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ON THE MECHANISMS OF SILICON ATOM ABSTRACTION REACTIONS

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Summary

A set of experiments were designed to verify that recoil ^{31}Si atoms abstract H and F atoms via a stepwise mechanism instead of a simultaneous mechanism to give silylenes such as $^{31}SiH_2$, $^{31}SiHF$ and $^{31}SiF_2$. In addition, a novel compound, 1-fluorosilacyclopent-3-ene, was synthesized.

Introduction

Silicon atoms have been generated either by the nuclear recoil, or by the thermal evaporation methods [1—4]. Such atoms are capable of undergoing abstraction, insertion, and addition reactions. Among these possible reaction channels, the H-abstraction to give SiH_2, and the F-abstraction to give SiF_2 are two of the well-established ones [5—9]. The resultant silylenes can then be captured by various reagents to give stable identifiable products.

The abstraction of univalent species such as H and F atoms by a multivalent species such as carbon atoms is generally believed to proceed via a stepwise mechanism [10,11]. However, as the size of the multivalent abstracting species increases, it is conceivable that geometrically it could overlap with the electron orbitals of two H (or F) atoms during a single reactive collision, and subsequently lead to simultaneous abstraction of two entities. The present work was designed to examine whether silicon atoms abstract univalent species with a stepwise or a simultaneous mechanism.

During the process of this mechanistic evaluation study, it became necessary to synthesize a novel compound, 1-fluorosilacyclopent-3-ene (FSCP). This monofluorinated silicon-containing compound has been successfully prepared and characterized.

Experimental

General procedure

The general procedure used for previous recoil ^{31}Si experiments was followed

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[6—8]. Mixtures of PH_3, PF_3, and 1,3-butadiene were sealed in 25 ml pyrex bulbs with the standard high vacuum techniques. The irradiation of the freshly prepared samples was carried out with the fast neutrons from a Triga nuclear reactor at the Texas A&M Nuclear Science Center. The samples in groups of four were irradiated for six minutes in an internal cadmium-lined boron rotisserie at an external total neutron flux of approximately 1×10^{12} neutrons/(cm^{2}s). Recoil ^{31}Si atoms were produced from the phosphorus-containing precursors, both PH_3 and PF_3, via the nuclear transmutation, $^{31}P(n,p)^{31}Si$. Products were analyzed with the standard radio-gas chromatography [12].

Sample analysis

The three major reaction products: Silacyclopent-3-ene-^{31}*Si* (SCP*); 1-fluorosilacyclopent-3-ene-^{31}*Si* (FSCP*); and 1,1-difluorosilacyclopent-3-ene-^{31}*Si* (DFSCP*), were all identified by the coinjection of synthesized authentic samples on four gas chromatographic columns: (i) a combined column of a 30-ft 20% silicone fluid (SF-96) segment operated at 55°C and a 7-ft 35% dimethylsulfolane (DMS) segment operated at 25°C; (ii) a 37-ft 20% SF-96 column operated at 38°C; (iii) a 20-ft 10% silicone oil (D.C.550) column operated at 25°C; and (iv) a 10-ft 35% DMS column operated at 25°C. The second column, 37-ft SF-96 at 38°C was used for most of the routine analyses to accumulate experimental data. All three major products were cleanly separated by this column with the elution order: DFSCP*, FSCP*, and SCP*. Some of the data were also obtained with the combined SF-96-DMS column. In this case, the elution order was: SCP*, DFSCP*, and FSCP* with the last two slightly overlapping. Graphical manipulation was applied for the separation of the two peaks, and the obtained results were generally consistent with those from the 37-ft SF-96 column.

Precautions were taken for the maximum preservation of the minute amounts of ^{31}Si-containing products. The analytical system was repetitively conditioned with SiH_4 prior to the injection of samples, and greaseless systems were employed throughout the analyses. In general, samples were transferred by condensing into an injection loop with liquid nitrogen. A metal injection system was occasionally used to crush the sample bulb directly in the gas chromatographic flow stream. For either mode of injection, appropriate carriers such as SCP and DFSCP were always added to the sample injection system prior to the breaking of the bulbs.

In addition to SCP*, FSCP*, and DFSCP*, a fourth product, 1-silacyclopent-2,4-diene-^{31}*Si*, was also observed. This compound was formed from the direct addition of ^{31}Si atoms to 1,3-butadiene [13]. However, since it is not instrumental to the present topic of mechanistic evaluation of silicon atom abstraction reactions, experimental conditions were not chosen for the maximum preservation of this compound. In order to get a high yield of the three major products, a rather high radiation dosage has been employed. As indicated by previous reports [13], a significant fraction of the 1-silacyclopent-2,4-diene-^{31}*Si* produced in the experiments would be removed through radiation damage at such a level of high radiation dosage. Therefore, no significance is to be attached to the observed yields of this product in the present experiments.

Synthesis of 1-fluorosilacyclopent-3-ene

Authentic samples of SCP and DFSCP were synthesized according to the established methods [14—17]. FSCP was converted from SCP through monofluorination. Four fluorination methods have been attempted. The first two methods failed to stop at the mono-fluorinated stage and apparently proceeded to give DFSCP as the obtained product: (i) fluorination with SbF_3 with $SbCl_5$ as a catalyst [18]; and (ii) fluorination with AgF [19] in a flow system. However, two other methods do give rather high yields of FSCP. (iii) Fluorination with SbF_3 [20,21]: Approximately 1.0 gram of powdered SbF_3 was placed in a reaction tube which was then evacuated. Approximately 2 mmol of SCP was condensed onto the SbF_3. The system was warmed up gradually and left undisturbed for 24 h at room temperature. For three separate trials the observed yields of FSCP were 82, 85, and 61%. The remainder included DFSCP and unreacted SCP. (iv) Monochlorination with AgCl [22—24] followed by fluorination with SbF_3: 8 g of $AgNO_3$ were dissolved in approximately 5 ml of distilled water and pipetted into a tube loosely packed with glasswool. 50 ml of dilute hydrochloric acid were then poured into the foil-covered tube. The water was removed and the deposited AgCl was thoroughly dried by heating at approximately 110°C under vacuum for about 20 h. When this chlorination bed was ready, approximately 0.2 mmol of SCP was drawn through the evacuated AgCl to a tube which was immersed in liquid nitrogen and contained approximately 0.5 mg SbF_3 [20,21]. The tube was warmed up to room temperature, and the resultant chlorinated SCP was allowed to undergo fluorination for 3 h. In two separate experiments the yields of FSCP were found to be 64 and 26%. The yield is probably dependent on the condition of the AgCl bed as a result of some uncontrolled factor during its preparation.

Disproportionation of FSCP was observed to take place after several days when stored at room temperature.

Identification of 1-fluorosilacyclopent-3-ene

The prepared FSCP was purified by gas chromatography and an infrared spectrum of the compound in the gas phase was taken on Beckman 4260

TABLE 1

NMR DATA (δ values) FOR SILACYCLOPENT-3-ENES

Compound	Proton	Chemical shift	Description
$\overline{CH_2CH{=}\overset{2}{C}H\overset{1}{C}H_2SiH_2}$ [a]	1	1.38	
	2	5.80	
	H(Si)	3.87	
$\overline{CH_2CH{=}\overset{2}{C}H\overset{1}{C}H_2SiF_2}$ [a]	1	1.33	Triplet of doublets
	2	5.94	Triplet of triplets
$\overline{CH_2CH{=}\overset{2}{C}H\overset{1}{C}H_2SiHF}$	1	1.52	Multiplet (15 peaks)
	2	5.98	Multiplet (6 peaks)
	H(Si)	5.28	Multiplet (18 peaks)

[a] Data from Ref. [17].

spectrometer. The observed characteristic bands are: 3060, 2950, 2190, 1620, 1415, 1220, 1110, 920, 775, 725, and 675 cm^{-1}. This spectrum is extremely similar to those reported earlier for SCP and DFSCP [17].

The proton NMR spectrum was also taken for freshly prepared FSCP with $CDCl_3$ as a solvent. A Varian XL-100 NMR spectrometer was used. The chemical shifts δ values are given in Table 1 with those reported for SCP and DFSCP values included for comparison [17]. The coupling is as follows: J(2H—F) 59 Hz; J(4H—F); 2.7 Hz; J(4H—H) 1.6 Hz; J(3H—H) $\simeq$ 0.98 Hz. The expected integrals for FSCP are 1/2/4 for $SiH/CH/CH_2$ hydrogens. The observed integrals, when normalized to one for the Si hydrogen, were found to be 1/2.1/4.1.

Results and discussion

Dependence of product yields on sample composition

The yields of SCP*, FSCP*, and DFSCP* as a function of the relative amounts of PH_3 and PF_3 have been studied. In all these systems, 30% 1,3-butadiene was employed to capture the ^{31}Si-labeled intermediate species derived from the nuclear transmutation of the phosphorus-containing precursors. The remaining 70% of the samples are mixtures of PH_3 and PF_3 in various proportions, ranging from pure PH_3 to pure PF_3. In Fig. 1, the absolute yields of SCP*, FSCP*, and DFSCP* are plotted as a function of the relative mole fraction of PH_3 among the total phosphorus-containing compounds in terms of $PH_3/(PH_3 + PF_3)$. The results indicate that as the mole fraction of PH_3 increases, the yield of SCP* increases, the yield of DFSCP* decreases, and the yield of FSCP* goes through a maximum.

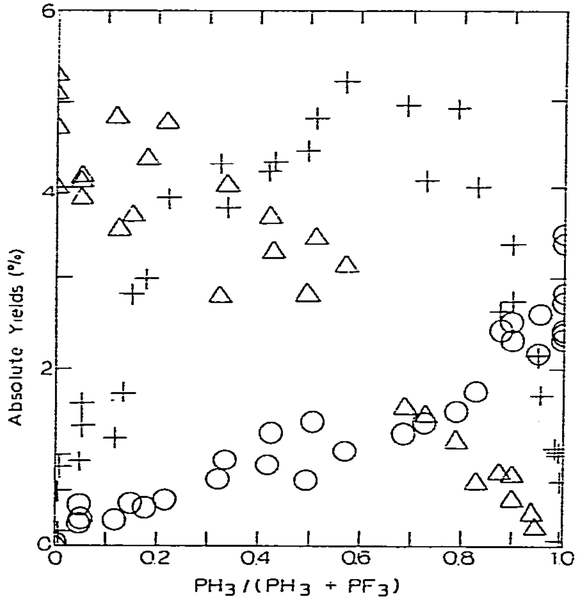
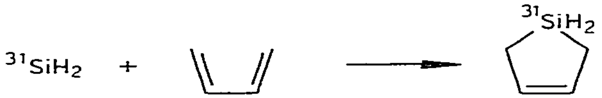


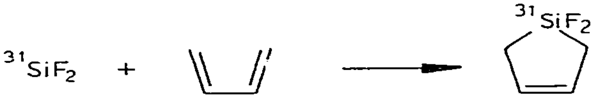
Fig. 1. The effect of sample composition on the product yields in recoil ^{31}Si atom reactions with PH_3/PF_3/1,3-butadiene systems: ○ SCP*; + FSCP*; △ DFSCP*.

Possible mechanisms of silicon atom abstraction reactions

In previous studies, it has been well-established that ^{31}Si atoms could abstract H atoms from PH_3 to give $^{31}SiH_2$, or F atoms from PF_3 to give $^{31}SiF_2$ [5—9]. The formation of such silylenes in the recoil ^{31}Si systems is evidenced by the capturing of such intermediates with 1,3-butadiene to give SCP* and DFSCP*.



(1)



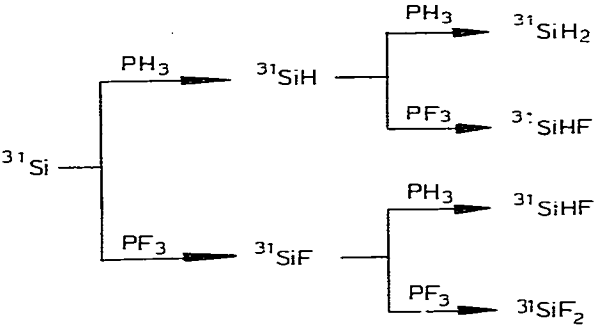
(2)

Information concerning the mechanism of Si atom abstraction reactions can be obtained from the results of the present PH_3/PF_3/1,3-butadiene mixture systems. If the abstraction of two entities by ^{31}Si atoms proceed via a simultaneous mechanism during a single reactive collision, only $^{31}SiH_2$ and $^{31}SiF_2$ will be formed in the mixture system, and consequently only SCP* and DFSCP* should be observed.

$$^{31}Si + PH_3 \rightarrow {}^{31}SiH_2 + PH \tag{3}$$

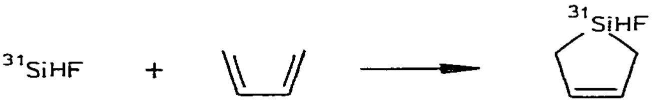
$$^{31}Si + PF_3 \rightarrow {}^{31}SiF_2 + PF \tag{4}$$

On the other hand, if the stepwise abstraction mechanism prevails, $^{31}SiHF$ will also be formed in addition to $^{31}SiH_2$ and $^{31}SiF_2$. The various possible abstraction steps involved are illustrated with the following scheme.



(5a)
(5b)
(5c)
(5d)

In fact $^{31}SiHF$ could be formed via two different abstraction routes: F-abstraction by ^{31}SiH via reaction 5b and H-abstraction by ^{31}SiF via reaction 5c. In the presence of 1,3-butadiene the resultant $^{31}SiHF$ could be captured to give FSCP* as the final product.



(6)

This means that if the ^{31}Si abstraction reactions proceed via a stepwise mechanism, all three silylenes, $^{31}SiH_2$, $^{31}SiHF$, and $^{31}SiF_2$, will be formed, and consequently all three 1,3-butadiene trapped products, SCP*, FSCP*, and DFSCP*, should be observed.

Since it is seen in Fig. 1 that in addition to SCP* and DFSCP*, the cross-abstraction product, FSCP*, is also obtained in large quantities, it can be concluded that the stepwise mechanism definitely operates during the H- and F-abstraction process by ^{31}Si atoms. Although this observation does not deny a possible limited occurrence of the simultaneous abstraction mechanism, the relative magnitude of the observed FSCP* yield surely indicates that the stepwise mechanism overwhelmingly predominates.

In spite of the strong support for the stepwise abstraction mechanism as presented above, there is always a chance that the simultaneous abstraction mechanism actually operates to give initially $^{31}SiH_2$ and $^{31}SiF_2$ which are subsequently converted to $^{31}SiHF$ via some secondary processes. Highly energetic silylenes might exchange H or F atoms with PH_3 or PF_3 to effect such a conversion.

$$^{31}SiH_2 + PF_3 \rightarrow {}^{31}SiHF + PHF_2 \quad (7)$$

$$^{31}SiF_2 + PH_3 \rightarrow {}^{31}SiHF + PH_2F \quad (8)$$

Reactions 7 and 8, though possible, are not very likely due to the reasons listed below: (i) Such exchange processes between silicon-containing intermediates and phosphorus compounds are unknown in the literature. (ii) After two abstraction reactions, the resultant $^{31}SiX_2$ definitely maintains some of the excitation from the nuclear recoil process, but its energy content is not likely to be high owing to the observation that there is a lack of decomposition and isomerization for the resulting SCP* and DFSCP*. (iii) In Fig. 1, it is observed that at 20% PH_3, the yields of FSCP* is about the same as that of DFSCP*, and at 20% PF_3 (80% PH_3), the yield of FSCP* is about three times as high as that of SCP*. If $^{31}SiHF$ were formed solely from reactions 7 and 8, the expected FSCP* yields should be much lower in both cases because there is only a one fifth chance for the major silylene formed in each case to collide with the correct phosphorus compound to give an effective H-for-F or F-for-H exchange process. Because of the above reasons, it is unlikely that $^{31}SiHF$ are predominently formed via reactions 7 and 8.

Relative efficiency of H- versus F-abstractions

Since it has been demonstrated that both $^{31}SiH_2$ and $^{31}SiF_2$ can be efficiently and quantitatively trapped by 1,3-butadiene as shown in eq. 1 and 2 to give SCP* and DFSCP* [5—9], the relative yields of these two products should represent the relative amounts of $^{31}SiH_2$ and $^{31}SiF_2$ being formed. This in turn should reflect the relative efficiency of H- versus F-abstraction by recoil ^{31}Si atoms. By using the data shown in Fig. 1, the information on the relative abstraction efficiency can be obtained from three different approaches. First, the absolute yield of SCP* from pure PH_3 sample is about 3% while the absolute yield of DFSCP* from pure PF_3 sample is about 5%. Such inter-sample comparison indicates that for recoil ^{31}Si atoms, the F-abstraction to give $^{31}SiF_2$

is approximately twice as efficient as the H-abstraction to give $^{31}SiH_2$. A second approach is to compare the yields of SCP* and DFSCP* in a mixture system containing 1/1 ratio of PH_3 and PF_3. Since their yields are 1 and 3%, respectively, it indicates that the F-abstraction is about three times more likely than the H-abstraction in an equimolar mixture to give the silylenes. A third approach is to locate the composition of the PH_3/PF_3 mixture which gave an identical yield of SCP* and DFSCP*. Since, as seen in Fig. 1, these two product yield lines intersect at approximately a mole fraction of 0.7 in terms of $PH_3/(PH_3 + PF_3)$, it again indicates that F-abstraction is about twice more likely than the H-abstraction.

In summary, all three approaches agree that for recoil ^{31}Si atoms, the F-abstraction to give $^{31}SiF_2$ is 2—3 times more efficient than the corresponding H-abstraction to give $^{31}SiH_2$. Such a difference may arise from the fact that the Si—F bonds are stronger than Si—H bonds and, therefore, they are more readily formed.

In order to gain some kinetic insight for the abstraction processes, a simple calculation has been attempted. The assumptions involved are the following: (i) the stepwise abstraction mode as shown in eq. 5 is the only operating one, while the contribution from the simultaneous abstraction mode is negligible; (ii) the H-abstraction efficiencies for ^{31}Si, ^{31}SiH, and ^{31}SiF are all similar; (iii) the F-abstraction efficiencies for these three species are the same; (iv) the efficiencies for the H- and F-abstraction processes have fixed values regardless whether the systems are pure or mixed. With these assumptions, the expected yields of SCP*, FSCP*, and DFSCP* were calculated as a function of sample composition. The lines obtained for the expected SCP* and DFSCP* yields are close to the experimental results as shown in Fig. 1. However, the calculated FSCP* line, although similar in shape to the observed results, lies much lower than the experimental data. These comparisons, although supporting the first assumption that the abstractions follow a stepwise mechanism, indicate that the second and/or third assumptions are not realistic. In referring to eq. 5, this observed disagreement means that ^{31}Si, ^{31}SiH, and ^{31}SiF probably have very different abstraction efficiencies for either H atoms from PH_3 or F atoms from PF_3.

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