[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Solubility of Cesium Antimony Chloride in Hydrochloric Acid Solutions at 25°

BY PAUL BENDER

In the isolation or purification of cesium salts the first step is normally the precipitation from hydrochloric acid solution of the double salt of cesium chloride with antimony trichloride. Since no adequate solubility data on this system have previously been recorded in the literature, the work of supplying them was undertaken. Before such measurements could be justified, however, an explanation of the variation in color and form regularly observed in the precipitate was required.

Experimental Details

Preparation of Materials.—Cesium chloride of spectroscopic purity was prepared from pollucite by the method of Wells.[1] All other compounds used were standard analytical reagents.

Analytical Methods.—Antimony was determined by titration with 0.1 *N* iodine solution standardized against arsenious oxide. Hydrochloric acid solutions were prepared by weight dilution of a stock solution standardized by means of silver chloride. Calibrated weights and glassware were employed in all determinations. A Bausch and Lomb large Littrow quartz spectrograph and Eastman Type O plates were used in the spectrographic work.

Solubility Measurements.—Standard procedures were followed in the solubility determinations. The thermostat temperature was maintained at 25.00 ± 0.05°, and attainment of equilibrium was checked by reanalysis after further equilibration. Duplicate samples of the saturated solutions were taken, and analyzed by volumetric determination of antimony. The hydrochloric acid concentrations were known to 0.1%, and, since the precision of the individual iodometric titrations was 0.1%, it is believed that the probable error in the solubility date is 0.3%. Pycnometrically determined densities were used to convert the results to the volume concentration basis.

Experimental Results

In the preparation of the double salt it was found that the character of the initial precipitate depends on the concentration of the hydrochloric acid used and the temperature. The addition of antimony trichloride to a cold solution of pure cesium chloride in concentrated hydrochloric acid produces an immediate finely divided white precipitate which on standing is converted into a macroscopically crystalline solid phase light yellow in color. The rate of the transformation at room temperature is inversely proportional to the concentration of acid used. With warmer and more dilute solutions the stable yellow form can be obtained at once.

Samples of both solid phases were obtained in several experiments and analyzed. Within the experimental error their compositions were identical and agreed at 25.35 ± 0.05% Sb with the value of 25.33% calculated from the formula $3CsCl \cdot 2SbCl_3$ established for the compound by Remsen and Saunders.[2] These results indicate that a stable solid phase of constant composition is obtained when equilibrium is established. In no case did the final product vary in color from the normal pale yellow when pure cesium chloride and antimony trichloride were used in its preparation.

The double salt as obtained in the course of routine recovery processes is invariably more highly colored. Four such samples, ranging in color from canary yellow to a brownish orange, were analyzed for antimony. The observed average value of 25.32 ± 0.05% Sb again corresponds to the formula $3CsCl \cdot 2SbCl_3$. Spectroscopic investigation was carried out to determine the origin of the abnormal color of these impure samples. The only extraneous element identified in the material was thallium, present in very small amount and detected by means of its sensitive line at 2768 Å.

Precipitation of the cesium antimony chloride in the presence of thallium was therefore carried out. It was found that as little as 0.005% of thallium in the cesium chloride used produced a definite change from the normal color of the pure double salt. Further investigation of this phenomenon is in progress, but these preliminary results suffice to show that the color variation in samples of cesium antimony chloride as ordinarily encountered may be ascribed to variations in the small amount of thallium present as an impurity.

Several hundred grams of the pure double salt were then prepared for the solubility measurements. Analysis of this material showed an antimony content of 25.38 ± 0.05%. Results of the solubility runs are summarized in Table I. It should be remarked that hydrolysis of the salt takes place if the hydrochloric acid concentration is reduced materially below 2 *M*.

TABLE I

THE SOLUBILITY OF CESIUM ANTIMONY CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS AT 25°

M HCl	G. salt/100 g. solvent	G. salt/100 cc. solution
2.086	1.732	1.778
2.953	1.389	1.444
4.027	1.236	1.304
4.869	1.178	1.256
6.875	1.114	1.217
9.957	1.083	1.218
12.92	1.093	1.258
16.20	1.134	1.333

Discussion

The only practical information previously available on the solubility of cesium antimony chloride is embodied in the statement of Lenher,[3] *et al.*,

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(1) H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

(2) I. Remsen and C. E. Saunders, *ibid.*, **14**, 152 (1892).

(3) V. Lenher, G. Kemmerer and E. Whitford, *Ind. Eng. Chem.*, **16**, 1280 (1924).

that the salt is sufficiently insoluble in 3 N HCl so that the filtrates from the precipitation can be discarded. The present results suggest that recovery of cesium from the filtrate is advisable. Recovery by precipitation of Cs_2SnCl_6 by addition of stannic chloride is recommended.

It had been expected that iron would be found in the impure samples, but only traces of this element were found in even the most highly colored material. A stable compound of thallium chloride and antimony trichloride, $SbCl_3 \cdot 3TlCl$, has been reported[4]; its existence makes the presence of thallium reasonable if unexpected, but inasmuch as the compound was not prepared under conditions comparable to those of the present work, a further investigation is necessary. A full discussion of this question will be given in a subsequent report.

Acknowledgment.—The author wishes to express his appreciation to Mr. Eugene F. Wilda for the spectrographic analyses.

Summary

Evidence has been presented confirming the composition of cesium antimony chloride as constant at $3CsCl \cdot 2SbCl_3$. Color variation in the salt has been shown to be due to the presence of thallium as an impurity.

The solubility of cesium antimony chloride at 25° in hydrochloric acid solutions of concentrations from 2 to 16 molal has been reported.

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[4] F. Ephraim and P. Barteczko, *Z. anorg.' Chem.*, **61**, 249 (1909).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Direct Synthesis of Phenylchlorosilanes

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The general reaction of hydrocarbon halides with elementary silicon to produce alkyl and aryl halosilanes has been described.[1] The purpose of the present investigation is to apply that general reaction to the synthesis of phenyl chlorosilanes from chlorobenzene and silicon, seeking conditions which would permit yields of diphenyldichlorosilane comparable to those obtained by substitution methods.[2]

Experimental

Chlorobenzene and Silicon.—Pure dry monochlorobenzene was introduced at a rate of 7 g. per hour into a heated glass tube of 2.5 cm. internal diameter containing 107 g. of granular pure silicon (99.8% Si). The tube was sealed to a water condenser, a thermocouple was embedded in the silicon, and the tube was heated until the temperature of the charge was 530°. Only slight reaction of the silicon with the stream of chlorobenzene occurred over a period of fifteen hours. When operated at 680° for a period of fifty-four hours, 13 g. of carbon was deposited in the tube and 367 g. of dark condensate was collected. From this liquid there was obtained by distillation 54 g. of silicon tetrachloride, 241 g. of unchanged chlorobenzene, and 65 g. of high-boiling material consisting of phenylchlorosilanes, biphenyl, chlorinated biphenyls and unknown materials of a tarry nature.

A larger glass tube (4 cm. internal diameter) in which was sealed a concentric thermocouple well was then charged with commercial silicon (97% Si) which had been pulverized to 325 mesh size and then sintered in hydrogen. The packed section was 120 cm. long. The tube was heated in an electric furnace to 570 ± 10° and chlorobenzene was introduced at the rate of 12 g. per hour. The products which condensed at water temperature were collected. From 2694 g. of condensate there was obtained by distillation 287 g. of low-boiling material (silicon tetrachloride and benzene), 1834 g. of unchanged chlorobenzene and 473 g. of fuming high-boiling material. Of the latter, 144 g. distilled near the boiling point of diphenyldichlorosilane, but analysis showed that only one-fourth of this was actually diphenyldichlorosilane and the rest was a mixture of chlorinated biphenyls having about the same boiling point. Phenyltrichlorosilane, triphenylchlorosilane and many other unidentified products also were obtained.

Chlorobenzene, Hydrogen Chloride and Silicon.—Apparatus similar to that employed in the preceding experiment was set up, but anhydrous hydrogen chloride was mixed with the chlorobenzene vapor and passed over the heated silicon. A variety of molar proportions of hydrogen chloride to chlorobenzene were employed at several temperatures. At 0.3 mole of hydrogen chloride per mole of chlorobenzene, and at a temperature of 500°, 9.4 g. of phenyltrichlorosilane was obtained per 100 g. of chlorobenzene charged, in one pass through the reactor. Twenty-four grams of silicon tetrachloride per 100 g. of chlorobenzene charged was obtained at the same time, but very little diphenyldichlorosilane.

Chlorobenzene, Silicon and Copper.—Copper had been found to be effective in facilitating the reaction of methyl chloride and silicon to produce dimethyldichlorosilane. A sintered mixture of commercial silicon and copper powders containing 20% Cu was found to react with chlorobenzene at an appreciable rate only above 550°, and the yield of phenylchlorosilanes was poor. When anhydrous hydrogen chloride was mixed with the chlorobenzene as in the previous experiment, phenyltrichlorosilane was obtained in a yield of 12.7 g. per 100 g. of chlorobenzene in a single pass, but the yield of diphenyldichlorosilane remained low. Experiments with sintered pellets containing 10% copper gave similar results.

Further experiments showed that chlorobenzene and bromobenzene would react with a commercial alloy of silicon and copper (50% Cu) in a rotating autoclave above the normal boiling point but below the critical temperature of the halide. To try the same reaction in the vapor phase, lumps of the same alloy (which had stood in the laboratory for over a year and had softened to a friable mass through inter-granular oxidation) were packed in a tube of 4-cm. diameter, and the vapor of chlorobenzene (mixed with 0.0004 g. of anhydrous hydrogen chloride per g. of chlorobenzene) was passed through at elevated temperatures at a rate of 29 g. per hour. The copper-silicon mass was found to have a comparatively high reactivity

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(1) E. G. Rochow, THIS JOURNAL, **67**, 963 (1945).

(2) Kipping and Murray, *J. Chem. Soc.*, 2734 (1927); Polis, *Ber.*, **19**, 1019 (1886); Dilthey and Edvardoff, *ibid.*, **37**, 1139 (1904).