[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY AND CARLETON COLLEGE]

Kinetics of the Hydrolysis of Hexachloroantimonate(V)

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Three methods (spectrophotometric, amperometric and solvent extraction) for measuring the kinetics of hydrolysis of $SbCl_6^-$ were investigated. The spectrophotometric method, which was superior to the other methods, was used for extensive measurements of the kinetics at 25° under varying conditions. The rates were determined under conditions where the reaction was pseudo first order; *i.e.*, the rate = $k_h[SbCl_6^-]$. Hydrogen ion accelerates the hydrolysis; at a total chloride concentration of 6 *M* the rate constant $k_h = (3.9 + 0.8[H^+]) \times 10^{-3}$ min.$^{-1}$. At a total chloride concentration of 9 *M*, $k_h = (5.3 + 1.6[H^+]) \times 10^{-3}$ min.$^{-1}$. Antimony(III) also accelerates the reaction, $SbCl_3$ apparently being the effective form. Mechanisms, consistent with these observations, are proposed.

The slow rate of hydrolysis of the hexachloroantimonate(V) ion, $SbCl_6^-$, was first reported by Weinland and Schmid.[1] Recent work[2] on the equilibrium aspects of the hydrolysis of $SbCl_6^-$ has also indicated the feasibility of investigating the kinetic aspects of the hydrolysis. More detailed knowledge of this hydrolysis is of value because of its relation to the rhodamine B method of analysis for antimony,[3] and because of its relation to the radioactive exchange between Sb(III) and Sb(V).[4] Of even greater value is the fact that this complex provides a convenient case for studying the factors affecting the kinetics of hydrolysis of halo-complexes. This type of reaction has not previously been studied extensively, primarily because of the rapid rate of reaction of most halo-complexes. As a result of this study of $SbCl_6^-$ some of the mechanistic features of the hydrolysis reaction are now evident.[5]

Experimental

Reagents.—The Sb(III) used for stock solutions was prepared from Sb_2O_3 that had been purified by the method of Schuhmann.[6] The Sb(V) stock solutions were prepared by two methods: (1) by chlorine oxidation of a concentrated Sb(III) solution, followed by boiling to remove excess Cl_2, and then dilution with hydrochloric acid, and (2) directly from Baker and Adamson reagent grade $SbCl_5$. The hydrochloric acid and lithium chloride, which were used without further purification, were Baker Analyzed reagent and Mallinckrodt analytical reagent, respectively. The LiCl-HCl mixtures were prepared by adding by means of a buret the desired volume of concentrated stock solutions of the two. The concentrations of the stock solutions had previously been determined by titration with standard $AgNO_3$ and standard NaOH.

Rate of Hydrolysis by Extraction Method.—It has been shown[3] that the well-known rhodamine B method extracts the anion $SbCl_6^-$ from hydrochloric acid solutions of Sb(V) and that the hydrolyzed species do not react with the dye to a measurable extent. Therefore it is sound in principle to follow the hydrolysis of $SbCl_6^-$ using this method. A solution of 0.0001 *M* $SbCl_6^-$ in 6.1 *M* hydrochloric acid was prepared by dilution of 0.5 ml. of 0.01 *M* $SbCl_6^-$ in concentrated acid with 49.5 ml. of 6.1 *M* acid. As the hydrolysis reaction occurred, 1-ml. samples were withdrawn at intervals and analyzed by the rhodamine B method. The extraction required only about one minute, during which time the formation reaction does not occur to an appreciable extent. The absorbance of the benzene extract was measured at 564 mμ with a Beckman Model B spectrophotometer.

Rate of Hydrolysis by Amperometric Method.—It was discovered that Sb(V) in concentrated hydrochloric acid is reduced to Sb(III) at the rotated platinum electrode to give a current voltage curve with a well-defined diffusion region. The diffusion current is proportional to the concentration of $SbCl_6^-$. It is possible to follow the hydrolysis of the latter by this method because the hydrolyzed species are reduced irreversibly at more negative potentials. This is made clear by consideration of Fig. 1. Linde nitrogen was used to remove oxygen from the solutions, which were prepared by dilution of a small volume of a concentrated hydrochloric acid solution of Sb(V) with a large volume of hydrochloric acid of the appropriate concentration. During a kinetics run the applied potential was constant at +0.1 volt *vs.* S.C.E. and the current was measured with a Weston Model 430 microammeter. The circuit was open except during measurement to minimize formation of Sb(III) by the electrode reaction.

Rate of Hydrolysis by Spectrophotometric Method.—Utilization of a spectrophotometric method, based on the ultraviolet absorption characteristics of $SbCl_6^-$ and its hydrolysis products, has been discussed previously.[2] Measurements were made with a Beckman Model DU spectrophotometer using fused silica cells having a light path of one cm. The cells were maintained at constant temperature in the spectrophotometer by means of a water jacket, through which water from a thermostated bath (25.0 ± 0.2°) was circulated.

To begin the reaction a small volume of a 0.5 *M* Sb(V) stock solution in concentrated HCl was added to a solution of the desired composition. For solutions containing only HCl and LiCl as additional components, a 20-microliter portion of the Sb(V) stock was added to 25 ml. total. "Absorbance" readings at this concentration (4×10^{-4} *M*) were convenient in the wave length region 290–320 mμ. Data were taken at time intervals dependent on the rate, and at several wave lengths. For the slower reactions data were taken at wave lengths of 290, 300, 310 and 320 mμ. For the faster reactions, where the time interval between readings was smaller, only two wave lengths, 300 and 310 mμ, were used.

For experiments involving antimony(III) it was necessary to use larger concentrations of Sb(V) so that the latter would still be the principal light absorbing species. Solutions 0.01 and 0.02 *M* in Sb(V) were used. Data were taken at several wave lengths in the region 340–400 mμ, the number of wave lengths used for any one experiment being from one to five depending on the rate.

Treatment of Spectrophotometric Data.—Although there are several reactions actually occurring, the system in essence is that of two reversible first-order reactions

$$A \underset{k_f}{\overset{k_h}{\rightleftarrows}} B$$

In this case A is $SbCl_6^-$, B is the mixture of hydrolytic species, k_h is the pseudo first-order rate constant for hydrolysis of $SbCl_6^-$, and k_f is the pseudo first-order rate constant for formation of $SbCl_6^-$. A plot of log $|A - A_\infty|$ *vs.* time, where *A* is the absorbance, gives the expected straight line, and from the slope of the line $(k_h + k_f)$ can be calculated.

In general we are interested in obtaining k_h rather than $(k_h + k_f)$. For reactions where k_f is small with respect to k_h, corresponding to reactions where the hydrolysis is essentially complete at equilibrium, the plot just described is sat-

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[1] R. F. Weinland and H. Schmid, *Z. anorg. allgem. Chem.*, **44**, 37 (1903).

[2] H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

[3] R. W. Ramette and E. B. Sandell, *Anal. Chim. Acta*, **13**, 455, (1955).

[4] H. M. Neumann and H. Brown, THIS JOURNAL, **78**, 1843 (1956).

[5] Some of the results of this work were reported at the Analytical Symposium, Syracuse University, June, 1955.

[6] R. Schuhmann, THIS JOURNAL, **46**, 52 (1924).

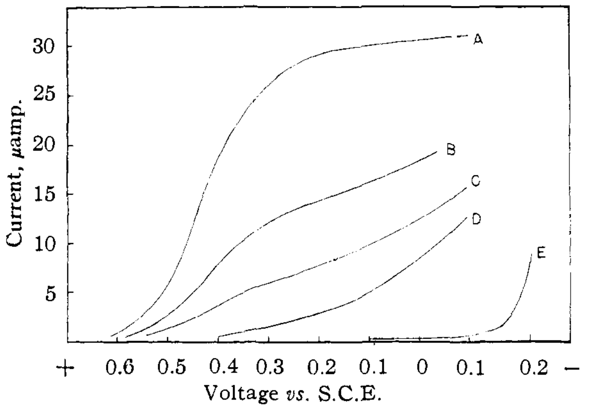

Fig. 1. Current–voltage curves obtained at various times during the hydrolysis of 2×10^{-4} M $SbCl_6^-$ in 6.1 M hydrochloric acid, using rotated platinum electrode: A, after 10 min.; B, 1.5 hours; C, 3 hours; D, 24 hours (∞); E, residual current.

isfactory for the determination of k_h. Solutions where the concentration of HCl is 6 M or smaller fall into this category, and the data were treated accordingly. For each experiment a rate constant was calculated from the data at each wave length, and an average value then taken. The total spread in the values obtained at the several wave lengths was generally about 5% of the average value.

When k_f is comparable to k_h one plots log $|A - A_B|$ vs. time, where A_B is the absorbance the solution would have if all A were converted to B. A_B can be calculated from the data and interpretation thereof given in an earlier paper,[2] but is clearly dependent on the assumptions and interpretation involved in that work.

The plot of log $|A - A_B|$ vs. time is initially a straight line (from the slope of which one can calculate k_h), but it curves when the rate of the reverse reaction is no longer negligible. The values of k_h obtained by this method are limited in accuracy because of two causes: (1) graphical determination of the initial slope is difficult, particularly when the equilibrium amount of $SbCl_6^-$ is large, and (2) the value of k_h will be dependent on the value chosen for A_B. The only experiments where this method was necessary were those in which the chloride ion concentration was 9 M. The likely accuracy of the k_h values has been estimated in the following way for each of the two limiting factors stated above: (1) The values of k_h calculated from data at the various wave lengths fell within ±5% of the average value. (2) After making the calculation of k_h from the best possible estimates of A_B at the various wave lengths, the calculation was repeated using as new values of A_B 75% of the previous values. The new values of k_h were uniformly lower by about 10% of the earlier value. Considering both these effects it is felt that the k_h values stated are reliable to ±20%.

Figure 2 provides an example of the graphical treatment of the data. The data were taken at 300 mμ on a 5 M HCl–4 M LiCl mixture.

Results

Comparison of Methods. (1) **Extraction Method.**—A plot of log $(A - A_\infty)$ vs. time, where A is the absorbance of the benzene extract, was linear with a slope corresponding to a value of 0.0093 min.^{-1} for the rate constant k_h in 6.1 M HCl. This is in good agreement with the values given below for the other methods. Because of the relative difficulty of this method no further experiments were tried.

(2) **Amperometric Method.**—Plots of log $(i - i_\infty)$ vs. time, where i is the measured current, were linear. The values obtained for the rate constant were in agreement with those by the spectrophotometric method except at low acidities. For example, for hydrochloric acid concentrations of 6, 4 and 2 M (chloride constant at 6 M using lithium chloride) the values of the rate constant were 0.0099, 0.0072 and 0.0042 min.^{-1}, respectively.

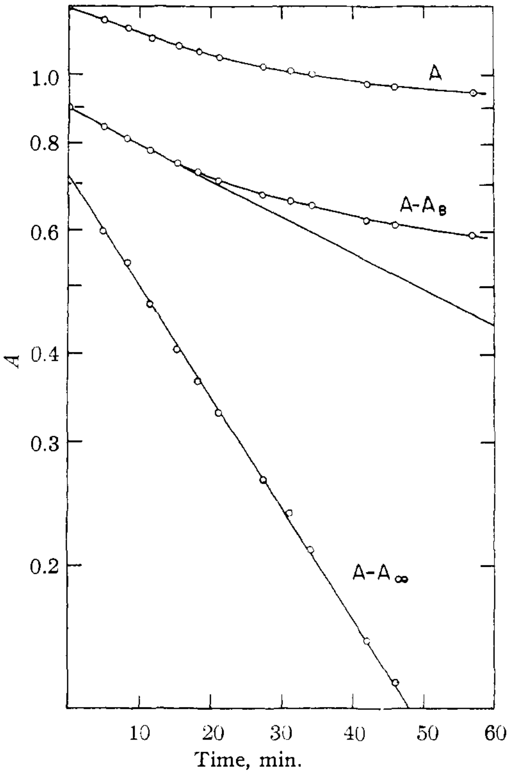

Fig. 2.—Example of treatment of spectral data to obtain the rate constants. The data were taken at 300 mμ on a 5 M HCl–4 M LiCl mixture. The $(A - A_\infty)$ plot has been displaced upward for convenience in plotting.

(3) **Spectrophotometric Method.**—Neither of the previous methods appeared to be capable of yielding results as precise as those of the spectrophotometric method. The latter method was thus the one used for the extensive measurements reported below.

Dependence on Acidity.—Cheek[7] has measured the rate of hydrolysis of $SbCl_6^-$ in hydrochloric acid solutions, and observed that the rate increases with increasing concentration of the acid. In the course of our work several similar experiments have been performed. Figure 3 shows these results.

With these data alone it is difficult to account for the observed trend, since $[H^+]$, $[Cl^-]$ and the ionic strength are all changing at once. Experiments performed at constant ionic strength and constant chloride concentration are more valuable. This was done, using HCl–LiCl mixtures, for total chloride concentrations of both 6 and 9 M, two sets of experiments being performed at each concentration. LiCl is the best chloride for such mixtures since data from the literature[8] shows that for HCl–LiCl mixtures of constant ionic strength, varying the ratio of HCl and LiCl changes only slightly the value of the mean ionic activity coefficient of HCl.

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(7) C. H. Cheek, Ph.D. Thesis, Washington University, St. Louis, January, 1953.

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950.

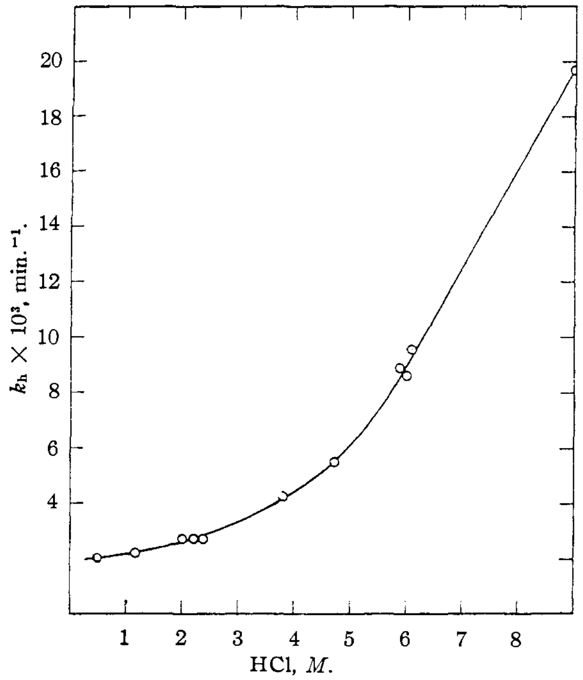

Fig. 3.—Rate constant for hydrolysis as a function of HCl concentration.

The results of the experiments in 6 *M* chloride solution are given in Table I. When the observed pseudo first-order rate constant is plotted *vs.* [H$^+$], one obtains a straight line that corresponds to the equation $k_h = (3.9 + 0.8[H^+]) \times 10^{-3}$ min.$^{-1}$.

Table I

Rate of Hydrolysis of $SbCl_6^-$ in Solutions Containing 6 *M* Cl^-

[H$^+$]	$k_h \times 10^3$ (min.$^{-1}$) 1st set	$k_h \times 10^3$ (min.$^{-1}$) 2nd set
1	4.8	4.7
2	5.4	5.4
3	6.3	5.9
4	7.0	7.1
5	..	7.8
6	8.7	8.5

The results in 9 *M* chloride are similar, and are given in Table II. The values of k_h are less accurate here because the initial slope must be used, and particularly at the higher acidities where the hydrolysis is not extensive. Considering these limitations, the straight line corresponding to the equation $k_h = (5.3 + 1.6\,[H^+]) \times 10^{-3}$ min.$^{-1}$ is consistent with the data obtained.

Table II

Rate of Hydrolysis of $SbCl_6^-$ in Solutions Containing 9 *M* Cl^-

[H$^+$]	$k_h \times 10^3$ min.$^{-1}$ 1st set	$k_h \times 10^3$ min.$^{-1}$ 2nd set	$k_{eq} \times 10^3$ 2nd set	$k_f \times 10^3$	k_f/k_h
0.01	..	5.3	5.3	0.0	0.0
1	7.2	6.9	9.1	2.2	0.3
2	8.7	7.9	12.6	4.7	0.6
3	10.0	9.8	21.5	11.7	1.2
4	11.6	12.3	27.2	14.9	1.2
5	12.5	12.6	35.7	23.1	1.8
6	15.3	13.8	47	33	2.4
7	15.6	14.4	53	39	2.7
8	21.3	19.8	76	56	2.8
9	19.0	23.1	100	77	3.3

A scheme of reactions that would account for the observed variation of k_h with [H$^+$] is

$$SbCl_6^- \xrightarrow{k_1} Cl^- + SbCl_5 \text{ (followed by rapid reaction of } SbCl_5 \text{ with water)} \quad (I)$$

$$SbCl_6^- + H^+ \overset{K}{\rightleftarrows} HSbCl_6 \quad (II)$$

$$HSbCl_6 \xrightarrow{k_3} HCl + SbCl_5 \text{ (followed by rapid reaction of } SbCl_5 \text{ with water)} \quad (III)$$

The equilibrium reaction (II) must be rapid with respect to reactions (I) and (III), and the equilibrium such that the amount of $HSbCl_6$ is small with respect to the amount of $SbCl_6^-$. These conditions would lead to the equation $k_h = k_1 + k_3K[H^+]$. Whether the species $HSbCl_6$ should be regarded as a true chloro-acid or as merely a transition state cannot be decided.

Because the dependence on water concentration remains undetermined the following scheme would also be consistent with the results

$$H_2O + SbCl_6^- \xrightarrow{k_1} Cl^- + Sb(H_2O)Cl_5 \quad (1)$$

(followed by rapid loss of H$^+$)

$$SbCl_6^- + H^+ \overset{K}{\rightleftarrows} HSbCl_6 \quad (2)$$

$$H_2O + HSbCl_6 \xrightarrow{k_3} HCl + Sb(H_2O)Cl_5 \quad (3)$$

(followed by rapid loss of H$^+$)

The same restrictions apply to equation 2. These two schemes obviously differ only in whether the first and third reactions are considered to be of the S$_N$1 or S$_N$2 type.

The rate going to equilibrium can be obtained as described in the Experimental section, the rate constant, k_{eq}, so obtained is given by $k_{eq} = k_h + k_f$. For any given experiment one can then obtain both k_{eq} and k_h, and hence k_f by difference. This was done for the second set of experiments in 9 *M* chloride in order to observe the dependence of k_f on [H$^+$]. The purpose was to obtain additional evidence in regard to the first hydrolytic form of Sb(V) present in these solutions. If the first hydrolytic species is $Sb(OH)Cl_5^-$, as is indicated in equilibrium studies,[2] then the equilibrium ultimately attained is

$$SbCl_6^- + H_2O \rightleftarrows Sb(OH)Cl_5^- + Cl^- + H^+$$

At equilibrium $k_h[SbCl_6^-] = k_f[Sb(OH)Cl_5^-]$, so that $k_f/k_h = [SbCl_6^-]/[Sb(OH)Cl_5^-]$. But from the equilibrium constant expression

$$[SbCl_6^-]/[Sb(OH)Cl_5^-] = K\,\frac{a_{H^+}a_{Cl^-}}{a_{H_2O}} = K'[H^+]$$

assuming that the activity coefficients are constant in these mixtures. It would then be expected that k_f/k_h would show a linear dependence on [H$^+$]. The ratio k_f/k_h is not known with great accuracy; the limitations on k_h have been discussed, and the accuracy of k_f is limited because it is obtained by taking the difference between k_{eq} and k_h. Bearing these limitations in mind, the data of Table II are consistent with k_f/k_h being directly proportional to [H$^+$].

If $Sb(H_2O)Cl_5$, rather than $Sb(OH)Cl_5^-$, were the first hydrolytic species, k_f/k_h should be independent of $[H^+]$. As a result it is clear that the amount of $Sb(H_2O)Cl_5$ must be small with respect to the amount of $Sb(OH)Cl_5^-$. Or expressing the same thing in another way, $Sb(H_2O)Cl_5$ is a strong acid in these solutions.

Although these kinetic data support the equilibrium data with respect to the identity of the first hydrolytic species, there is a disagreement as to the amounts of $SbCl_6^-$ and $Sb(OH)Cl_5^-$ present at equilibrium. Using the ratio of $k_f/k_h = 3.2$ in 9 *M* HCl, obtained by drawing the best straight line through the k_f/k_h *vs.* $[H^+]$ data, one calculates that 76% of the Sb(V) is present as $SbCl_6^-$ at equilibrium, whereas the equilibrium data gave a value of 60%. Since in both calculations an assumption was involved about the absorbancy of $Sb(OH)Cl_5^-$ at 300 and 310 mμ, various trial values were assumed in an attempt to obtain greater consistency between the kinetic and equilibrium data. All these attempts only led to other difficulties, such as greater disagreement between the rate constants determined from data at the two wave lengths for a given experiment.

There would seem to be two possible reasons for failure to achieve complete consistency: (1) there are small amounts of other Sb(V) species which have not been taken into account in the spectral analysis, or (2) the spectrum of an individual species changes somewhat as the HCl concentration changes. The conclusions resulting from the spectral analysis[2] are probably correct in so far as the identification of the predominant species is concerned, and for a semi-quantitative estimate of their amount as a function of acidity. The values of the equilibrium constants are questionable within a factor of two or three. The value of the equilibrium constant

$$K = \frac{[Sb(OH)Cl_5^-](a_{HCl})^2}{[SbCl_6^-]a_{H_2O}}$$

is 2.2×10^4 from the kinetic data as compared to 4.5×10^4 from the equilibrium data. The former is more reliable since the kinetic data are less sensitive to the assumptions involved.

Dependence on Sb(III).—Because of the importance of the hydrolysis in the understanding of the radioactive exchange between Sb(III) and Sb(V),[4] the effect of Sb(III) on the hydrolysis was investigated. A marked effect was observed.

Table III gives k_h for various HCl solutions containing 0.0385 *M* Sb(III). The accelerating effect is observed to increase with decreasing acidity, the reverse of the behavior in the absence of Sb(III). That the dependence on the Sb(III) concentration is first order is demonstrated by the data given in Table IV, in particular by the constancy of the values of $Sb(III)/(k_h - k_0)$. In the table k_0 is the rate constant when Sb(III) is absent. The quantity $(k_h - k_0)$ is the one of interest since it is the rate constant for the reaction proceeding by an Sb(III)-catalyzed mechanism.

TABLE III

RATE OF HYDROLYSIS OF $SbCl_6^-$ IN HCl SOLUTIONS CONTAINING 0.0385 *M* Sb(III)

	$k \times 10^3$ (min.$^{-1}$)		
$[H^+]$	k_h	k_0[b]	$(k_h - k_0)$
6.17	10.8	9.6	1.2
5.35	14.4	7.0	7.4
4.55	30	5.2	25
3.51	87	3.9	83
2.63	220	3.0	217
1.78	>350[a]	2.5	>350

[a] Formation of precipitate after 2.5 min. resulted in only a limiting value being obtained. [b] Values taken from the curve of Fig. 3.

TABLE IV

RATE OF HYDROLYSIS OF $SbCl_6^-$ IN 2.2 *M* HCl CONTAINING VARYING CONCENTRATIONS OF Sb(III)

[Sb(III)]	$k_h \times 10^3$ (min.$^{-1}$)	$(k_h - k_0) \times 10^3$ (min.$^{-1}$)	$\frac{[Sb(III)]}{(k_h - k_0)}$
......	2.7	0.0	...
0.000377	5.7	3.0	0.126
.00188	17.8	15.1	.125
.00376	31	28	.134
.00934	76	73	.128
.0185	141	138	.134

Since we have seen already that hydrogen ion can catalyze the hydrolysis by attack on chloride, it is reasonable that a Lewis acid such as $SbCl_3$ might also serve as a catalyst in the same way. The fact that $SbCl_3$ can be separated readily from HCl solutions of Sb(III) by volatilization suggests that a measurable amount of the Sb(III) actually is present as $SbCl_3$. At high HCl concentration essentially all of the Sb(III) is present as $SbCl_4^-$.[9] As the acidity decreases an increasingly larger fraction of the Sb(III) occurs as $SbCl_3$, leading to the observed rate dependence exhibited in Table III.

The transition state involving $SbCl_6^-$ and $SbCl_3$ is visualized to be $Cl_5Sb\text{–}Cl\text{–}SbCl_3^-$, *i.e.*, to have one bridging chlorine atom. Because $SbCl_5$ is a much stronger Lewis acid than $SbCl_3$ the transition state probably splits into the fragments $SbCl_6^-$ and $SbCl_3$ many more times than into the fragments $SbCl_5$ and $SbCl_4^-$.

It would be anticipated on this basis that any Lewis acid would catalyze the hydrolysis of $SbCl_6^-$. The difficulty in demonstrating this is that most Lewis acids will not exist as such in the solutions used. Addition of 0.02 *M* Sn(IV) to 4.7 *M* HCl was found to have no effect on the rate, presumably because insufficient Sn(IV) existed as $SnCl_4$. Addition of 0.02 *M* Al(III) to a solution originally 1.2 *M* in HCl gave a rate 10% larger than that in 1.2 *M* HCl alone, but this small increase is most likely due to an increase in the hydrogen ion concentration as a result of the hydrolysis of the added $AlCl_3$ itself.

Investigation of the kinetics of hydrolysis of other halo-complexes would be worthwhile to determine to what extent the mechanistic features reported here are unique to $SbCl_6^-$ or are common to other halo-complexes.

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[9] G. P. Haight, Jr., THIS JOURNAL, **75**, 3848 (1953).