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The Antimonous-Antimonic Complex in Hydrochloric Acid

FRANK EDWARDS, ADOLF VOIGT AND HARVEY DIEHL

A successful theory systematizing or correlating the color of inorganic complexes has not yet been advanced. Linus Pauling in his Richards Medal address (7) listed such a theory as one of the "puzzling unsolved problems of structural chemistry". The colors developed by solutions containing the same element in different valence states is particularly interesting, in that the color of the mixture may be radically different from that of either component. Cuprous chloride in concentrated hydrochloric acid is colorless, cupric chloride in a similar solution is green; present together they produce a dark brown or black solution(3). Similarly, a hydrochloric acid solution of antimony trichloride is colorless, of antimony pentachloride a pale yellow; a mixture of the two, however, possesses an intense red-brown color. Although ferrous hydroxide is white and ferric hydroxide brown, the ferrous-ferric hydroxide resulting from partial air oxidation of freshly precipitated ferrous hydroxide is black. Again, colorless tervalent ytterbium on reduction with metallic zinc to green, bivalent ytterbium passes through a purple stage, again probably a mixed valence complex(2). In the present paper a more detailed study is reported of the antimonous chloride-antimonic chloride-hydrochloric acid system.

Compounds containing both ter and quinquevalent antimony have been previously isolated. A black solid corresponding to the formula, $(\text{NH}_4)_2\text{SbBr}_6$ and designated ammonium hexabromohypoantimonate, and the rubidium compounds Rb_2SbBr_6 and Rb_2SbCl_6 have been obtained in crystalline form. Their crystal structure has been determined by Jensen (5) who found that these materials possess a face-centered, cubic lattice in which all of the antimony atoms are equivalent. The composition of these compounds implies a valence of four for antimony. Quadrivalent antimony, however, should be paramagnetic but Elliott(4) has found ammonium hexabromohypoantimonate to be diamagnetic and Asmussen(1) has reported that the systems antimonous-chloride-antimonic chloride and antimonous chloride-rubidium hexachloroantimonate to be without a paramagnetic component. In the crystalline compounds studied by Jensen the antimony-antimony distance is about 6.9 Å making improbable the suggestion that the color is due to the resonance of the electrons among the atoms of the metal. Presumably SbCl_6^- and SbCl_6^{\equiv} groups alternate in the crystal lattice. That double salts exist in the solid phase is well known, that such aggregations should persist on passage into solution is indicated by the unique colors of the examples cited is quite surprising. Compound formation is certainly implied in the failure of the rule of the additivity of optical densities on the mixing of two colored materials.

In the present work the method of continuous variations developed by Job(6) and recently reviewed and extended by Vosburgh(9) has been applied to hydrochloric acid solutions containing both antimonous chloride and antimonie chloride to determine the nature of the complexes present. Concentrated hydrochloric acid solutions of ter and quinquevalent antimony chlorides of the same molarity were prepared. A series of mixtures of these was made varying the ratio of ter to quinquevalent antimony and keeping the total antimony concentration the same in each solution. The absorption (optical density) of each solution was determined at appropriate wavelengths using a spectrophotometer. The absorption of the component solutions was also determined. The absorption that each solution would have had had no reaction occurred was calculated and this value subtracted from the observed absorption. The difference was plotted as a function of the mol fraction, x , of antimonie chloride. A maximum (or in some cases a minimum) is an indication of complex formation and the ratio of the components of the complex is related to the mol fraction, x at which the maximum occurs by the expression

$$n = \frac{x}{1-x}$$

as developed in the method of continuous variation.

Some further experiments were also made to determine the charge carried by the complex and the effect of variation in the concentration of hydrochloric acid.

EXPERIMENTAL WORK

Preparation and Standardization of Solutions. Crystalline antimonous chloride was dissolved in concentrated hydrochloric acid. The solution was standardized by titration with ceric sulfate(8); a 1.0 ml aliquot was diluted with 25 ml of concentrated hydrochloric acid and the titration carried out using methyl orange as indicator: found: 1.002 M.

In a similar manner liquid antimonie chloride was dissolved in concentrated hydrochloric acid and standardized by titration with ceric sulfate after reduction of the quinquevalent antimony by agitation with mercury; found: 1.007 M.

The various equimolar mixtures were made by pipetting appropriate volumes of the two component solutions, the total volume of all the mixtures being 10.0 ml. After mixing the color of the mixtures increased slightly and then faded somewhat, reaching a constant color in about twenty minutes. The spectrophotometric readings were made only after the solutions had stood one hour.

Spectrophotometric Measurements. A preliminary absorption study of hydrochloric acid solutions of antimonous chloride, of antimonie chloride, and of an equimolar mixture of antimonous chloride and antimonie chloride was made with a Jarrell-Ash, 21-foot, grating spectrophotometer. A hydrogen discharge tube was used as the light

source over the range 200 to 350 $m\mu$ and a tungsten filament bulb over the range 350 to 1,000 $m\mu$. This study indicated that the antimonous solution transmitted completely above 390 $m\mu$, that the antimonic solution transmitted completely above 440 $m\mu$, and that the mixture transmitted completely above 550 $m\mu$. Below these values absorption was complete and no regions of absorption were found above these values. The transition from complete transmission to complete absorption is very sharp with all three solutions, for example the optical density of an equimolar mixture 1.004 M in total antimony is 1.9 at 475 $m\mu$ and 0.14 at 550 $m\mu$. In the range 475 $m\mu$ to 525 $m\mu$ the absorption by the antimonous and antimonic solutions was so small that it could be neglected in the continuous variation treatment.

The spectrophotometric measurements on the various solutions were made using a Beckman quartz spectrophotometer at a band width maintained constant at 5 $m\mu$. Square cuvettes 1.0 cm in length were used.

The absorption of each member of the three series of mixtures mentioned above was measured at three wavelengths, 475, 500 and 525 $m\mu$. The results are shown in Figure 1. A maximum occurs in all cases at a ratio of one trivalent to one quinquevalent antimony.

Migration Study. Twenty-five milliliters of a concentrated hydrochloric acid solution, equimolar in antimonous chloride and antimonic chloride and having a total antimony concentration of 1 M, was placed in a "U" tube. Ten milliliters of concentrated hydrochloric acid was carefully added to each arm of the tube. A current of 0.060 amp was passed through this system for twelve hours. The red-brown boundary migrated toward the positive electrode and away from the negative electrode, showing the charge of the complex to be negative.

Effect of Hydrochloric Acid Concentration. Equimolar mixtures of antimonous chloride and antimonic chloride in solutions of varying hydrochloric acid concentration were prepared; the total antimony concentration was held constant at 0.258 M and the acid varied from 4.6 to 12.7 M. The optical densities of the solutions are given in Figure 2. The extent to which the complex is formed is seen to depend greatly on the concentration of the hydrochloric acid, maximum complex formation occurring at about 10.0 M.

DISCUSSION

It is apparent that the antimonous-antimonic complex in hydrochloric acid solution contains ter and quinquevalent antimony in the ratio of one to one.

There is undoubtedly a considerable amount of hydrochloric acid in the complex since the complex carries a negative charge. However, the number of chloride radicals or molecules of hydrochloric acid cannot be determined from the present work. No successful theoretical treatment of the data relating the extent of complex

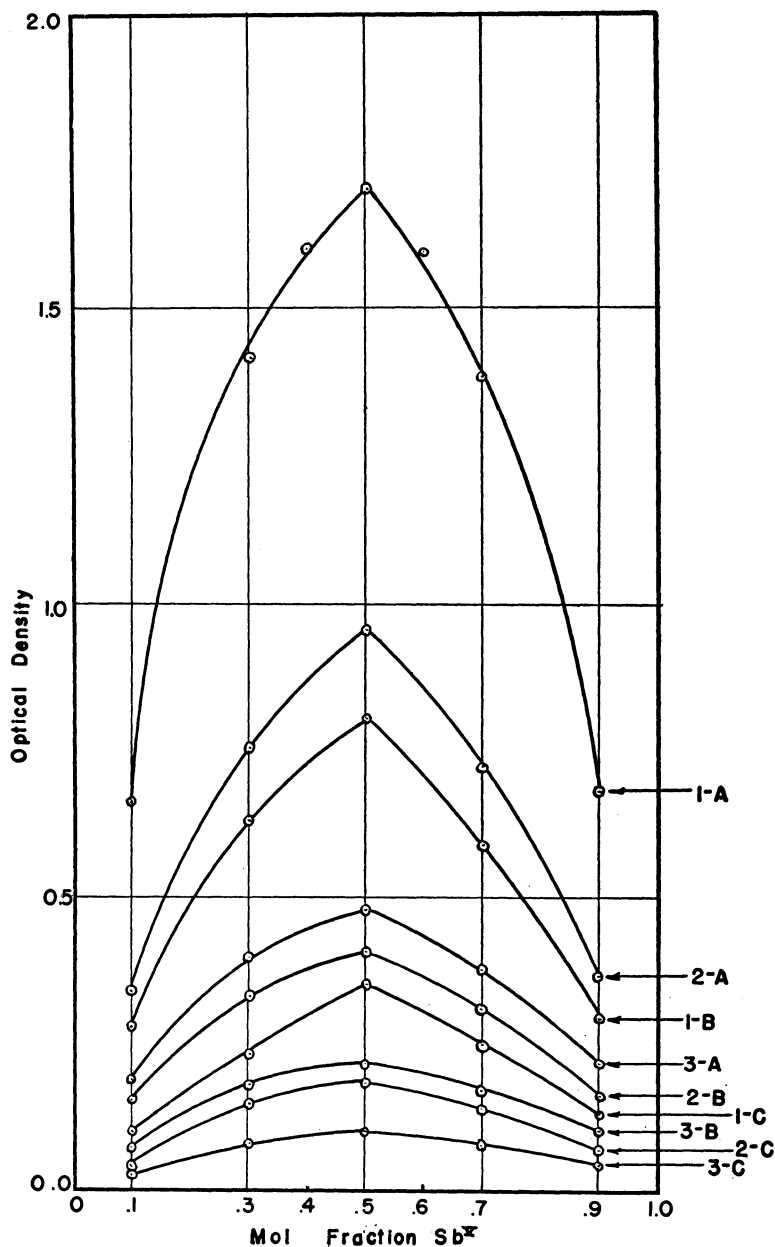


Figure 1. Spectrophotometric measurements of various equimolar mixtures of ter and quinquevalent antimony in concentrated hydrochloric acid solutions. The numbers index the total antimony concentration of the solutions: 1, 1.004 M; 2, 0.717 M; 3, 512 M. The letters index the wavelength at which the solutions were measured: A, 475 m μ ; B, 500 m μ ; C, 525 m μ .

formation and the hydrochloric acid concentration was devised. Owing to the high concentrations involved the interpretation of the activities concerned is difficult.

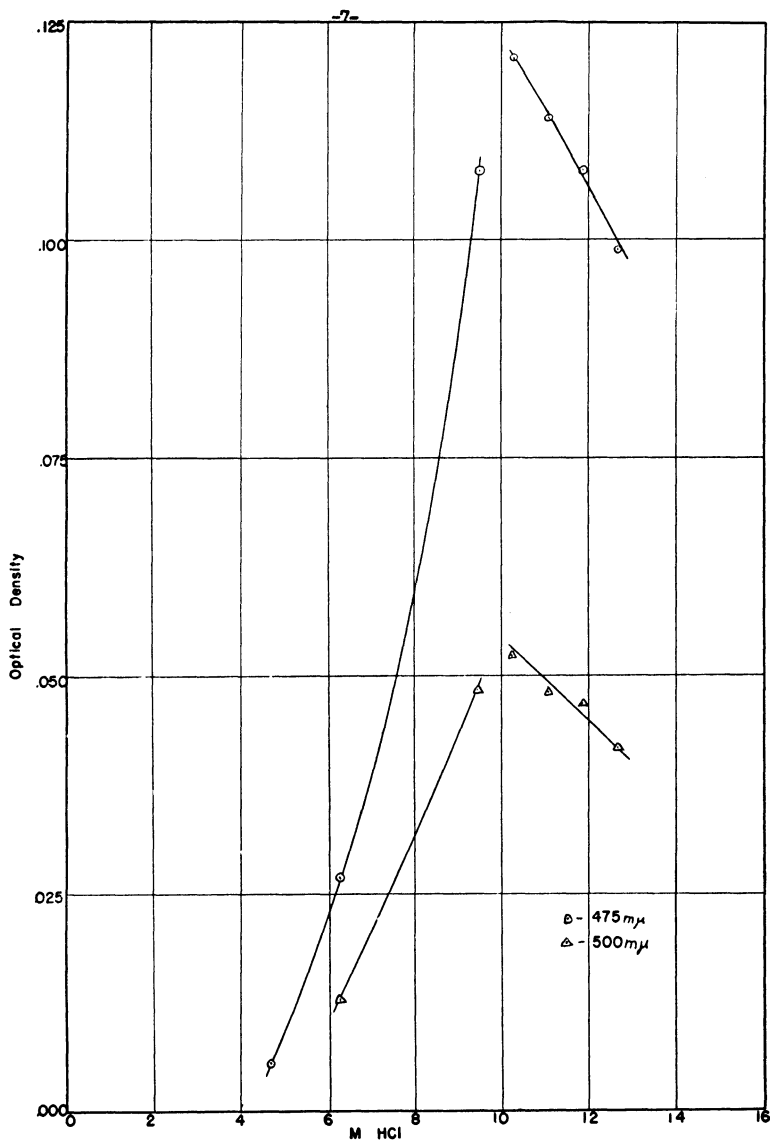


Figure 2. The effect of hydrochloric acid concentration on the mixed valence complex of antimony. Solutions were 0.258 M in total antimony.

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