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The Kinetics and Mechanism of Hydrolysis of Tetrachloroaurate(III)[1,2]

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The rate of hydrolysis of tetrachloroaurate(III) in aqueous solution was investigated by a spectrophotometric method at a number of different chloride ion and hydrogen ion concentrations. When an excess of chloride ion is present and the hydrogen ion concentration is kept constant by the use of a phosphate buffer, the change of absorbance as the hydrolysis proceeds follows first-order kinetics. The first-order rate constants calculated from the absorbancy change are independent of the initial tetrachloroaurate concentration, the buffer concentration, and the ionic strength, but they vary with the chloride and hydrogen ion concentrations. At 26.0° the observed first-order rate constants fall in the range $3.0\text{–}1.2 \times 10^{-2}$ sec^{-1} when the chloride ion concentration is varied from 0.5 to 0.05 *M* and the hydrogen ion concentration is varied from 12.6 to 1.1×10^{-7} *M*. A plot of the observed first-order rate constant *vs.* the product of the hydrogen ion and chloride ion concentrations is linear at high concentrations. On the basis of the experimental data, several possible mechanisms for the reaction can be eliminated. The mechanism which best fits the data is a slow, reversible aquation of the tetrachloroaurate, followed by a fast ionization of the acid, trichloroaquoaurate(III). The results lead to a clarification of the role of hydrolysis in a previously published study of the chloride ion exchange of tetrachloroaurate.

Introduction

Turkevich, Stevenson, and Hillier[4] have studied in some detail the formation of colloidal gold upon treatment of tetrachloroaurate with a variety of reducing agents. One of the steps which may be involved in the formation of the colloid is the substitution of one or more of the chlorides in $AuCl_4^-$. A survey of the literature indicated that little work had been done on the substitution mechanism of $AuCl_4^-$ despite the fact that it is one of the few common square-planar complex ions. Hydrolytic reactions of square-planar Pt(II) halide complexes have been studied extensively and it would be of interest to determine whether the reactions of Au(III) halide complexes were similar.[5] Early experiments indicated that the hydrolysis of $AuCl_4^-$ could be followed easily by spectral changes, and thus a kinetic investigation of the hydrolysis was undertaken.

The stoichiometry of the hydrolysis of the tetrachloroaurate(III) anion was established by Britton and Dodd,[6] and Bjerrum[7] evaluated potentiometrically the equilibrium constants for the successive hydrolytic steps. Rich and Taube[8] studied the exchange of $AuCl_4^-$ with chloride ion in aqueous solution, and their work gives some information on the hydrolysis of $AuCl_4^-$. However, the data on the kinetics of hydrolysis are scanty and the equilibrium results obtained by the various groups are not in agreement.

The present paper describes a kinetic study of the hydrolysis of $AuCl_4^-$ in 0.5–0.05 *M* chloride ion and $12.6\text{–}1.1 \times 10^{-7}$ *M* acid and over the temperature range 14.5 to 34.5°. The results are discussed in terms of possible mechanisms for the reaction.

Experimental Section

Materials and Equipment.—Chloroauric acid, Baker Analyzed reagent grade, was the source of the tetrachloroaurate anion. Solutions of the gold compound were prepared and standardized with iodine and thiosulfate. The sodium perchlorate and perchloric acid were the best grade available from G. F. Smith. All other chemicals were reagent grade or better. Chloride ion was added as NaCl. The water used in making up the solutions was purified before use by ion exchange and was then triply distilled. A Cary Model 14 spectrophotometer with a cell holder thermostated to ±0.1° was used for absorbance measurements. A Radiometer Model PHM4C, standardized against two commercial buffers of pH 4 and 7, was used for the pH measurements.

Method for Determining Acid Concentration.—In the experiments at 26° the acid concentration was determined by the glass electrode. At neutral pH the salt error of the electrode (Radiometer Model G202C) is small.

In the experiments at 34.5 and 15.3°, the method for determining the acid concentration was the following. Solutions were prepared identical with those used in the kinetics experiments, with the exceptions that no gold salt was added, and the phosphate was added entirely as Na_2HPO_4. A 50-ml aliquot of this solution was then titrated with 2.032 *N* $HClO_4$. Throughout the titration, the pH of the solution was measured (using the same electrode as in the kinetics experiments) after each 0.1-ml addition of the acid. Since the amount of added acid was accurately known, as well as the total amount of phosphate initially present, it was possible to calculate the ratio of dihydrogen phosphate anion to monohydrogen phosphate anion at each point in the titration. Then, using the concentration equilibrium constant (concentration quotient, ${}^cK_2$) of phosphoric acid, corrected by Hentola's formula[9] for the ionic strength effect of the sodium chloride present, the hydrogen ion concentration of the solution was calculated. The ratio of $[H^+]$ to ${}^cK_2$ was then calculated. Making use of the data of Hentola[9] and Bates and Acree,[10] ${}^cK_2$ for the other temperatures was estimated. Since the ratio of acid to base forms of buffer must remain essentially constant at all temperatures, the ratio $([H^+]/{}^cK_2)$ must also remain constant. Any change in ${}^cK_2$ due to temperature is corrected by a change in $[H^+]$ in such a way as to keep the ratio

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[2] Part of the Ph.D. thesis submitted in 1964 by F. H. Fry to the Graduate School of Princeton University. Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Division of Inorganic Chemistry; Abstracts of papers, p 35-O.

[3] Sayre Fellow 1960–1961. Esso Education Foundation Fellow 1962–1963.

[4] (a) J. Turkevich, P. C. Stevenson, and J. Hillier, *Discussions Faraday Soc.*, **11**, 55 (1951); (b) J. Turkevich, P. C. Stevenson, and J. Hillier, *J. Phys. Chem.*, **57**, 670 (1953).

[5] D. Martin, Jr., and R. J. Adams in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 579.

[6] H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 2464 (1932).

[7] N. Bjerrum, *Bull. Soc. Chim. Belges*, **57**, 432 (1948).

[8] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

[9] Y. Hentola, *Kemian Keskusliiton Julkaisuja*, **13**, No. 2, 62 (1964); *Chem. Abstr.*, **44**, 5192*i* (1950).

[10] R. G. Bates and S. F. Acree, *J. Res. Natl. Bur. Std.*, **34**, 373 (1945).

constant. Consequently, the hydrogen ion concentration at a second temperature may be obtained by multiplication of the ratios ($[H^+]/{}^cK_2$) at $T = 26°$ by the value of ${}^cK_2$ at the second temperature.

Kinetic Method.—The hydrolysis reaction was followed spectrophotometrically. The spectrum of $AuCl_4^-$ has been recently reported[11,12] to have two intense absorption maxima, at 226 mμ (ε 25,600) and 315 mμ (ε 4800) in 1 *M* HCl. Beer's law holds for $AuCl_4^-$ solutions at 360 mμ (ε 669) over the concentration range studied. As $AuCl_4^-$ is hydrolyzed, a blue shift in the spectrum is observed. There is an isosbestic point at 295 mμ (ε 3.02×10^3) which holds to $[H^+][Cl^-] \sim 10^{-4}$. We assume that under conditions in which absorbance at the isosbestic point does not change, $AuCl_4^-$ and $AuCl_3OH^-$ are the only species present.

For the kinetic experiments, 1 ml of the thermostated tetrachloroaurate solution containing 0.5–0.05 *M* Cl^-, 5×10^{-3} *M* $AuCl_4^-$ (except where noted), and sufficient HCl to make the acid concentration 0.01 *M* was pipetted into the cuvette in the instrument. After the solution had come to temperature equilibrium, 30 μl of KH_2PO_4–K_2HPO_4 solution (approximately 2.5 *M* in phosphate and having the same chloride ion concentration as the thermostated solution) was added with rapid agitation to the gold solution in the cuvette. The time lapse between adding the buffer and starting the spectrophotometer was about 5 sec. No attempt was made to keep the ionic strength constant since preliminary experiments indicated that variations in the ionic strength did not affect the rate of the reaction. In every case the reaction was followed at 360 mμ and for over 10 half-lives (the half-times were of the order of 3 to 8 min). Observed first-order rate constants (k_{obsd}) were calculated from the data in the usual manner. The linearity to 80% completion was usually excellent, but some deviation from first-order dependence was observed at low chloride ion concentrations and high pH. Duplicate runs gave first-order rate constants which differed by less than 5%.

Results

Kinetic Effect of Buffer Concentration, Ionic Strength, and Total Gold Concentration.—Initial experiments demonstrated that the rate of the hydrolytic reaction varied with the H^+ and Cl^- concentrations. Also, it was found that the rate could be easily measured in phosphate buffers at pH 6–7. Before beginning a series of experiments to determine the effect of H^+ and Cl^- concentrations on the rate, the effects of the buffer concentration, ionic strength, and gold concentration were investigated.

At 23°, 0.1 *M* chloride ion, 5.6×10^{-7} *M* hydrogen ion, and initially 5×10^{-3} *M* $AuCl_4^-$, the observed first-order rate constant was found to be 1.55×10^{-2} sec^{-1} when the phosphate buffer concentration was 0.073 *M*, and 1.57×10^{-2} sec^{-1} when the buffer concentration was 0.037 *M*. These are within experimental error, and thus the buffer concentration has no apparent effect on the rate of the hydrolysis reaction. In Table I are shown some results of experiments in which the ionic strength was varied by adding sodium perchlorate. Any changes due to the increased ionic strength can be ascribed to changes in the observed hydrogen ion concentration. The results summarized in Table II indicate that the observed first-order rate constant does not depend on the initial $AuCl_4^-$ concentration.

TABLE I

KINETIC EFFECT OF IONIC STRENGTH[a]

$[Cl^-]$, *M*	$[ClO_4^-]$, *M*	$[H^+]$, $M \times 10^7$	$10^2 k_{obsd}$, sec^{-1}
0.3	0.0	7.3	2.32
0.3	0.2	8.0	2.32
0.3	0.0	3.4	2.00
0.3	0.2	4.2	2.03
0.2	0.0	5.8	2.05
0.2	0.3	10.5	2.07
0.2	0.0	2.8	1.77
0.2	0.3	4.3	1.75

[a] In all cases the initial $AuCl_4^-$ concentration was 5×10^{-3} *M*, the phosphate buffer concentration was 0.073 *M*, and the temperature was 26.0°.

TABLE II

KINETIC EFFECT OF THE INITIAL GOLD CONCENTRATION[a]

$[AuCl_4^-]_i = 5 \times 10^{-3}$ *M*		$[AuCl_4^-]_i = 3.5 \times 10^{-3}$ *M*	
$[H^+]$, $M \times 10^7$	$10^2 k_{obsd}$, sec^{-1}	$[H^+]$, $M \times 10^7$	$10^2 k_{obsd}$, sec^{-1}
9.1	2.27	6.9	2.17
5.8	2.05	4.4	2.00
2.8	1.77	2.3	1.77
1.7	1.70	1.3	1.55
1.2	1.58	0.89	1.52

[a] In all cases the Cl^- concentration was 0.2 *M*, the phosphate buffer concentration was 0.073 *M*, and the temperature was 26.0°.

Kinetic Effects of Hydrogen and Chloride Ion Concentrations.—The results from a series of experiments with different H^+ and Cl^- concentrations are given in Table III. Most of the rate constants were determined at 26.0°, but some of the results shown in Table III were obtained at other temperatures so that the energy of activation (E_a) and frequency factor (A) could be estimated. In general, the observed first-order rate constant increases when either the H^+ or Cl^- concentration is increased. The only previous observation of a rate constant for the hydrolysis of $AuCl_4^-$ was reported by Rich and Taube,[8] who obtained a value of 2.8×10^{-3} sec^{-1} at 0° in 6.6×10^{-4} *M* HCl.

Discussion

Several mechanisms can be envisaged for the hydrolysis of the first chloride ion of tetrachloroaurate(III). In general, these differ in their rate dependence on the H^+ and Cl^- concentrations. A large number of such mechanisms have been considered and many can be eliminated on the basis of the data given in Table III. It is clear from the data that the observed first-order rate constant increases as the H^+ and Cl^- concentrations increase. Thus, the hydrolysis does not proceed by a direct displacement of OH^- on $AuCl_4^-$; such a mechanism predicts that the observed rate constant should be inversely dependent on the H^+ concentration. Also, mechanisms involving a rapid initial reversible aquation of $AuCl_4^-$ ($AuCl_4^- + H_2O \rightleftarrows AuCl_3H_2O + Cl^-$) followed by some slow reactions of $AuCl_3H_2O$ are eliminated because the rate of such reactions would be inversely proportional to the Cl^- concentration. Further analysis of the data indicates that $HAuCl_4$ is not an intermediate in the hydrolysis. Any reasonable mechanism involving this intermediate predicts a greater dependence of the observed rate constant on the H^+ concentration than is obtained.

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[11] A. Chakravorty, *Naturwissenschaften*, **9**, 375 (1961).

[12] A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, **35**, 2206 (1961).

TABLE III

KINETIC EFFECTS OF CHLORIDE AND HYDROGEN ION CONCENTRATIONS[a]

$[Cl^-] = 0.5\ M$		$[Cl^-] = 0.3\ M$		$[Cl^-] = 0.2\ M$		$[Cl^-] = 0.07\ M$		$[Cl^-] = 0.05\ M$	
$[H^+]$, $M \times 10^7$	10^2k_{obsd}, sec^{-1}	$[H^+]$, $M \times 10^7$	10^2k_{obsd}, sec^{-1}	$[H^+]$, $M \times 10^7$	10^2k_{obsd}, sec^{-1}	$[H^+]$, $M \times 10^7$	10^2k_{obsd}, sec^{-1}	$[H^+]$, $M \times 10^7$	10^2k_{obsd}, sec^{-1}
12.6	3.05	11.0	2.48	9.1	2.27	8.3	1.83	8.1	1.67
8.0	2.68	7.3	2.32	5.8	2.05	4.9	1.68	6.2	1.28
3.7	2.22	3.4	2.00	2.8	1.77	2.3	1.60	2.3	1.38
2.6	1.88	2.2	1.78	1.7	1.70	1.5	1.50	1.6	1.33
1.7	1.77	1.7	1.73	1.2	1.58	1.1	1.43	1.1	1.28
		6.4	4.55[b]			4.5	3.30[b]	3.8	3.18[b]
		2.3	3.68[b]			2.2	3.00[b]	3.7	0.58[c]
		6.8	0.93[c]			4.3	0.63[c]		
		2.2	0.75[c]			2.2	0.63[c]		

[a] In all cases the initial gold concentration was $5 \times 10^{-3}\ M$, the phosphate buffer concentration was 0.073 M, and the temperature was 26.0° unless specified otherwise. [b] Temperature 34.5°. [c] Temperature 15.3°.

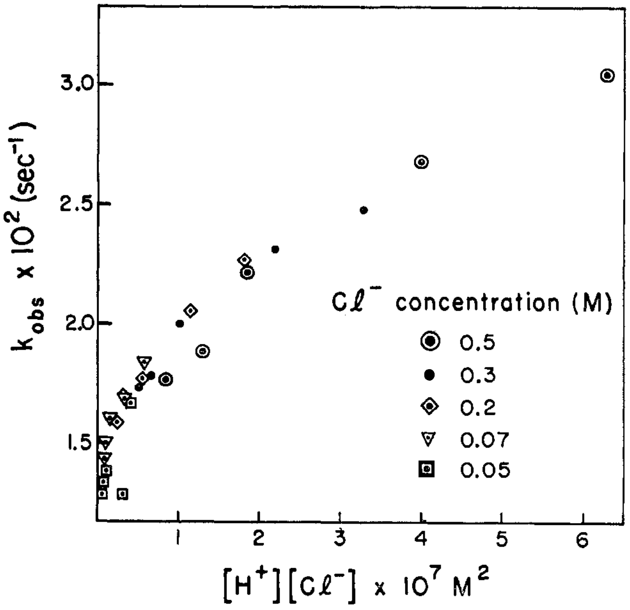

Figure 1.—The dependence of the observed first-order rate constant at 26° on the product of the H^+ and Cl^- concentrations.

The mechanisms which are most consistent with the data are ones which involve as the initial step a *slow* reversible aquation of $AuCl_4^-$. In the simplest such mechanism (1) the $AuCl_3H_2O$ is assumed to be in rapid equilibrium with its ionized form. If this is the correct

$$AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3H_2O + Cl^-$$

$$AuCl_3H_2O \overset{K}{\rightleftharpoons} AuCl_3OH^- + H^+ \tag{1}$$

mechanism for the reaction, then the observed first-order rate constant would be given by

$$k_{obsd} = k_1 + \frac{k_2[Cl^-]}{(1 + K/[H^+])} \tag{2}$$

This equation can be simplified to

$$k_{obsd} = k_1 + \frac{k_2}{K}[H^+][Cl^-] \tag{3}$$

because $K/[H^+]$ is probably much greater than 1 for all the experiments reported here. The acid ionization constant for the charged acid $PtCl_3H_2O^-$ is 10^{-7}.[13] Since $AuCl_3H_2O$ is neutral (and since Au has a greater nuclear charge than platinum), it would be expected to have a much greater acid ionization constant than the platinum compound. Consequently, if mechanism 1 is correct, a plot of k_{obsd} *vs.* the product of the H^+ and Cl^- concentrations should be linear. In Figure 1 the data obtained at 26° (see Table III) are plotted in this way. At high H^+ and Cl^- concentrations the points approximate a line, but at low concentrations k_{obsd} is less than expected if a straight-line relationship holds. The rate constants obtained at low concentrations of H^+ and Cl^- may be somewhat in error because poor first-order kinetics were obtained in some cases, and, in addition, some further reactions of $AuCl_3OH^-$ undoubtedly occur. At low concentrations of H^+ and Cl^- the isosbestic point (at 295 mμ) for the conversion of $AuCl_4^-$ to $AuCl_3H_2O$ did not remain constant but decreased as the hydrolysis proceeded.

Several simple variations on mechanism 1 (for example, the rate of the ionization step being comparable to the rate of the initial step, etc.) have been considered, but none of these predicts the observed curve exactly. However, the fact that k_{obsd} increases linearly with the product of the H^+ and Cl^- concentrations over most of the range studied strongly suggests that the initial steps in the mechanism are those given by mechanism 1. Thus, the slope of the straight-line portion of Figure 1 should be equal to k_2/K and the intercept should be k_1. In Table IV are listed estimates of these constants at a number of temperatures. The values are only approximate because it is difficult to determine where the line becomes straight. However, the intercept (k_1) is probably accurate to ±10%. At 26° the equilibrium constant for the first hydrolysis step (k_1K/k_2) as calculated from the results shown in Table IV is $4.4 \times 10^{-7}\ M^2$. Some values which have been reported for this equilibrium constant are: $1.2 \times 10^{-7}\ M^2$ at 20° (obtained by a potentiometric method[7]), $6.8 \times 10^{-7}\ M^2$ at 0° (obtained from exchange experiments[8]), and $1.2 \times 10^{-6}\ M^2$ at 24.5° (obtained by spectrophotometric measurements at equilibrium[14]). Considering the disparity in the re-

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(13) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955).

(14) F. H. Fry, Ph.D. Thesis, Department of Chemistry, Princeton University, 1964.

Table IV

Effect of Temperature on the Derived Constants

Temp, °C	k_1, $\sec^{-1} \times 10^2$ [a]	k_2/K, M^{-2} $\sec^{-1} \times 10^4$ [a]	$10^2k'$, $\sec^{-1}$ [b]
34.5	3.10	6.7	. . .
26.0	1.55	3.5	. . .
20.0	0.97[c]	. . .	0.60
15.3	0.60	2.0	. . .
10.0	0.40[d]	. . .	0.45

[a] This work. [b] From Rich and Taube.[8] [c] Interpolated. [d] Extrapolated.

ported values, the value obtained from the kinetics seems reasonable.

From the data shown in Table IV one can calculate that E_a for the k_1 step is 15 kcal/mole and the frequency factor, A, is 10^9 $\sec^{-1}$. For $PtCl_4^{2-}$ the rate constant for displacement of chloride ion by water is 3.8×10^{-5} $\sec^{-1}$ at 25°[13]; E_a is 21 kcal and A is 8×10^{10} $\sec^{-1}$. Therefore, the aquation of $AuCl_4^-$ is more rapid than that of the platinum compound because the energy of activation is lower. Possibly increased nuclear charge on the gold or decreased negative charge on the complex facilitates nucleophilic attack by the solvent.

Role of Hydrolysis in the Chloride Exchange of $AuCl_4^-$.—Rich and Taube[8] found that the rate of exchange (R) between chloride ion and $AuCl_4^-$ is given by an equation of the form

$$R = k'[AuCl_4^-] + k''[AuCl_4^-][Cl^-] \qquad (4)$$

The second term in eq 4 is due to a bimolecular reaction between Cl^- and $AuCl_4^-$ and the first term is due to exchange which occurs by some mechanism which does not involve Cl^- in the rate-determining step. Two general mechanisms can be envisaged which are consistent with the first term: (1) the reversible reaction of $AuCl_4^-$ with water to give Cl^- and $AuCl_3H_2O$ as an intermediate, and (2) same as (1) except that $AuCl_3H_2O$ exchanges rapidly with chloride ion before the reverse of the first step occurs to give back $AuCl_4^-$. If (1) were the reason for the first term in eq 4, then it can be shown that k' obtained by Rich and Taube should be the same as k_1 obtained in the present work. If (2) is the partial mechanism for exchange, it can be shown that k' should be equal to $4k_1$ (each time $AuCl_3$-H_2O is formed from $AuCl_4^-$, all four chlorides would exchange). The values of k' (obtained by Rich and Taube[8]) are listed in Table IV for comparison with k_1 obtained in this work. It can be seen that k' is approximately equal to k_1. Thus, presumably all the Cl^--independent exchange occurs by the reversible aquation of $AuCl_4^-$. The energy of activation for the k' step obtained by Rich and Taube[8] is quite different from that obtained here for k_1. However, inspection of their Figure 2 shows that an error of only a few per cent in one of their data points at 10° would have a large effect on the calculated activation energy. Thus, although a discrepancy exists between the two sets of data, it is not clear that it is significant. The value reported in the present work is probably more nearly the correct value.

It is interesting to compare these results with those obtained by Grantham, Elleman, and Martin[13] on the chloride exchange of $PtCl_4^{2-}$. They found that $PtCl_4^{2-}$ does not exchange its chloride by direct attack of chloride ion. The exchange apparently occurs by two mechanisms: (1) the reversible aquation of $PtCl_4^{2-}$ and (2) exchange of the intermediate $PtCl_3H_2O^-$ with chloride ion, the latter by a first-order chloride-independent process. The direct attack of the chloride ion is probably inhibited by the double negative charge on the platinum complex, but the mechanism is possible with the less charged gold complex. Both the platinum and gold complexes exchange by the reversible aquation reaction. The exchange of the trichloroaquo complex is only observed with the platinum complex probably because it can go to a neutral species by reacting with solvent and splitting out a chloride ion, but the gold intermediate is already neutral and would have to develop a positive charge if the same reaction occurred.