Reactions of Monomeric Difluorosilylene with Ethylene

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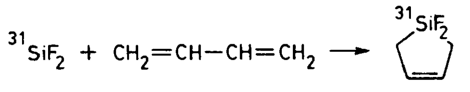
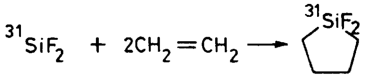
Summary Monomeric $^{31}SiF_2$ reacts efficiently with two molecules of ethylene to give 1,1-difluoro[^{31}Si]silacyclopentane as the final product, but competition experiments indicate that ethylene is about ten times less reactive than buta-1,3-diene for the trapping of the silylene.

Owing to the relative instability of the silacyclopropanes,[1] studies thus far have indicated that monomeric difluorosilylene can be conveniently trapped only by conjugated dienes rather than simple alkenes.[2–5] For example, monomeric $^{31}SiF_2$ prepared by the nuclear recoil method has been successfully trapped by buta-1,3-diene to give 1,1-difluoro[^{31}Si]silacyclopent-3-ene (DFSCPE) as shown in reaction (1).[2] We now report that monomeric $^{31}SiF_2$ can also be efficiently trapped by ethylene to give 1,1-difluoro-[^{31}Si]silacyclopentane (DFSCPA) as the final product, as shown in reaction (2). The interaction of ethylene with SiF_2 formed by the high-temperature reactions of Si and SiF_4 has been studied.[6] In this system, 1,1,2,2-tetrafluoro-1,2-disilacyclobutane and 1,1,2,2-tetrafluoro-1,2-disilacyclohexane were obtained, indicating the involvement of dimeric $(SiF_2)_2$.



(1)



(2)

Recoil ^{31}Si atoms were formed *via* the nuclear transmutation $^{31}P(n,p)^{31}Si$ under irradiation with fast neutrons from a Triga nuclear reactor at the Texas A&M Nuclear Science Center.[2] PF_3 served both as the source of ^{31}P atoms for the nuclear reaction, and as the source of F atoms for the abstraction during the formation of $^{31}SiF_2$. Products were analysed with standard radio-gas chromatography.[7] The major product of the system was identified as DFSCPA, as shown by comparison with authentic samples on three gas chromatographic columns of different separating characteristics. Four unidentified products with shorter retention times were also observed in lower yields.

Since in previous experiments it was shown that $^{31}SiF_2$ could be trapped quantitatively by buta-1,3-diene as DFSCPE,[2] a set of competition experiments with ethylene and butadiene mixtures has been designed to demonstrate that both DFSCPA and DFSCPE are derived from the same precursor. Systems containing 70% PF_3 and 30% of the olefins were used, in which the olefinic composition varied from pure butadiene to pure ethylene. The results are displayed in the Figure, which shows a plot of the absolute yields of both DFSCPA and DFSCPE as a function of the mole fraction of butadiene. Essentially the same amount of $^{31}SiF_2$ was captured by ethylene and butadiene when only they were present. As the mole fraction of butadiene increases, the yield of DFSCPA decreases sharply as the yield of DFSCPE increases. The two yields are nearly complementary to each other; a plot of the sum of the yields of DFSCPA and DFSCPE against the mole fractions of the olefins shows a shallow minimum corresponding to a decrease in total yield of *ca.* 15% at the composition where the yields of the two products are similar. This decrease is probably due to the formation of a presently undetected ethylene-butadiene cross-product, resulting from the interaction of an initially formed $^{31}SiF_2$–C_2H_4 adduct with butadiene. These results also provide information about the relative reactivities of the two olefins. The olefinic composition where the DFSCPA and the DFSCPE yields are identical corresponds to 3% of butadiene and 27% of C_2H_4 in the mixture, implying that butadiene is about ten times more reactive than ethylene for the trapping of $^{31}SiF_2$.

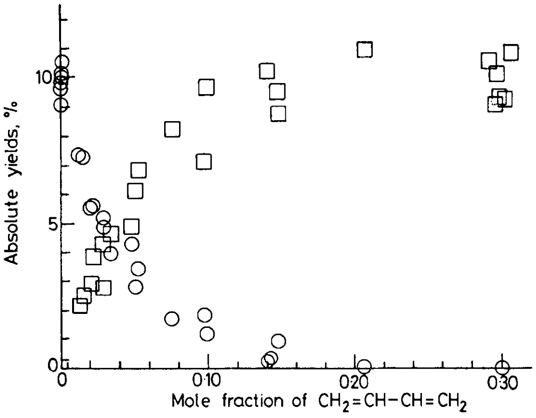


Figure. Absolute yields from the competition of ethylene and buta-1,3-diene for the trapping of $^{31}SiF_2$. ○, DFSCPA; □, DFSCPE. The mole fractions of C_2H_4 in the samples equal 0·30 minus the mole fractions of buta-1,3-diene.

Besides the ethylene–butadiene competition systems, other experiments have shown a maximum in the DFSCPA yield when the relative amounts of PF_3 and C_2H_4 were varied, confirming that both compounds are precursors of the product. The lack of a scavenger effect (with NO or O_2) indicates that the $^{31}SiF_2$–C_2H_4 adduct is probably a molecular intermediate, while the increase in the DFSCPA yield with Ne-moderation shows that reaction (2) is a low-energy process. The combination of the results with the scavenger and the moderator also indicates that the reacting $^{31}SiF_2$ is in its singlet ground state.

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