of CuO are dependent upon particle size; the susceptibility increases with a decrease in particle size. The deviations of the measured magnetic susceptibilities for sample III from the theoretical predictions are very likely due to a contamination of the sample with finely divided copper oxide suspended on the copper benzoate. It is interesting to note that not one of the eight samples of anhydrous copper benzoate prepared during the course of this study was found to have a higher percentage of carbon than the calculated percentage. We interpret this to mean that the copper arylcarboxylates undergo some decarboxylation upon heating with the formation of CuO and the loss of volatile organic decomposition products.

The initial goal of this research was the determination of the magnetic properties of a series of copper salts with substituted benzoic acids. It soon became evident that the magnetic properties of samples were very sensitive to the method of preparation and the history of the sample.[12] We wish to report only one additional set of representative data which illustrates this effect.

The magnetic properties of copper *p*-methylbenzoate were determined on two samples from the same monoethanolate preparation. Sample A was taken after heating $Cu(CH_3C_6H_5CO_2)_2 \cdot C_2H_5OH$ in air for 2 hr. at 70°, and sample B after heating sample A for 40 hr. at 90° in air. The magnetic properties of the compound were greatly affected by the heating process. The large increase of susceptibility at low temperature after prolonged heating may arise from a finely divided CuO impurity.

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Contribution from The Research Institute of Temple University, Philadelphia, Pennsylvania

Formation of Xenon Difluoride from Xenon and Oxygen Difluoride or Fluorine in Pyrex Glass at Room Temperature[1]

By L. V. Streng and A. G. Streng

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The synthesis of $XePtF_6$ by Bartlett[2] opened an entirely new chapter of chemistry, the chemistry of noble gases. Since then, a series of binary noble gas compounds has been obtained, first at the Argonne National Laboratory[3] and then by others. Thermal and electric-discharge methods,[3] photolysis,[4] and high-pressure technique[5] have been used to induce the reaction of xenon with fluorine. With oxygen difluoride, xenon reacted when a 1:1, by volume, mixture of OF_2 and Xe was heated in a nickel tube to 300–400° at 3.25–3.75 atm. pressure, or when the Xe–OF_2 mixture was fed into a reaction vessel in which a high-voltage electric discharge was established, at low temperature and pressure.[6]

Recently, in the course of the study of slow reactions of oxygen fluorides under gentle conditions,[7] we found that both oxygen difluoride and fluorine reacted with xenon at room temperature and ordinary pressure when exposed (in a Pyrex glass flask) to ordinary daylight without any artificial addition of energy.

Experimental Procedure and Results

A series of experiments was made. A typical one is described here in detail.

A 2-l. Pyrex glass flask was filled with the gaseous mixture of 350 mm. of Xe and 374 mm. of F_2. The total pressure in the flask was 724 mm. at 25°. The flask was kept for 3 weeks at room temperature exposed to ordinary daylight.

The formation of tiny crystals was noticed on the second day of standing. The crystals grew with time to a size of 3–5 mm. These large transparent glistening crystals are identical in appearance with xenon fluorides. The initial rate of formation of the reaction product was about 35 mg./day. The yield varied depending on the intensity of sunlight, temperature, etc. The total amount of product obtained during 3 weeks varied from 0.5 to 0.75 g.

The product was analyzed and found to be XeF_2. The analysis was made by hydrolysis, as described elsewhere.[6,8] A 40-mg. sample of product on hydrolysis with water gave 0.25 mmole of Xe, 0.12 mmole of O_2, and 0.55 mmole of HF; *i.e.*, the reaction proceeded in accordance with the equation

$$XeF_2 + H_2O \longrightarrow Xe + 0.5O_2 + 2HF \qquad (1)$$

Only HF was obtained in slight excess, $\simeq$ 0.55 mmole instead of the theoretical amount of 0.48 mmole.

Infrared absorption spectra of the gaseous phase of the product taken on a Beckman IR-9 spectrophotometer confirmed the results of the chemical analysis. Two characteristic peaks, at 570 and 555 $cm.^{-1}$, were obtained identical with those described by Smith.[9]

Oxygen difluoride, as expected, also reacts with xenon at the conditions described above. A 1:1, by volume, mixture of xenon and OF_2 at 1 atm. pressure produced crystals with an initial rate of 35 mg./day. The formation of the crystals was noticed on the third day of standing. Chemical analysis and the infrared spectrum showed that the reaction product was also XeF_2. It is possible that at different Xe:OF_2 ratio, temperature, pressure, and light intensity, the composition of the reaction product may be different. The possibility of formation of XeF_4 and $XeOF_2$, for example, is not excluded.

Similar experiments with OF_2–Xe and F_2–Xe mixtures repeated in darkness for a period of 4 weeks gave no visible trace of xenon fluorides.

Discussion

The fact that there was no formation of XeF_2 in the dark proves that the reactions between F_2 or OF_2 and Xe described above are photochemical.

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Weeks and Matheson[4b,10] studied the photochemistry of formation of xenon difluoride from Xe and F_2. They irradiated the $Xe–F_2$ mixture (in an all-nickel system with sapphire windows at room temperature and 1000 mm. pressure) with ultraviolet light at 3130 Å. The intensity of light varied from 0.8×10^{15} to 50×10^{15} quanta/sec. The quantum yields were of the order of 0.3–0.7. In our experiments the gaseous $Xe–F_2$ or $Xe–OF_2$ mixtures were irradiated with normal daylight. Thus, the intensity of the radiation energy over the entire absorption bands of F_2 and OF_2, as well as the transmission coefficients of window and Pyrex glass, have to be taken into consideration. Fluorine absorbs light over practically the whole ultraviolet range with the maximum at about 2900 Å.[11] Its absorption in the visible range is very low. The absorbance of OF_2 is different[12]; its extinction coefficient is negligible down to about 2400 Å. and increases sharply at lower wave lengths. The transmission coefficient of glass, on the contrary, is negligible below 3100 Å. and increases rapidly at higher wave lengths.[13,14] The intensity of the sunlight at our latitude in winter (when the experiments were made) is considered to be about 1000 μwatts/cm.[2,13,15] An estimate of the amount of radiation energy passed through the window glass and through the Pyrex glass walls of the flasks and absorbed by fluorine at the conditions of our experiments with the $Xe–F_2$ mixtures (10-cm. thick layer of F_2 at 0.5 atm. pressure) gave a value of 0.37×10^{20} quanta/hr. The production of XeF_2 (relating to the four most luminous hours of a day) was about 9 mg./hr. or 0.32×10^{20} molecules/hr. Thus, in view of the approximate character of our calculations, the formation of XeF_2 should be completely accounted for by the photochemical reaction between Xe and F_2 with a quantum yield of about 1.

In the process of formation of XeF_2 from $Xe–OF_2$ mixtures, the oxygen difluoride probably does decompose first to oxygen and fluorine under the action of ultraviolet light.[16] The liberated fluorine then reacts with xenon as in the experiments with the $Xe–F_2$ mixtures.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY, THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL

The Preparation of Chlorodisilazanes and Some of Their Derivatives

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The only chlorodisilazanes reported in the literature are trimethyltrichlorodisilazane[1] and 1,3-dichlorotetramethyldisilazane.[2] Trimethyltrichlorodisilazane was prepared from hexamethyldisilazane and silicon tetrachloride; 1,3-dichlorotetramethyldisilazane was prepared by brominating 1,3-diphenyltetramethyldisilazane to 1,3-dibromotetramethyldisilazane (yield ~15%) and converting it to the corresponding dichlorodisilazane with silver chloride (yield ~18%). It has also been reported that dimethyldichlorosilane does not react with hexamethyldisilazane.[3]

Attempts to prepare silazanes of the type $Cl{-}\overset{|}{\underset{|}{Si}}{-}NH{-}\overset{|}{\underset{|}{Si}}{-}Cl$ by partial reaction of chlorosilanes with ammonia were unsuccessful.[2] We tried to find a suitable method for the preparation of these highly reactive materials. We find that hexamethyldisilazane, when refluxed with dimethyldichlorosilane using a Lewis acid as a catalyst, results in an exchange of silyl groups

$$(CH_3)_3SiNHSi(CH_3)_3 + (CH_3)_2SiCl_2 \longrightarrow \underset{\text{I}}{(CH_3)_3SiNHSi(CH_3)_2Cl} + (CH_3)_3SiCl$$

$$(CH_3)_3SiNHSi(CH_3)_2Cl + (CH_3)_2SiCl_2 \longrightarrow \underset{\text{II}}{Cl(CH_3)_2SiNHSi(CH_3)_2Cl} + (CH_3)_3SiCl$$

If a long-chain silazane polymer, or the cyclic trimeric or tetrameric polysilazane, is allowed to react with dimethyldichlorosilane, an analogous reaction takes place, yielding 1,3-dichlorotetramethyldisilazane (II). These latter reactions proceed even without a catalyst.

As monochlorosilanes react in the same way, we obtained pentamethylphenyldisilazane and 1,3-diphenyltetramethyldisilazane by the reactions

$$(CH_3)_3SiNHSi(CH_3)_3 + C_6H_5Si(CH_3)_2Cl \longrightarrow (CH_3)_3SiNHSi(CH_3)_2C_6H_5 + (CH_3)_3SiCl \quad (1)$$

$$(CH_3)_3SiNHSi(CH_3)_2C_6H_5 + C_6H_5Si(CH_3)_2Cl \longrightarrow C_6H_5(CH_3)_2SiNHSi(C_6H_5)(CH_3)_2 + (CH_3)_3SiCl \quad (2)$$

We find further that 1,3-dichlorotetramethyldisilazane (II) reacts with lithium phenylate to yield 1,3-diphenyltetramethyldisilazane (III). Compound III

$$Cl(CH_3)_2SiNHSi(CH_3)_2Cl + 2LiC_6H_5 \longrightarrow \underset{\text{III}}{C_6H_5(CH_3)_2SiNHSi(C_6H_5)(CH_3)_2} + 2LiCl$$

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