TABLE V

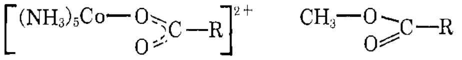
RATES OF UNCATALYZED ACID HYDROLYSIS

Complex	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu	Ref
$Co(NH_3)_5O_2C_2ClH_2$	26.3	−1.6	*a*
$Co(NH_3)_5O_2C_2Cl_2H$	26.4	−3.5	*a*
$Co(NH_3)_5O_2C_2Cl_3$	25.7	−3.0	*a*
$Co(NH_3)_5O_2C_2CF_3$	26	−2	*b*

[a] K. Kuroda, *Nippon Kagaku Zasshi*, **82,** 572 (1961). [b] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24,** 1241 (1962).

ing have lower activation enthalpies for the trifluoroacetato than for the dichloroacetato complex. Therefore, the $\Delta H^{\ddagger}$ for aquation of the latter complex should be higher whichever mechanism is operative. The conclusion is that the acid hydrolysis of these complexes is probably proceeding with both bond making and breaking in the transition state. The exact degree is still open to speculation.[6,7]

It would be interesting to determine the effect of the metal atom on reactivity by comparing the hydrolysis behavior of the inorganic complexes and the organic esters. Because of the differences in mechanism between the two systems, a quantitative comparison is not possible. However, the differences in mechanism do indicate the effect of the metal atom. The O–C bond breaking by a path first order in hydroxide ion occurs very little, if at all, in the inorganic complex, possibly owing to the increased double-bond character of this bond in the complex as compared to the organic ester.


$\left[(NH_3)_5Co{-}O{-}C(=O){-}R\right]^{2+}$ $CH_3{-}O{-}C(=O){-}R$

For the trifluoroacetato complex this effect would be greatest and therefore O–C bond breaking would be less favorable. However, there is the competing inductive effect making it easier for an OH^- to attack the acyl carbon. These two effects can be used to rationalize the rate parameters found for the carboxylatopentaamminecobalt(III) complexes.

Acknowledgment.—The authors wish to acknowledge the financial support of the National Research Council of Canada under Contract No. NRCA-2850.

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(6) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

(7) M. L. Tobe, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 79 (1966).

CONTRIBUTION FROM THE NATIONAL CHEMICAL RESEARCH
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Kinetics and Mechanisms of Reactions of Gold(III) Complexes. I. The Equilibrium Hydrolysis of Tetrachlorogold(III) in Acid Medium

BY WILLIAM ROBB

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The tetrachlorogold(III) anion reacts with water and establishes itself in equilibrium with other chlorogold(III) species as

$$AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3(H_2O) + Cl^-$$

$$AuCl_3(H_2O) \overset{K_a}{\rightleftharpoons} AuCl_3(OH)^- + H^+$$

$$AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AuCl_2(H_2O)(OH) + Cl^-$$

At 25° values of $k_1 = 2.2 \times 10^{-2}$ sec^{-1}, $k_2/K_a = 9.3 \times 10^3\ M^{-2}$ sec^{-1}, $k_3 = 3.3 \times 10^{-4}$ sec^{-1}, and $k_4 = 8.3 \times 10^{-2}\ M^{-1}$ sec^{-1} were obtained. The activation parameters were found to be: $\Delta H_1^{\ddagger} = 15.5$, $\Delta H_2^{\ddagger} = 9.1$, $\Delta H_3^{\ddagger} = 26.9$, and $\Delta H_4^{\ddagger} = 15.4$ kcal/mole; $\Delta S_1^{\ddagger} = -15.5$, $\Delta S_2^{\ddagger} = -25$, $\Delta S_3^{\ddagger} = 14$, and $\Delta S_4^{\ddagger} = -13$ eu. The value for K_a is $\sim 10^{-3}\ M$.

Introduction

A perusal of the literature reveals that no more than four studies on the rates and mechanism of reactions in the gold(III) system have been reported. These are the now well-known chloride ligand exchange reactions of tetrachlorogold(III) by Rich and Taube,[1] the polarographic study of Beran and Vlček[2] on the formation of the ethylenediaminedichlorogold(III) complex from $AuCl_4^-$ in acid medium, the studies in the diethylenetriaminehalogold(III) system by Baddley and Basolo,[3] and, finally, the recent report on the hydrolysis of $AuCl_4^-$ by Kazakov.[4]

Gold(III) and platinum(II) are isoelectronic, they both form square-planar complexes, and they behave similarly[5] from a mechanistic viewpoint, but they have very dissimilar rates. Thus $[Au(dien)Cl]^{2+}$ reacts

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

(2) P. Beran and A. A. Vlček, *Collection Czech. Chem. Commun.*, **24**, 3572 (1959).

(3) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

(4) V. P. Kazakov, *Zh. Neorgan. Khim.*, **10**, 1276 (1965).

(5) F. Basolo, Symposium on Mechanisms of Inorganic Reactions, Lawrence, Kansas, June 1964.

some 10^4 times faster than the analogous Pt(II) complex with bromide ion.[6] This dissimilarity in rates is once again highlighted by the present study on the hydrolysis of $AuCl_4^-$ in which there is ample scope for comparison with the very thorough study of Martin, *et al.*,[7] on the $PtCl_4^{2-}$ system.

The reactions of the $AuCl_4^-$ anion in aqueous medium can be quite complex, leading to the formation of no less and perhaps more than five species. It was imperative that the reactions from which these species originate be characterized since $AuCl_4^-$ would commonly be used as the starting material for complex formation.

Experimental Section

A. **Materials.**—The gold, in the form $HAuCl_4 \cdot H_2O$ (Merck), was standardized against "fine gold" obtained from the Spectrographic Division of the National Physical Research Laboratory, Pretoria. All other chemicals were of AR grade, except the sodium perchlorate, which was laboratory reagent grade.

B. **Kinetic Experiments.**—A 10^{-3} M solution of $AuCl_4^-$ was made up in 0.800 M sodium perchlorate medium and allowed to reach equilibrium over a period of several hours in a thermostated water bath. A measured aliquot was then transferred to a cell housed in a constant-temperature cell holder fitted to a Cary 15 recording spectrophotometer. Working at a constant wavelength of 310 mμ, the equilibrium in the solution was disturbed by injecting a measured amount of a chloride-containing solution of ionic strength 0.80. A trace of the change in the optical density with time was displayed on the chart. Hydrogen ion concentrations were measured with a Metrohm Model E300 pH meter.

C. **Tracer Work.**—A 10^{-5} M solution of $HAuCl_4$ was labeled with gold-198 and allowed to equilibrate. The solution was quantitatively transferred to a Dowex 50-X8 cation-exchange resin in the hydrogen form. A small fraction of the total activity (0.1%) was strongly absorbed on the column and could be removed only by elution with a 1 M HCl solution.

Results

A. The Hydrolysis of $AuCl_4^-$.—That $AuCl_4^-$ does undergo reversible hydrolysis was demonstrated by making up five solutions, each having the same initial concentration of $AuCl_4^-$ but containing 0.000, 0.040, 0.050, 0.100, and 0.200 M initial Cl^-. The ionic strengths were all adjusted with $NaClO_4$ to a value of 0.80. The absorption λ_{max} moved toward 312 mμ and the peak height increased as the initial chloride ion concentration increased, suggesting that the reaction

$$AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3(H_2O) + Cl^- \qquad (1)$$

takes place. The pH values of these solutions also increased with increasing initial chloride ion concentration, indicating that $AuCl_3(H_2O)$ dissociated as

$$AuCl_3(H_2O) \overset{K_a}{\rightleftharpoons} AuCl_3(OH)^- + H^+ \qquad (2)$$

The equilibrium expression for reaction 1, *viz.*

$$K = \frac{k_1}{k_2} = \frac{[AuCl_3(H_2O)][Cl^-]}{[AuCl_4^-]} = \frac{[AuCl_3(OH)^-][H^+][Cl^-]}{K_a[AuCl_4^-]} \qquad (3)$$

was used as the basis for measuring k_1 and k_2/K_a.

By simply diluting an equilibrium mixture by, say, a factor of 2, it is clear that in order to satisfy eq 3 "relaxation" occurs; *i.e.*, $AuCl_4^-$ hydrolyzes into $AuCl_3(H_2O)$ and Cl^- to reestablish the equilibrium. The rate of change in the concentration of $AuCl_4^-$ with time can be expressed as

$$\frac{-d[AuCl_4^-]}{dt} = k_1[AuCl_4^-] - \frac{k_2}{K_a}[AuCl_3(OH)^-][H^+][Cl^-] \qquad (4)$$

By using a high initial Cl^- concentration when disturbing the equilibrium and employing the noninterfering[8] acetic acid–sodium acetate buffer to keep $[H^+]$ constant, eq 4 reduces to the pseudo-first-order form

$$\frac{-d[AuCl_4^-]}{dt} = k_1[AuCl_4^-] - k_2'[AuCl_3(OH)^-] \qquad (5)$$

where

$$k_2' = \frac{k_2}{K_a}[H^+][Cl^-] \qquad (6)$$

Equation 5 can be treated as a simple first-order–first-order equilibration[9] and can be integrated as such. The fact that the reaction goes from one equilibrium position to the next does not alter the final integrated expression

$$\ln \frac{(A_0 - A_\infty)}{(A_t - A_\infty)} = (k_1 + k_2')t \qquad (7)$$

where A refers to concentration of $AuCl_4^-$ at times zero, t, and infinity. Equation 7 can be written as[10]

$$R_{obsd} = 0.693/t_{1/2} = k_1 + k_2' = k_1 + k_2''[Cl^-] \qquad (8)$$

where

$$k_2'' = k_2[H^+]/K_a$$

A plot of R_{obsd} *vs.* $[Cl^-]$ yielded a straight line of intercept k_1 and slope k_2''. Hence, knowing what $[H^+]$ is, it is then possible to estimate the value of k_2/K_a.

Table I gives the results of all of these experiments as well as the experimental conditions that applied. Table II shows the hydrogen ion concentration dependence of the slope of the R_{obsd} *vs.* $[Cl^-]$ plot. A temperature-dependence study yielded $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the rate constants k_1 and k_2/K_a. These results are summarized in Table III.

B. The Hydrolysis of Trichlorohydroxygold(III) Anion.—It can be seen from Figure 1 that the plot of $\ln (A_t - A_\infty)$ *vs.* t showed an initial nonlinear portion and then finally gave a straight line. The curve was resolved into its straight-line components by merely extrapolating the straight line to time zero and subtracting from the initial curved plot. The faster reaction represents the equilibration hydrolysis of $AuCl_4^-$, and the much slower reaction is ascribed to

$$AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AuCl_2(H_2O)(OH) + Cl^- \qquad (9)$$

Once again, the same integrated rate expressions hold, since the $t_{1/2}$ for this reaction is $>10t_{1/2}$ for the initial equilibrations. The results are summarized in Table IV

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[6] H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

[7] L. F. Granthan, T. S. Elleman, and D. S. Martin, Jr., *ibid.*, **77**, 2965 (1955).

[8] This buffer did not affect the ultraviolet spectrum of the $AuCl_4^-$ ion in solution.

[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 172.

[10] W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).

TABLE I

RATE DATA FOR THE EQUILIBRIUM REACTION

$$\mathrm{AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3(H_2O) + Cl^-}$$

$[\mathrm{Cl^-}]$, M	Temp, °C	pH	$10^2 R_{\mathrm{obsd}}$, sec^{-1}
0.060	20.5	3.80	9.2
0.050	20.5	3.80	7.7
0.040	20.5	3.80	6.6
0.033	20.5	3.80	5.4
0.025	20.5	3.80	4.6
0.020	20.5	3.80	4.2
0.067	25.0	3.80	12.2
0.050	25.0	3.80	9.6
0.040	25.0	3.80	8.3
0.033	25.0	3.80	6.8
0.025	25.0	3.80	5.8
0.020	25.0	3.80	5.3
0.067	30.4	3.80	16.5
0.050	30.4	3.80	12.9
0.040	30.4	3.80	11.0
0.033	30.4	3.80	9.9
0.025	30.4	3.80	8.6
0.020	30.4	3.80	7.5
0.100	25.0	4.15[a]	6.8
0.080	25.0	4.15[a]	5.8
0.025	25.0	4.15[a]	3.2
0.050	25.0	4.15[a]	4.3
0.050	25.0	4.10[a]	5.0
0.050	25.0	3.90[a]	7.2
0.050	25.0	3.75[a]	12.7

[a] pH values are those of initial solutions before reaction and are unbuffered.

TABLE II

VARIATION OF SLOPE OF R_{obsd} *vs.* $[\mathrm{Cl^-}]$ PLOT WITH HYDROGEN ION CONCENTRATION FOR THE REACTION

$$\begin{tikzcd} \mathrm{AuCl_4^- + H_2O} \arrow[r, shift left, "k_1"] & \mathrm{AuCl_3(H_2O) + Cl^-} \arrow[l, shift left, "k_2"] \arrow[d, shift left, "K_a"] \\ & \mathrm{AuCl_3(OH)^- + H^+} \arrow[u, shift left] \end{tikzcd}$$

Temp, °C	$10^6[\mathrm{H^+}]$, M	Slope, M^{-1} sec^{-1}	$10^{-3}k_2/K_a$, M^{-2} sec^{-1}
30.4	16	1.97	12.3
30.4	2.5	0.35	14.0
25.0	16	1.50	9.3
25.0	56	5.33	9.3

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION

$$\begin{tikzcd} \mathrm{AuCl_4^- + H_2O} \arrow[r, shift left, "k_1"] & \mathrm{AuCl_3(H_2O) + Cl^-} \arrow[l, shift left, "k_2"] \arrow[d, shift left, "K_a"] \\ & \mathrm{AuCl_3(OH)^- + H^+} \arrow[u, shift left] \end{tikzcd}$$

Temp, °C	10^2k_1, sec^{-1}	k_2/K_a, M^{-2} sec^{-1} [d]
20.5	1.4	8.0×10^3
25.0	2.2	9.3×10^3
30.4	3.3	12.3×10^3
$\Delta H^{\ddagger}$, kcal/mole	15.5	9.1
$\Delta S^{\ddagger}$, eu	−15	−25
0.0[a]	0.3	0.7×10^3 [e]
1.0[b]	0.3	...
4.0[b]	0.5	...
8.0[b]	0.8	...
20.0[c]	6×10^{-2}	...

[a] Value taken from ref 1. [b] Value taken from ref 4. [c] Value calculated from second-order rate constant $k_{\mathrm{OH^-}} = 9.6 \times 10^5$ M^{-1} sec^{-1} according to ref 2. [d] Assuming a value of 10^{-3} M for K_a, then the values become 8.0, 9.3, and 14.0 M^{-1} sec^{-1}, respectively. [e] Calculated from equilibrium constant given in ref 1, *viz.*, 0.5×10^{-5} M^2.

and the temperature-dependence parameters are given in Table V.

Discussion

Perhaps it would be worthwhile to discuss each of the rate constants in turn. The rate constant k_1 describing the hydrolysis of $\mathrm{AuCl_4^-}$ has a $\Delta H^{\ddagger}$ value of 15.4 kcal/mole and a corresponding $\Delta S^{\ddagger}$ at 25° of −15.5 eu. When compared with the $\mathrm{PtCl_4^{2-}}$ system where k_1 has a $\Delta H^{\ddagger}$ of 21 kcal/mole and a $\Delta S^{\ddagger}$ of −8 eu, it is seen that the rate constants are in the ratio of $k_1(\mathrm{AuCl_4^-})/k_1(\mathrm{PtCl_4^{2-}}) = 550/1$ at 25°. This is a rather striking example of the difference in reactivities of these two very similar complexes differing by only one electrostatic unit of charge on the central metal ion. A factor that cannot be ignored is the deprotonation of the aquo complex which in the case of the gold(III) complex is virtually complete at pH 3.80, whereas the platinum(II) complex is still largely undissociated at this pH having a $\mathrm{p}K_a \approx 7$.

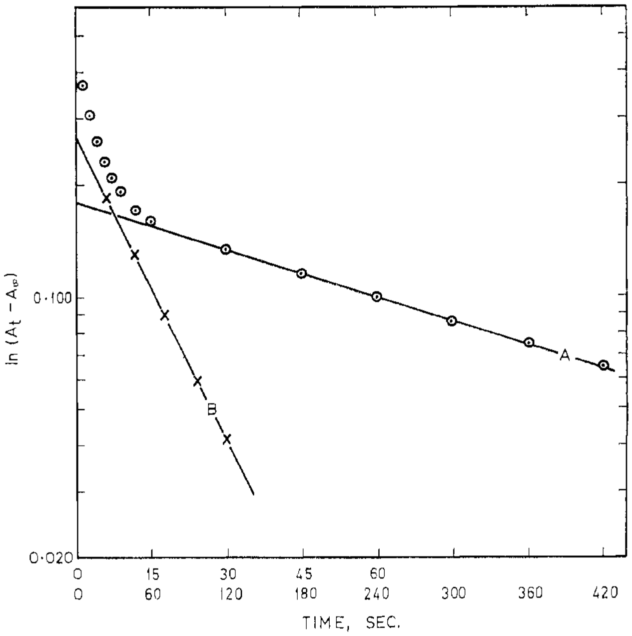

Figure 1.—Typical plot of ln ($A_t - A_\infty$) *vs.* time; $T = 20.5°$ and $[\mathrm{Cl^-}]_0 = 0.040$ M: A, equilibration of $\mathrm{AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}}}$; B, equilibration of $\mathrm{AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}}}$, on expanded time scale.

According to Beran and Vlček,[2] k_1 is really a second-order rate constant describing a direct attack by $\mathrm{OH^-}$ on the $\mathrm{AuCl_4^-}$ complex. If this were so, it would mean that at 20.5° the value for $k_{\mathrm{OH^-}} = k_1[\mathrm{H^+}]/K_w$ would be 4.3×10^8 M^{-1} sec^{-1} for this study. This is about 500 times greater than the value of 9.6×10^5 M^{-1} sec^{-1} found for such a process when ethylenediamine reacted with $\mathrm{AuCl_4^-}$ in a buffered medium at the same temperature. However, if the $k_{\mathrm{OH^-}}$ value of

TABLE IV

RATE DATA FOR THE EQUILIBRIUM

$$AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AuCl_2(H_2O)(OH) + Cl^-$$

$[Cl^-]$, M	Temp, °C	pH	$10^3 R_{obsd}$, sec^{-1} [a]
0.060	20.5	3.80	3.3
0.050	20.5	3.80	2.8
0.040	20.5	3.80	2.5
0.033	20.5	3.80	2.0
0.025	20.5	3.80	1.5
0.020	20.5	3.80	1.3
0.067	25.0	3.80	5.6
0.050	25.0	3.80	4.7
0.040	25.0	3.80	3.8
0.033	25.0	3.80	3.0
0.025	25.0	3.80	2.3
0.020	25.0	3.80	2.0
0.013	30.4	3.80	2.3
0.020	30.4	3.80	3.0
0.025	30.4	3.80	3.5
0.033	30.4	3.80	4.7
0.040	30.4	3.80	5.5
0.050	30.4	3.80	6.5
0.060	30.4	3.80	7.8
0.050	25.0	3.25	16.5
0.050	25.0	4.80	1.2

[a] R_{obsd} is the rate of equilibration for a first-order–first-order system.

TABLE V

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION

$$AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AuCl_2(H_2O)(OH) + Cl^-$$

Temp, °C	$10^4 k_3$, sec^{-1}	$10^2 k_4$, sec^{-1} [a]
20.5	1.7	5.3
25.0	3.3	8.3
30.4	6.7	11.8
$\Delta H^{\ddagger}$, kcal/mole	26.9	15.4
$\Delta S^{\ddagger}$, eu	+14	−13

[a] k_4 Treated as a second-order rate constant although it is also dependent on $[H^+]$ as shown in the last two results given in Table IV.

9.6×10^5 M^{-1} sec^{-1} is converted to an acid hydrolysis rate constant, the value of 6×10^{-4} sec^{-1} compares quite favorably with the second aquation rate constant $k_3 = 1.7 \times 10^{-4}$ sec^{-1} reported here in Table V. The small difference could be accounted for by the difference in ionic strength of the reactant media. Furthermore, it was found that even a threefold change in the hydrogen ion concentration had practically no effect on the intercepts of rate *vs.* $[Cl^-]$ plots from whence k_1 was obtained in this study. This is in accord with the finding of Rich and Taube[1] that the chloride ligand exchange reaction of $AuCl_4^-$ showed no hydrogen ion concentration dependence. One factor that still remains unreconciled is the value for the activation energy of 14.5 ± 1 kcal/mole reported for the study of the ethylenediamine substitution reaction. This is much lower than the value obtained for the hydrolysis of the $AuCl_3(OH)^-$ species.

Finally, it may be observed that the hydrolysis reaction described by k_1 is in variance with the conclusion[11] that the first-order process found to operate in the chloride ligand exchange reaction studied by Rich and Taube[1] was due to a hydrolysis reaction. The single value of 2.8×10^{-3} sec^{-1} for the hydrolysis rate constant for $AuCl_4^-$ at 0° reported in that study falls on the Arrhenius plot obtained in this work. Furthermore, the recent study by Kazakov[4] gave k_1 values at 1, 8, and 12° of 0.0027, 0.0052, and 0.0083 sec^{-1}, respectively, which also are in good agreement with the present study. The difference, of course, lies in the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values between the aquation process and the first-order exchange process. It is therefore unlikely that the exchange process with $\Delta H^{\ddagger} = 4.5$ kcal/mole and $\Delta S^{\ddagger} = -50$ eu occurs *via* the hydrolysis reaction with $\Delta H^{\ddagger} = 15.5$ kcal/mole and $\Delta S^{\ddagger} = -15.5$ eu. Yet this would be expected when comparing the ligand-exchange reaction of $AuCl_4^-$ to that of the $PtCl_4^{2-}$ system in which the exchange rate was almost entirely accounted for in terms of a hydrolysis reaction. It should be noted that if, in fact, k_1 was a product of a second-order rate constant and the OH^- concentration, a corresponding $\Delta S^{\ddagger}$ value of +15 eu would be found at 25°. This would be a change from generally large negative[5] entropies of activation to a fairly large positive value, as have been recorded, for example, in platinum(II) systems.[12,13]

The anation rate constant k_2 was determined in the form of a quotient containing K_a, the acidity constant for $AuCl_3(H_2O)$. The value of K_a was estimated as being no smaller than 10^{-3} M. This estimate was made on the following grounds.

(a) A 10^{-3} M solution of $HAuCl_4$ in 10^{-3} M NaOH gives a pH value of 3.20 at 25°. In the absence of any initial chloride ion the equilibrium lies far over to the trichloroaquogold(III) side. A simple calculation yields a K_a value that cannot be smaller than 10^{-3} M.

(b) Rich and Taube[1] found that even at $[H^+] = 0.08$ M the trichloroaquogold(III) species was absent suggesting in fact a value for $K_a > 10^{-3}$ M.

(c) Granthan, Elleman, and Martin[7] concluded that $AuCl_3(H_2O)$ is a strong acid compared to $PtCl_3(H_2O)^-$ by utilizing the argument of Ricci[14] that there is a difference in the standard free energy of ionization of −12 kcal for one unit of formal charge on the central atom of an oxy acid.

Hence, at 25°, k_2 would be at least 9.3 M^{-1} sec^{-1}. Assuming that K_a does not vary with temperature, a $\Delta H^{\ddagger}$ value of 9 kcal/mole is obtained for the anation reaction described by k_2. This is accompanied by a $\Delta S^{\ddagger}$ of some −25 eu. If this reaction is compared to the $[Au(dien)OH]^{2+}$ reaction with Cl^- in acid medium, it is found that the latter reaction is about 50 times faster if one takes into account the hydrogen ion contribution to the rate and considers the value of k_2/K_a in this study. This is in keeping with the observation that the cationic complexes react faster than the anionic

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[11] D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 131.

[12] F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

[13] W. Robb, Ph.D. Thesis, University of Melbourne, 1963.

[14] J. E. Ricci, *J. Am. Chem. Soc.*, **75**, 1548 (1953).

complexes and supports the theory[15] that bond making plays a more important role in the transition state than does bond breaking.

The one significant observation regarding the rate constant k_3 at 25° is that it is more than 50 times lower than k_1. A large part of the difference is due to the high $\Delta H^{\ddagger}$ for the latter reaction. There is also a considerable difference between the $\Delta S^{\ddagger}$ values, especially if it is considered that in both cases an ionic complex bearing a unit negative charge reacts with water to give the product. In the report of $PtCl_4^{2-}$ aquation studies,[7] it was remarked that the rate of aquation of $PtCl_3(H_2O)^-$ was also much slower than that of $PtCl_4^{2-}$ itself.

Finally, the rate constant k_4, describing the chloride anation reaction of $AuCl_2(H_2O)(OH)$, seems to be quite "normal" for the system with a $\Delta H^{\ddagger}$ value of 15.4 kcal/mole and $\Delta S^{\ddagger} = 13$ e.u. There is some evidence for the existence of a cationic species, probably $AuCl_2(H_2O)_2^+$, in acid medium (pH 4) as seen from the ion-exchange experiments using a radioactive gold tracer.

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[15] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 195.

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The Thermochemistry of Some Phosphorus Halide–Boron Halide Complexes

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The standard enthalpies of formation of four complexes of the general formula $PX_3 \cdot BY_3$ (X, Y = Br or I) are reported. These data are discussed in terms of the strength of the donor–acceptor bond. Estimates of this bond strength are: $PI_3 \cdot BI_3$, 22; $PI_3 \cdot BBr_3$, 65; $PBr_3 \cdot BI_3$, 34 and $PBr_3 \cdot PBr_3$, 7 kcal mole^{-1}.

Introduction

The 1:1 complexes formed from boron trihalides and phosphorus trihalides have been studied in connection with their stability with respect to dissociation,[1] their halogen-exchange reactions,[1] and their solid-phase structure.[2,3] Only the complexes involving the heavier halogen atoms are stable with respect to disproportionation or dissociation at room temperature. These complexes are presumably σ bonded from the phosphorus to the boron atom. This is in contrast to the phosphoryl halide–boron halide adducts, which have also been examined thermochemically,[4] where bonding is most probably from oxygen to boron.

Experimental Section

Materials.—Carbon disulfide used as solvent in the syntheses was British Drug Houses AnalaR grade, successively shaken with aqueous potassium permanganate and mercury followed by distillation immediately prior to use. The boron and phosphorus tribromides were supplied by BDH and distilled prior to use. Boron triiodide was supplied by L. Light and Co. and phosphorus triiodide (mp 60–61°, lit.[5] 60.5°) was synthesized by the method of Germann and Traxler[5] and recrystallized from carbon disulfide. Handling was performed in a nitrogen-filled drybox as the compounds are sensitive to both oxidation and hydrolysis.

Syntheses.—All complexes were synthesized by mixing equimolar quantities of the boron and phosphorus halides dissolved in carbon disulfide. The adducts were yellow solids (white, in the case of PBr_3BBr_3) and precipitated from carbon disulfide.

Phosphorus Triiodide–Boron Triiodide.—This was prepared by the method of Mitchell, *et al.*,[2] and vacuum dried; mp 250°. *Anal.* Calcd for PI_3BI_3: I, 94.8. Found: I, 95.7. Halogen analyses were performed by silver nitrate titrations using adsorption indicators.

Phosphorus Triiodide–Boron Tribromide.—This adduct was prepared by the method of Cowley and Cohen[3] and crystallized from carbon disulfide; mp 159–160°; lit.[3] 160°. *Anal.* Calcd for PI_3BBr_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.0; I, 56.5; mol wt (by cryoscopy in benzene), 651.

Phosphorus Tribromide–Boron Tribromide.—The method of Tarible[6] was used to synthesize this adduct; mp 59–61°, lit.[1] 61°. *Anal.* Calcd for PBr_3BBr_3: Br, 91.9. Found: Br, 91.0.

Phosphorus Tribromide–Boron Triiodide.—The method of Armington, *et al.*,[7] was used to prepare this adduct; mp 178–182°. *Anal.* Calcd for PBr_3BI_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.2; I, 55.7; mol wt (by cryoscopy in benzene), 646.

Calorimetry.—The calorimeter was of the constant-temperature environment type fully immersed in a thermostat maintained at 25 ± 0.01°. A full description may be found elsewhere.[8] The precision and accuracy of the equipment were checked by two standard reactions, one endothermic and the other exothermic. For the dissolution of potassium chloride in water, ΔH ($N = 200$, $T = 25°$) $= 4.23 \pm 0.03$ kcal mole^{-1} (mean of five determinations), and for the neutralization of tris(hydroxymethyl)aminomethane in excess 0.1 M hydrochloric acid, ΔH ($N = 600$, $T =$

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