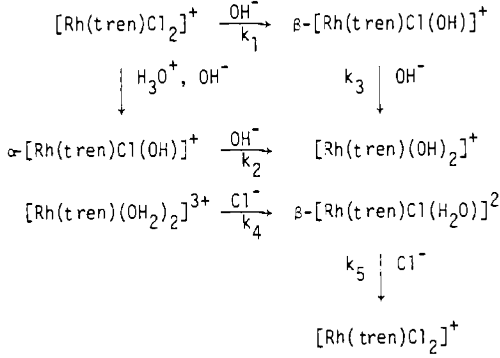

Scheme II. Summary of Base Hydrolysis and Chloride Anation Reactions

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 ($\Delta S^\ddagger \simeq 100$ J K^{-1} mol^{-1}) to the rhodium(III) ammines ($\Delta S^\ddagger \simeq 0$) 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 ($\Delta H^\ddagger = 59$ kJ mol^{-1}, $\Delta S^\ddagger = -132$ 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).

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

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

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 $\Delta H^\ddagger$ but the very favorable $\Delta S^\ddagger$ 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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in equilibrium 1 and the volume decrease inherent in the charge separation effect of reaction 2.

The study of the CB mechanism in liquid ammonia is extended to rhodium(III) complexes. The larger ionic radius of Rh^{3+} may be expected to decrease dielectric saturation, thus decreasing the difference between the entropy changes in the two reactions. In addition, the less pronounced dissociative character of the rhodium CB reaction[10-14] could bring about a larger role for solvent assistance in the rate-determining step, expressing itself in a lowering of both $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for reaction 2 compared to analogous cobalt(III) complexes. To test these predictions we present here an investigation into the ammoniation reactions of bromopentaamminerhodium(III) and (nitrato)pentaamminerhodium(III) ions. For comparison the ammoniation of the (nitrato)pentaamminecobalt(III) ion is included.

Experimental Section

Materials. $[Co(NH_3)_5NO_3](NO_3)_2$,[15] $[Rh(NH_3)_5NO_3](NO_3)_2$,[16] and $[Rh(NH_3)_5Br]Br_2$[17] were prepared according to published methods. The purified compounds were dissolved in water of pH 8.5 (borax) and precipitated with a saturated aqueous solution of lithium perchlorate of the same pH in order to free the complexes from acidic impurities and convert them into the perchlorates. As this method was not successful for $[Co(NH_3)_5NO_3](ClO_4)_2$ a similar procedure was followed with dimethyl sulfoxide as a solvent. The compounds were identified from their UV-vis spectra.[18,19] The metal analyses agreed within 1% with the calculated values. Potassium perchlorate was prepared and dried as described.[20] Ammonium perchlorate used was reagent grade. All compounds were dried and stored over phosphorus pentoxide. Liquid ammonia was dried by distilling from potassium metal.

Kinetics. Concentrations are expressed as mol kg^{-1} (*m*). All experiments were performed at constant ionic medium[5] of 0.20 *m* by adding a calculated amount of potassium perchlorate. Because of extensive ion pairing this concept is difficult to relate to ionic strength. In this ionic medium of 0.20 *m* the amine complexes can be considered as completely ion associated.[21] Reactions were followed in a thermostated stainless-steel cell with quartz windows inside a Beckmann 25 spectrophotometer. Details of the experimental setup and the procedure, employing a fully closed system, have been described elsewhere.[5] The accuracy of the temperature control was 0.1 °C. First-order rate-constants were obtained by a computerized least-squares fitting procedure.[22] Reactions were followed for at least 4 half-lives. The accuracy expressed as the mean deviation from a first-order rate law was in all cases better than 1%. Two series of experiments were performed.

(A) Experiments with Added Ammonium Perchlorate. (Nitrato)pentaamminecobalt(III) perchlorate was studied at a complex concentration of 10^{-2} *m*. The ammonium perchlorate concentration was varied between 1.3×10^{-3} and 5×10^{-2} *m*. Isosbestic points were found at 484 and 410 nm. Reactions were followed at 530 and at 370 nm; within experimental error no wavelength dependence was found. (Nitrato)pentaamminerhodium(III) perchlorate was studied at a complex concentration of 4×10^{-3} *m*. The ammonium perchlorate concentration was varied between 4×10^{-4} and 5×10^{-3} *m*. Isosbestic points were found at 303 and 294 nm. Reactions were followed at 350 and 265 nm; no wavelength dependence could be detected.

Table I. Kinetic Parameters for Ammonitation

complex	t, °C	$10^6 k_1 K_s^{CB}$, m s^{-1} obsd	calcd[a]
$[Co(NH_3)_5NO_3](ClO_4)_2$	−54.5	0.90 ± 0.03	0.94
	−48.7	2.80 ± 0.15	2.72
	−43.0	7.26 ± 0.26	7.31
	−37.3	19.75 ± 0.08	18.75
	−31.8	44.8 ± 1.0	44.7
	−26.3	99 ± 7	102
$[Rh(NH_3)_5NO_3](ClO_4)_2$	−24.8	0.066 ± 0.004	0.068
	−17.9	0.205 ± 0.013	0.201
	−11.1	0.558 ± 0.009	0.552
	−5.1	1.32 ± 0.10	1.29
	1.3	2.99 ± 0.04	3.07
$[Rh(NH_3)_5Br](ClO_4)_2$	14.6	0.0302 ± 0.0008	0.0297
	19.6	0.050 ± 0.003	0.051
	24.6	0.087 ± 0.004	0.087
	29.6	0.1453 ± 0.0003	0.1454
	34.7	0.243 ± 0.001	0.241

[a] Calculated from the activation parameters of Table II.

Bromopentaamminerhodium(III) perchlorate was studied at a complex concentration of 3×10^{-3} *m*. The ammonium perchlorate concentration was varied between 2×10^{-4} and 2×10^{-3} *m*. Isosbestic points were found at 325 and 286 nm. In all cases the reactions were first order in complex concentration. Within experimental error no influence of complex concentration upon the first-order rate constants was found. For each complex at each temperature four to six different concentrations of ammonium perchlorate were selected.

(B) Experiments without the Addition of Ammonium Perchlorate. A second series of experiments was performed without ammonium perchlorate. The complex now is the only acid in solution. The influence of complex concentration and temperature on the reaction rate was studied. (Nitrato)pentaamminecobalt(III) perchlorate was studied at complex concentrations between 3.5×10^{-3} and 2×10^{-2} *m* in the temperature range −64.5 to −44.7 °C. (Nitrato)pentaamminerhodium(III) perchlorate was studied at complex concentrations varying between 2×10^{-3} and 2×10^{-2} *m* in the temperature range −30.3 to −11.1 °C. Bromopentaamminerhodium(III) perchlorate was studied at complex concentrations varying between 2.5×10^{-3} and 1×10^{-2} *m* in the temperature range of 14.6–34.7 °C. The reactions were followed at the same wavelengths as in series A. Two to four different complex concentrations at four to five different temperatures, with intervals of about 5 °C, were chosen.

Results

As earlier studies of ammoniation reactions in our laboratory were performed on chloro- and bromopentaamminecobalt(III) perchlorate,[5] the initial intention was to study their rhodium(III) analogues. However, the solubility of hexaamminerhodium(III) perchlorate in liquid ammonia is too low in the presence of chloride to allow the study of chloropentaamminerhodium(III) spectrophotometrically. As a substitute for the chloro complex, (nitrato)pentaamminerhodium(III) perchlorate was chosen. The solubilities of the nitrato and bromo complexes in liquid ammonia were high enough to allow spectrophotometric monitoring. For a comparison (nitrato)pentaamminecobalt(III) perchlorate was included in the present study.

In the three cases mentioned, the product is the hexaamminemetal(III) complex. As found earlier for cobalt(III)–amine complexes in liquid ammonia[5,6] the reactions are base catalyzed. The observed rate constants for the ammoniation of bromo- and nitratopentaamminerhodium(III) perchlorate at excess ammonium perchlorate are given by expression 3, where k_s is the acid-independent part (apparently

$$k(\mathrm{obsd}) = k_s + k_b[NH_4ClO_4]^{-1} \qquad (3)$$

spontaneous ammoniation) of the rate constant, giving a small or negligible contribution to the overall rate. The main route of the ammoniation is the base-catalyzed pathway exemplified by the rate constant k_b in eq 3. Therefore the ammoniation

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Table II. Pseudoactivation Parameters of Ammoniation for $k_1K_5^{\mathrm{CB}}$ and $k_1(K_5^{\mathrm{CB}})^{1/2}$

	$k_1K_5^{\mathrm{CB}\,a}$		$k_1(K_5^{\mathrm{CB}})^{1/2}$	
complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
$[Co(NH_3)_5NO_3](ClO_4)_2$	72.67 ± 0.80	−25.37 ± 3.38	78.1 ± 1.4	57 ± 6
$[Rh(NH_3)_5NO_3](ClO_4)_2$	80.45 ± 0.78	−56.65 ± 2.97	74.2 ± 0.9	−19.9 ± 3.5
$[Rh(NH_3)_5Br](ClO_4)_2$	74.28 ± 0.74	−130.6 ± 2.50	70.3 ± 1.7	−79.7 ± 5.5

[a] The number of decimals is determined by the use as regression parameter in the comparison between observed and calculated rate constants in Table I.

Table III. Comparison of $\Delta H^{\ddagger}$ (kJ mol^{-1}) and $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) Values for Base-Catalyzed Ammoniation Base Hydrolysis and Aquation

	base-catalyzed ammoniation						base hydrolysis		aquation		
	k_1K^{CB}		k_1		K^{CB}		$k_1K^{\mathrm{CB}\,a,b}$		$k_{\mathrm{aq}}{}^a$		
complex	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔH	ΔS	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ref
$[Co(NH_3)_5Cl](ClO_4)_2$	87	−13	95	116	−8	−172	171	33	96	−34	5[c]
$[Co(NH_3)_5Br](ClO_4)_2$	72	−29	73	96	−1	−125	171	45	100	−13	5[c]
$[Co(NH_3)_5NO_3](ClO_4)_2$	73	−25	84	139	−11	−164	176	67	102	8	[d]
$[Rh(NH_3)_5Br](ClO_4)_2$	74	−131	66	−29	9	−102	179	−21	102	−40	[d]
$[Rh(NH_3)_5NO_3](ClO_4)_2$	81	−57	68	17	13	−74	171	−4	97	−13	[d]
$Ru(NH_3)_6Cl_3$			79[e]	−6[e]	96[b,e]	40[b,e]	175	34	60	−91	26[e]

[a] Parameters for aquation and base hydrolysis from ref 13. [b] Converted to the formulation of eq 1 with $\Delta H^{\circ} = 56$ kJ mol^{-1} and $\Delta S^{\circ} = -113$ J K^{-1} mol^{-1} for K_{W}.[27] [c] Reference for ammoniation. [d] Ammoniation (this work). [e] Aqueous values.

of rhodium(III) complexes appears to follow the conjugate-base mechanism. Working out eq 1 and 2 for M = Rh(III) and X = NO_3^- or Br^-, with the realization that the complexes are completely associated, gives[21,23] eq 4–6. K_5^{CB} and K_6^{CB}

$$[Rh(NH_3)_5X](ClO_4)_2 + NH_3 \overset{K_5^{\mathrm{CB}}}{\rightleftharpoons} [Rh(NH_3)_4(NH_2)X](ClO_4) + NH_4ClO_4 \quad (4)$$

$$[Rh(NH_3)_4(NH_2)X]ClO_4 \xrightarrow{k_1} [Rh(NH_3)_4(NH_2)]X(ClO_4) \quad (5)$$

$$[Rh(NH_3)_6](ClO_4)_3 + NH_3 \overset{K_6^{\mathrm{CB}}}{\rightleftharpoons} [Rh(NH_3)_5(NH_2)](ClO_4)_2 + NH_4ClO_4 \quad (6)$$

refer to rapid acid–base equilibria, and k_1 represents the rate-determining step, which is followed by a fast consecutive formation of the hexaammine. No direct study of the base-catalyzed reaction is possible, because the addition of amide ions produces consecutive proton dissociation steps, followed by condensation and precipitate formation.[24] Without the addition of amide further proton dissociation steps can be neglected. For the reactions under conditions of excess acid a rate equation in the form of eq 3 with $k_b = k_1K_5^{\mathrm{CB}}$ is predicted. The values of $k_1K_5^{\mathrm{CB}}$ and k_s, obtained by fitting eq 3 to the observed first-order rate constants, are presented in Table I. The mean deviations between the observed and calculated rates were generally better than 2%. Activation parameters of $k_1K_5^{\mathrm{CB}}$ were calculated by a weighted least-squares method on the basis of the Eyring formula.[25] No curvature was found. The calculated values of $k_1K_5^{\mathrm{CB}}$ in Table I stem from the activation parameters in Table II. In the case of (nitrato)pentaamminerhodium(III) and -cobalt(III) the intercept k_s was zero within experimental error. For bromopentaamminerhodium(III) a small intercept was found, indicating a small contribution of spontaneous ammoniation to the overall rate.

The situation becomes more complicated when extra acid is not added, because then the acidity of the solution is determined by all ammine acid–base equilibria implicit in eq 4, together with eq 6. For the moment we shall assume that only one acid–base equilibrium (eq 4) leading to the reactive conjugate base need be considered, but we will come back to this issue later. In spite of the complexity of the problem, this type of reaction was studied to give the relevant CB acidity constants of the ammine complexes.[5,23]

Only in the case that $K_5^{\mathrm{CB}} = K_6^{\mathrm{CB}}$ may a first-order rate law be expected. The resulting observed pseudo-first-order rate constant is then given by expression[5] 7, where $[\mathrm{Rh}]_t$ denotes the total rhodium concentration. All three systems studied showed first-order behavior within 1%, while the dependence of the rate on the complex concentration obeyed eq 7 (see Figure 1). (Because of the high rates in the absence of acid the spontaneous reaction is not observed.) Consequently K_5^{CB} equals K_6^{CB} within the limits of the experimental detection in every case. Thus for each temperature $k_1(K_5^{\mathrm{CB}})^{1/2}$ can be obtained by fitting the observed rates at different complex concentrations to eq 7. Because of the limited number of observations at each temperature the pseudo activation parameters of $k_1(K_5^{\mathrm{CB}})^{1/2}$ were determined directly by subjecting $k(\mathrm{obsd})[\mathrm{Rh}]_t^{1/2}$, i.e., $k_1(K_5^{\mathrm{CB}})^{1/2}$, determined at different complex concentrations and different temperatures, to a least-squares activation analysis.[25] The resulting parameter values are presented in Table II. Now it is possible to calculate the activation parameters of the rate-determining step (k_1) and the thermodynamic parameters of K_5^{CB} (Table III).

$$k(\mathrm{osbd}) = k_1(K_5^{\mathrm{CB}})^{1/2}[\mathrm{Rh}]_t^{-1/2} \quad (7)$$

Discussion

Base hydrolysis of cobalt(III) amines is characterized by very high values of the entropy of activation, reflecting a high degree of rearrangement of the first and probably the second coordination sphere.[2] Studies of the ammoniation of cobalt(III) amines in liquid ammonia gave the possibility of separating reactions 4 and 5.[5] The results for the rate-determining step still show large values for $\Delta S^{\ddagger}$ but for $\Delta H^{\ddagger}$ values of the same order of magnitude as $\Delta H^{\ddagger}$ for aquation (Table III). The entropy gain on activation could be located in the second coordination sphere.[4,6] The ammoniation of (nitrato)pentaamminecobalt(III) follows this pattern of activation parameters.

On the other hand the ammoniation of (nitrato)pentaamminerhodium(III) and bromopentaamminerhodium(III)

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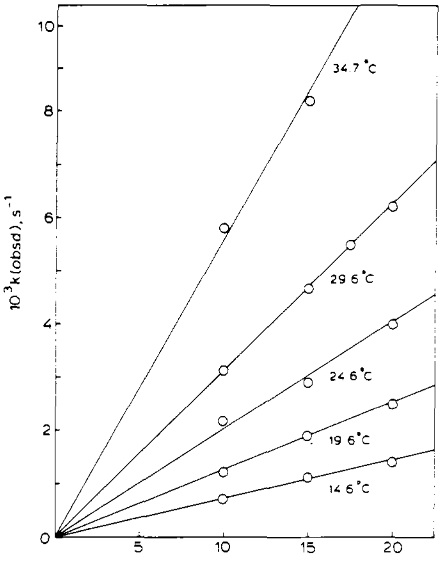

Figure 1. Variation of the observed rate constant of ammoniation with the inverse square root of the total rhodium(III) complex concentration for bromopentaamminerhodium(III) perchlorate at different temperatures.

shows a different behavior. From the entries in Table III it is clear that the activation entropies for the rate-determining step are much lower than those for their cobalt(III) analogues, whereas the entropy differences for the acid–base equilibrium (K_5^{CB}) are higher for the rhodium(III) complexes. These results are in agreement with the volume profile worked out for cobalt(III) complexes.[4] In this model the expected volume increase connected with the reduction of the effective charge on the metal in equilibrium 4 and the volume decrease due to charge separation in reaction 5 both are diminished by dielectric saturation around the small cobalt(III) ion. In the case of the larger rhodium(III) ion we expect a smaller dielectric saturation effect bringing the two values ΔS for K^{CB} and $\Delta S^{\ddagger}$ for k_1 closer together than for the cobalt(III) case. Consequently rhodium(III) is closer to the "normal" case, where charge separation effects may be expected[13] to bring $\Delta S^{\ddagger}$ close to zero. Indeed the present values of activation parameters for the rate-determining step of rhodium(III) complexes are very close to the ones found[26] for base hydrolysis of $\mathrm{Ru(NH_3)_6}^{3+}$, again with $\Delta S^{\ddagger}$ close to zero.

It is interesting to compare $\Delta H^{\ddagger}$ values for k_1 and the spontaneous aquation (k_{aq}). In the case of rhodium(III), $\Delta H^{\ddagger}$ values for k_1 are significantly smaller than those for k_{aq}. This is not found for cobalt(III). The absence of this effect in the ammoniation of cobalt(III) complexes has been sought[4] in the limiting dissociative mode of activation for the rate-determining loss of the leaving group, where solvent assistance is no longer operative, thus nearly completely obliterating the decrease of $\Delta H^{\ddagger}$ on account of the labilizing effect of the $\mathrm{NH_2}^-$ group. The appearance of solvent assistance for the rhodium(III) complexes is in line with earlier conclusions that octahedral substitution at rhodium(III) in general has a less strictly dissociative character[10] than at cobalt(III). This conclusion would imply a further reduction of $\Delta S^{\ddagger}$ for the rate-determining step on going from cobalt(III) to rhodium(III), so the low $\Delta S^{\ddagger}$ (k_1) values for rhodium(III) may stem from two causes (vide supra). In fact entropies of activation are almost always lower for rhodium(III) than for cobalt(III).[11,16,28] Summing up the conclusions from the comparison of cobalt(III) and rhodium(III) ammines we may say that the outer-sphere model[4] is also applicable to rhodium(III) complexes and that extrapolations from cobalt(III) to rhodium(III) on the basis of this model have been borne out by the experiments.

Recent results obtained by Palmer[29] on the volume of activation for the base hydrolysis of the series $[\mathrm{Rh(NH_3)_5X}]^{2+}$ (with X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_3^-}$) can be fitted in the mechanistic picture worked out above. Palmer has interpreted his results on the assumption that $\bar{V}([\mathrm{Rh(NH_3)_4(NH_2)}]^{2+}) \simeq \bar{V}([\mathrm{Rh(NH_3)_6}]^{3+})$. This assumption works well for the cobalt(III) ammines[4] but not for the rhodium(III) complexes, as argued above. With use of this assumption[29] a volume profile diagram for a dissociative activation reproduced the experimental values rather well, with the unexplainable exception of $[\mathrm{Rh(NH_3)_5I}]^{2+}$. We have used Palmer's experimental volumes of activation to calculate the volume $V^{\ddagger}$ of the activated complex $[\mathrm{Rh(NH_3)_4(NH_2)\cdots X}]^+$ (in our formulation) from eq 8.[4] With $\bar{V}(\mathrm{H_2O}) = 18$ and $\bar{V}(\mathrm{OH^-}) = 0.5$ cm³ mol⁻¹ we

$$V^{\ddagger} = \Delta V^{\ddagger}_{\text{exptl}} + \bar{V}([\mathrm{Rh(NH_3)_5X}]^{2+}) - \bar{V}(\mathrm{H_2O}) + \bar{V}(\mathrm{OH^-}) \tag{8}$$

get the following values ($\mathrm{cm^3\ mol^{-1}}$) for $V^{\ddagger}$: 83.5 (82.3) for X = $\mathrm{Cl^-}$; 94.2 (91.5) for X = $\mathrm{Br^-}$; 97.0 (94.1) for X = $\mathrm{I^-}$; 98.0 (93.2) for X = $\mathrm{NO_3^-}$. In parentheses are the values[29] ($\mathrm{cm^3\ mol^{-1}}$) for $\bar{V}([\mathrm{Rh(NH_3)_5X}]^{2+})$. The close parallel between $V^{\ddagger}$ and $\bar{V}([\mathrm{Rh(NH_3)_5X}]^{2+}$ makes it reasonable to assume that X has not left the first coordination sphere to an appreciable extent on activation. In fact the small increase of volume of the activated complex compared to $[\mathrm{Rh(NH_3)_5X}]^{2+}$ can be interpreted along the lines set out above as a volume increase resulting from the decreased formal charge of the complex, which is incompletely compensated by the volume decrease inherent in the associative activation: the displacement of a water molecule from the second to the first sphere.[30] This interpretation has the advantage that no exceptions are created, as with the iodo complex in Palmer's treatment.

Up to now we have not touched the fundamental question of different acidity of geometrically different coordinated $\mathrm{NH_3}$ groups[31-33] in the rhodium(III) complexes, leading to the problem of the position of the amido group in the reactive conjugate base.[34-37] For liquid ammonia this problem seems to be less severe because of the leveling effect of the solvent on acidity constants[38] which is evidenced by the invariance of $\mathrm{p}K_6^{\text{CB}}$ values of ammine complexes in general[6,39] and in the noted near equality of $\mathrm{p}K^{\text{CB}}$ values for our rhodium(III) ammines.

Formally the systems are treated here as consisting of one acid–base equilibrium leading to the one and only reactive conjugate base. Therefore it is not excluded that the parameter values reported in Table III will need a correction consisting of a statistical factor and/or an equilibrium constant between conjugate bases.[6]

As mentioned before,[5,6] for many of the amine complexes studied so far, the differences in overall activation parameters for base-catalyzed ammoniation and hydrolysis are close to

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the thermodynamic transfer functions for the proton between water and ammonia ($\delta_m\Delta H^\circ = -96$ kJ mol^{-1}, $\delta_m\Delta S^\circ = -96$ J K^{-1} mol^{-1}).[40] The new compounds in Table III conform to this picture, with the exception of $Rh(NH_3)_5NO_3^{2+}$. Consequently the higher rates of solvation in liquid ammonia should be primarily attributed to the more favorable heat of solvation of the proton in liquid ammonia. Contrary to the conclusions drawn so far, this would suggest that the solvent dependence of the rate-determining step is only slight. A similar conclusion has been drawn by Goodall and Hardy[41] from a kinetic study of cobalt(III) ammine complexes in Me_2SO–water mixtures. The postulate of solvent independence of k_1 can be checked by calculating K^{CB} for aqueous solutions. For the compounds under study the calculated pK^{CB} values at 25 °C are then 18.3, 17.7, and 17.5 for (nitrato)pentaamminecobalt(III), bromopentaamminerhodium(III), and (nitrato)pentaamminerhodium(III), respectively. In view of the fact that for hexaammineruthenium(III) and tris(ethylenediamine)cobalt(III) aqueous pK^{CB} values of 14.9[26] and 13.1[41] (25 °C), respectively, have been reported, our calculated values are definitely too large. This means that the suggested assumption of medium independence of k_1 cannot be maintained.

Bromopentaamminerhodium(III) gave a small contribution of spontaneous ammoniation (k_s) to the overall rate. The activation parameters of k_s are $\Delta H^\ddagger = 59 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -132 \pm 6$ J K^{-1} mol^{-1}. These values both are considerably lower than the ones found for spontaneous aquation (k_{aq}) (see Table III). The only cobalt(III) complex studied so far that showed spontaneous ammoniation is *trans*-dichlorobis(ethylenediamine)cobalt(III), with $\Delta H^\ddagger = 58$ kJ mol^{-1} and $\Delta S^\ddagger = -47$ J K^{-1} mol^{-1} for k_s.[6] The activation parameters for spontaneous aquation for this complex are[42] $\Delta H^\ddagger = 115$ kJ mol^{-1} and $\Delta S^\ddagger = 55$ J K^{-1} mol^{-1}, so in both cases almost the same differences between spontaneous ammoniation and aquation appear. The relatively low values for $\Delta H^\ddagger$ as well as $\Delta S^\ddagger$ in both cases may indicate a more pronounced degree of solvent assistance in liquid ammonia than in water.[6]

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Registry No. $[Co(NH_3)_5NO_3](ClO_4)_2$, 15156-24-8; $[Rh(NH_3)_5NO_3](ClO_4)_2$, 75908-19-9; $[Rh(NH_3)_5Br](ClO_4)_2$, 14282-99-6.

Supplementary Material Available: Tables containing the observed and calculated rate constants as a function of complex concentration and ammonium perchlorate concentration at different temperatures (6 pages). Ordering information is given on any current masthead page.

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Oxidation and Dismutation of Superoxide Ion Solutions to Molecular Oxygen. Singlet vs. Triplet State

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Photon counting and chemical trapping have been used to determine the yields of dimeric $^1\Delta_g$-state O_2 that result from oxidation and proton-induced dismutation of $O_2^-\cdot$. The results are consistent with theoretical predictions and indicate that those processes that involve adiabatic electron transfer or a triplet transition state favor formation of $^3\Sigma_g^-$-state O_2 (e.g., the $Fe^{III}(ClO_4)_3$–$O_2^-\cdot$ and the $HClO_4$–$O_2^-\cdot$ systems), and those that involve a singlet transition state favor formation of $^1\Delta_g$-state O_2 (e.g., the ferrocenium ion–$O_2^-\cdot$ system).

Several recent investigations describe the formation of singlet oxygen $O_2(^1\Delta_g)$) by oxidation of superoxide ion ($O_2^-\cdot$) with ferrocenium ion[1] and diacyl peroxides[2] and by dismutation of superoxide with proton sources.[3-5] To further test the reaction chemistry of $O_2^-\cdot$, we have undertaken a study to determine by photon counting and chemical quenching the yield of dimeric[6] $^1\Delta_g$-state O_2 from the oxidation and dismutation of $O_2^-\cdot$ in aprotic media.

Reaction by electron transfer to a cation radical from an anion radical such as $O_2^-\cdot$ is likely to result in excited-state product molecules which may emit characteristic fluorescence.[7-10] Mayeda and Bard have shown that in the reaction of ferrocenium ion with $O_2^-\cdot$ singlet oxygen is a product.[1] This was detected by the chemical quencher 1,3-diphenylisobenzofuran (DPBF), which has the largest rate constant, 8×10^8 M^{-1} s^{-1}, for quenching $O_2(^1\Delta_g)$.[11] However, luminescence was not observed.

Under suitable conditions we have been able to measure the chemiluminescence due to the $O_2(^1\Delta_g)$ that results from the oxidation of $O_2^-\cdot$. Consistent with theoretical calculations, the formation of $O_2(^1\Delta_g)$ is dependent upon substrates which favor singlet transition states in the electron-transfer process. Systems involving either adiabatic electron transfer or a triplet transition produce directly the $^3\Sigma_g^-$ state of O_2. To verify that

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