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Mechanism of Base Hydrolysis of Some Rhodium(III) Complexes

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*The base catalysis of the reactions of cis-
$[Rh(en)_2NO_2Cl]^+$ and of trans-$[Rh(en)_2NH_2CH_3Cl]^+$
with NO_2^- and with N_3^- in dimethylsulfoxide solution
is reported. The same complexes were allowed to
react with NO_2^- and N_3^- in the presence of OH^- in
aqueous solution and the ratio of the acido and
hydroxo products were determined. The ratio of
products depends on the reagent anion but is indepen-
dent of the OH^- concentration and of the leaving group.
The results are explained on the basis of an S_NICB
mechanism.*

Introduction

The base hydrolysis of cobalt(III) ammines has been
extensively investigated and recent reviews[1] provide
detailed discussions of the results obtained. These
reactions appear to take place by an S_NICB mechanism
in which the rate determining step is the dissociation
of the conjugate base.[2] This is illustrated for the
complex $[Co(NH_3)_5X]^{2+}$ by equation (1), (2) and (3).

$$[Co(NH_3)_5X]^{2+} + OH^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} [Co(NH_3)_4NH_2X]^+ + H_2O \quad (1)$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + X^- \quad (2)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} \quad (3)$$
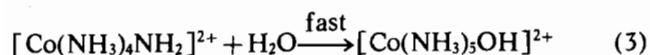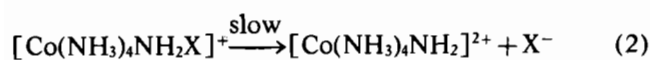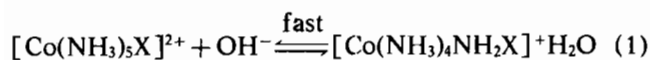
There is considerable evidence in support of this
mechanism, but the most direct evidence comes from
competition experiments[3,4,5] which demonstrate the pre-

sence of an active intermediate, e.g., $[Co(NH_3)_4NH_2]^{2+}$
in (2). The results of these experiments definitely
exclude an S_N2 mechanism for the second order base
hydrolysis reactions of these cobalt(III) ammines.

This paper reports the results of competition ex-
periments on the base hydrolysis of cis-$[Rh(en)_2NO_2X]^+$
and trans-$[Rh(en)_2NH_2CH_3X]^{2+}$ in dimethylsulfoxide
and water solutions. Kinetic studies[6,7,8,9] have been
made on some rhodium(III) ammines and it is found
that hydroxide ion has a smaller effect on their rates of
reaction than on the reactions of corresponding cobalt
(III) complexes.[10] Also base hydrolysis of cobalt(III)
complexes generally take place with rearrangement,
whereas rhodium(III) complexes often react with
retentetion of configuration.[7] Because of these differ-
ences it is important that the base hydrolysis reactions
of rhodium(III) complexes be subjected to further tests
in order to get more information on the mechanism of
reaction in these systems.

Experimental Section

«Analar» reagents were used throughout after further
purification by recrystallization. Matheson «anhydrous»
dimethylsulfoxide was distilled over $Mg(ClO_4)_2$ and the
middle fraction was redistilled using a 30 cm. fractionat-
ing column. The rhodium(III) compounds that had
been prepared in this laboratory[9,11] were made by the
same method and characterized by comparing their
spectra (UV, Vis, IR) with those reported for the
known compounds.

New compounds were prepared by the method used
to prepare similar compounds. For example, cis-
$[Rh(en)_2NO_2N_3]ClO_4$ was prepared from cis-
$[Rh(en)_2NO_2Cl]ClO_4$. An aqueous solution contain-
ing 0.4 g of the chloronitro complex in 15 ml. of 1 M
NaOH was heated on a steam bath for 15 min. After

(1) F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reac-
tions», John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., pp. 177-193
(1967).
(2) F. J. Garrick, *Nature*, 139, 507 (1937).
(3) R. G. Pearson, H. H. Schmidtke and F. Basolo, *J. Am. Chem. Soc.*,
82, 4443 (1960).
(4) M. Green and H. Taube, *Inorg. Chem.*, 2, 948 (1963).
(5) D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *J. Am. Chem.
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(6) A. B. Lamb, *J. Am. Chem. Soc.*, 61, 699 (1939).
(7) S. A. Johnson, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*,
85, 1741 (1963).
(8) G. W. Bushnell, G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem.
Soc.*, (A), 719 (1966).
(9) U. Klabunde, Doctorate Thesis, Northwestern University (1967).
(10) J. A. Broomhead, F. Basolo and R. G. Pearson, *Inorg. Chem.*,
3, 826 (1964).
(11) S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1, 925 (1962).

cooling to room temperature, the solution was passed through an anion exchange resin (Dowex 1-X8,50-100 mesh) in the hydroxide ion form. The eluate was neutralized with dilute $HClO_4$ and 0.5 g of NaN_3 was added. After concentrating on the steam bath to about 5 ml., the solution was passed through an anion exchange resin in the perchlorate ion form. The eluate was concentrated to about 5 ml. in vacuum and 3 g of $NaClO_4$ was added. The pale yellow crystals that separated were collected on a filter, washed with small amounts of ethanol and ether and dried at room temperature in vacuum. Yield, 34%.

Anal. Calcd. for cis-[Rh(en)₂NO₂N₃]ClO₄: C, 11.6 H, 3.93; N, 27.3. Found: C, 12.0; H, 4.03; N, 28.7.

The same type of procedure was used to prepare the other compounds for which the analyses are given here.

Anal. Calcd. for trans-[Rh(en)₂NH₂CH₃Br](ClO₄)₂: C, 11.3; H, 3.97; N, 13.21. Found: C, 10.9; H, 3.9; N, 12.8.

Anal. Calcd. for trans-[Rh(en)₂NH₂CH₃I](ClO₄)₂ : C, 10.3; H, 3.6; N, 11.9. Found: C, 10.5; H, 3.5; N, 12.1.

Anal. Calcd. for trans-[Rh(en)₂NH₂CH₃NO₂](ClO₄)₂: C, 12.0; H, 4.2; N, 16.8. Found: C, 11.9; H, 4.32; N, 16.6.

Anal. Calcd. for trans-[Rh(en)₂NH₂CH₃N₃](ClO₄)₂: C, 12.1; H, 4.3; N, 22.6. Found: C, 12.0; H, 4.2; N, 22.4.

Base Catalysis in Dimethylsulfoxide. The procedure used in these experiments was essentially the same as that employed earlier[3] to study the base catalysis of reactions of cobalt(III) complexes in dimethylsulfoxide solution. The rhodium(III) compounds used were cis-[Rh(en)₂NO₂Cl]ClO₄ and trans-[Rh(en)₂NH₂CH₃Cl]-(ClO₄)₂, both complexes being known to undergo base hydrolysis.[9]

The reactions of these compounds were examined spectrophotometrically by scanning the absorption spectra (290-400 mμ) of appropriate reaction mixtures at various times. Reaction mixtures generally contained the complexes at a concentration of approximately 0.001 M, an equivalent concentration of hydroxide ion and 0.1 M NO_2^- or N_3^-. The reaction mixtures were kept at 25°C and four different experiments were carried out with each complex. To solutions of the complexes were added the following: (1) A solution containing NO_2 or N_3^- plus OH^-, (2) A solution containing NO_2^- or N_3^-, (3) A solution containing OH^-, (4) A solution containing OH^- and after complete reaction (approx. 20 min.) a solution of NO_2^- or N_3^-.

The ions NO_2^- and N_3^- were added as the sodium salts. The OH^- was added as either $(C_2H_5)_4NOH$ or $(C_6H_5CH_2)(CH_3)_3NOH$ in the form of a concentrated (>50%) dimethylsulfoxide solution. The quarternary ammonium hydroxides were obtained (from Eastman Organics) as a methanol solution and the methanol was removed at 0°C under vacuum. Dimethylsulfoxide was then added to the bases to prepare the concentrated stock solutions. The catalytic activity of these solutions

decreased with time[12] and for this reason our experiments were carried out with freshly prepared solutions.

Although the spectral changes showed conclusively that the nitro and azido derivatives were formed in the presence of OH^-, direct evidence was also obtained by isolating the compounds from these reaction mixtures. For example a reaction mixture containing 0.050 g. cis-[Rh(en)₂NO₂Cl]ClO₄, one equivalent of $C_6H_5CH_2$-$(CH_3)_3NOH$ and 1.0 g $NaNO_2$ in 5 ml. dimethylsulfoxide was allowed to stand at room temperature for 20 min. Ether (50 ml) was added to the reaction mixture and the precipitate was collected and washed with ether. The precipitate was dissolved in 10 ml of water and 0.5 g of $NaB(C_6H_5)_4$ was added to precipitate the complex as the $B(C_6H_5)_4^-$ salt. This was dissolved in 3 ml. of methanol-acetone (1:1) and 0.025 g $NaNO_3$ was added. The white crystals that separated in approximately a 70% yield were identified as cis-[Rh(en)₂(NO₂)₂NO₃ by means of its infrared spectrum. The same procedure was followed starting with trans-[Rh(en)₂NH₂CH₃Cl](ClO₄)₂ and the product isolated was trans-[Rh(en)₂NH₂CH₃NO₂](NO₃)₂.

Competition Ratios in Water Solution. Aqueous solutions of the complexes cis-[Rh(en)₂NO₂X]⁺ and trans-[Rh(en)₂NH₂CH₃X]²⁺ were allowed to react with either NO_2^- or N_3^- in the presence of OH^- and the amounts of products formed were determined. The concentrations of the complex were approximately 0.1 M and that of the reagents was varied from 0.05-1.5 M. The reaction mixtures were kept at 54°C for nine half-lives (approx. 3 hr. for 0.05 M NaOH). Under the conditions of these experiments there is no detectable reaction of either the nitro or azido derivatives with OH^-. Likewise there is no reaction of cis-[Rh(en)₂NO₂OH]⁺ with either NO_2^- or N_3^-, but there is a slight reaction of trans-[Rh(en)₂NH₂CH₃OH]²⁺ with these anions.

The reaction products were separated on a cation exchange resin (Bio-Rad analytical 50 WX-2, 200-400 mesh) and the concentrations of the complexes eluted from the column were determined spectrophotometrically. A material balance on the reaction products of the aquo and nitro (or azido) derivatives was never less than 98% of the total expected and duplicate runs gave concentrations of the nitro (or azido) species that were reproducible to ±5%.

In order to avoid any reaction of the aquo compound with NO_2^- or N_3^-, these ions were immediately removed by passing the alkaline reaction mixture through an exchange column containing the Na^+ form of the resin. Also to compensate for any impurities that may arise and be present in the final solutions of the nitro (or azido) products, simultaneous duplicate runs were made without the added NO_2^- (or N_3^-) and these solutions were used as a blank in the reference cell. The discussion that follows gives the details of the experimental procedure.

One millimole of the complex was dissolved in 40 ml. of water. One half of this solution was added to a flask containing the required weighed amount of NaOH, and also to another flask containing the same amount of NaOH as well as the required amount of
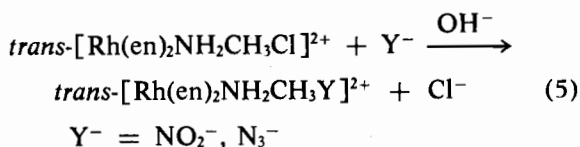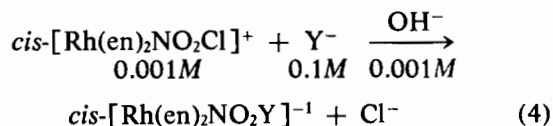
(12) W. T. Miller, J. Fried and H. Goldwhite, *J. Am. Chem. Soc., 82,* 3091 (1960).

NaNO₂ (or NaN₃). The two flasks were then put in a thermostated bath at 54.0°C and maintained at this temperature until the reaction was complete (approx. 3 hr.). After cooling to room temperature, the solutions were passed through separate exchange columns (10 × 150 mm) of resin in the Na⁺ form. The columns were then thoroughly washed with dilute NaOH and water to remove the anions before converting the complex to the aquo fomr. The addition of a slight excess of dilute HClO₄ to the column converts the hydroxo to the aquo complex in order that it have a one unit more positive charge than the acido species and allow the latter to be removed from the column first. This was done with a solution of 0.5N NaClO₄ adjusted to a pH of 3 with HClO₄.

The lower end of the column was connected to a continuous flow sample cell, from which the eluate could flow to the collection container. The optical density at a suitable wave length was recorder to show the appearance and final depletion of the acido (nitro or azido) complex from the column. This fraction was collected as well as the same volume from the blank column (no added NO₂⁻ or N₃⁻). The volumes of the two solutions were reduced to 25 ml. in a freeze drying apparatus and the spectrum of the solution containing the acido complex was determined with the other solution in the reference cell. The molar absorbancy of an authentic sample of the acid compound was determined in another portion of the same eluant blank. This spectrum was used to permit a more precise estimate of the amount of acido complex in the unknown solution. The aquo complex that remains on the column can all be removed as the chloro complex using a 1M HCl solution.

Results

The significant results obtained for the base catalysis reactions in dimethylsulfoxide are illustrated by equations (4) and (5).

$$cis\text{-}[Rh(en)_2NO_2Cl]^+ + Y^- \xrightarrow{OH^-} $$
$$0.001M \qquad 0.1M \quad 0.001M$$

$$cis\text{-}[Rh(en)_2NO_2Y]^{-1} + Cl^- \qquad (4)$$

$$trans\text{-}[Rh(en)_2NH_2CH_3Cl]^{2+} + Y^- \xrightarrow{OH^-}$$

$$trans\text{-}[Rh(en)_2NH_2CH_3Y]^{2+} + Cl^- \qquad (5)$$

$$Y^- = NO_2^-, N_3^-$$

The reactions are complete in 20 min. at 25°C and give the acido complexes in very high yield (greater than 90%). Under the same conditions with no added hydroxide ion there is no reaction. Also there is no reaction if the hydroxide ion is added first and followed 20 min. later by the addition of nitrite or azide ions. These results are shown for the reaction of trans-[Rh(en)₂NH₂CH₃Cl]²⁺ by the spectra in Figure 1.

In water solution the reactions of these complexes with OH⁻ and Y⁻ yield largely the hydroxo complex, but small amounts of the acido compounds are also produced, (6) and (7).
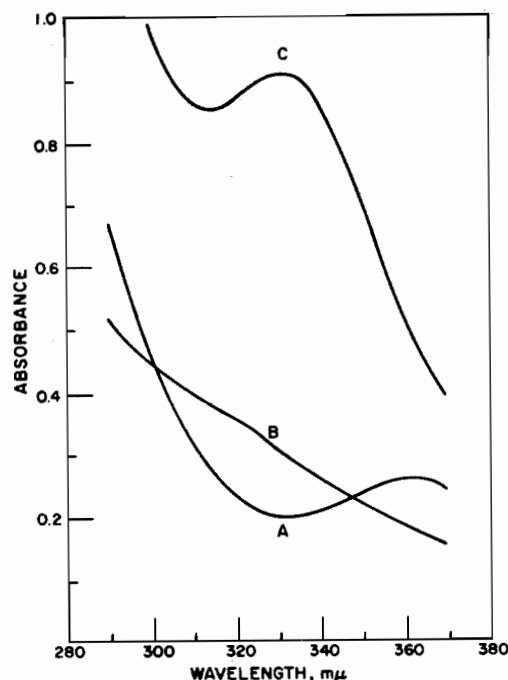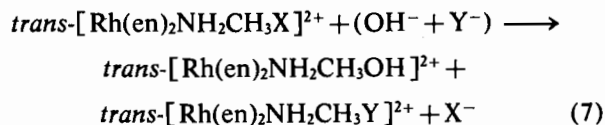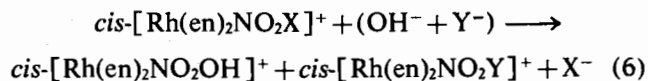
$$cis\text{-}[Rh(en)_2NO_2X]^+ + (OH^- + Y^-) \longrightarrow$$

$$cis\text{-}[Rh(en)_2NO_2OH]^+ + cis\text{-}[Rh(en)_2NO_2Y]^+ + X^- \quad (6)$$

$$trans\text{-}[Rh(en)_2NH_2CH_3X]^{2+} + (OH^- + Y^-) \longrightarrow$$

$$trans\text{-}[Rh(en)_2NH_2CH_3OH]^{2+} +$$

$$trans\text{-}[Rh(en)_2NH_2CH_3Y]^{2+} + X^- \qquad (7)$$

Figure 1. The absorption spectra of trans-[Rh(en)₂NH₂CH₃Cl]²⁺, I, and its reaction products in dimethylsulfoxide solution. A, 0.001 M I and also 0.001 M I + 0.10 M NaN₃ after 20 min.; B, 0.001 M I + 0.001 M OH⁻ after 20 min. and also this solution + 0.10 M NaN₃ after 20 min.; C, 0.001 M I + (0.10 M NaN₃ and 0.001 M OH⁻) after 20 min. and also 0.001 M trans-[Rh(en)₂NH₂CH₃N₃]²⁺. All at 25°C.

Table I. Formation of [A₅RhY] in the Base Hydrolysis of [A₅RhX] in the Presence of Y⁻ at 54°C

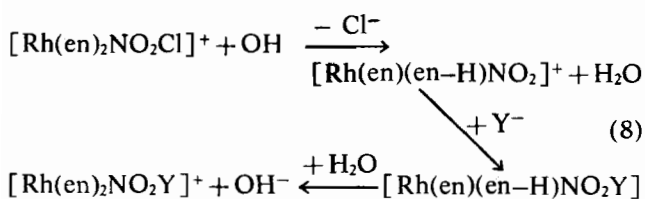| X =	Cl	Br	I
trans-[Rh(en)₂NH₂CH₃X]²⁺:			
N₃⁻	2.0 M	2.0 M	2.0 M
OH⁻	0.05 M	0.05 M	0.05 M
% [A₅RhN₃]²⁺	3.6	3.2	3.8
NO₂⁻	2.0 M	1.5 M	2.0 M
OH⁻	0.05 M	0.05 M	1.00 M
% [A₅RhNO₂]²⁺	2.7	1.8	2.8
cis-[Rh(en)₂NO₂X]⁺:			
N₃⁻	1.5 M	1.0 M	1.5 M
OH⁻	1.0 M	1.0 M	0.05 M
% [A₅RhN₃]⁺	1.1	0.8	1.1
NO₂⁻	1.5 M	1.0 M	
OH⁻	1.0 M	1.0 M	
% [A₅RhNO₂]⁺	0.9	0.6	

cis-[Rh(en)₂NO₂Br]⁺:
N₃⁻ 1.5 M, OH⁻ 1.0 M, % [A₅RhY]⁺ = 1.2

NO₂⁻ 1.5 M, OH⁻ 1.0 M, % [A₅RhY]⁺ = 0.8

The amounts of acido complexes produced in these experiments are given in Table I. The amounts of these products increase with increasing concentrations of Y^-, but are independent of the concentration of OH^- or of the nature of the leaving group X^-.
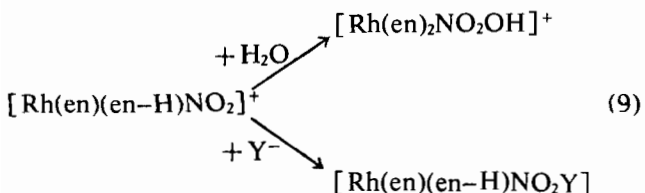
Discussion

The results obtained in this investigation for these two rhodium(III) complexes are very similar to those reported earlier for coresrponding studies of some cobalt(III) complexes.[3,5] It was suggested that the results do not permit an S_N2 mechanism for the reaction of cobalt(III) ammines with hydroxide ion and that they are best explained by an S_N1CB process (equations 1-3). This same mechanism also adaquately explains the observations reported here for the reactions of these rhodium(III) complexes.

For example, the base catalysis observed for reactions (4) and (5) in dimethylsulfoxide cannot be explained in terms of an initial direct displacement (S_N2) reaction by hydroxide ion. This would require that the reaction products formed by the reaction of the rhodium(III) complexes with hydroxide ion react rapidly with nitrite and azide ions. Since this does not happen, an alternative mechanism is necessary. The results can be explained providing the hydroxide ion produces some active intermediate which can in turn react with the reagent in solution. This is represented by scheme (8) for the complex cis-$[Rh(en)_2NO_2Cl]^+$ in terms of the conjugate base dissociation mechanism. It is seen that the hydroxide ion which is involved

$$[Rh(en)_2NO_2Cl]^+ + OH \xrightarrow{-Cl^-}$$
$$[Rh(en)(en-H)NO_2]^+ + H_2O$$
$$\searrow +Y^- \qquad (8)$$
$$[Rh(en)_2NO_2Y]^+ + OH^- \xleftarrow{+H_2O} [Rh(en)(en-H)NO_2Y]$$

initially in a rapid acid-base reaction is regenerated in a similar reaction in the final step, thus it behaves as a catalyst for the overall substitution reaction.

This same mechanism explains the results obtained for the competition experiments in water solution. However because of the coordinating ability of water and because of the acidity of coordinated water, the reaction products in these experiments are largely the hydroxo complexes. Starting with the conjugate base intermediate, the competition for it between water and the reagent anion is shown by (9).

$$\qquad\qquad\qquad \nearrow +H_2O \qquad [Rh(en)_2NO_2OH]^+$$
$$[Rh(en)(en-H)NO_2]^+ \qquad\qquad\qquad (9)$$
$$\qquad\qquad\qquad \searrow +Y^- \qquad [Rh(en)(en-H)NO_2Y]$$

Not shown is the rapid step of the amido-acido complex taking on a proton from the solvent to give the final acido product.

The competition scheme (9) readily permits an explanation of all of the results reported in Table I. Thus the amount of acido complex formed shows a direct dependance on the concentration of Y^- which is expected in its role of capturing the active intermediate in competition with the solvent. However, the amount of acido prdouct formed does not depend on the concentration of hydroxide ion nor on the nature of the leaving group X^-. This too is the expected result for the proposed mechanism where only water competes with Y^- for the five-coordinated intermediate. Since such an intermediate does not contain the leaving group, it cannot exert an influence on the ratio of products.

It is of interest to note that within the limitations of our experiments it appears that the leaving group is not present in the active intermediate. This indicates that the reaction is not of the S_N2CB type, although it had been suggested[7] that rhodium(III) complexes have a greater tendency to undergo S_N2 reactions than do corresponding cobalt(III) complexes. The five-coordinated amido intermediate of cobalt(III) complexes is believed[13] to have a trigonal bipyramidal structure which allows more efficient π-bonding between the amido group and cobalt(III). This can account for the extensive rearrangement that accompanies base hydrolysis reactions of cobalt(III) complexes. However the reactions of rhodium(III) complexes take place largely with retention of configuration[7] which implies that the active intermediate has a tetragonal pyramidal structure. For this structure the crystal field stabilization energy is greater in a low-spin d^6 system than for the trigonal bipyramidal structure.[14] Because of the greater crystal field strength of rhodium(III) relative to cobalt(III), it is suggested that the greater loss in CFSE would make it more difficult to produce a trigonal bipyramidal structure in the rhodium(III) systems.[10]

The data in Table I also show that the nucleophilic strength of N_3^- is only slightly greater than that of NO_2^- towards the rhodium(III) intermediate. This is the same order observed for their reactions with $[Co(NH_3)_4NH_2]^{2+}$ for which there is considerable data and it is found that the nucleophilic character of various anions do not differ greatly.[15] Taking the average of the nucleophilic character and redefining the competition ratio as

$$R = [MA_5Y^{2+}]/[MA_5OH^{2+}][Y^-]$$

to make it independent of $[Y^-]$, one obtains the data collected in Table II. As previously reported for cobalt(III),[5] the rhodium(III) systems also show an increase in R with an increase in charge on the active intermediate. For a charge of $+2$ where data are available for both cobalt(III) and rhodium(III) complexes, the competition ratio is less for the rhodium system. Unfortunately the complexes are different so that it cannot be concluded that cobalt(III) has a greater relative affinity for anions than water compared

(13) R. G. Pearson and F. Basolo, *J. Am. Chem. Coc.*, **78**, 4878 (1956).
(14) F. Basolo and R. G. Pearson, «Mechanisms of Inorganic Reactions», John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., p. 69 (1967).
(15) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

Table II. Comparison of Competition Ratios, $R = [A_5MY^{2+}]/[A_5MOH^{2+}][Y^-]$

Charge	Assumed Intermediate		Average R	
	Rh(III)	Co(III)	Rh(III)	Co(III)
+3	-----	$[Co(NH_3)_5]^{3+}$	-----	0.4 [a]
+2	$[Rh(en)_2NHCH_3]^{2+}$	$[Co(NH_3)_4NH_2]^{2+}$	0.02	0.06 [b]
+1	$[Rh(en)(en-H)NO_2]^{1+}$	-----	0.005	-----

[a] From reference 15. [b] From reference 5.

to rhodium(III).   The reverse is to be expected because rhodium(III) is *softer* than cobalt(III) and the anions are softer bases than water suggesting a greater relative (to water) rhodium(III)-anion interaction compared to cobalt(III)-anion.[16]

(16) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).