HYDROLYSIS OF HEXACHLOROANTIMONATE(V)

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TABLE OF CONTENTS

Chapter

LIST OF TABLES

Table Page

LIST OF ILLUSTRATIONS

SUMMARY

The purpose of this investigation was to study the hydrolysis of the $SbCl_6^-$ ion and to learn the effect of acid and base concentration on the rate of this reaction. Because the reaction had been thoroughly studied in strongly acidic solutions, and because the reaction becomes too fast to measure above pH 12, the rate of the reaction was studied in the pH range 2-12.

A stock solution of $SbCl_5$ in concentrated HCl was injected into various buffer media and the absorption due to $SbCl_6^-$ was measured with a Beckman DU spectrophotometer. Because the absorption is proportional to the concentration of the absorbing species, the slope of a plot of log absorption against time should give the rate of the reaction.

The final product of the hydrolysis was determined to be the $Sb(OH)_6^-$ ion in both the acid and basic pH's used in this study.

The plots of log absorption vs. time usually showed deviation at high pH from the straight line expected for a first-order or pseudo first-order reaction. Most of the curves could be resolved into two straight line components, one of which was attributed to the $SbCl_6^-$ hydrolysis, and the other to the decay of some intermediate or product characteristic of the basic buffer system. The rate of the hydrolysis of $SbCl_6^-$ is almost constant from pH 2 to pH 6. It is essentially first-order in hydroxide in the pH range 9-11. The rate of decay of the intermediate shows dependence on hydroxide within the NH_4Cl-NH_4OH buffered runs, but there appears to be dependence on the type of buffer as well.

CHAPTER I

INTRODUCTION

One of the areas of interest and importance in contemporary inorganic chemistry is the study of substitution reactions of complex ions. Many reactions, which in the past have merely been called hydrolysis reactions, are in fact reactions of this type with water molecules being the substituting reactant. This thesis reports the investigation of the hydrolysis of the $SbCl_6^-$ ion.

The hydrolysis of $SbCl_6^-$ to $SbCl_5OH^-$ has been studied by Neumann and Ramette (1) in HCl concentrations from 1 to 9 M. They determined rates under conditions where the reaction was pseudo first-order: i. e., the rate $= k_h \cdot [SbCl_6^-]$. The reaction was accelerated by the presence of hydrogen ions. The rate constant k_h was $(3.9 + 0.8[H^+]) \cdot 10^{-3}$ min.$^{-1}$ in 6 M Cl^-. At a total chloride concentration of 9 M, k_h was $(5.3 + 1.6[H^+]) \cdot 10^{-3}$ min.$^{-1}$. They also observed that Sb(III) accelerated the reaction and that $SbCl_3$ was apparently the active species.

Bonner and Goishi (2) reported a thorough study in hydrochloric acid of the kinetics of electron exchange between Sb(III) and Sb(V) species and of the hydrolysis of $SbCl_6^-$. Their data on the hydrolysis was obtained from both spectrophotometric measurements and from the exchange reaction studies. These results are in very good agreement with those of Neumann and Ramette.

Mazeika (3) attempted to study the hydrolysis in higher pH ranges. Certain difficulties in the work and irregularities in the results made it desirable to study further the pH 2-12 region in order to improve or explain his experimental data.

All previous work indicated that the final product in acidic chloride solutions is an equilibrium mixture of ions of the type $Sb(OH)_xCl_y^-$. There was no evidence as to what the final product is in basic solution, although $Sb(OH)_6^-$ might be expected. The behavior of antimony(V) in chloride-free solution will be discussed briefly because of its pertinence.

Jander and Ostmann (4) report that at pH greater than 12 a reversible equilibrium exists between two monomeric species, probably $Sb(OH)_6^-$ and $SbO(OH)_5^=$. Although they do not use their data to calculate K_a for $Sb(OH)_6^-$, it is possible to estimate the value from data in Figure 2 of their article. The ultra-violet spectrum of $KSb(OH)_6$ at pH 12 is identical to that at pH 6.8, indicating that $Sb(OH)_6^-$ is the only species present. The spectra are different at pH's 13 and 14. From the spectra, and assuming that at pH 14 the predominant species is $SbO(OH)_5^=$, it appears that about 25 per cent of the antimony(V) is present as $SbO(OH)_5^=$ at pH 13. This would correspond to an ionization constant of $3 \cdot 10^{-14}$ for $Sb(OH)_6^-$. They report that condensation of $Sb(OH)_6^-$ in the acid region is concentration dependent; in 10^{-3} M solutions only monomeric species exist, but in 10^{-2} M solutions $Sb(OH)_6^-$ aggregated at pH 3.6-4.0 to a species with ionic weight of 960 (hexaantimonate).

Souchay and Peschanski (5) report that the antimonate ion is $Sb(OH)_6^-$ at high pH, and $HSb_6O_{17}^{\equiv}$ at pH below 2.5 with no appreciable amounts of other ions occurring above pH 0.9. According to Ricca, D'Amore, and Bellomo (6), the species present in weakly acid solutions are $Sb(OH)_6^-$ and $HSb_2O_6^-$ along with $HSb_6O_{17}^{\equiv}$. They calculate the following equilibrium constants from their data:

$$H_3O^+ + 2\ Sb(OH)_6^- \rightleftarrows HSb_2O_6^- + 7\ H_2O$$

$$K_1 = \frac{[H_3O^+][Sb(OH)_6^-]}{[HSb_2O_6^-]} = 2.5 \cdot 10^{-6}$$

$$3\ HSb_2O_6^- \rightleftarrows HSb_6O_{17}^{\equiv} + H_2O$$

$$K_2 = \frac{[HSb_2O_6^-]^3}{[HSb_6O_{17}^{\equiv}]} = 3.3 \cdot 10^{-5}.$$

If the hydrolysis of $SbCl_6^-$ proceeds to the point where all chlorides are replaced, the final product would then be expected to be $Sb(OH)_6^-$ or its condensation products, depending on the solution conditions.

CHAPTER II

EXPERIMENTAL

The $SbCl_6^-$ ion exhibits a strong absorption peak at 2700 A (extinction coefficient = $7.84 \cdot 10^3$). If one assumes that none of the hydrolysis products show appreciable absorption in this region, the reaction

$$SbCl_6^- \rightarrow SbCl_5(OH)^-$$

can be followed by spectrophotometric methods. Absorbance readings were taken with a Beckman DU spectrophotometer at several wavelengths (usually 3000, 2800, 2700, and 2600 A). The readings at 3000 A were taken in those runs in which the initial $SbCl_6^-$ concentration was too great to allow useful absorbance readings at the absorbance peak. Those readings at 2800 A and 2600 A provided a check on the readings at the absorbance maximum (2700 A) and also some assurance that the reaction products did not contribute to the recorded absorbance.

Fused silica cells with a path length of 1 cm. were used in the initial runs both to contain the reaction and for the absorbance measurements. Some of the later runs were contained in 250-ml. volumetric flasks with aliquots removed for absorption measurements. The cells were maintained at a constant temperature ($25.0 \pm 0.4^\circ$) by means of a water jacket, through which water from a thermostated bath was pumped. Those runs which were made in volumetric flasks were maintained at $25.0 \pm 0.2^\circ$ by a separate water bath in which they were immersed. For readings from these flasks, the cells were rinsed two or three times with the solution, filled, and placed in the thermostated DU spectrophotometer cell holder where the readings were made. The time recorded was the time that the absorbance measurement was actually made.

Two concentrations of Sb(V) stock solution were used in the runs. They were prepared by transferring Baker and Adamson Reagent Grade $SbCl_5$ to a graduated test tube and diluting to 100 ml. with concentrated HCl. Because the $SbCl_5$ reacts with water vapor in the air, the volume of $SbCl_5$ could not be accurately measured. Spectrophotometric measurements showed the concentrations to be 0.12 M and 0.45 M. In each run about one microliter of the $SbCl_5$ solution was added for each ml. of buffer. This gave an initial absorbance of about 0.9 at 2700 A when the 0.12 M $SbCl_5$ stock solution was used and of about 0.9 at 3000 A when the 0.45 M stock solution was used.

Buffer solutions of $NaC_2H_2O_2Cl$, $KC_2H_2O_2Cl$, $NaC_2H_3O_2$, $KC_2H_3O_2$, KH_2PO_4, K_2HPO_4, K_3BO_3, K_2CO_3, and NH_4Cl were used. In most runs the concentration of the positive ion (Na^+, K^+, NH_4^+) was maintained as close as possible to 0.1 N. The pH was adjusted with the appropriate acid or base.

In general, the runs after number 15 used water which had been distilled from alkaline $KMnO_4$ solution. This water was used for two reasons: first, the results seemed to be somewhat better, and second, this water was considered to be about as consistently pure as possible.

Absorbance readings were taken at intervals dependent upon the rate of the reaction. For the faster reactions, readings were taken as often as every 1.5 minutes. However, if the reaction was going slowly, readings were not needed this frequently. Usually, five to ten readings per half-time were satisfactory. The reaction was usually first-order or pseudo first-order, as shown by the linearity of plots of $\log(A-A_\infty)$ vs. time, where A is the absorbance or optical density at a time t. The half-times of the reactions were determined from the slopes of these plots. Some typical runs are shown in Figure 1.

In an attempt to study several runs simultaneously, it was decided to perform the runs in volumetric flasks kept in a constant temperature bath. At convenient intervals a spectrophotometer cell was filled with the solution and absorbance readings made. In these runs, what was termed the "cell effect" was first observed. An example of this is run number 66. A plot of this run proceeded in a reasonably linear manner and with a half-time of more than 200 minutes, based upon readings made on portions freshly removed from the volumetric flask. The portion that was placed in the silica cell for the reading began to hydrolyze in a normal manner but with a half-time of about 30 minutes. After the cell effect was observed, most of the runs were made in both the glass volumetric flask and in the silica cell. In general, the volumetric flask produced a longer half-time than the silica cell. The reason for this difference is not clear. The most simple explanation is that it is just a surface effect; the surface area of the silica cell was about 4.2 $\text{cm.}^2/\text{ml.}$ compared with 0.64 $\text{cm.}^2/\text{ml.}$ for the volumetric flask. The volumetric flasks were always washed with concentrated HCl before runs to be sure that no reaction products were on the surface before the run. On occasions, the silica cells were washed with concentrated HCl between readings of the portions from the volumetric flasks without any decrease in the cell effect. Attempts were made to "isolate the solution from the cell" by the use of a thin

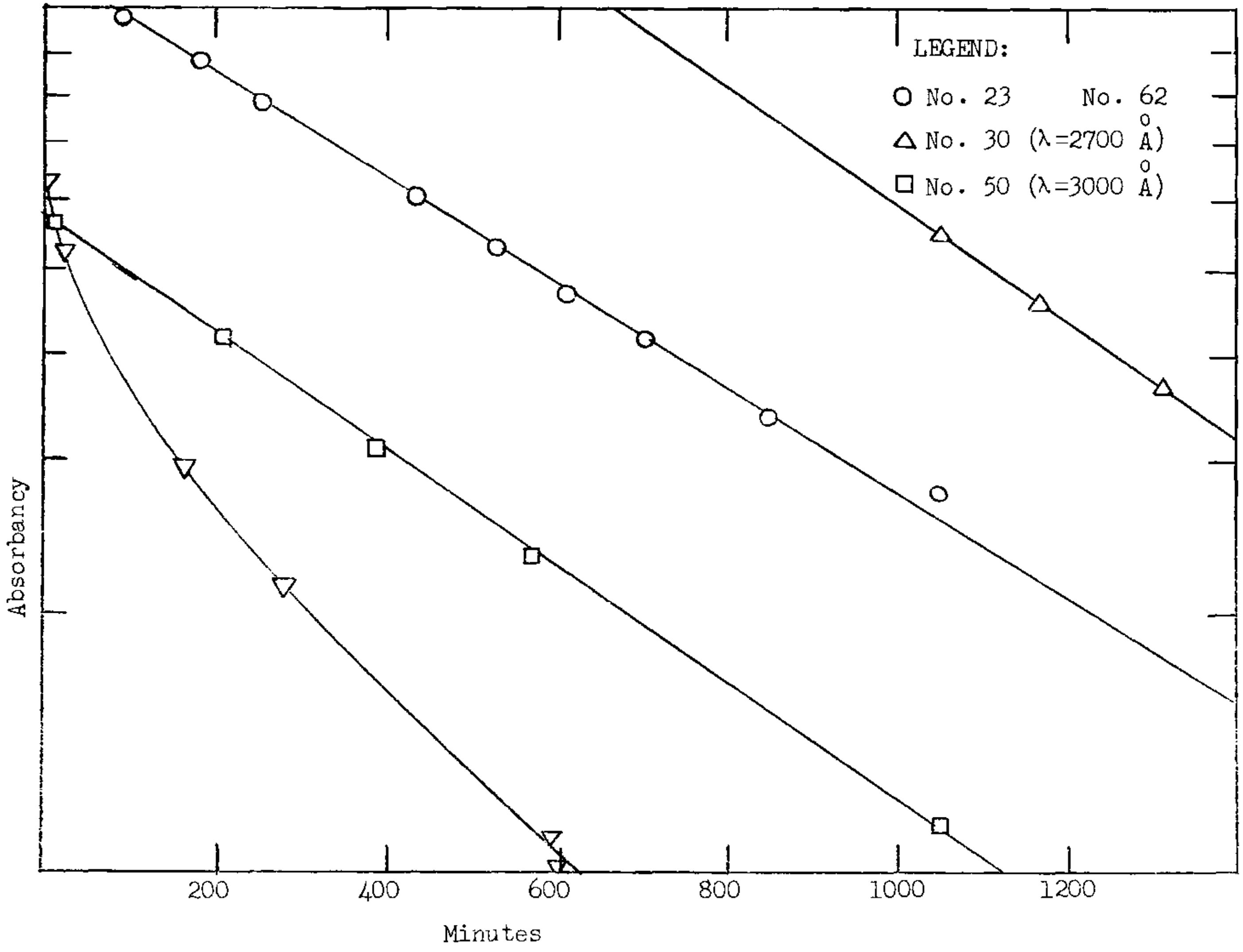

Figure 1. Plots of Typical Runs.

covering of paraffin on the inside of the cells. This seemed to help lessen the cell effect in some of the runs, but cracking or peeling of the coating occurred in some cases, making interpretation of the data difficult.

In an attempt to determine if the reaction products had any effect on the rate of the reaction, several runs were made by adding more $SbCl_6^-$ stock solution to an already used $NaC_2H_3O_2$ buffer solution (pH 5). While the kinetic results of these runs were inconclusive, there was an interesting occurrence. Small crystals of some substance were formed on the cell surfaces. Larger amounts of the stock $SbCl_6^-$ were added to the buffer and a white crystalline precipitate formed. A similar treatment of a Na_2CO_3 buffer also resulted in the formation of the white precipitate. Various analyses indicate that the precipitate in both cases is $NaSb(OH)_6 \cdot 1/2H_2O$ (Table 1). The method used for determination of antimony(V) was basically that described by Willard and Diehl (7), in which Sb(V) oxidizes iodide in strong acid, and the liberated iodine is titrated with thiosulfate. The results indicated that the end product of the reaction is the same in all buffer solutions, as well as characterizing the end product of the hydrolysis.

Because some of the runs at high pH showed curvature and an intermediate product was suspected to be responsible, several spectra were made on a Cary 14 recording spectrophotometer of solutions prepared by passing a stream of dry air over $SbCl_5$ and bubbling this gas through various buffer solutions. The resulting curves had a single absorption maximum located either about 2700 A or 2900 A. The 2700 A maximum is assumed to be caused by $SbCl_6^-$. The solutions that produced the maximum

Table 1. Analyses of Antimonates Precipitated from Buffered Solutions.

Material	% C	% H	% Sb
Unknown from $NaC_2H_3O_2$	0.21	2.80	----
Buffered Solution	0.46	2.78	----
Unknown from Na_2CO_3	----	----	47.6
Buffered Solution	----	----	47.5
$NaSb(OH)_6$	0.0	2.45	49.4
$NaSb(OH)_6 \cdot H_2O$	0.0	3.05	45.9
$NaSb(OH)_6 \cdot 1/2H_2O$	0.0	2.76	47.5

at 2900 A were solutions of high pH. The material which produced the peak at 2900 A was acid sensitive and disappeared immediately, if the solution was acidified.

CHAPTER III

RESULTS

The rate of hydrolysis was measured in solutions covering the pH range 2-12. For clarity, the results will be presented in groups depending on the pH range and/or composition of the buffer medium.

In many of the runs with high pH, the plots of $\log(A - A_\infty)$ vs. time were not linear. Serious deviations from linearity were first observed in runs buffered with NH_4Cl and K_3BO_3. In these runs, the rate accelerated as the reaction proceeded. Such an effect can occur whenever the product of the reaction is a catalyst for the reaction. However, addition of enough $KSb(OH)_6$ to saturate the solution was observed to have no effect (run 81), indicating that some other effect was causing the deviations.

A second possibility is that there is an intermediate of measurable life-time which has an appreciable absorbancy at the wavelength used. If such is the case, the intermediate will probably be disappearing by a first-order or pseudo first-order reaction. Assuming the reaction follows the pattern of consecutive first-order reactions

$$X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$$

the concentrations of X and Y are given by (8)

$$[X] = [X^o]\, e^{-k_1 t}$$

and

$$[Y] = \frac{k_1}{k_2 - k_1} [X^o] (e^{-k_1 t} - e^{k_2 t})$$

where $[X]$ and $[Y]$ are the concentrations of species X and Y at time t, and $[X^o]$ is the concentration of X at the start of the reaction.

The variation of absorbance with time for the case where X and Y are the only absorbing species can be derived in the following manner:

$$A_X = \varepsilon_X [X]\, l = A^o{}_X\, e^{-k_1 t}$$

$$A_Y = \varepsilon_Y [Y]\, l = \frac{k_1}{k_2 - k_1} \frac{\varepsilon_Y}{\varepsilon_X} A^o{}_X (e^{-k_1 t} - e^{-k_2 t})$$

$$A = A_X + A_Y$$

where A_X and A_Y are the absorbances due to the species X and Y, respectively; ε_X and ε_Y are the extinction coefficients of those species; and l is the path length of the solution. $A^o{}_X$ is the initial absorbance of the solution due to species X and $A^o{}_X = \varepsilon_X [X^o]\, l$. By rearrangements of the above equations one can arrive at the following relationships.

$$A = A^o{}_X\, e^{-k_1 t} + \frac{\varepsilon_Y}{\varepsilon_X} A^o{}_X \frac{k_1}{k_2 - k_1} e^{-k_1 t} - \frac{\varepsilon_Y}{\varepsilon_X} A^o{}_X \frac{k_2}{k_2 - k_1} e^{-k_2 t}$$

$$= A^o{}_X \left(1 + \frac{\varepsilon_Y}{\varepsilon_X} \frac{k_1}{k_2 - k_1}\right) e^{-k_1 t} - A^o{}_X \frac{\varepsilon_Y}{\varepsilon_X} \frac{k_1}{k_2 - k_1} e^{-k_2 t}$$

A system behaving in this way is best analyzed by plotting $\log(A - A_\infty)$ vs. t. Such a curve should be capable of resolution into two straight line components, one having a slope equal to $-k_1/2.303$ and the other

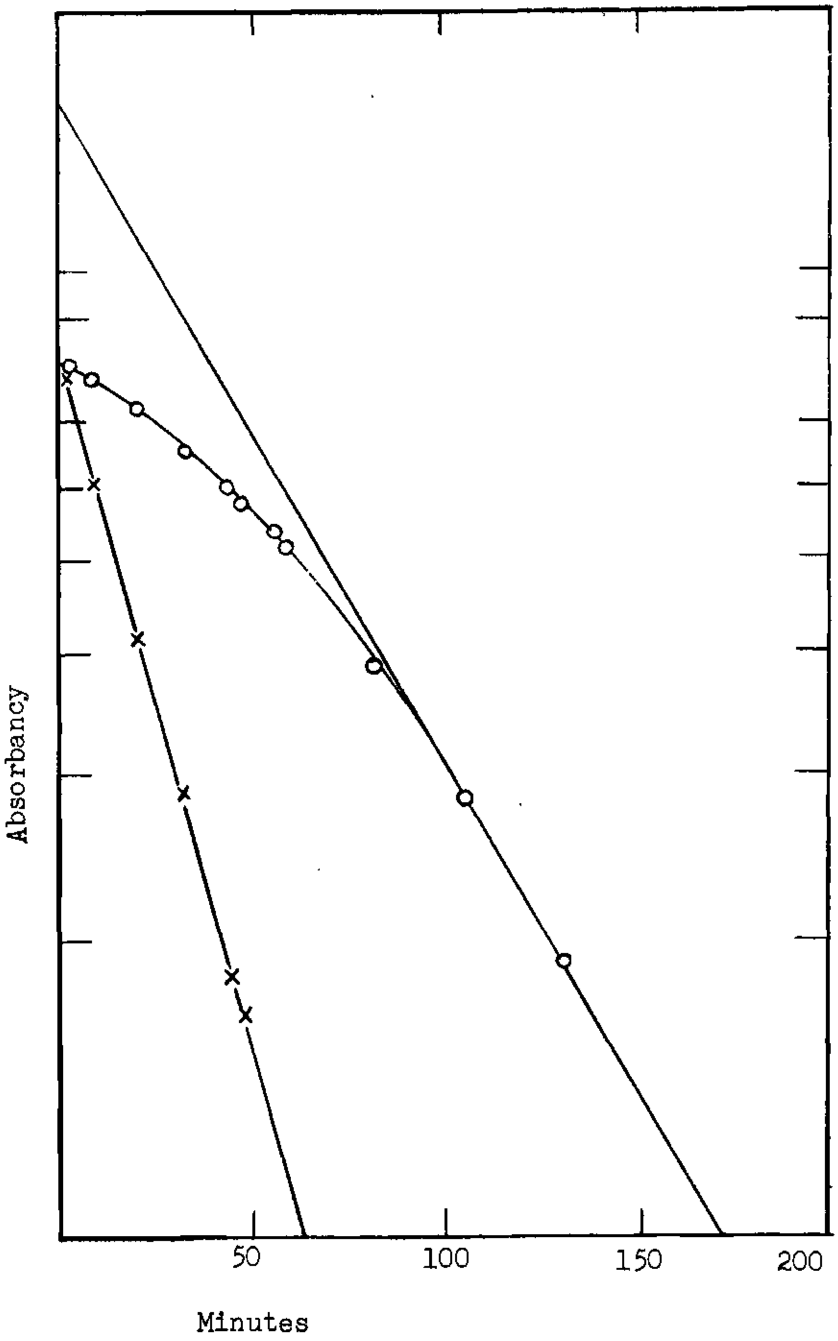

Figure 2. Resolution of an Accelerating Run.

equal to $-k_2/2.303$.

Because after a sufficiently long time the longest lived component determines the slope of the curve, this resolution is easily made by extension of the late straight line section of the plot to t_0, subtraction of the observed curve from the extended line, and plotting the log of the absolute value of the resulting numbers vs. time (Figure 2). In practice this resolution works best when the difference in k_1 and k_2 is large. However, if the curves to be resolved are in reasonably good order, one should be able to determine the half-lives of the components within 15 per cent.

It should be noted that the curve will be convex if k_2 is greater than k_1, and concave if k_2 is less than k_1. Most of the K_2CO_3 and NH_4Cl buffered runs gave curves that could be resolved into two more or less straight line compounds. The curves in the K_2CO_3 buffers were generally concave; those in the NH_4Cl buffers were convex. A clear resolution was not possible in most of the K_3BO_3 buffered runs. An explanation of this is that the components have similar half-times.

pH Range 2-6

Buffer solutions in this pH range are generally made from a combination of sodium acetate and acetic acid. The initial experiments were performed in such a medium. These runs usually gave relatively straight lines in the $\log(A - A_\infty)$ vs. time plots. Because of this good behavior in each individual run, and because of the convenience, use of this medium was continued. The work of Mazeika (3) indicated that the half-time observed depended on the source of the water used in the solutions.

This point was reinvestigated and the results are included in Table 2. Distilled water usually gave half-times markedly shorter than did tap water (Table 2, runs 1 and 2). Deionized water gave values between that of tap and distilled water (Table 2, run 4). The cause of this difference was thought to be the Cl_2 which is present in small amounts in the tap water. Several runs were made where portions of a saturated Cl_2 solution were added to the water used. The Cl_2 concentration in these runs was about 100 times greater than the concentration in tap water. The additional Cl_2 did not seem to make much difference in the rate. Because it did not seem really proper to be adding Cl_2 to a solution just because it gave a longer half-time, it was decided to attempt to improve the quality of the water. It was found that water which had been redistilled from alkaline permanganate solution gave a half-time very close to that of tap water and in the same range as those runs that had excess Cl_2 added. It was decided that water distilled from alkaline permanganate solution would be used for the remaining runs.

Since Sb(III) is known to catalyze the hydrolysis of $SbCl_6^-$ in hydrochloric acid solutions, it was thought that the scattering of the results might arise from the presence of variable amounts of Sb(III) formed by the action of reducing impurities. However, addition of an aliquot of Sb(III) from a stock solution in concentrated HCl to give an Sb(III) concentration of 10^{-4} M did not produce a decrease in the half-time (Table 2, run 26). Apparently, the Sb(III) does not catalyze the hydrolysis in the pH ranges studied here.

In an experiment at pH 4 in which the Sb(V) concentration was relatively large, small colorless crystals were formed on the walls of

Table 2. pH Range 2-6 with Sodium Salts as Buffers.

Run	pH	Half-time (min.)		
12	2.30	5400	distilled water + Cl_2 10.0 M acetic acid	sodium acetate
13	2.95	310	$KMnO_4$ distilled water	sodium monochloroacetate
14	3.00	350	$KMnO_4$ distilled water	sodium monochloroacetate
16	3.30	413	$KMnO_4$ distilled water	sodium monochloroacetate
32	3.89	420	$KMnO_4$ distilled water + Sb(III)	sodium acetate
31	3.90	290	$KMnO_4$ distilled water	sodium acetate
10	4.39	469	distilled water + Cl_2	sodium acetate
30	4.51	450	$KMnO_4$ distilled water	sodium acetate
29	4.53	505	$KMnO_4$ distilled water + Sb(III)	sodium acetate
33	4.55	330	$KMnO_4$ distilled water	sodium acetate
27	4.55	450	$KMnO_4$ distilled water + Sb(III)	sodium acetate
28	4.60	500	$KMnO_4$ distilled water + Cl_2	sodium acetate
33	4.64	290	distilled water	sodium acetate
26	5.00	445	$KMnO_4$ distilled water + Sb(III)	sodium acetate
23	5.20	490	$KMnO_4$ distilled water + Cl_2	sodium acetate
21	5.28	495	$KMnO_4$ distilled water + Cl_2	sodium acetate
9	5.33	505	distilled water + Cl_2	sodium acetate
24	5.40	440	$KMnO_4$ distilled water	sodium acetate
25	5.42	445	$KMnO_4$ distilled water	sodium acetate
7	5.48	560	distilled water + Cl_2 treated stock $SbCl_6^-$ + Cl_2	sodium acetate
6	5.48	315	distilled water + Cl_2 treated stock $SbCl_6^-$	sodium acetate

5	5.49	450	distilled water + Cl 2	sodium acetate
4	5.62	330	deionized water	sodium acetate
2	5.62	430	tap water	sodium acetate
1	5.62	253	distilled water	sodium acetate

the spectrophotometer cell. In a separate experiment larger amounts of this product were produced by further increasing the antimony concentration. The product was identified as the well-known $NaSb(OH)_6 \cdot 1/2\ H_2O$ (Table 1). Because of the low solubility of this salt, micro-crystals might form and affect the behavior of the reacting system. Since potassium antimonate is much more soluble than sodium antimonate, it was decided to use potassium salts rather than sodium salts for all buffer solutions.

The results in the pH range 2-6 using potassium salts are shown in Table 3. The improvement which had been hoped for in the consistency of the data was realized and is apparent in the tabulated results.

The only runs which appear abnormal in this set are the two which contain 1.0 M acetic acid (Table 3, runs 11 and 41). The marked slowing in rate is apparently due to the large percentage of acetic acid in the solutions; in the other solutions the acid content was generally not more than 0.1 M. The same effect is more obvious in a 10 M acetic acid run which had a half-time of 5400 minutes (Table 2, run 12).

If one excludes the runs with high acetic acid content, the rate is independent of the buffer composition and is constant to within experimental error. The average value of the half-time is 425 minutes in

Table 3. pH Range 2-6 with Potassium Salts as Buffers

Run	pH	$t_{1/2}$ (min.)	Comment	Buffer
15	2.42	440	$KMnO_4$ distilled water + Cl_2	potassium monochloroacetate
46	2.80	410	$KMnO_4$ distilled water	potassium phosphate
57	3.15	460	$KMnO_4$ distilled water	potassium phosphate
19	3.15	444	$KMnO_4$ distilled water + Cl_2	potassium acetate
20	3.28	450	$KMnO_4$ distilled water	potassium acetate
11	3.45	660	distilled water + Cl_2 1.0 M acetic acid	potassium acetate
41	3.64	640	$KMnO_4$ distilled water 1.0 M acetic acid	potassium acetate
43	3.89	435	$KMnO_4$ distilled water	potassium phosphate
40	4.53	440	$KMnO_4$ distilled water	potassium acetate
39	4.55	410	$KMnO_4$ distilled water	potassium acetate
52	5.30	390	distilled water	potassium phosphate
36	5.30	400	$KMnO_4$ distilled water	potassium acetate
63	5.50	415	$KMnO_4$ distilled water in a volumetric flask	potassium acetate
38	5.55	415	$KMnO_4$ distilled water	potassium acetate
37	5.55	425	$KMnO_4$ distilled water	potassium acetate
63a	5.55	420	$KMnO_4$ distilled water in a polyethylene bottle	potassium acetate
60	5.63	365	$KMnO_4$ distilled water	potassium acetate

this buffer range.

pH Range 6-8

Buffer solutions in this pH range were made by use of 0.05 F K_2HPO_4, 0.1 F KH_2PO_4, or mixtures of these solutions. The general quality of these runs was not as good as those in the pH 2-6 range. The plots showed some curvature but not enough to allow a resolution of the curve. The results are presented in Table 4. The phosphate buffers from the pH range 2-6 are included in this table. The rate in this pH region appears to change very little with pH, showing only a slight increase in rate as one approaches pH 8.

Table 4. pH Range 6-8. The Phosphate Buffers.

Run	pH	$t_{1/2}$ $SbCl_6^-$ (min.)	$t_{1/2}$ Intermediate (min.)	Container
46	2.80	410	---	silica cell
57	3.15	460	---	silica cell
43	3.89	435	---	silica cell
52	5.32	390	---	silica cell
47	6.30	380	---	silica cell
48	7.20	387 388	--- ---	silica cell
49	7.51	415 410	--- ---	silica cell
53	7.80	360 350	---	silica cell
50	8.05	354 374	--- ---	silica cell

pH Range 8-9.3

The buffers in this pH range were prepared by addition of KOH to H_3BO_3 solutions. Plots of $\log(A - A_\infty)$ vs. time showed an acceleration as time increased in each of the runs. Some of the convex curves could be resolved into two straight line components. The results obtained from the borate buffered runs are presented in Table 5. While the values of the half-times are highly irregular, one can see a trend toward a faster rate as the pH increases.

Table 5. pH Range 8-9.3 . The Borate Buffers.

Run	pH	$t_{1/2}$ $SbCl_6^-$ (min.)	$t_{1/2}$ Intermediate (min.)	Container
70	8.90	332	---	volumetric flask
67	9.18	100	34	silica cell
		370	---	volumetric flask
62	9.25	54	347	volumetric flask
		32	302	polyethylene
61	9.25	53	290	volumetric flask
66	9.30	227	---	volumetric flask

pH Range 9.3-10.5

NH_4OH - NH_4Cl buffers were used to attain this pH range. In each run curvature was observed, and resolution was possible in most cases. The data for these runs are presented in Table 6. There is in general a more rapid acceleration in the hydrolysis rate with pH than in the more acidic ranges. It is reasonable to assume that the reaction in this pH range is proceeding by two paths; one a pH independent mechanism, and the

Table 6. pH Range 9.3-10.5. The Ammonium Buffers.

Run	pH	$t_{1/2}$ $SbCl_6^-$ (min.)	$t_{1/2}$ Intermediate (min.)	Container
78	9.30	185	53	silica cell
		185	80	volumetric flask
77	9.60	88	43	silica cell
		90	47	volumetric flask
82	9.97	52	17	silica cell
		55	22	volumetric flask
80	10.00	62	33	silica cell
		68	34	volumetric flask
79	10.00	40	18	silica cell
		41	22	volumetric flask
74	10.01	13	8	silica cell
		16.2	9	volumetric flask
81	10.01	46	17	silica cell
92	10.07	32.5	14.5	silica cell
		40	----	volumetric flask
		37.5	16	paraffin-silica cell
91	10.20	21	9	silica cell
		25	10.5	volumetric flask
		20	6.5	paraffin-silica cell
75	10.49	20.2	9.8	silica cell
		14.8	8.0	volumetric flask
83	10.68	12	4.8	silica cell

other a base-catalyzed mechanism. If this assumption is correct, the rate would most probably be given by an expression of the form

$$\text{Rate} = (k_c + k_2\,[OH^-]^n)\,[SbCl_6^-]$$

where the expression in parenthesis is equal to the pseudo first-order constant, k, observed in a given experiment. The constants, k and k_c, are related to the half-times in the following way:

$$k = {}^{0.693}/_{t_{1/2}} \qquad \text{and} \qquad k_c = {}^{0.693}/_{t_{1/2}c}$$

The quantity $t_{1/2}c$ is the average value for the half-time of the runs in the pH range where the rate was independent of pH. Since $t_{1/2}c$ = 425 minutes, $k_c = 1.63 \times 10^{-3}$ min.$^{-1}$.

The relation

$$k = k_c + k_2\,[OH^-]^n$$

can be tested by plotting log(k-k_c) vs. pH. Such a plot is shown in Figure 3. For resolutions of this type an error of 10-15 per cent in k is not unreasonable. The uncertainty in (k-k_c) corresponding to a 10 per cent error in k is indicated on certain of the runs in Figure 3 in order that one can see the size of such an error relative to the graph scale.

pH Range 10.5-11

Buffers in this pH range were prepared by the use of K_2CO_3 solutions. Concave curvature (deceleration) was observed with the runs which used carbonate as buffers. The data for these runs are given in Table 7. The rate is increasing as the pH increases and becomes too fast to measure with convenience at about pH 11. These runs are included in Figure 3, the plot of $\log(k-k_c)$ vs. pH.

For those runs which could be resolved into two components, the rates of disappearance of the intermediate could not be treated in a manner completely analogous to that of Figure 3, since there was no evidence for a pH independent path. In this case k is plotted vs. pH (Figure 4). Note that the k in Figure 4 is the k of the intermediate. For the more easily resolved runs a 10 per cent error is a reasonable estimate of the uncertainty. An uncertainty of this amount is indicated for some of the runs in order that one may see the magnitude of such an error.

Table 7. pH Range 10.5-11. The Carbonate Buffers.

Run	pH	$t_{1/2}$ $SbCl_6^-$ (min.)	$t_{1/2}$ Intermediate (min.)	Container
93	10.55	6	50	silica cell
		28	140	volumetric flask
		6	none	paraffin-silica cell
85	10.70	13	77	silica cell
		29	170	volumetric flask
90	10.90	2.6	19	silica cell
		3.0	18	volumetric flask
		6.25	none	paraffin-silica cell

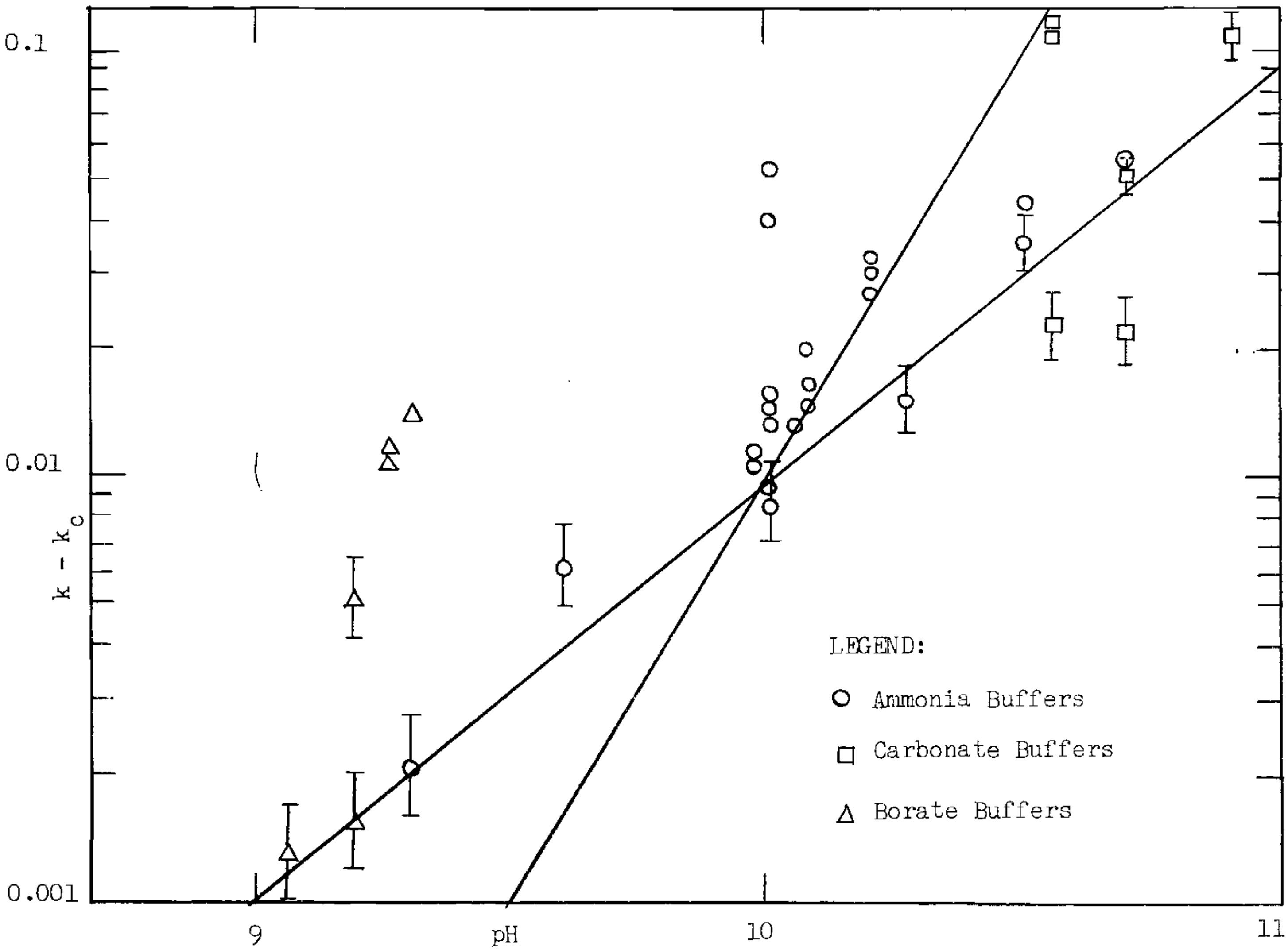

Figure 3. Plot of $(k - k_c)$ vs. pH.

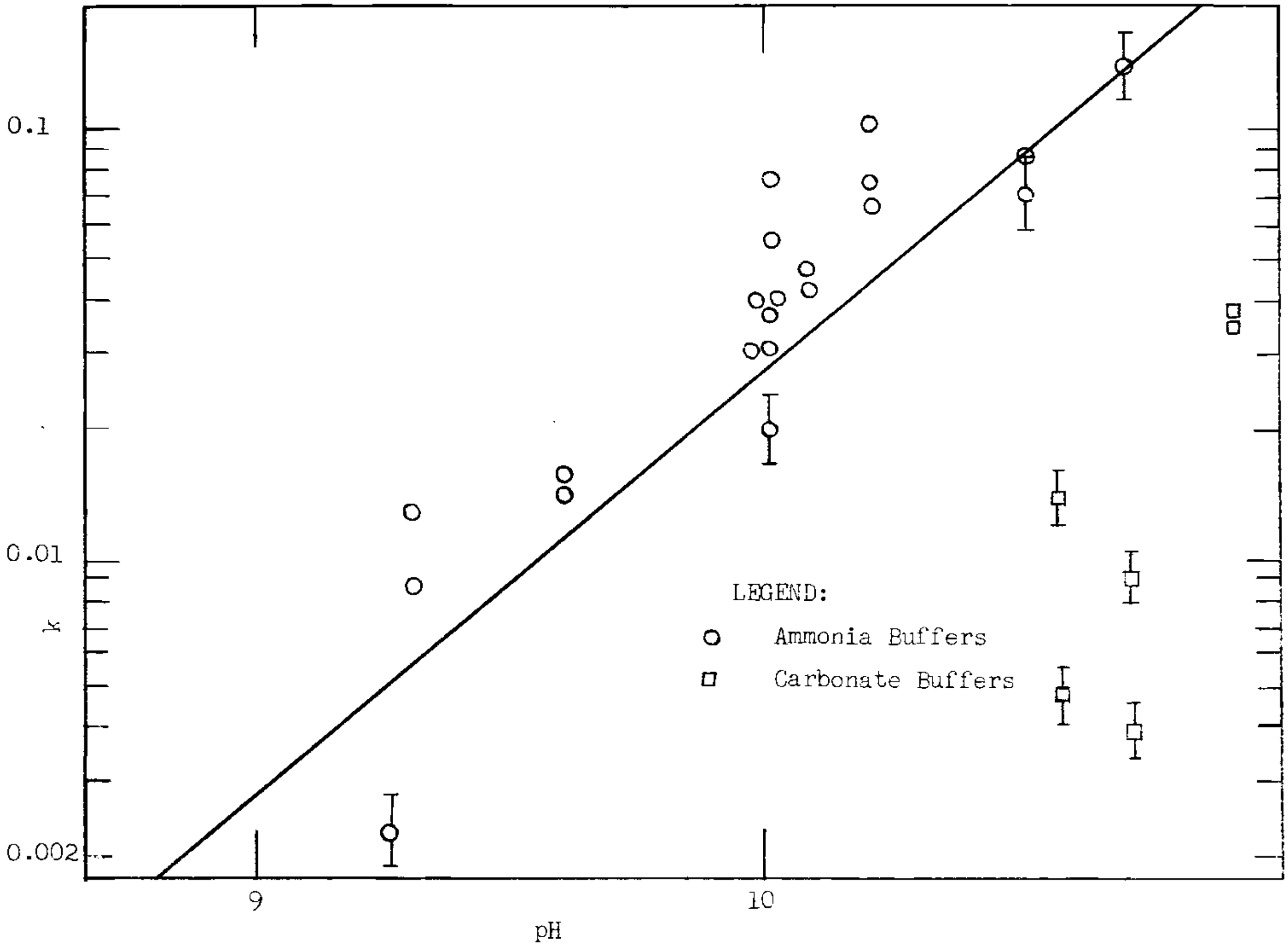

Figure 4. Plot of log k vs. pH for the Intermediate.

CHAPTER IV

CONCLUSIONS

The hydrolysis of the $SbCl_6^-$ ion apparently occurs by at least two mechanisms in the pH region studied. One of these is independent of pH and is the dominant one in pH 2-8 solutions. At pH above 9 there is apparently a hydroxide catalyzed path which is the predominant reaction.

Figure 3 is a plot of $\log(k-k_c)$ vs. pH, k and k_c being the rate constant for the combined mechanisms and the pH independent mechanism, respectively. The great scatter of the data points reflects the "cell effect" mentioned earlier. Lines of slope 1 and slope 2 have been drawn on the figure. It is obvious that the line with slope 1 not only fits the data better, but has most of the scatter above the line indicating the presence of catalysis. This line corresponds to the equation

$$\log(k-k_c) = \log(9.3 \times 10^{-13}) + \mathrm{pH}$$

Taking this line to be representative of the base catalyzed path for the reaction, the best quantitative rate law for the results is

$$\mathrm{Rate} = (k_c + k_2[OH^-])\ [SbCl_6^-],$$

where $k_c = 1.63 \times 10^{-3}$ min.$^{-1}$ and $k_2 = 93$ min.$^{-1}$ M^{-1}, at 25°C.

In solutions containing hydrochloric acid and lithium chloride, Neumann and Ramette (1) observed a rate law of the form

$$\mathrm{Rate} = (k_3 + k_4[H^+])\ [SbCl_6^-].$$

The constant k_3 is a measure of the acid independent portion of the rate. They obtained values of 5.3×10^{-3} min.$^{-1}$ in 9 M Cl^-, and 3.9×10^{-3} min.$^{-1}$ in 6 M Cl^-. These values are consistent with the value of 1.63×10^{-3} min.$^{-1}$ obtained for k_c in the 0.1 M acetate buffers.

In each reaction at pH > 9 there appears to be an intermediate that has an absorption maximum near that of $SbCl_6^-$. The best support for the presence of an intermediate is the fact that the plots of $\log(A - A_\infty)$ vs. time could be resolved, and that some of the curves were concave. Catalysis by a product would give only convex curvature.

Figure 4, the plot of log k vs. pH for the proposed intermediate, suggests that for a given buffer solution the rate is pH dependent. Despite the scatter of the data, there is sufficient difference between the ammonium and carbonate buffers to indicate there is some dependence upon the kind of buffer used. There are two possible interpretations to account for the differences: (1) there is one intermediate that reacts differently in the two buffers, or (2) there are two different intermediates. Although no convincing evidence can be presented about the identity of the intermediate or intermediates, some arguments can be made about possible structures.

In the acid solutions the results obtained are consistent with a step-wise hydrolysis of $SbCl_6^-$ to $Sb(OH)_6^-$ with only the first step being measurable.

$$\mathrm{SbCl_6^-} \xrightarrow{k} \mathrm{SbCl_5OH)^-} \xrightarrow{\text{fast}} \mathrm{SbCl_4(OH)_2^-} \xrightarrow{\text{fast}}$$

$$\mathrm{SbCl_3(OH)_3^-} \xrightarrow{\text{fast}} \mathrm{SbCl_2(OH)_4^-} \xrightarrow{\text{fast}} \mathrm{SbCl(OH)_5^-} \xrightarrow{\text{fast}}$$

$$\mathrm{Sb(OH)_6^-}$$

The intermediate that appears in the basic solutions cannot be any of the ions above, as there is no reason to expect base to prolong their lifetimes.

Since all of the ions above, with the exception of $SbCl_6^-$, are potentially acidic, species such as $SbCl_5O^=$, $SbCl_4(OH)O^=$, $SbCl_3(OH)_2O^=$, <u>etc</u>., are probably present. However, each of these would react more rapidly than the corresponding conjugate acid. Hence, it is unlikely that the long-lived intermediates are of this form.

If the individual steps proceed by an SN-1 mechanism, and the evidence in acid solution suggests this (3), five-coordinate intermediates, such as $SbCl_5$, $SbCl_4O^-$, <u>etc</u>., are present. Although these would be expected to be short-lived, some one of them might be stabilized for reasons unknown. Such a single intermediate would react differently in the ammonium and carbonate buffers.

A more likely possibility is that the five-coordinate intermediate is short-lived, and that it forms the observed intermediates by its reaction with the medium. Formation of the observed intermediate would be a simple acid-base reaction in the Lewis sense. Hence, in the carbonate buffers the intermediate might be $SbCl_5(CO_3)^=$ or $SbOCl_4(CO_3)^{\equiv}$. Such species are very reasonable. The ability of $SbCl_5$ to form adducts with oxygen containing molecules is verified by a variety of examples (9). The adducts most closely resembling the postulated intermediates are those with dimethyl carbonate and diethyl carbonate (10).

Although in principle the same argument can be applied to the ammonium buffers, <u>i</u>. <u>e</u>., suggesting $SbCl_5(NH_3)$ or $SbOCl_4(NH_3)^-$ as the intermediate, there is less supporting evidence. Although there are many examples of Sb-O bonds in $SbCl_5$ adducts, there are few examples with Sb-N bonds. Substances of formulas $SbCl_5 \cdot 3NH_3$, $SbCl_5 \cdot 4NH_3$, and $SbCl_5 \cdot 6NH_3$ have been recorded in the literature (11, 12), but the work was done in the years 1830-1861 and has not been repeated since then. The compounds $SbCl_5 \cdot C_5H_5N$ and $2SbCl_5 \cdot 3C_5H_5N$, reported in 1931 (13), are the only known adducts containing Sb-N bonds.

Recognition that specific effects occur in the carbonate buffers leads to the conclusion that in future experiments with basic solutions care must be exercised to exclude or control the carbonate ion. Some of the erratic behavior with the borate buffers may have been due to varying and unknown amounts of carbonate.

In an attempt to learn more about this intermediate, a stream of dry air was passed over liquid $SbCl_5$ and then bubbled through various buffers. The spectrum of such a solution usually showed an absorption peak at either 2700 A or 2900 A. The material causing the peak at 2700 A is assumed to be $SbCl_6^-$. The material causing the peak at 2900 A was formed only in basic buffers and disappeared immediately if the solution was acidified. This behavior is consistent with the non-appearance of the intermediate in the kinetic runs in acid buffers. Since most of the runs that were non-linear were the ones with a higher Sb(V) concentration, the curvature was found in lines composed chiefly of readings taken at 3000 A. Thus an intermediate with an absorption maximum at 2900 A could be, for practical purposes, hidden behind the huge $SbCl_6^-$ peak and still have appreciable absorption at 3000 A.

The end product of the hydrolysis, except in strong acid, is apparently $Sb(OH)_6^-$. This is demonstrated by the analyses of the solid which precipitated from a pH 4 solution buffered with acetate and the solid from a pH 9 solution buffered with carbonate which established the solid as $NaSb(OH)_6 \cdot 1/2H_2O$ in both cases (Table 1). Condensation of the $Sb(OH)_6^-$ in the acid region is concentration dependent. However, at the low Sb(V) concentrations used in these experiments, only the monomeric species is present (4).

In retrospect, the precipitation of $NaSb(OH)_6$ is not surprising once it is recognized that $Sb(OH)_6^-$ is the end product of the hydrolysis. The solubility of $NaSb(OH)_6$ is 0.0012 moles per liter of water (14), indicating a solubility product constant of $1.4 \cdot 10^{-6}$. Thus, in the buffer solutions containing 0.1 M sodium acetate, precipitation of $NaSb(OH)_6$ should be thermodynamically possible whenever hydrolysis has produced $SbCl_6^-$ to the extent of 10^{-5} M. Since the initial concentration of $SbCl_6^-$ was generally about 10^{-3} M, formation of solid $NaSb(OH)_6$ is possible after one per cent of the $SbCl_6^-$ has completed hydrolysis to $Sb(OH)_6^-$. Viewed in this way, the surprising feature is that solid crystals were not observed more frequently. In contrast, $KSb(OH)_6$ has a solubility of 0.11 moles per liter (14) and so one would expect no precipitation of $KSb(OH)_6$ at the concentrations studied. The improved behavior when potassium salts were used supports the feeling that the presence of small crystals of $NaSb(OH)_6$ in the runs buffered with sodium salts was real and should be avoided.

The reaction is obviously sensitive to the surfaces in contact with the reaction medium. Whether this effect is dependent on the amount of surface available or the type of surface is not clearly established. The surface sensitivity of the reaction can also be connected with the general lack of reproducible data in the runs with sodium salts used as buffers. Obviously, if crystals of $NaSb(OH)_6$ existed in the solution, the type and amount of surface would change markedly.

It would be of some interest to study further the reaction and attempt to characterize the proposed intermediate. In connection with this, one could study the species that result when the $SbCl_5$ vapors are bubbled into the various buffers. An effort to reproduce selected runs with freshly prepared stock solutions of $SbCl_6^-$ would be interesting as Sb(V) solutions are known to show aging effects in lower concentrations of hydrochloric acid.

78

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[*] Abbreviations here follow the form in Chemical Abstracts, 55, 1 J (1961).