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Photolysis of Hexafluoroazomethane

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Hexafluoroazomethane is decomposed by light of 2537 A to yield nitrogen, hexafluoroethane, perfluorotetramethyl hydrazine, and perfluorohexamethyl tetrazine. The relative amounts of the various products vary with the pressure: the compounds of higher molecular weight being produced more abundantly at higher pressures. A free radical mechanism is proposed for the reaction.

INTRODUCTION

HE photolysis of azomethane has been studied by a number of investigators,¹⁻³ and it is generally agreed that the decomposition takes place by a free radical mechanism. The primary step is the formation of a nitrogen molecule and two methyl radicals. The methyl radicals react with one another and with the starting material so that the products of the reaction are variable amounts of simple hydrocarbons and nitrogen. Since it is known from the work of Ruff⁴ that the ultraviolet adsorption spectrum of hexafluoroazomethane resembles that of azomethane, it was concluded that the fluorinated compound would probably decompose in a manner similar to azomethane. Thus it was hoped that hexafluoroazomethane would be a good source of trifluoromethyl radicals for further investigations of their reactions. The present paper describes the preliminary work on photolysis of hexafluoroazomethane.

EXPERIMENTAL

Preparation of Hexafluoroazomethane

Hexafluoroazomethane was prepared by a modification of the method used by Ruff,⁴ who showed that cyanogen iodide and iodine pentafluoride would react at 125°C to give hexafluoroazomethane and a number of other products. Whereas Ruff carried out the reaction at high pressure in an iron bomb, we found it more convenient to use Pyrex apparatus at ordinary pressure. The reaction vessel consisted of a two liter flask the neck of which had been replaced by a tube 100 cm long and 5 cm in diameter. This extended neck acted as an air cooled condenser to collect the iodine formed by the reaction. The top of the condenser was connected through a standard taper to a train of two traps cooled by liquid air.

The main impurity in the iodine pentafluoride was hydrofluoric acid which was removed by shaking with dry potassium fluoride. After filtering, the pentafluoride was placed in the bottom of the flask by means of a long funnel and the flask cooled in an ice bath.

An equal weight (200 g) of cyanogen iodide, recrystallized from ether, was added and the flask shaken until a slurry was formed. The flask was then heated on an oil bath until the temperature reached 85° where gaseous products were formed and collected in the cooled traps. After the reaction had subsided the temperature was raised slowly to 135° above which no further products were formed. The mixture of products was passed through a train of scrubbers containing sodium hydroxide, soda lime, and anhydrous calcium sulfate. The product was further purified by several distillations the final fractionation being made with a Podbielniak column. Hexafluoroazomethane is a pale greenish yellow liquid boiling under 760 mm at -32.2 °C. A yield of 35 percent was obtained by the above procedure.

Description of the Photolysis Apparatus

The photolysis was carried out in a silica cell, 10 cm deep and 5 cm in diameter, which was illuminated with light of 2537 A wavelength. The light source was a mercury resonance lamp the output of which was collimated by a lens system. The intensity of the light was determined by actinometry using potassium ferrioxalate.5

The reaction cell was part of a closed circuit which contained a volume of 3600 ml when the reaction pressure was below 1 cm and 300 ml when higher pressures were used. The reacting gas was continually circulated around this circuit by means of a magnetically operated all-glass pump. A U-tube trap was included in the circuit. The closed circuit was connected through a stopcock to a vacuum manifold. Beyond the stopcock, and also connected to the manifold, was a McLeod gauge.

Procedure

In making a run the reaction space was first evacuated and then filled to the desired pressure through the stopcock. The stopcock was then closed and the circulating pump started. Traces of mercury vapor were removed from the gas by allowing it to circulate for several hours over gold or indium which had been placed in the U-tube.⁶ The photolysis was then started by opening

1302

¹ M. Burton *et al.*, J. Am. Chem. Soc. **60**, 10 (1938); J. Am. Chem. Soc. **59**, 1989 (1937); J. Chem. Phys. **7**, 1080 (1939). ² H. A. Taylor and A. Gordon, J. Am. Chem. Soc. **63**, 3435 (1941).

³ H. C. Ramsperger, J. Am. Chem. Soc. **50**, 123 (1928). ⁴ O. Ruff and W. Willenberg, Ber. **73B**, 724 (1940).

⁵ C. A. Parker, Proc. Roy. Soc. (London) A220, 104 (1953)

⁶ E. A. Flood and R. D. Heyding, Can. J. Chem. 32, 591 (1954).

a shutter between the reaction vessel and the lamp. After the run was terminated, which was usually after about 10 percent of the reacting gas had decomposed, liquid air was placed around the U-tube. With all the condensable gases frozen in this trap, the pressure of the noncondensable gases was measured by opening the system to the McLeod gauge. The noncondensable gases were then removed by pumping and the trap allowed to warm, whereupon the pressure of the condensable products and the remaining starting material was measured. The products were then removed for analysis.

The products were separated with a Podbielniak column when a sufficient amount was available. A Ward still, similar to that described by LeRoy⁷ was used to separate small amounts of product. Mass spectrograph analyses were obtained of the products of several runs and separately on the higher and lower boiling fractions.

RESULTS

Light Absorption of Hexafluoroazomethane

The light absorption of hexafluoroazomethane was determined between 2000 and 4500 A by means of a Beckman spectrophotometer. The results are shown in Fig. 1 which also gives the absorption of azomethane taken from Ramsperger⁸ and the data of Ruff⁴ for hexafluoroazomethane in solution in methyl chloride.

Products of the Reaction

The photolysis of hexafluoroazomethane yields nitrogen, hexafluoroethane, and two new compounds, perfluorotetramethyl hydrazine and perfluorohexamethyl tetrazine. The latter two compounds were identified by means of molecular weight determinations and analysis.



FIG. 1. — The absorption of hexafluoroazomethane. – – – The absorption of azomethane from the data of Ramsperger (see reference 3). … The absorption of hexafluoroazomethane in methyl chloride solution from the data of Ruff (see reference 4).

Perfluorohexamethyl tetrazine was found to have a molecular weight by gas density of 468 while the calculated value is 470. The total fluorine by analysis was 72.27 percent while the calculated value is 72.75 percent. It is a colorless liquid boiling at $100.4^{\circ}C$.

Perfluorotetramethyl hydrazine had a molecular weight of 305, calculated value 304. The fluorine analysis gave 77.58 percent, calculated value 74.97 percent. It is a colorless liquid boiling at 32°C.

Effect of Pressure on the Products of the Reaction

It was found that at pressures below 1 mm the main products of the decomposition were nitrogen and hexafluoroethane, while at higher pressures increasing amounts of the tetrazine and hydrazine were formed. In Fig. 2 the fraction of the condensible products consisting of hexafluoromethane is plotted against the logarithm of the reaction pressure. The two curves are data obtained at different light intensities. For the upper curve the intensity was 1.2×10^{17} quanta per sec entering the cell, while for the lower curve it was 6.7 $\times 10^{16}$ quanta per second.

The ratio of tetrazine to hydrazine in the products increased as the pressure increased. At 10 mm pressure this ratio was 1:6.6 while at 100 mm it was 1:2.6.

Quantum Yield

The quantum yield was determined at 50 cm and at 28 cm pressure. The average value was 0.25.

DISCUSSION

Mechanism of the Reaction

There is no doubt that the initial step in this photolysis is the division of the hexafluoroazomethane into



FIG. 2. The fraction of the condensable products consisting of hexafluoroethane plotted against the $\log p$ in mm. For the upper curve the light intensity was 1.2×10^{17} quanta per sec and for the lower curve 6.7×10^{16} quanta per sec.

⁷ D. J. LeRoy, Can. J. Research **B28**, 492 (1950).

⁸ H. C. Ramsperger, J. Am. Chem. Soc. 50, 123 (1928).

1304

a molecule of nitrogen and two trifluoromethyl radicals.

$$CF_3 - N = N - CF_3 \rightarrow N_2 + 2CF_3.$$
(1)

Whether this occurs in two stages or not is impossible to determine from these experiments and in fact would make no difference to the subsequent steps of the over-all reaction. The radicals formed by reaction (1) may react with one another to form hexafluoroethane or with the parent material to form a new free radical.

$$2CF_3 + M \rightarrow C_2F_6 + M \tag{2}$$

$$CF_3 + CF_3 - N = N - CF_3 \longrightarrow N - N$$
 $CF_3 (3)$
 CF_3

The hydrazo radical formed by reaction (3) may react with a trifluoromethyl radical to form perfluorotetramethyl hydrazine or two hydrazo radicals may join together to form perfluorohexamethyl tetrazine



The tetrazine, however, could also be formed by the reaction of the hydrazo radical with the starting material forming a tetrazo radical which would in turn react with a trifluoromethyl radical.





Since the quantum yield is considerably less than unity no chain reactions occur. Hence the CF_3 radical, at least at room temperature, does not break the carbonnitrogen bond of hexafluoroazomethane, but prefers to open the nitrogen-nitrogen double bond. It is also interesting to note that the CF_3 radical will not, at room temperature, abstract a fluorine atom from another structure containing a CF_3 group. No carbon tetrafluoride was found among the products at any time.

At constant light intensity the rate of formation of trifluoromethyl radicals is proportional to the pressure, except at the highest pressure used where an appreciable amount of the total light is absorbed. Therefore, the ratio of the chance of a trifluoromethyl radical colliding with another trifluoromethyl radical to the chance of it colliding with a molecule of hexafluoroazomethane is independent of the pressure. Despite this the formation of hexafluoroethane is favored by low pressures. We, therefore, conclude that this process takes place mainly on the walls of the vessel. For a low pressure we may calculate the average time required for a trifluoromethyl radical to diffuse from the body of the gas to the wall. The number of collisions between such a radical and the molecules of hexafluoroazomethane during this time may also be calculated. The result of such a calculation, together with the experimental data, is that only one collision in 2×10^7 is effective in forming a hydrazo radical. If one assumes a steric factor of 0.1 this gives an activation energy for reaction (3) of 8700 cal per mole.

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