reduction of $CoOH^{2+}_{aq}$, $Co(NH_3)_2OH^{2+}_{aq}$, and $Co(NH_3)_5OH^{2+}_{aq}$ by Cr^{2+}_{aq} are 3.3,[10] 3.0, and 1.5 M^{-1} s^{-1},[35] respectively at 25 °C, suggesting a common rate-determining step, presumably substitution at Cr^{2+}_{aq}, for these systems. It is worth noting that oxygen atom exchange has been observed in other Cr^{2+}_{aq} reductions of cobalt ammines.[36]

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Registry No. Co, 7440-48-4; I^-, 20461-54-5; hydroquinone, 106-51-4; $Fe(o\text{-phen})_3^{2+}$, 14708-99-7; Fe^{2+}, 15438-31-0; V^{2+}, 15121-26-3; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Table I, showing kinetic data for the reduction of $Co(NH_3)_2{}^{3+}_{aq}$ species (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanism of the Anation of Hexaaquorhodium(III) Ion by Bromide Ion in Acidic Aqueous Solution. Kinetic Trans Effect as a Mechanistic Criterion for Ligand Water Replacement Processes[1]

R. J. BUCHACEK and G. M. HARRIS*

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Rate constants over the temperature range 50–80 °C have been obtained for the title reaction at $I = 2.00$ M, with $[H^+]$ varied between 0.50 and 2.00 M and $[Br^-]$ varied between 0.10 and 1.00 M. The data have been interpreted in a manner analogous to that employed for previous studies of aquorhodium(III) complex ions and show that the rate-limiting process for bromide anation is identical within experimental error with that for the corresponding chloride reaction and very close to the water-exchange rate of the parent complex ion. These findings, reinforced by some observations on the kinetic trans-effect phenomenon for anation of complexes of the form $Rh(H_2O)_5X^{2+}$ ($X^- = OH^-$, Cl^-, or Br^-), support the simple dissociative (D) mechanism concept for reactions of this type. Comparisons are also made with rate constant and trans-effect data for various reactions of the species $Rh(en)_2X(H_2O)^{3+}$ ($X = H_2O$, OH^-, Cl^-, or Br^-) and $Rh(NH_3)_5H_2O^{3+}$ and discussed in terms of possible mechanisms.

Introduction

Previous studies originating in this laboratory have dealt with the chloride anation kinetics of the complete family of chloroaquorhodium(III) complex ions, including the hexaaquo,[2] chloropentaaquo,[3] *trans*- and *cis*-dichlorotetraaquo,[4] *mer*- and *fac*-trichlorotriaquo,[4] *trans*-tetrachlorodiaquo,[4] *cis*-tetrachlorodiaquo,[5] and the pentachloroaquo species.[6] An argument based on the acid dependence of the anation kinetics of the monochloro congener[3] provides effective evidence that a five-coordinate intermediate or dissociative (D)[7] mechanism is to be preferred for at least two members of the series. This type of kinetic analysis has also supported the D-mechanism concept for chloride anation of the related species *trans*-diaquobis(ethylenediamine)rhodium(III) complex.[8] Furthermore, the recently reported study[4] of the dichloro, trichloro, and tetrachloro species offers additional kinetic evidence for the D mechanism and also for a fixed square-pyramidal geometry of the assumed five-coordinate intermediate.

If, in truth, anation of the hexaaquorhodium(III) ion is purely dissociative, use of some other similar anion in place

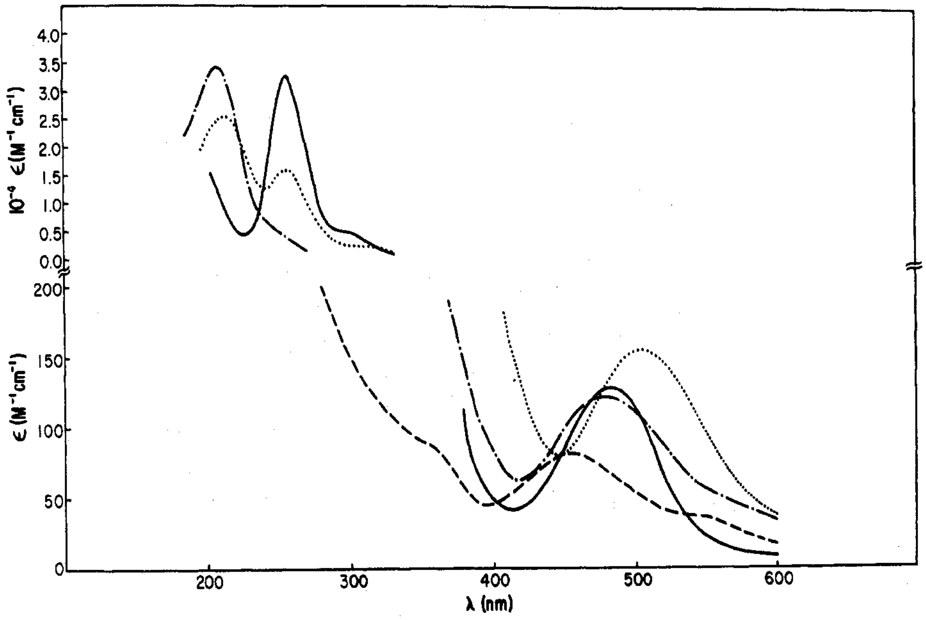

Figure 1. Spectra of various bromoaquorhodium(III) complexes: - - - - - -, $Rh(H_2O)_5Br^{2+}$; ———, *trans*-$Rh(H_2O)_4Br_2^+$; — · — · , *cis*-$Rh(H_2O)_4Br_2^+$; · · · · · ·, *mer*-$Rh(H_2O)_3Br_3$.

of chloride as the entering species should enable kinetic confirmation of this conclusion, since the rate-determining step in such mechanisms is essentially independent of the nature of the entering anion. In the present study, bromide ion has been selected to provide this kind of a test, with convincingly supportive results. Alternative evidence can be based on the observation throughout the chloride anation studies of a consistently distinctive kinetic trans effect exhibited by the chloride ligands in the various chloroaquo complexes, such that the site of entry of subsequent chloride ion in the anation process is totally predetermined by those already present in the complex.[4] This suggests the possibility of utilizing an anion which is known from other research to have a greater (or less) trans-orienting influence as a ligand than does chloride. In substituting bromide for chloride, we have indeed found the expected trans-effect enhancement as one would predict from previous comparisons of chloride and bromide ligands. Comparisons have also been made with previously published rate data for anation reactions of the species $Rh(en)_2(H_2O)_2^{3+}$ and $Rh(NH_3)_5H_2O^{3+}$, particularly in terms of the trans-effect phenomenon.

Experimental Section

Materials. $Rh(H_2O)_3Cl_3$ was prepared from the pure metal by the standard method[9] and converted to solid $Rh(H_2O)_6[ClO_4]_3$ by the procedure of Ayres and Forester.[10] Stock solutions of hexaaquorhodium(III) perchlorate were prepared by dissolving the air-dried yellow perchlorate crystals in distilled water and storing at 0 °C. The rhodium concentration of the stock solution was quantitatively determined by two different spectrophotometric methods. In one, the absorbance of an acidified solution is measured at 395 nm; at this wavelength $Rh(H_2O)_6^{3+}$ has an extinction coefficient[2] of 57.9 M^{-1} cm^{-1}. In the second method,[11] solutions of rhodium(III) are treated with $SnBr_2$ and concentrated $HClO_4$ and heated at 50 °C for 20 min to develop the color completely. The absorbance is read at 427 nm, at which wavelength ϵ is 28900 M^{-1} cm^{-1}. The results of the two methods agree within 2%.

Stock solutions of NaBr, LiBr, NaOH, and $HClO_4$ were prepared from reagent grade chemicals. $LiClO_4$ and $NaClO_4$ were prepared by neutralizing the respective carbonate salts with $HClO_4$. The resulting perchlorate salts were recrystallized twice from distilled water, and the stock solutions were adjusted to pH 7.0. Standardization of the stock solutions was accomplished by passing aliquots through an ion-exchange column containing Dowex 50W-X8 (acid form) resin and titrating the effluent with standard NaOH to a phenolphthalein end point.

Table I. Elution Data for Bromoaquorhodium(III) Complexes

Order of elution	Color of band	Br:Rh	Assignment	Spectral data[a]
1	Reddish purple	3.0 ± 0.1	*mer*-Tribromo	505 (155) 256 (1.6×10^4) 213 (2.5×10^4)
2	Pink-orange	2.0 ± 0.1	*trans*-Dibromo	483 (130) 256 (3.3×10^4)
3	Red-orange	2.1 ± 0.1	*cis*-Dibromo	478 (122) 208 (3.4×10^4)
4	Yellow-orange	1.0 ± 0.1	Monobromo	550 sh (37) 454 (81) 350 sh (90)
5	Pale yellow		Hexaaquo	395 (57.9)[b] 323 (32.5)[b]

[a] Wavelength maxima (nm), corresponding absorption coefficients (M^{-1} cm^{-1}) in brackets. [b] See ref 2.

Stoichiometry. The stoichiometry of the reaction was determined by permitting acidified solutions containing a rhodium:bromide molar ratio of 1:1 to react for various lengths of time at 70 °C. The reaction was quenched by submerging the solution in an ice bath. The products of the reaction were separated by passing the product solution through a previously cooled ion-exchange column, containing Dowex 50W-X8 (acid form). The column was first washed with 0.01 M perchloric acid solution, which eluted a reddish purple band. Elution by 0.2 M $HClO_4$ developed two bands, the first pink-orange and the second red-orange. A fourth band was eluted with 1.0 M perchloric acid and was yellow-orange. Unreacted $Rh(H_2O)_6^{3+}$ was eluted with 2.0 M $HClO_4$. The rhodium content of each fraction collected was determined by the $SnBr_2$ method[11] and showed there to be 98% recovery of all the rhodium initially present in the system. The bromide content of each complex was determined by potentiometric titration with standard $AgNO_3$ after reduction of the rhodium(III) to metal with magnesium turnings. The complete spectra of the complexes were recorded on a Cary Model 15 spectrophotometer as shown in Figure 1. The analytical data and absorbance maxima (absorbance coefficients in brackets) are presented in Table I. The identity of the various species was determined on the basis of these data and of their ion-exchange column behavior. Further experiments showed that under preparative conditions of large excess of bromide ion, only the *trans*-dibromo compound appears in the product mixture in acidic solution.

A check was made of the effect of substituting bromide medium for perchlorate medium on the first p*K* of the hexaaquorhodium(III) ion. The procedure previously described[3] was employed in making the p*K* determination in 2.00 M perchlorate and 2.00 M bromide, respectively, at 25 °C. The results obtained were 3.4 ± 0.1 and 3.3 ± 0.1, respectively, the former figure being in excellent agreement with the earlier similar determination.[2] Since the measurement in bromide medium is identical within experimental error, no corrections have been deemed necessary in analyzing the experimental data in the varying perchlorate–bromide concentrations encountered in the experiments.

Kinetics. Preliminary results showed that in acidities in excess of 0.05 M, the only observable initial product of the aquation is the *trans*-dibromo complex, as expected from the earlier studies of chloride anation.[2,3] The rate data were obtained spectrophotometrically using the *trans*-$Rh(H_2O)_4Br_2^+$ absorbance maximum at 483 nm. The ionic strength was fixed at 2.00 M by addition of appropriate amounts of $LiClO_4$ to the other reagents in making up the reactant solution. The latter was placed in a thermostat and aliquots were withdrawn at suitable intervals and chilled to room temperature, and their absorbances (A) were determined on a Beckman DU spectrophotometer equipped with a Gilford digital read-out attachment. The pseudo-first-order rate constants, k_{obsd}, were derived from the conventional log ($A_\infty - A_t$) vs. time plots. The calculated value of the infinite-time absorbance (A_∞) was employed, since in excess bromide further anation of the first-formed dibromo product may take place to produce a tribromo complex. The plots were, however, linear for at least 2 half-lives of reaction, notwithstanding the additional anation, which must obviously be very much slower.[12]

Results and Discussion

Runs were carried out at 50, 60, 70, and 80 °C at a series of hydrogen ion and bromide ion concentrations, the complex concentration being fixed at $\sim 3 \times 10^{-3}$ M. These results are summarized in Table II and have been analyzed in a manner analogous to that utilized in the two recent related studies.[3,8] Specifically, the D mechanism is assumed, which for our present system is of the form given by eq 1–8. This leads to

$$Rh(H_2O)_6^{3+} \rightleftarrows Rh(H_2O)_5OH^{2+} + H^+ \quad K_h \tag{1}$$

$$Rh(H_2O)_6^{3+} \rightleftarrows Rh(H_2O)_5^{3+} + H_2O \quad k_1, k_2 \tag{2}$$

$$Rh(H_2O)_5^{3+} + Br^- \rightarrow Rh(H_2O)_5Br^{2+} \quad k_3 \tag{3}$$

$$Rh(H_2O)_5OH^{2+} \rightleftarrows Rh(H_2O)_4OH^{2+} + H_2O \quad k'_1, k'_2 \tag{4}$$

$$Rh(H_2O)_4OH^{2+} + Br^- \rightarrow Rh(H_2O)_5(OH)Br^+ \quad k'_3 \tag{5}$$

$$Rh(H_2O)_5Br^{2+} \rightleftarrows Rh(H_2O)_4(OH)Br^+ + H^+ \quad K'_h \tag{6}$$

$$Rh(H_2O)_5Br^{2+} + Br^- \xrightarrow{\text{fast}} Rh(H_2O)_4Br_2^+ + H_2O \tag{7}$$

$$Rh(H_2O)_4(OH)Br^+ + Br^- \xrightarrow{\text{fast}} Rh(H_2O)_3(OH)Br_2 + H_2O \tag{8}$$

the rate expression[13] given by eq 9.

$$k_{obsd} = \frac{k_1\dfrac{k_3}{k_2}[Br^-]}{1 + \dfrac{k_3}{k_2}[Br^-]} + \frac{k'_1\dfrac{k'_3}{k'_2}K_h[Br^-]}{1 + \dfrac{k'_3}{k'_2}[Br^-]}\left(\frac{1}{[H^+]}\right) \tag{9}$$

It is clear that each set of data at a fixed [Br⁻] can be plotted in the form of eq 10. A linear regression analysis computation

$$k_{obsd} = A + B/[H^+] \tag{10}$$

has been carried out on the kinetic data to evaluate the magnitudes of A and B at each temperature and constant [Br⁻], and these values with their standard deviations also appear in Table II. In theory, inverse plots of A and B vs. [Br⁻] should yield values for k_1, k_3/k_2, k'_1, and k'_3/k'_2, since

$$1/A = \frac{1}{k_1} + \frac{1}{(k_1k_3/k_2)[Br^-]} \tag{11}$$

and

$$1/B = \frac{1}{k'_1K_h} + \frac{1}{(k'_1k'_3/k'_2)K_h[Br^-]} \tag{12}$$

and K_h is known from previous work.[14] However, due to the limited range of [Br⁻] of the present experiments and the relatively small magnitude of k_3/k_2 and k'_3/k'_2, the intercepts $1/k_1$ and $1/k'_1K_h$ are experimentally indistinguishable from zero. However, reasonably precise values of the slopes of the plots of the data according to eq 11 and 12 enable accurate determinations of k_1k_3/k_2 and $k'_1k'_3/k'_2$, which are recorded with their standard deviations in Table III. The temperature parameters of these quantities, with their standard deviations, are also presented in this table, along with the corresponding values for chloride anation.[2] The rate constant values applicable at 50 °C for these reactions together with those of a number of other related reactions are collected for ease of comparison in Table IV.

It is obvious from Table III that chloride and bromide anations of $Rh(H_2O)_6^{3+}$ occur at almost identical rates, as expected if the rate-determining step is water dissociation from the parent complex (k_1 or k'_1) and if the scavenging abilities of the two ions for the five-coordinate intermediate relative to water are the same (i.e., the rate ratios k_3/k_2 and k'_3/k'_2 remain fixed). While it has not been possible to evaluate either of these latter rate constant ratios for bromide in the present study, they are known for chloride from earlier work[2] and are of the order of magnitude of unity (essentially temperature independent), and halide anation studies of other aquorhodium(III) ions[17] confirm the near identity of these ratios for chloride and bromide ions.[18] Thus, for the systems under consideration in the present work, the quantities k_1k_3/k_2 and $k'_1k'_2/k'_3$ should be of the same magnitude as the corresponding water-exchange rate constants since k_3/k_2 for water exchange is also unity. On comparing the rate constants for reactions 1, 2, and 15 in Table IV, such is seen to be the case, within the uncertainties introduced by the unavoidable extrapolations of the $Rh(H_2O)_6^{3+}$–water exchange data. This differs from the situation one would expect to observe for the dissociative interchange (I_d) mechanism,[7] where one expects to find differences between halide ions due to differences in ion-pair association constants. One notes, for example, that both SCN⁻ and N₃⁻, typical "pseudohalide" ions, differ very significantly from Cl⁻ in this respect, at least on the basis of kinetic data[19] concerning $Co(NH_3)_5H_2O^{3+}$ anation, the classic I_d example. Similar data[20] for Br⁻ fail to yield a value for its ion-association constant, presumably because of its small magnitude. This view is supported by the fact that the second-order rate constant for Br⁻ anation of $Co(NH_3)_5H_2O^{3+}$ at 25 °C (kK in the Langford–Muir terminology)[19a] is only 1/50th as great as that for Cl⁻ anation at 45 °C, a much greater decrease than the temperature difference would predict.[21]

Returning now to the question of the relative scavenging abilities of the two halide ions for the highly reactive five-coordinate intermediates produced in steps 2 and 4 of the mechanism given above, it is clear that the halides are both more effective than water by a factor of about 50, the concentration of solvent water. This is apparently not the case at the other end of the chloroaquorhodium(III) series, since for chloride and bromide anation of $RhCl_5(H_2O)^{2-}$ ion the k_3/k_2 ratios are down to 0.021 and 0.016, respectively,[17] about 1/50th of the corresponding values of about unity in the present investigation. This change is undoubtedly a result of the Coulombic repulsive forces which deter the encounter of like-charged ions in solution, the main factor to be considered, since k_2 and k_3 are most likely limited by relative rates of diffusion. In fact, a simple calculation based on the theory of diffusion-controlled reactions in aqueous solution[23] predicts a rate difference for 3+, 1– or 2+, 1– encounters as compared to 2–, 1– of close to 50 if the distance of separation of the

Table II. Observed Rate Constants for Anation of $Rh(H_2O)_6^{3+}$ Ion by Bromide Ion[a]

	[H⁺], M								
[Br⁻], M	0.50	0.60	0.75	0.85	1.00	1.50	2.00	10^7A, s⁻¹	10^7B, M s⁻¹
50 °C									
0.10	0.71		0.56		0.39	0.33		0.12 ± 0.05	0.30 ± 0.03
0.20	1.26		0.90		0.74			0.21 ± 0.02	0.52 ± 0.01
0.50	3.02		2.03		1.73	1.23		0.35 ± 0.10	1.32 ± 0.07
0.75	3.87		2.87		2.30			0.76 ± 0.09	1.56 ± 0.06
1.00	4.97		3.64		2.81	2.25		0.82 ± 0.11	2.08 ± 0.08
60 °C									
0.10	2.86	2.70	2.10	1.97	1.75		1.06	0.48 ± 0.11	1.24 ± 0.08
0.12	3.68	3.10	2.52		2.13			0.51 ± 0.15	1.57 ± 0.10
0.20	5.66	5.34	4.30	3.80	3.51		2.00	0.88 ± 0.24	2.52 ± 0.18
0.50	13.8	12.0	9.74	9.54	8.12		4.96	2.20 ± 0.32	5.86 ± 0.23
0.75	19.1	16.6	13.6	12.9	12.1		7.26	3.73 ± 0.49	7.71 ± 0.36
1.00	24.4	21.3	17.1	15.1	15.0		8.72	3.65 ± 0.79	10.38 ± 0.58
70 °C									
0.10	14.6	13.3	11.2	9.33	8.52		4.89	1.77 ± 0.51	6.66 ± 0.38
0.12	18.1	17.1	13.2		10.3			2.32 ± 1.87	8.23 ± 1.21
0.20	34.3	25.6	21.0	19.3	16.7		10.6	1.76 ± 1.82	15.2 ± 1.3
0.50	72.9	59.2	49.8	46.8	41.6		22.8	7.78 ± 1.97	32.1 ± 1.4
0.75	108	89.5	69.5	66.7	58.8		32.0	7.11 ± 2.71	49.7 ± 2.0
1.00	136	108	89.1	83.4	71.3		40.0	8.49 ± 3.38	62.1 ± 2.5
80 °C									
0.10	75.0	72.0	58.0	46.2	40.8		23.5	5.23 ± 4.69	36.9 ± 3.4
0.12	84.3	77.8	64.2		46.1			10.5 ± 8.5	38.4 ± 5.5
0.20	143	130	104	93.2	81.7		43.1	12.2 ± 4.5	67.9 ± 3.3
0.50	332	286	234	219	194		126	56.4 ± 3.0	137 ± 2
0.75	471	429	335	300	259		160	49.2 ± 13.5	216 ± 10
1.00	593	501	424	368	326		188	55.3 ± 7.4	269 ± 5

[a] Units of k_{obsd} are 10^{-7} s⁻¹.

Table III. Rate Parameters for Anation Reactions of Hexaaquorhodium(III) Complex

Entering ligand	Temp, °C	$10^7k_1k_3/k_2$, M^{-1} s^{-1}	$10^4k'_1k'_2/k'_2$, M^{-1} s^{-1}	$\Delta H^{\ddagger}_1$, kcal mol⁻¹	$\Delta H^{\ddagger}_2$, kcal mol⁻¹	$\Delta S^{\ddagger}_1$, eu	$\Delta S^{\ddagger}_2$, eu
Bromide[a]	50	1.3 ± 0.1	4.4 ± 0.2	29.0 ± 1.0	31.6 ± 1.4	−1.3 ± 2.8	23.0 ± 4.3
	60	4.6 ± 0.2	15.7 ± 0.4				
	70	20 ± 6	68 ± 2				
	80	60 ± 10	300 ± 17				
Chloride[b]	50	(1.6)[c]	(5.9)[c]				
	75	50	190	30.4 ± 4.0	30.7 ± 1.6	3.8 ± 11.4	21.1 ± 4.4
	80	84	380				
	85	175	670				

[a] This work (I = 2.0 M). [b] Calculated from data of ref 2, Table I (I = 2.5 M). (Error limits were stated to be ~10% for each constant recorded.) [c] Extrapolated values using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ figures given.

colliding ions is about 4 Å, a very reasonable distance for the systems under discussion.

We turn now to discussion of the trans-effect phenomenon mentioned earlier. A few bromide anation experiments were performed in the present work (at 70 °C, I = 2.0 M and $[H^+] = [Br^-] = 1.0$ M), utilizing the monobromo complex ion $Rh(H_2O)_5Br^{2+}$ prepared by the ion-exchange separation procedure described in the Experimental Section. The results enabled determination of the limiting second-order rate constant for formation of the *trans*-dibromo product of 5.5×10^{-4} M^{-1} s^{-1}, which can be ascribed to reaction 7 above.[23] This figure has been adjusted to 50 °C by use of the same temperature parameters as those known for the chloro analogue,[3] giving the value of 5.5×10^{-5} M^{-1} s^{-1} which appears in Table IV. Some enlightening comparisons are now possible concerning the various types of reaction illustrated. First, one can evaluate the overall anation rate ratio for several different types of chloride vs. bromide comparisons, as is shown in column 6 of the table. The ratio is seen to be almost constant and only a little greater than unity, attesting further to the arguments already presented in favor of the dissociative mechanism. Other conclusions relate to the figures given in column 7, which are the ratios of the composite rate constant for the specified reaction to that of the corresponding reaction at comparable ionic strength of the parent aquo complex (either $Rh(H_2O)_6^{3+}$ or $Rh(en)_2(H_2O)_2^{3+}$)—i.e., the kinetic trans effect of the ligand OH^-, Cl^-, or Br^-, as the case may be. For both types of complex ion, the trans effects of hydroxide are very large, accounting for the very substantial acidity dependences of reactions of the parent species, inasmuch as only minor amounts of hydroxoaquo congener can have a large accelerating influence on the overall reaction. In the case of the hexaaquo series, the bromide effect (420—see reaction 6) is about one-ninth that of hydroxide (~3500—see reactions 3 and 4), while that of chloride (180—see reaction 5) is only about 1/20th. However, the effect for both halide ions easily accounts for the fact that the first observable kinetic product of the anation of the hexaaquo ion by these species is the dihalo product. For the *trans*-diaquobis(ethylenediamine) series, one notes that the rate constants for anation are of the order of 10 times greater than for comparable hexaaquo complexes (cf. reactions 1–6 with reactions 7–12 in Table IV). There is also a contrast in the trans-effectiveness of the various X groups between the two series. The bromide effect (~1900—see reactions 13 and 14) is nearly half as great as the hydroxide (~4700—see reactions 9 and 10), though chloride (~200 —see reactions 11 and 12) is again only about 1/20th as effective as hydroxide. Briefly stated, one concludes that the trans-effect order is OH >> Br > Cl for the hexaaquo series and OH > Br >> Cl for the *trans*-$(en)_2$ series. This

Table IV. Rates of Some Anation Reactions of the Type *trans*-$RhL_4X(H_2O) + Y \rightarrow RhL_4XY + H_2O$ at 50 °C

Reaction				10^5k,[a] $M^{-1}\ s^{-1}$	I,[b] M	Cl^-: Br^- rate ratio	Trans-effect ratio[c]	Ref
No.	L	X	Y					
1	H_2O	H_2O	Cl^-	0.016	2.5	1.2		2[d]
2	H_2O	H_2O	Br^-	0.013	2.0			This work
3	H_2O	OH^-	Cl^-	59	2.5	1.3	3700	2[d]
4	H_2O	OH^-	Br^-	44	2.0		3400	This work
5	H_2O	Cl^-	Cl^-	2.9	2.0		180	3
6	H_2O	Br^-	Br^-	5.5	2.0		420	This work
7	$^1/_2$en	H_2O	Cl^-	0.13	1.0			8
8	$^1/_2$en	H_2O	Br^-	0.33	0.2			8[e]
9	$^1/_2$en	OH^-	Cl^-	640	1.0		4900	8
10	$^1/_2$en	OH^-	Br^-	1500	0.2		4500	8[e]
11	$^1/_2$en	Cl^-	Cl^-	72	0.2	1.2	220	15
12	$^1/_2$en	Cl^-	Br^-	62	0.2		190	15
13	$^1/_2$en	Br^-	Cl^-	680	0.2	1.3	2100	15
14	$^1/_2$en	Br^-	Br^-	530	0.2		1600	15
15	H_2O	H_2O	$H_2{}^{18}O$	~0.03[f]	~2			16

[a] Limiting second-order rate constants (k_1k_3/k_2 for the D mechanism, kK for the I). [b] The variations in ionic strength do not cause major changes in the composite rate constants, as can be seen by comparing reactions 7 and 8, where the k's are decreased by a factor only of about 2 when I is increased by a factor of 5. [c] Relative to the corresponding anation of the appropriate parent complex ($X = H_2O$) at comparable ionic strength. Thus, the comparisons for reactions 3 and 5 are to reaction 1; those for (4) and (6), to (2). For (9) the comparison is with (7), and for the remaining reactions, the comparisons are all with (8). [d] Extrapolated values—see Table III. [e] Estimated by use of pK's of the $X = H_2O$ complex given in ref 8 and the rate constant data given by A. J. Poë and K. Shaw, *J. Chem. Soc. A*, 393 (1970). [f] First-order exchange rate constant (units s^{-1}).

change in the relative magnitudes of the trans effect in reactions of complexes which differ only in the identity of the nonparticipating ligands has not been discussed theoretically. Contrasts have also been noted in the trans-effect behavior of otherwise similar complexes which differ only in the central metal ion.[4]

In conclusion it should be pointed out that studies of the reactions of aquopentaamminerhodium(III) complexes have tended to support the associative interchange type of mechanism. Thus, pressure effect studies of the solvent–water exchange reaction of $Rh(NH_3)_5H_2O^{3+}$ show that $\Delta V^{\ddagger}$ is negative,[24] and kinetic data for the chloride and bromide anation[25] of the same ion also appear to conform to the associative pattern. We thus have the anomalous situation in which one line of evidence, as presented in this paper and earlier studies,[3,8] tends to support the dissociative mechanism view for octahedral rhodium(III) reactions, while other evidence is to the contrary. Unfortunately, the considerable amount of new experimental data needed to resolve this apparent discrepancy is not yet available.

Registry No. *mer*-$Rh(H_2O)_3Br_3$, 52242-54-3; *trans*-$Rh(H_2O)_4Br_2{}^+$, 58002-44-1; *cis*-$Rh(H_2O)_4Br_2{}^+$, 58073-27-1; $Rh(H_2O)_5Br^{2+}$, 48019-52-9; $Rh(H_2O)_6{}^{3+}$, 16920-31-3; $Rh(H_2O)_5OH^{2+}$, 58073-28-2; Br^-, 24959-67-9.

References and Notes

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(12) For the chloride system[4] the corresponding reaction is slower by a factor of over 1000.
(13) This derives from eq A22 of the Appendix to ref 3, modified by the plausible assumption that $P = K_h$ (since K_h is independent of whether the medium is $ClO_4{}^-$ or Br^-) and the fact that $[H^+] >> K_h$. Note that this equation is mathematically identical with that used to interpret the Cl^- anation data[2] but is based on the D mechanism rather than the I_d mechanism, as explained in ref 3. Note also that while ion pairing is not excluded from consideration, ion-paired species do not make a significant contribution to the limiting D-mechanism rate expression (see Appendix to ref 3).
(14) Values for K_h at the given temperatures were interpolated and extrapolated from the data of ref 2 and are as follows: 50 °C, 7.1×10^{-4}; 60 °C, 8.3×10^{-4}; 70 °C, 1.0×10^{-3}; 80 °C, 1.2×10^{-3}.
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(18) It is also of interest that in the classic series of D reactions, $Co(CN)_5H_2O^{2-} + X^-$, k_3/k_2 is 0.11 for both $X^- = Cl^-$ and $X^- = Br^-$: see R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).
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