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

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

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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(1) R. Teichmann and E. Wolf, *Z. Anorg. Allgem. Chem.*, **347**, 145 (1966).
(2) M. Schmeisser and P. Voss, *ibid.*, **334**, 50 (1964).
(3) P. W. Schenk and H. Blocking, *ibid.*, **334**, 57 (1964).
(4) P. L. Timms, R. A. Kent, T. D. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

Results

Condensation of $SiCl_2$ gas, prepared in better than 95% yield from silicon and silicon tetrachloride at 1350°, on a liquid nitrogen cooled surface, gave a brown polymer. On warming this to room temperature it turned white and evolved small quantities of volatile perchlorosilanes. The amount of perchlorosilanes formed appeared to be proportional to the amount of silicon tetrachloride also condensed with the $SiCl_2$.

The white polymer remaining at room temperature had the properties reported by Schenk and Blocking for $(SiCl_2)_n$.[3] However, with 10% hydrofluoric acid it was observed to evolve a mixture of silanes. This mixture contained relative amounts of silanes from SiH_4 through at least Si_5H_{12}, similar to those reported by Timms, *et al.*,[4,5] from the action of hydrofluoric acid on silicon monoxide or silicon difluoride polymer.

The Reaction with Boron Trichloride.—Cocondensation of $SiCl_2$ with boron trichloride in a 1:1 mole ratio, gave a blue solid at low temperatures. This liberated a mixture of volatile perchlorosilanes and another liquid slightly more volatile than Si_2Cl_6 when warmed to room temperature. The mass spectrum of this liquid showed the same ions reported by Massey and Urch[6] for the compound $SiBCl_5$, which they had prepared in tiny amounts by a discharge reaction in a $SiCl_4$–BCl_3 mixture. The relative ion abundances obtained in this work are shown in Table I.

Table I

Mass Spectra at 50 EV for $SiCl_3BCl_2$ and $SiCl_3PCl_2$

Ion	Rel intens	Ion	Rel intens (approx)
BCl^+	9.1	$SiCl^+$	25
$SiCl^+$	65.0	PCl^+	16
BCl_2^+	100.0	$SiCl_2^+$	10
$SiCl_2^+$	92.5	PCl_2^+	22
$SiCl_3^+$	23.7	$SiCl_3^+$	100
$SiBCl_4^+$	8.8	$SiCl_4^+$	6.5
$SiBCl_5^+$	14.9	$SiPCl_4^+$	4.5
		$SiPCl_5^+$	15

The gas-phase infrared spectrum of $SiBCl_5$ showed absorptions at 960 (s), 924 (vs), 596, and 524 (s) cm^{-1}. The frequencies can be tentatively assigned to the B^{10}–Cl and B^{11}–Cl stretches and the two Si–Cl stretches, respectively, as expected for $SiCl_3BCl_2$.

Trichlorosilylboron dichloride melts at −72° and appears to be quite stable at room temperature in the absence of air.

The same compound was also made by passing boron trichloride over silicon, or silicon tetrachloride over boron, at a temperature of 1400–1700°, condensing the volatile products in the same way as for $SiCl_2$.

Under no conditions was the compound $SiCl_3$-$SiCl_2BCl_2$ found in the reaction products, although Si_3Cl_8, probably of similar volatility, was easily detected. Thus the action of $SiCl_2$ on boron trichloride is quite unlike that of SiF_2 on boron trifluoride. In the latter case, $SiF_3SiF_2BF_2$ and its higher homologs are the products, but SiF_3BF_2 is not formed.[7]

The Reaction with Phosphorus Trichloride.—A reddish brown solid was obtained by cocondensing $SiCl_2$ with phosphorus trichloride at −196°. The solid liquefied on warming to room temperature and evolved a mixture of perchlorosilanes with another liquid a little less volatile than Si_2Cl_6.

The mass spectrum of the liquid showed that it contained silicon, phosphorus, and chlorine. The ions of lowest appearance potential were a group at m/e 234–239. Their relative intensity indicated that they came from a compound containing five chlorine atoms, assuming a normal $^{35}Cl/^{37}Cl$ isotope ratio. The large $SiCl_3^+$ and PCl_2^+ fragments seen in the mass spectrum suggested the compound generating the parent ions at m/e 234–239 was $SiCl_3PCl_2$. The approximate abundances of the ions in the mass spectrum are given in Table I.

The gas-phase infrared spectrum of the compound showed absorptions at 642 (s), 622 (vs), and 513 (s) cm^{-1}. These frequencies are in reasonable positions for the two Si–Cl stretches and the P–Cl stretch expected from $SiCl_3PCl_2$.

Trichlorosilyldichlorophosphine melts at −64°. It is fairly unstable at room temperature, decomposing into silicon tetrachloride and depositing yellow PCl polymers. It is much more stable than the products of cocondensation of SiF_2 and phosphorus trifluoride,[8] which decomposed at very low temperatures into perfluorosilanes and PF polymers.

The Reaction with Other Chloro Compounds.—The main product of cocondensation of $SiCl_2$ with carbon tetrachloride was a white polymer, together with a small yield of a white, slightly volatile solid. This solid was shown by its mass spectrum, infrared spectrum, and melting point (mp 114°, lit. 115–156°) to be $SiCl_3$-CCl_3, already described by DiGiorgio, Summer, and Whitmore.[9]

The reaction of $SiCl_2$ with stannic chloride gave only a bright yellow polymer which was partly soluble in ether. No simple volatile compounds such as $SiCl_3$-$SnCl_3$ seemed to have been formed.

The Reaction with Benzene and Acetylene.—The brown solid obtained from $SiCl_2$ and benzene at −196° evolved only small amounts of unchanged benzene and some perchlorosilanes on warming to room temperature. After prolonged pumping at room temperature to remove absorbed volatiles, the polymer was hydrolyzed either with 10% hydrofluoric acid or with potassium hydroxide solution, and any volatiles obtained were separated by gas chromatography. The main product of either acid or base hydrolysis of the polymer was 1,4-cyclohexadiene, mixed with about 20% of 1,3-cyclohexadiene and a little cyclohexene.

Similarly, the polymer from the cocondensation of

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[7] P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Am. Chem. Soc.*, **87**, 3819 (1965).

[8] P. L. Timms and J. L. Margrave, unpublished work.

[9] P. A. DiGiorgio, L. H. Summer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 3512 (1948).

$SiCl_2$ with acetylene evolved no volatiles on pumping at room temperature or slightly above. On acid or base hydrolysis, this polymer evolved acetylene and no other volatile product except hydrogen.

Discussion

The reactions of $SiCl_2$ form an interesting comparison with those of SiF_2. The former inserts readily into M–Cl bonds, and this provides a new synthetic route from M–Cl to M–$SiCl_3$. Reactions of this type are rare with SiF_2, which most frequently forms compounds containing at least two silicon atoms. It has been postulated that the initial step in the reaction of SiF_2 with another compound at $-196°$ is the formation of a diradical $\cdot Si_2F_4 \cdot$ which then reacts with other molecules. This accounts for the observed reactions with boron trifluoride to give $SiF_3SiF_2BF_2$,[7] with benzene to give $C_6H_6Si_2F_4$,[10] and with acetylene to give $HC{\equiv}CSiF_2SiF_2CH{=}CH_2$.

The molecules $C_6H_6Si_2F_4$ and $HC{\equiv}CSiF_2SiF_2CH{=}CH_2$, or the polymers from which they had been pumped, were readily hydrolyzed to 1,4-cyclohexadiene and acetylene, respectively. As 1,4-cyclohexadiene and acetylene were also obtained on hydrolysis of the corresponding $SiCl_2$ reaction product, this suggests that in nonchlorinated systems, where insertion into a bond is not favored, $SiCl_2$ may, like SiF_2, polymerize *via* reactive diradicals.

Experimental Section

Silicon dichloride was prepared in the same type of apparatus described by Timms[11] for the preparation of boron monofluoride. In this case, silicon tetrachloride vapor was passed at the rate of about 50 mg/min through an inductively heated graphite container containing about 8 g of 99.9% pure silicon in pea-sized lumps. The maximum temperature in the container was kept below 1380° to prevent sintering of the silicon. The pressure in the container dropped from 5 mm at the top to about 0.2 mm near the nozzle. The silicon dichloride, mixed with unchanged silicon tetrachloride, sprayed out through the nozzle into a liquid nitrogen cooled evacuated flask in which the pressure of permanent gas was below 2×10^{-6} mm. Slight blocking of the nozzle occurred, limiting running time to about 30 min.

When the dichloride was cocondensed with other chlorides, these were added through a Pyrex nozzle mounted below the nozzle from the graphite container. The rate of addition was controlled so that roughly equimolar quantities of silicon dichloride and the other chloride were condensed together.

At the end of a run, the furnace was cooled, and the condensate was warmed to room temperature. Volatiles liberated were pumped into a trap from which they could be transferred to a standard vacuum line. The volatiles were separated by distillation on a low-pressure, low-temperature distillation column. This was capable of giving a clean separation between mixtures of $SiCl_3BCl_2$ and Si_2Cl_6 and of $SiCl_3PCl_2$ and Si_2Cl_6 although these separations were not possible by trap to trap distillation.

$SiCl_3PCl_2$ and $SiCl_3BCl_2$.—The mass spectra of these compounds were taken with a Bendix Model 1400 time-of-flight mass spectrometer equipped with an all-glass direct inlet system allowing evaporation directly from the condensed phase into the ion source of the spectrometer. The spectra showed the compounds to be free of admixed Si_2Cl_6.

The compounds were analyzed for chlorine content by dissolving them in 5% NaOH, acidifying with HNO_3, adding a little $NaNO_2$ to oxidize any lower boron or phosphorus compounds to the +3 or +5 state, respectively, removing oxides of nitrogen, and determining the chloride by the Volhard method. *Anal.* Calcd for $SiCl_3BCl_2$: Cl, 82.1. Found: Cl, 82.7. Calcd for $SiCl_3PCl_2$: Cl, 74.8. Found: Cl, 73.8.

The melting points were obtained by the Stock ring method, using a calibrated pentane thermometer for temperature measurement.

Infrared spectra were taken in a 10-cm glass gas cell with silver chloride windows, using a Perkin-Elmer 211 spectrophotometer.

Polymeric residues left in the flask on the furnace system after volatiles had been pumped off could not be removed efficiently. They were treated with aqueous reagents added to the flask, and the volatiles formed were carried into a trap in a stream of helium. The silanes liberated from $(SiCl_2)_x$ on treatment with 10% HF were separated by gas chromatography at room temperature on a 6-ft column packed with 10% Silicone 702 on Chromosorb P. They were identified by their known relative retention times, with benzene as internal standard, and their relative abundances were estimated from the peak areas using a thermal conductivity detector. The C_6 hydrocarbons obtained by the action of acid or base on the benzene–$SiCl_2$ polymer were separated on a 6-ft column packed with 10% tritolyl phosphate on Chromosorb P. Individual peaks were collected and identified by their mass spectra and infrared spectra. Acetylene liberated from the $SiCl_2$–acetylene polymer was purified on a vacuum line and identified by its infrared spectrum.

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The Synthesis of Iridium Disulfide and Nickel Diarsenide Having the Pyrite Structure

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The pyrite structure (space group T_h^6[Pa3]) is in general a densely packed arrangement and, therefore, tends to be favored when synthesis is attempted between the transition metals and groups Va and VIa elements at high pressure. The preference of copper disulfide for the pyrite structure when synthesized under pressure allows the realization of the 1:2 cation to anion stoichiometry, which cannot be obtained at all if the synthesis is attempted below 15 kbars pressure.[2] The two syntheses which we wish to report here were performed in the "belt" superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. Both syntheses were carried out at 60 kbars pressure. Pressure and temperature calibration have been described.[2] Compositions have been determined by thermogravimetric analysis.

At 1 atm iridium is known to combine with sulfur to

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[1] Bureau of Mines, Metallurgy Research Center, College Park, Md. 20740.

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