

interaction of  $\text{PtCl}_4^-$  and  $\text{PtCl}_6^-$ , or by the nuclear radiation.

The compound  $\text{Cs}_2\text{PtCl}_5$  is described in the literature.<sup>9</sup> It is formed when  $\text{Cl}_2$  is passed into a cold solution of  $\text{Cs}_2\text{PtCl}_4$ , with  $\text{PtCl}_4^-$  kept in excess, but not by mixing  $\text{PtCl}_6^-$  and  $\text{PtCl}_4^-$  in the presence of  $\text{Cs}^+$ . The compound was prepared and tested as a catalyst for the exchange of  $\text{PtCl}_4^-$  and  $\text{PtCl}_6^-$ . Even when used in amounts representing 12% of the total Pt in the system, no catalytic effect is observed in 5 min. We consider this observation not to weaken the case which has been presented for reactions of Pt(III), but rather to show that  $\text{Cs}_2\text{PtCl}_5$  does not yield  $\text{PtCl}_5^-$  in solution, probably because it does not contain this ion.

An interesting question is the reason for the exceptional exchange lability of Pt(III). It is con-

(9) L. Wöhler and F. Martin, *Ber.*, **42**, 3958 (1909).

sidered to be caused by the existence of this ion in states of different coordination numbers with approximately the same energy. Along the series  $\text{PtCl}_6^-$ ,  $\text{PtCl}_5^-$ ,  $\text{PtCl}_4^-$ , there is compensation for the energy required to remove  $\text{Cl}^-$ , because the odd electron finds itself left in orbitals of increasing stability. Alternation of Pt(III) between a pair of these structures may account for the rapid exchange. The first two would seem particularly suitable because the ion  $\text{PtCl}_6^-$  makes all Cl's equivalent.

The induced exchange effects demonstrated should be a useful tool in diagnosing mechanisms of reduction of  $\text{PtCl}_6^-$  and of oxidation of  $\text{PtCl}_4^-$ . The reactions studied in this brief survey are only a few of those which suggest themselves for investigation.

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[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

## Antimony(V) Species in Hydrochloric Acid Solution<sup>1</sup>

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Analysis of the ultraviolet spectra of solutions of antimony(V) in hydrochloric acid solutions, ranging in concentration from 2 to 12 *M*, has allowed determination of the kind and amounts of the various species present. The spectrum characteristic of  $\text{SbCl}_6^-$  has been observed in solutions of hydrated  $\text{HSbCl}_6$  in ether, and in antimony(V) solutions in concentrated HCl. With decreasing acidity the presence of  $\text{Sb}(\text{OH})\text{Cl}_5^-$ ,  $\text{Sb}(\text{OH})_2\text{Cl}_4^-$ , etc., has been demonstrated, and the amounts of each determined for various acidities. The  $\text{Sb}(\text{OH})\text{Cl}_5^-$  ion is the predominant form in 8 *M* acid;  $\text{Sb}(\text{OH})_2\text{Cl}_4^-$ , in 6 *M* acid. Below 5 *M* acid  $\text{Sb}(\text{OH})_3\text{Cl}_3^-$  and the more hydrolyzed species are the most important.

There has been little evidence available concerning the nature of the species present when antimony(V) is dissolved in hydrochloric acid, and this lack of information has made difficult the interpretation of many experiments concerned with such solutions. It has been the belief for some time that solutions of antimony(V) in moderately concentrated hydrochloric acid contain the antimony primarily as the ion  $\text{SbCl}_6^-$  but the existence of this ion in solution had not been demonstrated. Both polarographic<sup>2</sup> and spectrophotometric<sup>3</sup> work indicated that hydrolysis of  $\text{SbCl}_6^-$  is probably important at lower acidities, but the hydrolytic species remained unidentified. It was clear from Bonner's work<sup>4</sup> on the radioactive exchange between Sb(III) and Sb(V) that some knowledge of the species involved would be necessary to interpret the exchange results. As a preliminary then to an investigation of the radioactive exchange a study has been made of the ionic species of Sb(V) present in hydrochloric acid solutions.

This study has primarily utilized spectrophotometric<sup>5</sup> methods. The spectrum of  $\text{SbCl}_6^-$  was

established by use of ether solutions of salts. Comparison of this spectrum with the spectra of aqueous hydrochloric acid solutions has allowed decomposition of the spectra into their component parts. As a result, the ions present have been identified, and the amounts of each determined as a function of acidity.

### Experimental

**Spectral Measurements.**—All 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. The spectra of equilibrium mixtures in hydrochloric acid were obtained from 215 to 400  $\mu$ . Absorbency values were obtained at 5  $\mu$  intervals, except in the regions of maxima where readings were taken at 2  $\mu$  intervals. A large slit width was necessary, varying from 2.0 mm. at 215  $\mu$  to 0.4 mm. at 400  $\mu$ . So that the spectra of solutions of varying acidity would be comparable the slit width was maintained constant for a given wave length for all solutions.

Solutions  $2.01 \times 10^{-4}$  *M* in Sb(V) were prepared in acids ranging from 2 through 12 *M* by adding 100 microliters of a 0.1005 *M* stock solution to 50 ml. of HCl of approximately the desired concentration. It was necessary to allow the solutions to stand for several days; equilibrium was considered to be reached when no change in the spectrum was observed over a period of 48 hours. After equilibrium had been attained the acidity was determined by titration. Solutions  $4.02 \times 10^{-5}$  *M* were also prepared by using a 20-microliter portion of stock solution. The stock solution was prepared from "J. T. Baker Analyzed" antimony pentachloride and hydrochloric acid. Solvent blanks for the spectrophotometer were prepared in a manner analogous

(1) Presented in part at the Chicago Meeting of the American Chemical Society, September, 1953.

(2) J. J. Lingane and F. Nishida, *THIS JOURNAL*, **69**, 530 (1947).

(3) J. Whitney and N. Davidson, *ibid.*, **69**, 2076 (1947); **71**, 3809 (1949).

(4) N. A. Bonner, *ibid.*, **71**, 3909 (1949).

(5) The nomenclature used here for spectrophotometric terms is that given in Letter Circular LC-857 of the National Bureau of Standards.

to the preparation of the samples. Measurements were made at three temperatures, 18.0, 25.6 and 34.8°. The most extensive measurements were at 25.6° where solutions differing by increments of about 0.5 *M* in acidity were used. At the other temperatures the acidities varied in 1 *M* increments.

The compounds  $\text{HSbCl}_6$  and  $\text{MgSbCl}_7$  were prepared by the method of Weinland.<sup>8</sup> Both are easily soluble in ether, and solutions approximately  $10^{-4}$  *M* in concentration were used for spectral analysis.

**Analysis of Spectra.**—An attempt was made to decompose the observed spectra into the component parts and identify these components. This attempt has been successful enough to allow identification of the ionic species present, and to make possible the estimation of the concentration of the various species at any acidity. Figure 1, illustrating the change in the spectra with acidity, shows some of the spectra obtained at a temperature of 25.6°. Casual observation of the data indicates that four or five species must be involved, with three of them having absorption maxima in the observed spectral region.

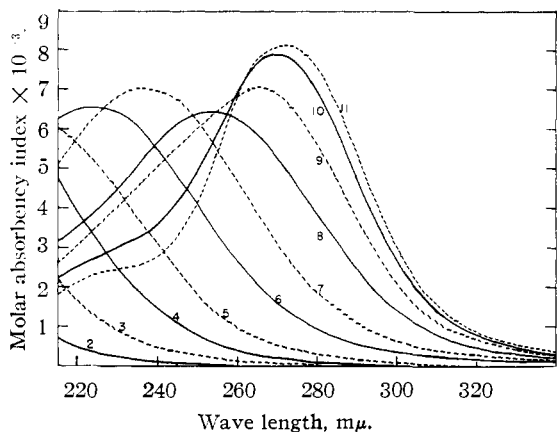


Fig. 1.—Spectra of solutions of  $\text{Sb(V)}$  as a function of  $\text{HCl}$  concentration at 25.6°; concentrations of acids are: 2, 1.99 *M*; 3, 2.98 *M*; 4, 4.09 *M*; 5, 4.96 *M*; 6, 6.10 *M*; 7, 7.01 *M*; 8, 8.11 *M*; 9, 8.94 *M*; 10, 9.97 *M*; 11, 11.45 *M*. Concentration of  $\text{Sb(V)}$  is  $2.01 \times 10^{-4}$  *M* and the cell length is one cm.

Quantitative analysis of the spectra began with those obtained at the highest acid concentrations and proceeded to the lower. The species will be referred to as A, B and C as they result from the analysis. Comparison of the spectrum in concentrated  $\text{HCl}$  with that of  $\text{SbCl}_6^-$  in ether (Fig. 2) indicates the presence of the single species A; *i.e.*,  $\text{SbCl}_6^-$ . The spectra of solutions 9 to 12 *M* in  $\text{HCl}$  exhibit an isosbestic point at 262  $\text{m}\mu$ , indicating the presence of only A and B. Reconstruction of the spectra of pure B proceeded in the following manner.

In first approximation it is assumed that only A contributes to the absorption at 300  $\text{m}\mu$ . Comparison of the absorption at 300  $\text{m}\mu$  by a solution of given acidity with the absorption at the same wave length of a solution in concentrated acid allows calculation of the fraction of antimony(V) that is present as A. The contribution of A to this particular spectrum can then be calculated, and the contribution by B obtained by difference. This defines the spectrum of B fairly well in the region of its absorption maximum, but leaves the region  $> 270$   $\text{m}\mu$  poorly defined. Now the assumption is made that the shape of the spectrum of B is the same as that of A (this assumption is restricted to the shape only and does not imply that the molar absorptivity indexes are the same), and the spectrum at the longer wave lengths is drawn accordingly. This procedure indicates that B does have some absorption at 300  $\text{m}\mu$ , and using the value so obtained a second approximation is then made. Calculations of this type were done for each of the acidities where the isosbestic point indicated only A and B were present, and

averaged to obtain the spectrum of B. The result is shown in Fig. 2, where a smooth curve of the same shape as A is drawn through the calculated values. Within the limitations of the method both A and B have the same value of the molar absorptivity index at the wave length of maximum absorption.

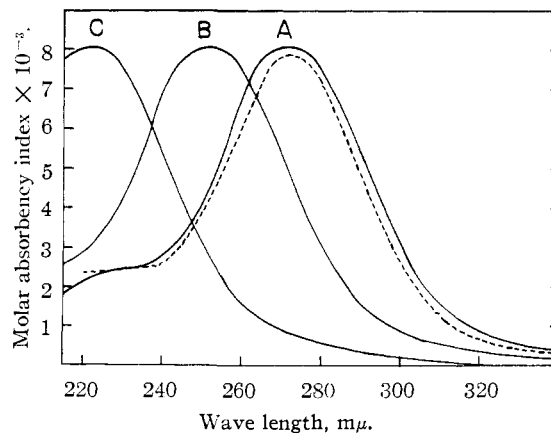


Fig. 2.—Spectra of individual ions: -----,  $8.09 \times 10^{-6}$  *M*  $\text{SbCl}_6^-$  in diethyl ether; A,  $2.01 \times 10^{-4}$  *M*  $\text{SbCl}_6^-$  in concentrated  $\text{HCl}$ ; B, reconstructed spectrum of  $\text{Sb(OH)Cl}_5^-$ ; C, reconstructed spectrum of  $\text{Sb(OH)}_2\text{Cl}_4^-$ .

The same process is extended to species C using the spectra of solutions 6 to 9 *M* in  $\text{HCl}$ . In this case the absorption at 262  $\text{m}\mu$  (the isosbestic point of A and B) is used to determine the total amount of A and B. The individual amounts of A and B are determined from equilibrium constant data. Subtraction of the contributions by A and B then gives the absorption due to C. As might be expected the spectrum of C is not as well defined as that of B, but the best fit to the data is given by the curve in Fig. 2. Again the shape has been drawn like that of A, and again the absorption at the maximum seems to have the same value as those of A and B.

## Results

**Spectrum of  $\text{SbCl}_6^-$ .**—Antimony(V) forms a number of salts where the antimony appears in a chloro anion. Typical examples of these salts are  $\text{KSbCl}_6$ ,  $\text{MgSbCl}_7$  and  $\text{FeSbCl}_8$ . Sidgwick<sup>7</sup> has called attention to the fact that in all these cases the  $\text{SbCl}_6^-$  ion can be shown to be present regardless of the empirical formula of the salt. The evidence here is that from aqueous solutions of  $\text{MgSbCl}_7$  and  $\text{FeSbCl}_8$  only one and two atoms of chlorine, respectively, are precipitated immediately on the addition of silver nitrate.

A solid hydrate of  $\text{HSbCl}_6$  is also known, and an ether solution of this salt was used to obtain the spectrum of the  $\text{SbCl}_6^-$  ion. This hydrate has been reported in the literature as  $\text{HSbCl}_6 \cdot 4.5\text{H}_2\text{O}$  and as  $\text{HSbCl}_6 \cdot 0.5\text{H}_2\text{O}$ . The solid would be expected to be the hydronium salt and hence the half-hydrate formula is open to a suspicion. The solid prepared and isolated in this work was a dihydrate, best formulated as  $\text{H}_3\text{OSbCl}_6 \cdot \text{H}_2\text{O}$ . The spectrum of the ether solution of this salt is shown in Fig. 2, along with the spectrum of  $\text{Sb(V)}$  in concentrated hydrochloric acid. It is observed that these spectra are practically identical.

This solid is also of interest in connection with

(8) Weinland and Schmid, *Ber.*, **38**, 1080 (1905); Weinland and *ibid.*, **36**, 244 (1903).

(7) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, The Clarendon Press, 1950, p. 800.

the fact that Sb(V) can be extracted into ethers from hydrochloric acid solutions. In analogy with the known extractable  $H_3OFeCl_4$ ,  $H_3OAuCl_4$ , etc., it would be expected that  $H_3OSbCl_6$  would be the actual form extracted. That this is actually the case is illustrated in Fig. 3, where the spectra of the isopropyl ether fractions obtained by extracting solutions of Sb(V) in 3 and 6 M HCl are shown. The appearance of the absorption maximum at 272 m $\mu$  demonstrates the presence of  $SbCl_6^-$ . Figure 3 also illustrates the fact that ether solutions of  $MgSbCl_7$  contain the antimony in the form of  $SbCl_6^-$ .

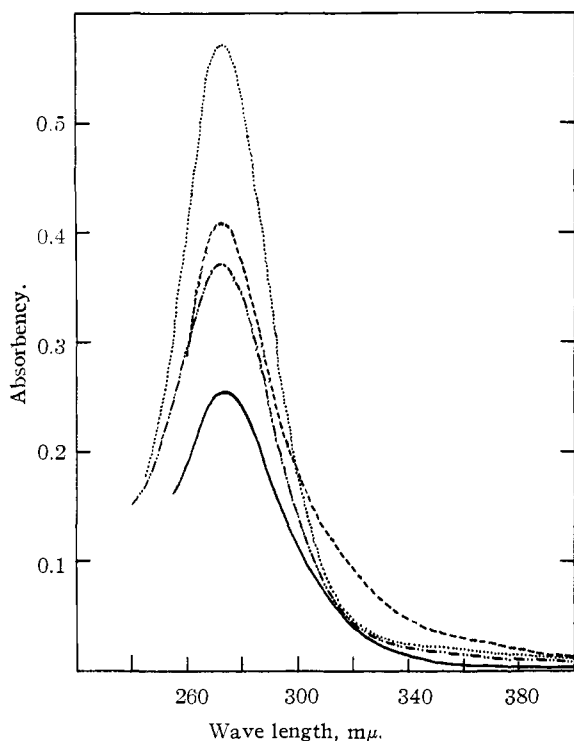


Fig. 3.—Spectra of systems containing  $SbCl_6^-$ : ..... approximately  $7 \times 10^{-5} M$   $SbCl_5 + 0.05 M$  HCl in chloroform; — — —, approximately  $5 \times 10^{-5} M$   $MgSbCl_7$  in ethyl ether; - - - - -, isopropyl ether fraction resulting from extraction of  $5 \times 10^{-5} M$  Sb(V) in 6 M HCl with equal volume of ether; —, isopropyl ether fraction resulting from extraction of  $5 \times 10^{-4} M$  Sb(V) in 3 M HCl with equal volume of ether.

It was thought of interest to see whether a similar absorption could be obtained in other organic solvents by the interaction of  $SbCl_6^-$  and HCl. The result of such an experiment using chloroform as solvent is shown in Fig. 3. No attempt was made to prevent water vapor from being taken up by the solvent, and the solution probably contained sufficient water to allow formation of  $H_3OSbCl_6$ , leading to the characteristic absorption at 272 m $\mu$ .

**Qualitative Aspects of Aqueous Species.**—The number of possible species that one might postulate as being present in hydrochloric acid solutions is quite large. Some qualitative evidence allows the elimination of many of these. Migration experiments reported by Bonner<sup>4</sup> indicate that all of the

species containing antimony are anionic. This is consistent with the observation that there is essentially no retention of antimony on cation-exchange resins, and almost complete retention on anion exchangers. Species containing antimony with a coordination number other than six are felt unlikely, and in particular the evidence against  $SbCl_7^-$  and  $SbCl_8^{2-}$  has been pointed out.

Solutions at the two concentrations,  $2.01 \times 10^{-4} M$  and  $4.02 \times 10^{-5} M$ , used in the spectral studies, adhered to Beer's law, suggesting that polymerization does not occur at these concentrations. It is also possible to test for polymerization by observing the distribution ratio of Sb(V) between an aqueous HCl solution and an ether as a function of Sb(V) concentration. The results of two such experiments are shown in Fig. 4, where the ordinate and abscissa are the logarithms of the respective concentrations. The acid concentration is 3.5 M and the aqueous concentration of Sb(V) varies from  $6 \times 10^{-4}$  to  $1.4 \times 10^{-2}$ . The slope has a numerical value of one, corresponding to a constant extraction ratio, verifying that there is no polymerization at these concentrations. Whitney and Davidson<sup>8</sup> report deviations from Beer's law for solutions 0.1 to 1 M in Sb(V) dissolved in 3.5 M HCl. However, as will be pointed out shortly, hydrolysis is extensive under these conditions, and the equilibrium acidity is considerably greater than 3.5 M. The observed absorption is totally consistent with an increase in acidity (a possibility clearly stated by Whitney and Davidson), and does not require postulation of polymerization.

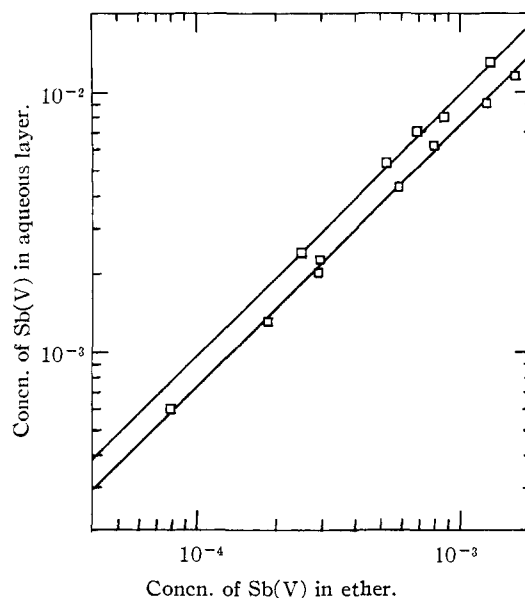


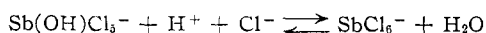
Fig. 4.—Distribution of Sb(V) between 3.5 M HCl and dichloroethyl ether as a function of Sb(V) concentration.

The most reasonable anionic species retaining a coordination number of six are then the ions resulting from stepwise hydrolysis of  $SbCl_6^-$ , namely,  $Sb(OH)Cl_5^-$ ,  $Sb(OH)_2Cl_4^-$ ,  $Sb(OH)_3Cl_3^-$ , etc. The spectral changes have been interpreted in this way,

and the over-all consistency resulting from this interpretation lends great credence to it.

**Identification of Species in Aqueous HCl.**—Analysis of the spectra into the component parts provides a measure of the number of species involved but does not identify the particular species. From the qualitative arguments presented hydrolytic species with coordination number six are most probable, although species of the type  $\text{SbOCl}_4^-$  and  $\text{SbO}_2\text{Cl}_2^-$  also have been postulated.<sup>2</sup>

A possible approach to the identification of the spectral species is to assume that each species is a particular kind, and see if plausible equilibrium constants can be calculated on this basis. For example, let us suppose that species B is  $\text{Sb(OH)Cl}_5^-$ . Then the equilibrium relating it to species A, *i.e.*,  $\text{SbCl}_6^-$ , is



and the equilibrium constant is given by

$$K = \frac{[\text{Sb(OH)Cl}_5^-](a_{\text{HCl}})^2}{[\text{SbCl}_6^-]a_{\text{H}_2\text{O}}} = \frac{[\text{B}](a_{\text{HCl}})^2}{[\text{A}]a_{\text{H}_2\text{O}}}$$

where  $a_{\text{HCl}}$  is the mean ionic activity of HCl and  $a_{\text{H}_2\text{O}}$  is the activity of water. The activities of  $\text{H}_2\text{O}$  and HCl can be calculated from the data of Akerlof and Teare.<sup>8</sup> The only assumption involved in the calculation is that the activity coefficients of  $\text{SbCl}_6^-$  and  $\text{Sb(OH)Cl}_5^-$  are the same, and this is probably not an extreme assumption. The amounts of the two species are determined from the absorption at 300  $m\mu$ , in conjunction with the molar absorptivity indexes of the reconstructed spectra (Fig. 2) at this wave length.

The results of the calculation are given in Table I. Equilibrium constants have been calculated

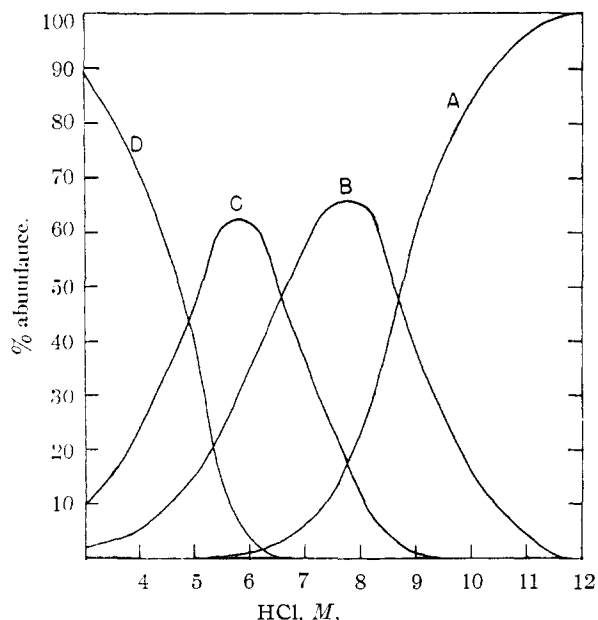


Fig. 5.—Abundances of Sb(V) species as a function of HCl concentration at 25.6°: A,  $\text{SbCl}_6^-$ ; B,  $\text{Sb(OH)Cl}_5^-$ ; C,  $\text{Sb(OH)}_2\text{Cl}_4^-$ ; D,  $\text{Sb(OH)}_3\text{Cl}_3^- + \text{Sb(OH)}_4\text{Cl}_2^-$ , etc.

(8) G. Akerlof and J. W. Teare, *THIS JOURNAL*, **59**, 1855 (1937).

for B being one of three possible species;  $\text{Sb(OH)Cl}_5^-$ ,  $\text{Sb(OH)}_2\text{Cl}_4^-$  or  $\text{SbOCl}_4^-$ . It is apparent from these values that B is  $\text{Sb(OH)Cl}_5^-$ .

TABLE I

EQUILIBRIUM CONSTANTS FOR SPECIES B

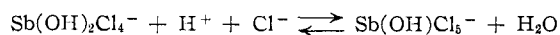
$$\text{If B is } \text{Sb(OH)Cl}_5^- \quad K = \frac{[\text{B}](a_{\text{HCl}})^2}{[\text{A}]a_{\text{H}_2\text{O}}}$$

$$\text{If B is } \text{Sb(OH)}_2\text{Cl}_4^- \quad K = \frac{[\text{B}](a_{\text{HCl}})^4}{[\text{A}](a_{\text{H}_2\text{O}})^2}$$

$$\text{If B is } \text{SbOCl}_4^- \quad K = \frac{[\text{B}](a_{\text{HCl}})^4}{[\text{A}]a_{\text{H}_2\text{O}}}$$

Acidity, <i>M</i>	$K^-$		
	$\text{Sb(OH)Cl}_5^-$	$\text{Sb(OH)}_2\text{Cl}_4^-$	$\text{SbOCl}_4^-$
10.75	$3.9 \times 10^4$	$2.2 \times 10^{10}$	$5.3 \times 10^9$
10.31	$4.8 \times 10^4$	$1.6 \times 10^{10}$	$4.5 \times 10^9$
9.97	$4.0 \times 10^4$	$9.1 \times 10^9$	$2.7 \times 10^9$
9.20	$4.5 \times 10^4$	$3.8 \times 10^9$	$1.3 \times 10^9$
8.94	$4.1 \times 10^4$	$2.4 \times 10^9$	$9.0 \times 10^8$
8.23	$5.3 \times 10^4$	$1.3 \times 10^9$	$5.4 \times 10^8$
8.11	$4.8 \times 10^4$	$9.7 \times 10^8$	$4.3 \times 10^8$
Av. value	$4.5 \times 10^4$		

If this stepwise process continues, species C should be  $\text{Sb(OH)}_2\text{Cl}_4^-$ , and the equilibrium constant for the reaction



should be calculable. For solutions where this reaction predominates (6–9 *M* HCl) the sum of  $[\text{Sb(OH)Cl}_5^-]$  and  $[\text{SbCl}_6^-]$  comes from the absorption at 262  $m\mu$ , the actual value of each from calculation using the previously determined equilibrium constant, and the  $[\text{Sb(OH)}_2\text{Cl}_4^-]$  by difference. The calculations are summarized in Table II. The constancy supports the assignment of  $\text{Sb(OH)}_2\text{Cl}_4^-$  to species C, and it seemed unnecessary to test other postulated species.

TABLE II

EQUILIBRIUM CONSTANT FOR SPECIES C

$$K = \frac{[\text{Sb(OH)}_2\text{Cl}_4^-](a_{\text{HCl}})^2}{[\text{Sb(OH)Cl}_5^-]a_{\text{H}_2\text{O}}}$$

Acidity, <i>M</i>	8.23	8.11	7.31	7.01	6.14	6.10
$K \times 10^{-3}$	3.2	2.6	3.1	2.4	2.4	2.3

Av. value of  $K = 2.7 \times 10^3$

The abundances of the various species as a function of acidity are shown in Fig. 5. The data plotted are those used to calculate the equilibrium constants, and are not obtained from the constants except for the abundances of  $\text{SbCl}_6^-$  in 6 and 7 *M* HCl. At acidities less than 6 *M* the amounts of  $\text{Sb(OH)Cl}_5^-$  and  $\text{Sb(OH)}_2\text{Cl}_4^-$  are calculable, and the remainder is attributed to more hydrolyzed species. Because these latter do not show appreciable absorption in the spectral region observed a more detailed analysis is impossible.

**Temperature Effect on Spectra.**—Changes in temperature do not drastically change the spectra. At a constant acidity there is a shift of the absorption maximum to shorter wave length with decreasing temperature, indicating that the more hydrolyzed species are favored by lower tempera-

ture. For acidities where no maximum occurs the absorbency at 220  $m\mu$  is taken as a qualitative measure of the amount of hydrolysis. At these acidities the absorbency decreases with temperature, indicating again more extensive hydrolysis at the lower temperatures.

**Rates of Reaction.**—The work of Whitney and Davidson<sup>8</sup> pointed to the fact that the equilibria involving  $SbCl_6^-$  are established at a measurable rate. In the extraction experiments already cited it became apparent that considerable time was required before equilibrium was attained, indicating that the rate of formation of  $SbCl_6^-$  is slow, at least in 3.5  $M$  acid.

The attainment of equilibrium in such cases results from a series of reactions, and interpretation in terms of the separate reactions is not possible. The only individual reaction that can be studied easily is the hydrolysis of  $SbCl_6^-$ . This can be done spectrophotometrically by observing the rate of change of absorbency at a wave length of 300  $m\mu$  after diluting a solution in concentrated HCl to some desired acidity. It may be argued that the absorption at 300  $m\mu$  is not solely due to  $SbCl_6^-$  since we have seen that  $Sb(OH)Cl_5^-$  also shows appreciable absorption at this wave length, and hence that the observed rate is not truly the rate of hydrolysis. The evidence, however, points to the fact that even though  $Sb(OH)Cl_5^-$  may be the initial product of the hydrolysis of  $SbCl_6^-$ , it is itself hydrolyzed rapidly. This is illustrated by an experiment where a 12  $M$  acid solution was diluted to 2  $M$  and the rate of change of absorbency followed at wave lengths of 240, 250 and 300  $m\mu$ . There was no increase in absorbency at 240 and 250  $m\mu$  which

would have been expected if appreciable amounts of  $Sb(OH)Cl_5^-$  had accumulated; and in fact, all three absorbencies decreased at the same rate.

If one examines the entire spectrum at various times during such an experiment and plots these spectra, an isosbestic point occurs. The wave length at which the isosbestic point occurs will vary with the final acidity. These observations and the points raised in the previous discussion are consistent with the interpretation that once the initial step of hydrolysis is complete the products come to the equilibrium determined by the acidity. That is, under these conditions all of the species, with the exception of  $SbCl_6^-$ , are in equilibrium. For fairly low acidities there is then no contribution by hydrolysis products to the absorbency at 300  $m\mu$ , and the actual rate of hydrolysis is being measured. Preliminary experiments indicate the hydrolysis to have a half-time of two hours at 25°.

Only qualitative information is available on the rates of reactions that lead from the more hydrolyzed to the less hydrolyzed species. If a solution of low acidity is mixed with concentrated acid the rate of attainment of equilibrium is strongly dependent on the resulting acidity. If the final acidity is greater than 9  $M$  equilibrium is reached within a few minutes; in a 6  $M$  solution equilibrium is reached after a few hours. Several days are necessary for the formation of  $SbCl_6^-$  (as determined by extraction experiments) when the acidity decreases to less than 3  $M$ . Here again the qualitative evidence points to a rapid equilibrium between the hydrolyzed species, followed by a slow rate of formation of  $SbCl_6^-$ .

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Relationships among the Absorption Spectra of the 5,7-Dihalo-8-quinolinol Chelates of Gallium(III) and Indium(III)

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The absorption spectra of chloroform solutions of 5,7-dihalo-8-quinolinol (dichloro-, dibromo-, chloroiodo- and diiodo-) chelates of gallium(III) and indium(III) resemble those of comparable solutions of the unsubstituted 8-quinolinol chelates in that only three absorption bands, all lying in the near ultraviolet and violet regions, are detectable in the wave length range 300–600  $m\mu$ . Absorptions in the 392.5–417  $m\mu$  region are major and most characteristic and are apparently due to bathochromic shifts in the spectra of the chelating agents as a result of chelate formation. The wave lengths and equivalent extinction coefficients characterizing these absorption bands increase generally with increasing molecular weights of the chelates. Absorptions at the major peaks are in accord with Beer's law at low metal concentrations. Chloroform solutions of these chelates all undergo photochemical decompositions.

### Introduction

The ability of 8-quinolinol to form stable chelates with a variety of metal ions is well established.<sup>1–3</sup> Since such chelates result through substitution of metal ions for the acidic hydrogen in the parent compound, they are structurally similar

to 8-quinolinol itself, and their properties may be expected to reflect those of 8-quinolinol with suitable modifications depending upon the metal ions themselves. Similar chelates are formed by many of the substituted 8-quinolinols.<sup>4,5</sup> Although the properties of these chelates again reflect those of the parent chelating agents, they differ somewhat from

(1) F. L. Hahn, *Z. angew. Chem.*, **39**, 1198 (1926).  
 (2) R. Berg, *J. prakt. Chem.*, **115**, 178 (1927).  
 (3) R. Berg, "Das O-Oxychinolin 'Oxine,'" F. Enke, Stuttgart, 1935.

(4) R. Berg, *Z. anorg. allgem. Chem.*, **204**, 208 (1932).  
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