

# Silicon Difluoride, a Carbene Analog. Its Reactions and Properties

JOHN L. MARGRAVE\* AND PAUL W. WILSON†

Department of Chemistry, Rice University, Houston, Texas 77001

Received May 21, 1970

The chemistry of the divalent compounds of the group IVb elements has received considerable attention in recent years. These studies have embraced carbene ( $\text{CH}_2$ ), the carbon dihalides, silylene ( $\text{SiH}_2$ ), dimethylsilylene, the silicon dihalides, and the germanium dihalides. This interest has been stimulated by the realization that these compounds are important intermediates in many reactions. More importantly, they can be used to make new compounds, both organic and inorganic, that can be prepared in no other way.

Since this field has proved to be so fruitful, it is somewhat surprising that much of its development has occurred over only the last decade. One reason is that the difluoride is invariably the most stable and long-lived divalent compound of a group IV element; *e.g.*, carbene has a half-life of about 1 msec in the gas phase whereas carbon difluoride has a half-life of 1 sec. The entire field of fluorine chemistry has been retarded by the lack of suitable materials for constructing apparatus, but this should have been less of a handicap for the group IVb fluorides than for other fluorides inasmuch as  $\text{CF}_4$  and  $\text{SiF}_4$  do not attack glass. Apparently the lack of development of the general fluorine field also delayed the investigation of the group IV fluorides. Since the most stable members of this family were not studied, the members of lesser stability received virtually no attention, with the exception of carbene itself.

Another problem which delayed the study of the group IV dihalides is the fact that many of them are transient species under the conditions in which they are normally prepared. Improvements in instrumentation over the last decade have permitted studies of these short-lived species which were not possible earlier.

At Rice University studies of the divalent compounds of group IV elements have become a major research area. Investigations have ranged over many of the divalent species— $\text{SiO}$ ,  $\text{SiS}$ ,  $\text{GeF}_2$ ,  $\text{GeCl}_2$ ,  $\text{GeO}$ ,  $\text{GeS}$ ,  $\text{SnF}_2$ ,  $\text{PbF}_2$ , etc.—but silicon difluoride has been the compound of principal interest. In this Account, some of its properties and reactions are described. Many of these reactions have led to unusual products, suggesting that use of this compound will become very important in the synthesis of organic and inorganic silicon compounds.

In the early literature, there are several reports claiming the preparation of  $\text{SiF}_2$ . Actually these reports deal with reactions of polymeric silicon difluoride.

Such polymers can be prepared by reducing  $\text{SiF}_4$  using heated Si, Al, or Mg.<sup>1</sup> Although it was suggested that monomeric  $\text{SiF}_2$  was an intermediate in the formation of these polymers, its presence was not definitely established. At about the same time, spectroscopic<sup>2</sup> and mass spectrometric investigations<sup>3</sup> showed that at least small amounts of gaseous  $\text{SiF}_2$  could be prepared. All of this led to an extensive and systematic study of the properties of silicon difluoride.

**Preparation of Silicon Difluoride.** Silicon difluoride is relatively easy to make.<sup>4</sup> The apparatus used is shown in Figure 1. Commercially available  $\text{SiF}_4$  is passed into a reservoir and then, using needle valve controls, it is passed over lumps of Si heated to  $1200^\circ$ . This gives a yield of about 50%  $\text{SiF}_2$ , with the remainder being  $\text{SiF}_4$ . If the pressure of  $\text{SiF}_2$  is more than 1–2 Torr, there is some disproportionation. To avoid this the system is pumped continuously. As soon as the  $\text{SiF}_2$  is formed, it is swept through the vacuum line to a point where it can react or its physical properties can be examined.

A major point of the initial studies was to show that monomeric  $\text{SiF}_2$  was being formed.<sup>4</sup> The  $\text{SiF}_2$ - $\text{SiF}_4$  mixture was led from the hot column into a 5-l. bulb which was connected to a mass spectrometer inlet. It was found that the gas contained only  $\text{SiF}_4$  and monomeric gaseous  $\text{SiF}_2$ . Surprisingly, there was no evidence of a gas-phase reaction to give  $\text{Si}_2\text{F}_6$ . (The other silicon dihalides all undergo gas-phase reactions producing  $\text{Si}_2\text{X}_6$ . The carbon dihalides also react in the gas phase.) Within the flask, the concentration of  $\text{SiF}_2$  fell to half its original value in about 150 sec. The  $\text{SiF}_2$  decayed by reacting at the walls of the flask to form a polymer, and not by gas-phase reaction.

The half-life of gaseous  $\text{SiF}_2$  was only slightly affected by adding  $\text{BF}_3$ , CO, or  $\text{PF}_3$  to the flask. Apparently there is no reaction between these compounds and  $\text{SiF}_2$  in the gas phase. Oxygen did significantly reduce the half-life of  $\text{SiF}_2$ ; the  $\text{SiF}_2$  and  $\text{O}_2$  reacted at the walls of the flask and silicon oxyfluorides were detected mass spectrometrically. This contrasts with the behavior of singlet  $\text{CF}_2$ , which is not affected by  $\text{O}_2$ .

(1) For a summary of this early work see M. Schmeisser and P. Voss, *Fortschr. Chem. Forsch.*, **9**, 165 (1967); also see D. C. Pease, U. S. Patent 2,840,588 (June 24, 1958).

(2) J. W. C. Johns, G. W. Chantry, and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1589 (1958).

(3) T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).

(4) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 2824 (1965).

† Present address, A.A.E.C. Research Estb., Lucas Heights, Australia.

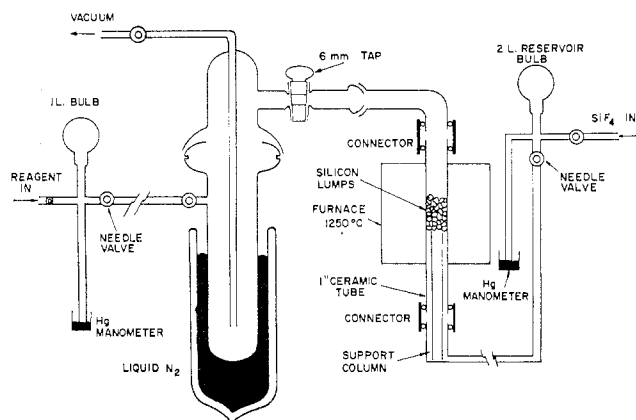


Figure 1. Apparatus for the preparation and reaction of  $\text{SiF}_2$ .

**Some Properties of Polydifluorosilylene.** When an  $\text{SiF}_2$ - $\text{SiF}_4$  mixture is condensed into liquid  $\text{N}_2$ , a red-yellow deposit is formed. If this deposit is warmed to room temperature, it gradually turns white. The deposit is pliable, somewhat elastic, and quite tough; it can be cut with scissors. The overall stoichiometry of the deposit is  $(\text{SiF}_2)_x$ . With respect to its plastic properties and composition,  $(\text{SiF}_2)_x$  is very much like its important relative, polytetrafluoroethylene,  $(\text{CF}_2)_x$ . Unfortunately  $(\text{SiF}_2)_x$  is not inert; in fact, it is pyrophoric, burning spontaneously in air and reacting vigorously with water.

Two recent studies of  $(\text{SiF}_2)_x$  have shown that its structure is very similar to that of  $(\text{CF}_2)_x$ . The Raman spectra of  $(\text{SiF}_2)_x$  and  $(\text{CF}_2)_x$  are comparable.<sup>5</sup> The spectrum of  $(\text{SiF}_2)_x$  confirms that the polymer does contain Si-Si bonds, as intuitively expected. The strength of these Si-Si bonds was established indirectly using fluorine bomb calorimetry.<sup>6</sup> In this useful technique, some sample is placed in a container and this container is placed inside a second container filled with 4-5 atm of  $\text{F}_2$ . A tungsten diaphragm separates the sample and the fluorine. This diaphragm is ignited electrically and the sample is exposed to the  $\text{F}_2$  in which it then burns vigorously. The temperature rise of the calorimeter is related to the energy released in the reaction. The Si-Si bond energy was determined to be  $47 \pm 7$  kcal mol<sup>-1</sup>. This compares with  $51 \pm 10$  kcal mol<sup>-1</sup> determined for some fluorosilanes by a mass spectrometric technique.<sup>7</sup>

One of the more useful properties of  $(\text{SiF}_2)_x$  is that it can be used to prepare perfluorosilanes.<sup>4</sup> When  $(\text{SiF}_2)_x$  is heated to  $\sim 200^\circ$  it begins to decompose. All of the perfluorosilanes,  $\text{Si}_n\text{F}_{2n+2}$ , from  $\text{SiF}_4$  through  $\text{Si}_{16}\text{F}_{34}$  have been detected as products; undoubtedly still higher silanes are also formed. These compounds can currently be prepared in no other way. Silanes containing above six silicon atoms are unusual and above ten silicon atoms very unusual. This preparation, yielding silanes with 16 silicon atoms, has therefore

great potential for the preparation of high molecular weight silanes.

**Some Properties of Gaseous Silicon Difluoride.** Before the reactions of  $\text{SiF}_2$  can be discussed, something must be said of its physical parameters. These parameters have been measured in a number of experiments and are now well documented.

Possibly the most instructive study of gaseous  $\text{SiF}_2$  has been the observation of its microwave spectrum.<sup>8</sup> This was done simply by passing a  $\text{SiF}_4$ - $\text{SiF}_2$  mixture through a conventional microwave absorption cell. In the singlet ground state, the Si-F bond distance was determined to be 1.591 Å and the F-Si-F bond angle to be  $100^\circ 59'$ . The dipole moment is  $1.23 \pm 0.015$  D.

The Si-F bond length is longer and the F-Si-F bond angle is smaller than might have been expected. For example, compare the bond angle ( $100^\circ 59'$ ) with the bond angle ( $119^\circ 30'$ ) for  $\text{SO}_2$ , which is isoelectronic with  $\text{SiF}_2$ . This has led to the suggestion that the bonding in  $\text{SiF}_2$  involves mainly  $p^2$  hybridization of the Si orbitals. The two nonbonding silicon electrons may have either pure s or sp character, although with silicon the possibility of d-orbital involvement must always be considered.

The infrared spectrum of gaseous  $\text{SiF}_2$ <sup>9</sup> was recorded between 1050 and 400  $\text{cm}^{-1}$ . Two of the expected three absorption bands were observed. The other band was below the limits of the spectrometer. The two bands centered at 855 and 872  $\text{cm}^{-1}$  were assigned to the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_2$ ) stretching modes, respectively. The fundamental bending frequency ( $\nu_3$ ) 345  $\text{cm}^{-1}$  was already available from other studies.<sup>2,8,10</sup> From these vibration frequencies and the bond lengths and angles determined in the microwave studies, the force constants of the molecule were calculated, as were its thermodynamic functions.

Ultraviolet emission spectra studies first proved the existence of monomeric gaseous  $\text{SiF}_2$ . The  $\text{SiF}_2$  was produced in small yield by passing an uncondensed electric discharge through  $\text{SiF}_4$ . Unfortunately in the first two studies band numberings were erroneous, so the early interpretations are incorrect.<sup>2</sup> An ultraviolet absorption study was undertaken in this laboratory,<sup>10</sup> and 28 absorption bands were observed in the region between 2325 and 2130 Å. An interesting feature of this spectrum was the presence of a long progression in the bending frequency of the upper electronic state. This suggests that the F-Si-F angle undergoes a considerable change during transition. A series of bands with a periodicity of 252  $\text{cm}^{-1}$  was associated with the bending frequency of the excited state. The vibrationless transition lies at 2266.4 Å and is probably a  ${}^1\text{B}_1 \leftarrow {}^1\text{A}_1$  transition.

A further study of interest was a mass spectrometric

(5) J. L. Margrave and P. W. Wilson, *Eur. Polym. J.*, in press.

(6) G. P. Adams, J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Chem. Thermodyn.*, **2**, 439 (1970).

(7) J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, *Advan. Chem. Ser.*, No. 72, 681 (1968).

(8) V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965).

(9) V. M. Khanna, R. Hauge, R. F. Curl, and J. L. Margrave, *ibid.*, **47**, 5031 (1967).

(10) V. M. Khanna, G. Besenbruch, and J. L. Margrave, *ibid.*, **46**, 2310 (1967).

determination of the heat of formation of  $\text{SiF}_2(\text{g})$ .<sup>3</sup>  $\text{CaF}_2$  and Si were placed in a Knudsen cell and heated. The emission from the cell was monitored mass spectrometrically. The following data were obtained:  $\Delta H_a^\circ_{298}(\text{SiF}_2, \text{g}) = 12.33 \pm 0.2$  eV and thence  $\Delta H_f^\circ_{298}(\text{SiF}_2, \text{g}) = -139 \pm 2$  kcal mol<sup>-1</sup>. This value for  $\Delta H_f^\circ_{298}$  is not very close to that estimated from transpiration studies,  $-148 \pm 4$  kcal mol<sup>-1</sup>.<sup>11</sup> It is thought that the formation of higher perfluorosilanes can explain the results of the transpiration study.<sup>12</sup>

Most of these properties are tabulated in Table I. Also listed are the corresponding values for  $\text{CF}_2$  and  $\text{GeF}_2$  which are also known.<sup>13</sup> One of the more interesting comparisons is the M-F bond strengths. The Si-F average bond dissociation energy is higher than that of any other group IV elements for both the  $\text{MF}_2$  and  $\text{MF}_4$  species.<sup>14</sup> This has important repercussions in the reaction chemistry of  $\text{SiF}_2$ .

### Reactions of Silicon Difluoride

One of the first reactions of  $\text{SiF}_2$  to be studied was that with  $\text{BF}_3$ .<sup>15</sup> The reaction was carried out in what has now become the "usual" way.  $\text{BF}_3$  was continuously mixed with the  $\text{SiF}_2$ - $\text{SiF}_4$  mixture emerging from the furnace and then the whole mixture was condensed at  $-196^\circ$ . When reactions are studied in this way, it is not completely clear whether most reactions occur upon condensation or while the mixed reagents are warming to room temperature. Studies of  $\text{SiF}_2$  reactions in low-temperature matrices are required to answer this question. With some reagents a highly colored polymer is formed, indicating there must have been some interaction between the reagents upon condensation. In other cases, however, there is no visible change and possibly reaction occurs upon warming. In either case, condensing the reagents presumably serves to cause reaction by increasing the local reagent concentration. As described earlier, there is no reaction in the gas phase; to get reaction the reagents must be condensed.

With  $\text{SiF}_2$ - $\text{BF}_3$  a green condensate was formed. The condensate turned white upon warming and about 10% of the material condensed was evolved as volatile products. Excess  $\text{SiF}_4$  and  $\text{BF}_3$  were removed from the products by pumping on the condensate while cooling it to  $-90^\circ$ . The products were then separated by passing them through a series of U tubes cooled to different temperatures. Two fractions were obtained, one at  $-50^\circ$  and another at  $-25^\circ$ . The relative amounts were 3:1.

When the first product was examined mass spectro-

Table I  
Some of the Properties of  $\text{CF}_2$ ,  $\text{SiF}_2$ , and  $\text{GeF}_2$ <sup>a</sup>

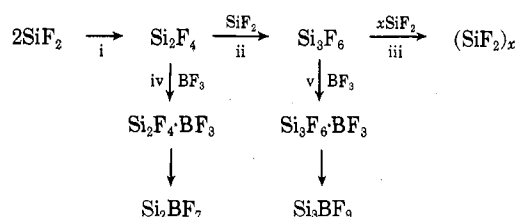
Property	$\text{CF}_2$	$\text{SiF}_2$	$\text{GeF}_2$
Bond length, Å	1.300	1.591	1.7321
Bond angle	104° 56'	100° 59'	97° 10'
Dipole moment, D	0.46	1.23	2.68
$\Delta H_f^\circ_{298, \text{g}}$ , kcal mol <sup>-1</sup>	-39.3	-139	-136.9
$\bar{D}$ , kcal mol <sup>-1</sup>	125	143	131
$T_{1/2}$ , sec	1	150	Stable
Infrared fundamental frequencies $\nu_1, \nu_2, \nu_3$ , cm <sup>-1</sup>	1222, 668, 1102	855, 345, 872	692, 263, 663

<sup>a</sup> These properties were all measured in the gas phase.

metrically, the heaviest ion had  $m/e$  181 ( $\text{Si}_2\text{BF}_6^+$ ). *PVT* methods indicated the molecular weight to be  $201 \pm 2$  and thus the molecular formula to be  $\text{Si}_2\text{BF}_7$ . The infrared spectrum showed bands in the Si-F and B-F region. The structure of the compound was conveniently determined using <sup>19</sup>F and <sup>11</sup>B nuclear magnetic resonance. This proved that the compound was  $\text{SiF}_3$ - $\text{SiF}_2\text{BF}_2$ . By similar methods the less volatile product was shown to be  $\text{SiF}_3\text{SiF}_2\text{SiF}_2\text{BF}_2$ .

Not very much is known about these two compounds. They thermally decompose at  $\sim 500^\circ$ . On reaction with iodine, they form  $\text{BF}_3$ ,  $\text{BI}_3$ ,  $\text{SiI}_4$ ,  $\text{SiF}_4$ , and  $\text{Si}_2\text{F}_6$ . The presence of  $\text{Si}_2\text{F}_6$  indicates that the iodine is attacking the Si-B bond rather than the Si-Si bond. With triethylamine, the liquid complex  $\text{Si}_2\text{BF}_7 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  is formed. When  $\text{SiF}_3\text{SiF}_2\text{BF}_2$  and  $\text{CO}$  are mixed in the gas phase a number of products are formed, one of which has the molecular formula  $\text{Si}_2\text{BF}_5\text{CO}$ .

It is interesting to speculate about the  $\text{SiF}_2$ - $\text{BF}_3$  reaction mechanism. There are four considerations. (1)  $\text{SiF}_2$  and  $\text{BF}_3$  do not react in the gas phase. (2) The  $\text{BF}_3$  must be present when the  $\text{SiF}_2$  is condensed. When  $\text{BF}_3$  is condensed onto a layer of  $\text{SiF}_2$ , no reaction occurs. When  $\text{SiF}_2$  is condensed onto  $\text{BF}_3$ , reaction does occur. (3) The simplest member of the series  $\text{SiF}_3\text{BF}_2$  is not formed. (4) When  $\text{SiF}_2$  is condensed alone,  $(\text{SiF}_2)_x$  is formed. Polymerization must proceed via a radical species  $\cdot\text{SiF}_2(\text{SiF}_2)_x\text{SiF}_2\cdot$ . These facts suggest the following reactions occur.



If reactions ii and iii are fast compared with iv and v, the low yields, the need for cocondensation, and the products formed are all simply explained.

When  $\text{BCl}_3$  was allowed to react with  $\text{SiF}_2$ , no new products other than  $\text{SiF}_n\text{Cl}_{4-n}$  were found. Apparently any silicon-boron product formed was too unstable to be purified.

The next reactions studied were those with benzene

(11) J. L. Margrave, A. S. Kana'an, and D. C. Pease, *J. Phys. Chem.*, **66**, 1200 (1962).

(12) A. S. Kana'an and J. L. Margrave, *Inorg. Chem.*, **5**, 729 (1966).

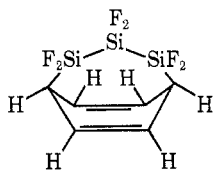
(13) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *Top. Curr. Chem.*, in press, and references herein.

(14) G. P. Adams, J. L. Margrave, R. P. Steiger, and P. W. Wilson, *J. Chem. Thermodyn.*, in press.

(15) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Amer. Chem. Soc.*, **87**, 3819 (1965); J. L. Margrave, P. L. Timms, and T. C. Ehlert, U. S. Patent 3,379,512 (April 23, 1968).

and some substituted benzenes.<sup>15</sup> This series of reactions is particularly interesting since it is known that carbenes add to multiple bonds to form three-membered rings.

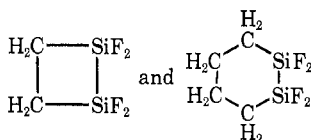
When  $\text{SiF}_2$  and  $\text{C}_6\text{H}_6$  were cocondensed at  $-196^\circ$ , a brown polymer formed. On warming, this turned yellow and liberated unchanged benzene and perfluorotetrasilane. When the condensate was heated to  $140^\circ$ , a mixture of liquids and solids was produced. Mass spectrometric examination of this distillate showed that it contained a series of compounds of the type  $\text{C}_6\text{H}_6(\text{SiF}_2)_n$ , where  $n$  varied from 2 to at least 8. At low electron voltages only ions of the type  $\text{C}_6\text{H}_6^+$  and  $\text{C}_6\text{H}_6(\text{SiF}_2)_n^+$  were seen. The most abundant compound was  $\text{C}_6\text{H}_6\text{Si}_3\text{F}_6$ . When this compound was hydrolyzed, the product was 1,4-cyclohexadiene. Infrared and ultraviolet studies showed that the compound does not have a conjugated double-bond system. These data, plus proton nmr studies, suggest that the compound has the structure



Although the compound with three  $\text{SiF}_2$  units in the chain was produced in highest yield, all the compounds with from two to eight units were observed. When the reaction was repeated using toluene, the same products with methyl substitution were obtained. Fluorobenzene and *p*-difluorobenzene gave products equivalent to those obtained from toluene. These compounds are most unusual and cannot be synthesized by any other technique available at present. Little is known about their chemistry.

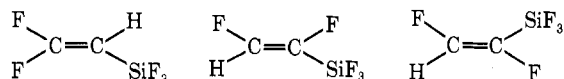
When hexafluorobenzene and  $\text{SiF}_2$  react, products differing from those above are obtained. The major product has the molecular formula  $\text{C}_6\text{F}_5\text{SiF}_3$  and was shown to be simply pentafluorophenyltrifluorosilane. Smaller amounts of the compound  $\text{C}_6\text{F}_4(\text{SiF}_3)_2$  were also produced (ortho:para:meta  $\sim 1:6:9$ ).

The reactions described above differ for fluorinated and for nonfluorinated aromatic systems. This difference was investigated further with respect to ethylene and fluorinated ethylene derivatives.<sup>17</sup> With ethylene, two main products were obtained with molecular formulas  $\text{C}_2\text{H}_4\text{Si}_2\text{F}_4$  and  $\text{C}_4\text{H}_8\text{Si}_2\text{F}_4$ . The nmr spectra of the compounds showed that they had the structures

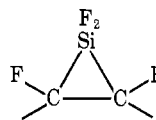


When fluorinated ethylene derivatives were used, different products were formed. With tetrafluoroethylene only a white polymer was produced. When heated, this polymer exploded. This is simply explained: the Si-F bond is stronger than the C-F bond; upon heating the polymer rearranges to give carbon and  $\text{SiF}_4$ . Cautious heating of the polymer enabled compounds of the general formula  $\text{C}_2\text{F}_4(\text{SiF}_2)_n$  ( $n = 1, 2, 3$ ) to be seen in a mass spectrometer. Possibly these species are three-, four-, and five-membered-ring systems.

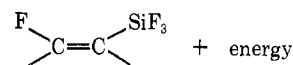
From the reaction of trifluoroethylene and  $\text{SiF}_2$  several products were isolated. These were



These reactions show that there are differences between fluorinated and nonfluorinated systems. In the  $\text{BF}_3\text{-SiF}_2$  reaction, a mechanism based on the formation of diradical dimers, trimers, etc., was suggested. The same mechanism adequately explains the reaction of  $\text{SiF}_2$  with benzene and ethylene. With hexafluorobenzene, however, it is difficult to imagine how the observed proportions of ortho, meta, and para derivatives could have been formed by diradicals. Also, the major products from both hexafluorobenzene and trifluoroethylene were monosilanes. In these cases monomeric silicon difluoride is the attacking species, probably forming the intermediate



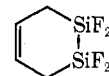
By considering the bond energies, one finds that this system should rapidly rearrange to give



Several other multiple bond systems have been investigated. One of these is the butadiene- $\text{SiF}_2$  reaction.<sup>18</sup> It is known that 1,3-butadiene reacts with tetrafluoroethylene to give, ultimately, the two compounds<sup>19</sup>



With butadiene,  $\text{SiF}_2$  reacts to give a compound of molecular formula  $\text{C}_4\text{H}_6\text{Si}_2\text{F}_4$ . Nmr examination showed the compound to have the structure



This product is analogous to that from  $\text{C}_2\text{F}_4$  reaction, possibly indicating that a diradical mechanism operated in its formation.

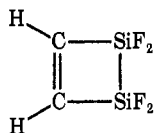
(16) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Amer. Chem. Soc.*, **88**, 940 (1966); J. L. Margrave and P. L. Timms, U. S. Patent 3,485,862 (Dec 23, 1969).

(17) J. C. Thompson and J. L. Margrave, *Chem. Commun.*, 566 (1966).

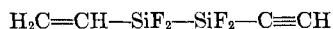
(18) Work done in this laboratory, but as yet unreported, including studies by G. Besenbruch, F. Catrett, T. W. Harbaugh, J. Hastie, R. Hauge, G. Maass, K. G. Sharp, N. Szczepanski, J. C. Thompson, P. L. Timms, D. Williams, and P. W. Wilson.

(19) J. J. Drysdale, U. S. Patent 2,831,025 (Nov 1958).

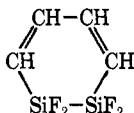
$\text{SiF}_2$  also reacts with a number of acetylene derivatives.<sup>18</sup> With acetylene itself two products were formed. One of these was identified as



The other product was a little more difficult to identify. The mass spectrum showed the molecular formula to be  $\text{C}_4\text{H}_4\text{Si}_2\text{F}_4$ ; the molecular weight was confirmed by *PVT* methods. Hydrolysis of the compound yielded equal volumes of acetylene and ethylene. The compound therefore is

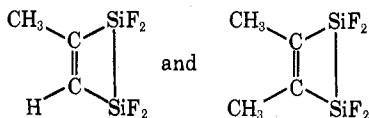


A mechanism whereby this product might have been formed can be proposed by analogy with the ethylene reaction. An intermediate compound with the structure



may have formed. This would be unstable and should easily rearrange to give the observed product.

In reactions similar to that of acetylene, propyne and 2-butyne react with  $\text{SiF}_2$  to give the compounds<sup>18</sup>



### Some Studies of the Silicon Difluoride Condensate.

In the reactions described above, it appears that in most cases the reactive silicon intermediate is the diradical  $\cdot\text{SiF}_2-\text{SiF}_2\cdot$ . This species was therefore sought in the  $\text{SiF}_2-\text{SiF}_4$  condensate.

The first method used to study this problem was infrared spectroscopy.<sup>20</sup> An  $\text{SiF}_2-\text{SiF}_4$  mixture was diluted with argon (1:700) and the mixture was condensed onto a CsI window which had been cooled to 20°K using liquid hydrogen. This matrix was then allowed to warm gradually, and changes in the spectrum were noted. The resultant spectra are shown in Figure 2.

The first observation is that the peak at 811  $\text{cm}^{-1}$  disappears more rapidly than any other peak. Also, the peak is not observed at all if the furnace-to-window distance is long (10 ft or more). This suggests that the peak is due to some highly reactive species, possibly triplet  $\text{SiF}_2$  or  $\text{SiF}$  and  $\text{SiF}_3$  impurities. The next feature to observe is the appearance of the two bands at 892 and 830  $\text{cm}^{-1}$  as the matrix warms. As these bands grow, the band due to monomeric  $\text{SiF}_2$  (855  $\text{cm}^{-1}$ ) decreases. These two new bands reach a maximum intensity at 38°K. At higher temperatures the new bands begin to disappear, and bands due to polymeric

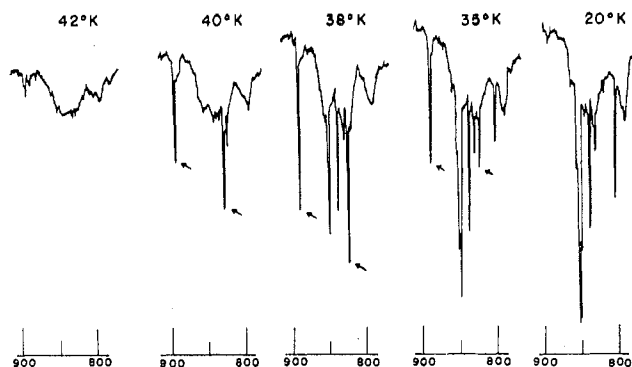


Figure 2. Infrared spectrum of  $\text{SiF}_2$  in argon matrices.

silicon difluoride,  $(\text{SiF}_2)_z$ , appear. By 50°K polymerization appears to be complete. The behavior of the species in these spectra strongly indicates that monomeric  $\text{SiF}_2$  is reacting to give polymeric diradicals and that these diradicals react to give the polymer.

Recently, there have been two reexaminations of the infrared spectrum of matrix-isolated  $\text{SiF}_2$ .<sup>21</sup> These studies were oriented more to quantitative measures of physical parameters than to qualitative behavior. The  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  fundamental frequencies were observed at 851, 343, and 865  $\text{cm}^{-1}$ , respectively. Isotopic splitting was used to calculate a bond angle of 97–102°. These results agree with those obtained in the gas-phase studies.

A more definitive experiment, proving the presence of radicals in the condensate, was an electron spin resonance study.<sup>22</sup> When the gaseous  $\text{SiF}_2-\text{SiF}_4$  mixture was allowed to flow through the cavity of an esr spectrometer, no signal was observed. This confirms that the concentration of any triplet  $\text{SiF}_2$  is very low, as the results of the microwave and electronic spectral studies suggested.

When the  $\text{SiF}_2-\text{SiF}_4$  mixture was condensed on a cold finger in the cavity, a signal was produced. Radicals must be present in the condensate. The *g* factor for the resonance was determined to be  $g = 2.003 \pm 0.002$ , very close to the value that is usually found for a free electron.

As long as the condensate was kept cold, the signal intensity was constant. When the condensate was allowed to warm, the signal intensity began to drop. When the condensate reached room temperature, there was no residual signal.

The experiment also showed that the radicals are produced by interaction of  $\text{SiF}_2$  molecules. A mixture of  $\text{SiF}_4$ ,  $\text{SiF}_2$ , and Ar was condensed in the cavity; there was sufficient Ar to effectively isolate each  $\text{SiF}_2$  molecule. This condensate gave no signal. If the amount of Ar diluent was too low to ensure isolation, a signal was produced.

The infrared and esr studies show that there are

(20) J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, **5**, 729 (1966).

(21) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *J. Amer. Chem. Soc.*, **91**, 2536 (1969); D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **49**, 4269 (1968).

(22) H. P. Hopkins, J. C. Thompson, and J. L. Margrave, *J. Amer. Chem. Soc.*, **90**, 901 (1968).

radicals in the condensate. These radicals are undoubtedly  $\cdot(\text{SiF}_2)_n$ , where  $n = 2, 3, \dots$ . Unfortunately neither experiment is quantitative, so it is impossible to tell if the radical concentration is high or low. In the  $\text{SiF}_2$ -benzene reaction it appears that biradical chains must be the major reacting species. In the  $\text{SiF}_2$ - $\text{C}_6\text{F}_6$  reaction the monomeric species seems to be the major reacting species. Apparently, then, both monomeric and polymeric  $\text{SiF}_2$  species are present in the condensate. The specific reactants and reaction conditions determine which of the two species will be the major reactant.

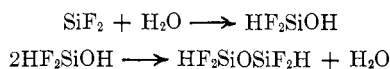
### Further Reactions of Silicon Difluoride

The first few reactions of  $\text{SiF}_2$  studied were with organic molecules: benzene, toluene, alkenes, and alkynes. Since then a number of inorganic compounds have also been found to react, and these reactions have yielded new and interesting products.

Possibly one of the most interesting reactions of  $\text{SiF}_2$  with an inorganic compound is its reaction with water.<sup>23</sup> When most silicon halides are hydrolyzed, polymeric oxides are formed. Intuitively, one might expect that the same would happen with  $\text{SiF}_2$ , especially in view of the fact that such polymers are produced in the reaction of  $\text{SiF}_2$  with  $\text{O}_2$ .<sup>18</sup> It has been reported that  $\text{SiF}_4$  can be hydrolyzed to give volatile products if the conditions are strictly controlled. Under carefully controlled conditions it was hoped that nonpolymeric compounds might also be formed with  $\text{SiF}_2$ .

When  $\text{H}_2\text{O}$  and  $\text{SiF}_2$ - $\text{SiF}_4$  were cocondensed, a multi-colored condensate formed; the color varied from yellow through green to white as the amount of  $\text{H}_2\text{O}$  was increased. When the condensate was warmed a number of products were formed. Several were easily identified as  $\text{SiF}_3\text{H}$ ,  $\text{SiF}_3\text{OSiF}_3$ , and  $\text{SiF}_3\text{OSiF}_2\text{OSiF}_3$ . The latter two compounds were probably formed by the reaction of  $\text{SiF}_4$  with  $\text{H}_2\text{O}$ .

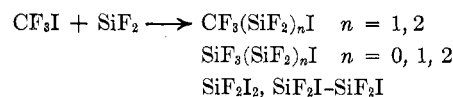
Another product that formed was a new substance. By means of the usual physical methods of investigation, it was shown that this compound was 1,1,1',1'-tetrafluorodisiloxane,  $\text{HF}_2\text{SiOSiF}_2\text{H}$ . The most likely route for the formation of  $(\text{SiF}_2\text{H})_2\text{O}$  is



Other reaction routes can be proposed, however, and may also play a part. The chemistry of  $(\text{SiF}_2\text{H})_2\text{O}$  was studied in some detail to see if the Si-H or Si-O-Si bonds were more reactive than normal due to the presence of the fluorine atoms. The compound behaved in a similar fashion to other silanes and disiloxanes, so apparently the fluoride has little effect on the reactivity.

Another interesting reaction was that with  $\text{CF}_3\text{I}$ .<sup>24</sup> It was expected that the  $\text{SiF}_2$  would simply insert into the  $\text{CF}_3$ -I bond to give  $\text{CF}_3(\text{SiF}_2)_n\text{I}$ -type products.

( $\text{CF}_3\text{I}$  and  $\text{CF}_2\text{CF}_2$  react to give  $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ .) Actually three separate series of products were characterized



If  $\text{CF}_3\text{I}$  was in excess,  $\text{CF}_3\text{SiF}_2\text{I}$  was the major product; if  $\text{SiF}_2$  was in excess, the number of higher silanes increased. It is interesting that, while each compound containing the  $\text{CF}_3$  group also contained iodine, the reverse is not true. This observation led to the suggestion that  $\text{SiF}_2$  initially abstracts an I atom from the  $\text{CF}_3\text{I}$  and that the resulting  $\cdot\text{SiF}_2\text{I}$  reacts either with the residual  $\cdot\text{CF}_3$  or with other neighboring groups.

To investigate further the reaction of  $\text{SiF}_2$  with iodides, the reaction with  $\text{I}_2$  itself was studied.<sup>25</sup> The products were  $\text{SiF}_2\text{I}_2$  and  $\text{SiF}_3\text{I}$  (yield 3:1). It is possible that the initial products were  $\text{SiF}_2\text{I}\cdot\text{SiF}_2\text{I}$  and other di- or trisilanes.  $\text{I}_2$  might cleave the Si-Si bonds to give monosilanes. On the other hand, the  $\text{SiF}_2\text{I}\text{SiF}_2\text{I}$  produced in the  $\text{CF}_3\text{I}$ - $\text{SiF}_2$  reaction was stable to  $\text{I}_2$ , as are  $\text{Si}_2\text{H}_5\text{I}$  and  $\text{Si}_2\text{H}_4\text{I}_2$ . It is probable then that monosilanes were the initial products, and so the reacting species must have been monomeric  $\text{SiF}_2$ .

$\text{SiF}_2$  and  $\text{H}_2\text{S}$  react to give mainly  $\text{SiF}_2\text{HSH}$  and  $\text{Si}_2\text{F}_5\text{H}$ .<sup>26</sup> The analog to the product obtained in the  $\text{H}_2\text{O}$ - $\text{SiF}_2$  reaction,  $\text{SiF}_2\text{HSSiF}_2\text{H}$ , was not observed. The disilanethiol,  $\text{SiF}_2\text{HSiF}_2\text{SH}$ , expected from insertion of  $\text{SiF}_2$  into the H-SH bond was recovered in only small amounts, although this might have been due to its instability.

Several reactions of  $\text{SiF}_2$  with silanes and germanes have been reported.  $\text{SiF}_2$  and  $\text{GeH}_4$  react to give products of the type  $\text{GeH}_3(\text{SiF}_2)_n\text{H}$ ,  $n = 1-3$ .<sup>27</sup> The stability of these compounds decreases rapidly as  $n$  increases. To date, the reaction of  $\text{SiF}_2$  with  $\text{SiH}_4$  has not been reported.  $\text{SiF}_2$  does not appear to react with  $\text{Si}(\text{CH}_3)_4$ ,  $\text{Si}(\text{CH}_3)_3\text{Cl}$ , or  $\text{Ge}(\text{CH}_3)_4$ .<sup>28</sup>  $\text{SiF}_2$  reacted with  $\text{Si}(\text{CH}_3)_3\text{OCH}_3$  to give  $\text{Si}(\text{CH}_3)_3\text{F}$ ,  $\text{Si}(\text{CH}_3)_3\text{Si}(\text{CH}_3)_2\text{F}$ ,  $\text{CH}_3\text{OSiF}_3$ , and  $\text{Si}(\text{CH}_3)_3\text{SiF}_3$ .<sup>28</sup> The formation of these products suggests that the  $\text{SiF}_2$  initially inserted into the Si-O bond but that the product was unstable and decomposed.

The reaction of  $\text{SiF}_2$  with  $(\text{CH}_3)_2\text{SO}$  gives  $(\text{CH}_3)_2\text{SF}_2$  and  $(\text{SiF}_3)_2\text{O}$ .<sup>18</sup> In some way, the oxygen has been abstracted from the sulfur. Much the same happened in the reaction with  $\text{SOF}_2$ . The only silicon-containing products were cyclic fluorosiloxanes.<sup>18,29</sup> The mechanisms of these reactions are not understood.

A class of reactants which gives products that are very hard to characterize is carbonyl compounds, especially ketones and acid halides. In most cases liquids of very low vapor pressure have been formed with re-

(25) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *ibid.*, **32**, 1813 (1970).

(26) K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, **8**, 2655 (1969).

(27) D. Solan and P. L. Timms, *ibid.*, **7**, 2157 (1968).

(28) J. L. Margrave, D. L. Williams, and P. W. Wilson, *Inorg. Nucl. Chem. Lett.*, in press.

(29) K. G. Sharp, Ph.D. Thesis, Rice University, 1969.

(23) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Amer. Chem. Soc.*, **92**, 1530 (1970).

(24) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, **32**, 1817 (1970).

actants such as  $(CF_3)_2CO$ ,  $CF_3COF$ , and  $CF_3COCl$ . These liquids have not yet been successfully characterized. It is interesting that  $CF_2$  does not react with the carbonyl group.<sup>13</sup>

The reactions of  $SiF_2$  with nitrogen-containing compounds have not as yet yielded new compounds.<sup>18</sup> Deeply colored polymers are formed, indicating that some reaction has occurred upon cocondensation. When the condensate is warmed, however, no compounds containing both Si and N are found. Reagents used have been  $N_2O$ ,  $NO$ ,  $NO_2$ ,  $NOCl$ ,  $NOF$ , and  $NH_3$ .

When  $BF_3$  is passed over B at  $2000^\circ$ ,  $BF$  is produced. This  $BF$ - $BF_3$  mixture has been condensed with a  $SiF_2$ - $SiF_4$  mixture. Two new compounds,  $F_2Si(BF_2)_2$  and  $FSi(BF_2)_3$ , were recovered from this condensate.<sup>30</sup>

Another reaction yielding new products was that with methanol.<sup>31</sup> The products recovered indicated however that the  $CH_3OH$  first reacted with the  $SiF_4$  in the gas phase, forming  $CH_3OSiF_3$  and  $HF$ . The  $HF$  and the  $SiF_2$  reacted upon condensation to give  $SiF_3H$ . There was some reaction of  $SiF_2$  with methanol, probably to form  $CH_3OSiF_2H$ , which then reacted with excess  $CH_3OH$  to form the recovered product,  $(CH_3O)_2SiF_2$ .

The reactions of  $SiF_2$  with  $NaF$  and  $LiF$  have been studied.<sup>18</sup> The alkali fluorides were evaporated from a Knudsen cell and cocondensed with  $SiF_2$ . Although it appears that new products are formed at low temperatures, they are not thermally stable. Probably the low-temperature species ( $M^+, SiF_3^-$ ) are formed. When warmed to about  $0^\circ$  they decompose to give  $M_2SiF_6$  and  $Si$ . Reaction between  $SiF_2$  and  $Na$  to yield ( $Na^+, SiF_2^-$ ) has also been observed in matrix studies.<sup>18</sup>

There have also been attempts to observe reaction of  $SiF_2$  with the compounds  $GeF_4$ ,  $CF_4$ ,  $\cdot CF_3$ ,  $CF_2$ ,  $CF_2=CF_2$ ,  $C_2F_6$ , and perfluorocyclobutane. The course of these reactions is easily predicted since the Si-F bond is considerably stronger than other M-F bonds for group IV elements. There is normally a rapid (sometimes explosive) exchange giving  $SiF_4$  and C or Ge. Reactions with this type of compound should be approached cautiously.

Finally, it is necessary to point out that sometimes products cannot be recovered from the condensate. When  $SiF_2$  reacts with nitriles ( $CF_3CN$ ,  $CH_3CN$ ,  $CNCl$ ,  $(CN)_2$ ), a black condensate forms. The only products that have been recovered from this condensate, even after strong heating, are perfluorosilanes and triazine derivatives.<sup>18</sup>

Thus far in the development of the chemistry of  $SiF_2$  it has only been possible to predict the course of a specific reaction in broad terms. In some cases the reactive species seem to be polymeric diradicals, notably

$Si_2F_4$ , and in other monomeric  $SiF_2$ . From consideration of all of the reactions studied, two hypotheses emerge. First, diradicals only take part in reaction when a bond of sufficient reactivity to be attacked by monomeric  $SiF_2$  is not present. The extreme negative extension of this case is seen in the reaction of  $SiF_2$  with  $CCl_3H$ ;<sup>18</sup> unreacted  $CCl_3H$  and polymeric  $(SiF_2)_x$  are recovered from the condensate. This idea can be expressed in another way. There are two competing reactions: (a) the reaction of  $SiF_2$  with the reagent, and (b) the polymerization of  $SiF_2$ . The rate of reaction seems to be far more important than the thermodynamic stability of the products. In turn, the reaction rate depends on activation energy. The activation energy for polymerization is low (say 1 or 2 kcal mol<sup>-1</sup>), and if monomeric  $SiF_2$  is to react with the other species, the activation energy for this reaction must be even lower. Second, with attention especially to the  $CF_3I$  and  $H_2S$  reactions, it appears that monomeric  $SiF_2$  may react in a stepwise fashion, abstracting a single atom or group from the reactant and then reacting with any nearby species.

## Conclusions

The studies described above have shown that  $SiF_2$  is a versatile reagent which reacts with both organic and inorganic compounds. The products obtained are often unique and almost invariably interesting. New classes of compounds have been prepared with many reagents, and with others new members have been added to existing classes. Development of the chemistry of  $SiF_2$  will doubtless provide many more new organic, inorganic, and organometallic compounds.

Rather than suggest new reagents to try, however, it seems important here to point out that there are some fields of  $SiF_2$  chemistry which have received little attention to date. First, all of the work so far was with singlet  $SiF_2$ . Techniques leading to the production of triplet or excited  $SiF_2$  should be investigated. Triplet  $CF_2$  has a broadly developed gas-phase chemistry and that of triplet  $SiF_2$  should also be interesting. Second, it has been noted by Pease<sup>1,32</sup> that if gaseous  $SiF_2$  and any halogen were passed through a furnace at  $1200^\circ$ , gas-phase reaction occurred. Some of the gas-phase chemistry of monomeric singlet  $SiF_2$  could be investigated in this way. Finally, all the reactions reported to date have been initiated by cocondensation at  $-196^\circ$ . It appears that the reaction rate is the most important factor in controlling the ultimate course of  $SiF_2$  reactions. The rates of reactions with low activation energies (3-5 kcal mol<sup>-1</sup>) are strongly affected by small temperature differences. Cocondensation at temperatures higher than  $-196^\circ$  may lead to reactions that do not occur at lower temperatures and may also alter the course of those reactions that are known to occur.

(30) R. W. Kirk and P. L. Timms, *J. Amer. Chem. Soc.*, **91**, 6315 (1969).

(31) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *Inorg. Nucl. Chem. Lett.*, **5**, 995 (1969).

(32) D. C. Pease, U. S. Patent 3,026,173 (March 20, 1962).

Research in the areas of high-temperature chemistry, fluorine chemistry, optical and mass spectroscopy, and thermodynamics, which have all been explored during nearly a decade of SiF<sub>2</sub> research, has been supported at Rice University by the U. S. Atomic

Energy Commission, U. S. Army Research Office (Durham), National Aeronautics and Space Administration, Petroleum Research Fund, administered by the American Chemical Society, and Robert A. Welch Foundation.

## Symmetry Rules for Chemical Reactions

RALPH G. PEARSON\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 10, 1970

Recently there has been great interest in the devising of symmetry rules for predicting the course of chemical reactions. Much of this interest is due to the well-known work of Woodward and Hoffmann. Their method is based upon a correlation of the molecular orbitals of the reactant(s) with those of the product(s), and can be considered quite general. In this Account we present symmetry rules, derived in quite a different manner, whose predictions are not expected to differ from the most generalized application of the Woodward-Hoffmann rules but which are usually easier to apply.

Molecular orbital theory is still used as a basis, but the chemical reaction is considered as a perturbation on the reactant system. In particular, a small displacement along the reaction coordinate is taken as the perturbing influence. Using the quantum mechanical method of second-order perturbation theory, the symmetry rules for an elementary process of any molecularity can be stated in a rigorous way. This was first done by Bader<sup>1</sup> for the decomposition of an activated complex, a special example of a unimolecular reaction. The corresponding rules for bimolecular reactions have only recently been stated.<sup>2</sup> However the same conclusions can be drawn from a number of other perturbation theories of chemical reactivity.<sup>3</sup>

The mathematical language of group theory is useful in stating the symmetry rules in a concise way. Fortunately the conclusions can also be stated in a simple, pictorial manner. It is necessary to have some knowledge of the molecular orbitals of the system. In particular, the symmetry properties are needed. These are simply the changes in sign (plus or minus) of the

wave function, corresponding to the MO, at different parts of the molecule.

Chemical reactions consist of the breaking of certain bonds between atoms and the making of new bonds. All MO's correspond to the bonding together of certain atoms, the antibonding of other atoms, and the non-bonding of the remaining atoms. It follows that in a chemical reaction certain molecular orbitals must be vacated of electrons and others must be filled to create the new bonding situation.

The most important of these changes is a flow of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The importance of these orbitals has been stressed by Fukui, who in 1952 named them the frontier orbitals.

Electron movement between two orbitals cannot occur unless the orbitals meet the symmetry requirement. For a bimolecular reaction, the requirement is simply that the two have a net overlap. For a unimolecular reaction, the symmetries of the two must match up with the symmetry of the motion of the nuclei. The nuclear motion can be regarded as equivalent to one or more of the normal modes of vibration of the molecule.

### Theory

Consider an elementary process (concerted reaction) of any molecularity. The question is, how does symmetry enter into the variation of potential energy with changing nuclear coordinates? Group theory will first be used to obtain an exact answer to this question. The applications made later do not require the use of group theoretic language, but it is obvious that there are many reasons for chemists today to become familiar with the symbols used.

Figure 1 shows the usual adiabatic plot of potential energy vs. reaction coordinate. The points marked A, B, and C will be used to derive the symmetry rules since they represent characteristic features of such a plot. Any point on the diagram corresponds to some arrangement of the nuclei of the reactants. This ar-

\* Recipient of the 1970 American Chemical Society Award for Distinguished Service in the Advancement of Inorganic Chemistry, sponsored by Mallinckrodt Chemical Works.

(1) (a) R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962); (b) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(2) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).

(3) M. J. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341 *et seq.* (1952); K. Fukui, *Bull. Chem. Soc. Jap.*, **39**, 498 (1966); K. Fukui and H. Fujimoto, *ibid.*, **41**, 1989 (1968); G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **7**, 165 (1967); L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).