Fluorine Atom Shift in 1,2-Difluoroethyl Radicals

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Summary Subsequent to the addition of tritium atoms to *trans*- and *cis*-1,2-difluoroethylene, the resultant 1,2-difluoroethyl radical undergoes a 1,2-F-shift *via* a bridged intermediate to give $CHT{=}CF_2$ as a final decomposition product

THE shift of chlorine and bromine atoms in free radicals has been well established for at least two decades[1,2] However, unambiguous evidence for the occurrence of the corresponding fluorine atom shift in fluorine-containing radicals is still lacking In 1975, Guillory and Andrews observed that during vacuum u v photolysis, *trans*-1,2-

difluoroethylene, *cis*-1,2-difluoroethylene, and 1,1-difluoroethylene underwent partial interconversion.[3] But they neither gave an explanation for the 1,2-isomerization, nor speculated as to whether or not it was molecular or free-radical in nature. The apparent migration of F atoms in complex aromatic and vinylic compounds was also observed during flash vacuum pyrolyses.[4] In the present work, we have studied recoil tritium reactions[5] with *trans*- and *cis*-1,2-difluoroethylene, and in each case tritium-labelled 1,1-difluoroethylene was observed as a major product. There is ample evidence to show that subsequent to the addition of tritium atoms (T) to CHF=CHF, the resultant 1,2-difluoroethyl radical will undergo a 1,2-F-shift to give $CHT=CF_2$ as a final decomposition product.

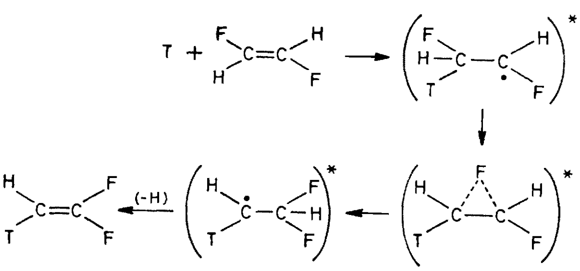
• Recoil tritium atoms were generated *via* the nuclear transmutation, $^3He(n,p)^3H$. *trans*- and *cis*-1,2-Difluoroethylene were obtained from PCR Inc. as a mixture which was separated and purified by gas chromatography. Samples containing ^3He and the parent compound were irradiated with the Texas A&M Nuclear Science Center reactor. The tritium-labelled products were analysed by radio-gas chromatography.[6]

The major products observed in these systems included HT (the H-abstraction product), the tritium-labelled parent compound, its geometric isomer, C_2H_2TF (the apparent T-for-F substitution product), and $CHT=CF_2$ (the structural isomer of the parent compound). Of these products, the observation of the structural isomer was totally unexpected.

The geometric isomer of the parent compound can be formed *via* two different routes: (i) T-for-H substitution followed by isomerization, and (ii) the addition of tritium atoms to the double bond of CHF=CHF to give the CHTF–CHF radical which subsequently decomposes by H-elimination.[5] The fact that the *trans-/cis-* product ratio is 7/3 from *trans-* and 3/7 from *cis-*, together with the fact that such ratios are not sensitive to the addition of He as a moderator means that most of the observed CHF=CTF was formed *via* the direct T-for-H substitution process.

The $CHT=CF_2$ yields are of similar magnitude to those of *trans-* and *cis*-CHF=CTF. Its yield relative to those of the parent compounds decreases with increasing pressure and with the addition of O_2 as a radical scavenger. This indicates that $CHT=CF_2$ is formed *via* the decomposition of a hot radical. The excitation energy of the hot radical must be derived mainly from the exothermicity of the addition reaction of the T atom to the double bond. This conclusion was arrived at after the observation that the yield of $CHT=CF_2$ was not diminished when a large excess of He was added to thermalize the tritium atoms.

A possible mechanism for the formation of $CHT=CF_2$ in the present system involves the addition of tritium atoms to CHF=CHF to give a CHTF–CHF radical which isomerizes *via* a 1,2-F-shift to give a CHF_2–CHT radical; this radical subsequently decomposes by eliminating an H atom to give the final product. A bridged intermediate similar to those proposed in the rearrangement process of chloro- and bromo-compounds[1,2] is also probably involved in the present 1,2-F-shift radical isomerization process. The single electron on the carbon interacts with the unbonded electron pairs of F atoms to form the bridge. The sequence of steps is illustrated in equation (1) with *trans*-CHF=CHF as the parent compound.



(1)

$$T + CH_2{=}CF_2 \longrightarrow CH_2T{-}\dot{C}F_2 \qquad (2)$$

In the corresponding system of recoil tritium reactions with $CH_2=CF_2$, the observed yields of CHF=CTF amount only to *ca.* 4% relative to those of the tritium-labelled parent compound. This is due to the fact that the tritium atom addition should take place almost exclusively at the $=CH_2$ group [equation (2)].[7,8] It is difficult for the resultant $CH_2T–CF_2\cdot$ radical to form a bridged intermediate to facilitate the 1,2-F-shift process.

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