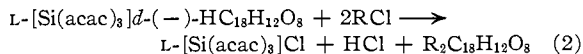


minutes, and the resulting precipitate of the diastereoisomer, $L\text{-}[\text{Si}(\text{acac})_3]d\text{-}(-)\text{-HC}_{18}\text{H}_{12}\text{O}_8$, was filtered quickly, washed with four 2-ml. portions of anhydrous acetone, and dried at room temperature by passing dry air over the product; yield 0.384 g. (56.2%). Calcd. for $L\text{-}[\text{Si}(\text{C}_8\text{H}_7\text{O}_2)_3]d\text{-}(-)\text{-HC}_{18}\text{H}_{12}\text{O}_8$: C, 58.11; H, 5.02; Si, 4.12. Found: C, 59.06; H, 5.01; Si, 4.25.

The filtrate (after a fivefold dilution) showed a high positive rotation (α obsd. = 0.650°) which decayed to a constant value of -0.340° after several hours, indicating that not all of the $(-)$ -dibenzoyl- d -tartrate had been removed during the precipitation.

Replacement of the Resolving Anion.—The precipitated diastereoisomer, $L\text{-}[\text{Si}(\text{acac})_3]d\text{-}(-)\text{-HC}_{18}\text{H}_{12}\text{O}_8$ (0.1334 g.), was suspended in water and mixed (with constant stirring) with five grams of Dowex 1-X8 anion-exchange resin in the chloride form (50–100 mesh) for 15 minutes (total volume = 100 ml.). The precipitated diastereoisomer dissolved and the resolving anion exchanged with chloride according to the equation



where R = the unipositive resin cation. That the hydrogen ion is separated from the resolving anion in the resin procedure is shown by (a) the observed drop in $p\text{H}$ after the resin treatment, and (b) the appearance of two chloride ions in the filtrate for every silicon, as determined by chloride and silicon analyses on the filtrate containing the enantiomer. That the resin effectively removes all the resolving anion is shown by treating 0.001 mole of sodium monohydrogen $(-)$ -dibenzoyl- d -tartrate with resin under the conditions described above. This treatment produces a filtrate without any observable rotation.

The filtrate from the initial precipitation reaction was treated with resin in the manner described above and a 0.209% solution showed $\alpha_{\text{obs.}} = +0.908 \pm 0.003^\circ$; $[\alpha]_{\text{D}}^{15} + 435^\circ$ at 15° . The relatively low value is due to incomplete separation of the *levo*-enantiomer of the complex during the precipitation process. The separation of the *dextro*-isomer from the *levo* is improved if, in the initial precipitation reaction, equimolar quantities of the resolving agent and racemic silicon complex are used. The specific rotation of the *dextro*-isomer prepared in this manner is 680° at 22.7° . The half-life for racemization of the *dextro*-isomer at 22.7° is 64 minutes, which is the same as that for the *levo*-enantiomer.

Hydrolysis Studies.—Ultraviolet absorption spectra were taken of $[\text{Si}(\text{acac})_3]\text{Cl}\cdot\text{HCl}$ immediately after dissolving it in water and after it had undergone hydrolysis (6 hr.), as well as of free acetylacetone (see Fig. 2). Since neither the hydrolysis products nor free acetylacetone shows any appreciable absorption at $305\text{ m}\mu$, whereas the complex has

appreciable absorption at this wave length, it was chosen as the wave length to study the hydrolysis rate (see Fig. 2). All solutions studied were thermostated to within $\pm 0.1^\circ$. In order to obtain measurable transmittance values, it was frequently necessary to dilute aliquots of the solution immediately before transmittance measurements were made. These were usually fifty-fold dilutions resulting in a final concentration of about $1.5 \times 10^{-5} M$ in silicon.

1. **Behavior of the Aqueous Solution of $[\text{Si}(\text{acac})_3]\text{Cl}\cdot\text{HCl}$.**—While the complex was allowed to stand in water, its ultraviolet absorption spectrum changed with time. After 6 hr., there was no further change and the spectrum at that time corresponded exactly to the spectrum of free acetylacetone in water at a concentration of three times the initial molar concentration of the complex. The $p\text{H}$ values of the untreated solutions of the complex at concentrations of 7.5×10^{-4} , 3.0×10^{-3} and 1.5×10^{-5} mole per liter were 3.2, 4.9, 5.4, respectively. After long standing, these values decayed to 2.95, 4.48 and 5.0, respectively. In order to be better able to observe the decay of $p\text{H}$ of the aqueous solution of the complex with time, it was decided to add sodium hydroxide to the solution at the instant of dissolution to neutralize the associated hydrochloric acid. This raised the $p\text{H}$ to about 9, thereby enabling a plot of $p\text{H}$ vs. time of standing to be made (see Fig. 1).

2. **Titration of the Complex.**—This was carried out in the usual fashion using a $p\text{H}$ meter as the detector and sodium hydroxide as the titrant (see Fig. 5).

Racemization Studies.—These were carried out with the $L\text{-}[\text{Si}(\text{acac})_3]\text{Cl}$ isomer obtained from ion-exchange treatment of the diastereoisomer $L\text{-}[\text{Si}(\text{acac})_3]d\text{-}(-)\text{-HC}_{18}\text{H}_{12}\text{O}_8$.¹ The concentration of the complex was about 7.5×10^{-4} mole per liter. Experiments also were performed where the complex concentration was 3.0×10^{-5} and 1.5×10^{-5} molar. No difference in the kinetic order of the reaction could be observed by these concentration changes.

Instruments.—Ultraviolet spectra were obtained with a Spectracord automatic recording spectrophotometer using 1 cm. quartz cells. The hydrolysis data at $305\text{ m}\mu$ were taken with a Beckman model DU spectrophotometer using 1 cm. quartz cells. Determinations of optical rotation were carried out at the sodium-D line on a Rudolph High Precision Visual Polarimeter, Model 80. The $p\text{H}$ determinations were made with a Leeds and Northrup $p\text{H}$ Indicator.

Acknowledgment.—The authors wish to express their appreciation to the Union Carbide Corporation for a research fellowship grant which contributed significantly to the progress of this investigation.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY, CHEMICAL ENGINEERING DIVISION]

Preparation, Properties and Reactions of Bismuth Pentafluoride¹

BY JACK FISCHER AND EDGARS RUDZITIS

RECEIVED JUNE 1, 1959

Bismuth pentafluoride was prepared by synthesis from bismuth and fluorine at 500° . Its crystal structure, density of the solid and liquid, triple point temperature and vapor pressure were determined and the latent heat of vaporization and Trouton constant were calculated. Various chemical reactions of bismuth pentafluoride, such as its reduction with hydrogen and fluorination reactions with various elements and compounds, were studied. Bismuth pentafluoride acts as a strong fluorinating agent.

A literature search revealed little information about bismuth pentafluoride. There have been some unsuccessful attempts to prepare bismuth pentafluoride in aqueous solution.^{2,3} The com-

pound was first prepared by von Wartenberg⁴ by fluorination of bismuth trifluoride at 550° . Bismuth pentafluoride was found to be extremely reactive and no positive identification was carried out. Gutman and Emeleus⁵ next investigated the chemistry of bismuth pentafluoride. They studied

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Weinland and Lauenstein, *Z. anorg. Chem.*, **20**, 46 (1899).

(3) Wuorinen, *Suomen Kemistilehti*, **B**, 3 (1940).

(4) H. von Wartenberg, *Z. anorg. Chem.*, **240**, 337 (1940).

(5) V. Gutman and H. J. Emeleus, *J. Chem. Soc.*, 1046 (1950).

the reactions of bismuth pentafluoride in bromine trifluoride. An attempt to prepare bismuth pentafluoride by the reaction of compounds of trivalent bismuth with bromine trifluoride failed.⁶

This report describes synthesis of bismuth pentafluoride from bismuth and fluorine and an investigation of its physical and chemical properties.

Experimental

Materials.—Commercial 99.99% bismuth was used after it had been checked for impurities by spectroscopic analysis. Other reagents were commercial high-purity grades and were used without further purification.

Apparatus.—The central part of the apparatus consisted of a manifold made from $\frac{3}{8}$ inch tubing which joined gas, vacuum lines, reaction vessels and pressure measuring equipment made of nickel, Monel and copper. Components of the system were separated by nickel Hoke valves. The components were joined by either silver soldered connections or flare and compression fittings, which were sealed with Teflon or copper gaskets.

Pressure measuring equipment consisted of helicoid gages and well-type mercury manometers employing Booth-Cromer pressure transmitters.⁷ Temperatures were measured by chromel-alumel thermocouples and recorded by a recording potentiometer. In cases where higher precision was required, a Rubicon Type B potentiometer was used.

The chemical reactions and triple point determination of bismuth pentafluoride were carried out in closed nickel tubes provided with thermocouple wells.

Some of the reactants and products, especially bismuth pentafluoride, were very sensitive to moisture; therefore, all of the external operations were performed in a helium filled dry box. Helium was dried by passing it through "Molecular Sieves." The water content in the dry box was determined to be less than 10 parts per million.

Analytical Procedures

Determination of Bismuth and Fluorine.—The bismuth contents in the pentafluoride and trifluoride were analytically verified to be within 1.5% of the theoretical value by precipitation with cupferron and ignition to bismuth trioxide, Bi₂O₃. Bismuth pentafluoride, because of its high reactivity, had to be carefully hydrolyzed and reduced to the trivalent state. Bismuth trifluoride was dissolved directly in 1 *N* hydrochloric acid.

Because of the high reactivity of bismuth pentafluoride with water, the fluorine content was determined indirectly by reducing it to the trifluoride and bismuth stepwise with hydrogen: $\text{BiF}_5 + \text{H}_2 \rightarrow \text{BiF}_3 + 2\text{HF}$ at 180° and $\text{BiF}_3 + \frac{3}{2}\text{H}_2 \rightarrow \text{Bi} + 3\text{HF}$ at 430°. The hydrogen fluoride formed was absorbed and acidimetrically determined in a standard solution of sodium hydroxide. This result was compared with the weight loss incurred during the reaction. Both methods yielded the fluorine content of bismuth pentafluoride within 1% of the theoretical value.

Preparation and Purification of Bismuth Pentafluoride.—About 100 g. of bismuth was melted in an Alundum crucible within a Monel vessel and treated with fluorine at 1500 mm. The beginning of the reaction, which occurred near 600°, was observed by a temperature increase, which was measured by an Alundum protected thermocouple immersed in the melt. An induction period which usually preceded the reaction could be shortened by evacuation and re-admission of fluorine to the reaction vessel. After the process was initiated the reaction temperature could be reduced to 500° without interrupting the reaction. A lowering of the reaction temperature improved the yield of the pentafluoride. The rate of fluorine reaction was approximately 0.1 mole per hour. The reaction product, in the form of white needles, had condensed on the cooled upper portion of the vessel. No indications of attack on Alundum by the reactants had been observed. The crude bismuth pentafluoride, containing some bismuth trifluoride, was purified by repeated sublimation in a Vycor tube at 120°, which bismuth pentafluoride does not attack even at 220° for short periods of time.

(6) H. J. Emeleus and A. A. Woolf, *J. Chem. Soc.*, 164 (1950).

(7) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.

It was observed that slow crystallization in a closed vessel under fluorine pressure yielded needle-shaped crystals of up to 2 cm. long.

Physical Properties of Bismuth Pentafluoride: Solid and Liquid Densities.—Powder density determinations were carried out using Halocarbon Oil, Series 11-14, as a pycnometer liquid. Halocarbon oil is manufactured by Halocarbon Products Corporation and consists of saturated low polymers of chlorotrifluoroethylene. The oil completely wet the powdered bismuth pentafluoride, and no immediate reaction occurred at room temperature. However, slow gas evolution was observed after prolonged contact. On heating to 100° a fast decomposition to bismuth trifluoride and fluorine was observed. No appreciable solubility of bismuth pentafluoride in halocarbon oil was found. The average of three density determinations gave a value of 5.4 g./cc. at 25° which is in good agreement with the X-ray density of 5.52 g./cc. A liquid density of 3.7 g./cc. at 160° was obtained by measuring the volume of a known weight of molten bismuth pentafluoride.

Triple Point.—A triple point determination by thermal analysis yielded a value of $151.4 \pm 0.5^\circ$. The triple point did not change after repeated thermal cycling. There seems to be no appreciable solubility of bismuth trifluoride in molten bismuth pentafluoride near the melting point. The addition of bismuth trifluoride to pentafluoride did not change the melting point of the latter and the trifluoride remained in suspension.

Thermal Decomposition.—Bismuth pentafluoride decomposes on heating into bismuth trifluoride and fluorine. This was indicated from a vapor density determination yielding a value of 43 as the average molecular weight of the gas phase over liquid bismuth pentafluoride at 174° (mol. wt. of F₂ = 38). The determination was carried out in a nickel vessel using the method of Dumas. Determinations of the dissociation pressure had to be discontinued after the pressure exceeded the range of the Booth-Cromer pressure transmitter. Another attempt to obtain a provisional value of the dissociation pressure using a helicoid gage connected to a test-tube with bismuth pentafluoride in a heated box was also discontinued because of the failure of the equipment after reaching a fluorine pressure of 6000 mm. at 200°. The dissociation pressure indicates a negative value for the ΔF of the decomposition reaction at 200°. The decomposition rate, starting with 0.1 mole of bismuth pentafluoride, was approximately 5×10^{-4} mole/hr. at 167°.

Vapor Pressure and Derived Data.—Because of continuous decomposition most of the vapor pressure determination methods were not applicable. In the liquid range a method could be used in which boiling points at different temperatures were determined by observation of ebullition as the vapor pressure of the bismuth pentafluoride became equal to the variable pressure of helium measured with a helicoid gage. Eleven determinations were made in the temperature range between 167 and 223°. A plot of the vapor pressure in mm. against the reciprocal of the absolute temperature was made and a linear equation was obtained

$$\log P_{\text{mm}} = 9.340 - 3250/T \quad (1)$$

The experimental values for the vapor pressure of bismuth pentafluoride agree with values calculated from equation 1 with an average deviation of $\pm 6.5\%$. The temperature was measured to $\pm 1^\circ$ and the pressure measurements are accurate to ± 5 mm. Extrapolation of the line gave a boiling point of 230° at 760 mm. and a vapor pressure of 48 mm. at the triple point, 151°. Application of the Clausius-Clapeyron equation yielded 14.9 kcal./mole as the latent heat of vaporization. A Trouton constant of 29.5 cal./deg. mole was calculated, which is indicative of molecular association.

Crystal Structure.—Powder diffraction patterns of bismuth pentafluoride indicate that it has the same structure as the body-centered tetragonal α -polymorph of uranium pentafluoride. The X-ray density was calculated to be 5.52 g./cc. assuming that there are two molecules per unit cell.

Chemical Reactions of Bismuth Pentafluoride. Hydrolysis.—Bismuth pentafluoride is very reactive toward water. The first step is a fast hydrolysis reaction during which a voluminous dark brown precipitate is formed. This compound, probably a hydrated oxyfluoride of pentavalent bismuth, undergoes a relatively slow reduction to a white fluoride containing trivalent bismuth compound. The product and intermediates of the aqueous reactions were not

further investigated. Gram amounts of bismuth pentafluoride may hydrolyze explosively. Attempts to determine bismuth pentafluoride quantitatively, by oxidation reduction reactions in aqueous solutions, gave erratic results.

Reduction of Bismuth Pentafluoride by Hydrogen.—Bismuth pentafluoride can be reduced with hydrogen at elevated temperatures stepwise as described previously. The reductions were carried out in an all-nickel system using a slow stream of hydrogen. The temperature was raised slowly to the appropriate reduction temperature.

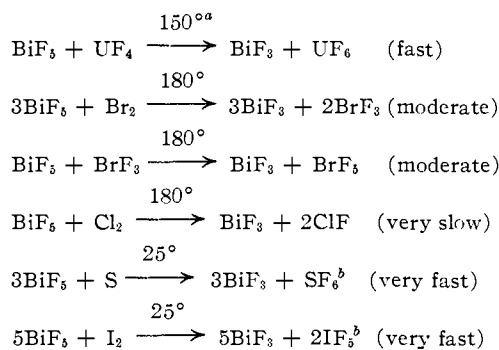
Reproducible results could be obtained only when the reductions were carried out slowly in a system pretreated with hydrogen fluoride at the respective temperatures.

Bismuth Pentafluoride as a Fluorinating Agent.—Investigation of some of the chemical reactions of bismuth pentafluoride were made to obtain some knowledge of it as a fluorinating agent. The free energy of formation of bismuth pentafluoride is not known. Bismuth trifluoride exhibits the characteristics of an ionic compound. Bismuth pentafluoride, however, has strong covalent characteristics. The average bond strength of the two additional fluorine bonds in bismuth pentafluoride is probably much weaker than the average fluorine-bismuth bond in bismuth trifluoride.

Some estimate of the average free energy per gram atom of fluorine in reactions involving the reduction of bismuth pentafluoride to bismuth trifluoride was made by treating bismuth pentafluoride with elements and compounds which were oxidized to higher valent states.

Chemical reactions that were studied are shown in Table I. The reaction products, uranium hexafluoride, bromine trifluoride, bromine pentafluoride and chlorine monofluoride were isolated in approximately 50% yields and identified by their vapor pressures and hydrolytic reactions. Bismuth trifluoride was identified by its X-ray powder pattern and quantitative analysis for bismuth and fluorine. Temperatures at which the reactions are initiated and relative rates of the reactions are shown in Table I.

TABLE I
FLUORINATION REACTIONS OF BISMUTH PENTAFLUORIDE



^a Temperature at which reaction was initiated. ^b Product not positively identified.

One can estimate, from the chemical reactions of bismuth pentafluoride and the free energies, that the average free energy per gram atom of fluorine in fluorinating bismuth trifluoride to bismuth pentafluoride is less negative than -14 kcal. at 180° .

Further qualitative investigation of fluorination properties showed that uranium dioxide was fluorinated easily to uranium hexafluoride by an excess of bismuth pentafluoride at 135° . Upon contacting dry oxygen with molten bismuth pentafluoride no signs of a reaction were observed.

Addition Compounds.—The tendency of bismuth pentafluoride to form addition compounds was observed by Gutman and Emeleus⁸ when they isolated addition compounds of bismuth pentafluoride with silver fluoride and bromine trifluoride, respectively, from bromine trifluoride solutions.

In the present investigation a series of addition compounds has been prepared by treating bismuth pentafluoride with lithium fluoride at 150° , sodium fluoride at 85° , potassium fluoride at 150° and silver fluoride at 90° . Equimolar amounts (approximately 0.1 mole) of the reaction components were heated in closed nickel test-tubes. In all cases exothermic heat effects were observed.

An attempt to form an addition compound by the reaction of bismuth pentafluoride with hydrogen fluoride failed. There was no evidence of a reaction between bismuth pentafluoride and bismuth trifluoride up to 300° .

Quantitative hydrogen reductions of KBiF_6 and LiBiF_6 -hexafluorobismuthates(V) of potassium and lithium, were carried out in a similar fashion as described previously for the reduction of bismuth pentafluoride. A stepwise reduction of potassium hexafluorobismuthate(V) first to potassium tetrafluorobismuthate(III) and then a mixture of bismuth and potassium fluoride was carried out at 300 and 430° , respectively. When the reduction was carried out at 180° for 15 hr., a temperature sufficient to reduce bismuth pentafluoride to trifluoride, only 3% reduction occurred. Lithium hexafluorobismuthate(V) was 25% reduced at 180° after 15 hr. It should be noted that although the addition of potassium fluoride or lithium fluoride to bismuth pentafluoride seems to stabilize the pentavalent state toward reduction with hydrogen, there is no appreciable stabilization of the trivalent state which was completely reduced at the same temperature as the uncomplexed bismuth trifluoride.⁸

X-Ray powder diffraction patterns of the addition compounds of pentavalent bismuth were obtained. None of them had been known previously. The pattern of potassium hexafluorobismuthate(V) indicated that the structure was similar to the antimony salt, KSbF_6 . The patterns of other addition compounds so far have been evaluated only qualitatively indicating that in all cases the product showed a different pattern from that of the starting materials.

Notes on Behavior of Bismuth Trifluoride.—Bismuth trifluoride prepared by reduction of the pentafluoride was identified by chemical analysis. X-Ray powder diffraction patterns obtained from hydrogen and bromine, reduced bismuth pentafluoride and that of partially fluorinated bismuth show a molecular species considered to be bismuth trifluoride.⁸

It was observed that bismuth trifluoride forms a relatively stable addition compound with bromine trifluoride. The white solid decomposed between 200 and 300° , under reduced pressure.

Acknowledgments.—The authors wish to acknowledge the assistance of W. H. Gunther in the experimental determinations. The X-ray work was performed by D. S. Flikkema and B. Tani.

LEMONT, ILLINOIS

(8) B. Aurivillius, *Acta Chem. Scand.*, **9**, 1206 (1955).