

of sucrose decomposed per photon absorbed by the system. The variation in ϕ with the concentration of sucrose was given by $\phi = a[1 - \exp(-g[\text{sucrose}])]$. At 254 $m\mu$, $a = 0.3$ and $g = 0.6$ when [sucrose] was expressed in moles per liter and solutions were buffered with acetate. ϕ increased when the solutions were not buffered, but the pH then decreased slightly due to subsequent reactions. ϕ was independent of (1) the light intensity over a 200-fold range, (2) the temperature between 10 and 35°, (3) the pH between

3 and 6, and (4) the concentration of uranyl sulfate between 0.0008 and 0.008 molar.

The kinetics of the reaction have been discussed.

Extinction coefficients of uranyl sulfate solutions were obtained at intervals of 0.1 in the logarithm and are given for the dip in absorption about 366 $m\mu$. Beer's law was obeyed and sucrose concentrations up to 100 times those of uranyl sulfate did not affect the measurements.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Aquation of Carbonato Pentammine Cobaltic Bromide

BY ARTHUR B. LAMB AND ROGER G. STEVENS

Carbonate tetrammine cobaltic salts undergo little or no aquation in pure aqueous solution at ordinary temperatures. In other words, the carbonate group is not readily displaced from the complex ion by molecules of water. This is explained by its firm attachment, presumably by two covalent links.

In carbonato pentammine salts the carbonato group appears to be held by one polar and one covalent link. While the former would permit dissociation, the latter holds the carbonato group firmly, so that it cannot function as a separate ion. In agreement with this, their freshly prepared solutions, like those of the corresponding carbonato tetrammine salts, do not give the characteristic tests for the carbonate ion and exhibit the conductance to be expected of uni-univalent electrolytes.

One might expect, however, that carbonato pentammine salts with but a single covalent link holding the carbonato group, would undergo aquation more readily than the carbonato tetrammine salts. Yet, Werner and Gosling,¹ to whom we owe most of our knowledge of the carbonato pentammines, appear never to have observed any aquation of these substances, and Schwartz and Tede² state that dilute solutions of the nitrate are stable both in the dark and when exposed to ultraviolet light, as shown by the constancy of their electrical conductance. Duff,³ to be sure, found that while dilute solutions of the nitrate showed

no change in conductance at 25° by themselves, an increase in conductance took place when the solutions were left in contact with platinum electrodes. Solely on the basis of this evidence he inferred that carbonato pentammine nitrate does not aquate spontaneously, but does so under the catalytic influence of the platinum. The latter part of this inference was and is quite unjustified, because no such catalytic effect on aquation has ever been observed by others, while it has long been recognized that the decomposition of cobalt ammines is markedly accelerated by contact with platinum electrodes.⁴

In this situation it appeared of interest to examine solutions of these carbonato pentammines more particularly for possible aquation, and this we have now done by means of measurements of the conductance of dilute solutions of the bromide at 25 and 0°.

The carbonato pentammine cobaltic bromide was prepared through the nitrate following the methods of Werner and Gosling.¹ The conductances were measured using "dip" electrodes following the procedure previously described in another connection.⁵ Duplicate readings were taken over an interval of more than an hour with and without the removal of the electrodes from the solution. Identical changes in conductance took place in each instance indicating that the platinum electrodes exerted no perceptible effect under the circumstances.

(1) Werner and Gosling, *Ber.*, **36**, 2380 (1903).

(2) Schwartz and Tede, *ibid.*, **60**, 65 (1927).

(3) Duff, *J. Chem. Soc.*, **123**, 573 (1923).

(4) Lamb and Larson, *THIS JOURNAL*, **42**, 2025 (1920); Lamb and Yngve, *ibid.*, **43**, 2354 (1921); Brønsted, *ibid.*, **40**, 439 (1927).

(5) Lamb and Stevens, *ibid.*, **54**, 2643 (1932).

The resulting data are collected in Table I.

TABLE I
CHANGE IN CONDUCTANCE OF A 0.004 *M* SOLUTION OF
CARBONATO PENTAMMINE COBALTIC BROMIDE

AQUATION			
0°		25°	
Time, min.	Mol. cond. 1/ohm	$a - x$ 1/ohm	$k_1 + k_2$ 1/min.
0	(54.8)	(19.7)	
4	55.5	19.0	0.0089
5	55.7	18.8	.0094
7	56.1	18.4	.0097
10	56.6	17.9	.0097
11	56.8	17.7	.0097
15	57.5	17.0	.0099
16	57.6	16.9	.0097
25	58.9	15.6	.0092
50	61.7	12.8	.0085
101	66.0	8.5	.0083
145	68.8	5.7	.0085
205	71.6	2.9	.0084
	(74.5)	0	
Average		0.0092	
		± .0004	
Time, min.	Mol. cond. 1/ohm	$a - x$ 1/ohm	$k_1 + k_2$ 1/min.
0	(102)	(69.2)	
1	108.9	62.2	0.106
2	115.8	55.3	.113
4	127.2	43.9	.113
5	131.4	39.7	.111
6	135.5	35.6	.111
8	142.0	29.1	.111
10	147.3	23.8	.106
12	151.8	19.3	.106
15	156.0	15.1	.101
20	161.9	9.2	.101
25	165.4	5.7	.099
35	168.6	2.5	.094
60	171.0	0.1	.105
86	171.1	0	
444	171.2		
Average		0.106	
		± .005	

It can be seen that the conductance increases slowly, indicating a slow aquation. A stationary state is reached after about an hour at 25° and after perhaps ten hours at 0°.

It was possible, to be sure, that the observed increase in conductance was caused by a decomposition of the ammine. If this occurred, free ammonia should be present. A current of air was therefore bubbled through a solution of the ammine and thence into Nessler reagent, blank tests having shown that minute amounts of ammonia in a solution can be detected in this way. With the ammine solution at 0° no trace of ammonia was indicated until after an hour's bubbling. At 25° a trace was indicated in thirty minutes and a marked test was obtained in seventy minutes. Since the change in conductance is nearly complete before any decomposition is detectable, the observed change in conductance cannot be ascribed to decomposition.

Tests were also made to confirm the presence of the bicarbonate ions produced by the aquation. For this purpose a weakly ammoniacal solution of barium chloride was added to freshly prepared solutions of the bicarbonato ammine bromide at 0°. At first no indication of carbonate or bicarbonate was obtained, but after the solution had stood for an hour at this temperature a small precipitate was formed. A similar solution kept at 25° for seventy minutes and then cooled to 0° gave an immediate and copious precipitate when the barium hydroxide was added. These results

confirm the inference drawn from the conductance measurements that aquation of the carbonato pentammine does indeed take place.

From the data in Table I values of k in the formula for a unimolecular reaction have been computed taking a , the concentration of the reacting substance, as equal to the total change in conductance and $a - x$ as equal to the change in conductance at the time t . Since the final state reached is, on the basis of all our previous studies of aquation, an equilibrium, the constants thus obtained represent the sum of the individual constants for the direct and the reverse reaction, *i. e.*, $k_1 + k_2$. They are given in the last column of Table I and show a reasonable constancy at each temperature.

The Mechanism of the Aquation

Aquation is usually looked upon as a direct replacement of a complexly held anion by a molecule of water. An alternative mechanism would be the primary addition of hydrogen ion to the complexly held anion with the formation of the undissociated acid which is then replaced by a molecule of water. It is, however, unlikely that this latter is the sole mechanism of aquation, because then the anions of weak acids should aquate more rapidly and completely than those of strong acids, and this does not appear to be the case.

This mechanism is, however, presumably operative in the case of the carbonato pentammines. They react rapidly with acids to give carbonic acid and aquo pentammine salts. Direct replacement of the complexly attached carbonato group by water certainly could not account for so rapid a reaction. There can, therefore, be little doubt that the hydrogen ion here combines directly with carbonato group to form the bicarbonato group. The resulting ion, for electrostatic reasons, would aquate much more rapidly than the carbonato ion itself. Indeed, it might aquate with sufficient rapidity to account entirely for the observed aquation of the carbonato ammine.

Aquation and Anation of the Bicarbonato Pentammines.—To ascertain how rapidly and completely the aquation of the bicarbonato pentammine takes place, we have measured the conductance of dilute solutions of its nitrate at 0° and at successive intervals of time. The data are given in the second column of Table II.

It can be seen that a relatively rapid rise in conductance takes place, indicating rapid aquation, a stationary state being reached in about

TABLE II

CHANGE IN CONDUCTANCE OF A 0.00286 *M* SOLUTION OF BICARBONATO PENTAMMINE COBALTIC NITRATE AND BROMIDE AT 0°

Time, min.	AQUATION		$a - z$, 1/ohm	$k_1 + k_2$, 1/min.
	Molecular conductance Nitrate, 1/ohm	Molecular conductance Bromide (calcd.), 1/ohm		
0	(124.2)	(130.0)	(21.2)	
6	138.1	143.9	7.3	0.177
7	139.4	145.2	6.0	.179
8	141.1	146.9	4.3	.198
9	141.9	147.7	3.5	.200
10	142.5	148.3	2.9	.198
11	143.2	149.0	2.2	.205
12	143.8	149.6	1.6	.214
13	144.2	150.0	1.2	.221
15	144.5	150.3	0.9	.209
18	144.8	150.6	0.6	.198
	(145.4)	(151.2)	0	

Average 0.20 ± 0.01

eighteen minutes. The extrapolated initial molecular conductance, 124.2 1/ohm, is what would be expected from the previously observed⁶ conductance of hydroxo pentammine chloride, 132 1/ohm.

To ascertain whether this final stationary state represents an equilibrium, we have also carried out the reverse process, *i. e.*, the anation⁷ of the aquo pentammine. For this purpose we added an equivalent weight of aquo pentammine bromide to a solution of sodium bicarbonate and followed the change of the conductance with the time. The resulting data are collected in Table III.

TABLE III

CHANGE OF CONDUCTANCE OF A 0.00286 *M* SOLUTION OF SODIUM BICARBONATE AND OF AQUO PENTAMMINE COBALTIC BROMIDE AT 0°

Time, min.	ANATION		$a - z$, 1/ohm	$k_1 + k_2$, 1/min.
	Molecular conductance Observed, 1/ohm	Molecular conductance Corrected, 1/ohm		
0		(183.3)	(32.5)	
1	0.6624	174.8	24.0	0.304
2	.6393	166.8	16.0	.318
3	.6261	162.2	11.4	.346
4	.6166	158.9	8.1	.348
5	.6107	156.8	6.0	.337
7	.6029	154.0	3.2	.332
10	.5972	152.0	1.2	.330
18	.5937	150.8	...	
38	.5935	150.8	...	
∞		(150.8)		

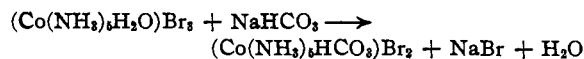
Average 0.33 ± 0.005

The observed specific conductances are given in the second column of the table. They exhibit a rapid *decrease*, indicating the formation of the

(6) Lamb and Stevens, ref. 5, p. 2649.

(7) A. B. Lamb, *THIS JOURNAL*, **61**, 609 (1939),

bicarbonato pentammine ion, *i. e.*, anation. To compare these data with those obtained in the previous aquation experiment it was necessary to eliminate the conductance of the sodium bromide present here as shown by the equation



and not present in the aquation experiment. This was accomplished by multiplying the observed specific conductance of the sodium bicarbonate solution before the addition of the ammine (0.0001334 1/ohm) by the ratio of the molecular conductances of sodium bromide and sodium bicarbonate at the prevailing concentration, and subtracting the product from the observed specific conductances. The resulting corrected specific conductances were then converted to molecular conductances and were corrected for the diminished conductances, both of the ammine and of the sodium bicarbonate, in the mixture. These corrected molecular conductances are given in the third column of Table III and are shown graphically as the upper curve in Fig. 1. The

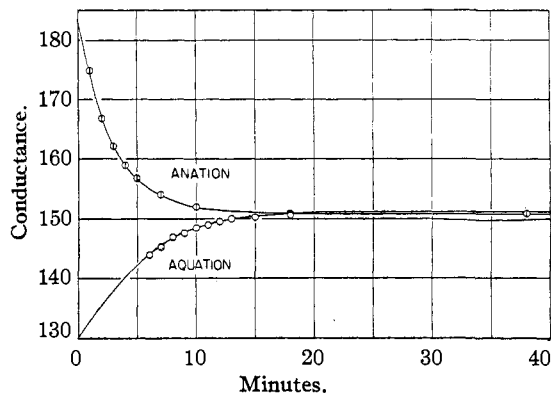
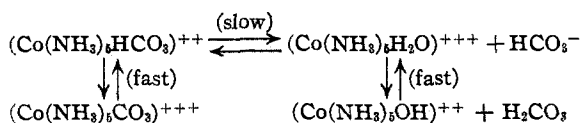


Fig. 1.—Change in conductance (corrected) of a solution of bicarbonatopentammine cobaltic bromide (aquation) and of a solution of aquopentammine cobaltic bromide and sodium bicarbonate (anation) at 0°.

corresponding molecular conductances observed with the bicarbonato pentammine nitrate, corrected to bromide by addition of 5.8 1/ohm for the difference in mobility between two bromide and two nitrate ions, are given in the third column of Table II and are also shown as the lower curve in Fig. 1. It can be seen that these two curves approach each other and after about eighteen minutes become nearly coincident. This indicates that the stationary condition reached both by aquation and anation is indeed an equilibrium.

The composition of the solution of aquo pentammine bromide and sodium bicarbonate at the start, before any bicarbonato pentammine has been formed by anation, can be computed from the known dissociation constants of aquo pentammine ion and carbonic acid. The reactions involved in this equilibrium can be represented as follows



Calling Aq^{+++} and Hy^{++} the concentrations of aquo and hydroxo pentammine ions, respectively, and considering solely the above equilibria on the right

$$\text{Hy}^{++}/\text{Aq}^{+++} = \sqrt{\frac{K_{\text{Aq}}}{K_{\text{H}_2\text{CO}_3}}} = \sqrt{\frac{1 \times 10^{-7}}{4 \times 10^{-7}}} = 1/2$$

That is, $\text{Aq}^{+++} = 2\text{Hy}^{++}$ at the start.⁸ Taking the molecular conductances of the aquo and hydroxo pentammine bromide, sodium carbonate and sodium bromide at 0°, and at the prevailing concentration, as 222, 130, 47.5 and 62.6 1/ohm, respectively, the initial conductances of the system on the right, before any bicarbonato had formed, would be 222 + 47.5 - 62.6, or 206.9 1/ohm, if the pentammine were exclusively aquo, and 130 1/ohm, if exclusively hydroxo. Since, however, $\text{Aq}^{+++} = 2\text{Hy}^{++}$, the initial conductance should be 206.9 - 1/3(206.9 - 130) = 181.3 1/ohm. This value corresponds closely with the extrapolated value shown in Fig. 1.

The concentrations of the various ions in these solutions at any time during the aqutation or anation could likewise be calculated from the observed conductances and the known dissociation constants of aquo pentammine ion and carbonic acid if the dissociation constant for the bicarbonato pentammine ion were also known. From these concentrations velocity constants for aqutation and anation could then be directly evaluated with a good deal of certainty. Lacking this information as to the bicarbonato ammine, we have simply assumed, as usual, that the extent of the reaction is proportional to the change in conductance, and since an equilibrium is attained we have taken the total concentration of reacting substance as equal to the amount transformed at equilibrium. The resulting apparent velocity

(8) From the data of Brønsted, *Z. physik. Chem.*, **134**, 133 (1928); and MacInnes, *This Journal*, **55**, 2638 (1933); **57**, 1084 (1935), by application of the observed temperature coefficients.

constants for a unimolecular reaction of this sort, $k_1 + k_2$, the sum of the unimolecular velocity constants of the simple aqutation and anation reactions, respectively, are given in the final columns of Tables II and III.⁷

It can be seen that the individual values for $k_1 + k_2$ are in each series reasonably constant. The average of the values obtained in the anation measurements is, however, considerably larger than the average obtained in the aqutation measurements. This may well be due to a lack of rigor in our assumption of direct proportionality between the change in conductance and the concentrations of the ions undergoing either aqutation or anation, or to the failure of the approximate unimolecular formula to represent adequately the bimolecular anation reaction when corrected for the kinetic salt effect.⁷

Aqutation in Mixtures of Carbonato and Bicarbonato Pentammine.—We have also made measurements of the change in conductance of solutions of carbonato pentammine bromide to which aliquot amounts of hydrochloric acid have been added. This has afforded a convenient means of obtaining mixtures of the carbonato and bicarbonato amines. The observed conductances of the ammine immediately upon the addition of the acid and at intervals thereafter are given in Table IV. Velocity constants computed in the same way as for the pure compounds are also given.

It can be seen that the solution to which an equivalent amount of acid was added showed substantially the same initial conductance and the same rate of aqutation as a solution of pure bicarbonato pentammine. Solutions containing lesser amounts of acid showed progressively smaller velocities of aqutation. Indeed, the velocity constants for the aqutation of the several solutions followed closely the formula

$$k_1 + k_2 = 0.214 \frac{(\text{Co}(\text{NH}_3)_5\text{HCO}_3)^{++}}{0.00286}$$

the calculated values for $k_1 + k_2$ when 1/10 and 1/4 equivalents of hydrochloric acid were added, being 0.0214 and 0.0535, respectively, whereas 0.0233 and 0.0515 were actually observed.

The application of this formula to the 0.00286 *M* solution of pure carbonato pentammine bromide where the velocity constant of aqutation is 0.0092 1/min. would indicate a concentration of bicarbonato pentammine = 0.0092 × 0.00286/0.214, or 0.00012 *M*, provided aqutation takes

TABLE IV

CHANGE IN CONDUCTANCE OF A 0.00283 *M* SOLUTION OF CARBONATO PENTAMMINE COBALTC CHLORIDE CONTAINING VARIOUS CONCENTRATIONS OF HCl AT 0°

HCl = 0.000286 <i>M</i>				HCl = 0.000715 <i>M</i>				HCl = 0.00286 <i>M</i>			
Time, min.	Mol. cond. obsd., 1/ohm	$a - x$, 1/ohm	$k_1 + k_2$, 1/min.	Time, min.	Mol. cond. obsd., 1/ohm	$a - x$, 1/ohm	$k_1 + k_2$, 1/min.	Time, min.	Mol. cond. obsd., 1/ohm	$a - x$, 1/ohm	$k_1 - k_2$, 1/min.
0	(64.4)	(27.8)		0	(74.6)	(26.6)		0	(130.0)	(25.3)	
1	65.0	27.2		2	77.2	24.0	0.0516	3	142.0	13.3	0.215
2	65.7	26.5	0.0240	3	78.5	22.7	.0528	4	144.9	10.4	.217
3	66.3	25.9	.0235	4	79.6	21.6	.0521	5	147.3	8.0	.230
4	67.0	25.2	.0244	5	80.7	20.5	.0521	6	149.0	6.3	.232
5	67.5	24.7	.0237	6	81.7	19.5	.0518	7	150.5	4.8	.237
6	68.1	24.1	.0237	7	82.7	18.5	.0518	8	151.5	3.8	.237
7	68.7	23.5	.0240	9	84.5	16.7	.0518	9	152.4	2.9	.240
8	69.3	22.9	.0242	11	86.1	15.1	.0516	10	153.0	2.3	.240
10	70.3	21.9	.0240	13	87.5	13.7	.0512	11	153.3	2.0	.230
12	71.2	21.0	.0235	16	89.4	11.8	.0510	12	153.8	1.5	.235
15	72.7	19.5	.0237	19	91.0	10.2	.0506	14	154.2	1.1	.224
20	74.7	17.5	.0230	22	92.5	8.7	.0510	17	154.5	0.8	.206
25	76.6	15.6	.0230	26	94.1	7.1	.0510		(155.3)	0	
30	78.2	14.0	.0228	31	95.7	6.5	.0510				
35	79.7	12.5	.0228	36	96.9	4.3	.0507				
45	82.1	10.1	.0226	41	97.8	3.4	.0502				
55	84.0	8.2	.0221	51	99.3	1.9	.0516				
70	86.2	6.0	.0219	66	100.4	0.8	.0530				
90	88.4	3.8	.0221		(101.2)	0					
125	90.5	1.7	.0223								
160	91.6	0.6	.0240								
195	91.9	.3	.0233								
	(92.2)										
	Average	0.0233		Average	0.0515			Average	0.228		
		= .0006			= .0006				= .007		

place exclusively via the bicarbonato ammine, that is, with no direct aquation of the carbonato. This concentration of bicarbonato in equilibrium with the carbonato in pure water would correspond to a dissociation constant of about 4×10^{-10} . A direct determination of this constant would show the actual concentration of bicarbonato in equilibrium with the carbonato and thus permit a decision as to what part of the aquation of the carbonato takes place directly and what part via the bicarbonato pentammine.

Summary

1. It has been found from conductance measurements that carbonato pentammine bromide undergoes a slow aquation to give an equilibrium mixture of bicarbonato, aquo and hydroxo pentammines. Bicarbonato pentammine salts undergo a much more rapid aquation, reaching an

equilibrium with the opposing anation reaction by which aquo pentammine is converted into bicarbonato pentammine. The velocities of these aquation and anation reactions have been measured and velocity constants have been computed.

2. Evidence is presented to show that in the equation of the carbonato pentammine salts a rapid, reversible addition of hydrogen ion to the complexly held carbonato group takes place, followed by a relatively slow, but reversible, aquation of the bicarbonato group.

3. It has been pointed out that these measurements, coupled with measurements of the dissociation constant of the bicarbonato pentammine ion would permit an estimate of how much of the aquation of the carbonato pentammine takes place directly and how much through the intermediate formation of the bicarbonato pentammine.

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