Interaction of Triplet Silicon Difluoride with Paramagnetic Molecules

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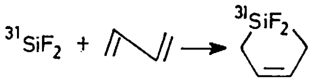
Summary Recoil ^{31}Si atom reactions with PF_3 resulted in the formation of both singlet and triplet $^{31}SiF_2$ in the ratio 1·0:3·5 where the triplet species was found to interact with paramagnetic molecules forming $^{31}SiF_2$-donor complexes towards buta-1,3-diene.

Essentially all the present information on the chemistry of silicon difluoride is due to Margrave and his co-workers through their cocondensation experiments.[1] Spectroscopic evidence points to a singlet ground electronic state for SiF_2.[2] The absence of an e.s.r. signal indicates that the SiF_2 formed by the Si + SiF_4 reaction in the cocondensation studies is ground state singlet.[3] Even now, excited triplet SiF_2 is unknown chemically.[1b]

Recently we reported the formation of monomeric $^{31}SiF_2$ by the nuclear recoil technique[4] and the addition of the $^{31}SiF_2$ thus formed to buta-1,3-diene giving 1,1-difluoro[^{31}Si]-silacyclopent-3-ene (DFSCP).[5] A study of the effect of various additives on this reaction has revealed three basic patterns. For the first type, which includes N_2O, CO, propene, and isobutene, the addition of as much as 20% of each of these molecules has no apparent effect on the observed DFSCP specific yields. The second type includes NO and NO_2 which surprisingly increase the yield by a factor of 4·5. Such an increase can be caused by as little as 0·25% NO, and no further change was observed up to 20% NO. The third type of behaviour is observed with O_2. In this case, the yield also increases sharply by a factor of 4 in the presence of *ca.* 0·1% O_2, but further addition of O_2 causes a decrease until at *ca.* 10% O_2 the yield returns to virtually the same as that of the pure samples. Addition of O_2 beyond 10% causes no significant decrease.

These results indicate that two kinds of species, A and B, give rise to DFSCP. Species A always gives DFSCP with or without additives, while species B only reacts to give DFSCP in the presence of molecules such as NO, NO_2, or O_2. Species A is likely to be ground state singlet $^{31}SiF_2$ primarily because of its insensitivity to typical radical scavengers such as NO and O_2. It reacts according to reaction (1) to give DFSCP. Species B is likely to be triplet $^{31}SiF_2$ because of the nature of the final product and because of its sensitivity to paramagnetic molecules. This triplet species either does not react with buta-1,3-diene or reacts with it in a stepwise fashion to initiate chain reactions forming polymeric products instead of DFSCP. It is fairly stable and unreactive and survives for at least several hundred collisions in a PF_3–buta-1,3-diene system before it interacts with NO. Such stability would not be expected for a ^{31}Si atom or a ^{31}SiF radical in a PF_3–buta-1,3-diene system because they are likely to undergo either F-abstraction or double-bond additions. However, triplet $^{31}SiF_2$, though electronically excited, may possess stability similar to that of its singlet counterpart whose half-life at 0·1 Torr is 150 s.[6]


(1)

Explanation of the effect of paramagnetic molecules on triplet $^{31}SiF_2$ in terms of a spin conversion process giving singlet $^{31}SiF_2$ which then adds to buta-1,3-diene to give DFSCP, is ruled out by results from O_2-addition systems. It is impossible for traces of O_2 to initiate a spin conversion which is then reversed by further addition of O_2.

A more plausible explanation is that paramagnetic molecules form complexes with triplet $^{31}SiF_2$ which then act as $^{31}SiF_2$-donors on collision with buta-1,3-diene to give DFSCP thereby regenerating the paramagnetic molecules. (In the cocondensation experiment, singlet SiF_2 has been postulated to form complexes with NO dimers.[7]) In the case of O_2, the $^{31}SiF_2$–O_2 complex may either react with buta-1,3-diene to give DFSCP or be tied up with other O_2 molecules to give some species which can no longer donate $^{31}SiF_2$. Since the latter process is somewhat more efficient than the former, only a 10% O_2 concentration is required to destroy all the $^{31}SiF_2$-donating agents.

The quantitative results show that the ratio of singlet $^{31}SiF_2$ to triplet $^{31}SiF_2$ formed in this recoil ^{31}Si system is *ca.* 1·0:3·5.

The authors acknowledge financial support by the U.S. A.E.C. and the irradiation time provided by the Texas A&M cyclotron Institute and Nuclear Science Center.

(*Received*, 20*th November* 1974; *Com.* 1410.)

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