

edge, or a face of the anion octahedron. The value of R for dimethyl sulfoxide is slightly larger than 4 Å. This indicates that in this solvent the cation approaches the face, since other configurations do not allow enough space for the electron clouds. The value of R for D_2O is 7–8 Å. This clearly suggests that regardless of configuration, there is at least one layer of water molecules between the counterions in the ion pair; *i.e.*, the cation lies outside the second coordination sphere of the anion. In 30% D_2O –70% dimethyl sulfoxide, the distance is intermediate, and this suggests an equilibrium between “contact” and “solvent-separated” ion pairs.

The values of R for the other anions in Table III differ by about 1 Å from $M(CN)_6^{3-}$. This is consistent with their difference of 1 Å in radius from $M(CN)_6^{3-}$, which suggests similar configurations for these anions.

The variation in R over the temperature range 10–75° is quite small (about 1 Å maximum) and suggests that the ion pair undergoes only minor configuration changes in this temperature range.

The previous studies^{2,4} involved use of tetraalkylammonium ions with chain lengths up to *n*-butyl. As the chain length increases and as concentration increases, the greater will be the probability of micelle formation.¹⁰ In the present study, both the length of the alkyl chain (ethyl) and the concentration of the cation (0.05 *M*) are such that it is unlikely that micelles are present.¹⁰ It was also observed that when the concentration of the cation is increased fivefold, the

(10) C. W. Davies, “Ion Association,” Butterworth Inc., Washington, D. C., 1962, pp 117–127.

observed interaction parameter ratios are unchanged within experimental error, indicating that micelles are also not present in this system even at the higher concentrations.

The Solomon relaxation model⁵ is not strictly speaking applicable to the present case. In these systems with strongly anisotropic g factors, T_2 will have an angular dependence. This dependence could be taken into account by using the Solomon treatment if g -factor components in solution were known. Unfortunately, neither the components themselves nor the extent to which ion pairing influences the components is known, so the effect cannot be explicitly accounted for in our calculations. However, examination of the Solomon equations indicates that inclusion of g -factor anisotropy would result in an expression which would be the sum of a large number of terms, each containing the geometric factor r^{-6} . If the expression excluding the geometric factor has the same or approximately the same numerical value for both methyl and methylene protons (when averaged over all configurations), then eq 3 will be at least approximately correct. Since the ion-pair model involves many configurations and since the cation itself is highly symmetric, the approximation is probably justified. Certainly the reasonable results of the calculations support the approximation.

Acknowledgments. We thank Mr. Raymond F. Novak for synthesizing some of the compounds used in this study. Support of the Office of Water Resources Research through Grants A-012-MO and A-022-MO is gratefully acknowledged.

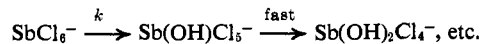
Hydrolysis and Nucleophilic Substitution of the Hexachloroantimonate(V) Ion in the pH Range 2–12

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Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia. Received October 21, 1968

Abstract: The hydrolysis reaction of $SbCl_6^-$ has been investigated in the pH range 2–12. The final product of the reaction is the $Sb(OH)_6^-$ ion. The rate of the reaction has been measured by use of a spectrophotometric method in acetate, phosphate, borate, ammonia, and carbonate buffers. In the acid region the rate is independent of pH. In the basic region the reaction is catalyzed by OH^- and by the basic component of the buffer. In ammonia buffers at ionic strength = 0.10, the pseudo-first-order rate constant is given by $k = k_0 + k_{OH^-}[OH^-] + k_{NH_3}[NH_3]$, where $k_0 = 2.74 \times 10^{-5} \text{ sec}^{-1}$, $k_{OH^-} = 1.56 \text{ sec}^{-1} M^{-1}$, and $k_{NH_3} = 8 \times 10^{-5} \text{ sec}^{-1} M^{-1}$. Intermediates of measurable lifetime are formed with the buffer bases. The behavior in basic solution provides a good example of an S_N2 mechanism in the substitution reactions of an octahedral complex.

In hydrochloric acid solution the hexachloroantimonate(V) ion, $SbCl_6^-$, undergoes hydrolysis at a measurable rate.² The observations are consistent with the interpretation that the hydrolysis occurs stepwise, with only the rate of the first step being measurable.



(1) Taken in part from a thesis submitted by S. B. Willis in partial fulfillment of the requirements for the M.S. degree, June 1966.

(2) H. M. Neumann, *J. Am. Chem. Soc.*, **76**, 2611 (1954).

The final product of the hydrolysis depends on the H^+ and Cl^- concentrations, but in any case is an equilibrium mixture of complexes of type $Sb(OH)_xCl_{6-x}^-$.

Quantitative measurements of the rate were made by Neumann and Ramette.³ Using a spectrophotometric method they determined rates under conditions where the reaction was pseudo first order; *i.e.*, rate = $k_h \cdot [SbCl_6^-]$. The reaction was accelerated by hydrogen ions. At a total chloride concentration of 6 *M*, the

(3) H. M. Neumann and R. W. Ramette, *ibid.*, **78**, 1848 (1956).

pseudo-first-order rate constant, k_b , was equal to $(6.5 + 1.3[\text{H}^+]) \times 10^{-5} \text{ sec}^{-1}$ and at a total chloride concentration of 9 M it was $(8.8 + 2.7[\text{H}^+]) \times 10^{-5} \text{ sec}^{-1}$. Thus the rate includes both a pH-dependent and a pH-independent term. They also observed that Sb(III) accelerated the reaction and suggested that SbCl_3 was the active species.

As part of a thorough study of the kinetics of electron exchange between Sb(III) and Sb(V) in hydrochloric acid, Bonner and Goishi⁴ reported measurements of the rate of hydrolysis of SbCl_6^- . Their data on the hydrolysis were obtained from both spectrophotometric measurements and from the exchange reaction studies. The results are in very good agreement with the earlier work.³

The work reported here began as an attempt to measure the rate of hydrolysis of SbCl_6^- in the pH 2–12 region. Measurements in basic media were of particular interest, since there seemed to be a good possibility of an SN2 mechanism. Such displacement mechanisms are uncommon for octahedral complexes, and it has been suggested⁵ that examples might be found more readily among the complexes of nontransition elements. Often data which are consistent with an SN2 mechanism can be explained in other ways.⁶ The relative simplicity of the SbCl_6^- ion, compared to some of the other ions studied, does not allow for such ambiguity. Difficulties encountered and complexities observed in the present work made it clear that in addition to hydrolysis other reactions are occurring. The data indicate that these other reactions are substitution reactions of the SN2 type.

Experimental Section

Final Product of the Reaction. All previous work^{2–4} indicated that the final product in acidic chloride solutions is an equilibrium mixture of ions of the type $\text{Sb}(\text{OH})_x\text{Cl}_{6-x}^-$. There was no prior evidence as to the identity of the final product in basic solution, although $\text{Sb}(\text{OH})_6^-$ might be expected. By allowing a sufficiently large amount of SbCl_6^- to hydrolyze in a $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ buffer solution (pH 5), a white crystalline precipitate was obtained. Analyses indicated the precipitate to be $\text{NaSb}(\text{OH})_6 \cdot 0.5\text{H}_2\text{O}$. A similar treatment of a Na_2CO_3 buffer also resulted in the formation of the same white precipitate.

Anal. Calcd for $\text{NaSb}(\text{OH})_6 \cdot 0.5\text{H}_2\text{O}$: Sb, 47.5; H, 2.76; C, 0.00. Found: Sb, 47.5; H, 2.79; C, 0.33.

Kinetic Experiments. The SbCl_6^- ion exhibits a strong absorption peak in the region of 270 m μ . The actual position of the maximum is dependent on the medium; in concentrated HCl² the maximum is at 272 m μ , and in 7 M HCl⁴ it is at 271 m μ . In 2×10^{-4} M HCl we have observed the peak to be at 268.5 m μ . These values are sufficiently displaced from the peak of $\text{SbCl}_6^-(\text{OH})^-$, which appears at approximately 252 m μ .² Because none of the known or expected hydrolysis products has appreciable absorption in this region a spectrophotometric method is feasible. In the present work the hydrolysis reaction of SbCl_6^- was followed on a Beckman Model DU spectrophotometer using fused silica cells having a light path of 1 cm.

Buffer solutions were prepared as follows. For acetate and phosphate systems, the appropriate acid was added to a solution of $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$, KH_2PO_4 , or K_2HPO_4 . For monochloroacetate and borate systems, KOH was added to a solution of the appropriate acid. For carbonate buffers, mixtures of KHCO_3 , and K_2CO_3 were used. For ammonia buffers, mixtures of NH_4Cl and aqueous NH_3 were used. In most buffer solutions the concentration of the positive ion (K^+ and/or NH_4^+) was maintained as close as possible

(4) N. A. Bonner and W. Goishi, *J. Am. Chem. Soc.*, **83**, 85 (1961).

(5) R. G. Pearson, D. N. Edgington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., 1967, pp 234–238.

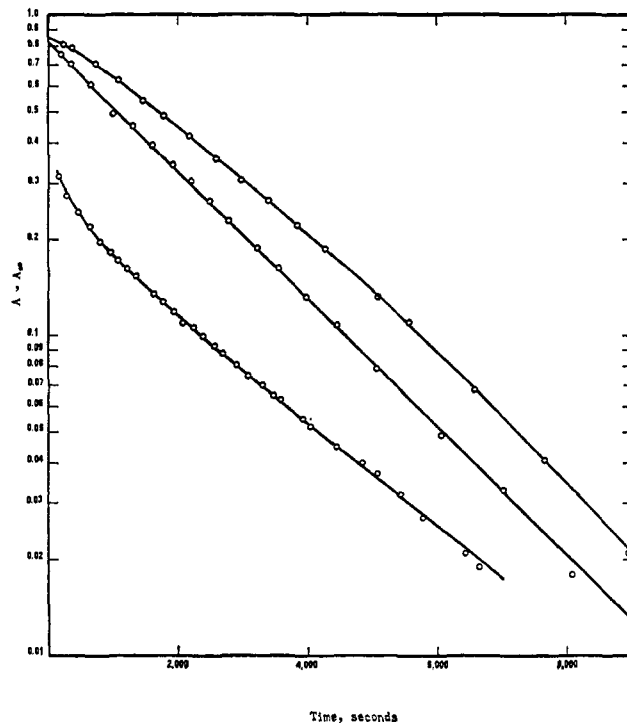


Figure 1. Examples of kinetic behavior in hydrolysis of SbCl_6^- : upper curve, $[\text{NH}_4^+] = 0.1024$, pH 10.29, λ 270 m μ ; middle curve, $[\text{NH}_4^+] = 0.0124$, pH 10.83, λ 270 m μ ; lower curve, 0.25 M K_2CO_3 , 280 m μ (absorbancy values plotted are one-half the values observed).

to 0.1 M. Measurements of pH were made with a Beckman Zeromatic pH meter.

Stock solutions of Sb(V) in concentrated HCl were prepared by transferring Baker and Adamson reagent grade SbCl_5 to a 100-ml volumetric flask and diluting with concentrated HCl. Three different stock solutions were used at various times; spectrophotometric measurements showed their concentrations to be 0.12, 0.45, and 0.53 M.

To begin a kinetic experiment, a small volume from one of the stock solutions was injected into a solution of the desired composition. In all experiments in ammonia buffers 20 μl . of the 0.53 M SbCl_6^- stock solution was injected into 100 ml of buffer solution. In other experiments the aliquot ranged in volume from 20 to 100 μl .

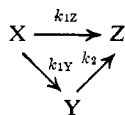
After thorough mixing, a portion of the solution was transferred to a spectrophotometer cell. During the reaction the cells were maintained at a constant temperature ($25.0 \pm 0.1^\circ$) by means of a water jacket, through which water from a thermostated bath was pumped. Initial concentrations of SbCl_6^- ranged from 1×10^{-4} to 5×10^{-4} M. Absorbance readings at these concentrations are convenient in the wavelength region 260–300 m μ . Readings were taken at time intervals dependent on the rate, and at several wavelengths. One wavelength was selected to give an initial absorbance in the 0.7–0.9 range; other wavelengths had smaller initial values. For the faster reactions data were taken at one or two wavelengths and for the slower reactions at four wavelengths at 10-m μ intervals. For the faster reactions, data were taken as often as every 90 sec. Usually five to ten readings were taken per half-time.

Analysis of Data for Individual Kinetic Experiments. In most cases the reaction was first order or pseudo first order as shown by the linearity of plots of $\log(A - A_\infty)$ vs. time, where A is the absorbancy at time t . The rate constants for the reactions were determined from the slopes of these plots. One such run is shown in Figure 1.

In several of the runs in basic solution the plots of $\log(A - A_\infty)$ vs. time were not linear. In some cases the curves were convex, and in other cases they were concave. An example of each type is shown in Figure 1.

Either behavior can be accounted for in a given reaction if there is an intermediate of measurable lifetime which has an appreciable absorbancy at the wavelength used. If such is the case, the inter-

mediate will probably be disappearing by a first-order or pseudo-first-order reaction. Assuming the reaction follows the pattern



the concentrations of X and Y are given by

$$[X] = [X]_0 e^{-k_1 t}$$

and

$$[Y] = \frac{k_{1Y}}{k_2 - k_1} [X]_0 (e^{-k_1 t} - e^{-k_2 t})$$

where $k_1 = k_{1Z} + k_{1Y}$, and $[X]_0$ is the concentration of X at the start of the reaction.

For the case in which X and Y are the only absorbing species

$$A = A_X + A_Y = \epsilon_X [X]l + \epsilon_Y [Y]l$$

where A is the absorbancy of the solution; A_X and A_Y are the absorbancy due to species X and Y, respectively; ϵ_X and ϵ_Y are the molar absorbancy indices of those species; and l is the path length of the solution.

The variation of A with time is given by

$$A = A_0 \left(1 + \frac{\epsilon_Y}{\epsilon_X} \frac{k_{1Y}}{k_2 - k_1} \right) e^{-k_1 t} - A_0 \frac{\epsilon_Y}{\epsilon_X} \frac{k_{1Y}}{k_2 - k_1} e^{-k_2 t}$$

where A_0 is the initial absorbance of the solution due to X. 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 with a slope 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 extrapolation of the late straight-line section of the plot to $t = 0$, subtraction of the observed curve from the extrapolated line, and plotting the log of the absolute value of the resulting numbers vs. time. In practice, this resolution works best when the difference in k_1 and k_2 is large.

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 . The curves obtained, whether convex or concave, resolved nicely into two straight-line components, supporting the suggested interpretation.

Results

General Observations. The initial experiments were performed in buffer solutions made from a combination of sodium acetate and acetic acid. These runs usually gave straight lines in the $\log(A - A_\infty)$ vs. time plots. In spite of this good behavior in each individual run, it was found difficult to obtain reproducibility from one run to another. This erratic behavior is apparently due to the presence of sodium ions, since it ceased to be a difficulty when potassium salts were used.

Convex curvature, like that in the upper curve of Figure 1, can occur whenever the product of the reaction is a catalyst for the reaction. This possibility was investigated in experiments in which enough KSb(OH)_6 was added to saturate the solution. The rate was unaffected, indicating that some other effect must be causing the curvature. The assumption of the presence of intermediates as the cause is consistent with all the data obtained and explains both convex and concave curvature.

Reaction in pH Range 2-8. The results in the pH range 2-8 using potassium salts are shown in Table I. In the range 2-6 the rate is independent of the buffer composition and is constant to within experimental error. The average value of the rate constant is $(2.74 \pm 0.12) \times 10^{-5} \text{ sec}^{-1}$ in this buffer range.

Table I. Rates of Hydrolysis in the pH Range 2-8 at 25°, $[\text{K}^+] = 0.1 \text{ M}$

pH	$k \times 10^5, \text{ sec}^{-1}$	Buffer
2.42	2.65	Monochloroacetate
2.80	2.84	Phosphate
3.15	2.54	Phosphate
3.15	2.63	Acetate
3.28	2.59	Acetate
3.89	2.68	Phosphate
4.53	2.65	Acetate
4.55	2.84	Acetate
5.30	2.98	Phosphate
5.30	2.91	Acetate
5.50	2.80	Acetate
5.55	2.78	Acetate
6.30	3.07	Phosphate
7.20	3.01	Phosphate
7.51	2.82	Phosphate
7.80	3.28	Phosphate
8.05	3.20	Phosphate

Since Sb(III) is known to catalyze the hydrolysis of SbCl_6^- in hydrochloric acid solution,³ a few experiments were performed in which Sb(III) , added as an aliquot from a stock solution in concentrated HCl, was present in the reaction mixture at a concentration of 10^{-4} M . Experiments were performed in acetate solutions at pH 3.89, 4.55, and 5.00. In no case was there an acceleration in rate.

The linearity of the plots of $\log(A - A_\infty)$ vs. t was not as good in phosphate buffers at pH 6-8 as that in the pH 2-6 range. The plots showed some curvature but not enough to allow resolution of the curves. The rate constant changes only little with pH, showing a slight increase as the pH increases.

Reaction in Ammonia Buffers. In experiments with ammonia-ammonium chloride buffers two types of behavior were observed. In solutions of low NH_4^+ concentration ($\lesssim 0.01 \text{ M}$) good first-order behavior was observed; there was no deviation from linearity as the absorbancy decreased over a factor of at least 10. In solutions in which NH_4^+ was 0.1 M , the first-order plots were convex and could be resolved into two linear components. The accuracy of the k 's obtained from the resolution is, of course, dependent on establishing the slope in the late stages of the reaction. The difficulties associated with this procedure should be apparent from the convex curve shown in Figure 1. For cases in which resolution of the curve was necessary, an uncertainty of 10-15% in the k 's is not unreasonable. It is worth noting, however, that one is more likely to get a value of k_1 that is too small rather than one which is too large.

Values of k_1 and k_2 obtained from the slopes are given in Table II. In the case of two-component curves the intercepts can be used to calculate values of $(\epsilon_Y/\epsilon_X)k_{1Y}$. These values are also given in Table II. Two effects on k_1 are immediately apparent from these results; there is an acceleration of rate as the pH increases and as the salt concentration increases.

Reaction in Borate and Carbonate Buffers. A few reactions were performed at pH 8-9.3 using solutions prepared by addition of KOH to H_3BO_3 solutions. Plots of $\log(A - A_\infty)$ vs. time were convex and could be resolved into two straight-line components. Although no systematic study was made, values of k_1 increase as the pH increases.

Table II. Reaction Rates in Ammonia Buffers at 25°, $[\text{SbCl}_6^-]_0 = 1.1 \times 10^{-4} M$

pH	$[\text{NH}_4^+], M$	$[\text{NH}_3], M$	$k_1 \times 10^5, \text{sec}^{-1}$	$(\epsilon_Y/\epsilon_X)k_{1Y} \times 10^5, \text{sec}^{-1}$	$k_2 \times 10^5, \text{sec}^{-1}$
9.55	0.0034	0.0076	4.94
9.83	0.0124	0.048	8.89
10.09	0.0124	0.098	13.7
10.82	0.0124	0.50	45.5
11.72	0.0124	5.0	159
9.84	0.0124 ^a	0.048	13.4
10.14	0.0124 ^a	0.098	24.1
10.86	0.0124 ^a	0.50	91.9
11.17	0.0124 ^a	1.0	114
11.90	0.0124 ^a	5.0	309
8.99	0.1024	0.048	4.53	0.33	8.53
9.27	0.1024	0.098	6.42	0.98	13.7
9.95	0.1024	0.50	21.1	3.4	36.6
10.29	0.1024	1.0	46.9	21	77.0
11.02	0.1024	5.0	126	94	199

^a Also contains 0.0900 M K⁺. ^b Data taken at 270 mμ.

Several reactions were performed in carbonate buffers in the pH region 9.5–12. When nonlinearity was observed the curvature was concave, and the curves could be resolved into two components. Values of k_1 increase as the pH increases, and the rate becomes too fast to measure with convenience at about pH 11.

Discussion

Hydrolysis in Acid Solution. The hydrolysis of the SbCl_6^- ion apparently occurs by at least two mechanisms over the entire pH region studied. One of these is independent of pH and is the dominant one in pH 2–8.

In solutions containing hydrochloric acid and lithium chloride, Neumann and Ramette³ observed a rate law of the form

$$\text{rate} = \{k_0 + k_H[\text{H}^+]\}[\text{SbCl}_6^-]$$

The constant k_0 is a measure of the acid-independent portion of the rate. They obtained values of $8.8 \times 10^{-5} \text{ sec}^{-1}$ in 9 M Cl⁻, and $6.5 \times 10^{-5} \text{ sec}^{-1}$ in 6 M Cl⁻. These values are consistent with the value of $2.74 \times 10^{-5} \text{ sec}^{-1}$ obtained for k_0 in the 0.1 M acetate buffers.

The end product of the hydrolysis except in strong acid is apparently the $\text{Sb}(\text{OH})_6^-$ ion. This is demonstrated by the precipitation of $\text{NaSb}(\text{OH})_6 \cdot 0.5\text{H}_2\text{O}$ both from a pH 4 solution buffered with acetate and from a pH 9 solution buffered with carbonate. Polymerization of $\text{Sb}(\text{OH})_6^-$ in acid solution has been observed,⁷ but it is concentration dependent, and at the low Sb(V) concentrations used in the present kinetic experiments only the monomeric species is present.

Effect of Na⁺. The erratic behavior observed when sodium acetate buffers were used appears to be related to the solubility characteristics of $\text{NaSb}(\text{OH})_6$. The precipitation of this salt, formulated as $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ in the older literature,⁸ has been used in the past for qualitative identification and quantitative determination⁹ of sodium. The solubility of $\text{NaSb}(\text{OH})_6$

(7) P. Souchay and D. Peschanski, *Bull. Soc. Chim. France*, **15**, 439 (1948); B. Ricca, G. D'Amore, and A. Bellomo, *Ann. Chim. (Rome)*, **46**, 491 (1956); G. Jander and H. J. Ostmann, *Z. Anorg. Allgem. Chem.*, **315**, 241, 250 (1962).

(8) "Gmelins Handbuch der Anorganischen Chemie," System No. 21, "Natrium," Verlag Chemie, Berlin, 1928, p 968.

is 0.0012 mole/l.,¹⁰ indicating a solubility product constant of 1.4×10^{-6} . Thus, in the buffer solutions containing 0.1 M sodium acetate, precipitation of $\text{NaSb}(\text{OH})_6$ should be thermodynamically possible whenever hydrolysis has produced $\text{Sb}(\text{OH})_6^-$ to the extent of $10^{-5} M$. Since the initial concentration of SbCl_6^- was 1×10^{-4} to $5 \times 10^{-4} M$, formation of solid $\text{NaSb}(\text{OH})_6$ is possible after a few per cent of the SbCl_6^- has completed hydrolysis to $\text{Sb}(\text{OH})_6^-$. The formation of crystals could affect the apparent rate by trapping ions of SbCl_6^- in the crystal lattice. In contrast, $\text{KSb}(\text{OH})_6$ has a solubility of 0.11 mole/l.,¹⁰ so one would expect no precipitation of $\text{KSb}(\text{OH})_6$ at the concentrations used. Although solid crystals were not observed in the kinetic experiments with sodium salts, the consistent behavior of the kinetic runs when potassium salts were used supports the feeling that the presence of microcrystals of $\text{NaSb}(\text{OH})_6$ was real and should be avoided.

Reaction in Ammonia Buffers. The variation of k_1 shown in the experiments of Table II, and the appearance of convex curves in some of the experiments, can be accounted for by assuming that three mechanisms contribute to the rate of disappearance of SbCl_6^- . The mechanisms are: a pH-independent mechanism, attack by OH^- , and attack by NH_3 . The rate constant k_1 is then given by

$$k_1 = k_0 + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{NH}_3}[\text{NH}_3]$$

For a set of experiments at constant $[\text{NH}_4^+]$

$$k_1 = k_0 + \left(k_{\text{OH}^-} + \frac{k_{\text{NH}_3}[\text{NH}_4^+]}{k_b} \right) [\text{OH}^-]$$

in Figure 2, $\log(k_1 - k_0)$ has been plotted vs. pH. Although the value of k_0 probably changes with the nature of the medium, we have used the numerical value of 0.0000274 displayed in the 0.1 M $\text{KC}_2\text{H}_3\text{O}_2$ buffers. A line of slope one has been drawn through the points of smallest $[\text{NH}_3]$ for each set, since medium effects would not be unexpected at NH_3 concentrations as high as 1 and 5 M. The good adherence to linearity in 0.1024 M NH_4Cl suggests that the numerical value of k_0 in this medium cannot be much different from that chosen.

The two sets of experiments in which $[\text{NH}_4^+] = 0.0124$ can be accounted for solely in terms of the sensitivity of k_{OH^-} to ion concentrations. On the other hand, to explain the two sets of experiments in which $([\text{NH}_4^+] + [\text{K}^+]) = 0.1024$ one must first account for the curvature of the first-order plots in one of the sets. The assumption of the general mechanistic scheme indicated in the Experimental Section provides the basis of the explanation. The path indicated as $\text{X} \rightarrow \text{Z}$ corresponds to attack by OH^- ; the path indicated as $\text{X} \rightarrow \text{Y} \rightarrow \text{Z}$ corresponds to attack by NH_3 to yield an intermediate Y which then reacts further at a measurable rate. The differences in the values of k_1 in the two sets of experiments provide a measure of k_{NH_3} . Although they are not highly accurate because they are highly sensitive to the resolution procedure, the values of $(\epsilon_Y/\epsilon_X)k_{1Y}$ provide a further check of the over-all consistency. The linear portions of the two curves (Figure 2) for these sets of experiments give the values

(9) B. Kramer and F. F. Tisdall, *J. Biol. Chem.*, **46**, 467 (1921).

(10) A. F. Clifford, "Inorganic Chemistry of Qualitative Analysis," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1961, p 479.

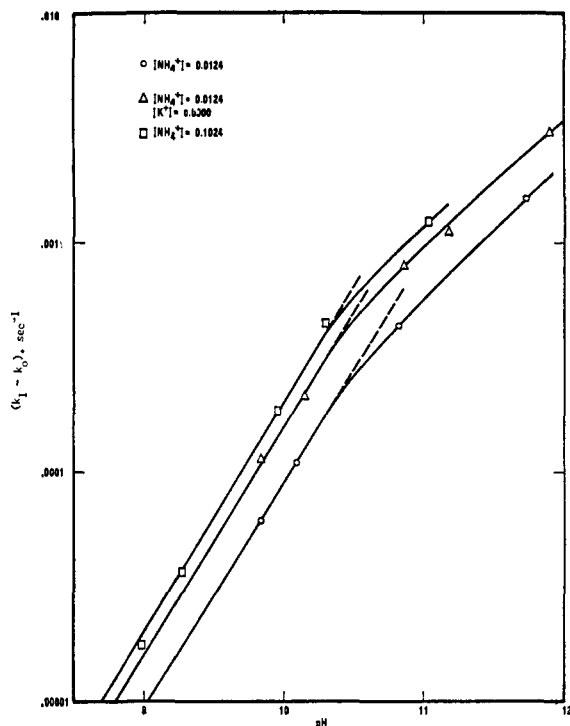


Figure 2. Variation of $(k_1 - k_0)$ with pH for ammonia buffers.

$k_{\text{OH}^-} = 1.56 \text{ sec}^{-1} M^{-1}$ and $k_{\text{NH}_3} = 8 \times 10^{-5} \text{ sec}^{-1} M^{-1}$.

Nature of the Intermediates. In each reaction at $\text{pH} > 9$ 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 $\log(A - A_\infty)$ could be resolved, and that some of the curves were concave. Catalysis by a product would give only convex curvature.

The intermediates are most likely acid-base adducts in the Lewis sense. Hence, in the carbonate buffers the intermediate might be $\text{SbCl}_5(\text{CO}_3)^{2-}$ or $\text{SbOCl}_4(\text{CO}_3)^{2-}$. Such species are very reasonable. The ability of SbCl_5 to form adducts with oxygen-containing molecules is verified by a variety of examples.¹¹ The adducts most closely resembling the postulated intermediates are those with dimethyl carbonate and diethyl carbonate.¹²

(11) I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Springer-Verlag, Berlin-Wilmersdorf (West), 1963.

Although in principle the same argument can be applied to the ammonia buffers, *i.e.*, suggesting $\text{SbCl}_5(\text{NH}_3)$ or $\text{SbOCl}_4(\text{NH}_3)^-$ 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 $\text{SbCl}_5 \cdot 3\text{NH}_3$, $\text{SbCl}_5 \cdot 4\text{NH}_3$, and $\text{SbCl}_5 \cdot 6\text{NH}_3$ have been recorded in the literature,^{13,14} but the work was done in the years 1830-1861 and has not been repeated since then. The compounds $\text{SbCl}_5 \cdot \text{C}_5\text{H}_5\text{N}$ and $2\text{SbCl}_5 \cdot 3\text{C}_5\text{H}_5\text{N}$, reported in 1931,¹⁵ are the only known adducts containing Sb-N bonds.

We are inclined to take the simplest view about the intermediate in ammonia buffers, *viz.*, that an SN_2 displacement of Cl^- by NH_3 leads to the intermediate SbCl_5NH_3 . The rate of disappearance of this intermediate (measured by k_2 , Table II) is catalyzed by base. Several mechanistic possibilities exist for the latter: SN_2 displacement of Cl^- by OH^- , SN_2 displacement of NH_3 by OH^- , or dissociation of Cl^- *via* an SN_1CB mechanism.

Mechanisms Involved. The evidence points to a general base catalysis in the hydrolysis of SbCl_6^- , with the reaction with each base proceeding by an SN_2 mechanism. The question then arises as to whether the pH-independent path proceeds *via* an SN_2 mechanism involving a water molecule. If so, $k_0 = k_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}]$, and $k_{\text{H}_2\text{O}} = 4.9 \times 10^{-7} \text{ sec}^{-1} M^{-1}$. Comparison of this value with $k_{\text{OH}^-} = 1.56$ and $k_{\text{NH}_3} = 8 \times 10^{-5}$ shows that the three reactants are in the expected order based on nucleophilicity. Quantitatively, however, the value of $k_{\text{H}_2\text{O}}$ is too large. Using any of three quantities which have been used to measure electron-donor tendencies¹⁶ suggests that $k_{\text{NH}_3}/k_{\text{H}_2\text{O}}$ should be greater than $k_{\text{OH}^-}/k_{\text{NH}_3}$. Since this is not the case, it seems likely that the pH-independent path is closer to an SN_1 description than an SN_2 description.

An interesting feature of the hydrolysis of SbCl_6^- is the variety of mechanistic paths by which it proceeds. The catalysis by H^+ and SbCl_5 , observed earlier in HCl solutions,³ provides evidence for SE_2 paths.

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(15) J. C. Hutton and H. W. Webb, *J. Chem. Soc.*, 1523 (1931).

(16) Reference 6, p 140.