THE HALOGEN FLUORIDES

HAROLD SIMMONS BOOTH
Department of Chemistry, Western Reserve University, Cleveland, Ohio
AND
JOHN TURNER PINKSTON, JR.
The Harshaw Chemical Company, Cleveland, Ohio

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I. Introduction

The halogen fluorides make up the most reactive class of chemical compounds known, with some members of the group approaching elemental fluorine itself in reactivity. Under the proper conditions, they appear to react with all organic materials, with all of the metals, and with all of the non-metals excepting the inert gases and nitrogen and oxygen. They decompose water to give ozone and oxygenated halogen acids. They react with most salts to form the corresponding fluorides. They have been used in the preparation of organic fluorides and should find a wide variety of other applications where the action of elemental fluorine in a modified degree is desired.

In view of the recent commercial availability of some of the halogen fluorides, it seems particularly timely to assemble all the published information pertaining to them. These substances appear to offer such a wealth of possibilities for attacks on both theoretical and applied problems that a summary of the available information relating to them should prove useful.

II. Iodine Pentafluoride

A. PREPARATION

In a historical sense, the fluorides of iodine take precedence over the other members of the group. The possibility of the formation of a compound of fluorine and iodine was recognized as early as 1845 by H. B. Leeson (12). This investigator thought that he had prepared such a compound by passing the gas generated from one part of manganese dioxide, three parts of calcium fluoride, and six parts of concentrated sulfuric acid through water containing iodine until the whole of the iodine was taken up. Since both of the known iodine fluorides react with water, it appears that Leeson was mistaken.

Although he did not recognize it and reached an incorrect conclusion, Kammerer (7) was probably the first to prepare iodine pentafluoride. He heated dry silver fluoride and iodine together in a sealed tube to 70–80°C. After 24 hr. the color of iodine disappeared. The gaseous portion of the reaction product was collected over mercury and absorbed by aqueous potassium hydroxide. Since the resulting solution gave no test for the iodide ion, Kammerer erroneously concluded that he had isolated fluorine.

The actual nature of this reaction was clarified by Gore (3, 4, 5), who showed that iodine and silver fluoride under the influence of heat yield silver iodide and a fluoride of iodine. At 90–315°C. iodine reacts only slowly with silver fluoride, but at red heat the reaction proceeds readily. The platinum vessels used for carrying out the reaction are corroded at the higher temperature, giving rise to the formation of a double salt of silver iodide and platinum fluoride.

Moissan (15, 17) reduced the preparation of iodine pentafluoride to a more practical basis. He found that fluorine ignites iodine, burning it with a pale blue flame to yield iodine pentafluoride. Likewise, he showed that fluorine reacts with metallic iodides and hydrogen iodide to produce iodine pentafluoride and the corresponding fluorides. The preparation of iodine pentafluoride was preferably carried out by causing a stream of fluorine to impinge on iodine contained in a platinum boat in a glass tube. The iodine pentafluoride was condensed in a cold end of the glass tube. The physical constants for iodine pentafluoride reported by Moissan and later investigators differ sufficiently from those reported by Gore as to cast doubt on the purity of the material obtained by the English investigator.

Prideaux (20) confirmed the analysis made by Moissan on iodine pentafluoride prepared by direct combination of the elements. In a further study of the reaction, he found that iodine was not soluble in liquid fluorine at atmospheric pressure, nor did any reaction take place between the elements as fluorine distilled from the mixture. When the tube containing iodine and liquid fluorine was sealed off and permitted to become warm, however, a dark color appeared in the fluorine next to the iodine and a reaction occurred with flame. A colorless liquid, iodine pentafluoride, condensed in the tube.

Ruff and Keim (26) devised an improved method for the preparation of iodine pentafluoride. Their apparatus consisted of a large-diameter copper tube connected by a small copper tube to a quartz spiral condenser and a receiver. Fluorine was passed over iodine placed in the large copper tube. The heat of the reaction caused the iodine pentafluoride to distill through the small copper tube and into the quartz condenser. The passage of fluorine was continued until all free iodine in the iodine pentafluoride was removed. The product was purified by redistillation in fused quartz at about 5°C. under reduced pressure, with the condenser kept at -20°C.

Ruff and Braida (25) preferred to have a slight excess of iodine present at the end of the reaction and thus minimize the formation of iodine heptafluoride. They purified iodine pentafluoride by distilling the crude product in quartz apparatus at approximately 10 mm. pressure and taking the fraction over at

−10°C. The residue consisted of iodine pentafluoride and iodine oxyfluoride, the presence of the latter being due to the reaction of some moisture present with the iodine pentafluoride.

B. PHYSICAL PROPERTIES

While Moissan (17), Gore (3, 4), Prideaux (19), and others have reported physical constants for iodine pentafluoride, the most recent and complete data are due to Ruff and Braida (24). These latter investigators have described iodine pentafluoride as a colorless liquid which freezes at 9.6°C. and boils at 98°C. The relation between the vapor pressure (millimeters of mercury) of the solid and temperature (°K.) is given by

$$\log p = 11.764 - \frac{3035}{T}$$

while that of the liquid corresponds to

$$\log p = 8.83 - \frac{2205}{T}$$

At 0°C. the density of the solid is approximately 3.75 g./ml., while at −193°C. it is 4.07 g./ml. The density of the liquid is given by the expression:

$$d = 4.38 - 0.004T$$

C. CHEMICAL PROPERTIES

1. Thermal decomposition (17)

Iodine pentafluoride distills at atmospheric pressure without decomposition. When it is heated to approximately 500°C., however, iodine vapors are produced. An increase in temperature accentuates this change only slightly. It seems highly improbable that fluorine is a dissociation product as well as iodine. Rather, Moissan suggested the possibility of the formation of a higher iodine fluoride, as:

$$7IF_5 \rightarrow I_2 + 5IF_7$$

2. Reactions with metals (17)

Silver, magnesium, copper, mercury, iron, and chromium are only very slightly attacked by iodine pentafluoride even on long contact. Molybdenum and tungsten burn in it after warming. At room temperature the alkali metals when plunged into iodine pentafluoride form a surface coating which stops further action. If the alkali metal is heated to its melting point, however, the reaction becomes so violent as to be almost explosive. Arsenic, antimony, and boron become incandescent or inflame in iodine pentafluoride, yielding iodine and the metalloid fluoride.

3. Reactions with other elements (17)

Iodine pentafluoride is not affected by distillation in hydrogen. At 100°C. it is not attacked by oxygen. The reaction between sulfur and warm liquid iodine pentafluoride results in a mixture containing sulfur hexafluoride and sulfur monoiodide and free iodine in small amounts. Red phosphorus burns vigorously in iodine pentafluoride, yielding iodine and phosphorus trifluoride. Chlorine does not react with iodine pentafluoride when cold, but if the temperature is raised the liquid becomes tinged with yellow. Likewise bromine does not react with iodine pentafluoride when cold, but bromine trifluoride and iodine bromide are formed when the mixture is heated. Iodine is very soluble in iodine pentafluoride, but does not react with it (*vide infra*). In the cold, iodine pentafluoride and carbon react to yield carbon tetrafluoride and iodine.

4. Reactions with inorganic compounds (17)

Iodine pentafluoride reacts violently with water and with aqueous solutions in general. Apparently the hydrolysis proceeds as follows:

$$6H_2O + 2IF_5 \rightarrow 2HIO_3 + 10HF$$

While calcium carbonate and calcium phosphate are inert to iodine pentafluoride, calcium carbide becomes incandescent when warmed with it. When potassium hydride is brought into contact with iodine pentafluoride it glows. The reaction products are hydrogen fluoride, potassium fluoride, and iodine.

Iodine pentafluoride is not soluble in concentrated sulfuric acid, but settles to the bottom of the container when added to it. There a reaction sets in at the interface between the liquids and a regular evolution of bubbles of hydrogen fluoride takes place. Iodine pentafluoride does not dissolve appreciably in concentrated nitric acid and does not react immediately with it.

5. Reactions with organic compounds

In a qualitative manner Moissan (17) noted that iodine pentafluoride reacts with such organic compounds as alcohols, ether, ethyl acetate, carbon tetrachloride, chloroform, *s*-tetrachloroethane, perchloroethylene, trichloroethylene, pyridine, benzene, and hydrocarbon mixtures such as gasoline and turpentine. The reactions with chlorine-containing compounds were characterized by the separation of iodine. Compounds rich in hydrogen yielded hydrogen fluoride and tended to inflame in the iodine pentafluoride.

Ruff and Keim (27) studied the action of iodine pentafluoride on benzene at temperatures below 50°C., the point at which the reaction suddenly became violent. The principal products were hydrogen fluoride, iodobenzene, and carbonized matter. Only a small amount of fluorobenzene was formed.

By maintaining iodine pentafluoride in contact with dry carbon tetrachloride at 30–35°C. for an extended period, Ruff and Keim (27) obtained a gas consisting chiefly of trichlorofluoromethane and a small amount of dichlorodifluoromethane. The reaction mixture contained an orange residue of iodine monochloride, iodine trichloride, and some iodine pentoxide resulting from attack on the glass vessel. Only a few per cent of trichlorofluoromethane was changed to dichlorodifluoromethane when trichlorofluoromethane was passed through boiling iodine pentafluoride and the resulting gas mixture heated first to 125°C. and then to 225°C.

Simons, Bond, and McArthur (35) showed that iodine pentafluoride begins to react with iodoform at the temperature of an ice–salt mixture. In their study the temperature was raised gradually to 80–90°C. as the reaction proceeded, and thereby a product mixture of fluoroform and difluorodiiodomethane in a ratio of about 15 to 1 was obtained. When carbon tetraiodide was a reactant under the same conditions, the product was hexafluoroethane.

Scott and Bunnett (32) found that iodine pentafluoride is partially soluble in dry 1,4-dioxane, and that the addition of an excess of iodine pentafluoride caused the precipitation of colorless crystals of a dioxanate having the formula $IF_5 \cdot C_4H_8O_2$. These crystals hydrolyzed in air and even over sulfuric acid in a desiccator. When hydrolysis was complete, the only solid residue was iodic acid. The melting of the dioxanate was accompanied by decomposition and the evolution of hydrogen fluoride and iodine vapor. The value of the melting point varied from 84°C. to more than 112°C., depending on the manner in which it was determined.

D. PHYSIOLOGICAL ACTION

Hanzlik and Tarr (6) found iodine pentafluoride to be a severe skin irritant, as shown by hyperemia, edema, vesication, necrosis, and ulceration.

III. Iodine Heptafluoride

A. PREPARATION

Moissan (17) observed that at 500°C. iodine pentafluoride began to decompose, liberating iodine vapor. He concluded that this was either a dissociation or a decomposition yielding a new fluoride of iodine. Undoubtedly, Moissan produced iodine heptafluoride by the reaction

$$7IF_5 \rightarrow I_2 + 5IF_7$$

Although he promised to investigate it, he failed to do so.

On redistillation of crude iodine pentafluoride Ruff and Keim (26) observed repeatedly the separation of a compound containing iodine and fluorine which was more volatile than iodine pentafluoride. The amount of this material available, however, was too small to permit its purification and identification. After producing chlorine trifluoride they concluded that iodine heptafluoride should exist and turned to its study.

On passing fluorine into liquid iodine pentafluoride no appreciable amount of a more volatile fluoride was obtained, but when a mixture of iodine pentafluoride and fluorine was heated, iodine heptafluoride was produced. Over the range of 100–270°C. the yield of iodine heptafluoride based on the fluorine used increased with increasing temperature. Platinum apparatus was used. In it at 250–270°C. a conversion of 83 per cent of the fluorine used to iodine heptafluoride was obtained.

The iodine heptafluoride was purified by pumping off silicon tetrafluoride at −90°C., followed by fractional distillation of iodine heptafluoride from the iodine pentafluoride.

B. PHYSICAL PROPERTIES (26)

Pure iodine heptafluoride at room temperature is a colorless gas with a sour, musty odor. It may be cooled to a dense, snow-white powder, to colorless crystals, or to a colorless, mobile, supercooled liquid. The compound sublimes at 4.5°C. and melts at 5–6°C.

The molecular weight based on determinations of vapor density at room temperature was found to average 260.2, while theory calls for 260.3. Ruff and Keim claimed that this indicated no association at a little above the boiling point.

The vapor pressure of the solid determined on a freshly sublimed sample was found to correspond to the expression:

$$\log p = 8.6604 - \frac{1602.6}{T}$$

C. CHEMICAL PROPERTIES (26)

1. Reactions with metals

With the possible exception of elements in the platinum group, iodine heptafluoride appears to react with all metals. The extent of the reaction seems to be determined by the stability of the fluoride film formed on the metal.

Copper and silver tarnish slightly when heated with iodine heptafluoride. Likewise, a stable film is formed on the surface of mercury which, even on moderate heating, protects the remainder of the metal from the iodine heptafluoride.

Iron, chromium, and cobalt react at a red heat, yielding compounds of undetermined composition. Molybdenum and tungsten form the volatile compounds molybdenum hexafluoride and tungsten hexafluoride. Thus these metals on slight warming with iodine heptafluoride react readily and completely.

The reactions of iodine heptafluoride with sodium, potassium, barium, magnesium, aluminum, and tin are vigorous and are accompanied by the evolution of heat and light. Reaction takes place immediately with the first three metals, but heating is required for the last three, since they are protected by a fluoride film at room temperature.

2. Reactions with other elements (26)

Sulfur reacts with iodine heptafluoride at room temperature producing iodine and sulfur fluorides of undetermined composition, but selenium and tellurium require heating to undergo the same type of reaction. Arsenic, phosphorus, boron, and silicon all react at room temperature to give the corresponding fluorides, iodine pentafluoride, and iodine.

Iodine reacts with iodine heptafluoride to produce iodine pentafluoride. Chlorine reacts with iodine heptafluoride with the formation of iodine monochloride, iodine trichloride, and chlorine monofluoride. Bromine, however, was found not to react with iodine heptafluoride. (This observation should be checked, for the formation of iodine bromide and bromine trifluoride would be expected to occur.)

While iodine heptafluoride was inert to hydrogen at room temperature, heating a mixture of the materials gave rise to reactions of explosive violence. A mixture of 1 volume of iodine heptafluoride and 3.5 volumes of hydrogen was exploded by an electric spark into hydrogen fluoride, hydrogen iodide, and some iodine.

Pure activated carbon immediately caught fire in iodine heptafluoride and free iodine was liberated.

3. Reactions with inorganic compounds (26)

Water quietly dissolved gaseous iodine heptafluoride, forming periodate and fluoride ions.

After being warmed slightly, carbon monoxide burned in iodine heptafluoride with a pale yellow flame. In the form of compact quartz silica was attacked only slowly by iodine heptafluoride, but in the form of glass it reacted with it more readily. With nitric oxide at room temperature iodine heptafluoride formed nitroxyl fluoride, nitrosyl fluoride, and iodine pentafluoride. Tungstic oxide and molybdic oxide reacted after heating with iodine heptafluoride to form oxyfluorides, but phosphorus pentoxide even on heating showed only a slight reaction.

Potassium bromide, silver nitrate, and sodium carbonate all reacted with iodine heptafluoride, but the reaction products were not determined satisfactorily. In the first case, it was observed that bromine was liberated. Silver iodide and metallic silver were the only products reported in the silver nitrate reaction. Sodium carbonate was merely observed to become hot in contact with iodine heptafluoride.

4. Reactions with organic compounds (26)

Organic compounds in general have been found to react with iodine heptafluoride to produce complex mixtures of degraded organic fluorides and iodine.

Benzene and light paraffin hydrocarbons took fire at once in iodine heptafluoride. This was also true of alcohol and ether. Methane burned to form hydrogen fluoride, iodine, and (presumably) carbon tetrafluoride, with no free carbon separating.

Paraffin oils, stopcock grease, cotton, and cellulose reacted slowly or with flame, depending on the amount of iodine heptafluoride present. Such oxygen-containing materials as acetone, acetic acid, and ethyl acetate reacted immediately and were heated by the reaction to boiling. The products in these cases included hydrogen fluoride, iodine pentoxide, and highly volatile organic fluorides.

Pyridine united with iodine heptafluoride with the evolution of considerable heat to form an orange product of undetermined composition.

Chloroform, carbon tetrachloride, tetrachloroethane, perchloroethylene, and trichloroethylene all reacted to yield a mixture of gases having a sweet odor.

IV. Lower Fluorides of Iodine (25)

The available information indicates that no fluoride of iodine lower than iodine pentafluoride has a stable existence. Measurements of the vapor pressure and melting point of a mixture of iodine pentafluoride and iodine gave no evidence of a lower fluoride. Fractional distillation of the mixture yielded only iodine and iodine pentafluoride. The direct reaction of iodine and fluorine to iodine pentafluoride or iodine heptafluoride further points to the absence of a compound like iodine trifluoride.

V. Bromine Monofluoride

A. PREPARATION

The existence of the monofluoride of bromine was suspected by Ruff and Menzel (30) when they noted that the product of the reaction of bromine trifluoride and bromine had a higher vapor pressure and a stronger etching action on vitreous quartz than bromine trifluoride, bromine pentafluoride, or bromine.

Ruff and Braida (24) undertook the preparation of bromine monofluoride, but were unable to obtain it in a pure form because of its instability. Mixtures of bromine trifluoride, bromine pentafluoride, bromine, and bromine monofluoride were produced by the reaction of fluorine and bromine diluted by nitrogen at 10°C. The reaction product was fractionally condensed at the successively lower temperatures of 10°, −20°, −50°, −120°, and −185°C. Based on analysis, density, and vapor-pressure data, the conclusion was reached by Ruff and Braida that the mixture condensed in one of the −120°C. traps contained almost 50 per cent bromine monofluoride. The present reviewers do not find the evidence altogether convincing.

B. PHYSICAL PROPERTIES

Ruff and Braida (24) estimated the boiling and freezing points of bromine monofluoride to be −20°C. and −33°C., respectively. The gas, liquid, and solid phases of bromine monofluoride were reported as being red-brown, red, and the color of dichromate, respectively.

C. CHEMICAL PROPERTIES

The chemical properties of bromine monofluoride are reported to resemble those of the other bromine fluorides in general. Its outstanding property is its thermal instability. At 50°C. the decomposition into bromine and bromine trifluoride was found to be so rapid that bromine monofluoride could no longer be detected. This low stability was found to be further decreased by exposure to light.

Bromine monofluoride quickly destroyed vitreous quartz and attacked gold and platinum vigorously under conditions which left these materials unaffected by bromine and fluorine.

VI. Bromine Trifluoride

A. PREPARATION

Moissan (16) found that fluorine combined violently with bromine vapor in the cold with "une flamme éclairante." When fluorine was passed through liquid bromine, combination was also immediate but without flame. The composition of the product was first established by Lebeau (8, 9, 10, 11) and was almost immediately verified by Prideaux (20) as corresponding to bromine trifluoride.

Lebeau prepared bromine trifluoride in a platinum crucible by passing fluorine beneath the surface of dry liquid bromine. The crucible itself was contained in a large glass cylinder judiciously cooled by dry ice to maintain a temperature slightly above the freezing point of bromine (−7.2°C.). The reaction was immediate and quite regular. The bromine trifluoride condensed completely in the crucible and formed an upper liquid layer rather insoluble in the liquid bromine. The bromine trifluoride dissolved enough bromine to give the resulting solution a yellow color.

Bromine trifluoride was also formed when metallic bromides were decomposed by fluorine (9):

$$\mathrm{KBr} + 2\mathrm{F}_2 \rightarrow \mathrm{KF} + \mathrm{BrF}_3$$

Ruff and Menzel (30) prepared bromine trifluoride by reacting fluorine with bromine at 200°C. (*vide infra*).

B. PHYSICAL PROPERTIES

Ruff and Braida (23, 24) found bromine trifluoride to be a colorless liquid which solidified at 8.8°C. At the melting point the density of the solid was 3.23 g./ml. and that of the liquid was 2.843 g./ml. The variation of the liquid density with absolute temperature is given by the equation:

$$\mathrm{d} = 3.623 - 0.00277T$$

Ruff and Braida (24) determined the vapor pressure of bromine trifluoride between 3.8 and 136 mm. of mercury in platinum apparatus of the Smith–Menzies type. The vapor pressure–absolute temperature relation could be expressed by the equation:

$$\log p = 8.41954 - \frac{2220.2}{T}$$

From this equation the boiling point was calculated to be 127.6°C. This extrapolated value appears to be too low, since Lebeau (8) by direct measurement was able to report a boiling point between 130° and 140°C.

By the use of the Clausius–Clapeyron equation and their vapor-pressure data Ruff and Braida showed that the heat of vaporization of bromine trifluoride was about 10 kg.-cal. per mole. Trouton's constant was calculated to be 25.3.

C. CHEMICAL PROPERTIES

1. Reactions with elements (8, 9, 10, 11)

Boron, silicon, powdered arsenic, and powdered antimony all burned in liquid bromine trifluoride with the evolution of heat and light. A crystal of iodine when placed on solid bromine trifluoride at first merely stained it brown. Then the bromine trifluoride melted rapidly and reacted with incandescence, evolving iodine pentafluoride and bromine vapor. The reaction was strongly exothermic. Sulfur, like iodine, did not appear to react with solid bromine trifluoride, but it inflamed vigorously with liquid bromine trifluoride, giving a mixture of the fluorides and bromides of sulfur. Graphite was not changed in the cold. Lampblack absorbed the liquid and when warmed slightly burned with a flash.

2. Reaction with water

Bromine trifluoride was found by Lebeau (8) and Prideaux (20) to react vigorously with water to give oxygen and an aqueous solution of hydrofluoric acid, hypobromous acid, and bromic acid. The reaction with aqueous alkali produced oxygen and the salts of the metals.

3. Reactions with organic compounds

Lebeau (8) and Ruff and Braida (23) observed that bromine trifluoride reacted violently with organic compounds. Ether, benzene, and turpentine took fire on contact with it. Methyl chloride at first dissolved bromine trifluoride, and then reacted with explosive violence. In none of these cases was the reaction controlled to give desired products.

Nutting and Petrie (19) have described the preparation of chlorofluoromethanes by the controlled action of bromine trifluoride on carbon tetrachloride.

McBee, Lindgren, and Ligett (13) carried out the preparation of a mixture corresponding approximately to the formula $C_6Br_2Cl_4F_6$ by the action of bromine trifluoride on perchlorobenzene and a mixture approximating $C_6Br_2Cl_3F_6(CF_3)$ when pentachloro(trifluoromethyl)benzene was the organic reactant. These mixtures were intermediates in the preparation of perfluorobenzene and perfluorotoluene, respectively.

D. PHYSIOLOGICAL ACTION

Hanzlik and Tarr (6) found bromine trifluoride to be a severe skin irritant, as shown by hyperemia, edema, vesication, necrosis, and ulceration.

VII. BROMINE PENTAFLUORIDE

A. PREPARATION

The successful preparation of iodine heptafluoride by the high-temperature combination of iodine pentafluoride and fluorine suggested that bromine pentafluoride might be made in a similar manner. Ruff and Menzel (30) heated bromine trifluoride to 90–100°C., mixed the bromine trifluoride vapors with fluorine, and then heated the mixture to 200°C. in a platinum tube. By fractional condensation of the gaseous products bromine pentafluoride was separated from the reaction mixture.

After an explosion, however, the two-step process in platinum was abandoned by Ruff and Menzel in favor of direct combination of bromine and fluorine to bromine pentafluoride in a copper apparatus at 200°C. Purification was accomplished by condensing the entire reaction mixture and then fractionally distilling it in quartz.

B. PHYSICAL PROPERTIES (30)

Ruff and Menzel showed bromine pentafluoride to be a colorless liquid which solidified at −61.3°C. and boiled at 40.5°C. The molecular weight at 330 mm. and 29°C. was found to be 174.7, while theory calls for 174.92. The claim was made that this excellent agreement shows no association of the molecules in the gas phase.

The relation between the vapor pressure of liquid bromine pentafluoride and absolute temperature was shown to be represented by the equation:

$$\log p = 8.0716 - \frac{1627.7}{T}$$

The heat of vaporization at the boiling point was calculated to be 7443 cal. per mole. Trouton's constant was calculated to be 23.7.

The density of solid bromine pentafluoride at the melting point was found to be 3.09 g./ml., while the following equation was shown to give the relation between the liquid density and absolute temperature:

$$\mathrm{d} = 3.496 - 0.00346T$$

C. CHEMICAL PROPERTIES (30)

It appears probable that bromine pentafluoride reacts with every known element except the rare gases and nitrogen and oxygen. With the exception of the inorganic fluorides, there is little doubt that it reacts under proper conditions with the vast majority of inorganic compounds. Even under mild reaction conditions, it attacked organic compounds vigorously.

1. Reactions with metals

There is no recorded failure of bromine pentafluoride to react with a metal. These reactions usually proceed sufficiently rapidly to be accompanied by a sharp rise in temperature and the emission of light. Little is known about the reaction products, except that they contain metallic fluorides. The main difference observed in these reactions is the ease with which they are initiated. The major portion of this difference is probably due to the varying effectiveness of the fluoride films first formed as a means of protection for the main body of metal.

Ruff and Menzel found that lithium powder, barium, zinc, mercury, molybdenum, tungsten, iron, cobalt, arsenic, and antimony react immediately with bromine pentafluoride at room temperature. Bismuth, gold, and manganese in bulk form and powders of aluminum, nickel, rhodium, and iridium required slight warming. Still higher temperatures ranging from about 300°C. to a dull red heat were necessary for the reaction of bromine pentafluoride with sodium, magnesium, calcium, cadmium, copper, tin, chromium, powdered titanium, and platinum.

2. Reactions with other elements

Ruff and Menzel found that powdered boron, carbon, and sulfur reacted immediately and vigorously with bromine pentafluoride, as did red phosphorus, selenium, and tellurium in bulk form. The exact nature of the products was not determined. Although iodine reacted with bromine pentafluoride at room temperature, heating to 250–300°C. was necessary to initiate reactions with chlorine and fluorine. The compositions of the halogen fluoride mixtures which resulted were not reported. Bromine pentafluoride reacted with bromine at 250°C. to give bromine trifluoride.

A violent explosion resulted when a mixture of bromine pentafluoride and hydrogen was ignited by a flame.

3. Reactions with inorganic compounds

Ruff and Menzel (30) reported that bromine pentafluoride reacted immediately with the following oxides, liberating heat: tungstic oxide, molybdic oxide, chromic acid, phosphorus pentoxide, iodine pentoxide, arsenic pentoxide, boric oxide, cadmium oxide, and magnesium oxide. Moderate warming was necessary to start the reaction with silica (kieselguhr) and with glass. While sulfur dioxide and carbon monoxide also reacted, ignition in a flame was required. Bromine pentafluoride reacted violently with water. Ruff and Menzel (30) suspected that the products were bromine oxyfluoride ($BrOF_3$) and hydrogen fluoride, but did not establish the point.

Sodium chloride and potassium bromide both reacted immediately with bromine pentafluoride to evolve chlorine and bromine, respectively. Potassium iodide and ammonium chloride inflamed instantly with bromine pentafluoride. Sodium nitrite, potassium nitrate, and nitric acid reacted with evolution of gases. Ammonia inflamed in bromine pentafluoride, and both sodium hydroxide and sulfuric acid reacted with it evolving heat.

4. Reactions with organic compounds

Ruff and Menzel (30) reported that reactions between bromine pentafluoride and organic compounds are usually accompanied by flame and often approach explosive violence. There is no recorded instance of a desired organic fluoride being made by the use of bromine pentafluoride. These generalizations are borne out by the action of bromine pentafluoride on such widely different organic materials as methane, acetic acid, ethanol, benzene, cork, picein, cotton, paper, textiles, and rubber.

VIII. CHLORINE MONOFLUORIDE

A. PREPARATION

The history of the preparation of chlorine monofluoride is remarkable for the number of failures to prepare it. Moissan (15, 16) found no apparent reaction when fluorine and chlorine were mixed at room temperature. Lebeau (8, 11) remarked that one may conclude that fluorine and chlorine do not react either directly or indirectly at room temperature, since fluorine displaces chlorine from chlorides without producing a chlorine fluoride. Lebeau also observed that fluorine dissolved freely in liquid chlorine at −80°C., but there was no indication that any definite compound was formed. The solution evolved fluorine when cooled to the freezing point of chlorine.

Ruff and Zedner (31) struck an electric arc in a solution of fluorine in liquid chlorine without success.

The first bit of progress was accomplished by Ruff and Ascher (22) in their investigation of the action of hydrogen chloride gas on liquid fluorine. When the hydrogen chloride came in contact with the fluorine gas above the liquid fluorine surface, a greenish light was observed and a white floc settled slowly in the liquid fluorine. Fractionation yielded an orange-colored liquid boiling between −100° and −80°C., but the quantity of this product was too small to permit identification.

Ruff and Ascher (22) had observed, however, that explosions occurred in their preparation of rhodium trifluoride by the passage of fluorine over the trichloride. They then passed a 2:1 mixture of fluorine and chlorine at 400°C. through a quartz tube containing a fluorite boat filled with rhodium to act as a catalyst. The condensate from this process contained an orange-red liquid which etched the quartz, with the formation of silicon tetrafluoride.

Because of this reactivity toward quartz, their later studies of the reaction between fluorine and chlorine were carried out in a copper block heated by an oil bath to 250°C. It was observed that the presence of rhodium was not necessary and that the union of fluorine and chlorine was accompanied by the evolution of heat and by occasional explosions. The chlorine monofluoride was isolated by the fractional condensation of the reaction products.

Ruff *et al.* (21) concluded that the reaction proceeds to an equilibrium and that even in the presence of a great excess of fluorine the product still contains free chlorine. They regarded the formation of chlorine monofluoride as due to the action of nascent chlorine on fluorine and indicated that it should be possible to find catalysts which would permit the reaction to proceed at lower temperatures with better yields.

Fredenhagen and Krefft (2), however, disposed of these views by sparking a mixture of chlorine and fluorine at room temperature and observing that a yellow-red flame spread through the mixture. The reaction resulted in either a detonation or a gentle "puff", depending on the mixture. In the absence of moisture there was no explosion. Fredenhagen and Krefft concluded that fluorine and chlorine actually have a great affinity for each other, and that Ruff's method of preparation prevented the combination of the elements from going to completion.

Ruff and Krug (28) found that a mixture of four parts of chlorine monofluoride and one part of chlorine trifluoride resulted from the reaction of fluorine with chlorine at −170°C. in the volume ratio of three to two.

B. PHYSICAL PROPERTIES

Ruff and Laass (29) found chlorine monofluoride at room temperature to be a colorless gas with a characteristic odor different from both that of fluorine and that of chlorine. In fused quartz it exhibits an orange cast, which is perhaps due to the presence of traces of chlorine monoxide formed from reaction with quartz. At −100.8°C. chlorine monofluoride condenses to a yellowish liquid and at −154°C. it freezes to a white solid.

The vapor pressure of the liquid corresponded to the expression:

$$\log p = 15.738 - \frac{3109}{T} + \frac{1.538(10)^5}{T^2}$$

where p is millimeters of mercury and T is °K.

Ruff and Laass found the heat of formation of chlorine monofluoride to be 25.7 kg.-cal. per mole. This value was based on their determination that

$$\mathrm{ClF} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{HF} + 58.6\ \text{kg.-cal.}$$

and Ruff's value of 62.3 kg.-cal. per mole for the heat of formation of hydrogen fluoride.

Wahrhaftig (36), from a study of the absorption spectrum of chlorine monofluoride between 3500 Å. and 7000 Å., and particularly a band at 4800 Å., concluded that while the heat of formation of chlorine monofluoride is appreciable, the value of 25.7 kg.-cal. per mole is too high.

C. CHEMICAL PROPERTIES (22)

1. Reactions with metals

Like fluorine and the other halogen fluorides, chlorine monofluoride appears to react with all metals, with the differences in degree being due to the varying protective qualities of the films of metallic fluoride originally formed. With chlorine monofluoride, sodium forms a white protective layer in the cold but inflames on heating. Magnesium and aluminum burn in chlorine monofluoride when heated strongly. Copper and zinc as powders and gold and platinum as foils react on slight heating. Iron powder glows on contact with chlorine monofluoride at room temperature. Mercury at first forms a brown-black coating, but on heating yields a white sublimate.

Arsenic, antimony, and amorphous boron all burn briskly at room temperature to arsenic pentafluoride, antimony pentafluoride and, presumably, boron trifluoride.

2. Reactions with other elements

Hydrogen required some heating before it ignited and burned in chlorine monofluoride. Bromine and iodine reacted to produce bromine trifluoride and, probably, iodine pentafluoride. Sulfur reacted slowly and without flame, but phosphorus burned briskly in chlorine monofluoride at room temperature.

3. Reactions with inorganic compounds

Chlorine monofluoride reacted vigorously with water. Oxygen and ozone were among the products formed. After warming, carbon monoxide and sulfur dioxide both reacted with chlorine monofluoride.

4. Reactions with organic compounds

No controlled reaction with any organic compound was observed. Under the test conditions paraffin oil, filter paper, cork, picein, and other organic materials all caught fire in chlorine monofluoride.

IX. CHLORINE TRIFLUORIDE

A. PREPARATION

The first evidence pointing toward the existence of chlorine trifluoride was obtained by Ruff and Laass (29) during their determination of the latent heat of evaporation of chlorine monofluoride. While carrying out their experiments on samples of chlorine monofluoride successively boiled off from the same storage vessel, these investigators obtained an increase in their values of the heat of evaporation. The presence of a higher fluoride in the chlorine monofluoride would account for the trend observed in these measurements.

Accordingly, Ruff and Krug (28) undertook the preparation of chlorine trifluoride. Since it was suspected that a low temperature would favor a good yield, 3 volumes of fluorine and 2 volumes of chlorine were passed into a quartz ampoule held at −170°C. Combination of the elements took place, yielding one part of crude chlorine trifluoride to four parts of chlorine monofluoride. By using 800 ml. of chlorine and 1200 ml. of fluorine per hour for 8 hr., there were prepared about 5 ml. of liquid chlorine trifluoride and 20 ml. of chlorine monofluoride. The chlorine was completely consumed.

The proportion of chlorine trifluoride in the reaction product appeared to be much greater at low temperatures than at high. While the ratio of chlorine monofluoride to chlorine trifluoride is approximately four to one at −170°C., at 250°C. the number of moles of chlorine monofluoride is many times that of chlorine trifluoride.

The production of chlorine trifluoride in Germany in pilot-plant quantities during the recent war has been reported (1, 18). The compound was made by heating the proper proportion of the gaseous elements to 280°C. in a U-shaped tube. The vapors were condensed at −80°C. and run into iron cylinders which were vented several times to allow fluorine, chlorine, and chlorine monofluoride to escape.

Apparently, the German Army intended to use chlorine trifluoride in shells against aircraft and tanks because of its incendiary properties (*vide infra*).

B. ANALYSIS

For analysis, chlorine trifluoride was distilled by Ruff and Krug (28) into a quartz tube which was cooled in liquid air, sealed off in a flame, and then weighed. The tube was broken under 10 per cent sodium hydroxide, which immediately reacted with the chlorine trifluoride. The hypochlorites were reduced by digesting with hydrazine hydrate or pieces of zinc. The total solution was made up to a known volume, from which aliquot portions were taken for the determination of fluoride as calcium fluoride and chloride as silver chloride. It was necessary to complete the reduction of hypochlorites by digesting several times with sulfurous acid after the silver nitrate solution had been added. In two trials the atomic ratio of chlorine to fluorine was found to be 1:2.997 and 1:3.07.

C. PHYSICAL PROPERTIES (28)

While in the liquid phase chlorine trifluoride has a pale green color, as a gas it is practically colorless. In the solid state it is white.

Chlorine trifluoride melts at −83°C. In the liquid phase the vapor pressure is given by the equation

$$\log p = 7.42 - \left(\frac{1.292(10)^3}{T}\right)$$

from which it can be seen that the boiling point is 11.3°C. At the boiling point the latent heat of evaporation is close to 5.9 kg.-cal. per mole, and the Trouton constant is 20.8. The critical temperature is estimated by the "three halves rule" to be 154°C.

In three trials by the density method, the molecular weight of the chlorine trifluoride gas was measured at 86.71, 87.49, and 87.93; theory requires 92.46. Whether the discrepancy is due to partial dissociation or to impurities is uncertain.

D. CHEMICAL PROPERTIES (28)

It appears probable that chlorine trifluoride reacts with every element except the rare gases, nitrogen, and possibly platinum and palladium. There is little doubt that it reacts under proper conditions with the vast majority of inorganic and organic compounds.

1. Reactions with metals

While some metals such as magnesium, aluminum, and copper form a protective fluoride film which can halt further action, at elevated temperatures these metals combine explosively with chlorine trifluoride. To varying extents this is true of other metals, including silver, lead, zinc, tin, sodium, and calcium. Although potassium, molybdenum, tungsten, iron, rubidium, iridium, and osmium are reported to inflame in chlorine trifluoride, it seems likely that under proper conditions protective fluoride films can be built up on at least some of these metals.

2. Reactions with non-metals

Such representative non-metals as silicon, red phosphorus, arsenic, antimony, sulfur, selenium, tellurium, bromine, and iodine inflame on contact with chlorine trifluoride.

3. Reactions with organic compounds

Organic compounds, even graphite and wood charcoal, react vigorously with chlorine trifluoride. Some of these reactions approach explosive violence. The behavior of benzene, ether, carbon tetrachloride, acetic acid, paraffin wax, cotton, and wool when brought in contact with chlorine trifluoride supports the generalization.

4. Reactions with hydrogen and other gases

Hydrogen, sulfur dioxide, hydrogen sulfide, ammonia, and illuminating gas all ignite in chlorine trifluoride.

5. Reactions with inorganic compounds

Chlorine trifluoride reacts actively with the following oxides: H_2O, MgO, CaO, Al_2O_3, La_2O_3, TiO_2, SnO_2, PbO_2, U_2O_5, Ta_2O_5, CrO_3, Cr_2O_3, MoO_3, WO_3, MnO_2, P_2O_5, B_2O_3, and As_2O_3. While no reaction is reported with ZnO, HgO, SiO_2, ZrO_2, ThO_2, and Fe_2O_3, it is probable that this is just a matter of test conditions. At an elevated temperature or in the presence of a trace of water these oxides should also react.

In the presence of chlorine trifluoride lively reactions are undergone by the following: potassium iodide, mercuric iodide, potassium carbonate, silver nitrate, sulfuric acid, nitric acid, and tungsten carbide. Under the conditions employed, no reaction was observed with sodium chloride, potassium sulfate, potassium nitrate, mercuric sulfate, and mercuric chloride.

X. HIGHER FLUORIDES OF CHLORINE

As yet no evidence has appeared to indicate the existence of higher fluorides of chlorine than chlorine trifluoride. The one mention of chlorine pentafluoride (33) was a typographical error (34).

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