

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Interconversion of Acido and Aquo Rhodium Pentammines

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In a study of the interconversion in aqueous solution of certain acido- and aquo-pentammines of iridium¹ it was found that equilibria were established after a number of hours at 80–90° and that, in contrast to the equilibria among the corresponding pentammines of cobalt, these equilibria lay well over toward the acido side. This made it possible for the first time to obtain satisfactory measurements of the velocity of conversion of an aquo into an acido ammine. These measurements showed that, surprisingly enough, although the conversion to acido involved the combination of two ions, namely, the aquo ammine ion and the bromide (or chloride) ion, nevertheless, like the conversion of acido to aquo ammine, it was characterized by a first-order reaction rate, that is, it followed the schedule of a unimolecular reaction.

The pentammines of rhodium, because of their remarkable stability and ease of preparation, are favorable substances for a further study of these phenomena. Similar measurements have therefore been made of the velocities of conversion of aquopentammine rhodium bromide and chloride into the corresponding bromo- and chloropentammines, and vice versa, and of the location of the equilibria thereby established.

The experimental procedure for determining the velocities of conversion was substantially that used in work with the iridium amines.¹ The change in conductivity of the solutions was measured at successive intervals of time and from these measurements the velocity of conversion was calculated, assuming direct proportionality. The location of the equilibrium attained in the conversion was ascertained by analysis of the quickly chilled samples for free (*i. e.*, directly precipitable) bromide (or chloride) ion. Since the velocity of conversion of the rhodium amines is greater than that of the iridium amines the heating could be less prolonged and the temperature lower, so that the conductivity cells and the containers for the equilibrium mixtures could be of glass rather than of silica.

The amines were prepared according to the

directions of Jörgensen.² The stability of the pentammine ions themselves was demonstrated by heating a sample of aquopentammine rhodium bromide in aqueous solution in a closed platinum autoclave in a steam-bath for ten hours. No turbidity or alkalinity developed, nor was there evidence of any other change in the sample. The dry chloro- and bromopentammine salts appear to be stable indefinitely at room temperatures. The dry aquo chloride and bromide, on the other hand, change into the corresponding acido salts under these conditions. After a few days, analysis shows several per cent. of precipitable chloride (or bromide); after several months, complete conversion to the acido ammine. The aquo amines were in general, therefore, freshly prepared immediately before use, by conversion of the acido ammine into hydroxo hydroxide by digestion on the steam-bath with a solution of sodium hydroxide, followed by precipitation of the chloride (or bromide) in the cold with an excess of hydrochloric (or hydrobromic) acid.

Results

Velocity Measurements.—To illustrate the experimental results obtained in the velocity measurements, the data for one series of conductance measurements with aquo- and of another series with bromopentammine rhodium bromide are shown graphically in Fig. 1 and are listed in Table I. In the figure it can be seen that the upper curve, representing the molar conductance of the aquo, and the lower curve, representing the molar conductance of the acido, ammine, both as functions of the time, become closely asymptotic after one hundred to two hundred minutes, showing that a mixture of substantially the same composition is reached from either direction. It also can be seen that these amines, like the corresponding amines of iridium but unlike those of cobalt, reach an equilibrium in which the acido ammine largely predominates.

From the conductance data (for instance, those in the second and fifth columns of Table I) reaction velocity constants were first calculated on the simple assumption that both the change of

(1) Lamb and Fairhall, *THIS JOURNAL*, **45**, 378 (1923).

(2) Jörgensen, *J. prakt. Chem.*, [2] **27**, 433 (1883); *ibid.*, [2] **34**, 394 (1886).

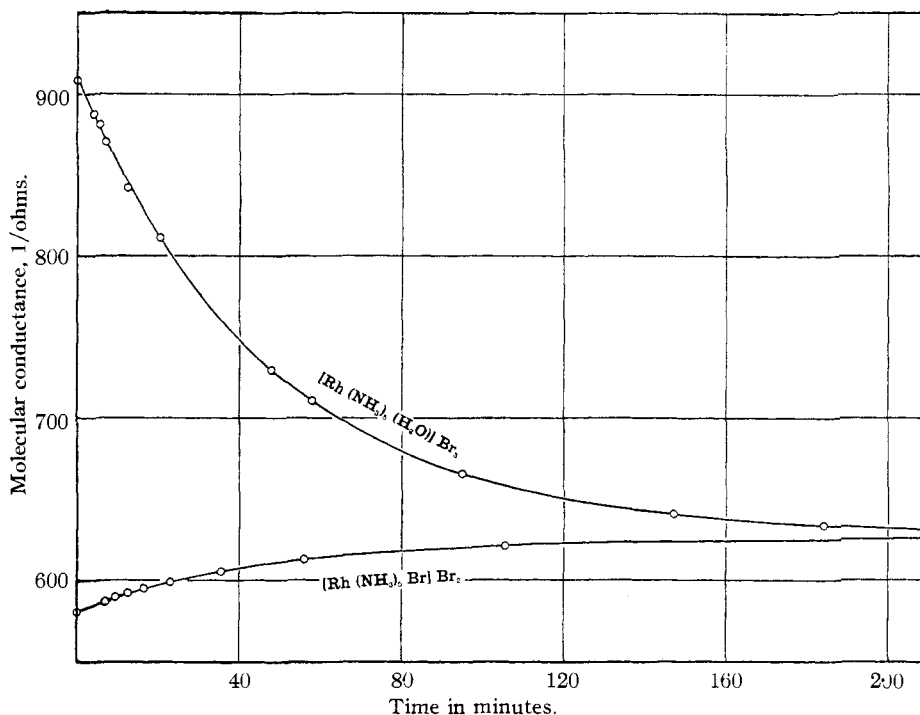


Fig. 1.—Change in conductance of aquo and bromo pentammine rhodium bromides with time

TABLE I
VELOCITY MEASUREMENTS, TEMPERATURE 84°

Aquation— $a = 0.00490 M$			Anation— $a = 0.00510 M$		
Time, min.	Molar cond. mhos $\times 10^2$	$(k' + k'')$ 1/min.	Time, min.	Molar cond. mhos $\times 10^2$	$(k' + k'')$ 1/min.
0	(909)		0	(581.7)	
4	888.4	1.91 ^a	7	587.9	2.10
5.2	881.2	2.01	9.5	590.0	2.13
7	870.6	2.11	12.5	592.5	2.18
12.2	842.2	2.18	16.5	595.2	2.15
20.2	809.2	2.17	23	599.5	2.17
48	730.0	2.12	35.5	605.9	2.16
58	711.4	2.11	56	613.3	2.14
95	666.5	2.12	105.5	622.1	2.12
147	641.8	2.13	∞	(626.9)	
184	634.5	2.13			Av. 2.14
∞	(629)				$\pm 1\%$
		Av. 2.133			
		$\pm 1\%$			

^a Not taken in av.

aquo into acido, which may well be called "acidation" or better "anation" and that of acido into aquo already known as aquation, are *unimolecular*. In such an instance, if the opposing reactions reach an equilibrium, the simple formula for a straightforward unimolecular reaction can be employed for either reaction, provided the concentration of the product formed at equilibrium is taken as the initial concentration of the reactant.³

(3) Mellor, "Chemical Statics and Dynamics," Longmans, Green & Co., London, 1904, p. 86.

Thus, calling a the total concentration of the pure acido or aquo ammine at the start, x the concentration of aquo or acido formed at the time t , ξ the value of x at equilibrium, and k' and k'' the velocity constants of aquation and anation, respectively, for aquation

$$1/t \log_e \frac{\xi}{\xi - x} = k' + k''$$

and for anation

$$1/t \log_e \frac{a - \xi}{a - \xi - x} = k' + k''$$

Assuming, further, proportionality between molar conductance and extent of transformation for aquation

$$1/t \log_e \frac{\mu_{\infty}' - \mu_0'}{\mu_{\infty}' - \mu_t'} = k' + k''$$

and for anation

$$1/t \log_e \frac{\mu_0'' - \mu_{\infty}''}{\mu_t'' - \mu_{\infty}''} = k' + k''$$

where μ_0' , μ_0'' , μ_t' , μ_t'' , and μ_{∞}' , μ_{∞}'' are the molar conductances at the start, at the time t and at equilibrium, for aquation and anation reactions, respectively.

The values of the combined velocity constants ($k' + k''$) obtained by substituting the observed data in these equations, are given in the third and sixth columns of Table I. The individual values in each series show very little variation ($\pm 1\%$) and the averages of ($k' + k''$), starting first with the acido and second with the aquo

TABLE II
 VELOCITIES OF TRANSFORMATION OF RHODIUM PENTAMMINES IN AQUEOUS SOLUTION

Temp., °C.	Rhodium pentammine	Concn. $M \times 10^3$	Added sub- stance	Concn. $M \times 10^3$	Molecular conductance 1/ohms			$k' + k''$ $\times 10^3$ 1/min.	No. meas.	$\Delta \pm \%$
					Initial	Final	Change			
64°	Aquobromide	4.852	665.1	509.7	155.4	2.34	7	0.4
64°	Aquobromide	4.919	672.3	514.7	157.6	2.35	7	1.9
64°	Aquobromide	4.961	728.0	510.0	218.0	2.38	9	2.7
64°	Aquobromide	5.007	728.7	508.0	220.7	2.33	7	5.4
64°	Bromobromide	4.898	475.4	513.9	38.5	2.19	6	2.0
64°	Bromobromide	5.039	481.4	520.0	38.6	2.38	8	3.6
64°	Chlorochloride	4.832	458.9	497.4	38.5	4.03	5	4.0
64°	Chlorochloride	4.982	460.3	498.6	38.3	4.01	6	6.0
84°	Aquobromide	4.640	918.6	638.6	280.0	20.9	13	0.7
84°	Aquobromide	4.880	895.0	626.0	269.0	21.0	9	1.0
84°	Aquobromide	4.870	854.4	627.1	227.3	18.6	11	0.1
84°	Aquobromide	4.901	909.6	628.6	281.0	21.0	10	2.2
84°	Aquobromide	5.450	KBr	14.0	805.8	596.6	209.2	34.5	11	3
84°	Aquobromide	4.677	KBr	19.0	733.0	522.0	211.0	36.8	9	5.5
84°	Aquobromide	5.103	KBr	19.4	733.0	522.0	211.0	36.4	8	3.1
84°	Aquobromide	5.003	HBr	0.69	905.0	612.3	292.7	23.7	8	0.9
84°	Aquobromide	5.021	HBr	.69	894.2	612.3	281.9	23.6	10	1.0
84°	Aquobromide	5.275	HBr	.99	849.3	594.3	255.0	23.8	14	0.8
84°	Aquobromide	4.948	NaOH	1.2	23.5	11	1.5
84°	Aquobromide	4.879	NaOH	2.2	24.6	10	5.0
84°	Bromobromide	4.790	573.5	631.0	57.5	21.1	4	0.8
84°	Bromobromide	4.800	582.9	633.5	50.6	19.4	7	4.8
84°	Bromobromide	4.863	582.4	629.0	46.6	19.5	6	3.5
84°	Bromobromide	5.096	581.4	626.9	45.5	21.3	7	1.0
84°	Aquochloride	0.970	1042	782	260	11.5	12	2.2
84°	Aquochloride	1.000	973	753	220	11.0	6	4
84°	Aquochloride	3.27	866	583	277	23.2	11	0.6
84°	Aquochloride	4.78	853.5	633.5	220.0	26.4	12	1.6
84°	Aquochloride	4.86	892.7	614.0	278.7	24.2	8	0.9
84°	Aquochloride	4.883	908.0	628.9	279.1	23.9	11	0.5
84°	Aquochloride	5.06	879.0	618.3	260.7	26.9	11	1.5
84°	Chlorochloride	2.38	568.8	635.4	66.6	20.4	4	4.2
84°	Chlorochloride	4.77	545.1	582.2	37.1	27.0	7	1.7

ammines, are practically identical, in agreement with the requirements of these equations.

The values of the individual constants are easily obtained from the values of the combined constants by the use of equilibrium data; namely,

$$k' = \frac{\xi}{a} (k' + k''), \text{ and } k'' = (k' + k'') - k'$$

On this basis $k' = 0.00315$ and $k'' = 0.0181$.

The values of $(k' + k'')$ calculated in the same way from all of our measurements would require too much space to justify their complete presentation here. Only the *averages*, therefore, of all the values obtained with each of the solutions studied will be given. These have been collected in Table II along with the values of the total concentrations, the extrapolated initial and final conductances, the number of the individual measurements of $(k' + k'')$ on which each average is based and the average deviations of the individual measurement from the average.⁴

(4) The extrapolated initial values of the conductances of the

It can be seen from Table II that the average deviations of the individual values of $(k' + k'')$ from the average in all the measurements with the pure aquo pentammines are in general only about ± 1 to $\pm 3\%$. The average deviations observed with the acido pentammines and with the pentamine solutions to which various additions were made are somewhat greater, corresponding to the greater experimental difficulties, but they are never greater than $\pm 6\%$. It can be seen also that substantially identical values of $(k' + k'')$ are obtained, irrespective of whether the transformation of aquo to acido or acido to aquo is being measured.

aquo and acido ammines show some variations in separate experiments. The occasional lower values for the aquo ammine indicate a slight, partial conversion to the acido ammine before the measurements had started. The higher values for the acido ammines, conversely, show a slight prior conversion to aquo ammine. The "Added Substances" were already present in the solutions to which the requisite weights of the solid ammines were added. The molecular conductance in such cases represents merely the increase in conductance as observed, without correction.

There is no doubt, therefore, that the transformations individually have first-order reaction rates, that is, they follow the schedule of opposed unimolecular reactions. The aquo rhodium pentammines, then, exhibit the same anomalous behavior as was found for the aquo iridium ammines, since on any simple interpretation of the conversion of aquo to acido ammines, the interaction of two molecular species is involved, namely, the aquo cation and the halogen anion, and these reactions should follow the equation of a bimolecular rather than a unimolecular reaction.

The explanation of this anomalous behavior may be, as was pointed out in connection with the study of the iridium ammines,¹ that the rate-determining step in this change is the slow loss of a molecule of water from the ion, preceded perhaps by an internal electronic rearrangement or by the formation of an activated variety of the ion. This slow step would then be followed by a very rapid combination of the new ion with the chloride or bromide ion present.

Evidence against this explanation is the greater rapidity of the change of aquo bromide to the bromo-bromide as compared with the rapidity of the change of the aquochloride into the chloro chloride, as found with the iridium ammines and now with the rhodium ammines (see Table II). If the speed of the reaction were governed only by the rate at which the water molecule leaves the aquo ammine ion, it should be independent of the nature of the unattached anion. In rebuttal to this objection, it might be argued that the undissociated molecule of the aquo ammine may share in the reaction, indeed may be the chief actor therein, in which case the undissociated chlorine atoms might accelerate the loss of the water molecule more than the bromine atoms. Supporting this argument is the fact that added amounts of bromide ions (KBr) increase decidedly the rate of the anation (Table II).

This latter fact, however, must be considered equally indicative of a bimolecular mechanism. Moreover, strong evidence against the unimolecular and in favor of a bi- or multimolecular mechanism is the fact that, while individually these anations follow the schedule of opposed unimolecular reactions, $(k' + k'')$ varies markedly with different initial concentrations of the ammine.

There is another explanation of this anomalous behavior which avoids these difficulties. The

reaction may be accepted as bimolecular, *i. e.*, the combination of aquo ion with the halogeno ion, but a correction may then be applied for the "kinetic salt effect" as set forth by Brönsted.⁵ If this is done, it turns out that the resulting kinetic expression for a bimolecular, opposed by a unimolecular, reaction does not differ significantly from the above expression for opposed unimolecular reactions.

The detailed development of the kinetic expression is as follows: Brönsted showed for a considerable number of ionic reactions that the reaction velocity is proportional to the product of the concentration of the reactants, multiplied by a factor consisting of the product of the activity coefficients of the reactants, divided by the activity coefficient of an assumed fugitive complex resulting from the collision of the reactants. Applied to a bimolecular reaction, this gives

$$dc/dt = kc_a c_b (f_a f_b / f_x)$$

where c and f represent the concentrations and activity coefficients, respectively, subscripts a and b indicating the reactants and x the collision complex. The value of the factor $f_a f_b / f_x$ can be computed for dilute solutions from the relation $\log f = -1/2 Z^2 \sqrt{\mu}$ where Z is the valence of the ion in question and μ the ionic strength; hence $\log f_a f_b / f_x = Z_a Z_b \sqrt{\mu}$ and $dc/dt = kc_a c_b 10^{Z_a Z_b \sqrt{\mu}}$. For a bimolecular reaction opposed by a unimolecular reaction the relation becomes

$$dc/dt = k'' c_a c_b 10^{Z_a Z_b \sqrt{\mu}} - k' c_c$$

where k_2'' and k_2' represent the velocity constants of the bi- and unimolecular reactions (anation and aquation), respectively, and c_c the concentration of the product formed in the bimolecular reaction.

Applied to the reaction under consideration, namely, $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})^{+++} + \text{Br}^- \rightleftharpoons (\text{Rh}(\text{NH}_3)_5\text{Br})^{++} + \text{H}_2\text{O}$, in dilute solution

$$dx/dt = k''(a - x)(3a - x)10^{Z_a Z_b \sqrt{\mu}} - k_2' x$$

where a is the initial concentration of the pure aquopentammine ion and x the amount of a transformed in time t . Since Z_a and $Z_b = +3$ and -1 , respectively, $\mu = 3(2a - x)$ and the expression becomes

(5) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); Brönsted and Livingston, *THIS JOURNAL*, **49**, 435 (1927), in a footnote reference to the finding of Lamb and Fairhall¹ that the formation of the acido pentammine iridium ion follows the scheme of a unimolecular reaction remarked, "This apparent anomaly may be explained on the basis of the present theory of reaction velocity when the negative salt effect to be expected is taken into consideration." So far as we are aware, no further development of this suggestion has appeared.

$$dx/dt = k_2'' \frac{(a-x)(3a-x)}{10^3 \sqrt{3(2a-x)}} - k_1' x \quad (1)$$

The limiting values of x are 0 and a , respectively; substituting them in the term $(3a-x)/10^3 \sqrt{3(2a-x)}$, this then has the limiting values of $3a/10^3 \sqrt{6a}$ and $2a/10^3 \sqrt{3a}$, respectively. The ratio of these limiting values is $(3/2)/10^3(\sqrt{6a} - \sqrt{3a})$ or, when a is 0.005, 1.06, so that the maximum variation in the expression for the bimolecular reaction due to terms other than $(a-x)$ is 6%. It follows that velocity constants computed on the assumption of opposed unimolecular reactions, that is, where the term $(3a-x)/10^3 \sqrt{3(2a-x)}$ is omitted, should not vary on this account by more than $\pm 3\%$ from the average.⁶ Therefore, one cannot conclude from the constancy of the calculated values of $(k' + k'')$ and hence of k'' , that the mechanism of the anation reaction is necessarily an anomalous unimolecular one; indeed it is more reasonable to conclude that the reaction is actually bimolecular, the term for the chloride ion being practically cancelled by the term for the salt effect, so that a kinetic formula substantially identical with that based on opposed unimolecular reactions is obtained.

To show definitely whether or not the results of our measurements are in agreement with the Brønsted formula based on a bimolecular reaction opposed by a unimolecular reaction, we have applied it to the same data used to illustrate the applicability of the simple formula based on opposed unimolecular reactions (Table I). In order to use formula (1) directly and avoid integration, the actual concentrations were first computed from the observed conductances; these were plotted on a large scale and the momentary velocities obtained by taking the tangents at these concentrations to the smooth curve drawn through them. These velocities are given in the third column and the values of k_2'' computed from them using formula (1) are given in the fourth column of Table III.

It can be that the values of k_2'' are indeed very constant (except for the final value which was unduly close to the equilibrium), the average deviation of the individual values from the mean (4.12) being only about 2%. The value of k_1' (the velocity constant for aquation) computed from formula (1) by substitution of equilibrium

(6) The actual variation on this account would be even smaller since x actually does not vary as widely as the limits taken above, and since the initial and final values used in the calculation of the constants were obtained by extrapolation.

TABLE III

Time, min.	$M \times 10^3$	$M \times 10^3 / \frac{dx}{dt}$ min.	k_2'' bimol. M/min.	k_1' unimol. l/min.
0	0			
4	.278	0.86	4.18	0.0188
5.2	.385	.81	4.05	.0182
7	.544	.78	4.08	.0183
12.25	.968	.70	4.17	.0186
20.25	1.461	.57	4.03	.0179
48	2.645	.32	4.07	.0180
58	2.922	.26	3.98	.0179
95	3.593	.120	4.35	.0182
147	3.962	.040	4.06	.0177
184	4.072	(.020)	(4.80)	(.0210)
∞	4.154	0		
			Av. 4.12 \pm 2.1%	0.0182 \pm 1.5%

values of x and equating to zero is 0.00318. This latter is substantially identical with the value of k' (*i. e.*, 0.0032) obtained by use of the integrated equation based on opposed unimolecular reactions. The value of k_2'' obtained for the bimolecular reaction is also very nearly identical with the product of the unimolecular constant k'' divided by the factor $(3a-x)/10^3 \sqrt{3(2a-x)}$. Thus when $a = 0.0049$ and x varies between 0 and a , the average value of this factor is $1/220$, and therefore, $0.0181 \times 220 = 4.10$. These agreements serve as a check on the accuracy of the computation and the plotting.

An independent check on the accuracy of the plotting is furnished by the values of k_1' given in the last column of Table III. These were computed from the differential equation for opposed unimolecular reactions using the same values of dx/dt used in the calculation of k_2'' , for a bimolecular opposed by a unimolecular reaction. The mean value 0.0182 agrees very exactly with the mean value of 0.0181 obtained previously using the integrated formula.

It is also of interest to inquire whether the observed larger value for the sum of the unimolecular constants of anation and aquation in the presence of added potassium bromide is also explicable on the assumption of a bimolecular anation reaction with the Brønsted correction. To test this we have taken the averages of all the experiments with added potassium bromide, the average values being for $a = 0.00490 M$ and $KBr = 0.0192 M$, $(k' + k'') = 0.0360$. Since no conductance measurements of bromo-bromide with added bromide were made, we have utilized the analytical data given later for the fraction of aquo ammine at equilibrium (0.125) (Table V) and have thus obtained the apparent unimolecu-

lar anation constant $k'' = 0.0315$. The conversion factor in these solutions, $(3a + 0.0192 - x)/10^3\sqrt{6a + 0.019 - 3x}$, is 1/136 for $x = 0$, and 1/123 for $x = a$, 1/129 average; which, taking the value of the bimolecular anation constant obtained from the 0.005 M solution without the addition of potassium bromide ($k_2'' = 4.12$), gives $k'' = 0.0320$, in agreement with the above value obtained directly for the measurements with added bromide.

A decided decrease in the values of the sums of the apparent unimolecular constants was observed when, as in the case of the chloride, the initial concentration of the ammine was lowered to 0.001 M . This would not be expected if only opposed unimolecular reactions were involved. To ascertain whether this decrease is also explainable on the assumption of a bimolecular anation with the Brönsted correction, we have computed the bimolecular anation constant for the aquopentammine chloride, both at 0.00490 and 0.001 M . The average conductance of the approximately 0.005 M solutions of aquo chloride at equilibrium and the single available value for the chloro-chloride give the apparent fraction of aquoammine at equilibrium as 0.127. The average value of $(k' + k'')$ is 0.0257 which gives k'' , or the unimolecular anation constant, as 0.0224. The average conversion factor for this ionic strength is, as was computed for the bromide, 1/226.7, which gives a bimolecular anation constant $k_2'' = 5.08$.

Similarly, from the conductance data for the 0.001 M solution, the apparent fraction of aquoammine at equilibrium is 0.28, which, with the observed value of $(k' + k'') = 0.01126$, gives $k'' = 0.0081$. The average conversion factor in this solution is 1/620 which gives the bimolecular anation constant $k_2'' = 5.02$, in agreement with the above value computed from the data for the more concentrated solution.

The addition of hydrobromic acid to the aquoammine had only a slight effect on the value of $(k' + k'')$. The average conversion factor for the experiment using 0.00099 hydrogen bromide is 1/210, which would give a value of $k'' = 0.0197$. The measured value of $(k' + k'')$ is 0.0238, which, combined with equilibrium values, gives the concordant value $k'' = 0.0202$. This slight increase in $(k' + k'')$ is therefore closely what would be expected from the bimolecular formula with the Brönsted correction.

The addition of sodium hydroxide to the aquopentammine also produced only a slight increase in $(k' + k'')$. Here, as a result of the recognized rapid formation of hydroxopentammine, the ionic strength is diminished so that, even though no additional halogen ions are present, the average conversion factors become 1/213 and 1/203 for 0.0121 M and 0.0223 M sodium hydroxide, which would give values of $k'' = 0.0194$ and 0.0206, respectively. The measured values of $(k' + k'')$, combined with the equilibrium data, give $k'' = 0.0200$ and 0.0209, respectively, in agreement with the calculated values.

The addition of sodium hydroxide to the solution of bromopentammine bromide brought about changes of conductivity which at first sight appeared anomalous. A slight initial increase in conductivity occurred prior to the addition of the sodium hydroxide. On the addition of the sodium hydroxide, after the consequent immediate considerable increase in conductivity, a rapid decrease took place at a steadily diminishing tempo, the conductance becoming practically constant after about an hour. This decrease contrasts sharply with the slow increase in conductance that accompanies aquation. The explanation of this behavior would appear to be that slow aquation of the bromopentammine bromide first takes place; on the addition of the sodium hydroxide a relatively rapid, direct reaction ensues between the bromopentammine ion and the hydroxyl ion. This results in the replacement of the fast moving hydroxyl ion by the relatively slow moving bromide ion, and since the hydroxoammine ion formed has substantially the same conductance as the bromoammine ion originally present, a net decrease in conductance takes place. The conductances as measured in the course of an experiment of this kind where sodium hydroxide sufficient to give a concentration of 0.00460 M was added to a 0.00512 M solution of bromopentammine bromide, are collected in Table IV.

In this experiment some aquation of the bromopentammine takes place after the preparation of the solution and before the addition of the sodium hydroxide, as is shown by the conductance data given in the second column. From the extrapolated value of the conductance at the moment of addition of the sodium hydroxide and the known conductance of the aquopentammine at this concentration and temperature, it follows that the concentrations of the bromo and aquo am-

TABLE IV
 EFFECT OF SODIUM HYDROXIDE ON THE TRANSFORMATION OF BROMOPENTAMMINE RHODIUM BROMIDE, TEMP. 84°

Time, min.	Sp. cond. $\frac{1}{\text{ohm}} \times 10^2$	Time after NaOH added, min.	Sp. cond. $\frac{1}{\text{ohm}} \times 10^2$	$x \times 10^3 M$	$\frac{dx}{dt} \times 10^6 M / \text{min.}$	$k'(a-x) \times 10^6 M / \text{min.}$	$\frac{dx_c}{dt} \times 10^6 M / \text{min.}$	$\frac{k_c}{1 \times M / \text{min.}}$
0		0	(0.5080)	0				
6.3	0.2936	1.5	.4919	0.766	520	12.1	508	41
7	.2959	2.2	.4845	1.119	465	10.9	454	45
9	.2973	3.2	.4745	1.595	385	9.4	376	51
12.5	.3018	4.25	.4672	1.942	290	8.3	282	51
13.5	.3030	6.25	.4578	2.388	238	7.0	231	64
14 ^a	(.3035)	8	.4514	2.693	146	6.0	140	55
		9.8	.4468	2.913	103	5.3	98	52
		12	.4430	3.093	81	4.7	76	54
		16.5	.4371	3.374	53	3.8	49	59
		24	.4318	3.627	32	3.1	28.9	74
		30	.4291	3.755	18	2.6	15.4	66
		37	.4260	3.092	8.8	2.2	6.6	74
		46	.4253	3.935	4.5	2.1	2.4	35
			(.4233)	(4.031)				Average 55

^a NaOH added at 14 min.

mines at that moment must have been 0.00521 and 0.000459 *M*, respectively. When the sodium hydroxide is added this aquopentammine reacts at once with an equivalent amount of hydroxyl ion to form hydroxopentammine, without, however, producing thereby any significant change in conductance, since the sum of conductances of the resultant hydroxopentammine and sodium ions is presumably substantially equal to that of the aquopentammine ion above. A slight decrease only will result from the elimination of the free hydrogen ions originally present in the solution of the aquopentammine bromide.

The amount of this decrease was ascertained by comparing the conductance of a 0.005 *M* solution of aquopentammine bromide when pure and when amounts of sodium hydroxide sufficient to give concentrations of 0.00122, 0.00224 and 0.00456 *M* had been added. In these latter solutions decreases of 0.00047, 0.00045 and 0.00036 $\frac{1}{\text{ohm}}$ were obtained.⁷ On this basis the decrease in the above-mentioned solution would be 0.00048 $\frac{1}{\text{ohm}}$, so that the corrected initial increment in conductance due to the sodium hydroxide was 0.002093 $\frac{1}{\text{ohm}}$. This, multiplied by the excess conductance of the hydroxyl ion over the bromide ion and divided by the conductance of sodium hydroxide, all at a concentration of 0.005 *M*, would require a decrease of 0.00090 $\frac{1}{\text{ohm}}$ in the conductance of the solution during the subse-

(7) These decreases indicate a dissociation constant for the aquopentammine ion at this temperature and concentration of 1.6×10^{-4} . Correcting this to 15°, assuming a temperature coefficient of 2.2 for a 10° change, gives 7×10^{-7} in close agreement with the value obtained independently by Brønsted and Volquartz [*Z. physik. Chem.*, **134**, 131 (1928)] at this temperature.

quent conversion of the bromopentammine into hydroxopentammine. The observed decrease was 0.00085 $\frac{1}{\text{ohm}}$. The close agreement of these quantities confirms the correctness of the above interpretation.

The formation of hydroxoammine conceivably might take place by the slow aquation of the bromopentammine followed by the very rapid reaction with hydroxyl ion to give the hydroxopentammine. It can, however, be seen from Table IV that the transformation is much more rapid than the previously measured aquations and one must therefore conclude that the transformation takes place chiefly by direct reaction of the bromopentammine ion with the hydroxyl ion. If this is the case, the reaction should exhibit second-order reaction rates since the two ions were present in nearly equivalent amounts.

To test this matter we have first computed the change in the concentration of the bromopentammine ion from the observed values of the specific conductance given in the fourth column of Table IV, assuming that the sodium hydroxide is substantially all consumed in the presence of the excess of bromopentammine and that the change in concentration is proportional to the relative decrease in conductance. The resulting values are given in the fifth column of Table IV. The velocity of the reaction was obtained graphically at the successive time intervals and these values are given in the sixth column. Since some formation of hydroxoammine must take place by an initial aquation of the bromoammine present, we have computed the velocity of this concurrent

reaction from the known value of its velocity constant (0.00315) and the corresponding concentrations of the bromopentammine ion. The values are given in the seventh column and the velocities of the bimolecular reaction corrected for them (dx_c/dt) are given in the eighth column. These corrected values divided by the product of the concentrations of the bromopentammine and hydroxyl ions give the values of the bimolecular reaction velocity constant (k_c) listed in the last column of the table. No correction for the kinetic salt effect is required since no change in ionic strength takes place. It can be seen that these values are quite constant and thus afford additional confirmation of the interpretation advanced.

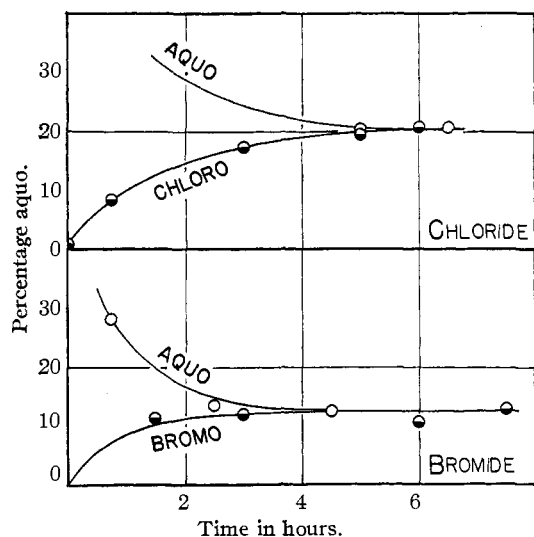


Fig. 2.—Attainment of equilibrium as shown by precipitable halide.

Finally, it should be pointed out that this very rapid direct reaction between bromopentammine rhodium bromide and hydroxyl ion as contrasted with the relatively slow aquation at the same temperature ($k_c = 55$ versus $k' = 0.00315$) finds its parallel in the corresponding reaction of bromopentammine cobaltic bromide at 25°. Brönsted and Livingston⁸ found a bimolecular velocity constant for this reaction of 355 while the corresponding velocity constant for the unimolecular aquation of that ammine is 3.9×10^{-4} at the same temperature.⁹

Equilibrium Measurements.—It is possible from the initial and final conductances of aquo and acido amines to compute the fraction of

(8) Brönsted and Livingston, *THIS JOURNAL*, **49**, 435 (1927).

(9) Lamb and Marden, *ibid.*, **33**, 1873 (1911).

each ammine present in the equilibrium mixture, and this procedure already has been utilized in computing the individual apparent unimolecular constants of anation and aquation from the directly determined sums of these constants. This method has the disadvantage that it assumes a direct proportionality between the conductances and the fraction of aquo salt present in the mixture. We have, therefore, as in the case of the cobalt and iridium amines, resorted to a direct analytical determination of this fraction.

The analytical procedure was that previously employed, namely, the determination of the precipitated halogen in the solutions that had reached equilibrium at a higher temperature (64 and 84°) and which then had been suddenly chilled by shaking with ice and an excess of acidified silver nitrate. Since the original amines, unless freshly prepared, contain small amounts of the complementary amines (acido or aquo), they were analyzed and allowance was made for this content in the calculations. A vacuum weight correction was also applied in the case of the bromide.

To demonstrate that equilibria were indeed obtained, analyses were made at successive intervals starting with acido amines on the one hand and aquo amines on the other. Results obtained with the chloride and with the bromide in the presence of 0.01 *M* hydrobromic acid are shown graphically in Fig. 2. It can be seen that substantially the same fraction of aquo ammine was attained starting either from the aquo or from the acido ammine, indicating that equilibrium was indeed established. The final data obtained for the equilibria at different temperatures and concentrations are collected in Table V.

These data inserted in the simple mass law give values of the equilibrium constant (K_1) which increase rapidly (over 100%) in passing from 0.001 to 0.010 molar solution. Inserted in the Debye limiting law for this equilibrium

$$\log K = \log K_0 + 3\sqrt{\mu}$$

these data give $\log K_0 = -3.20$ and -4.92 , respectively, for the bromo- and chloroammines. The values of $\log K$ calculated on this basis are given in the next to the last column of Table V. They are in fair agreement with the observed values. Inserted in the Storch-Bancroft empirical equation for the ionization of strong electrolytes

$$\left(\frac{\text{Aquo}^{+++} \times \text{Hal}^-}{\text{Acido}^{++}} \right)^n = K_{s.B.}$$

TABLE V
 EQUILIBRIUM BETWEEN AQUO AND ACIDO AMMINE IONS AND HALIDE IONS AT 84°

Initial ammine	Concn. $M \times 10^3$	Added substance	Concn. $M \times 10^3$	Mole fraction aquo Obsd. Av.	Obsd. $\log K$	Calcd.	$K_{S.B.}$
Bromide							
Acido	2.05	..		0.3756	-3.47	-3.41	0.052
Acido	5.07	..		.2226			
Acido	5.07	..		.2270			
				.2243	-3.51	-3.52	.044
Acido	5.07	..		.2195			
Acido	5.07	..		.2280			
Aquo	20.8	..		.1345	-3.84	-3.83	.055
Aquo	4.97	HBr	10.74	.1215			
				.1230	-3.48	-3.58	.040
Acido	4.99	HBr	10.74	.1245			
Acido	5.02	KBr	9.87	.1515			
Acido	5.05	KBr	9.87	.1575	-3.59	-3.58	.048
Acido	5.06	KBr	9.87	.1545			
Average							.048
Chloride							
Acido	1.24	..		0.3410	-3.17	-3.11	0.0201
Acido	4.97	..		.2030			
Acido	4.97	..		.2130			
Acido	4.98	..		.2050			
				.2037	-3.45	-3.32	.0275
Acido	4.98	..		.1915			
Aquo	5.00	..		.2085			
Aquo	5.00	..		.2010			
Acido	10.00	..		.1025			
				.1100	-3.42	-3.47	.0220
Acido	10.00	..		.1175			
Acido	19.9	..		.0755			
				.0751	-3.52	-3.68	.0230
Acido	20.1	..		.0747			
Acido	4.96	HCl	0.00684	.1030	-3.49	-3.46	.0287
Acido	4.97	HCl	0.0342	.0650	-3.30	-3.34	.0203
Average							0.0234 ±

these data give the values of $K_{S.B.}$ collected in the last column of Table V, taking $n = 0.77$ for the bromo- and $n = 0.80$ for the chloroammine. Here again a fair concordance is obtained.

This behavior parallels closely that observed with the corresponding amines of cobalt and iridium,¹ so that one may conclude that these acido rhodium amines also ionize quite as do strong electrolytes, except that the rate at which the equilibrium is established is relatively much slower.

Effect of Sodium Hydroxide.—Sodium hydroxide in excess is known to produce at 100° a rapid transformation of acido (purpureo) rhodium amines into hydroxoammines, so that on acidification, the corresponding aquo (roseo) amines result. To test the effect of less than equivalent amounts of sodium hydroxide on the equilibrium, 100-cc. portions of approximately 0.005 M chloro-pentammine rhodium chloride containing various

amounts of sodium hydroxide were heated for six to eight hours at 84°, the solution rapidly chilled as described above and the precipitated silver chloride determined. The data obtained are collected in Table VI.

 TABLE VI
 EFFECT OF SODIUM HYDROXIDE ON THE EQUILIBRIUM,
 TOTAL VOLUME 100 CC., TEMPERATURE 84°

Concn. chloro-pentammine chloride $M \times 10^3$	Vol. 0.1 M NaOH added, cc.	Calcd. concn. of ions, $M \times 10^{-3}$			Weight of silver chloride, g.	
		Aquo-pent-ammine	Chloro-pent-ammine	Chloride	Calcd.	Found
4.983	0.957	0.745	3.286	11.67	0.1673	0.1678
4.990	1.000	.734	3.256	11.71	.1679	.1690
5.000	1.949	.503	2.548	12.45	.1784	.1802
4.992	2.930	.493	1.569	13.41	.1922	.1972
4.996	4.99	0	0	14.99	.2145	.2146
4.990	9.98	0	0	14.97	.2147	.2157

A reasonable expectation on the basis of our kinetic results as to what takes place in these reaction mixtures is that a rapid formation of hy-

droxoamine ensues with a practically complete consumption of the hydroxyl ion. It is then reasonable to expect that the residual chloropentamine and aquopentamine chlorides adjust themselves in accordance with the above expressions which have been found to apply to this equilibrium.

To test this hypothesis we have computed from the observed value of $K_{S.B.}$ (*i. e.*, 0.0234) what the concentrations of the aquo, chloro and chloride ions should have been in these solutions, and from these values have then calculated the weights of silver chloride which would have been formed on the addition of silver nitrate in the cold. These are given in the next to the last column of Table VI. They agree quite closely with the weights of silver chloride actually found as given in the last column.

Summary

1. The rates at 64 and 84° of the direct transformation of aquopentamine bromide and chloride in aqueous solution into the corresponding acido pentamine salts and of the reverse transformation have been determined by means of conductivity measurements. The location of the equilibria reached in these transformations also has been ascertained by determinations of the precipitable halide.

2. Both the direct and the reverse transformations exhibit first-order reaction rates indicating a mechanism of opposed unimolecular reactions, in spite of the fact that in the conversion of aquo to acido amines two reactants are involved. This anomalous behavior is explained as due to changes in the ionic strength of the solutions during the reaction. The insertion of the Brønsted correction for this effect in the kinetic

equation for opposed bi- and unimolecular reactions gives a modified kinetic equation practically indistinguishable from the simple equation for opposed unimolecular reactions.

3. The experimental results for the velocities of transformation agree excellently with this modified equation over a range of initial concentrations and in the presence of added halides and of sodium hydroxide.

4. The equilibrium constants computed from the data obtained with these amines show the variation with the ionic strength to be expected from the Debye limiting law. They also fit the empirical Storch-Bancroft formula for the dissociation constants of strong electrolytes, which again emphasizes the similarity between these two classes of equilibria in spite of the fact that one is adjusted slowly and the other instantaneously.

5. The addition of sodium hydroxide to solutions of bromo- and chloropentamines results in the rapid conversion of these substances to the corresponding hydroxopentamines. This reaction when corrected for the concurrent formation of hydroxopentamine by primary aquation follows a simple second-order equation. No correction for the kinetic salt effect is required since no change in the ionic strength takes place.

6. Sodium hydroxide added to a solution containing an excess of ammine chloride does not affect the equilibrium directly. Determinations of the precipitable chloride show that hydroxopentamine is formed equivalent to the sodium hydroxide added and that the residual amines adjust their concentrations in conformity with the above expressions for the equilibrium constant.

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