liometer (Gallenkamp) using a thermistor sensing in boiling benzene and carbon tetrachloride.

Synthetic Reactions. Reaction of Gallium Isopropoxide with Acetyl Chloride in Molar Ratio 1:1.—Acetyl chloride (0.54 g) was added in two or three lots to a solution of gallium isopropoxide (1.67 g) in dry benzene (20 g). An exothermic reaction took place. The mixture was refluxed for 2 hr at a bath temperature of 90–100°. On cooling, nothing appeared to crystallize. The excess benzene was therefore distilled out under reduced pressure. Finally a white solid (1.51 g, yield 100%) was obtained by drying the product for 3 hr at 0.1 mm pressure at room temperature (25°). *Anal.* Calcd for $Ga(i\text{-}C_3H_7O)_2Cl$: Ga, 31.23; Cl, 15.91; $i\text{-}C_3H_7O$, 52.86. Found: Ga, 31.18; Cl, 15.87; $i\text{-}C_3H_7O$, 52.1.

The compound (0.41 g) was distilled at 110° (0.4 mm) to give a colorless liquid (0.28 g) which solidified after a few minutes. *Anal.* Found: Ga, 31.15; Cl, 15.85; $i\text{-}C_3H_7O$, 51.84. The melting point of this compound is 74.75°. The analogous bromo derivative melts at 95–96°.

The general method of synthesis was the same in every case; hence the other derivatives are described in Table II.

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Difluoramine: Reactions with Chlorine Fluorides

BY D. PILIPOVICH AND C. J. SCHACK

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The action of chlorine fluorides on organic compounds has been reviewed with respect to the more quantitative aspects of chlorofluorination and the degree of competition between the chlorination and fluorination processes.[1] Since difluoramine is a readily oxidized compound[2] we were interested in studying the system HNF_2–ClF_x in order to determine whether general halogenation occurred and to what extent competition existed between the chlorination and the fluorination processes.

Experimental Section

Materials.—Chlorine monofluoride was prepared by heating an equimolar mixture of chlorine and fluorine to 150° for several hours in a stainless steel cylinder. The product was purified by vacuum fractionation prior to use. Chlorine trifluoride was purchased from the Matheson Co. and purified by the method of Schack, *et al.*[3] Chlorine pentafluoride was prepared by the method of Pilipovich, *et al.*,[4] which involved the fluorination of $CsClF_4$. Chlorine fluorides of high purity were essential. Freedom from chlorine oxides was most important since such impurities often caused the reactions with difluoramine to occur with an explosive deflagration. Difluoramine was generated from difluorourea as reported by Lawton, *et al.*[5] Alkali fluorides were fused and then powdered in a drybox prior to use.

Apparatus.—Difluoramine was handled in a glass vacuum line and the chlorine fluorides in a stainless steel vacuum line fitted with Teflon U traps. Because difluoramine is decomposed by fluorine-passivated metal and the chlorine fluorides are difficult to manipulate in glass, the reactions of these materials were conducted in a Kel-F cylinder fitted with a Teflon valve. Reaction products were separated on the metal system.

Infrared spectra were taken on a Perkin-Elmer Infracord 137 using 5-cm Kel-F or stainless steel cells fitted with AgCl windows. Mixtures of chlorodifluoramine and tetrafluorohydrazine were not separable by fractional condensation and the relative proportions of such mixtures were determined by infrared absorbance measurements. Pure samples of $ClNF_2$ and N_2F_4 were employed to obtain the necessary coefficients. The experimental values are: $ClNF_2$, $a_{845\text{cm}^{-1}} = 7.2 \times 10^{-3}$ mm^{-1} cm^{-1} and $a_{685\text{cm}^{-1}} = 4.4 \times 10^{-3}$ mm^{-1} cm^{-1}; N_2F_4, $a_{735\text{cm}^{-1}} = 2.3 \times 10^{-3}$ mm^{-1} cm^{-1}. Errors in the analysis are probably on the order to 5% including the errors of gas volume measurements.

Reaction of ClF and HNF_2.—After pretreating the Kel-F reactor with ClF_3, it was evacuated and attached to the glass vacuum line. Difluoramine (32.1 cm^3, 1.43 mmol) was condensed into the reactor at −142°. The closed reactor was reattached to the metal vacuum line and ClF was condensed in at −142°, the quantity (32.0 cm^3, 1.43 mmol) being measured by pressure difference since ClF has a low vapor pressure at this temperature. After 30 min at −78°, the product gases were separated by fractional condensation at −142 and −196°. The high-temperature fraction was found to be HF without any infrared-observable contaminants. The low-temperature sample (31.9 cm^3) did not contain any unreacted ClF, but was composed of a mixture of 97% $ClNF_2$ and 3% N_2F_4. The latter may have arisen through incomplete reaction of the difluoramine and its subsequent decomposition in the metal line during fractionation[6] or through decomposition of $ClNF_2$ to N_2F_4 and Cl_2 as reported by Petry.[7]

Reaction of ClF_3 and HNF_2.—Chlorine trifluoride (8.1 cm^3, 0 362 mmol) was condensed into the Kel-F reactor at −196°. The valve was closed and the reactor connected to the glass line from which HNF_2 (24.2 cm^3, 1.07 mmol) was obtained by condensation at −142°. The reactor was then immersed in a bath cooled to −78°. After 30 min, the reactor was opened and the products were fractionated on the metal vacuum system. An infrared spectrum of the material trapped at −142° showed no Cl–F or N–F species but only HF. Similar inspection of the −196° condensate (16.2 cm^3) revealed a 1:1 mixture of N_2F_4 and $ClNF_2$ with less than 1% NF_3. Replicate measurements showed 7.8 and 8.4 cm^3 of $ClNF_2$ to be present in addition to 8.1 cm^3 of N_2F_4. Thus the reaction was complete and nearly quantitative in a 1:3 ratio of ClF_3 to HNF_2. Several experiments were carried out with lesser amounts of either reactant. In these cases the reaction ratio of 1:3 was still observed and the excess reactant was recovered.

Reaction of ClF_5 and HNF_2.—A sample of ClF_5 (37.6 cm^3, 1.68 mmol) was condensed into the reactor at −142° followed by HNF_2 (38.9 cm^3, 1.73 mmol). The closed reactor was warmed to −78° for 10 min before fractionation of the products was initiated. Some noncondensable gas was produced but not measured. Most of the ClF_5 was recovered unreacted (28.4 cm^3). No HNF_2 was recovered but 9.2 cm^3 of $ClNF_2$, 15.1 cm^3 of N_2F_4, and a trace of NF_3 were obtained along with 39 ml of HF. Thus, somewhat over 4 HNF_2 reacted for each ClF_5 producing 1 $ClNF_2$ and somewhat less than 2 N_2F_4.

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Results and Discussion

It was determined that the reaction of HNF_2 with pure ClF_3 proceeds rapidly and smoothly to yield chlorodifluoramine, $ClNF_2$, and tetrafluorohydrazine as in

$$ClF_3 + 3HNF_2 \longrightarrow ClNF_2 + N_2F_4 + 3HF \qquad (1)$$

Regardless of variation in experimental reactant ratios, $ClNF_2$ was smoothly generated according to eq 1. Although $ClNF_2$ was expected, the observed high yield obtained in these studies was of sufficient interest to determine the intermediates in the reaction. Since the reaction of chlorine and HNF_2 to form $ClNF_2$ is known to be slow,[8] the failure to find Cl_2 as a product in the reaction, regardless of stoichiometry, shows that the reduction of ClF_3 does not proceed to Cl_2 with a subsequent reaction to form $ClNF_2$. In addition, data for the equilibrium involving Cl_2 and N_2F_4 precluded the formation of $ClNF_2$ from these ingredients.

Two routes to the formation of $ClNF_2$ from HNF_2 and ClF_3 were then considered and are visualized as

$$ClF_3 + HNF_2 \longrightarrow ClF_2NF_2 + HF \qquad (2a)$$

$$ClF_2NF_2 + 2HNF_2 \longrightarrow ClNF_2 + N_2F_4 + 2HF \qquad (2b)$$

$$ClF_3 + 2HNF_2 \longrightarrow ClF + 2HF + N_2F_4 \qquad (3a)$$

$$ClF + HNF_2 \longrightarrow ClNF_2 + HF \qquad (3b)$$

Direct experimental evidence was obtained that strongly suggested the routes shown in (3a) and (3b). This was clearly demonstrated by mixing equivalent amounts of ClF and HNF_2 at −78° and obtaining $ClNF_2$ in near quantitative yields. A further check showed that the $ClF–N_2F_4$ system is unreactive and is therefore not responsible for $ClNF_2$ formation. Thus, in showing that HNF_2 rapidly reduces ClF_3 to ClF, a most convenient synthesis of $ClNF_2$ has been uncovered. These experiments do not preclude, however, an intermediate such as ClF_2NF_2.

The reaction of chlorine pentafluoride with HNF_2 also gave $ClNF_2$ and N_2F_4. Unlike the ClF_3 reaction at −78°, the ClF_5 reaction was not as precise with respect to the reproducibility of the reaction stoichiometry. At times, there appeared to be two distinct modes of reduction of ClF_5 occurring

$$ClF_5 + 4HNF_2 \longrightarrow ClF + 4HF + 2N_2F_4 \qquad (4)$$

$$ClF_5 + xHNF_2 \longrightarrow ClF_{5-2x} + xHF + xNF_3 \qquad (5)$$

The degree to which the reactions shown in (4) and (5) are competitive was not determined. However, in those reactions where NF_3 formation was negligible the observed stoichiometry suggests that the mode of formation of $ClNF_2$ appears to be the same as that in ClF_3

$$ClF_5 + 5HNF_2 \longrightarrow ClNF_2 + 4HF + 2N_2F_4 \qquad (6)$$

Because of the rapidity of the reactions of HNF_2 with chlorine fluorides some moderating effect was sought through reaction studies involving complexes of either the chlorine fluoride or HNF_2. For example, when BF_3 was used to complex either ClF_3 or HNF_2, treatment with the other reagent at −78° gave a system that slowly produced $ClNF_2$ over a 4-day period. The complexes examined were $HNF_2 \cdot BF_3$, $KF \cdot KClF_4$, $RbClF_4$, and ClF_2BF_4. The results of these as intermediates are unremarkable except that they all yielded $ClNF_2$ in varying amounts. From the rate of pressure increase at −78°, a definite order of reactivity of HNF_2 with the various chlorine fluorides and their complexes could be perceived. The relative order of reactivity appears to vary as

$$ClF_3–HNF_2 > ClF_5–HNF_2 \gg ClF_3–HNF_2 \cdot BF_3 > ClF_2BF_4–HNF_2 > KF \cdot KClF_4–HNF_2 \sim RbClF_4–HNF_2$$

The place of the $ClF–HNF_2$ system in the series was not established.

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Some Reactions of Silicon Dichloride

BY P. L. TIMMS

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The gaseous molecule silicon dichloride has been known for many years. Recently Teichmann and Wolf[1] have reported on the thermodynamics of the reaction $Si + SiCl_4 = 2SiCl_2$, and Schmeisser and Voss[2] and Schenk and Blocking[3] have described some properties of the polymer $(SiCl_2)_n$.

There has, however, been no previous report of the chemistry of monomeric silicon dichloride, which is a "carbene-like" molecule and potentially very reactive toward many compounds. Gaseous silicon dichloride is unstable at ordinary temperatures. It either decomposes by direct polymerization to $(SiCl_2)_n$ or gives higher perchlorosilanes by reaction with any $SiCl_4$ which may also be present. At pressures of the order of 1 μ, the lifetime of the species $SiCl_2$ may be only a few milliseconds. This contrasts with the species SiF_2 which is stable for several minutes at 1 μ pressure and which does not react with SiF_4.[4]

In this work, silicon dichloride gas has been prepared at high temperatures from silicon and silicon tetrachloride at a pressure low enough to allow it to be transferred from the furnace to a liquid nitrogen cooled surface, without appreciable gas-phase polymerization or reaction. Under these conditions it has been possible to study some of the reactions of the molecule $SiCl_2$.

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