

# Effect of Additives on the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene

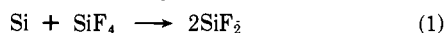
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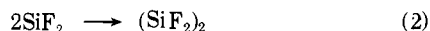
**Abstract:** Recoil  $^{31}\text{Si}$  atom reactions with  $\text{PF}_3$  resulted in the formation of both singlet and triplet  $^{31}\text{SiF}_2$  in the ratio of 1.0:3.3. Singlet  $^{31}\text{SiF}_2$  reacted with 1,3-butadiene to give difluorosilacyclopent-3-ene- $^{31}\text{Si}$ , but triplet  $^{31}\text{SiF}_2$  only gave this product in the presence of paramagnetic molecules such as  $\text{NO}$ ,  $\text{NO}_2$ , or  $\text{O}_2$ .

The nuclear recoil technique<sup>1-8</sup> and the thermal vaporization method<sup>9-15</sup> account for all the silicon atom reactions studied to date. Both processes have also been proven to be very effective in generating silicon analogues of carbenes. Using the nuclear recoil method of formation, silylene,  $\text{SiH}_2$ , has been shown to undergo  $\text{Si-H}^{2-6}$  and possibly  $\text{Si-Si}$  bond insertion.<sup>5</sup> Both singlet and triplet  $\text{SiH}_2$  also add to 1,3-butadiene, giving silacyclopent-3-ene.<sup>7,8</sup>

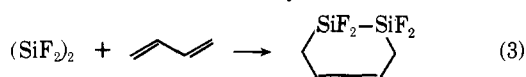
On the other hand, silicon difluoride, the best characterized carbene analogue, has been extensively studied by Margrave and co-workers employing the thermal vaporization method through the following formation process:<sup>10,11</sup>



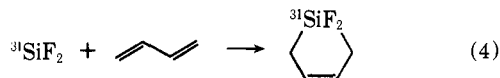
Spectroscopic evidence indicates that  $\text{SiF}_2$  possesses a singlet ground electronic state<sup>12</sup> with a bond angle of  $100^\circ 59'$ .<sup>13</sup> It is extraordinarily stable having a half-life at 0.1 Torr of 150 s. Even in the presence of 1 Torr of oxygen, its half-life is still 6 s.<sup>14</sup> However, in the majority of cocondensation studies where the  $\text{SiF}_2$  thus formed is allowed to react with other substrates, the products always contained a dimeric unit of  $\text{SiF}_2$ , indicating that dimerization predominates whenever  $\text{SiF}_2$  is in high concentration.



Accordingly, in the study of  $\text{SiF}_2$  reactions with 1,3-butadiene, Thompson and Margrave<sup>15</sup> have found that the major product formed was 1,1,2,2-tetrafluorodisilacyclohex-4-ene.



Using the nuclear recoil method by employing the transmutation,  $^{31}\text{P}(n,p)^{31}\text{Si}$ , we have found that energetic  $^{31}\text{Si}$  abstracts fluorine atoms from  $\text{PF}_3$  yielding  $^{31}\text{SiF}_2$ . Due to its extremely low concentration, the  $^{31}\text{SiF}_2$  thus formed reacts with 1,3-butadiene in its monomeric form to give difluorosilacyclopent-3-ene- $^{31}\text{Si}$  (DFSCP\*<sup>1</sup>).



In the present work, we have studied the effect of seven inorganic and organic additives on the yield of DFSCP\* from eq 4. From these studies, the possible existence of the previously unknown triplet  $^{31}\text{SiF}_2$  has been deduced.<sup>1b</sup> Such experiments also reveal certain interesting chemical properties of both singlet and triplet silicon difluoride.

## Experimental Section

**General Procedure.** The general procedure used in this study was the same as that used in other typical nuclear recoil experiments.<sup>16</sup> Phosphorus trifluoride and 1,3-butadiene along with other desired additives were sealed in Pyrex bulbs using high vacuum techniques. Sample analysis was performed using standard radio-gas chromatography.<sup>16</sup>

Silicon-31 from the  $^{31}\text{P}(n,p)^{31}\text{Si}$  nuclear transmutation<sup>3</sup> was formed using fast neutrons from two different sources. (1) A 16- or 20-MeV deuteron beam from the Texas A&M University cyclotron was focused on a beryllium target initiating the nuclear transformation,  $^9\text{Be}(d,n)^{10}\text{B}$ . (2) Fast neutrons from a Triga nuclear reactor at the Texas A&M Nuclear Science Center. Details regarding these irradiations are described in a previous publication.<sup>7</sup>

**Product Identification.** Identification of DFSCP\* was confirmed by coinjection of authentic samples of difluorosilacyclopent-3-ene (DFSCP) with irradiated samples on four different gas chromatographic columns. The authentic DFSCP was prepared using the method described by Chao et al.<sup>17</sup> and confirmed by its infrared spectrum. The four columns were: (1) a 30-ft 20% silicone fluid (SF-96) column operated at  $75^\circ\text{C}$ ; (2) a 2-, 5-, or 10-ft 35% dimethylsulfolane (DMS) column operated at  $25^\circ\text{C}$ ; (3) a 50-ft 15% silicone oil 550 column operated at  $75^\circ\text{C}$ ; and (4) a 50-ft 10% tri-*o*-tolylphosphate column operated at  $70^\circ\text{C}$ . The short DMS columns were used for routine analyses.

**Absolute Yield Measurement.** No direct measurement of the absolute yield of DFSCP\* was attempted. Instead, this value was indirectly evaluated by using the known  $^{31}\text{SiH}_4$  absolute yield (13%) from the recoil  $^{31}\text{Si}$  reactions in the  $\text{PH}_3/\text{SiH}_4$  system as a comparison standard.<sup>8</sup> Experimentally, two samples each of a 3:1  $\text{PF}_3$ /butadiene mixture and a 1:1  $\text{PH}_3/\text{SiH}_4$  mixture were simultaneously irradiated under normalized neutron flux conditions. The yield of DFSCP\* from the butadiene sample as measured on the 2-ft DMS or 50-ft silicone oil columns was compared to the  $^{31}\text{SiH}_4$  yield from the silane sample as measured on a 50-ft triisobutylene column at  $0^\circ\text{C}$ . After appropriate flow rate corrections, the ratio of the specific activities of these two products was calculated. The absolute yield of DFSCP\* was then evaluated by employing the 13% value for  $^{31}\text{SiH}_4$ . Three sets of experiments were performed for determining the absolute yield of DFSCP\* and the average value was found to be  $3.8 \pm 0.6\%$ . The addition of DFSCP carrier to the  $\text{PF}_3$ /butadiene sample before irradiation to ensure the preservation of DFSCP\* did not alter the observed yield.

**Chemicals.**  $\text{PF}_3$  (>97%) was obtained from PCR, Inc. Butadiene (>99.0%),  $\text{O}_2$  (>95%),  $\text{N}_2\text{O}$  (>98.0%),  $\text{NO}$  (>99%),  $\text{NO}_2$  (>99.5%),  $\text{CO}$  (>99.0%), propene (>99.0%), isobutene (>99.0%),  $\text{PH}_3$  (>99.5%) and  $\text{SiH}_4$  (>99.99%) were all obtained from Matheson. Each gas was used without further purification except for several cycles of degassing.

## Results

**Composition Study.** The dependence of DFSCP\* specific yields<sup>7</sup> on butadiene concentration is presented in Figure 1. In this as well as all later figures, the DFSCP\* specific yield for a 25% butadiene sample containing no additives has arbitrarily been assigned a value of 100. The results here indicate that in going from 2 to 75% butadiene, there is at most a 10% variation in the DFSCP\* specific yield. (Although the data in Figure 1 can be viewed as an increase to a maximum followed by a gradual decline similar to what Gaspar and co-workers have observed in their  $^{31}\text{SiH}_2$ -butadiene system,<sup>8</sup> the initial increment here nevertheless is much sharper and the decline is much less pronounced than in their system.) Even with 0.4% butadiene present the relative specific yield is already as high as 70.

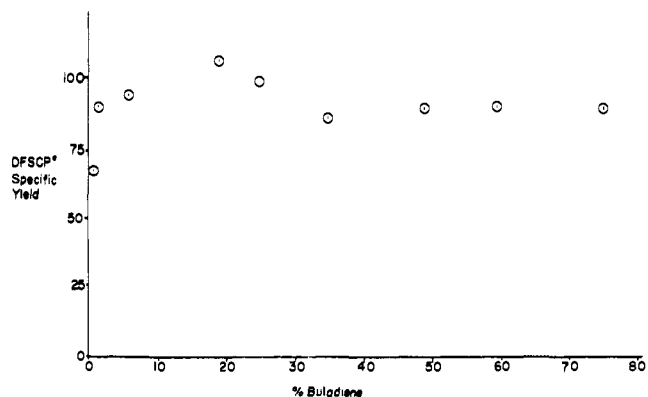


Figure 1. Dependence of difluorosilacyclopent-3-ene- $^{31}\text{Si}$  (DFSCP\*) specific activity on butadiene concentration.

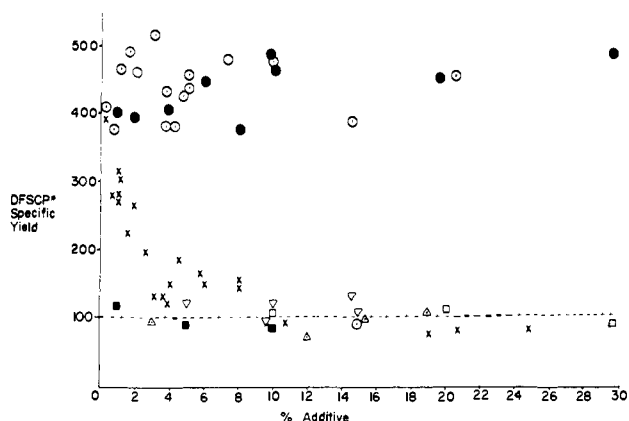


Figure 2. Effect of NO ( $\odot$ ),  $\text{NO}_2$  ( $\bullet$ ),  $\text{O}_2$  ( $\times$ ), CO ( $\blacktriangle$ ),  $\text{N}_2\text{O}$  ( $\nabla$ ), propene ( $\blacksquare$ ), and isobutene ( $\square$ ) on the DFSCP\* specific activity.

This points to the conclusion that the  $^{31}\text{SiF}_2$  reaction with butadiene is extremely efficient. In fact, the observed yield of 70 at 0.4% butadiene implies that the reaction of  $^{31}\text{SiF}_2$  with butadiene is at least 250 times more efficient than its further interaction with  $\text{PF}_3$ .

**Effect of NO and  $\text{NO}_2$  on the DFSCP\* Specific Yield.** A number of experiments were performed to study the effect of various additives on the DFSCP\* specific activity. Seven compounds, most of them known to be efficient radical scavengers, served as additives and their quantitative effects are shown in Figure 2. These effects can be classified into three different categories. The first type results from the addition of NO and  $\text{NO}_2$ <sup>18</sup> which causes a dramatically sharp rise in the DFSCP\* specific yield and is followed by an essentially constant plateau. An amplified illustration of the effect of small NO concentrations is shown in Figure 3. As observed in this figure, a concentration of 0.01% NO has already increased the DFSCP\* specific yield by a factor of three. In the entire range of 1–20% NO, the DFSCP\* yield is essentially constant and has a value  $4.3 \pm 0.5$  times higher than those from samples containing no additives.

As shown in Figure 2 the DFSCP\* specific yields from  $\text{NO}_2$ -addition samples have essentially the same values as their counterparts in the NO systems. The plateau region again has a value of  $430 \pm 50$ .

**Effect of  $\text{O}_2$  on the DFSCP\* Specific Yield.** The second type of additive effect as shown in Figures 2 and 4 is exhibited by the addition of  $\text{O}_2$  which causes a sharp rise in the DFSCP\* specific yield and is followed by an eventual decline to the level of no-additive samples. Figure 4 which is an amplified illustration of the effect of small  $\text{O}_2$  concentrations has the following features. The DFSCP\* yield starts to increase with the

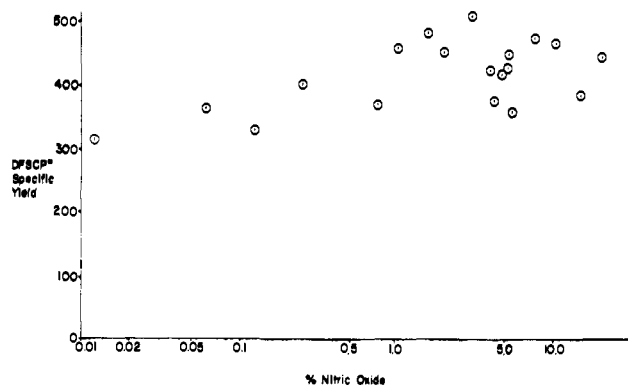


Figure 3. Effect of small nitric oxide concentrations on the DFSCP\* specific activity.

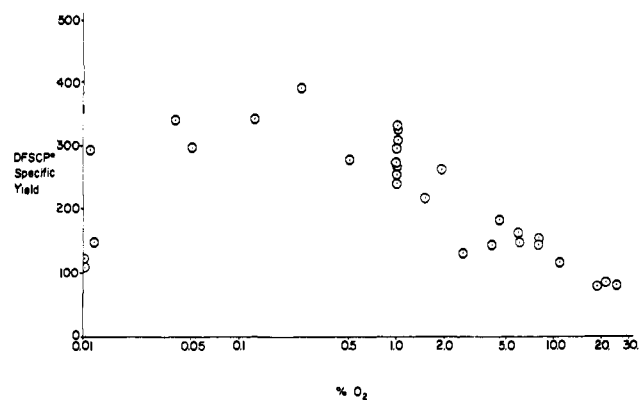


Figure 4. Effect of small oxygen concentrations on the DFSCP\* specific activity.

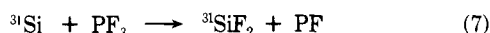
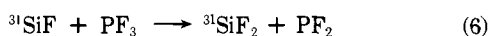
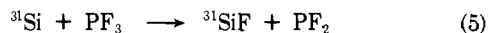
addition of 0.01%  $\text{O}_2$ , reaches a maximum region around 0.1%, decreases to a relative specific yield of about 100 at the 10% level, and remains nearly constant thereafter up to 20%  $\text{O}_2$ . The maximum yield attained in  $\text{O}_2$ -addition systems is approximately four times higher than those from samples containing no additives.

**Effect of Other Additives on the DFSCP\* Specific Yield.** The third type of additive includes carbon monoxide, nitrous oxide, propene, and isobutene which have virtually no effect on the DFSCP\* yield. As seen in Figure 2, even with the addition of up to 30% of these additives all the data points lie around the dotted line representing a relative specific yield of 100.

**Radiation Dose Effect.** A possible explanation for the high DFSCP\* yield in systems containing NO may be due to the fact that nitric oxide protects and preserves the actual original DFSCP\* yield, while in its absence either the products or their precursors are removed by species derived from radiation damage. Such a theory has been tested with two sets of experiments: (1) changing the neutron dose rate at constant total dose, and (2) changing the total dose by increasing the dose rate at constant irradiation time. In both cases there was no significant variation in DFSCP\* specific yield which therefore denies the possibility of such a theory.

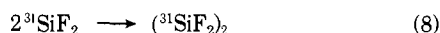
## Discussion

**Formation of Monomeric  $^{31}\text{SiF}_2$ .** The recoil  $^{31}\text{Si}$  atoms formed in the  $\text{PF}_3$ /butadiene system may undergo F abstraction after their energy has been degraded to the chemical reaction range. The apparent abstraction of two F atoms to give  $^{31}\text{SiF}_2$  may proceed through either a stepwise mechanism as shown in eq 5 and 6 or in a single step simultaneous abstraction process as in eq 7.

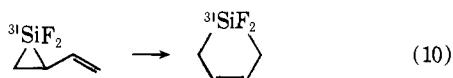
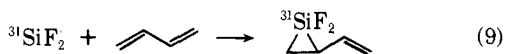


The heats of reaction for eq 5 and 6 are +7 and -20 kcal/mol, respectively, while that of eq 7 is exothermic by about 21 kcal/mol.<sup>19,20</sup> Although the thermodynamic data slightly favor the essentially unknown simultaneous abstraction process,<sup>21</sup> it is difficult to ascertain the extent of its occurrence without further direct evidence. However, the stepwise abstraction can only be effected by <sup>31</sup>Si atoms with kinetic energy in excess of at least 7 kcal/mol, while the simultaneous abstraction might be initiated by thermal <sup>31</sup>Si.

The <sup>31</sup>SiF<sub>2</sub> formed in this system must be reacting in its monomeric form because of its extremely low concentration. In the composition study we have shown that essentially all the <sup>31</sup>SiF<sub>2</sub> which can be directly captured by butadiene reacts very effectively to give DFSCP\*. In a typical sample of such kind, about 10<sup>7</sup> <sup>31</sup>SiF<sub>2</sub> species are formed in a system consisting of 10<sup>20</sup> PF<sub>3</sub> and butadiene molecules. Even if we assign a lifetime of 100 s to <sup>31</sup>SiF<sub>2</sub> in such a system its instantaneous concentration is so low that every <sup>31</sup>SiF<sub>2</sub> radical will be surrounded by about 10<sup>14</sup> bath molecules. Because of this the occurrence of the dimerization process, eq 8, should be negligible and therefore <sup>31</sup>SiF<sub>2</sub> must react in its monomeric form.

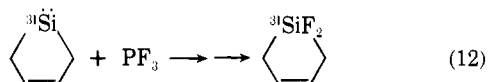
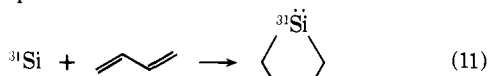


**Formation of Difluorosilacyclopent-3-ene-<sup>31</sup>Si.** The apparent 1,4-addition of <sup>31</sup>SiF<sub>2</sub> to butadiene giving DFSCP\*, in the pure PF<sub>3</sub>/butadiene system as shown in eq 4 may actually proceed through the 1,2-addition reaction, eq 9, followed by the isomerization reaction, eq 10.<sup>1a</sup>

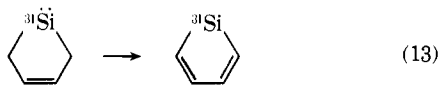


The strongest evidence to support this sequence is the nonstereospecific addition of SiH<sub>2</sub> to *trans*-2-*trans*-4-hexadiene.<sup>22</sup> The addition of singlet methylene to butadiene giving excited vinylcyclopropane which isomerizes to cyclopentene is also a well-known mechanism.<sup>23,24</sup>

DFSCP\* can also be formed through the addition of <sup>31</sup>Si atoms to butadiene as in eq 11 followed by the abstraction of two F atoms, eq 12.



The strongest evidence against this mechanism is the fact that silacyclopent-2,4-diene-<sup>31</sup>Si with a yield which is much higher than that of DFSCP\* has been deduced as an observed product by Gaspar and co-workers.<sup>8</sup> This implies that the intramolecular rearrangement, eq 13, is much faster and more likely to occur than the bimolecular F-abstraction reaction, eq 12, which probably involves an initial endothermic step.<sup>25</sup>

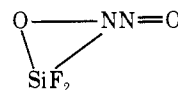


As discussed in a previous work the importance of <sup>31</sup>Si<sup>+</sup> as a product precursor in a butadiene-containing system should be minimal because of the low ionization potential of the latter molecule.<sup>7</sup>

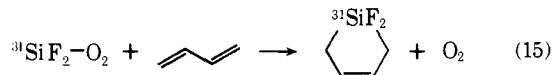
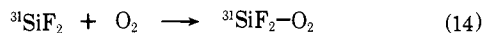
**Electronic States of Reacting <sup>31</sup>SiF<sub>2</sub>.** Free radical scavengers such as most of the additives which were employed in this work should interact with triplet <sup>31</sup>SiF<sub>2</sub>, but should be nonreactive towards its singlet counterpart. The results described here indicate that two kinds of <sup>31</sup>SiF<sub>2</sub> were formed in this system and both eventually give rise to DFSCP\*. The first kind (relative specific yield = 100) which always gives DFSCP\* with or without additives is likely to be ground state singlet <sup>31</sup>SiF<sub>2</sub> primarily because its yield is not altered by radical scavengers such as propene and isobutene. The second kind (relative specific yield = 430 - 100 = 330) only reacts to give DFSCP\* in the presence of paramagnetic molecules such as NO, NO<sub>2</sub>, or O<sub>2</sub>, which means the species is likely to be triplet <sup>31</sup>SiF<sub>2</sub>. In a system without such paramagnetic molecules this presumed triplet species either does not react with butadiene<sup>26</sup> or reacts with it in a stepwise fashion to initiate chain reactions forming polymeric products instead of DFSCP\*. Results here indicate that if triplet <sup>31</sup>SiF<sub>2</sub> is actually involved, it should possess stability similar to that of its singlet counterpart although it is electronically excited.

**<sup>31</sup>SiF<sub>2</sub>-Donor Complexes.** Previous discussion has already ruled out the possibility of a radiation dose effect for the dramatic increase in DFSCP\* specific yield in the presence of paramagnetic molecules, nor can this observation be explained by the fact that all these yield-promoting molecules are oxides, because other oxides such as N<sub>2</sub>O and CO gave negative results. A third possible explanation is that paramagnetic molecules will effect a spin conversion process changing triplet <sup>31</sup>SiF<sub>2</sub> into its singlet form which then adds to butadiene to give DFSCP\*. Although this supposition will explain the NO and NO<sub>2</sub> results, it fails to account for the detailed variations in the O<sub>2</sub> system.<sup>27</sup> It is unlikely that traces of O<sub>2</sub> initiate a spin conversion which is then reversed by further addition of O<sub>2</sub>.

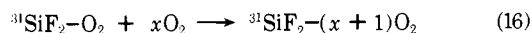
An explanation consistent with the observed facts is one involving complex formation of <sup>31</sup>SiF<sub>2</sub> with paramagnetic molecules thereby giving an entity having the capability of acting as an <sup>31</sup>SiF<sub>2</sub> donor. That is, molecules such as NO, NO<sub>2</sub>, and O<sub>2</sub> which have one or more unpaired electrons may interact with triplet <sup>31</sup>SiF<sub>2</sub> to give a <sup>31</sup>SiF<sub>2</sub>-NO type of complex which on collision with butadiene gives DFSCP\*. An SiF<sub>2</sub>-NO complex has actually been proposed to exist at low temperatures where NO is present as a dimer before reaction. The structure of such a complex has been proposed on the basis of ir matrix isolation studies.<sup>28</sup> In the gas phase, the <sup>31</sup>SiF<sub>2</sub>-NO complex may or may not have this structure.



The above complex formation mechanism involving O<sub>2</sub> as the paramagnetic molecule is illustrated in eq 14 and 15.



However, in the O<sub>2</sub> system an additional complication arises probably because of the high reactivity of the <sup>31</sup>SiF<sub>2</sub>-O<sub>2</sub> complex with other oxygen molecules as in eq 16 to give a species which can no longer donate <sup>31</sup>SiF<sub>2</sub>.



Kinetically, both reactions 15 and 16 are competing for the available <sup>31</sup>SiF<sub>2</sub>-O<sub>2</sub> complexes.

It is understandable that at very low O<sub>2</sub> concentrations reaction 14 determines the amount of complex being formed and therefore the DFSCP\* yield rises with increasing O<sub>2</sub>. Whenever there is enough O<sub>2</sub> in the system to complex all the triplet <sup>31</sup>SiF<sub>2</sub>, further increases in the oxygen level will enhance the

competition of eq 16 over 15 and therefore decrease the DFSCP\* yield. Eventually when the oxygen level in the system is such that reaction 16 overwhelmingly predominates over 15, none of the DFSCP\* will be derived from the complexed triplet  $^{31}\text{SiF}_2$ . At this point the DFSCP\* yield should return to that of the nonadditive systems where only the singlet  $^{31}\text{SiF}_2$  reaction product is observed. From the results as shown in Figures 2 and 4 it can be derived that eq 16 is about ten times more efficient than eq 15 and only a 10% oxygen concentration is sufficient to completely suppress the reactions of  $^{31}\text{SiF}_2\text{-O}_2$  complexes with butadiene.

The above proposed mechanism is simple, direct, and explains all the experimental observations very well. However, it is not necessarily the unique explanation for the present results.<sup>29</sup>

If the above mechanism is correct, the relative specific yields of singlet  $^{31}\text{SiF}_2$  as 100 and triplet  $^{31}\text{SiF}_2$  as 330 transcribe into 23% singlet and 77% triplet. In a previous study we have shown that the  $^{31}\text{SiH}_2$  formed in a similar  $\text{PH}_3$ /butadiene system consists of 20% singlet and 80% triplet.<sup>7</sup> Although the similarity is noted here, any further deduction is unwarranted unless more knowledge is obtained about the mechanism of F- and H-abstraction reactions by recoil  $^{31}\text{Si}$  atoms.

**Relative Reactivities of Other Olefins.** From the data presented in Figure 2, it is observed that the addition of 30% other alkenes such as propene or isobutene to the  $\text{PF}_3$ /butadiene system did not significantly decrease the DFSCP\* specific yield. Therefore the conjugated double bonds of butadiene are much more efficient in trapping singlet  $^{31}\text{SiF}_2$  than the double bonds in ordinary olefins. Quantitatively, it can be estimated that butadiene is more reactive by at least a factor of 20. In comparison with others,  $^{31}\text{SiF}_2$  in its singlet ground state, being the least reactive and most stable carbene-type species, discriminates among the olefins much more pronouncely.<sup>30</sup>

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- (18) For simplicity the equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at room temperature is designated  $\text{NO}_2$ . In preparing samples with  $\text{NO}_2$  it was noticed that its brown color was immediately removed when butadiene was added. While this reaction may have resulted in the loss of a large fraction of the  $\text{NO}_2$ , apparently enough was still available for  $^{31}\text{SiF}_2$  reactions, as evidenced by the results shown in Figure 2.
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- (25) The heat of reaction for eq 12 cannot be evaluated because of the lack of data for  $\Delta H_f^\circ$  of DFSCP. However, data for F abstraction by  $\text{SiF}_2$  giving  $\text{SiF}_3$  is endothermic by 15 kcal/mol. (Using the data given in ref 20.)
- (26) It has been shown that  $^{31}\text{P}$  carbon atoms react much slower than  $^{13}\text{C}$  carbon atoms with ethylene. See (a) F. F. Martinotti, M. J. Welch, and A. P. Wolf, *J. Chem. Soc. D*, 115 (1968), and (b) D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, **67**, 3166 (1971).
- (27) One plausible mechanism as suggested by a reviewer of this paper is that small quantities of paramagnetic molecules cause a conversion from triplet to singlet  $^{31}\text{SiF}_2$ . A nondonor type of complex with triplet  $^{31}\text{SiF}_2$  is possible with  $\text{O}_2$  (but not with  $\text{NO}$  or  $\text{NO}_2$ ) which removes  $^{31}\text{SiF}_2$  from the sequence yielding DFSCP\* in the  $\text{O}_2$  system. As the concentration of  $\text{O}_2$  increases to the point that reaction to form the complex competes with the rate for induced intersystem crossing, the observed DFSCP\* yield decreases from that found at small  $\text{O}_2$  concentrations. This mechanism requires that the spin conversion of all the triplet  $^{31}\text{SiF}_2$  by the long range dipole-dipole interaction be efficient and achieved by the presence of merely 0.1%  $\text{O}_2$ . On the other hand, it also requires that the spin conversion process be some 30 times slower than the complex formation reaction because the excess DFSCP\* yield decreases to about half of the 330 value at about 3%  $\text{O}_2$  concentration. Nevertheless, this mechanism gives the same conclusion as what has been proposed in this paper. That is, the excess relative yield of 330 is due to triplet  $^{31}\text{SiF}_2$ .
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