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Berkeley, California

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Abstract

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 $k(\text{min.}^{-1}) = 0.0050 + \frac{1.55 \times 10^{-5}}{[H^+]}$. The results are discussed in relation to existing data and in terms of a proposed mechanism.

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Introduction

The rate of aquation of dichlorotetraaquochromic ions, hereafter 1-5 referred to as $CrCl_2^+$, has been reported by several investigators.[1-5] These workers disagree either in 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 M to 0.008 M in $CrCl_2^+$.

Experimental Method

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 °C. Solid $(CrCl_2(H_2O)_4)Cl\cdot 2H_2O$ was prepared by the method outlined by Elving and 6 Zemel,[6] and characterized by analysis of percent water and chloride. The

salt prepared in this manner has been shown to be predominantly the <u>trans</u>
7 isomer.[7] 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 following equation can be written for the total absorbancy of the solution at any time t:

$$A = \ell \left\{ a_1[\mathrm{CrCl_2}^+] + a_2[\mathrm{CrCl}^{++}] + a_3[\mathrm{Cr}^{+++}] \right\} \qquad (1)$$

Since the rate of aquation of CrCl^{++} is known to be much smaller than that of the $\mathrm{CrCl_2}^+$ species, the concentration of Cr^{+++} ion at the early stages of the experiment will be very small. This factor and the fact that the absorbancy index of the Cr^{+++} ion is approximately 0.6 at 700 mμ permits us to neglect the contribution of the Cr^{+++} 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:

$$A = \ell\, [\mathrm{CrCl_2}^+]_0 \left\{ a_1\, e^{-kt} + a_2(1 - e^{-kt}) \right\} \qquad (2)$$

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

From this equation values of k at the various pH's were calculated. F1 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 $CrCl^{++}$, $a_2 = 4.0$, to Cr^{+++}, $a_3 = 0.6$, 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
8 a_2 as an average of the data reported by Gates and King[8] and Taube and
9 Myers.[9] For a_1, King[7] 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.

TI Table I shows the values of k measured at the various pH's and in
F2 Fig. 2 we have plotted k *versus* $1/[H^+]'$, where the symbol $[H^+]'$ = antilog ($-$pH).

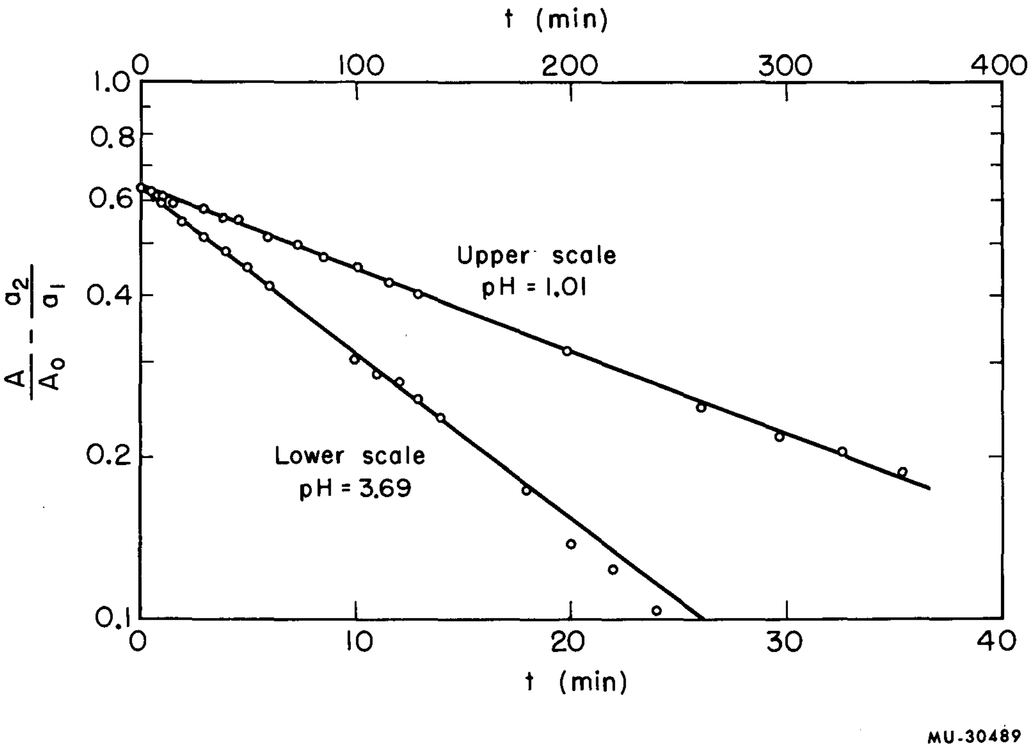
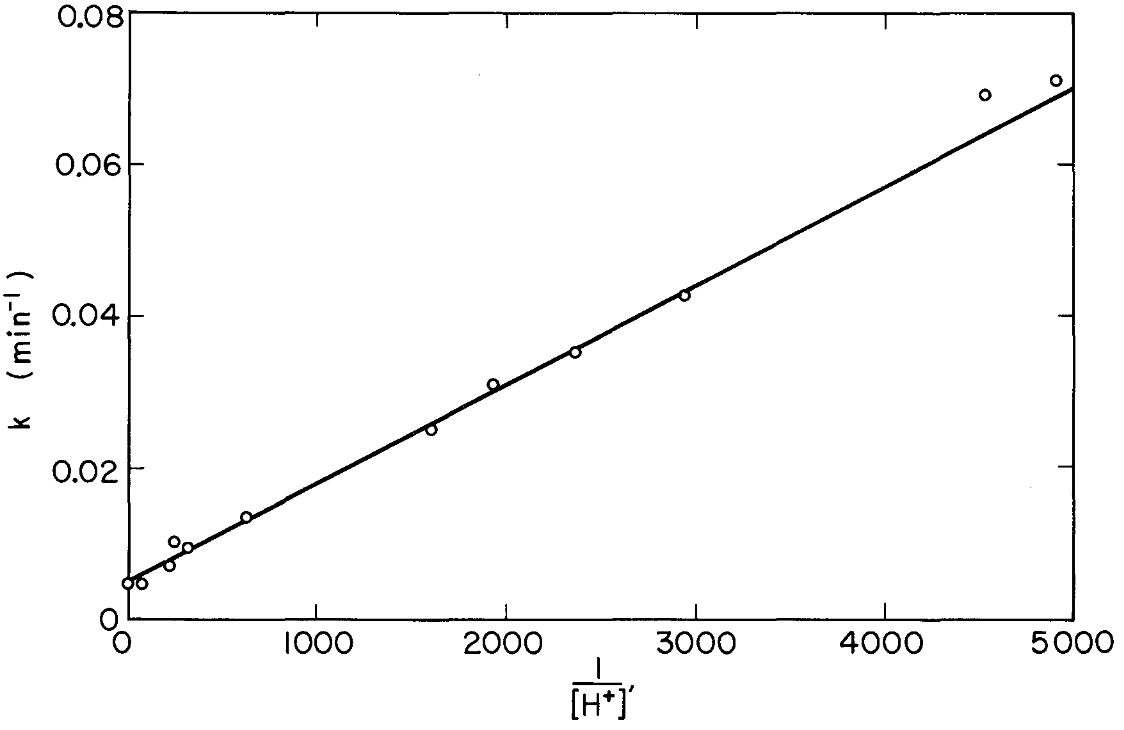

t (min)
0
100
200
300
400
1.0
0.8
0.6
0.4
0.2
0.1
$\frac{A}{A_0} - \frac{a_2}{a_1}$
Upper scale
pH = 1.01
Lower scale
pH = 3.69
0
10
20
30
40
t (min)
MU-30489

Fig. 1


0.08
0.06
0.04
0.02
0
k (min^{-1})
0
1000
2000
3000
4000
5000
$\frac{1}{[H^+]'}$

MU-30488

Fig. 2

TABLE I

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

pH	3.69	3.66	3.47	3.37	3.28	3.21	2.80	2.50	2.39	2.35	1.75	1.0
$k \times 10^3 (\text{min.}^{-1})$	70.80	69.20	42.80	35.40	31.10	25.40	13.50	9.45	10.40	7.22	4.72	4.7

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

$$k = 0.0050 + \frac{1.55 \times 10^{-5}}{[H^+]}, \qquad (4)$$

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 born 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.

The results of this investigation are compared with the existing data in Table II. TII

TABLE II

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

Investigator	Method	$k(\text{min.}^{-1})$	$k(\text{min.}^{-1})$ at 0.01 M
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}
Ibraz, Virgili and Costa[e]	Dropping mercury electrode	$0.00095 + \frac{7.6 \times 10^{-9}}{[H^+]^2}$	10.30×10^{-4}

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[a] Ref. 1.

[b] Ref. 2.

[c] Ref. 3.

[d] Ref. 4.

[e] Ref. 5.

[f] Referred to antilog (-pH) = 0.01; all other data referred to actual $[H^+]$.

It is apparent that our results are in substantial agreement with the data reported in refs. 1, 2, and 3. The disagreement shown by the entries for refs. 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 $CrCl^{++}$ as determined in this
10 Laboratory[10] 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 $CrCl^{++}$. This can be explained by assuming that the chromous ion formed at the electrode rapidly converts $CrCl_2^+$ to $CrCl^{++}$ according to the following fast reaction:

$$^{*}CrCl_2^{+} + Cr(II) \rightarrow {}^{*}Cr(II) + CrCl^{++} + Cl^{-} \qquad (5)$$

which has a rate constant[9] of roughly 10^4 $\underline{M}^{-1}$ min.$^{-1}$.

Mechanism.

Although the starting chromic salt used in these measurements has been shown to be predominately the trans isomer[8], our data cannot be said to refer only to the rate of aquation of this isomer. The absence of significant experimental deviation of the data from eq. 3 as shown in Fig. 1 does not rule out the possibility that part of the actual reaction path is conversion of the original trans isomer to the corresponding cis isomer and the aquation of the latter species. In view of the term 0.0050 min.$^{-1}$ in the rate eq. 4, this value may be taken as an upper limit for the aquation of the trans $CrCl_2^{++}$ species.

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.

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

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

$$H^+ + CrCl(H_2O)_4OH^+ \xrightleftharpoons{\text{rapid}} CrCl(H_2O)_5^{++}$$

This same type of mechanism is generally accepted in regard to many related
11 reactions.[11]

The rate constant for the aquation of $CrCl_2(H_2O)_3OH$ is 6.21 as compared with 0.0050 for the $CrCl_2(H_2O)_4^+$ species. This ratio of approximately 1240 is in agreement with that found in many analogous systems
12 and is subject to the same general interpretation.[12]

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Figure Captions

Figure 1. Experimental data analyzed by equation (3) at pH = 1.01 and 3.69.

Figure 2. The dependence of k on acidity at 25°C and $\mu = 0.5$ (NaCl added).