-toluenesulfonate).

ΔH^\ddagger terms but falls well within the experimental uncertainty for this parameter.

In the previous section, it was demonstrated (using the chromous reduction method for generating $Ru(NH_3)_5H_2O^{2+}$) that changing the pH from 6.30 to 4.30 did not result in a significant change in the second-order rate constant k_L when $L = \text{pyridine}$. The k_L value was based on the calculated concentration of free base alone. Since aquations of certain ruthenium(II)-ammine complexes have been reported¹¹ to display pathways first order in $[H^+]$, acid dependence for reaction 1 remains a definite possibility. In order to investigate this possibility, the rates of the benzonitrile reaction (eq 4) were measured at two very



different pH's (0.7 and 7.7) in water ($\mu = 0.20 M$ (*p*-toluenesulfonate)). Benzonitrile was the ligand of choice for this comparison since the Brønsted basicity of the nitrile group has been shown¹² to be sufficiently low that the reaction equilibrium constant will be unaffected by ligand protonation. The k_L ($0.275 \pm 0.024 M^{-1} \text{sec}^{-1}$) determined for pH 0.7 is identical with that measured at pH 7.7 (Table I, $0.268 \pm 0.018 M^{-1} \text{sec}^{-1}$), indicating that, at least for reaction 4, acid does not play an important rate-determining role between pH 0.7 and 7.7.

Rate Studies in Aqueous Methanol.—A number of the organonitrile ligands were insoluble in the aqueous medium used for rate studies with the various pyridine derivatives. For this reason, rate studies with these ligands were carried out in 50% (volume ratio) aqueous methanol solutions. The resulting rate constants are summarized in Table IV. These data include rates for

 TABLE IV
 VALUES OF k_L DETERMINED IN 50% AQUEOUS METHANOL^a

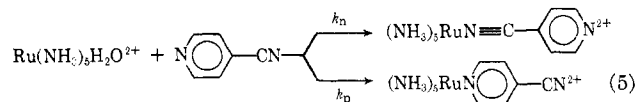
| Ligand | $10^3 k_L$, $M^{-1} \text{sec}^{-1}$ | Ligand | $10^3 k_L$, $M^{-1} \text{sec}^{-1}$ |
|-----------------------|---------------------------------------|----------------------|---------------------------------------|
| Pyridine | 4.8 ± 0.2 | Benzonitrile | 19.6 ± 1.1 |
| 4-Methylpyridine | 5.5 ± 0.2 | 4-Chlorobenzonitrile | 21.0 ± 1.5 |
| Perfluorobenzonitrile | 13.7 ± 2.9 | | |

^a At 25°; $\mu = 0.20 M$ (sodium *p*-toluenesulfonate); solvent 1:1 v/v aqueous methanol.

several ligands (notably 4-methylpyridine, pyridine, and benzonitrile) which were determined in both solvent systems in order to compare the solvent rate effect (Tables I and IV). Comparison of the data obtained in water to those obtained in 50% aqueous methanol show that the rates are 30–50% slower in the latter me-

dium. However, the same reactivity order is maintained; namely, benzonitrile is several times more reactive than either pyridine, and the more basic pyridine (4-methylpyridine) is also the more reactive pyridine. In the absence of data to assess the effect of substituents on the physical properties (*e.g.*, basicity) of the benzonitriles, it is difficult to interpret the effects of such substituents on the rates. The k_L for 4-chlorobenzonitrile is actually somewhat greater than the k_L for benzonitrile despite the fact that similar substitution of an electron-withdrawing group in the pyridine series would be expected to depress the rate. However, a more major perturbation by placing the electronegative fluorines at all five benzonitrile ring positions does lead to a decrease in the ligand reactivity (Table IV). Again, as in the pyridine series, the rate differences are relatively minor.

Rate Studies with $L = 3$ - or 4-Cyanopyridine.—The presence of two coordination sites on 3-cyanopyridine and 4-cyanopyridine, both sites capable of forming substitution-inert complexes with pentaammineruthenium(II), adds potential complications to rate studies with these ligands. Clarke and Ford^{3b} demonstrated that the synthesis of the 4-cyanopyridine (4-cp) complex ion $Ru(NH_3)_5(4-cp)^{2+}$ (from $Ru(NH_3)_5H_2O^{2+}$ plus the ligand) in strongly acidic solution gave exclusively the nitrile-coordinated isomer. Synthesis in roughly neutral solution, however, gave both the nitrile-coordinated complex and the pyridine-coordinated linkage isomer in an estimated (from spectral data) ratio of 9:1 (eq 5).^{3b} The pyridine-coordinated linkage isomer was not



detected in the 3-cyanopyridine complex synthesis; however, since the electronic spectra of the two isomeric types would be expected to be more similar for the 3-cyanopyridine complexes than for the 4-cyanopyridine complexes,² small percentages of the pyridine-coordinated linkage isomers might have been overlooked in the former case.

The formation rate for the nitrile coordinated isomer of $Ru(NH_3)_5(4-cp)^{2+}$ in neutral solution was determined by following the development of the visible absorption band of this species at λ_{max} 425 nm.^{3b} The plots of $\ln(A_\infty - A)$ vs. time were linear to give pseudo-first-order rate constants k' which were proportional to ligand concentration. The plots of k' vs. $[L]$ were linear, had zero intercepts, and gave the second-order rate constant k_L' (Table V). This k_L is essentially equal to k_n , the rate constant for formation of the nitrile-coordinated species, since the product distri-

 TABLE V
 VALUES FOR k_L DETERMINED FOR REACTIONS OF $Ru(NH_3)_5H_2O^{2+}$ WITH CYANOPYRIDINES^a

| L | μ, M | $10^3 k_L, M^{-1} \text{sec}$ |
|------------------------------------|----------|-------------------------------|
| 3-Cyanopyridine | 0.2 | 26.1 ± 2.1 |
| 4-Cyanopyridine | 0.2 | 23.8 ± 2.4 |
| 4-Cyanopyridine | 1.0 | 26.4 ± 0.9 |
| 4-Cyanopyridinium ion ^b | 1.0 | 23.9 ± 1.0 |

^a At 25°; ionic strength maintained with *p*-toluenesulfonate; solvent is 50% aqueous methanol at approximately neutral pH except where noted. ^b 4-Cyanopyridine ($pK_a = 2.72$) in 1.0 M *p*-toluenesulfonic acid.

(11) P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

(12) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 4239 (1932).

bution shows that k_n must be substantially larger than k_p and since the extinction coefficient of the pyridine-coordinated species (λ_{\max} 500 nm)^{3b} is undoubtedly quite small at 425 nm, λ_{\max} for the nitrile-coordinated isomer. The substitution rate was also determined in solution sufficiently acidic to protonate the pyridine site. In this case, the k_L (determined by following the reaction at 532 nm, λ_{\max} of the protonated nitrile-coordinated complex $\text{Ru}(\text{NH}_3)_5(4\text{-cpH})^{3+}$)^{3b} can be attributed to the exclusive formation of the nitrile-coordinated 4-cyanopyridinium complex.

The k_L for the reaction between $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and 3-cyanopyridine in neutral solution is also listed in Table V. Despite the failure to find the pyridine-coordinated isomer as a synthesis product, there is no clear-cut reason to expect that this isomer would not be formed to a degree comparable to that of the 4-cyanopyridine system. Nonetheless, the heavy predominance of the nitrile-coordinated isomer in the product,^{3b} plus the use of the nitrile coordinated isomer's developing charge-transfer band λ_{\max} to follow the reaction, suggests that the measured k_L is at least close to the reaction rate constant for nitrile attack.

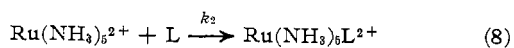
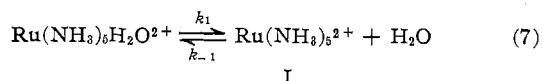
Examination of the respective rate constants shows that in 50% aqueous methanol the cyanopyridines are somewhat more reactive than benzonitrile, despite the fact that the rate constant for 4-cyanopyridine and probably for 3-cyanopyridine reflects only reaction at the nitrile. In addition, the rate constant for 4-cyanopyridine is somewhat greater at 1.0 M ionic strength than at 0.2 M. The most surprising result is the observation that the 4-cyanopyridinium ion (4-cpH⁺) is only about 10% less reactive than 4-cyanopyridine under similar conditions.

Discussion

Rate Law.—The reaction of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with each of the pyridines and organonitriles investigated proved to be second order, first order in complex and first order in ligand concentration. Observations are consistent with rate laws observed for anion replacement of coordinated water in analogous pentaammine complexes $\text{M}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ [eq 6, $\text{M} = \text{Rh}(\text{III}),^{13}$



$\text{Ru}(\text{III}),^{14}$ $\text{Co}(\text{III})^{15}$]. These reactions have been variously interpreted on the bases of rate laws and other experimental data as demonstrating associative (SN2) pathways [$\text{Ru}(\text{III})$ and $\text{Rh}(\text{III})$] and dissociative (SN1) pathways [$\text{Co}(\text{III})$]. The second-order rate law observed for the reaction under study is consistent with either limiting mechanism. The rate law (eq 9) for the dissociative mechanism (eq 7, 8) reduces to a



$$\text{rate} = \frac{k_1 k_2 [\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}] [\text{L}]}{k_{-1} + k_2 [\text{L}]} \quad (9)$$

simple second-order form ($k_L = k_1 k_2 / k_{-1}$) for L concentrations where $k_{-1} \gg k_2 [\text{L}]$. Similarly, a second-

order rate law (eq 11) is predicted for an associative mechanism requiring significant bond formation between L and a ruthenium(II) with an expanded coordination number during the rate-determining step.

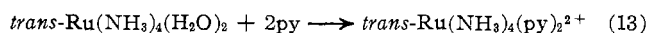
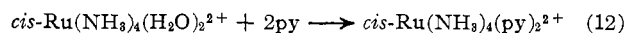


$$\text{rate} = k_3 [\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}] [\text{L}] \quad (11)$$

The failure to observe a departure from second-order rate behavior as predicted by eq 10 over the L concentration ranges studied does not distinguish between the two mechanisms. For the dissociative pathway, the second-order behavior simply implies $k_{-1} \gg k_2 [\text{L}]$ at the highest concentration studied (~ 0.1 M for pyridine). These terms embody the relative reactivities of solvent water and ligand L for the coordinatively unsaturated intermediate I. Since the k_{-1} term incorporates the concentration of water (55.4 M), for $k_2 [\text{L}]$ to be comparable to k_{-1} , L must be about 500 times as reactive toward I as is H_2O . Since changes in the identity of L lead to relatively small perturbations in k_L (Table I, also see below), it appears improbable that such might be the case.

Stereochemistry.—Reaction stereochemistry has commonly been used as an argument for selection between associative and dissociative pathways in octahedral substitution reactions. For example, retention of configuration for specific geometric and optical isomers was invoked¹⁴ as evidence supporting an octahedral-wedge geometry for an associative mechanism (cis attack) in the anation reactions of $\text{cis-Ru}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ and $\text{cis-Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})^{2+}$ (en = ethylenediamine). However, a similar stereochemical consequence is predicted by a dissociative pathway for which the pentacoordinate intermediate is a nonequilibrating tetragonal pyramid. The feasibility of such a pathway has been elegantly demonstrated by Buckingham, *et al.*,¹⁶ in some reactions of pentaamminecobalt(III) complexes.

The high symmetry of $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ does not allow for the stereochemical elucidation of the reactions reported in this paper. However, the stereochemistries of analogous ruthenium(II) substitutions, the reactions of pyridine with *cis*- and *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ (eq 12, 13), have been studied in this laboratory¹⁷ and have



been shown to give complete stereochemical retention in each case. Since these reactions apparently occur by stepwise addition of pyridine to replace the coordinated waters, the analogy to the $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ reactions is significant, and the reactions, no doubt, occur *via* similar pathways. If this analogy holds true, the stereochemical implication is that $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ reacts either by associative cis attack of L (as suggested for the aquoammineruthenium(III) complexes¹⁴) or by formation of a stereochemically nonequilibrating, pentacoordinate, dissociative intermediate.

Relative Rates.—Table VI summarizes the reaction parameters for the reactions of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ with various ligands L. The coordination site for each L

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(14) J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **10**, 85 (1971).

(15) A. Haim and H. Taube, *ibid.*, **2**, 1199 (1963).

(16) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satropa, *ibid.*, **6**, 1027 (1967); D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 597 (1967).

(17) P. C. Ford and C. Sutton, *Inorg. Chem.*, **8**, 1544 (1969).

TABLE VI
SECOND-ORDER RATE CONSTANTS^a AND ACTIVATION
PARAMETERS FOR THE REACTION

$$(\text{NH}_3)_5\text{RuH}_2\text{O}^{2+} + \text{L} \longrightarrow (\text{NH}_3)_5\text{RuL}^{2+} + \text{H}_2\text{O}$$

| L | k_L , $M^{-1} \text{sec}^{-1}$ | ΔH^\ddagger , kcal/mol | ΔS^\ddagger , eu | Ref |
|--|-------------------------------------|-----------------------------------|-----------------------------|-----------|
| Pyridine | 0.091 | 15.3 | -13 | This work |
| Acetonitrile | 0.260 | 16.2 | -7 | This work |
| Benzonitrile | 0.268 | 15.8 | -8 | This work |
| N ₂ O | 0.072 | 17.6 | -11 ^b | 10 |
| N ₂ | 0.073 | 18.3 | -2 | 9 |
| | 0.08 | 21.4 ^c | +8 ^c | 8 |
| Ru(NH ₃) ₅ N ₂ ²⁺ | 0.036 | 19.3 ^c | -1 ^c | 8 |

^a In aqueous solution at 25°. ^b As reported in ref 9. ^c Calculated from reported rate data.

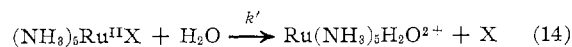
studied is an unsaturated nitrogen base. With the exception of pyridine, the steric properties of that coordination site are quite similar. Comparison of accurate space-filling models of the linear "end-on" coordinated $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{N}\equiv\text{X}$ systems shows no steric interaction between the $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ moiety and X even when the latter is a group as large as $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}\equiv$. In contrast, the space-filling model of the pyridine complex shows that while several conformations are relatively strain free, certain internal degrees of freedom, especially rotations about the metal-pyridine bond and the metal-cis-ammonia bonds, are affected by steric repulsion between pyridine ortho hydrogens and ammonia hydrogens. Other properties for the ligands in Table VI include wide variations in the Brønsted basicities (*e.g.*, pyridine $\text{p}K_a = 5.3$,¹⁸ acetonitrile $\text{p}K_a \approx -4$ ¹²) and in stabilities of the complexes with pentaammineruthenium(II). Aqueous solution equilibrium constants for eq 1 are $K_1 \simeq 10^7$ for L = pyridine,¹⁹ $K_1 = 3.3 \times 10^4$ for L = N₂,⁹ and $K_1 \simeq 8.3$ for L = N₂O¹⁰ (all at 25°).

Despite the differences in ligand properties listed above, the second-order rate constants (k_L , 25°) for reaction 1 are remarkably similar, with the fastest (benzonitrile) less than a factor of 5 more reactive than the slowest (3-chloropyridine) uncharged ligand reported to date. In addition, the activation parameters for the reactions (with the possible exception of those calculated for L = N₂ and L = Ru(NH₃)₅N₂²⁺ from the data of Page and coworkers⁸) are again quite analogously insensitive to ligand properties. We interpret these observations to indicate the operation of a *dissociative reaction pathway* similar to that described by eq 7 and 8. The same conclusion was recently forwarded by Armor and Taube⁹ on the basis of their data on the reactions with N₂ and N₂O. A limiting SN2 pathway is clearly ruled out by the reaction rate insensitivity to the stability of developing ruthenium(II)-ligand bond. The k_L 's for pyridine, N₂, and N₂O (Table VI) are exceedingly close; the reaction equilibrium constants differ by over six orders of magnitude. The activation parameters, in particular the negative ΔS^\ddagger values, fall into a range which has been interpreted as indicating a second-order associative pathway.²⁰ Equally convincing, however, is Tobe's correlation²¹ which illustrates that dissociative pathways occurring by trigonal-bipyramidal intermediates

give positive ΔS^\ddagger values, while negative ΔS^\ddagger values are observed with square-pyramidal intermediates. For ruthenium(II) substitutions, stereochemical retention is observed for reactions of *cis*- and *trans*-Ru(NH₃)₄(H₂O)₂²⁺, a fact which suggests tetragonal-pyramidal intermediates if the mechanisms are dissociative.

If eq 7 and 8 adequately describe the reaction mechanism, then $k_L = k_1 k_2 / k_{-1}$. In absence of major solvent perturbations, k_1 / k_{-1} would be independent of ligand identity and the k_L variations as a function of ligand identity would have to be reflected by proportional variations in k_2 . The term k_2 is the rate constant for the second-order nucleophilic attack of L on the coordinatively unsaturated Ru(NH₃)₅²⁺. As a result, k_2 should be a function of the ligand nucleophilicity with the exception of a diffusion-controlled reaction. Even then, small differences in ligand aqueous solution diffusion rates should influence k_2 . It is additionally possible that k_2 exceeds the diffusion-control limit and that I reacts only with ligands in its first solvation sphere ("interchange dissociative" mechanism²²). In this case, k_2 variations would reflect the population of L, which is uncharged or positively charged for all cases reported, in the outer coordination sphere of Ru(NH₃)₅H₂O²⁺ in competition with solvent. It is probable that both the k_2 step and the k_{-1} step (the nucleophilic attack of solvent water on Ru(NH₃)₅²⁺) would be quite rapid and that, owing to the small free energies of activation involved, Ru(NH₃)₅²⁺ would show relatively little selectivity toward various ligands. The greater the lifetime of I (*i.e.*, the less reactive it is with omnipresent solvent water) the more selective the reaction should be since the transition-state energy for the k_{-1} and k_2 steps should reflect the free energies of the developing metal-ligand bonds.

In the context of the above discussion, it would be especially interesting to know the relative reactivities of solvent water and ligand L toward the pentacoordinate intermediate I. These could be determined if k_1 were known; however, the best estimates available are the first-order rate constants which have been measured for reaction 14. These values (25°) are 20.1



and 17.5 sec⁻¹ for the uncharged oxygen-coordinated ligands formic acid and acetic acid,²³ respectively, and 5.3, 4.7, and 1.3 sec⁻¹ for the negative ligands trifluoroacetate,²³ chloride,²⁴ and formate,²³ respectively. By assuming that (14) is also a limiting dissociative reaction, we can estimate k_1 as 10 sec⁻¹, somewhat less than k' for the carboxylic acids since RC=O groups are electron withdrawing but somewhat greater than k' for the anions. On the basis of this estimate, the k_2 / k_{-1} ratio would be about 0.0091 M for L = pyridine and 0.0268 M for L = benzonitrile. The ratios must be multiplied by 55.4 M, the concentration of water, to give 0.5 and 1.5 as the estimated molar reactivity ratios for pyridine and benzonitrile, respectively, *vs.* H₂O. These estimates have little quantitative value but do suggest that (presuming the validity of the SN1

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(19) R. Sheppard and H. Taube, private communication.

(20) F. Monacelli and E. Viel, *Inorg. Chim. Acta*, **1**, 467 (1967).

(21) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

(22) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, pp 1-17.

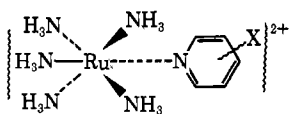
(23) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

(24) J. H. Baxendale, M. A. J. Rodgers, and M. D. Ward, *J. Chem. Soc. A*, 1246 (1970).

or the interchange dissociative pathway) the molar reactivities of H_2O and of the other ligands toward I are quite comparable.

Some selectivity, nonetheless, is displayed since k_L values depend somewhat on L's identity. However, as mentioned above, even the dissociative interchange mechanism would be expected to give different k_L 's. The interchange mechanism, which implies reaction of I primarily with L or H_2O in its first solvation shell, can be discounted by considering the k_L 's (25°) for nitrile coordination of 4-cyanopyridine ($0.261 M^{-1} \text{sec}^{-1}$) and of 4-cyanopyridinium ion ($0.238 M^{-1} \text{sec}^{-1}$). The k_L 's differ by less than 10% (Table V), yet the positive charge must dramatically alter the tendency for the cyanopyridinium ion to form an outer-sphere complex with the cationic $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$. Similarly, the reactivity of dinitrogen toward $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ is not significantly greater than that of cationic complexed dinitrogen $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ (Table VI), the difference being largely accountable to statistical phenomena: symmetrical N_2 has two potential coordination sites for attack while complexed N_2 has only one. On these bases, we conclude that the dissociative mechanism pentacoordinate intermediate must have a lifetime long enough to survive several collisions so that (1) the population of the first solvation sphere is not product determining and (2) a moderate selectivity is established in the competition for I between H_2O (k_{-1} step) and the various L's (k_2 step).

Substituent Effects.—The reactivities of the substituted pyridines follow the order of the ligand Brønsted basicities (Table I). Although the $\text{p}K_a$'s range from 6.23 for 3,5-dimethylpyridine to 2.83 for 3-chloropyridine, the k_L 's are much less sensitive, and 3,5-dimethylpyridine is only twice as reactive as 3-chloropyridine. Relative stabilities of the resulting $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complex ions have not been determined, and it would be difficult to predict these since the Ru(II) ligand bond has two important components. The σ -bonding donation ligand to metal of the nitrogen electron pair should be favored by electron-donating substituents while the π back-bonding of metal d electrons into unfilled π -symmetry ligand orbitals would be favored by electron-withdrawing substituents. The observation that the reactivity order follows ligand basicity suggests that, in the transition state of the k_2 step (the only ligand-dependent step), substituent-related differences in the σ bonding play the dominant role in the substituent effect. We believe that this result is to be expected for the k_2 step where the transition state may be envisioned to have an elongated metal-pyridine bond



Calculation of σ - and π -overlap integrals using Slater orbitals for ruthenium d orbitals and nitrogen sp^2 and p orbitals²⁵ leads to the qualitative conclusion that elongation of the ruthenium-nitrogen bond axis results in a much more precipitous decrease of π

overlap than of σ overlap. Consequently, regardless of relative contributions of σ and π interactions at the equilibrium bond length, σ -bonding effects should dominate in the activated complex suggested above. Substituent effects should be evident in the activation parameters, in particular ΔH^\ddagger ; however, the experimental uncertainty exceeds the small ΔH^\ddagger differences observed.

Steric Effects.—The organonitriles are more than twice as reactive (at 25°) as the substituted pyridines. Comparison of the activation parameters shows that the rate preference for the nitrile comes from more favorable ΔS^\ddagger terms while the ΔH^\ddagger values are actually less favorable by about 0.5 kcal/mol. These differences can be rationalized on the basis of bonding and steric effects in the k_2 step. The nitriles are much weaker Brønsted bases than the pyridines, a fact which suggests that their σ -donor capability would be lower. Consequently, in the activated complex having an elongated ruthenium-nitrogen bond, the pyridine should form the stronger σ bond, a fact which should result in a lower ΔH^\ddagger . The pyridine, however, should be sterically more restricted in attacking the tetragonal-pyramidal intermediate (I) owing to repulsive interactions between pyridine ortho hydrogens and the cis ammonias. Attack of the smaller nitrile group on the tetragonal-pyramidal intermediate should display significantly fewer steric interactions giving more internal degrees of freedom to the activated complex, and, consequently, a k_2 step with a more positive ΔS^\ddagger than for the pyridine k_2 step. In agreement, the nitrile reactions have ΔS^\ddagger values 5 eu more positive than the pyridine reactions, an effect sufficient to overbalance the less favorable ΔH^\ddagger terms. Also in agreement with these arguments are the results of Sheppard and Taube,¹⁹ who have determined the k_2 values for some ortho-substituted pyridines. These reactions are substantially slower than the reaction with unsubstituted pyridine, and the activation parameters demonstrate that the rate differences are largely the result of more negative ΔS^\ddagger terms.

Ionic Strength and Solvent Effects.—Higher ionic strength and a more polar solvent medium both lead to somewhat greater k_2 values (Tables I, III, IV, and V). Since in mixed solvent the ruthenium(II) reactant is actually $\text{Ru}(\text{NH}_3)_5\text{S}^{2+}$, the equilibrium mixture of the solvent complexes, interpretation of modest rate differences must be cautious. Nonetheless, the ionic strength and solvent effects observed are consistent with the argument that a pentacoordinate intermediate I is smaller and more highly solvated than the starting complex and that this species would be more stable in solutions at higher ionic strength and in more polar solvents.

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(25) W. Palke, private communication.