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THE UNCATALYZED EXCHANGE OF Cl^- AND $AuCl_4^-$

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The rate law for the reaction carrying exchange between $AuCl_4^-$ and Cl^- is $R = k_1(AuCl_4^-) + k_2(AuCl_4^-)(Cl^-)$. Neither k_1 nor k_2 depend on acidity, but a term depending on acidity enters when this is made sufficiently small. The values of E corresponding to the two paths are 4.5 and 16.5 kcal., respectively, and of pz are 10^3 min.$^{-1}$ and 2×10^{14} l. mole^{-1} min.$^{-1}$, respectively. The mechanism corresponding to the second term is of the S_N2 type. The mechanism corresponding to the first term may also be, but is not proven to be of the S_N2 type, nor is its relation to the rate of net hydrolysis settled.

Introduction

Kinetic studies on substitution reactions with complex ions have for the most part been conducted only for hexa-coördinated ions. Even in this field evidence contributing to a definite conclusion about mechanism has been presented only in a few cases. For square planar complex ions, which would seem to afford most interesting possibilities for composition and configuration of the activated complex, not only proofs of mechanism but even rate laws are lacking although there has been considerable speculation about mechanisms.

The kinetic data offered here for the reaction $AuCl_4^- + Cl^{*-} \rightarrow AuCl_4^{*-} + Cl^-$ make a beginning in this field. Some advantages of an exchange process in measuring the lability of a chemical system already have been discussed.[2] An additional feature of interest is that although the exchange may proceed by a path which involves ordinary chemical reactions (for example, exchange carried by a hydrolytic equilibrium), paths may exist which can be discovered only by the use of labeled atoms. The significance of these paths for the field of reaction kinetics and mechanisms is as great as that of the ordinary chemical paths.

Reagents.

Water.—It was found that ordinary distilled water, except in the precipitant solutions, induced some initial exchange. Therefore redistilled water was used in all but the earlier experiments.

$RbAuCl_4$.—The rubidium salt was used because of its fair solubility and its ease of recrystallization. Pure $HAuCl_4 \cdot 3H_2O$ and a 50% excess of C.P. RbCl were dissolved in hot water with subsequent cooling by ice. The resulting crystals of $RbAuCl_4$ were dissolved in hot water and the solution was filtered through a sintered glass filter while hot. After slow cooling and crystallization the excess solution was removed by suction and the $RbAuCl_4$ was dried at 110°. 4.244 g. of $RbAuCl_4$ and 2 ml. of 0.502 *f* HCl (to repress hydrolysis) were diluted to 100 ml. of stock solution 0.01004 *f* in HCl and presumably 0.1000 *f* in $RbAuCl_4$. By addition of excess KI to a portion of the stock and titration of the triiodide with thiosulfate the $RbAuCl_4$ was found to be 0.0992 *f*.

Other Salts and Acids.—Concentrated A.R. HCl, HNO_3, H_2SO_4 and $HClO_4$ were diluted to the desired volume and titrated with NaOH or Na_2CO_3. Solutions of NaCl, KNO_3 and $NaNO_3$ were similarly prepared from the purest salts with concentrations calculated from the weights taken.

Radioactive Chloride.—The Atomic Energy Commission at Oak Ridge supplied a sample of hydrochloric acid described as 1.2 ml. at 1.66 *f* concentration containing 10 microcuries of Cl^{36} (analysis showed the concentration of acid to be almost twice that stated.) This isotope emits 0.66 Mev. β-rays and has a half-life of about 10^5 years. The solution was diluted altogether about 1000-fold to give stock solutions. Experiments 1.13, 1.14 and 1.21 included 0.00122 *f* HCl from this source. Experiments 1.15, 1.22 and 1.23 similarly included 0.00106 *f* active HCl. Experiments 1.11 and 1.12 included 0.00070 *f* active HCl from an older source.

Precipitants.—Separation of chloroaurate and chloride at the end of exchange experiments was accomplished by precipitating the former as salt, $(C_6H_5)_4AsAuCl_4$. The precipitant used first, $((C_6H_5)_4As)_2SO_4$, was prepared by heating 100 g. of $(C_6H_5)_4AsCl$ with 40 ml. of concd. H_2SO_4 on the steam-bath until complete evolution of HCl and liquefaction, and by subsequent crystallizations with an addition of $BaCO_3$ to change bisulfate to sulfate. A later experiment (to determine whether coprecipitation of chloride was causing zero time exchange to appear larger than zero) showed

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[1] Atomic Energy Commission Predoctoral Fellow.

[2] H. Taube, *Chem. Revs.*, **50**, 76 (1952).

that even 0.5 f NaCl in the precipitant had a negligible effect on results. Thereafter $(C_6H_5)_4AsCl$ was used as the precipitant in about twice the concentration required by stoichiometry. Saturated C.P. $MgSO_4$ was usually used as a coagulant.

Experimental Procedure.

The Exchange Experiments.—Nearly all except the earlier experiments were carried out as follows. The reaction vessels were round-bottom 50-ml. flasks which had been partially divided, after heating the bottom of the bulb, by pushing in with the edge of a triangular file. On one side of the division was placed a total of 3 ml. of solutions containing the chloroaurate and acids or salts (HCl, NaCl, HNO_3 except where indicated otherwise) to adjust the chloride concentration, acidity and ionic strength. On the other side was placed 1 ml. of active HCl. The bulb of the (stoppered) flask was then immersed in ice and water or in water at 10 or 20°. After 15 minutes, found to be more than adequate for complete cooling, the vessel was shaken from side to side a few times to mix the solutions at time 0. At time t a mixture of 1 ml. of saturated $MgSO_4$ and 1 ml. of the precipitant was poured in, with immediate shaking to quench the reaction. This mixture was previously cooled for 10 minutes (to 0°) in a small glass tube whose surface had been exposed to the vapor of Dri-Film, coating the tube with a water repellent silicone layer that provided a reproducible pouring volume. The precipitated mixture was quickly filtered through porous porcelain crucibles and the filtrate was collected for counting of activity. The magnesium sulfate appeared to improve the filtering speed greatly, at least at 0°. Only one result, and that obtained by the slower centrifugation rather than filtration, indicated exchange between precipitate and solution.

The radioactivity of the filtrates was determined directly in a solution counter having a very thin glass wall between the solution and the counting chamber. The counting efficiency was about 5%. It was necessary neither to have quite complete filtration nor to dilute the filtrate since the counter tube required only 4.5 ml. of solution. Loss of counts due to coincidence was negligible with the counter used. Counting was long enough to give a standard deviation less than 1% of the count. After subtraction of background and the value found for "infinite" time the results were usually plotted *versus* time on semilog graph paper and half-times were determined graphically. Measurements of time were made with a stop watch, times 0 and t being taken, respectively, at the beginning of mixing and at the beginning of pouring of the precipitant.

The very insoluble $(C_6H_5)_4AsAuCl_4$ in the filtering crucibles was reduced to Au with $N_2H_5HSO_4$ and Na_2CO_3 and then removed with aqua regia. The reaction flasks were also treated first with a hydrazine solution but then with the usual dichromate cleaning solution. The counter tube was rinsed with water, methanol, ether and a current of air.

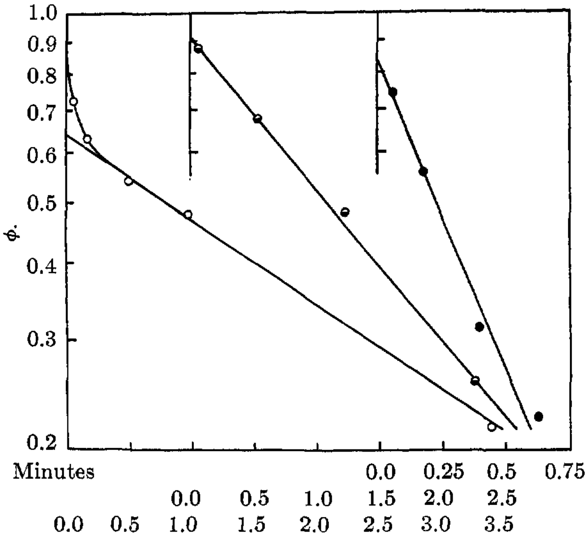

Fig. 1.—Three exchange experiments at the extremes of temperature and concentration: ○, conditions as in exp. 1.13 but with ordinary distilled water; ⊖, exp. 1.12; ●, exp. 1.23.

Kinetics of Hydrolysis.—Here the reaction vessels were ordinary 200-ml. round-bottom flasks. Into each of these was placed 2 ml. of a solution 0.0328 f in HCl and 0.0451 f in $RbAuCl_4$. The chloride included the active isotope which had several days to reach isotope equilibrium with the inactive chloride. Another flask, containing 100 ml. of 0.0884 f KNO_3, was cooled in ice-water at least 45 minutes, which was found sufficient to cool the contents to 0.0°. After similarly cooling the other flask the KNO_3 solution was quickly poured into it. After time t in the ice-bath a cold mixture of 25 ml. of sat. $MgSO_4$, 1 ml. of 0.3 N $((C_6H_5)_4As)_2SO_4$ and 10 ml. of water was poured into the flask to quench the reaction. A stopwatch was punched at the beginning of both pourings. The first several samples were filtered after half a minute through a large sintered glass filter. In the more hydrolyzed samples, however, a later clouding occurred which was found to increase the final count appreciably. The reported data are based on filtrations after six minutes, which gave filtrates remaining almost completely clear. Since no exchange with the precipitate was observed in exchange experiments we believe that these precipitates also remained unaltered after their formation. Five ml. of 0.1 f $AgNO_3$ was added to each filtrate. After coagulation and one washing of the AgCl it was dissolved in 5 ml. of 2 f NH_4OH and counted in solution. The proportionality between observed radioactivity and final free chloride concentration was used (as in equilibrium studies also) with the values calculated for no hydrolysis to determine the amount of hydrolysis.

Equilibrium of Hydrolysis.—The reaction volume for these experiments was 4 ml. as in the exchange studies. The temperature was 0.0°, exchange was complete, but the acidity was varied while keeping initial ionic strength at 0.088. The precipitant was added to the mixture after several hours or days. Complete precipitation of gold complexes in these experiments was shown by the absence of color or clouding in the final solution and by a negative stannous chloride test. ($AuCl_3OH_2$, for example, may be precipitated as $(C_6H_5)_4AsAuCl_3OH$). The first set of runs indicated that equilibrium was not quite established in 1.5 to three hours. A later series, in which equilibrium was established in half a day to two days, is reported among the results.

Equations

The general equations for isotope exchanges[3] can be written as follows for our case, assuming chemical equilibrium and the equivalence of the four chlorides in chloroaurate

$$\phi \equiv \frac{(\mathrm{Cl}^{*-})_t - (\mathrm{Cl}^{*-})_\infty}{(\mathrm{Cl}^{*-})_0 - (\mathrm{Cl}^{*-})_\infty} = e^{-k_{\mathrm{ex}}t} \qquad (1)$$

$$k_{\mathrm{ex}}t_{1/2} = \ln 2 \qquad (2)$$

$$R = \frac{(\mathrm{Cl}^-)(\mathrm{Cl_c})}{(\mathrm{Cl_c}) + (\mathrm{Cl}^-)}\, k_{\mathrm{ex}} \qquad (3)$$

where $(\mathrm{Cl}^{*-})_t$ is the concentration of active free chloride at time t, (Cl^-) is the total concentration of free chloride, $(\mathrm{Cl_c})$ is the concentration (equivalent) of the complexed chloride, k_{ex} is, under constant conditions, a constant defined in equation 1, $t_{1/2}$ is the half-time for the exchange and R is the chemical rate of exchange of chloride, active plus inactive, between the free and the complexed states. The results of some selected runs are shown in Fig. 1.

We find that the experimental values of R obtained in a fair range of conditions can be correlated by the equation

$$R = k_1'\,(\mathrm{Cl_c}) + k_2'\,(\mathrm{Cl_c})(\mathrm{Cl}^-) \qquad (4)$$

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[3] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 285-288.

TABLE I

RATE OF $AuCl_4^-$–Cl^- EXCHANGE AS A FUNCTION OF CONCENTRATIONS AND TEMPERATURE

	Formal concentrations								
No.	Cl^-	$AuCl_4^-$	H^+	Misc.	μ	T, °C.	$t_{1/2}$ obs., min.	$t_{1/2}$, calc.	$\frac{(Cl^-)k_{ex}}{(Cl_c)+(Cl^-)}$
1.11	0.0760	0.0124	0.076		0.088	0.0	1.64 ± 0.02		0.256
1.12	.0760	.0124	.076	0.160 KNO_3	.248	.0	1.25 ± .01		.335
1.13	.00351	.00310	.083		.088	.0	2.64 ± .05		.0576
1.14	.0167	.00620	.067		.088	.0	2.89 ± .03		.0969
1.15	.0162	.00310	.070		.088	.0	4.17 ± .04	4.15	
1.21	.0470	.0119	.032		.088	10.0	0.77 ± .01		.448
1.22	.00813	.00372	.077		.088	10.0	1.85 ± .04		.132
1.23	.0469	.0119	.032		.088	20.0	0.30 ± .01	0.31	
1.31	.021,[a] 0.028[b]	.0050	1.4	1.4 H_2SO_4	1.5	0.0	0.7 ± .2	3.3	
1.32	.035,[a] 0.036[b]	.0083	0.05	0.04 H_2SO_4	0.1	.0	2.15 ± .1	2.45	
1.33	.035	.0083	0.0018		0.043	.0	2.07 ± .02	2.45	
		Study of rate of hydrolysis							
1.4	0.000660[c]	0.000884	0.00066	0.0866 KNO_3	0.088	.0			
	0.001013[d]						1.6 ± .1		

[a] Calculation. [b] Observation. [c] At $t = 0$. [d] At $t = 30$.

Combining 3 and 4 we have

$$\frac{(Cl^-)k_{ex}}{(Cl_c) + (Cl^-)} = k_1' + k_2'(Cl^-) \qquad (5)$$

The rate law was tested in this form (Fig. 2). We can rewrite 4 as

$$R = k_1(AuCl_4^-) + k_2(AuCl_4^-)(Cl^-) \qquad (6)$$

where $k_1 = 4k_1'$ and $k_2 = 4k_2'$ since (Cl_c) is four times $(AuCl_4^-)$.

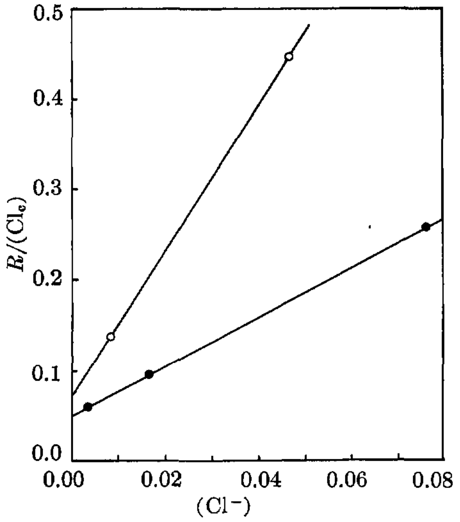

Fig. 2.—Evaluation of k_1 and k_2: ●, 0°; ○, 10°. Recalculation raises very slightly the intermediate point for 0°.

Results

Dependence on Chloride, Chloroaurate and Acid.—Table I summarizes the data on the kinetics of exchange between Cl^- and $AuCl_4^-$. In the concentration range studied a negligible amount of $AuCl_4^-$ is hydrolyzed. This was shown by the agreement of the activity found as free chloride at infinite time (over 30 minutes) with that calculated assuming the precipitate to be $(C_6H_5)_4AsAuCl_4$. The plot in Fig. 2 of the quantity in the last column of Table I permits evaluation of the parameters k_1 and k_2 of equation 6 at 0 and 10°. Experiment 1.15 (*cf.* $t_{1/2}$ calcd. and $t_{1/2}$ obs.), was performed to test the dependence of rate on $(AuCl_4^-)$ with this as the only variable. The rate law of equation 7 in unambiguously established by the data for the concentration range investigated.

Experiments 1.31, 1.32 and 1.33 were designed to determine the influence of acidity on rate. Only experiment 1.33 allows a definite conclusion to be drawn. The half-time observed is slightly shorter than that calculated using the values of k_1 and k_2 appropriate to 0° and somewhat higher ionic strength. It must be concluded therefore that at sufficiently low (H^+) a path inverse in (H^+) does contribute. However the increase in rate produced by lowering (H^+) 37-fold below the lowest concentration used to evaluate k_1 and k_2 at 0° is so slight that k_1 and k_2 are demonstrated to describe paths which are independent of (H^+).

The Effect of Oxy-anions.—The agreement in $t_{1/2}$ between experiments 1.32 and 1.33 must be construed as due to fortuitous cancellation of opposing effects, produced by variation in (H^+), μ and $(SO_4^=)$. Sulfate ion was observed to affect the stoichiometry. In experiment 1.31 the radioactivity in the free chloride after complete exchange corresponded to 0.028 M (Cl^-) rather than the 0.021 M (Cl^-) contributed by the original reagents. This suggests that Au(III) was precipitated partly as a sulfato complex, leaving additional free chloride to be counted. Participation of an equilibrium such as, $AuCl_4^- + SO_4^= \rightleftarrows AuCl_2SO_4^- + 2Cl^-$ would increase the exchange rate and may contribute to the results in experiments 1.31 and 1.32. The contribution by this path may be similar in 1.31 and 1.32 since $(SO_4^=)$ must be nearly the same in both; the greater rate in 1.31 may be due mainly to the change in μ. Another, but slower, equilibrium could contribute to the greatly altered stoichiometry in 1.31. The considerable kinetic irreproducibility observed in the presence of sulfuric acid is probably due to an accidental impurity in the acid.

Other early experiments showed that, within the error introduced by the precipitation of much $(C_6H_5)_4AsClO_4$, HNO_3 and $HClO_4$ are equivalent in the exchange studies.

Ionic Strength.—The term $k_2(\mathrm{AuCl_4^-})(\mathrm{Cl^-})$ in the rate law shows that two anions are combined in the corresponding activated complex. We then expect k_2 to vary with the ionic strength. The limiting law[4] describing this variation is

$$\log k_{2\mathrm{b}} - \log k_{2\mathrm{a}} = 2(0.49)Z_{\mathrm{Cl}} - Z_{\mathrm{AuCl4}} - (\sqrt{\mu_{\mathrm{b}}} - \sqrt{\mu_{\mathrm{a}}})$$

Experiments 1.11 (= a) and 1.12 (= b) in Table I show the effect of raising the ionic strength at a chloride concentration such that the k_2 path contributes 80% of the total rate at the lower μ. Assuming k_1 to be unchanged we calculate that k_2 has increased from 10.9 to 15.0. The left side of the equation is then found to be 0.14 while the right side is calculated to be 0.20, showing that the variation with ionic strength is consistent with the ionic type of the k_2 path of equation 6.

The Influence of Light and Impurities.—The observation that the rate of exchange in the system $\mathrm{PtCl_6^=}$–$\mathrm{Cl^-}$ is greatly increased even by diffuse daylight led us to test the effect of diffuse daylight on the $\mathrm{AuCl_4^-}$–$\mathrm{Cl^-}$ exchange. No effect was observed. A rapid initial exchange was noted especially at low $(\mathrm{Cl^-})$ (Fig. 1), when ordinary distilled water was used in the solutions. After the initial induced reaction the specific rate was reproducible and consistent with the rate law reported. This and other examples of catalysis and induced exchange are described in the following paper.

Variation with Temperature.—Table II summarizes the relevant data. The values recorded for 20° were obtained by graphical extrapolation since the exchange was too irreproducible at low $(\mathrm{Cl^-})$ to get good separation of the constants. These extrapolated values lead to a good calculated half-time for experiment 1.23 in which the k_1 path should account for 8% of the rate. The activation energy and pz factor for each path were calculated using the equation

$$\log k = \log pz - \frac{0.4343E}{RT}$$

TABLE II

A SUMMARY OF CONSTANTS

T, °C.	k_1, min.$^{-1}$	k_2, l. mole min.$^{-1}$	k_h, min.$^{-1}$
0.0	0.200	11.0	0.17
10.0	0.27$_0$	32.4	
extrap. 20.0	0.36	88	
E, kcal.	4.5	16.5	
log pz	2.9	14.3	

Rate of Hydrolysis.—The term $k_1(\mathrm{AuCl_4^-})$ in the rate law suggests an exchange mechanism involving loss of chloride from the complex as the first step. Such a dissociation of chloroaurate might involve hydrolysis. The last two rows of Table I describe the initial and final (after 30 minutes) conditions in a direct study of the reaction by observing the increase of $(\mathrm{Cl^-})$ with time. A graph of $\log((\mathrm{Cl^-})_\infty - (\mathrm{Cl^-})_t)$ *versus* t was found not to be quite straight, due to the reverse reaction, although the forward reaction is presumably first order and characterizable by a half-time. Experimental errors were fairly great. The initial rate was used to calculate k_h (= 0.17 min.$^{-1}$) in Table II, assuming this rate to be equal to $k_\mathrm{h}(\mathrm{AuCl_4^-})$ minus rate of reversal.

Equilibrium of Hydrolysis.—Three kinds of experiments yielded information on the hydrolytic equilibrium: (1) infinite time results from exchange studies, (2) final results from the study of rate of hydrolysis and (3) the separate investigation of the equilibrium. The data show that the behavior of the system is complex, and further study is necessary. The post-precipitation observed in experiment 1.4 suggests the formation of polynuclear complexes. The variation of hydrolysis with acidity shows that aquo complexes cannot be the only important hydrolyzed forms. Bjerrum's use of hydroxy complexes[5] to explain the data is also inadequate, as are some hypotheses employing binuclear complexes, alone or with mononuclear forms. It may be noted that Bjerrum determined $(\mathrm{H^+})$ by electrode potentials, that ionic strength was not constant and that small differences of large numbers were used.

Mercury and Thallium Complexes.—Some preliminary experiments had been performed to determine whether chloro-complexes of mercury, thallium, or gold had measurably slow exchange rates. The temperature was about 25°. After separation the radio-activity of the aqueous solutions was determined. Table IV shows the results. The exchanges may have been complete also in the first two experiments, in spite of the lower values of the apparent % exchange recorded. The high concentrations in the first solution, necessary to prevent dissociation of the complex, produced an extremely bulky precipitate and a very messy separation. The extraction of mercuric chloride from the second solution by phenylacetonitrile was known to be incomplete. From the known chemistry of these elements it seemed that gold offered the greatest possibilities for further investigation. About the mercury and thallium complexes we can say only that exchange is fast, but not necessarily immeasurably fast.

Discussion

The rate law for the k_2 path proves the presence of $\mathrm{Cl^-}$ and of $\mathrm{AuCl_4^-}$ in the activated complex, and shows the mechanism of replacement of $\mathrm{Cl^-}$ by $\mathrm{Cl^-}$ by this path to be of the $\mathrm{S_N2}$ type. This type of mechanism for a square planar complex ion, which has open coördination positions as well as a fairly stable vacant orbital (p), may prove to be fairly general for these ions. Such a path has in no case been proven for hexa-coördinated complex ions of the electronic structure type of Co(III), nor in fact has any simple net replacement of one anion for another been observed in these cases.

It will be recalled from the results that the pz factor for the k_2 path is normal. An entropy decrease would be expected for association of charges of the same sign in a dielectric medium. However, if in the activated complex the entering $\mathrm{Cl^-}$ and that being replaced are on opposite sides of the molecule $\mathrm{AuCl_5^=}$, such an effect would be quite

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[4] The value of the constant at 0° from H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solution," Reinhold Publ. Corp., N. Y., 1943, p. 119.

[5] N. Bjerrum, *Bull. soc. chim. Belg.*, **57**, 432 (1948).

TABLE III[a]

HYDROLYSIS OF $AuCl_4^-$

No.	Formal concentrations Initial (Cl^-)	Final (Cl^-)	Final ($AuCl_4^-$)	(Au_{hyd})[b]	Initial (H^+)	t	K[c]
1.13	0.00351	0.00353	0.00308	0.00002	0.083	30 min.	
1.4	.000660	.001013	.000531	.000353	.000660	30 min.	6.8×10^{-7}
3.1	.001845	.00246	.005585	.000615	.0833	1.6 days	2.3×10^{-5}
3.2	.001845	.00308	.00496	.00124	.0222	1.7 days	1.8×10^{-5}
3.3	.001845	.00358	.00447	.00173	.00694	1.8 days	1.2×10^{-5}
3.4	.001845	.00365	.00440	.00180	.00185	1.5 days	0.5×10^{-5}

[a] Ionic strength kept very nearly equal to 0.088. [b] (Au_{hyd}) = final (Cl^-) minus initial (Cl^-). [c] Assuming $K = (H^+)(Cl^-)(AuCl_3OH^-)/(AuCl_4^-)$ represents the only important equilibrium.

TABLE IV

EXPLORATORY EXPERIMENTS

Formal concentrations Cl^-	 Complex	 Misc.	t, min.	Separation	Apparent % exchange[a]
1.0 NaCl	0.3 Na_2HgCl_4		1	Ppt. $((C_6H_5)_4As)_2HgCl_4$	90
0.0002 HCl	.001 $HgCl_2$	0.05 Na_2SO_4	1	Ext. $HgCl_2$ by $C_6H_5CH_2CN$	70
.05 HCl	.025 $HTlCl_4$	.025 HNO_3	1	Ppt. $(C_6H_5)_4AsTlCl_4$	100
.004 HCl	.03 $RbAuCl_4$		30	Ppt. $(C_6H_5)_4AsAuCl_4$	100
.004 HCl	.03 $RbAuCl_4$	1.4 H_2SO_4	4	Ppt. $(C_6H_5)_4AsAuCl_4$	100

[a] % ex. $\equiv 100(1 - \phi)$.

small. In view of the p-orbital available in the ion $AuCl_4^-$, it seems likely that the configuration of the activated complex approaches that of a trigonal bipyramid, the entering group and that being replaced occupying the apical positions.

No definite conclusion can be drawn about the mechanism by the k_1 path. The very low value of the pz factor suggests hydrolysis by an SN2 path as the rate determining act (in many systems SN2 solvolyses have been observed to occur with pz factors *ca.* 10^4 lower than corresponding reactions by SN1 mechanisms[6]). Mere analogy, however, does not explain the phenomenon, does not bridge the large defect of pz from the normal values, nor explain the low activation energy observed. It is tempting to try to relate the special features of the k_1 path to the circumstance that two vacant coordination positions are open, and that two solvent molecules can be directly bound in the activated complex. To explain the large entropy decrease on activation, (*ca.* −50 e.u.) a large entropy decrease must be imposed on the solvent water, in addition to the decrease involved in the transfer of two water molecules from the solution to coordination positions about Au(III).

An important feature of the k_1 path is its relation to the net hydrolysis of $AuCl_4^-$. An SN2 mechanism for the exchange yielding hydrolyzed product would suggest that the rate of net hydrolysis and the exchange rate are directly related. It is difficult to study the rate of net hydrolysis under the conditions of the exchange experiments, because these conditions were purposely chosen to minimize hydrolysis. If the first-order specific rate of exchange corresponding to the conditions of the single experiment on rate of hydrolysis is computed, making use of the dependence on OH^- indicated by experiment 1.33 and estimating the correction for ionic strength, a value of 0.76 is calculated. The results are inaccurate enough so that the relation is consistent with the interpretation that the rate of exchange is just four times the rate of hydrolysis (this is the ratio expected if each $AuCl_3OH^-$ exchanges completely before returning to $AuCl_4^-$). However, an SN1 mechanism could lead to an accidental ratio of 4. Further work is in progress to define better the relation between the two processes.

REMARKS

W. K. WILMARTH (University of Southern California) raised the question of whether a difference in rate of exchange is observed corresponding to the change in the principal hydrolyzed form from $AuCl_3OH^-$ to $AuCl_3H_2O$. In response, we can only say that the rate of exchange is very little sensitive to acidity over the range 0.002 to 0.076 *M*. There are no data outside of our work on net hydrolysis indicating that $AuCl_3H_2O$ is a weak acid, and the assumption is usually made that it is strong. Further work on the hydrolysis, and on the relation of rates of hydrolysis and exchange may lead to a more satisfactory answer.

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[6] B. K. Morse and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 416 (1952).