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Substitution Reactions of Metallic Complexes of β,β′,β″-Triaminotriethylamine. 14. Base Hydrolysis, Chloride Anation, and Synthesis of Some Rhodium(III) Complexes of β,β′,β″-Triaminotriethylamine: Evidence for Chemically Nonequivalent Coordination Sites in the $[Rh(tren)XY]^{n+}$ Cation[1]

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The base hydrolysis of $[Rh(tren)Cl_2]^+$ generates β-$[Rh(tren)ClOH]^+$ identical with the photochemical product, while earlier work shows that aquation of $[Rh(tren)Cl_2]^+$ in acidic solution gives the α isomer. The kinetics of the hydrolysis of $[Rh(tren)Cl_2]^+$ and α- and β-$[Rh(tren)ClOH]^+$ in alkaline solution have been investigated, as have the kinetics of the acid hydrolysis of β-$[Rh(tren)Cl(H_2O)]^{2+}$. The hydrolyses of the dichloro and α-chlorohydroxo ions (k_1 and k_2) are accelerated by hydroxide, whereas the rate of hydrolysis of the β isomer (k_3) is only marginally affected by the presence of hydroxide. In acidic solution in the presence of excess Cl^-, $[Rh(tren)(OH_2)_2]^{3+}$ undergoes two distinct chloride anation steps (k_4 and k_5). Kinetic data were collected on the following reactions:

$$\begin{tikzcd} {[Rh(tren)Cl_2]^+} \arrow[r, "k_{-1}", "OH^-"'] & \beta\text{-}[Rh(tren)ClOH]^- \arrow[d, "k_3", "OH^-"'] \\ \alpha\text{-}[Rh(tren)Cl(OH)]^+ \arrow[r, "k_2", "OH"'] & {[Rh(tren)(OH)_2]^+} \end{tikzcd}$$

$$[Rh(tren)(OH_2)_2]^{3+} \xrightarrow[Cl^-]{k_4} \beta\text{-}[Rh(tren)ClOH_2]^{2+} \xrightarrow[Cl^-]{k_5} [Rh(tren)Cl_2]^+$$

Reaction products were characterized in solution by electronic spectra and chemical analyses. The stereospecific substitutions and differences in substitution rates, for both the hydrolyses and anations, are explained in terms of different environments of the two nonamine coordination sites in $[Rh(tren)XY]^{n+}$ complexes. The base hydrolysis and chloride anation data have been used in the synthesis of some new Rh(III)-tren complexes. These have been isolated as solids and characterized by elemental analysis and visible and ultraviolet spectra.

Introduction

In recent studies,[2,3] the thermal and photochemical reactions of $[Rh(tren)Cl_2]^+$ (tren = β,β′,β″-triaminotriethylamine) were found to be drastically different. It was postulated that α-$[Rh(tren)Cl(H_2O)]^{2+}$ was produced during the associative acid hydrolysis, while distortion toward a trigonal-bipyramidal (TBP) intermediate during photolysis led to the formation of β-$[Rh(tren)Cl(H_2O)]^{2+}$ (Figure 1). The nonequivalency of the two nonamine coordination sites was invoked to account for the stereospecificity of these reactions.

In an effort to further clarify this situation, we have investigated the kinetics of the base hydrolysis of $[Rh(tren)Cl_2]^+$ and α- and β-$[Rh(tren)ClOH]^{2+}$, respectively. If the coordination sites occupied by the chlorides are nonequivalent, these three complexes should differ significantly in their reactivity toward the hydroxide ion, since one of the chlorides is more susceptible to dissociative-type reactions. In addition, the kinetics of the chloride anation of $[Rh(tren)(OH_2)_2]^{3+}$ have been studied in an effort to characterize further the differences between these to nonamine coordination sites. Finally, the base hydrolysis and anation results have been used as an aid in the synthesis of some new Rh(III)-tren compounds.

Experimental Section

Preparation of Complexes. Dichloro(β,β′,β″-triaminotriethylamine)rhodium(III) Chloride. The method of Basolo and Johnson,[4] as amended by Martins and Sheridan,[2] was used to prepare this compound. Purity was established by checking electronic spectra against the known values.[5]

α-Aquochloro(β,β′,β″-triaminotriethylamine)rhodium(III) Cation. This species was isolated in solution by the method of Madan[3] as modified by Sheridan.[2] The corresponding α-chlorohydroxo cation was generated in solution by basifying solutions of α-$[Rh(tren)Cl(OH_2)]^{2+}$ with NaOH.

β-Aquochloro(β,β′,β″-triaminotriethylamine)rhodium(III) Cation. The procedure of Martins and Sheridan[2] was used. The β-chlorohydroxo species was generated in solution by the basification of solutions of β-$[Rh(tren)Cl(H_2O)]^{2+}$ as described for the α isomer.

New Complexes. Diiodo(β,β′,β″-triaminotriethylamine)rhodium(III) Iodide, $[Rh(tren)I_2]I$. One-fourth gram of $[Rh(tren)Cl_2]Cl$ was dissolved in 0.1 M NaOH at 80 °C and allowed to undergo base hydrolysis to $[Rh(tren)(OH)_2]^+$. The resulting solution was adjusted to neutral pH (as determined by multirange pH paper, Fisher Scientific Co.) by the dropwise addition of 0.5 M $HClO_4$. At this point NaI (1.16 g, a 10-fold excess) was added, and the solution was refluxed until the solution turned brown. The hot solution was filtered immediately and allowed to cool to room temperature. During this time, a rust-brown product crystallized. The complex was recrystallized by dissolving in hot water and filtering into a cold, saturated solution of NaI. The product was collected, washed with ethanol and ether, and air-dried. The yield was 0.31 g (70%). Anal. Calcd for $[Rh(C_6H_{18}N_4)I_2]I$: C, 11.43; H, 2.86; N, 8.89; Rh, 16.35. Found: C, 11.63; H, 3.02; N, 9.00; Rh, 16.60.

(Oxalato)(β,β′,β″-triaminotriethylamine)rhodium(III) Perchlorate Monohydrate, $[Rh(tren)ox]ClO_4{\cdot}H_2O$. One-fourth gram of $[Rh(tren)Cl_2]Cl$ was allowed to undergo base hydrolysis to the dihydroxo complex. The solution was adjusted to neutral pH with 0.5 M $HClO_4$ and a 10-fold excess of (0.23 g) of $NaC_2O_4{\cdot}H_2O$ was added. The solution was refluxed until colorless (~2 h) and then evaporated to a volume of (~5 mL). Saturated $NaClO_4$ (3 g, 5 mL) was added, and upon cooling, beautiful off-white crystals deposited in 82% yield. They were collected and washed with ethanol and ether. Anal. Calcd

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(2) Martins, E.; Sheridan, P. S. *Inorg. Chem.* **1978**, *17*, 2822.

(3) Zipp, S. G.; Madan, S. K. *J. Inorg. Nucl. Chem.* **1975**, *37*, 181.

(4) Johnson, S. A.; Basolo, F. *Inorg. Chem.* **1962**, *1*, 925.

(5) Martins, E., personal communication.

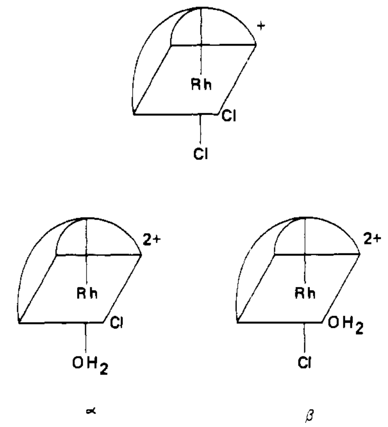

Figure 1. Possible geometric isomers for $[Rh(tren)ClX]^{n+}$ (X = Cl^-, H_2O).

for $[Rh(C_6H_{18}N_4)C_2O_4]ClO_4·H_2O$: C, 21.12; H, 4.40; N, 12.32; Rh, 22.66. Found: C, 20.99; H, 4.14; N, 11.96; Rh, 23.00.

Dibromo(β,β′,β″-triaminotriethylamine)rhodium(III) Perchorate Hemihydrate, $[Rh(tren)Br_2]ClO_4·{}^1/_2H_2O$. A solution of the dichloro complex (0.25 g) in 0.1 M NaOH was allowed to undergo base hydrolysis to $[Rh(tren)(OH)_2]^+$. After neutralization with 0.5 M $HClO_4$, NaBr (0.72 g) was added and the solution refluxed for 1 h. During this time the color of the solution turned a bright yellow-orange. After filtration, the volume was reduced to 10 mL, and 5 mL of concentrated $HClO_4$ were added. Upon cooling in an ice bath, a yellow-orange powder appeared. After filtration and washing with ethanol and ether, the yield was 0.23 g (63%). Anal. Calcd for $[Rh(C_6H_{18}H_4)Br_2]ClO_4·{}^1/_2H_2O$: C, 13.91; H, 3.67; N, 10.82; Rh, 19.90. Found: C, 14.27; H, 3.77; M, 11.09; Rh, 19.78.

Diazido(β,β′,β″-triaminotriethylamine)rhodium(III) Chloride, $[Rh(tren)(N_3)_2]Cl$. After the base hydrolysis and neutralization (with 0.5 M HCl) of $[Rh(tren)Cl_2]Cl$ (0.25 g), NaN_3 (0.46 g) was added and the solution refluxed until the color became a bright gold (~90 min). The solution was concentrated to a volume of about 5 mL, at which time crystallization occurred. The solid was dissolved in about 15 mL of water containing 5 g of DOWEX 1-X4 anion-exchange resin (Cl^- form). The resin was removed by filtration and the resulting solution evaporated to about 5 mL. After cooling in an ice bath, the yellow crystals of $[Rh(tren)(N_3)_2]Cl$ deposited in 61% yield. Anal. Calcd for $[Rh(C_6H_{18}N_4)N_3)_2]Cl$: C, 19.54; H, 4.88; N, 37.99; Rh, 27.95. Found: C, 19.45; H, 4.82; N, 37.88; Rh, 28.02.

Dinitro(β,β′,β″-triaminotriethylamine)rhodium(III) Nitrate, $[Rh(tren)(NO_2)_2]NO_3$. The dichloro complex (0.25 g) was base hydrolyzed to $[Rh(tren)(OH)_2]^+$ and the solution neutralized with 0.5 M $HClO_4$. Sodium nitrite (0.50 g) was added and the solution refluxed until colorless. After filtration, the solution was evaporated to 10 mL and 5 mL of concentrated HNO_3 added to destroy the excess nitrite. Upon cooling in an ice bath, beautiful white crystals appeared to 70% yield. The product was filtered and washed with ethanol and ether. Anal. Calcd for $[Rh(C_6H_{18}N_4)(NO_2)_2]NO_3$: Rh, 25.56. Found: Rh, 25.90.

Analyses. C, H, and N, analyses were performed by Strauss, Oxford, England. Rh was determined spectrophotometrically with stannous chloride.[6]

Electronic Spectra. A Beckman Acta MIV recording spectrophotometer was used to record all ultraviolet and visible spectra. Approximately millimolar solutions were scanned in matched quartz cells of 1-cm path length.

Infrared Spectra. All IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Solid samples in potassium bromide disks were scanned in the region 4000–250 cm^{-1}.

Kinetics. (1) Base Hydrolysis. The base hydrolysis of the dichloro ion was measured by dissolving the complex in a solution of the appropriate pH and temperature. The change in absorbance at 295 nm was monitored as a function of time. For the chlorohydroxo species, solutions of the appropriate complex in water at a given temperature were mixed with the appropriate volume of 0.2 N NaOH at the same temperature. Changes in absorbance were followed at 360 nm for both complexes.

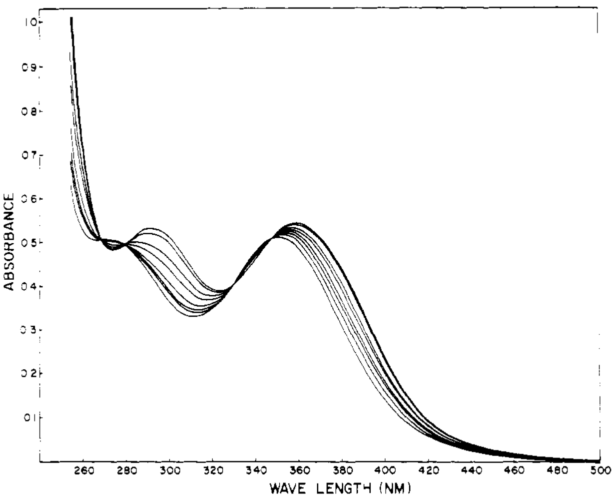

Figure 2. Spectophotometric scans during the base hydrolysis of $[Rh(tren)Cl_2]^+$ to β-$[Rh(tren)ClOH]^+$ at pH 13.0 and 25 °C.

Table I. Values of k_1 for the Base Hydrolysis of $[Rh(tren)Cl_2]^+$ [a]

T, °C	pH	μ, M[b]	10^3k_1, s^{-1}
20.0	13.02	0.104	1.33 ± 0.03
25.0	13.02	0.104	2.47 ± 0.01
25.0	12.50	0.104	0.727 ± 0.005
25.0	12.03	0.104	0.236 ± 0.002
30.0	13.02	0.104	4.59 ± 0.04
35.0	13.02	0.104	7.45 ± 0.10
35.0	13.02	0.204	5.81 ± 0.06
35.0	13.02	0.370	4.91 ± 0.08
35.0	13.02	0.500	4.09 ± 0.04
35.0[c]	13.02	0.500	4.13 ± 0.06

[a] [complex] = 5.0 × 10^{-4} M; λ = 295 nm. [b] Adjusted with $NaClO_4$. [c] [complex] = 1.0 × 10^{-3} M.

(2) Chloride Anation. In a typical experiment, a solution of $[Rh(tren)(H_2O)_2]^{3+}$ in 0.1 M $HClO_4$ was thermostated at the desired temperature, and then solid NaCl and $NaClO_4$ were added to give the desired chloride concentration and ionic strength. The reaction mixture was transferred to a spectrophotometric cell, and the rate of appearance of β-$[Rh(tren)Cl(H_2O)]^{2+}$ was monitored spectrophotometrically. The anation of β-$[Rh(tren)Cl(OH_2)]^{2+}$ was then subsequently followed in a similar manner. The method of calculating rate constants has been described previously.[7]

Results

Base Hydrolysis. $[Rh(tren)Cl_2]^+$. The reaction of $[Rh(tren)Cl_2]^+$ in basic aqueous solution leads to spectral changes with a shift of the d–d band maxima to lower wavelengths. Spectral scans of this reaction at pH 13.0 and 25 °C showed four isosbestic points (349, 330, 279, 269 nm) which were maintained throughout the reaction (Figure 2). Acidification of product solutions resulting from this reaction yielded solutions whose spectra were identical with (±5%) that previously reported for β-$[Rh(tren)Cl(H_2O)]^{2+}$.[2] This allows the assignment of the base hydrolysis product as β-$[Rh(tren)Cl(OH)]^+$.

The kinetics of the base hydrolysis of $[Rh(tren)Cl_2]^+$ were measured over a wide range of hydroxide ion concentrations, complex concentrations, ionic strengths, and temperatures. Pseudo-first-order rate plots were linear for more than 4 half-lives. Representative rate data are listed in Table I. Figure 3 shows a plot of the pseudo-first-order rate constant (k_1) for the base hydrolysis of $[Rh(tren)Cl_2]$ vs. the OH^- concentration. The line passes through the origin; the slope

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(6) (a) Sandell, E. B. "Colorimetric Determination of Trace Metals"; Interscience: New York, 1959; p 769. (b) Kolthoff, I. M., Elving, P. J., Eds. "Treatise on Analytical Chemistry"; Interscience: New York, 1963; Part II, Vol. 8, p 468.

(7) Madan, S. K.; Reiff, W. M.; Bailar, J. C., Jr. *Inorg. Chem.* **1965**, *4*, 1366.

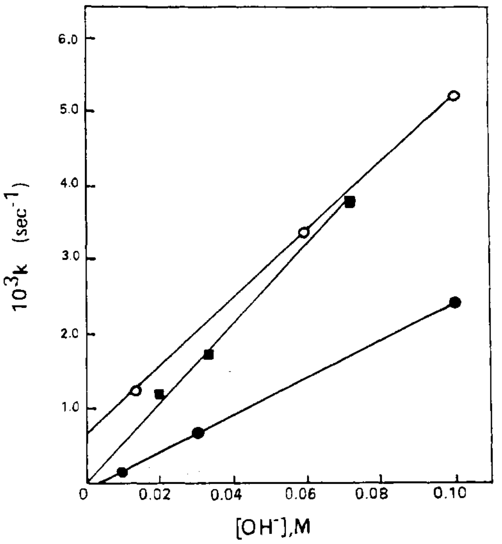

Figure 3. Plots of k vs. [OH$^-$] for the base hydrolysis of $[Rh(tren)Cl_2]^+$ (k_1, ●, 25 °C), α-$[Rh(tren)ClOH]^+$ (k_2, ■, 70.3 °C), and β-$[Rh(tren)ClOH]^+$ (k_3, ○, 75.0 °C).

Table II. Values of k_2 for the Base Hydrolysis of α-$[Rh(tren)Cl(OH)]^+$ [a]

T, °C	pH	μ, M[b]	10^3k_2, s^{-1}
55.0	12.84	0.069	1.03 ± 0.04
60.0	12.84	0.069	1.57 ± 0.06
60.0	13.00	0.100	2.19 ± 0.05
65.0	12.84	0.069	2.47 ± 0.10
70.3	12.84	0.069	3.81 ± 0.08
70.3	12.84	0.200	3.70 ± 0.01
70.3	12.84	0.350	3.52 ± 0.03
70.3	12.50	0.069	1.67 ± 0.04
70.3	12.32	0.069	1.17 ± 0.04
70.3[c]	12.32	0.069	1.21 ± 0.06

[a] [complex] = 1.0 × 10^{-3} M; λ = 360 nm. [b] Adjusted with $NaClO_4$. [c] [complex] = 2.0 × 10^{-3} M.

corresponds to the second-order rate constant, k_{OH}, and has a value of 2.38 (±0.10) × 10^{-2} M^{-1} s^{-1}.

Arrhenius plots were obtained from the data in Table I, and the following activation parameters were calculated: $\Delta H^* = 21.0 \pm 0.2$ kcal mol^{-1}; $\Delta S^* = -0.2 \pm 0.7$ cal deg^{-1} mol^{-1}.

α-$[Rh(tren)Cl(OH)]^+$. Thermally produced α-$[Rh(tren)Cl(H_2O)]^{2+}$ is thermally inert in acidic aqueous solution. Thermally produced α-$[Rh(tren)Cl(OH)]^+$, however, undergoes hydrolysis in alkaline solution. Spectral scans of this reaction at pH 13.0 and 60 °C exhibit isosbestic points at 333, 307, 262, and 256 nm, and the d–d band maxima shift to higher energies.[2] In addition, spectra of the product solutions after acidification with $HClO_4$ are identical with that of $[Rh(tren)(OH_2)_2]^{3+}$.[2] This behavior is consistent with the formation of $[Rh(tren)(OH)_2]^+$ as the base hydrolysis product.

Pseudo-first-order rate constants (k_2) for this reaction were determined under a variety of conditions as indicated in Table II. A plot of k_2 vs. [OH$^-$] at 70.3 °C yielded a straight line (Figure 3) which corresponded to a second-order rate constant of 5.44 (±0.25) × 10^{-2} M^{-1} s^{-1}. The linear Arrhenius plots yielded $\Delta H^* = 18.4 \pm 0.4$ kcal mol^{-1} and $\Delta S^* = 16.0 \pm 0.7$ cal deg^{-1} mol^{-1}.

β-$[Rh(tren)Cl(H_2O)]^{2+}$ and β-$[Rh(tren)Cl(OH)]^+$. Photochemically produced β-$[Rh(tren)Cl(H_2O)]^{2+}$ is thermally reactive in acidic solution at pH 1 and 70 °C; spectral changes occur with four isosbestic points: 335, 305, 279, and 262 nm.[2] These points hold throughout the aquation, and the final spectrum is identical with that of $[Rh(tren)(OH_2)_2]^{3+}$. At pH 13 and 75 °C, however, the reaction leads to $[Rh(tren)(OH)_2]^+$ as the product. The kinetics of hydrolysis were measured over the pH range 1–13 at a number of temperatures and ionic strengths. The results are given in Table III. Only a slight increase in the hydrolysis rate occurs even in 0.1 M NaOH.

Table III. Values of k_3 for the Hydrolysis of β-$[Rh(tren)(H_2O)Cl]^{2+}$ [a]

T, °C	pH	μ, M[b]	10^4k_3, s^{-1}
65.0	13.0	0.100	26.9 ± 0.8
70.0	1.0	0.100	3.76 ± 0.07
75.0	1.0	0.100	5.45 ± 0.10
75.0	1.0	0.302	5.40 ± 0.07
75.0	1.0	0.500	5.38 ± 0.14
75.0	7.0	0.100	5.52 ± 0.12
75.0	10.0	0.100	11.3 ± 0.5
75.0	12.05	0.100	12.5 ± 0.6
75.0	12.75	0.100	33.5 ± 0.9
75.0	13.0	0.100	53.2 ± 0.7
80.0	1.0	0.100	8.60 ± 0.7
80.0	13.0	0.100	78.3 ± 0.6
85.0	1.0	0.100	12.7 ± 0.9
85.0	13.0	0.100	108 ± 7

[a] [complex] = 1.0 × 10^{-3} M; λ = 360 nm. [b] Adjusted with $NaClO_4$.

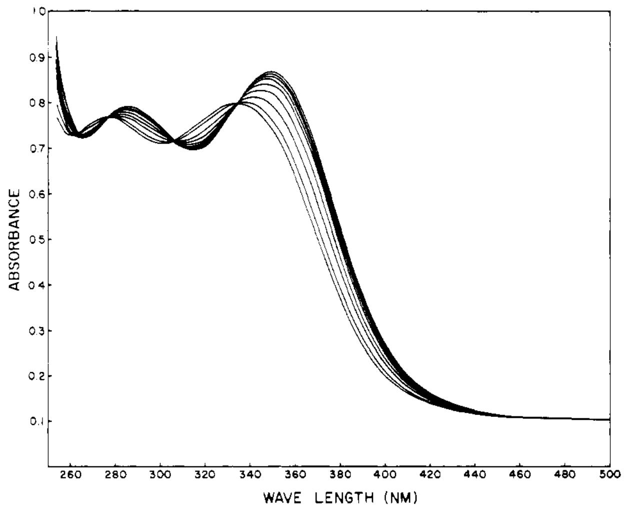

Figure 4. Spectrophotometric scans during the chloride anation of $[Rh(tren)(H_2O)_2]^{3+}$ to β-$[Rh(tren)Cl(H_2O)]^{2+}$ at pH 1, [Cl$^-$] = 0.73, and 45.0 °C.

Figure 3 shows a plot of k_3 vs. [OH$^-$] at 75 °C. The slope of the line (equal to the second-order rate constant) is 4.56 (±0.45) × 10^{-2} M^{-1} s^{-1}, and the intercept is 7.36 (±0.70) × 10^{-4} s^{-1}. Activation parameters were evaluated under both acidic and basic conditions: at pH 1, $\Delta H^* = 19.4 \pm 0.4$ kcal mol^{-1} and $\Delta S^* = -18 \pm 1.0$ cal deg^{-1} mol^{-1}; at pH 13, $\Delta H^* = 18.9 \pm 0.9$ kcal mol^{-1} and $\Delta S^* = -19.0 \pm 1.1$ cal deg^{-1} mol^{-1}.

Chloride Anation of $[Rh(tren)(OH_2)_2]^{3+}$. In acidic aqueous solution in the presence of excess chloride ion, $[Rh(tren)(OH_2)_2]^{3+}$ undergoes two successive chloride anation steps. Scans of the first in the region 500–250 nm show four isosbestic points (335, 306, 277, 265 nm) which hold throughout the reaction and which are the same wavelengths as those observed for the aquation of β-$[Rh(tren)Cl(H_2O)]^{2+}$ (Figure 4). Furthermore, the product has an electronic spectrum which agrees with that of β-$[Rh(tren)Cl(H_2O)]^{2+}$.

During the second reaction, which corresponds to the chloride anation of β-$[Rh(tren)Cl(H_2O)]^{2+}$, spectral changes occur with the maintenance of four more isosbestic points at 363, 319, 282, and 275 nm, respectively. The final spectrum is identical with that of $[Rh(tren)Cl_2]^+$.

The kinetics of the chloride anation of $[Rh(tren)(OH_2)_2]^{3+}$ were measured at 363 nm. This is an isosbestic point of the

Table IV. Values of k_4 for the Chloride Anation of $[Rh(tren)(OH_2)_2]^{3+}$ [a]

T, °C	pH	$[Cl^-]$, M	μ, M[b]	10^3k_4, s^{-1}
40.0	1.0	1.90	2.00	2.54 ± 0.04
45.0	1.0	1.90	2.00	3.85 ± 0.07
45.0	1.0	0.37	2.00	1.75 ± 0.14
45.0	1.0	0.73	2.00	2.40 ± 0.10
45.0	1.0	1.09	2.00	2.69 ± 0.03
45.0	1.0	1.59	2.00	3.58 ± 0.18
50.0	1.0	1.90	2.00	5.50 ± 0.09
60.0	1.0	1.90	2.00	9.70 ± 0.17

[a] [complex] = 1.0×10^{-3} M; λ = 363 nm. [b] Adjusted with $NaClO_4$.

Table V. Values of k_5 for the Chloride Anation of β-$[Rh(tren)Cl(H_2O)]^{2+}$ [a]

T, °C	pH	$[Cl^-]$, M	μ, M[b]	10^4k_5, s^{-1}
55.0	1.0	1.90	2.00	7.34 ± 0.11
60.0	1.0	0.37	2.00	2.16 ± 0.08
60.0	1.0	0.73	2.00	4.50 ± 0.03
60.0	1.0	1.09	2.00	6.63 ± 0.05
60.0	1.0	1.59	2.00	9.94 ± 0.14
60.0	1.0	1.90	2.00	11.7 ± 0.6
65.0	1.0	1.90	2.00	17.8 ± 0.4
70.0	1.0	1.90	2.00	27.3 ± 0.8

[a] [complex] = 1.0×10^{-3} M; λ = 390 nm. [b] Adjusted with $NaClO_4$.

second anation, and any absorbance changes at this wavelength must be due to the first reaction only. Pseudo-first-order rate constants (k_4) were linear for 3 or more half-lives. Representative values of k_4 under a variety of conditions are given in Table IV. The effect of the chloride ion concentration on the rate constant is illustrated in Figure 5. The slope of this line which is the second-order anation constant k_{AN} is 1.42 (±0.35) × 10^{-3} M^{-1} s^{-1}.

The kinetics of the chloride anation of β-$[Rh(tren)Cl(H_2O)]^{2+}$ were also measured: the results are presented in Table V. Rate plots were linear for at least 4 half-lives. The value of k'_{AN} resulting from a plot of k_5 vs. $[Cl^-]$ (Figure 5) is 6.25 (±0.27) × 10^{-4} M^{-1} s^{-1}. Activation parameters were determined for both anations as follows: for $[Rh(tren)(OH_2)_2]^{3+}$, $\Delta H^* = 13.6 \pm 0.5$ kcal mol^{-1}, $\Delta S^* = -26.3 \pm 1.0$ cal deg^{-1} mol^{-1}; for β-$[Rh(tren)Cl(H_2O)]^{2+}$, $\Delta H^* = 18.3 \pm 0.3$ kcal mol^{-1}, $\Delta S^* = -17.0 \pm 1.5$ cal deg^{-1} mol^{-1}.

Synthesis of New Complexes. A number of new Rh(III)–tren compounds have been synthesized via the base hydrolysis of the $[Rh(tren)Cl_2]^+$ ion. These compounds were characterized be elemental analysis (see Experimental Section) and visible (Table VI) and infrared spectra (see Discussion).

Discussion

Base Hydrolysis. In basic aqueous solution, $[Rh(tren)Cl_2]^+$ undergoes hydrolysis to β-$[Rh(tren)ClOH]^+$. Evidence for this reaction includes (1) the shift of d–d band maxima to lower wavelengths, (2) the similarity of the spectra of acidified product solutions to that of β-$[Rh(tren)Cl(H_2O)]^{2+}$, and (3) further reactions of β-$[Rh(tren)ClOH]^+$ in alkaline media.

Previously reported studies of the acid hydrolysis[3] and photochemistry[2] of $[Rh(tren)Cl_2]^+$ have shown that the two nonamine coordination sites are nonequivalent. The chloride trans to the tertiary nitrogen is in close proximity to amine protons which can interact with solvent molecules. The chloride cis to the tertiary nitrogen, however, is surrounded by the aliphatic chains of the tren ligand and is thus located in a hydrophobic region. It is reasonable to assume, therefore, that a dissociative reaction would lead to loss of the cis chloride, while the trans chloride would be lost if an associative mechanism were in operation. The base hydrolysis of Rh(III) has been demonstrated to be dissociative in other cases.[8]

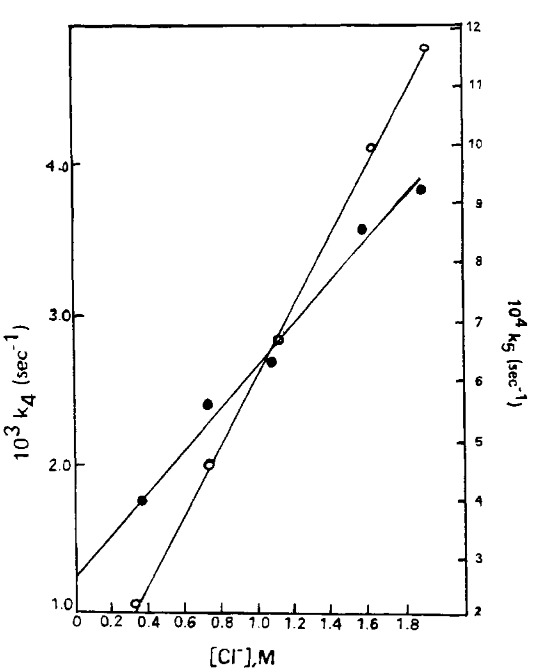

Figure 5. Plots of k vs. $[Cl^-]$ for the chloride anation of $[Rh(tren)(H_2O)_2]^{3+}$ (k_4, ●, 45.0 °C) and β-$[Rh(tren)Cl(H_2O)]^{2+}$ (k_5, ○, 60.0 °C).

Table VI. Electronic Spectra for Various Rh(III)–Amine Complexes

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[Rh(tren)_2Cl_2]NO_3$[a]	352 (155), 295 (180)
$[Rh(tren)Cl_2]Cl$[b]	364 (321), 292 (330)
$[Rh(tren)C_2O_4]ClO_4 \cdot H_2O$[c]	328 (290)
$[Rh(tren)I_2]I$[c]	395 sh (1350)
$[Rh(tren)Br_2]Br \cdot {}^1/_2H_2O$[c]	382 (260)
$[Rh(tren)(N_3)_2]Cl$[c]	357 (320)
$[Rh(tren)(NO_2)_2]NO_3$[c]	295 (800)

[a] Reference 4. [b] Reference 5. [c] This work.

Application of a dissociative mechanism to the base hydrolysis of $[Rh(tren)Cl_2]^+$ leads to a prediction of β-$[Rh(tren)ClOH]^+$ as the product. Acidified solutions of this product have the same spectra as photochemically produced β-$[Rh(tren)Cl(H_2O)]$.$^{2+}$ These results support the previous assignments of the isomers of $[Rh(tren)Cl(H_2O)]^{2+}$.[2]

The rate of base hydrolysis at 25 °C is more rapid than the rates of the analogous reaction of other Rh(III)–tetraamine complexes.[9] This is characteristic of tren complexes and may be due to strain induced by the tren ligand[10] or to the presence of the hydrophilic pocket.

Photochemically produced β-$[Rh(tren)Cl(H_2O)]^{2+}$ is thermally reactive (Table III). The rate constants and activation parameters for the acid hydrolysis of β-$[Rh(tren)Cl(H_2O)]^{2+}$ are typical of those of other Rh(III)–amine complexes[9,11] and require no further comment. At higher pHs, however, there is only a slight acceleration of the hydrolysis rate. Furthermore, the line in Figure 3 has a positive intercept of 7.36 (±0.7) × 10^{-4} s^{-1}. This intercept corresponds to the rate of aquation of β-$[Rh(tren)ClOH]^+$. Thus, the rate constant k_3 can be represented as a combination of two terms

$$k_3 = k + k'[OH^-]$$

where k is the first-order rate constant for the aquation of

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(8) Panunzi, A.; Basolo, F. *Inorg. Chim. Acta* **1967**, *1*, 223.

(9) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

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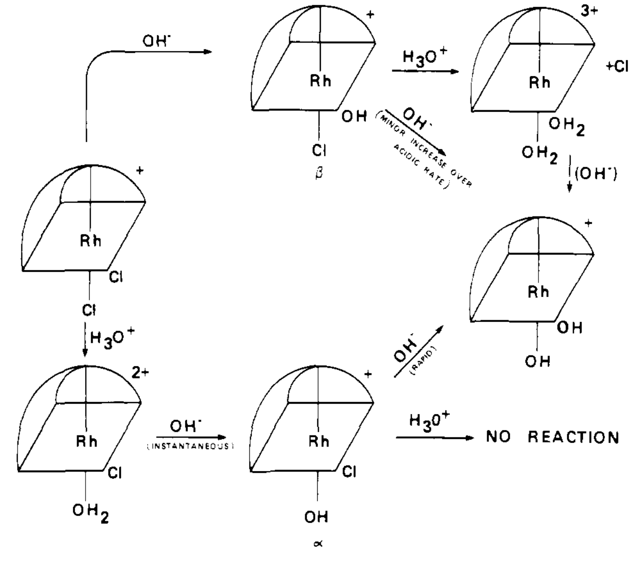
(11) Martins, E.; Kaplan, E. B.; Sheridan, P. S. *Inorg. Chem.* **1979**, *18*, 2195.

Scheme I



β-[Rh(tren)ClOH]$^+$. The activation parameters for the base hydrolysis of β-[Rh(tren)ClOH]$^+$ are similar to those calculated for the acid hydrolysis, again indicating the lack of any marked change in reactivity when hydroxide is the entering ligand.

In contrast, α-[Rh(tren)ClOH]$^+$ is very reactive toward the hydroxide ion (Table II). Comparison of the rates of the base hydrolysis of this complex to those for the β-chlorohydroxo ion reveals that the α isomer reacts approximately 10 times faster. A more important comparison, however, is that between the rates of reaction of both isomers in acidic and basic solution. As stated earlier, the β isomer aquates smoothly at pH 1; addition of hydroxide (pH 13) increases the rate of hydrolysis by a factor of ~10. The α isomer, however, is thermally inert at pH 1.[3] In this case, adjustment of the pH to 13 results in an efficient and relatively fast base hydrolysis. These reactions are summarized in Scheme I.

The effects of added hydroxide ion on the reactions of these two complexes can be rationalized on the basis of the dissociative mechanism proposed above. As indicated earlier, such a mechanism would favor the formation of a TBP intermediate and loss of the nonamine ligand cis to the tertiary nitrogen. In the case of the α isomer, such a distortion would lead to the cleavage of a Rh–Cl bond. Hydroxide exchange, however, would be predicted in the case of the β isomer, although we have no experimental evidence to support this supposition. A dissociative mechanism, therefore, accounts nicely for the differences in the base hydrolysis reactions of these two complexes.

It is worthwhile to note that the results presented here differ from those reported during a previous investigation[9] of the base hydrolysis of [Rh(tren)Cl$_2$]$^+$. It was reported then that the second chloride was inert to base hydrolysis. This was presumably due to the fact that amino protons trans to the leaving group were required if an (S$_N$1)CB mechanism was in operation. Thus, β-[Rh(tren)ClOH]$^+$ was thought to be inert. However, the present study, together with the recent acid hydrolysis and photolysis studies, unequivocally confirms that the chloride trans to the tertiary amine is reactive in both acidic and basic media.

Chloride Anation. The chloride anation of [Rh(tren)(OH$_2$)$_2$]$^{3+}$ in acidic solution proceeds in two steps: the formation of β-[Rh(tren)Cl(H$_2$O)]$^{2+}$ and its subsequent anation to the dichloro ion. The kinetics of both reactions have been studied.

The experimental data do not allow an unambiguous determination of the mechanisms of these anation reactions. The anation of both [Rh(tren)(OH$_2$)$_2$]$^{3+}$ and β-[Rh(tren)Cl(H$_2$O)]$^{2+}$ are first order in both [Rh(III)] and [Cl$^-$] (see Figure 5). The linearity of both plots in Figure 5, even at high Cl$^-$ concentrations, is not consistent with a dissociative mechanism.[9,12] Whenever such cationic species are present in solution with high concentrations of anionic species, the formation of outer-sphere complexes[9] must be considered. The resulting outer-sphere to inner-sphere interchange process is consistent with the observed kinetic behavior and is a likely reaction pathway.

It is interesitng to note that the first anation product is the β isomer, i.e. the one with a chloride occupying the hydrophilic site. It is reasonable that a reaction in which chloride ions must be obtained from the solvent shell would occur more quickly at the hydrophilic pocket. The stereochemistry of these anation reactions, therefore, lends further support to the notion of the noneqivalency of the two nonamine coordination sites.

Synthesis of New Complexes and Spectral Studies. The results of the base hydrolysis and chloride anation studies were used as a guide for the preparation of some new Rh(III)–tren compounds. The [Rh(tren)(OH$_2$)$_2$]$^{3+}$ cation was generated in solution by the acidification of solutions of [Rh(tren)(OH)$_2$]$^+$ which had been prepared via the base hydrolysis of the dichloro starting materials. Introduction of the appropriate sodium salt and subsequent refluxing led to the formation of the desired acido cations. Complexes with the following ligands were isolated: Br$^-$, I$^-$, N$_3^-$, C$_2$O$_4^{2-}$, and NO$_2^-$.

Attempts to isolate [Rh(tren)(N$_3$)$_2$]N$_3$ were successful, but the resulting solid decomposed in a matter of hours. The chloride salt, however, is stable for at least 3 months at room temperature. The infrared spectra of [Rh(tren)(N$_3$)$_2$]Cl and [Rh(tren)C$_2$O$_4$]ClO$_4$·H$_2$O were very similar to those of other Co(III)–[13] and Rh(III)–tetraamine[4,14] complexes.

An interesting point is the mode of bonding in [Rh(tren)(NO$_2$)$_2$]NO$_3$. Some Co(III)[15] and Rh(III)[16] compounds which contain M–ONO moieties have been isolated. The IR spectra of such complexes do not exhibit the wagging absorption present at 594 cm^{-1} in the N-bonded species. The tren complex does exhibit this abosrption. In addition, the UV–visible spectrum of this species is very similar to that reported for *cis*-[Rh(en)$_2$(NO$_2$)$_2$]NO$_3$.[4] Both these observations are evidence for bonding of the nitrite via nitrogen in [Rh(tren)(NO$_2$)$_2$]NO$_3$.

Species containing ionic perchlorate show the characteristic broad absorption in the region 1050–1150 cm^{-1},[17] and the bands in the regions 3550–3200 and 1650–1620 cm^{-1} in complexes containing waters of hydration were attributed to the antisymmetric and symmetric O–H stretching modes and to the H–O–H bending mode, respectively.[17] The infrared absorptions in the regions 3300–3200, 1600, and 800–750 cm^{-1} are due to the tren ligand and are similar to those found in Co(III)- and Cr(III)-tren complexes.[10,13]

The electronic spectral data of the new Rh(III)–tren species are given in Table VI; the wavelengths of the d–d absorption maxima are consistent with the positions of the respective ligands in the spectrochemical series. Interpretation of many of these data is difficult due to the intense charge transfer or intraligand transitions which tend to partially obscure the d–d

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(12) (a) Haim, A.; Wilmarth, W. R. *Inorg. Chem.* **1962**, *1*, 573. (b) Haim, A.; Wilmarth, W. R. *Inorg. Chem.* **1967**, *6*, 237.

(13) Kuo, K.-W.; Miller, W. V.; Madan, S. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 957.

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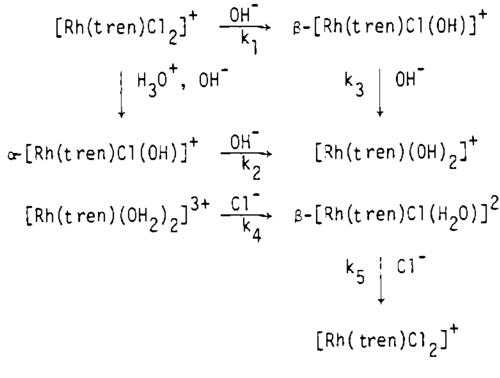
(15) Nakamoto, K.; Fujita, J.; Murata, H. *J. Am. Chem. Soc.* **1958**, *80*, 4817.

(16) (a) Basolo, F.; Hammaker, G. S. *J. Am. Chem. Soc.* **1960**, *82*, 1001. (b) Basolo, F.; Hammaker, G. S. *Inorg. Chem.* **1962**, *1*, 1.

(17) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.

Scheme II. Summary of Base Hydrolysis and Chloride Anation Reactions



bands. For the complexes whose d–d band extinction coefficients can be determined accurately, it can be seen that the intensities here are greater than those observed for the analogous bis(ethylenediamine) complexes.[4] The intensity of a d–d band is increased by the absence of a center of symmetry in the ligand field,[18] so the known distortions induced by the tren ligand should cause the new complexes to have higher d–d intensities than the analogous ethylenediamine complexes.

In summary, the base hydrolysis reactions of $[Rh(tren)Cl_2]^+$ and α- and β-$[Rh(tren)Cl(OH)]^+$ can be interpreted in terms of dissociative mechanisms. Hydroxide ion causes a dramatic increase in the rates of hydrolysis of the dichloro and α-chlorohydroxo species but a lesser effect on the β-chlorohydroxo ion. The chloride anation of $[Rh(tren)(OH_2)_2]^{3+}$ leads to the formation of β-$[Rh(tren)Cl(H_2O)]^{2+}$, which in turn anates to the dichloro ion. These reactions are summarized in Scheme II. Finally, the base hydrolysis and anation studies have led to a viable pathway for the synthesis of some new Rh(III)–tren complexes which contain acido ligands. These compounds have been isolated and characterized.

Registry No. $[Rh(tren)Cl_2]^+$, 56026-84-7; α-$[Rh(tren)Cl(OH)]^+$, 75766-27-7; β-$[Rh(tren)Cl(H_2O)]^{2+}$, 67179-21-9; $[Rh(tren)(OH_2)_2]^{3+}$, 75717-78-1; β-$[Rh(tren)Cl(OH)]^+$, 75717-79-2; $[Rh(tren)I_2]I$, 75717-80-5; $[Rh(tren)ox]ClO_4$, 75717-82-7; $[Rh(tren)Br_2]ClO_4$, 75717-84-9; $[Rh(tren)(N_3)_2]Cl$, 75717-85-0; $[Rh(tren)(NO_2)_2]NO_3$, 75717-87-2; $[Rh(tren)Cl_2]Cl$, 67124-80-5; Cl^-, 16887-00-6.

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Conjugate-Base Mechanism and Activation Parameters for the Ammoniation of Bromopentaamminerhodium(III) Perchlorate and (Nitrato)pentaamminerhodium(III) Perchlorate in Liquid Ammonia

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The kinetics of ammoniation of $[Rh(NH_3)_5Br](ClO_4)_2$ and $[Rh(NH_3)_5NO_3](ClO_4)_2$ were studied at constant ionic medium of 0.20 *m* in the temperature ranges 15–35 °C and −30 to +2 °C, as a function of the acidity of the solution. $[Co(NH_3)_5NO_3](ClO_4)_2$ was included for comparison. The base-catalyzed reaction of the rhodium(III) ammines follows the conjugate-base mechanism. Separate activation parameters were obtained for the acid–base preequilibrium and the rate-determining step. The decrease in entropy of activation for the latter on going from cobalt(III) amines ($\Delta S^* \simeq 100$ J K^{-1} mol^{-1}) to the rhodium(III) ammines ($\Delta S^* \simeq 0$) is in line with the outer-sphere activation model, proposed earlier, and the expected more associative character of rhodium(III)-substitution reactions. A comparison of aqueous and liquid-ammonia parameters for the conjugate-base reactions also proves the rate-determining step to be solvent dependent. A spontaneous, i.e., base-independent, solvolysis reaction could be detected only for $[Rh(NH_3)_5Br](ClO_2)_2$. The activation parameters found in this case ($\Delta H^* = 59$ kJ mol^{-1}, $\Delta S^* = -132$ J K^{-1} mol^{-1}) indicate a pronounced degree of solvent assistance.

Introduction

The conjugate-base (CB) mechanism[1–3] operative in octahedral amine complexes of chromium(III), cobalt(III), ruthenium(II) and -(III), rhodium(III), and iridium(III) generally involves a combination of a rapid acid–base preequilibrium (eq 1) and a dissociative rate-determining step (eq 2) (omitting charges).

$$\mathrm{NH_3(L_4M)X \overset{K^{CB}}{\rightleftharpoons} NH_2(L_4M)X + H(solv)} \qquad (1)$$

$$\mathrm{NH_2(L_4M)X \xrightarrow{k_1} NH_2(L_4M) + X} \qquad (2)$$

In contrast to water, ammonia gives the possibility to separate the processes to obtain activation parameters for both reactions 1 and 2.[4–6] Results on cobalt(III) complexes have led to the surprising conclusion that for reaction 2 not the expected lowering of ΔH^* but the very favorable ΔS^* is the rate-enhancing factor compared to spontaneous solvolysis. This result has previously been worked out by one of us in an outer-sphere model[4] in which the entropy increase associated with the liberation of the leaving group into the second sphere is responsible for a large part of the reactivity of the conjugate base. For consistent volume profiles for the CB mechanism to be drawn up, the phenomenon of dielectric saturation[7,8] due to the high electric field of the Co^{3+} ion had to be invoked. This effect is thought to diminish for the metal complex both the increase in partial molar volume (and consequently entropy[9]) connected with the reduction of the effective charge

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[4] Balt, S. *Inorg. Chem.* **1979**, *18*, 333.

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