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The Rate of Aquation of Dichlorotetraaquochromic Ion as a Function of pH in Chloride Media

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The first-order rate constant for the aquation of $Cr(H_2O)_4Cl_2^+$ ions has been determined in chloride media of ionic strength 0.5 as a function of pH over the range 1.0 to 3.7 and found to be k (min.^{-1}) $= 0.0050 + 1.55 \times 10^{-5}/[H^+]'$. The results are discussed in relation to existing data and in terms of a proposed mechanism.

Introduction

The rate of aquation of dichlorotetraaquochromic ions, hereafter referred to as $CrCl_2^+$, has been reported by several investigators.[1-6] These workers disagree either on the dependence of the rate on hydrogen ion concentration or the value of the rate constant or both.

In the present work the rate of aquation was followed spectrophotometrically over a pH range of 1.0 to 3.7 and a concentration of 0.005 to 0.008 M in $CrCl_2^+$.

Experimental

A Cary Model 11 spectrophotometer was used to measure the change in absorbancy of the solution at 700 mμ as a function of time. Stoppered Corex 10-cm. cells were employed and air was used as a reference. The absorbancy of the solutions without the chromic salt was measured against air and this value was subtracted from the absorbancy of the chromium solutions. All determinations were made at 25 ± 0.05°. Solid $CrCl_2(H_2O)_4Cl \cdot 2H_2O$ was prepared by the method outlined by Elving and Zemel[7] and characterized by analysis of per cent water and chloride. The salt prepared in this manner has been shown to be predominantly the *trans* isomer.[8] Weighed amounts of this salt were dissolved in solutions of HCl and NaCl of suitable ionic strength and the pH was determined by a Beckman Model G pH meter.

Results and Calculations

Determination of the Rate Constants.—The solution prepared as described above initially contained only the dichlorochromic ion species, presumably all in the *trans* form.[8] The amount of $CrCl_2OH$ formed by hydrolysis was calculated using the hydrolysis constant of 1.9×10^{-6} reported by Lamb and Fonda.[2] The resulting concentration of $CrCl_2OH$ at the highest pH used experimentally was found to be less than 0.5% of the total chromium. This is in agreement with the magnitude of the change in pH observed immediately after dissolution of the solid chromic salt. Also the apparent absorbancy index of these solutions at zero time showed no experimentally significant dependence upon pH. This implies that the contribution of the small amount of $CrCl_2OH$ present to the absorbancy of the solution can be neglected.

From Bjerrum's reported hydrolysis constant of 8×10^{-6} for $CrCl^{+2}$, the fraction of chromic ions as $CrClOH^+$ was calculated as less than 2% at pH 3.69, the highest pH used. We have assumed that the absorbancy index of $CrClOH^+$ is similar in magnitude to that of $CrCl^{+2}$ and have neglected the contribution of $CrClOH^+$ to the total absorbancy.

Within the above limitations the following equation can be written for the total absorbancy of the solution at any time t

$$A = l\{a_1[CrCl_2^+] + a_2[CrCl^{+2}] + a_3[Cr^{+3}]\} \qquad (1)$$

Since the rate of aquation of $CrCl^{+2}$ is known to be much smaller than that of the $CrCl_2^+$ species, the concentration of Cr^{+3} ion at the early stages of the experiment will be very small. This factor and the fact that the absorbancy index of the Cr^{+3} ion is approximately 0.6 at 700 mμ permits us to neglect the contribution of the Cr^{+3} ion to the total absorbancy at the early stages of the experiment. Within this approximation and neglecting the back reaction, the following expression can be derived for the total absorbancy as a function of time

$$A = l[CrCl_2^+]_0\{a_1e^{-kt} + a_1(1 - e^{kt})\} \qquad (2)$$

Dividing through by A_0 and rearranging, we can write

$$\log\left(\frac{A}{A_0} - \frac{a_2}{a_1}\right) = -\frac{kt}{2.3} + \log\left(\frac{a_1 - a_2}{a_1}\right) \qquad (3)$$

where A is the total absorbancy at time t, A_0 is the total absorbancy at time $t = 0$, k is the first-order rate constant for the aquation of $CrCl_2^+$, a_1 is the molar absorbancy index of $CrCl_2^+$, a_2 is the molar absorbancy index of $CrCl^{+2}$, $[CrCl_2^+]_0$ is the molar concentration of $[CrCl_2^+]$ at $t = 0$, and l is the length of the cell.

From this equation values of k at the various pH values were calculated. Figure 1 shows typical plots of eq. 3 for the lowest and highest pH used. The rate constant, k, was evaluated from the slope of the straight portion of these curves. In all determinations the linear region covers approximately two half-lives. At times greater than two half-lives the conversion of significant amounts of $CrCl^{+2}$, $a_2 = 4.0$, to Cr^{+3}, $a_3 =$

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(1) N. Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907).

(2) A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43**, 1154 (1921).

(3) Yu. P. Nazarenko, *Zh. Neorgan. Khim.*, **4**, 1829 (1959).

(4) R. E. Hamm and C. M. Shull, Jr., *J. Am. Chem. Soc.*, **73**, 1240 (1951).

(5) J. Ibarz, J. Virgili, and J. M. Costa, *Anales real. soc. espan. fis. quim.*, **57B**, 489 (1961); **58B**, 89 (1962).

(6) H. B. Johnson and W. L. Reynolds, *Inorg. Chem.*, **2**, 468 (1963).

(7) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

(8) E. L. King, M. J. M. Woods, and H. S. Gates, *ibid.*, **80**, 5015 (1958).

TABLE I

RATE OF AQUATION OF $CrCl_2^+$ AS A FUNCTION OF pH

pH	$k \times 10^3$, min.$^{-1}$	pH	$k \times 10^3$, min.$^{-1}$
3.69	70.80	2.80	13.50
3.66	69.20	2.50	9.45
3.47	42.80	2.39	10.40
3.37	35.40	2.35	7.22
3.28	31.10	1.75	4.72
3.21	25.40	1.01	4.71

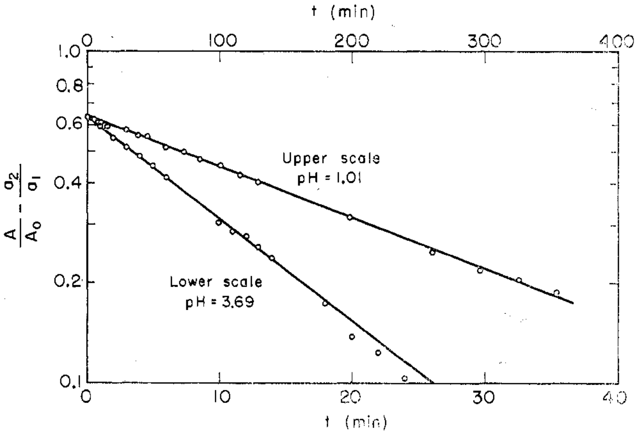

Fig. 1.—Experimental data analyzed by eq. 3 at pH 1.01 and 3.69.

TABLE II

REPORTED FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF DICHLOROTETRAAQUOCHROMIC ION

Investigator	Method	k, min.$^{-1}$	k, min.$^{-1}$ at 0.01 M H^+
Present study	Spectrophotometrically	$0.0050 + \frac{1.55 \times 10^{-5}}{[H^+]'}$	6.55×10^{-3}[f]
Bjerrum[a]	Conductometrically	$0.00272 + \frac{1.62 \times 10^{-5}}{[H^+]}$	4.30×10^{-3}
Lamb and Fonda[b]	Conductometrically	$0.00265 + \frac{1.42 \times 10^{-5}}{[H^+]}$	4.10×10^{-3}
Nazarenko[c]	Argentimetric titration	...	5.30×10^{-3}
Hamm and Shull[d]	Dropping mercury electrode	$\frac{5.2 \times 10^{-6}}{[H^+]}$	5.20×10^{-4}
Ibarz, Virgili, and Costa[e]	Dropping mercury electrode	$0.00095 + \frac{7.6 \times 10^{-8}}{[H^+]^2}$	10.30×10^{-4}

[a] Reference 1. [b] Reference 2. [c] Reference 3. [d] Reference 4. [e] Reference 5. [f] Referred to antilog (−pH) = 0.01; all other data referred to actual $[H^+]$.

0.6, leads to a larger decrease in light absorption with time than that predicted by eq. 3, as shown by the data in Fig. 1.

In analyzing the experimental data, a value of 4.0 was obtained for a_2 as an average of the data reported by Gates and King[9] and Taube and Myers.[10] For a_1, King[8] gives 11.6 for the *cis* isomer and 13.2 as the value for the *trans* isomer. Since the rate of isomerization of these species is unknown, we chose to use an average value of 12.4 for a_1 in the evaluation of our data. This leads to an uncertainty of ±6% in the ratio of a_2/a_1, which in turn leads to an uncertainty of ±3% in the reported values of k.

Dependence of the Rate Constant on pH.—Table I shows the values of k measured at the various pH values and in Fig. 2 we have plotted k *vs.* $1/[H^+]'$, where the symbol $[H^+]'$ = antilog (−pH).

The data in Table I were analyzed graphically to obtain the following equation for the rate of conversion of $CrCl_2^+$ to $CrCl^{+2}$.

$$k\ (\text{min.}^{-1}) = 0.0050 + \frac{1.55 \times 10^{-5}}{[H^+]'} \qquad (4)$$

In evaluating these data, two effects that influence the pH during an experiment need to be considered. First there is the initial hydrolysis of the added $CrCl_2^+$, which gives rise to a change in pH that is easily measured before any significant amount of reaction has occurred. It is these measured initial pH values that are reported in Table I and Fig. 2. The second factor is the hydrolysis of the $CrCl^+$ species formed during the reaction, which gives rise to a continuous change in pH during the reaction. In the determination at pH 3.69, for example, the pH decreased to 3.50 over a 24-min. interval as determined in a separate experiment. This should be borne in mind in regard to the reliability of the data as given in Table I and Fig. 2 at pH greater than 3.3.

Discussion

Comparison with Existing Data.—Our pH-independent term of the rate law is 5.0×10^{-3} min.$^{-1}$ and is in excellent agreement with the value of 4.94×10^{-3} recently reported for the rate of aquation of *trans*-$CrCl_2^+$ at pH 0 by Johnson and Reynolds.[6] The results of this investigation are compared with previously existing data in Table II.

It is apparent that our results are in substantial agreement with the data reported in ref. 1, 2, and 3. The disagreement shown by the entries for ref. 4 and 5 in Table II suggests a systematic error is involved in following this reaction at the dropping mercury electrode. In fact, the rate law found for aquation of $CrCl^{+2}$ as determined in this laboratory[11] is in substantial agreement with that given in Table II for ref. 5. It would thus appear that the reaction actually being followed at the dropping mercury electrode is that of the aquation of $CrCl^{+2}$. This can be explained by assuming

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[9] H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

[10] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[11] Unpublished results.

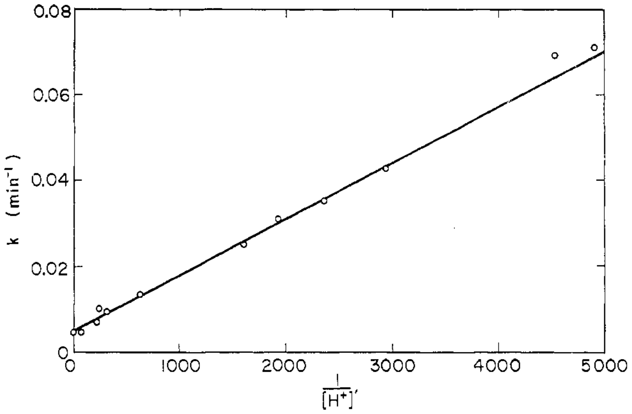

Fig. 2.—The dependence of *k* on acidity at 25° and μ = 0.5 (NaCl added).

that the chromous ion formed at the electrode rapidly converts $CrCl_2^+$ to $CrCl^{+2}$ according to the fast reaction

$$*CrCl_2^+ + Cr(II) \longrightarrow *Cr(II) + CrCl^{+2} + Cl^- \tag{5}$$

which has a rate constant[10] of roughly 10^4 M^{-1} min.$^{-1}$.

Mechanism.—The first term in eq. 4 may be taken as the rate of aquation of the *trans*-$CrCl_2^+$ species, as is shown in the recent work of Johnson and Reynolds.[6]

The second term in eq. 4 represents the dependence of the forward reaction on the concentration of hydrogen ion. In light of the inverse hydrogen dependence the following mechanism is assumed, in agreement with that outlined by Hamm and Shull,[4] to account for this term in the rate law.

$$CrCl_2(H_2O)_4^+ \overset{\text{rapid}}{\rightleftarrows} CrCl_2(H_2O)_3OH + H^+$$

$$CrCl_2(H_2O)_3OH + H_2O \xrightarrow{\text{slow}} CrCl(H_2O)_4OH^+ \; Cl^-$$

$$H^+ + CrCl(H_2O)_4OH^+ \overset{\text{rapid}}{\rightleftarrows} CrCl(H_2O)_5^{+2}$$

This same type of mechanism is generally accepted in regard to many related reactions.[12]

The rate constant for the aquation of $CrCl_2(H_2O)_3OH$ is 8.15 as compared with 0.0050 for the $CrCl_2(H_2O)_4^+$ species. This ratio of approximately 1630 is in agreement with that found in many analogous systems and is subject to the same general interpretation.[13]

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[12] R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

[13] R. Pearson and F. Basolo, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

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The Characterization of $[Cr(H_2O)_4OH]_2^{+4}$ and Its Formation by Oxygen Oxidation of Chromous Solutions[1]

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The dinuclear Cr(III) species formed by O_2 oxidation of Cr^{+2} solutions, which is the same species as the early product of boiling Cr^{+3} solutions and of electrochemical reduction of $Cr_2O_7^{-2}$, was shown by O^{18} exchange studies to be $[Cr(H_2O)_4OH]_2^{+4}$. The fact that but five O atoms per Cr show a measurable exchange rate eliminates the possibility of an oxo bridge. The rate of the oxidation was found to be second order in Cr^{+2} but was directly proportional to the flow rate of O_2 gas. Isotope labeling showed that all of the O atoms of the oxidizing agent, O_2, are transferred to the product. These results are understood in terms of a mechanism which involves a peroxide-bridged intermediate.

When chromous perchlorate solutions are oxidized by air or O_2, a dinuclear product of total charge +4 results.[3] The same product is formed as the first step in hydrolytic polymerization of heated chromic perchlorate solutions,[4] or by electrolytic reduction of $Cr_2O_7^{-2}$.[5] The charge found for the species[3] is consistent with its being either $[(H_2O)_5CrOCr(H_2O)_5]^{+4}$ or $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{+4}$. Because of the importance of this species in a wide variety of different processes, and because of the general difficulty in deciding between oxo and hydroxo bridging in Cr(III) polymers, the present experiments were undertaken.

If to a solution of the dinuclear species, H_2O^{18} is added, thoroughly mixed, and the solvent is promptly sampled, the amount of exchangeable O atoms is found. By difference, the number of O atoms "held back" in the dinuclear species is obtained as was done in establishing coordination number six for the simple Cr^{+3} ion.[6] In this way, decision can be made between the oxo-bridged structure, O/Cr = 5.5, and the hydroxy-bridged one, O/Cr = 5.0.

Once the structure of the dinuclear Cr(III) has been established, further experiments could indicate its mechanism of formation by the O_2 oxidation of Cr^{+2}.

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[1] Supported by the United States Air Force through the Air Force Office of Scientific Research and Development Command.

[2] Based on a thesis presented in partial fulfillment of the degree of Doctor of Philosophy.

[3] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[4] J. A. Laswick and R. A. Plane, *ibid.*, **81**, 3564 (1959).

[5] J. Levitan, Hebrew University, Jerusalem, private communication.

[6] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).