The Dihalides of Group IVB Elements

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The elements of Group IVB (C, Si, Ge, Sn, and Pb) all possess the ground state configuration $n_2^2p_2^2$. This configuration suggests that oxidation states of either two or four are especially probable for the elements in the group, and to a greater or lesser extent, both states are observed for each number. There is a continuous increase in the stability of the divalent state with respect to the tetravalent state with increasing atomic number, so that with carbon the (II) oxidation state is restricted to the very reactive carbenes and to "special" compounds such as isonitriles, whereas (II) is the prevalent state in the inorganic compounds of tin and lead.

Two factors probably contribute to this increase in stability of the divalent state. For one, the $M-X$ bond energies generally decrease down the group, with the exception that the bonds between silicon and the most electronegative elements are usually stronger than the corresponding bonds to carbon.\(^1\) Secondly, repulsive interactions between non-bonding and bonding electron pairs are larger for the smaller atom at the top of the group.\(^2\)

There has been some uncertainty as to the relative electronegativities of the various members of Group IVB. The current consensus seems to favor the order $C > Ge > Si - Sn > Pb$, but the difference in electronegativity between Si and Pb may be small.\(^3\) At any rate, electronegativity differences seem inadequate to explain the monotonic increase of stability of the (II) state as one goes down the group.

The "inert pair" concept has sometimes been advanced to account for the extra stability of atoms or ions which contain a lone pair of $s$-electrons (e.g. $Hg^{+1}$ or $TI^{+1}$); however, this effect does not seem to be particularly
operative in Group IV, since the 3rd ionization potentials are similar for the elements Si through Pb.

The chemistry of the dihalides of the Group IVB elements has developed along several lines. One approach has been to use the dihalides as reactive intermediates in liquid phase studies. For example, CCl₂ is produced by the alkaline hydrolysis of chloroform; this CCl₂ can then react with other reagents in the system. A very large amount of work has been done on this type of study and since it is already extensively described in the literature it will only be briefly discussed in this article. The dihalides of Group IVB elements, particularly CF₂, are also intermediates in a number of gas phase reactions. Another important approach has been to design experiments that produce the dihalides in conditions that prevent their immediate reaction with other reagents in the system. This has permitted the direct measurement of some of their physical properties and also the determination of some of their descriptive chemistry. It has been principally this technique that has been used in the chemistry department of Rice University, Houston. In this article some of the results obtained using all of these approaches are described although the last technique will be emphasized.

A. Difluoromethylene

CF₂ is unique among carbenes because of its high stability and low reactivity. Investigations of the ultraviolet absorption spectrum of CF₂ have led to estimates of roughly 10 milliseconds to one minute for the half-life of CF₂ at pressures in the region of one atmosphere. The gas-phase molecule does not react with BF₃, N₂O, SO₂, CS₂ or CF₃I at 120°C.
The nature of CF$_2$ is perhaps best presented in separate sections discussing its preparation, structure and physical properties, reaction chemistry, and reaction kinetics.

**Preparation.** The majority of the preparations of CF$_2$ reported in the literature involve photolytic or pyrolytic processes. Table I contains a representative list of methods used to produce CF$_2$. Most of the reactions produce the molecule in its singlet ground state, but the reaction of O ($^3$P) atoms with C$_2$F$_4$ and the decomposition of CF$_4$ in a glow discharge appear to produce triplet CF$_2$. In this connection it is interesting to note that the reaction of Hg ($^3$P) atoms did not give rise to triplet CF$_2$; the authors suggested that the triplet C$_2$F$_4$ initially formed passes through an excited singlet prior to dissociation.

**Structure.** The ultraviolet emission spectrum of CF$_2$ was first examined by Venkateswarlu$^{22}$, who prepared the molecule by passing an uncondensed transformer discharge through CF$_4$. An extensive band system between 3250 and 2400 Å was observed. The similarity of the band system to that of NO$_2$ suggested that a non-linear triatomic molecule was responsible for the spectrum. Venkateswarlu identified the band system with the transition $^1B_2 \rightarrow ^1A_1$.

The ultraviolet absorption bands were examined by Laird, Andrews and Barrow$^{23}$ who obtained much the same results as Venkateswarlu although they suggested that the band numbering previously assigned might be incorrect. They demonstrated that the observed system involves the ground state of CF$_2$. Since their equipment design permitted examination of only long-lived species, they estimated that the half-life of CF$_2$ is approximately 1 second at a pressure of 1 mm Hg.
Table 1

Methods of Production of CF₂

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Products</th>
<th>Multiplicity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolytic methods:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₂=CF₂</td>
<td>2CF₂</td>
<td>singlet</td>
<td>6</td>
</tr>
<tr>
<td>CF₂=CF₂ (Hg-sensitized)</td>
<td>2CF₂</td>
<td>singlet</td>
<td>7</td>
</tr>
<tr>
<td>CF₂N₂</td>
<td>CF₂ + N₂</td>
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</tr>
<tr>
<td>O (³P) + C₂F₄</td>
<td>CF₂ + CF₂O</td>
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<td>9</td>
</tr>
<tr>
<td>Fluorocarbons</td>
<td>CF₂ + various compounds</td>
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<td>10</td>
</tr>
<tr>
<td>ClF₂COClF₂</td>
<td>CF₂ + ClCOCF₂Cl</td>
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<td><strong>Pyrolytic methods:</strong></td>
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</tr>
<tr>
<td>CF₃COCF₃</td>
<td>CF₂ + CF₃COF</td>
<td>singlet</td>
<td>12</td>
</tr>
<tr>
<td>CF₂=CF₂</td>
<td>CF₂ + CF₂O</td>
<td>singlet</td>
<td>13</td>
</tr>
<tr>
<td>CF₃Sn(CH₃)₃</td>
<td>CF₂ + FSn(CH₃)₃</td>
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<td>14</td>
</tr>
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<td>(CF₃)₃PF₂</td>
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</tr>
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<td>CF₂ + CX₂=CX₂</td>
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<td>15</td>
</tr>
<tr>
<td>Fluorocarbons</td>
<td>CF₂ + other products</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td><strong>Other methods:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₄</td>
<td>CF₂ + several other species</td>
<td>triplet</td>
<td>16</td>
</tr>
<tr>
<td>C + CF₄</td>
<td>CF₂</td>
<td>singlet</td>
<td>17</td>
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<td>CF₂ + HF</td>
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<td>CF₂=CF₂</td>
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<td>unknown</td>
<td>20</td>
</tr>
<tr>
<td>CH₂ + CF₂=CF₂</td>
<td>CF₂ + CH₂=CF₂</td>
<td>unknown</td>
<td>21</td>
</tr>
</tbody>
</table>
More recent experiments\(^{24}\) have resulted in the re-assignment of the band system origin, the extension of spectral measurements to shorter wavelengths, and the correlation of the observed absorption spectra solely with the bending modes of the two states involved. In addition, Simons\(^{25}\) and Margrave\(^{26}\) have suggested that the spectra are due to the transition \(^1\text{B}_1 \leftrightarrow ^1\text{A}_1\), rather than \(^1\text{B}_2 \leftrightarrow ^1\text{A}_1\), as originally proposed. Mathews\(^{27}\) has analyzed the rotational fine structure of the band at 2540 Å, and obtained the following values for molecular parameters: upper state, \(\langle \text{FCF} \rangle = 134.8^\circ\), \(r_{\text{C-F}} = 1.30\) Å; lower state, \(\langle \text{FCF} \rangle = 104.9^\circ\), \(r_{\text{C-F}} = 1.30\) Å.

The infrared spectrum of matrix-trapped CF\(_2\) (produced by the photolysis of difluorodiazirine, CF\(_2\)N\(_2\)) has been examined\(^{28}\). The three fundamental vibrational frequencies were determined to be 668, 1102, and 122 cm\(^{-1}\). The intensities of the two stretching fundamentals were sufficiently strong to permit observation of the corresponding absorption of \(^{13}\text{CF}_2\), from which the bond angle of CF\(_2\) was calculated to be approximately 108°. The gas-phase infrared spectrum of CF\(_2\) has been observed by Pimental and Herr\(^{29}\). Difluorodiazirine was flash-photolyzed and the infrared spectrum of the products was immediately taken with a rapid-scan infrared spectrometer. Absorptions due to CF\(_2\) were seen but the resolution of the instrument was insufficient for determination of the symmetry of the absorptions. The half-life of CF\(_2\) was estimated to be 2.5 m secs.

Powell and Lide\(^{30}\) observed the microwave spectrum of CF\(_2\) using a fast-flow microwave spectrometer. The CF\(_2\) was prepared by passing a weak r.f. discharge through C\(_2\)F\(_3\)Cl, CF\(_4\) or (CF\(_3\))\(_2\)CO. The absence of fine structure and observable Zeeman shifts provided evidence that the CF\(_2\) was in
the singlet ground state. The bond angle was determined to be 104.9° and
the bond length to be 1.30 Å, in complete agreement with Matthews' values
(see ref. 27). For comparison, the C-F bond length in CF₄ is 1.317 ± 0.005 Å.³¹

The Heat of Formation of CF₂. A number of experimental approaches
has been used to determine ΔH°ᵢ(CF₂). The most common technique involves
mass spectrometric measurement of appearance potentials. The earlier
appearance potential measurements indicated that ΔH°ᵢ(CF₂) = -30 ± 10 kcal. mole⁻¹,³²
but it now appears this value is too high. Margrave and co-workers³³ reported
a mass spectrometric study of the C₂F₄/CF₂ equilibrium between 1127-1244°K.
Both second and third-law determinations of the enthalpy of reaction for
C₂F₄ → 2CF₂ were made, yielding -39.3 ± 3 kcal. mole⁻¹ for ΔH°₂₉₈(CF₂, g).

Two groups have studied the pyrolysis of CF₂HCl and have calculated
ΔH°ᵢ(CF₂) to be -43 and -39.1 kcal. mole⁻¹, respectively.³⁴ Shock waves
were also used to study the formation of CF₂ from C₂F₄ and CHF₃; values
of ΔH°ᵢ(CF₂) = -39.7 ± 3.0 and -40.2 ± 4.0 kcal. mole⁻¹ respectively¹⁸,¹⁹
were obtained. Other methods that have been used to determine ΔH°ᵢ(CF₂)
include the pyrolysis of CF₄ on graphite³⁵ and the observation of predissociation
in ultraviolet absorption spectra³⁶.

Reaction Chemistry of CF₂. The reactions of CF₂ that have been studied
to date fall conveniently into two categories: reaction in solution and
reaction in the gas phase. Recently, however, there have also been some
investigations of the reactions of matrix-isolated CF₂. No attempt will be
made in this article to recount the large number of investigations into
solution-phase dihalocarbene chemistry; a brief summary of dihalocarbene
solution chemistry will be given in the following section. The interested reader is directed to several reviews of this subject.

In solution, dihalocarbenes are often produced from the basic hydrolysis of haloforms:

\[ \text{CHXYZ} + \text{OH}^- \rightarrow \text{CXYZ}^- + \text{H}_2\text{O} \]
\[ \text{CXYZ}^- \rightarrow \text{CXY} + \text{Z}^- \]

Hine has shown that the relative ability of substituent halogens to enhance trihalo anion formation is

\[ \text{I} \sim \text{Br} > \text{Cl} > \text{F} \]

and that halogens facilitate carbene formation in the order

\[ \text{F} \gg \text{Cl} > \text{Br} > \text{I} \]

This latter sequence has been attributed to the relative ability of the halogens to supply unshared pairs to the electron-deficient carbon atom, as represented by the hybrids shown below:

\[ \text{X} - \text{C} - \text{X} \]
\[ \text{X} = \text{C} \]
\[ \text{X} = \text{X} \]

In the case of difluoromethylene, Hine suggested that formation of the carbene is so favored that dehydrohalogenation occurs in a concerted fashion, with no carbanion intermediate.

Several other methods of generating dihalocarbenes in solution have been reported; the most useful of these appears to be the thermolysis of phenyltrihalomethyl mercury compounds as reported by Seyferth and co-workers, although other organometallic precursors have also been employed.

\[ \phi - \text{Hg} - \text{CF}_3 + \phi - \text{Hg} - \text{F} + :\text{CF}_2 \]
\[ \phi - \text{Hg} - \text{CCl}_2\text{Br} + \phi - \text{Hg} - \text{Br} + :\text{CCl}_2 \]

The advantages of this method of carbene synthesis are that reaction can be carried out in neutral solution, and that reaction yields are often dramatically improved. Thus, although reactions of dihalocarbenes generally do not give
rise to products corresponding to single bond insertion, Seyferth has reported insertion of phenyl(trihalomethyl) mercury-generated carbenes into C-H, Si-H, Ge-H, O-H, B-C, Hg-X, Sn-X, Si-Hg, Ge-Hg and Sn-Sn bonds.37

Much of the literature regarding dihalocarbenes is concerned with reactions of CX₂ with olefinic substrates to give 1,1-dihalocyclopropane derivatives. These reactions occur with retention of stereospecificity, as expected for singlet carbenes. Dihalocarbenes also exhibit strong electrophilic behavior towards olefins, and will often not react with weakly nucleophilic species if stronger nucleophiles are present.

Gas-phase Reactions of CF₂. In the gas phase, CF₂ is remarkably unreactive as compared to CH₂. This situation has been dramatically demonstrated by Mahler, who did not observe reaction between CF₂ (as produced from the pyrolysis of trifluoromethylfluorophosphoranes at 120°C) and BF₃, H₂, CO, NF₃, CS₂, PF₃, SO₂, CF₃I or N₂O. Mahler did report the following reactions:

\[
\begin{align*}
\text{CF}_2 + \text{I}_2 &\rightarrow \text{CF}_2\text{I}_2 + \text{CF}_2\text{ICF}_2\text{I} + \text{I(CF}_2)_3\text{I} + \frac{\text{CF}_2}{\text{CF}_2} \\
\text{CF}_2 + \text{HCl} &\rightarrow \text{CF}_2\text{HCl} \\
\text{CF}_2 + \text{Cl}_2 &\rightarrow \text{CF}_2\text{Cl}_2 \\
\text{CF}_2 + \text{O}_2 &\rightarrow \text{COF}_2 \\
\text{CF}_2 + \text{MoF}_6/\text{WF}_6 &\rightarrow \text{CF}_4 + \text{reduced metal fluorides} \\
\text{CF}_2 + \text{CF}_3\text{C≡CCF}_3 &\rightarrow \frac{\text{CF}_3}{\text{CF}_2} + \frac{\text{CF}_3}{\text{CF}_2} + \frac{\text{CF}_2}{\text{CF}_2} \\
\text{CF}_2 + \text{F}_3\text{PO} &\rightarrow \text{CO} + \text{PF}_5 + \text{COF}_2 + \text{PF}_3
\end{align*}
\]

The CF₂/I₂ reaction is complicated by the fact that I₂ reacts with C₂F₄ to give CF₂I-CF₂I.39 The HCl reaction is interesting since, as Mahler points
out, it is the reverse of a reaction often used to produce CF₂. The reaction of CF₂ with O₂ is surprising in light of the many kinetic studies of the reactions of CF₂ in the presence of O₂, to be discussed later.

Mitsch⁴⁰ studied the reaction of CF₂ produced from the photolysis of CF₂N₂, and reported the following reactions:

\[
\begin{align*}
\text{CF}_2 + \text{Cl}_2 & \rightarrow \text{CF}_2\text{Cl}_2 \\
\text{CF}_2 + \text{I}_2 & \rightarrow \text{CF}_2\text{I}_2 \\
\text{CF}_2 + \text{N}_2\text{O}_4 & \rightarrow \text{CF}_2\text{NO}_2 \\
\text{CF}_2 + \text{NO}_2\text{Cl} & \rightarrow \text{CF}_2\text{ClNO}_2 \\
\text{CF}_2 + \text{O}_2& \rightarrow \text{CF}_2\text{O}_2 \\
\text{CF}_2 + \text{R}-\text{C}-\text{OH} & \rightarrow \text{R}-\text{C}-\text{OCF}_2\text{H} \\
\text{CF}_2 + \text{R}-\text{OH} & \rightarrow \text{R}-\text{O} \cdot \text{CF}_2\text{H} \\
\text{CF}_2 + \text{RSO}_3\text{H} & \rightarrow \text{CF}_3\text{SO}_3\text{CF}_2\text{H} \\
\end{align*}
\]

Perfluoro-1,4-pentadiene and perfluoropropene undergo similar reactions.

Atkinson and McKeagen⁴¹ reported two similar reactions:

\[
\begin{align*}
\text{CF}_3 = \text{CF} = \text{CF}_2 + \text{CF}_2 &= \text{CF} \rightarrow \\
\text{C}_2\text{H}_4 + \text{CF}_2 & \rightarrow \text{CH}_2 = \text{CH}_2, \text{ low yield}.
\end{align*}
\]
Behind a shock wave CF$_2$ reacts with NO$^{42}$:

\[
\begin{align*}
\text{CF}_2 + \text{NO} & \rightarrow \text{CF}_2\text{NO} \\
2\text{CF}_2\text{NO} & \rightarrow 2\text{CF}_2\text{O} + \text{N}_2 \\
\text{CF}_2\text{NO} + \text{NO} & \rightarrow \text{CF}_2\text{O} + \text{N}_2\text{O}
\end{align*}
\]

CF$_2$ also reacts with NOF. In this case the CF$_2$ used was prepared by the photolysis of C$_2$F$_4$ and the reaction was complicated by the reaction between C$_2$F$_4$ and NOF.$^{43}$

Mastrangelo$^{20}$ has reported some interesting work on the reactions of CF$_2$ trapped in matrices. A stream of octafluorocyclobutane was passed through a radio frequency discharge and condensed on a liquid nitrogen-cooled cold finger. The resultant deposit was an intense dark blue which persisted until the cold finger warmed to ca. 95$^\circ$K. When radical generation times exceeded 15 minutes, however, the blue condensate slowly changed to a red color believed to be associated with CF$_3^-$ radicals. On warming, the blue condensate gave rise to C$_2$F$_4$ and unreacted c-C$_4$F$_8$, but no polymeric residue. When chlorine was condensed on the blue deposit before warmup, CF$_2$Cl$_2$ and CF$_2$Cl-CF$_2$Cl, with smaller amounts of CF$_3$Cl, were observed in the products. Mastrangelo attributed the blue color to the presence of CF$_2$ radicals, and the ensuing red color to the disproportionation of CF$_2$ to CF and CF$_3$. No determination of the spin state of either the gas-phase or condensed species was reported; in view of the intense color of the condensate, the absence of polymeric radical chains, and the proposed disproportionation of CF$_2$ to CF and CF$_3$, the presence of triplet CF$_2$ seems quite possible.

Milligan and Jacox$^{44}$ have recently reported an elegant synthesis of CF$_2$ in an argon matrix. Carbon atoms, produced from the photolysis of
cyanogen azide, were allowed to react with molecular fluorine, and the presence of CF₂ was demonstrated from infrared spectra. Use of radiation effective in photolyzing F₂ produced CF₃ from the reaction of the CF₂ with atomic fluorine.

Kinetic Studies of the Gas-Phase Reactions of CF₂. As mentioned above, when gaseous CF₂ is produced in the presence of substances with which it does not react, the products obtained are tetrafluoroethylene and perfluorocyclopropane. The decay of CF₂ was originally thought to follow zero-order kinetics (that is, removal of CF₂ by means of diffusion to the walls of the apparatus). A study of the flash-photolysis of C₂F₄ by Dalby, however, showed that CF₂ decay follows second order kinetics, and a rate constant of 1.7x10⁻⁷ (liter/mole·sec) at 25°C was determined for dimerization of CF₂ to CF₂=CF₂. Dalby further observed that the rate of disappearance of CF₂ was independent of the concentration of oxygen, C₂F₄ or C₂H₄ at pressures as high as 40 cm for the latter two. He was thus able to set an upper limit to the rate constant for the reaction of CF₂ with these molecules of approximately 10⁴ liter/mole·sec.

Cohen and Heicklen investigated the mercury-sensitized photolysis of C₂F₄ and were able to determine the rate constant for the reaction

$$\text{CF}_2 + \text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{F}_6$$

to be $$k_{\text{C}_2\text{F}_4} = 6.4 \times 10^7 \exp (-7500/RT)$$ or 4.5x10⁳ liter/mole·sec at 25°C. The ratio of $$k_{\text{C}_2\text{F}_4}$$ to the rate constant for dimerization was also found:

$$k_{\text{C}_2\text{F}_4}/k_{\text{dim.}}^{1/2} = 395 \exp (-6700/RT) \text{ (liter/mole·sec)}^{1/2}$$. This ratio has a value of approximately 5.6x10⁻³ at 25°C. Although this method of CF₂ production apparently does not yield triplet CF₂, the molecule may be
generated via the reaction of ground-state oxygen atoms (3P) with C2F4 to yield 3CF2 and CF2O9,47. Triplet CF2, like the singlet molecule, can add to C2F4 to form c-C3F6. Triplet CF2 can also revert to singlet CF2 through a bimolecular reaction involving an excited C2F4 intermediate:

\[
2 \text{3CF}_2 + \text{C}_2\text{F}_4^* \rightarrow 2 \text{1CF}_2
\]

The self-annihilation reaction occurs much faster than addition to C2F4. If molecular oxygen is added to the system, 3CF2 may then react with O2 to give CF2O2. This reaction is slightly faster than the combination of 3CF2. The CF2O2 radicals produced in the reaction with O2 are removed via

\[
2\text{CF}_2\text{O}_2 \rightarrow 2\text{CF}_2\text{O} + \text{O}_2
\]

The presence of triplet CF2 was inferred from the fact that in this system all of the CF2 species are scavenged by O2 if the O2 pressure is greater than 5 torr, coupled with previous observations that the rate of reaction of singlet CF2 with O2 is extremely slow6,7,48.

Modica and LaGraff19 have conducted a series of examinations of the production and kinetic aspects of the reactions of CF2 in shock waves. C2F4, diluted 1:100 with argon, was shocked over the temperature range 1200-1800°K. Ultraviolet absorption of the shocked mixture revealed that dissociation of the C2F4 to CF2 was virtually complete within 1 usec. The dissociation reaction was found to be second order,

\[
\frac{1}{2} \frac{d[\text{CF}_2]}{dt} = K_{\text{Ar}} [\text{C}_2\text{F}_4][\text{Ar}], \text{ with } K_{\text{Ar}} = 7.82 \times 10^{15} T^{1/2} \exp \left(-\frac{55690}{RT}\right) \text{ cc/mole \cdot sec}
\]

The equilibrium constant for the reaction C2F4 $\rightarrow$ 2CF2 was determined to be

\[
\log K_c (\text{mole/cc}) = 69432/2.303RT + 4.62
\]

The value of $\Delta H_f^0$ (CF2) calculated from the measured heat of the above reaction agrees well with that obtained by other methods33,34, and lends
strength to the assumption that equilibrium conditions prevail in the system.

When oxygen was added to the C2F4/Ar mixture, no reaction with the O2 was observed below 1400°K. At temperatures above 1700°K, however, the bimolecular oxidation of CF2 to (initially) CO + 2F + O was found to occur with

$$K_{ox} = 2.82 \times 10^{10} \frac{T^4}{s} \exp \left( -\frac{-13280}{RT} \right)$$

At temperatures in the range 2600–3700°K CF2 itself decomposes to CF + F, with equilibrium expressed by

$$\log K_c \text{ (mole/cc)} = \frac{-103000 \pm 5700}{2.303 RT} - 0.41 \pm 0.11$$

B. Other Carbon Dihalides

Despite the large body of literature discussing the preparation and reaction chemistry of dichloromethylene in solution, very few reports of the isolation of the molecule have appeared. The technique of forming Group IV dihalides from the reduction of the tetrahalide with the metal has proved to be of great utility for production of SiX2 and GeX2, but has not been successful in the case of carbon. Schmeisser and Schröter studied the reaction of CCl4 with activated charcoal at 1300°, and originally reported isolation of CCl2 itself as a mobile, volatile liquid boiling at -20°C. A subsequent publication retracted the claim, explaining that an equimolar mixture of dichloroacetylene and chlorine had comprised the "CCl2." The paper further stated the CCl4 was in fact undergoing a surface-catalyzed pyrolysis rather than reaction with the charcoal. Carbon is known to catalyze the decomposition of CCl4 to C + 2Cl2. Schmeisser et al. obtained the following products from CCl4 pyrolysis (yields in parentheses):

C(35); C2Cl2 (20); C2Cl4 (40); C2Cl6 (5); C4Cl6 (0.1); C6Cl6 (0.1). Dichloromethylene was presumably the precursor of the C2Cl4, although the latter
compound could have resulted from disproportionation of C$_2$Cl$_6$ to Cl$_2$ and C$_2$Cl$_4$. Blanchard and LeGoff$^{50}$ studied the decomposition of CCl$_4$ on a tungsten ribbon in the temperature range 1300-2000 K. The CCl$_4$ vapor, at a pressure of 10$^{-5}$ mm Hg, was made to flow past the ribbon and directly into the ionization source of a mass spectrometer, which was then utilized to analyze the products. Between the temperatures of 1300 and 1600$^\circ$, the major pyrolysis products were CCl$_2$ and Cl$_2$; between 1600 and 1900$^\circ$ CCl$_2$ and Cl prevailed. When a carburized tungsten ribbon was used virtually identical results were obtained, indicating that the reaction

$$\text{C + CCl}_4 \rightarrow 2\text{CCl}_2$$

was not important under the existing conditions. The ionization potential of CCl$_2$ was determined to be 13.2 ± 0.2 eV, and the appearance potentials of the various C-Cl$_n^+$ ions were used to calculate approximate bond dissociation energies of the corresponding neutral species.

Three groups have recently claimed to have isolated CCl$_2$ in low-temperature matrices and to have observed the molecule spectroscopically. Milligan and Jacox$^{51}$ prepared CCl$_2$ in a manner analogous to that described for their matrix synthesis of CF$_2$. Carbon atoms formed in situ from the photolysis of N$_2$CN were allowed to react with Cl$_2$ in an argon or nitrogen matrix at 140 K. Subsequent to irradiation, two new bands at 721 and 748 cm$^{-1}$ were observed in the infrared spectrum of the matrix. The relative intensity of the bands remained constant under varying conditions. The features disappeared rapidly on warmup of the matrix, with corresponding growth of bands assigned to CCl$_4$. Moreover, $^{13}$C isotopic studies demonstrated that the compound in question contained only one carbon atom. The above observations were taken as evidence for the existence of CCl$_2$ as the species in question, and the bands at 721 and 748 cm$^{-1}$ were assigned to the stretching fundamentals.
of the molecule. The bond angle for CCl2 was estimated to lie in the range 90-110°. The authors also reported a weak band system between 4400 and 5600 cm⁻¹, with a band spacing of 305 cm⁻¹, to be associated with CCl2-containing matrices. By analogy with known electronic spectra of CF₂, the system was attributed to a transition from the singlet ground state to the first excited state, with an extensive progression in the upper state bending vibration.

Andrews⁵² isolated CCl₂ in an argon matrix by means of the reaction of Li atoms with CCl₄. CCl₃⁻ radicals are formed from the abstraction of a Cl atom from CCl₄ by Li, and CCl₂ is produced from the secondary reaction

$$\text{Li + CCl}_3^- = \text{LiCl + CCl}_2$$

The loss of CCl₂ absorption on matrix warmup was accompanied by the growth of bands attributed to C₂Cl₄. A complete isotopic analysis of the CCl₂ spectra supported the assignment of the stretching fundamentals as \( \nu_1 = 719.5 \) and \( \nu_3 = 745.7 \) cm⁻¹, in excellent agreement with the work of Milligan and Jacox. The weak \( \nu_2 \) (bending) mode was not observed. The bond angle of CCl₂ was estimated to be 100° ± 9°, which strongly indicates that the observed species is in the singlet electronic configuration. Stretching force constants were calculated, and \( F_{\text{C-Cl}} \) was found to be lower than the corresponding value for CCl₄—a fact which Andrews claims to be evidence for lack of significant pi-bonded contributions to the C-Cl bonds. This result is surprising since doubly-bonded resonance hybrids have long been invoked to explain the stability of dihalocarbenes.

About the same time as the publication of Milligan and Jacox⁷ and Andrews¹ work, Steudel⁵³ claimed to have observed the infrared spectrum of CCl₂ condensed from the pyrolysis (or decomposition in a high-frequency
discharge) of several C-Cl compounds. CCl₄, C₂Cl₆, CHCl₃, and CS₂Cl₂ were passed individually through a furnace at 900°C, and immediately condensed on a KBr window at 89°K. In each instance, a broad band in the IR spectrum at 896 cm⁻¹ was seen. The absorption diminished in intensity as the matrix was warmed, finally disappearing at 160-200°K. Since the pyrolysis products in each case included C₂Cl₄, CCl₂ was assumed to be the common intermediate in each reaction.

Although CCl₂ may well have been an intermediate in the pyrolytic reactions reported by Steudel, it seems clear that the molecule is not responsible for the observed band at 896 cm⁻¹. Andrews has recently described the infrared spectrum of matrix-isolated CCl₃, and located one of the stretching modes (v₃) at 898 cm⁻¹. Since the reactions discussed in Steudel’s work all produce C₂Cl₆ as well as C₂Cl₄, he likely observed the CCl₃ radical.

The area of gas-phase chemistry of dichloromethylene is as yet largely unexplored. Haszeldine and co-workers have prepared CCl₂ from the pyrolysis of CCl₃SiCl₃ and CCl₃SiF₃. The CCl₂ thus produced was observed to react with ethylene and a number of butenes in 85-95% yield, and with C₂Cl₄ in 69-85% yield. Addition to cis- or trans-2-butene occurred with retention of stereospecificity. No report of the dimerization of CCl₂ to C₂Cl₄ was given. These preparations belong to the general class of α-elimination reactions of trihaloalkyl organometallics, several of which were discussed in the section on CF₂. In a variation of this type of work Skell and Cholod prepared CCl₂ in the gas phase by pyrolysing CHCl₃ at 1400°K. This pyrolysis was carried out immediately above a solution of olefins and the CCl₂ reacted with these olefins to give dichlorocyclopropane derivatives. The authors argue that this confirms the fact that free CCl₂ is
indeed the intermediate in α-elimination reactions.

Other than some solution chemistry very little indeed is known about CBr₂ and Cl₂ or about mixed dihalocarbenes. Tyerman⁵⁶ has observed the band spectrum of CFCl between 3736-3466 Å. Its main feature is a progression of bands with an average spacing of 386 cm⁻¹. He also observed that, in contrast with CF₂, CFCl reacts with O₂ at room temperature.

\[
\text{CFCl} + \text{O}_2 \rightarrow \text{CFClO} + \text{O}
\]

C. Silicon Difluoride

If the gaseous species resulting from passing SiF₄ over elemental silicon at 1100-1400°C are condensed at temperatures below -80°C and subsequently allowed to warm to room temperature, a waxy, tough white polymer of composition (SiF₂)ₙ is obtained⁵⁷. Mass spectrometric analyses of the gas phase products of the Si/SiF₄ reaction indicate that SiF₂ and SiF₄ account for over 99% of the species present, with the percentage of SiF₂ typically near 60%⁵⁸. Gaseous silicon difluoride is extraordinarily stable compared to dihalocarbenes and other silicon dihalides. Its half-life at a pressure of 0.2 mm has been estimated to be 150 seconds⁵⁸. Unlike other Group IV difluorides, SiF₂ shows no tendency to form gas phase dimers, and is essentially unaffected by the addition of many other gases (except for oxygen, which facilitates formation of Si-O-F polymers on the walls of the apparatus).

The low-temperature condensate of SiF₂ is a yellow-brown paramagnetic solid which remains unchanged when maintained at -196°C. If, however, another substance is co-condensed with the SiF₂, the low-temperature species can be made to react—usually on warming. The reaction chemistry thus investigated has proved to be quite extensive, and likely represents the
most comprehensive study of the low-temperature chemistry of a high-
temperature molecule. Results of the various examinations of the physical
and chemical properties of SiF₂, most of which have been conducted in this
laboratory, will be discussed in the following sections.

Gas Phase Spectra

Ultraviolet Spectra. The first direct evidence for the existence of
gas phase monomeric silicon difluoride resulted from observation of emission
spectra of the molecule in electric discharges through SiF₄⁵⁹. The emission
band system was subsequently extended⁶⁰; however, both of these investigations
are now thought to have resulted in erroneous vibrational numberings. The
ultraviolet absorption spectrum was reported by Khanna, Besenbruch and
Margrave⁶¹, who employed the "usual" preparative technique of reducing the
tetrafluoride with the metal. They measured 28 absorption bands in the
region between 2325 and 2130 Å. The most striking feature of the spectrum
was the appearance of a series of bands with a periodicity of 252 cm⁻¹.
This progression was correlated with the bending frequency of the excited state.
As was the case of CF₂, no direct evidence for excitation of stretching
frequencies was obtained. The vibrationless transition is thought to lie
at 2266.4 Å, and is likely a ¹B₁ - ¹A₁ transition.

Microwave Spectrum. Rao, et al.⁶² were able to observe the microwave
spectrum of SiF₂ by generating the molecule from the high-temperature
Si/SiF₄ reaction and pumping the reaction mixture through an absorption
cell. The Si-F bond distance and F-Si-F bond angle were calculated to be
1.591 Å and 100°59', respectively. The bond angle is smaller, and the bond
distance longer than one might anticipate, suggesting that bonding involves
mainly p² hybridization of the silicon orbitals.
Infrared Spectrum. The infrared spectrum of gaseous SiF₂ has been recorded from 1050 to 400 cm⁻¹. Two absorption bands, centered at 855 and 872 cm⁻¹, were assigned to the symmetric (ν₁) and antisymmetric (ν₃) stretching modes, respectively. The assignment was rendered difficult because of the considerable overlap of the two bands. The fundamental bending frequency occurs below the instrumental range of the study, but a value of 345 cm⁻¹ can be determined from the ultraviolet study. The vibrational frequencies were combined with data from a refined microwave study⁶⁴ and utilized to calculate force constants and revised thermodynamic functions.

Mass Spectrum. There have been two investigations of the mass spectrum of SiF₂. In one experiment⁵⁸ the gaseous mixture of silicon fluorides obtained after passing SiF₄ over a column of Si held at 1150°C was passed into a 5 lt. bulb and thence into a mass spectrometer. Only SiF₄ and monomeric SiF₂ were observed; no polymeric species of SiF₂ were seen. By isolating the 5 lt. bulb containing the SiF₂ from the furnace and then monitoring the decay of SiF₂, it was estimated that SiF₂ has a half-life of 120 seconds. In a second investigation⁶⁵a SiF₂ was produced by heating a mixture of Si and CaF₂ to about 1500°C. From this study the following values were obtained: \( \Delta H_{a,298}^{\circ} \text{SiF}_2,g = 12.33 \pm 0.2 \text{ eV} \) and thence \( \Delta H_{f,298}^{\circ} \text{SiF}_2,g = -139 \pm 2 \text{ kcal mole}^{-1} \). This value for the heat of formation of SiF₂ is not too close to that determined by a transpiration method, \(-148 \pm 4 \text{ kcal mole}^{-1} \)⁶⁵b. The discrepancy probably arises from the interaction between SiF₄ and SiF₂ to form Si₇F₂X⁺ at the higher pressures⁶⁵c.
Studies of SiF₂ Condensate

Infrared Spectrum. Since the reaction chemistry of SiF₂ known to date occurs at low temperatures in the condensed phase rather than in the gas phase, it is naturally of interest to investigate the low-temperature condensate formed from gaseous SiF₂. The first such investigation was conducted by Bassler, Timms, and Margrave⁶⁶, and involved recording the infrared spectrum of matrix-isolated SiF₂ between the temperatures of 20-40°K. Figure (1) illustrates spectra obtained when a gas-phase SiF₂/SiF₄ mixture was condensed on a CsI window at 20°K and allowed to warm. One notes that the peak at 811 cm⁻¹ disappears much faster than the rest of the spectrum as the matrix is warmed. Furthermore, when the furnace-to-window distance is increased to 10 feet, or when nitric oxide is co-condensed with the SiF₂, the peak is absent altogether. This behavior suggests that the species responsible for the absorption is more reactive than monomeric singlet SiF₂—perhaps triplet SiF₂, excited singlet SiF₂, or SiF₃. The second spectral feature evident on warmup is the appearance of two new bands at 830 and 892 cm⁻¹. These absorptions first appear at about 35°, grow to maximum intensity at 38° (at the expense of bands now known to be due to monomeric SiF₂), and disappear rapidly on further warming. When the matrix is warmed to 50°K, the spectrum consists of broad bands identical with those of thin layers of (SiF₂)ₙ at room temperature. These facts, especially when viewed in conjunction with the chemical characteristics of SiF₂ condensates, lead to the conclusion that the new bands are due to SiF₂ dimer. The same study also examined some of the earlier
Figure 1 - Infrared spectra of SiF₂ in argon matrix during warm-up.

The bands attributed to Si₂F₄ are shown by arrows.
SiF₂ chemistry by co-condensing potential reactants in the matrix. Most illuminating of these experiments was that involving BF₃. Previous work had shown that the reaction of SiF₂ with BF₃ (to be discussed in more detail later) leads to a series of compounds BF₂(SiF₂)ₙF, with n at least two. When the BF₃/SiF₂ matrix was allowed to warm, a series of bands not associated with "pure" SiF₂ spectra appeared. The bands began to appear when those associated with (SiF₂)₂ reach a maximum. Moreover, the new absorptions corresponded closely with those of the gas-phase spectrum of SiF₃SiF₂BF₂, the major product of the SiF₂/BF₃ reaction on a macroscopic scale.

Two re-examinations of the infrared spectra of matrix-isolated SiF₂ have been reported very recently. This work was characterized by improved matrix isolation and by the use of both neon and argon matrices. Hastie, Hauge, and Margrave established the stretching fundamentals in a Ne matrix to lie at 851 (ν₁) cm⁻¹ and 865 (ν₃) cm⁻¹, representing a red shift of approximately 8 cm⁻¹ from the gas phase. A bond angle of 97-102° was calculated from observed isotopic splitting; molecular geometry is thus not greatly perturbed by the matrix environment. Milligan and Jacox, who generated SiF₂ from the vacuum photolysis of SiF₂H₂ or SiF₂D₂, were able to directly observe the bending fundamental of 343 cm⁻¹ (in an Ar matrix). These authors also measured a series of bands in the ultraviolet which correspond closely to those seen in the gas phase spectrum of SiF₂ (see ref. 61).
ESR Studies. Both the low-temperature chemistry and the colored appearance of SiF$_2$ condensate strongly suggest the presence of radical species containing unpaired electrons. Consequently, an attempt was made in this laboratory to detect an electron spin resonance signal from the condensate. A gaseous SiF$_2$/SiF$_4$ mixture was condensed on a liquid nitrogen-cooled cold finger in the spectrometer cavity. The condensate generated in this manner gave rise to a broad signal whose intensity was invariant with time as long as the low temperature was maintained. The $g$ factor for the resonance was 2.003 ± 0.002, essentially that of a free electron. When the condensate was allowed to warm, the signal decayed rapidly, and could not be regenerated by subsequent cooling—indication that polymerization is irreversible and complete. The nature of the signal is similar to that found upon irradiation of polytetrafluoroethylene.

Reactions of SiF$_2$

One of the first reactions of SiF$_2$ to be investigated was that with boron trifluoride. The apparatus used to study this reaction is shown in Figure (2); this apparatus is typical of those used in all of the following reactions of SiF$_2$. When SiF$_2$ and BF$_3$ are co-condensed at -196°C, a green solid results. Warmup of the condensate leads to a number of volatile species, including the new compounds SiF$_3$SiF$_2$BF$_2$ and SiF$_3$(SiF$_2$)$_2$BF$_2$. The reaction products each contain at least two silicon atoms, and a gas phase
Figure 2 - Apparatus used to study condensed phase reactions of SiF$_2$. 
reaction does not occur. These observations lead to the suggestion of the mechanism shown below:

\[
\begin{align*}
2\text{SiF}_2 & \rightarrow \text{SiF}_2\text{SiF}_2, \\
\text{SiF}_2 & \rightarrow \text{SiF}_2\text{SiF}_2\text{SiF}_2, \\
\text{SiF}_2 & \rightarrow (\text{SiF})_4 \\
\text{iv} + \text{BF}_3 & \rightarrow \text{v} + \text{BF}_3 \\
(\text{Si}_2\text{F}_4\text{BF}_3) & \rightarrow (\text{Si}_3\text{F}_6\text{BF}_3) \\
& \rightarrow \\
\text{SiF}_3\text{SiF}_2\text{BF}_2 & \rightarrow \text{SiF}_3\text{SiF}_2\text{SiF}_2\text{BF}_2
\end{align*}
\]

where reactions ii and iii are fast compared to iv and v. In a more recent study a mixture of SiF₂ and SiF₄ was reacted with a mixture of BF and BF₃. The compound F₂Si(BF₂)₂ was isolated from the resultant products. Diboron tetrafluoride was also reacted with SiF₂ but any new products that were formed were too unstable to be recovered.

The next series of reactions examined involved simple unsaturated and aromatic hydrocarbons and their fluorocarbon analogs. The SiF₂/benzene reaction produces a series of compounds of formulae C₆H₆(SiF₂)ₙ with n = 2 to at least 8. Both infrared and ultraviolet spectra indicate the absence of conjugated π-systems for the n = 3 (highest yield) product. Hydrolysis of the product mixture gives 1,4-cyclohexadiene. These facts, along with the proton nmr spectrum of the compound, permit the conclusion that the products possess the bridged structure shown

\[
\begin{align*}
(S\text{F}_2)_n
\end{align*}
\]

where n = 2-8

The reaction of SiF₂ with ethylene yields the two cyclic molecules

\[
\begin{align*}
\text{CH}_2 - \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{SiF}_2\text{SiF}_2
\end{align*}
\]

and

\[
\begin{align*}
\text{CH}_2 - \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 - \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{SiF}_2\text{SiF}_2
\end{align*}
\]

both of which are of quite limited stability. The SiF₂/acetylene reaction
proceeds similarly to give
\[
CH = CH
\]
\[
\text{SiF}_2 \text{-SiF}_2
\]
and
\[
\text{CH} \text{-CH}
\]
\[
\text{SiF}_2 \text{-SiF}_2
\]
but here the six-membered ring is not isolated and is instead recovered as the rearrangement product, \( \text{HC}=\text{C-SiF}_2 \text{-SiF}_2 \text{-CH}=\text{CH}_2 \). Another cyclic compound

\[
\text{SiF}_2
\]
\[
\text{SiF}_2
\]
was isolated from the reaction of \( \text{SiF}_2 \) with butadiene\(^76\).

The above reactions reinforce the "diradical" mechanism proposed for the \( \text{BF}_3 \) reaction. Hexafluorobenzene and the various fluorinated ethylenes\(^73,74\), however, react quite differently. The products in these reactions formally correspond to C-F bond insertion by an \( \text{SiF}_2 \) monomer.

\[
\text{SiF}_2 + \text{SiF}_2 \text{F}_3 \rightarrow \text{SiF}_2 \text{F}_3 + \text{C}_6 \text{F}_4(\text{SiF}_3)_2
\]

\[
\text{SiF}_2 + \text{CFH}=\text{CF}_2 \rightarrow \text{CFH}=\text{CFSiF}_3 + \text{F}_3 \text{SiC} \text{CF}_2
\]
(cis and trans)

Attack of a C-F bond was shown to be preferential to attack of a C=C bond.

Several quite recent investigations into \( \text{SiF}_2 \) chemistry conducted in this laboratory have further indicated the versatility of \( \text{SiF}_2 \) as a reactant. Hydrogen sulfide reacts with \( \text{SiF}_2 \) to form predominantly \( \text{SiF}_2 \text{HSH} \) and \( \text{Si}_2\text{F}_5\text{H} \)\(^77\). The disilanethiol, \( \text{SiF}_2 \text{HSiF}_2 \text{SH} \), expected from addition of \( \text{H}_2\text{S} \) to \( \text{Si}_2\text{F}_4 \), was
obtained in limited yield and was observed to be quite unstable. The \( \text{H}_2\text{S} \) reaction closely paralleled an earlier study of the \( \text{SiF}_2/\text{GeH}_4 \) reaction \(^7\) in which the products were the germysilanes \( \text{GeH}_3(\text{SiF}_2)_n\text{H} \), \( n = 1-3 \). The \( n = 1 \) homolog was the major product and compound stability decreased dramatically with increasing \( n \).

The reaction of \( \text{SiF}_2 \) and iodotrifluoromethane was studied \(^7\) in expectation of obtaining the products corresponding to "addition" of \( \text{CF}_3\text{I} \) to \( (\text{SiF}_2)_n \) species, \( \text{CF}_3(\text{SiF}_2)_n\text{I} \). The reaction of \( \text{CF}_3\text{I} \) with tetrafluoroethylene has been shown to yield (mainly) \( \text{CF}_3\text{CF}_2\text{CF}_2\text{I} \). In fact, three separate homologous series of products were characterized:

\[
\begin{align*}
\text{CF}_3\text{I} + \text{SiF}_2 &= \text{CF}_3(\text{SiF}_2)_n\text{I} \quad n = 1,2 \\
\text{SiF}_3(\text{SiF}_2)_n\text{I} &= n = 0,1,2 \\
\text{SiF}_2\text{I}_2; \text{SiF}_2\text{ISiF}_2\text{I}
\end{align*}
\]

Excesses of \( \text{CF}_3\text{I} \) in the condensing mixture afforded large yields of \( \text{CF}_3\text{SiF}_2\text{I} \); excesses of \( \text{SiF}_2 \) resulted in the formation of most or all of the compounds listed above. The \( \text{CF}_3\text{I} \) reaction is of interest as regards reaction mechanisms in \( \text{SiF}_2 \) chemistry. As in many other reactions not involving unsaturated reactants, the product obtained in highest yield contained a single silicon atom. Moreover, while each product which contained a \( \text{-CF}_3 \) moiety also included an I atom, the converse was not true. Similar behavior was exhibited in the \( \text{H}_2\text{S} \) reaction: \( \text{SiF}_3\text{H} \) and \( \text{Si}_2\text{F}_5\text{H} \) were products; \( \text{SiF}_3\text{SH} \) and \( \text{Si}_2\text{F}_5\text{SH} \) were not. One may make two suggestions from these observations. The first is that diradical species play a major role in \( \text{SiF}_2 \) chemistry only when there is no bond of sufficient lability to be attacked by \( \text{SiF}_2 \) monomers. (Such reactive bonds include \( \text{C-F} \) in \( \text{C}_5\text{F}_5 \); \( \text{C-I} \) in \( \text{CF}_3\text{I} \); and the \( \text{O-H} \) and \( \text{S-H} \) bonds in \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \).) Secondly, attack by \( \text{SiF}_2 \) or \( (\text{SiF}_2)_n \) often appears to be
stepwise with, in the case of CF₃I, abstraction of an I atom followed by attack on the resultant CF₃ fragment or abstraction of iodine or fluorine from another molecule.

The low-temperature condensate of SiF₂ and elemental iodine produces only SiF₂I₂ and SiF₃I, in the approximate ratio of 3:1, on warming. One must consider the question of whether compounds containing silicon-silicon bonds, such as SiF₃SiF₂I or SiF₂ISiF₂I, are formed in the reaction, and suffer Si-Si bond cleavage by unreacted I₂. Although some disilanes do undergo fission reactions with I₂, the hydrogen analogs of the compounds in question (i.e., Si₂H₅I and Si₂H₄I₂) react only to give further substitution, eventually yielding Si₂I₆. Moreover, Si₂F₅I and Si₂F₄I₂, which were formed in the CF₃I/SiF₂ reaction, exhibited moderate stability in the presence of small amounts of I₂ generally present in the product mixtures of that reaction, and no evidence of these molecules was found even when large SiF₂/I₂ ratios were employed. It seems likely, then, that only SiF₂ monomers are involved in the I₂ reaction.

Hydrolysis of a silicon-halogen bond often results in formation of oxygen-containing polymers such as silicones. However the siloxanes Si₂OCl₆ and Si₃O₂Cl₈ can be recovered from careful hydrolysis of SiCl₄. The reaction of SiF₄ with excess water produces fluorosilicic acid and hydrated silica, but if SiF₄ is passed over wet magnesium sulfate, one obtains the perfluorosiloxanes Si₂OF₆ and Si₃O₂F₈. The controlled hydrolysis of SiF₂ might therefore be expected to lead to any of several products. Several oxygen-containing molecules other than water have been observed to react with SiF₂ to produce homologous series of both linear and cyclic oxyfluorides; alternatively, insertion of an SiF₂ monomer or telomer into an O-H bond
would result in formation of the silanols H(SiF₂)ₙOH, which would almost certainly be unstable with respect to condensation to siloxanes.

The SiF₂/H₂O reaction was conducted in a manner designed to minimize the contact of reactants before condensation in the cold trap. Reactions in which the SiF₂/H₂O ratio varied from 1:1 to 7:1 were conducted, but in all cases the only products not attributable to hydrolysis of SiF₄ were 1,1',2,2'-tetrafluorodisiloxane, SiF₂HOSiF₂H, and a voluminous white polymer. No evidence for volatile compounds containing more than two silicon atoms was obtained. The polymer was of interest inasmuch as it, unlike virtually all other SiF₂ copolymers, was not pyrophoric. Infrared analysis demonstrated the absence of Si-H bonds in the polymer. The structure of the polymer is as yet unknown, but it must differ from the Si-O-F polymers formed in various other SiF₂ reactions.

The reaction of SiF₂ with methanol proceeded a different course from the water reaction. Here, the reaction products were CH₃OSiF₃, SiF₃H, and (CH₃O)₂SiF₂. Again, the competing reaction with SiF₄ represents a complication. In a separate experiment conducted under similar conditions, SiF₄ was shown to react readily with CH₃OH to form CH₃OSiF₃ + HF. Further methanolysis of the product to form (CH₃O)₂SiF₂, however, occurred only very slowly. From these and other observations, the authors formulated the following reaction scheme:

\[
\begin{align*}
\text{SiF}_4 + \text{CH}_3\text{OH} & = \text{SiF}_3\text{OCH}_3 + \text{HF} \\
\text{SiF}_2 + \text{HF} & = \text{SiF}_3\text{H} \\
\text{SiF}_2 + \text{CH}_3\text{OH} & = \text{SiF}_2\text{HOCH}_3 \\
\text{SiF}_2\text{HOCH}_3 + \text{CH}_3\text{OH} & = \text{SiF}_2(\text{OCH}_3)_2 + \text{H}_2
\end{align*}
\]

Since the Si-H bond has been observed to react readily with methanol, failure to observe SiF₂HOCH₃ is not surprising.
Reactions of SiF₂ with NaF and LiF have been studied⁸⁷. The alkali fluorides were vaporized from a Knudsen cell and co-condensed with approximately equal amounts of SiF₂ on a liquid-nitrogen cooled cold finger. The reactions are complicated by gas-phase reactions of SiF₂ and MF and also by the reactions of SiF₄ with the fluorides. The gas phase SiF₂/MF reactions lead to deposition of M₂SiF₆ and elemental silicon on the walls of the apparatus. The low-temperature condensate is a reddish-brown at -196°, and in all cases decomposes suddenly on warmup. The nature of the low-temperature solid is as yet undetermined.

Conclusions. The utility and versatility of silicon difluoride as a chemical reagent has clearly been demonstrated. Although the region of reactions of SiF₂ with small (i.e., volatile) organic molecules has been rather well covered, there remain a great number of potentially rewarding reactions with inorganic substances. Rather than dwell on this point, however, the authors would prefer to mention two potential areas for expanding SiF₂ chemistry.

No direct evidence for the observation of triplet gaseous SiF₂ exists. If such species could be generated in reasonably high yield (by mercury-sensitized photolysis, for example), their chemistry from both synthetic and kinetic points of view would merit considerable interest. Heicklen and co-workers⁴⁶ have successfully conducted similar studies with triplet CF₂ as generated from the reaction of C₂F₄ with ground-state oxygen atoms.

An aspect of Pease's early work with SiF₂ systems may have significance for the future of SiF₂ chemistry. In a variation of the usual "matrix-trapping" technique, Pease studied the reaction of SiF₂ with Br₂ by passing
the gases through an 8" length of tubing heated to 1200° prior to condensation. Although the same product, SiF₂Br₂ was collected on warmup of the condensate, none of the usual room-temperature polymer was retained in the reaction trap—indicative of a quantitative gas-phase reaction. The heretofore unknown gaseous chemistry of SiF₂ might well be discovered via a similar approach on a general basis.

D. Other Silicon Dihalides

SiCl₂ has long been postulated to be an intermediate in gas-phase pyrolyses of various chlorosilanes, and in such reactions as that of Si and HCl to form SiCl₃H, or the reduction of perchlorosilanes with H₂. Direct observation of SiCl₂ monomer, or successful attempts to investigate the reaction chemistry of the monomer have, however, been very sparse until quite recently. This situation is in large part due to the fact that the gas-phase lifetimes of the heavier dihalides are several orders of magnitude less than that of SiF₂. Thus, although equilibrium measurements of the system Si + SiCl₄ = 2SiCl₂ indicate that K_p = 1 at 1350°C, techniques similar to those utilized for production of SiF₂ lead to (SiCl₂)ₙ and perchlorosilanes.

Timms has recently studied SiCl₂ reaction chemistry by employing fast pumping speeds and low (5x10⁻⁶ torr) permanent gas pressures. Under these conditions the SiCl₂, which is produced from reduction of the tetrahalide with the metal at 1350°C, can successfully be condensed on cooled surfaces. Condensation of the equilibrium SiCl₂/SiCl₄ mixture at liquid nitrogen temperatures gives rise to a brown solid which turns white and evolves perchlorosilanes on warming. Co-condensation of PCl₃, BCl₃, or CCl₄ yields
products corresponding to insertion of SiCl₂ into a M-Cl bond; products containing more than one silicon are not found. SiCl₂ may behave more similarly to SiF₂ (that is, diradicals may be important) in its reactions with unsaturated and aromatic compounds; Timms reported that such reactions lead to involatile polymers which incorporate the organic molecule.

Spectroscopic observations of SiCl₂ have been reported by Asandi, Karim and Samuel⁹⁴ and Milligan and Jacox⁹⁵. The early work of Asandi et al. was concerned with the emission spectra from the products of an electric discharge through SiCl₄. The spectrum attributable to SiCl₂ consisted of a number of features superimposed on a continuous band from 3160 to 3550 Å. The spectral features were used to tentatively assign two of the ground state vibrational fundamentals as 250 and 540 cm⁻¹. Milligan and Jacox generated SiCl₂ from the vacuum photolysis of SiH₂Cl₂ (or SiD₂Cl₂) in argon matrices at 140 K. Examination of infrared spectra taken subsequent to photolysis revealed the stretching fundamentals to occur at 502 and 513 cm⁻¹. It was not possible to assign the symmetries of the two absorptions.

Much of the known high-temperature chemistry of silicon-chlorine compounds is indirectly concerned with SiCl₂. The reactions discussed below will serve as examples of those in which the intermediacy of SiCl₂ is indicated.

The "direct synthesis" of SiCl₃H from Si and HCl has been shown⁹⁹ by kinetic studies to proceed via

\[
\text{Si} + 2\text{HCl} = \text{SiCl}_2 + \text{H}_2 \\
\text{SiCl}_2 + \text{HCl} = \text{SiHCl}_3
\]

Synthesis of organosilanes from silicon and RC₁ is facilitated if a silicon-copper alloy is employed⁹⁶. The catalytic action of the copper is due to the formation of CuCl, which then reacts with silicon to form SiCl₂:
The existence of SiCl₂ as an intermediate was indicated from an experiment in which the volatile product of a Si/CuCl reaction was allowed to react with CH₃Cl to form methylchlorosilanes.

The high-temperature (1000–2000°K) reactions

\[
\text{SiCl}_4 + 2\text{H}_2 = \text{Si} + 4\text{HCl} \\
\text{SiCl}_3\text{H} + \text{H}_2 = \text{Si} + 3\text{HCl}
\]

were examined by Sirtl and Reuschel. Considerations of silicon yield as a function of temperature and mole fraction of reactants lead to the conclusion that SiCl₂ is an important reaction intermediate.

The SiCl₄/Si reaction may lead to several different products, depending on reaction conditions. Thus, under conditions of high vacuum and fast pumping, SiCl₂ may be isolated by rapidly quenching the reaction products. Under less stringent vacuum conditions, (SiCl₂)ₙ is deposited just beyond the hot zone, and the perchlorosilanes SiCl₂ₙ₂⁺ can be trapped further downstream. If, however, SiCl₄ is recycled over hot silicon in a closed system, viscous subchlorides of formulae SiCl₂ₙ are obtained. The value of n varies from 12 at 900° to 16 at 1200°. The presumably cyclic compounds were characterized only by standard quantitative analyses; no spectroscopic or other physical data were reported. Bromination of the compounds produced some SiCl₃Br, indicating that at least some open-chain compounds were present.
Since \( \text{SiCl}_2 \) reacts readily with \( \text{SiCl}_4 \) under other conditions, it is difficult to explain the apparently quantitative production of \( \text{SiCl}_2 \) necessary to form high-molecular weight rings. At any rate, the closed system reaction certainly merits further investigation.

Recent thermochemical data for \( \text{SiCl}_2 \) have been reported by Schafer and co-workers\(^{91a} \), and by Teichmann and Wolf\(^{91b} \) from transpiration studies of the \( \text{SiCl}_4/\text{Si} \) system. The heat of formation of the gaseous monomer now seems well established:

\[
\Delta H_f^\circ(\text{SiCl}_2, \text{g, } 298^\circ\text{K}) = -38.2 \pm 1.5 \text{ kcal.}
\]

Mass spectrometric investigations of the silicon-chlorine system do not seem to have been made.

Although for the dibromide and diiodide, the respective \( \text{SiX}_4 + \text{Si} = 2\text{SiX}_2 \) equilibria and the reaction chemistry of the \( (\text{SiX}_2)_n \) polymers have been well characterized, the physical and chemical properties of the monomeric dihalides remain virtually unknown. In a preliminary report, Timms\(^{98} \) related the formation of \( \text{SiBr}_2 \) in 90% yield with the apparatus and procedures employed in \( \text{SiCl}_2 \) production. The only reaction reported was that with \( \text{BF}_3 \). The sole product was \( \text{BF}_2\text{SiF}_3 \)--presumably formed from disproportionation of the expected \( \text{BF}_2\text{SiBr}_2\text{F} \).

Production of \( \text{SiI}_2 \) under similar (i.e., low-pressure high-temperature) conditions is difficult due to the appreciable decomposition of \( \text{SiI}_2 \) to \( \text{Si} \) and I atoms at the temperatures required. Indeed, the diiodide has been utilized for the transportation and deposition of silicon\(^{99} \).

E. Germanium Difluoride

Germanium difluoride differs dramatically from \( \text{CF}_2 \) and \( \text{SiF}_2 \) in that it can be isolated as a stable compound at room temperature. Thus, it is surprising that few of its properties have been described.
GeF$_2$ can be prepared by reducing GeF$_4$ with Ge at temperatures above 120°C$^{100}$. It can also be prepared by heating germanium powder with anhydrous HF (225°C, 16 hrs)$^{101}$.

Ge + HF $\rightarrow$ GeF$_2$ + H$_2$

A number of the physical properties of GeF$_2$ have been measured including its infrared, ultraviolet and mass spectrum. The crystal structure of GeF$_2$ has also been determined.

The ultraviolet absorption spectrum of GeF$_2$ has been measured by Hauge, Khanna and Margrave$^{102}$. The spectrum is fairly simple and is probably due to the perpendicular $^1B_1 \leftrightarrow ^1A_1$ transition. All progressions were explained in terms of bending frequencies of the lower and upper electronic states, which are $v_2'' = 263$ cm$^{-1}$ and $v_2' = 164$ cm$^{-1}$. The 0,0,0 - 0,0,0 transition is reported to lie at 2280.1 Å.

The infrared spectrum of GeF$_2$ has also been reported$^{103}$. Both the gas phase and the matrix-isolated infrared spectra were determined. It was necessary to study the matrix-isolated spectrum for two reasons. First, the examination of the ultraviolet absorption spectrum of GeF$_2$ indicated that at least ten of the bending states were populated, and second, germanium has five abundant isotopes. These suggested that the gas phase spectrum would be broad and ill defined at the temperatures required to vaporize GeF$_2$ (150°C). As anticipated the authors found that the gas phase spectrum of GeF$_2$ did consist of broad absorbances centered at 663 and 676 cm$^{-1}$.

The spectrum of GeF$_2$ trapped in a neon matrix is shown in Figure 3. The ratio of GeF$_2$/rare gas in the matrix was 1:1000. When new matrices were prepared similar spectra were obtained, even when the ratio of diluent was changed or the temperature of deposition was altered. This indicated that
Figure 3: IR absorption spectrum of GeF$_2$ matrix isolated in Neon at $\sim$5 K.
the splitting seen in the spectrum was due to isotope effects and was not due to matrix effects. As can be seen the intensities at the various peaks are in the same ratio as the abundant isotopes of germanium, providing additional evidence that the splitting is due to isotope effects.

One may calculate the bond angle of GeF₂ from the isotope splitting. If one assumes that the lower frequency absorption is \( \nu_3 \), the bond angle is 94 ± 4°. If the higher frequency were \( \nu_3 \) the bond angle is 82 ± 3°. Since CF₂ and SiF₂ have bond angles of 104.9° and 100.9°, respectively, the value of 94 ± 4° seems more likely to be the correct value.

There have been several mass spectrometric examinations of GeF₂. The first was by Ehlert and Margrave⁶⁵a. GeF₂ was prepared by heating Ge and CaF₂. The appearance potential of GeF₂ was determined to be 11.6 ± 0.3 eV and the heat of atomization of GeF₂(g) to be \( \Delta H_a^{298} = 16.0 ± 0.8 \) eV, thence \( \Delta H_f^{298} \) (GeF₂, c, 298) = -140 ± 17 kcal mole⁻¹. The second investigation⁷⁰₄a has required repetition since it is suspected that possibly the sample used was not pure GeF₂.⁷⁰₆ In this more recent examination⁷⁰₄b the vapor species over pure GeF₂ was monitored over the temperature range 70 – 95°C. Only GeF₂ and (GeF₂)₂ were found; no GeF₄ was detected. The thermodynamic data determined from this experiment are listed in Table 2.

The heat of formation of GeF₂ has very recently been determined by fluorine bomb calorimetry⁷⁰⁵. The value of \( \Delta H_f^{298} \) (GeF₂, c, 298.15°C) = -157.3 ± 1.0 kcal mole⁻¹ was determined. This is probably the best value currently available.
Table 2

Thermodynamic Data from Mass Spectrometer Experiments

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_{365}^{o}$</th>
<th>$\Delta S_{365}^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF$_2$(c) = GeF$_2$(g)</td>
<td>19.4 ± 1.0</td>
<td>44.7 ± 2.5</td>
</tr>
<tr>
<td>2GeF$_2$(c) = (GeF$_2$)$_2$(g)</td>
<td>18.3 ± 2.4</td>
<td>36.7 ± 6.0</td>
</tr>
</tbody>
</table>
The crystal structure of GeF$_2$ was reported by Trotter, Akhtor and Bartlett$^{107}$. They describe GeF$_2$ as "a strong fluorine-bridged chain polymer, in which the parallel chains are cross-linked by weak fluorine bridges. The structural unit of the strongly bridged chains is a trigonal pyramid of three fluorine atoms and an apical germanium atom." They found that the Ge-F distances are 1.79, 1.91 and 2.09 Å and the F-Ge-F angles are 85°, 85.6° and 91.6°. The two fluorine atoms at 2.09 Å are equivalent and join the germanium atoms into chains. The F atoms at 1.79 Å are weakly bonded to germanium atoms in neighboring chains whose distance is 2.57 Å. The poor packing of fluorine atoms in this arrangement is due to steric activity of the non-bonding valence electron pair on the germanium. The GeF$_4$ group is a distorted trigonal bipyramid with four fluorine atoms and a lone pair (in the equatorial plane) around a germanium atom.

Only a few reactions of GeF$_2$ have been reported; however, those currently known indicate that GeF$_2$ is a strong reducing reagent$^{100b}$. 

\[ \text{GeF}_2 + \text{I}_2 \rightarrow \text{GeF}_2\text{I}_2 \quad \text{decomposes} \quad \rightarrow \text{GeI}_4 + \text{GeF}_4 \]
\[ \text{GeF}_2 + \text{Cl}_2 \rightarrow \text{GeF}_2\text{Cl}_2 \quad \text{decomposes} \quad \rightarrow \text{GeCl}_4 + \text{GeF}_4 \]
\[ 2\text{GeF}_2 + \text{SeF}_4 \rightarrow 2\text{GeF}_4 + \text{Se} \]
\[ \text{GeF}_2 + \text{SO}_3 \rightarrow \text{explosion} \quad \text{(products are probably GeOF}_2, \ \text{SO}_2) \]
\[ \text{GeF}_2 + \text{H}_2\text{O} \rightarrow \text{"Ge(OH)}_2" \]

Muetterties has described some of the reactions of GeF$_2$ in solution$^{108}$. He isolated the salts, KGeF$_3$ and CsGeF$_3$, by dissolving GeF$_2$ in concentrated solutions of KF and CsF. In solution there must be rapid exchange between F$^-$ and GeF$_3^-$ since the $^{19}\text{F}$ nmr signal from a solution containing both species is midway between the signal due to either species alone. If a solution of GeF$_2$
is acidified, hydrogen is released. When GeF$_2$ is dissolved in dimethyl sulphoxide the complex GeF$_2$·OS(CH$_3$)$_2$ is formed. No report of bond insertion or additions to multiple bonds by GeF$_2$ exist.

F. Other Germanium Dihalides

The other germanium dihalides have been known for a very long time. The first reported preparation of GeCl$_2$ was later withdrawn; Winkler claimed to have formed GeCl$_2$ by reacting heated germanium with HCl but the product was actually HGeCl$_3$. Moulton and Miller have shown that HGeCl$_3$ is very unstable, and decomposes to GeCl$_2$ and HCl when distilled at low pressure. GeCl$_2$ can be prepared by passing GeCl$_4$ over Ge at 350°C. It is also formed by the action of AgCl on Ge and by the action of Cl$_2$ on Ge at 650°C. When GeCl$_4$ is reduced by hydrogen, germanium subchlorides of limiting composition GeCl$_{0.9}$ are formed. When these subchlorides are distilled under vacuum at 210°C, GeCl$_2$ can be isolated.

GeBr$_2$ and GeI$_2$ are much easier to prepare than the difluoride or dichloride. GeBr$_2$ can be prepared by reducing HGeBr$_3$ with Zn, or by the vacuum distillation of HGeBr$_3$. GeI$_2$ can be very easily prepared by precipitation from Ge$^{2+}$ solutions. It can also be prepared by the action of HI on GeS.

Although GeF$_2$ has been examined by a variety of spectroscopic techniques the other dihalides have not been examined in such detail.

The chemiluminescent emission spectrum of GeCl$_2$ was obtained by burning GeCl$_4$ in potassium vapor using a diffusion flame technique. The spectrum consisted of a series of closely spaced diffuse bands in the region 4900-4100 Å with an underlying continuum. The bands resemble those of SnCl$_2$. 
These results were taken to indicate that GeCl₂ is non-linear in the gas phase. If the diffuse nature of the bands is due to predissociation, then the dissociation energy of the ClGe-Cl bond is less than 64 kcal.

Both the absorption and the emission spectra of GeCl₂ were observed by Hastie, Hauge and Margrave¹¹⁹. GeCl₂ was produced either by vaporization from liquid GeCl₂ or by the reduction of GeCl₄ with Ge. Absorption occurred between 3301-3140 Å. The transition is probably X¹A₁ → ¹B₁, as is observed for CF₂, SiF₂ and GeF₂. Bands in the spectrum were interpreted in terms of progressions in the bending frequencies of the lower and upper states. The ground state bending frequency is 162 cm⁻¹ and that of the upper state is 95 cm⁻¹.

A microwave discharge through GeCl₄ vapor at low pressure produced a continuous emission from 3125 to 3341 Å, the same range as that observed in the absorption spectrum of GeCl₂.

The thermodynamics of the reactions

\[ \text{Ge (s)} + \text{GeX₄ (g)} \rightarrow 2\text{GeX₂ (g)} \]

\[ X = \text{Cl, Br, I} \]

have been studied by a number of workers using weight loss methods, static vapor pressure measurements and mass spectrometric techniques. The mass spectrometric investigation showed that GeCl₂ and GeBr₂ do not form polymers in the gas phase in contrast with the behavior of GeF₂. The numerical results of these various investigations are summarized in Table 3¹²⁰.

Reactions of Germanium Dihalides. Due to its ease of preparation, GeI₂ possesses the best characterized reaction chemistry of the dihalides of germanium.
Table 3

Heats of Formation and Atomization of Gaseous Germanium Dihalides, and Stabilities of Ge-X Bonds, kcal mole\(^{-1}\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\Delta H_F^{\circ},298)</th>
<th>(\Delta H_{\text{atoms}}^{\circ})</th>
<th>(\overline{E}(\text{Ge-X}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF(_2)</td>
<td>(-136.9 \pm 2^{104b,105})</td>
<td>(266.3 \pm 2^{104a,105})</td>
<td>(133.2 \pm 1^{104a,105})</td>
</tr>
<tr>
<td>GeCl(_2)</td>
<td>(-42 \pm 1^{120,121})</td>
<td>(188 \pm 5^{120})</td>
<td>(94 \pm 2^{120})</td>
</tr>
<tr>
<td>GeBr(_2)</td>
<td>(-13 \pm 1^{120})</td>
<td>(164 \pm 5^{120})</td>
<td>(82 \pm 2^{120})</td>
</tr>
<tr>
<td>GeI(_2)</td>
<td>(13 \pm 2^{123})</td>
<td>(142 \pm 5^{123})</td>
<td>(71 \pm 2^{123})</td>
</tr>
</tbody>
</table>
GeCl₂, GeBr₂ and GeI₂ all undergo the following reactions:

\[
\text{GeX}_2 + X_2 \rightarrow \text{GeX}_4
\]

\[
\text{GeX}_2 + \text{HX} \rightarrow \text{GeHX}_3
\]

GeCl₂ and GeBr₂ hydrolyze to give "Ge(OH)₂". GeCl₂ begins to decompose at 75°C, and reacts with H₂S to give GeS.¹²⁴

Just as Cₓ₂ is formed in solution by the basic hydrolysis of CₓHₓ₃, so can Geₓ₂ be formed from HGeₓ₃ in solution. For example, when HGeCl₃ is dissolved in ether it forms the complex 2(Et₂O)HGeCl₃ which is thought to have the ionic structure

\[
\left[\text{Et}_2\text{O} + \text{H}^+ + \text{OEt}^-\right] \left[\text{GeCl}_3^-\right]
\]

and thus it readily forms GeCl₂. Typical reactions of the complex are

\[
2(\text{Et}_2\text{O})\cdot\text{HGeCl}_3 \rightarrow \left[\text{GeCl}_2\right] + 2\text{Et}_2\text{O}\cdot\text{HCl}
\]

\[
\text{GeCl}_2 + \text{HCC} \rightarrow \left[\begin{array}{c}
\text{H} \\
\text{GeCl}_2
\end{array}\right] \text{GeXCl}_2-\text{CH}=\text{CH}-\text{GeCl}_3
\]

\[
\text{GeCl}_2 + \text{H}_2\text{C}=\text{CH} \rightarrow \left[\begin{array}{c}
\text{H}_2\text{C} \\\n\text{GeCl}_2
\end{array}\right] \text{GeXCl}_2-\text{CH}_2-\text{CH}_2-\text{GeCl}_3
\]

GeBr₂ is observed to undergo similar reactions.¹²⁴ No direct reaction was observed between carbonyl compounds and germanium dihalides.¹²⁵

The reactions of GeI₂ have received more attention. GeI₂ will react with a carbon halogen bond.¹²⁶

\[
\text{GeI}_2 + \text{RI} \rightarrow \text{RGeI}_3
\]

R = Bu, Ph, CH₂I, I(CH₂)₂.

\[
\text{GeI}_2 + \text{BuBr} \rightarrow \text{trihalogenated products} + \text{Et}_3\text{GeBu}
\]
Most of these reactions were carried out in sealed tubes. \( \text{GeI}_2 \) also reacts with multiple bonds.\(^{127} \)

\[
\text{R-C=CR} + \text{GeI}_2 \rightarrow \left[ \begin{array}{c}
\text{C} \\
\text{R} \\
\text{R} \\
\text{C} \\
\text{R} \\
\text{R} \\
\text{GeI}_2
\end{array} \right]_n
\]

\( \text{R} = \text{H, C}_6\text{H}_5 \)

\( \text{GeI}_2 \) inserts into metal-metal bonds,\(^{128,129} \)

\[
\left[ \pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2 \right]_2 + \text{GeI}_2 \rightarrow \left[ \pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2 \right]_2\text{GeI}_2
\]

\( (\text{CO})_4\text{CoCo(CO)}_4 + \text{GeI}_2 \rightarrow (\text{CO})_4\text{Co-GeI}_2-\text{Co(CO)}_4. \)

Similar reactions have been observed for \( \text{GeCl}_2 \).\(^{130} \) The halide atoms in these compounds are very labile and are easily changed for groups such as \(-\text{Me}, -\text{OCH}_3, -\text{SC}_2\text{H}_5, -\text{NCS}, \) and \(-\text{OCOCH}_3 \) or other halides\(^{128,130} \).

\( \text{GeI}_2 \) also reacts with organo-mercury compounds.\(^{131} \)

\[
\begin{align*}
\text{GeI}_2 + \text{HgEt}_2 & \rightarrow \text{GeEt}_2 + \text{HgI}_2 \\
\text{GeI}_2 + \text{HgBu}_2 & \rightarrow \text{Bu}_2\text{Ge-GeIBu}_2
\end{align*}
\]

(dissolved in acetone)

\( \text{GeI}_2 \) is also of considerable importance in the transport and purification of germanium.
G. Tin and Lead Dihalides

The dihalides of tin and lead are so very well known that it is unnecessary to summarize the extensive chemical knowledge of these compounds. The chemistry of divalent tin and lead has been reviewed several times recently. A few points that are relevant to the material already discussed will be made.

The ultraviolet absorption spectra of gaseous SnF₂, SnCl₂, PbF₂ and PbCl₂ have all been recently reported. For SnF₂ a weak absorption with a regular banded structure was seen at around 2425 Å. The bending frequency of the ground electronic state is 180 cm⁻¹ and for the excited state is 120 cm⁻¹. For PbF₂ no discrete band system was observed; a plot of the bending frequencies of the other Group IVB difluorides against the reciprocal of their internuclear separations enabled ν₂'' to be estimated as 145 cm⁻¹ and ν₂' 105 cm⁻¹. For SnF₂ and PbF₂ the 0,0,0 - 0,0,0 transitions are estimated to occur at 40,741 and 40,560 cm⁻¹, respectively.

In the ultraviolet SnCl₂ showed a continuous absorption with a maximum intensity at about 21,044 cm⁻¹(3220 Å). The absence of discrete bands is probably due to overlapping of closely spaced diffuse bands. For PbCl₂ three regions of continuous absorption were observed. These had maximum intensities at 3600, 3200 and below 2916 Å. The SnCl₂ and PbCl₂ spectra were interpreted as being due to ¹A₁ → ¹B₁ transitions.

The mass spectra of the vapors over hot SnF₂ and PbF₂ were also examined recently. SnF₂ undergoes some polymerization. Species found over molten SnF₂ at 616°C were SnF₂ 79.5%, Sn₂F₄ 20.5%, and Sn₃F₆ 0.027%. No dimers were found over PbF₂; this was probably due to the ready decomposition of
these dimers into PbF₄ and Pb. The heats of dimerization for all of the Group IVB difluorides are listed in Table 4.¹³⁵ In the same study a number of the thermodynamic functions of the fluorides of tin and lead were measured using Knudsen cell effusion techniques.¹³⁴ These values do not agree very well with previously available data. This area has recently been surveyed and interested readers should refer to this survey.¹³⁶

Conclusions

A varied and productive chemistry is now established for most of the Group IV dihalides. By combining high temperature and low temperature techniques, one may now isolate and observe molecular parameters, as well as physical and chemical properties for AX₂-species. The CX₂ (carbenes) and SiX₂ (silylenes) molecules have a rich chemistry and provide new and unique opportunities for organic and organo-metallic syntheses.

Acknowledgments

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Table 4

Heats of Dimerization of Group IVb Difluorides (kcal mole⁻¹)

\[(\text{MX}_2)_n(g) \rightarrow (\text{MX}_2)_{n-1}(g) + \text{MX}_2(g)\]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( n = 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₂</td>
<td>76.3 ± 3</td>
</tr>
<tr>
<td>SiF₂</td>
<td>—</td>
</tr>
<tr>
<td>GeF₂</td>
<td>18.3 ± 3</td>
</tr>
<tr>
<td>SnF₂</td>
<td>39 ± 2</td>
</tr>
<tr>
<td>PbF₂</td>
<td>—</td>
</tr>
</tbody>
</table>
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65. a) T. C. Ehlert and J. L. Margrave, J. Chem. Phys., 41, 1066 (1964);  
b) J. L. Margrave, A. S. Kana'an and D. C. Pease, J. Phys. Chem., 66, 1200 (1962);  
100. a) L. M. Dennis and A. W. Laubengayer, Z. Physik Chem., 130, 520 (1927);
106. Apparently GeF₂ reacts with GeF₄ to form either a complex or a new compound. Possibly Zmbov et al used this new compound instead of GeF₂ since they prepared their GeF₂ sample in an excess of GeF₄. This reaction is being investigated.
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