

## 1,2-Fluorine Atom Migration in the 1,1,2-Trifluoroethyl Radical

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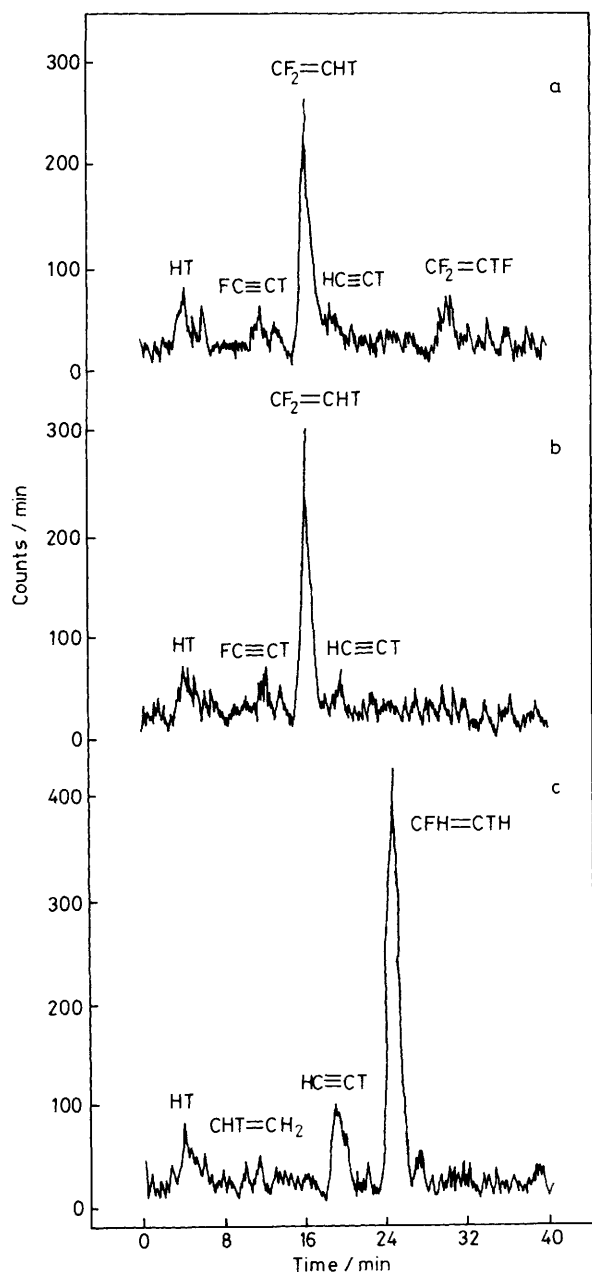
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The reactions of energetic tritium (T) with 1,1,2-trifluoroethylene suggest that the excited  $\cdot\text{CF}_2\text{CHTF}$  radical formed by tritium addition undergoes 1,2-fluorine migration, and eventually gives  $\text{CF}_2=\text{CHT}$  as the major product.

Chlorine and bromine have been found to undergo 1,2-migration readily in various chemical species,<sup>1-3</sup> whereas 1,2-migration of fluorine is rare.<sup>4-6</sup> Recently, Siefert *et al.* have investigated the reactions of recoil tritium with *cis*- and *trans*-difluoroethylenes, and found that the tritium-labelled parent molecules are formed mainly by the direct T-for-H substitution process, and that the  $\text{CHTF}-\dot{\text{C}}\text{HF}$  radical formed by the recoil tritium addition process undergoes 1,2-fluorine

migration to give  $\text{CF}_2=\text{CHT}$  as final decomposition product.<sup>7</sup> In the present work, reactions of energetic tritium atoms with 1,1,2-trifluoroethylene and with 1,1-difluoroethylene and vinyl fluoride for comparison have been studied.

Energetic tritium atoms were produced by the nuclear reaction  ${}^3\text{He}(\text{n,p})\text{T}$ . Sample mixtures containing the fluorinated ethylenes and  ${}^3\text{He}$  were exposed to neutrons in an irradiation chamber of the TRIGA Mark II reactor of the



**Figure 1.** Radio-gas chromatograms of tritium-labelled products from the reactions of energetic tritium atoms with (a)  $\text{CF}_2=\text{CHF}$ , (b)  $\text{CF}_2=\text{CH}_2$ , and (c)  $\text{CFH}=\text{CH}_2$ .

Musashi Institute of Technology. The radioactive tritium-labelled products in each irradiated sample were assayed using radio-gas chromatography.

The results, examples of which are in Figure 1, show the following. (i) In energetic tritium reactions with 1,1,2-trifluoroethylene (Figure 1a), tritium-labelled 1,1-difluoroethylene  $\text{CF}_2=\text{CHT}$  was produced in unexpectedly high yield, whereas the tritium-labelled parent compound  $\text{CF}_2=\text{CTF}$  was a minor product, as were  $\text{TC}\equiv\text{CF}$  and  $\text{TC}\equiv\text{CH}$ . (ii) In the cases of 1,1-difluoroethylene and vinyl fluoride (Figure 1b and c) the major products were the tritium-labelled parent compounds  $\text{CF}_2=\text{CHT}$  and  $\text{CFH}=\text{CHT}$ , respectively; the minor products were  $\text{TC}\equiv\text{CF}$ ,  $\text{TC}\equiv\text{CH}$ , and  $\text{CHT}=\text{CH}_2$ . It is well known that thermal hydrogen atoms preferentially add to the less substituted carbon atom of fluorinated ethylenes.<sup>8</sup>

Therefore, tritium should also add to the less fluorinated carbon atom. In the case of 1,1,2-trifluoroethylene, most of the tritium atoms should add to the  $=\text{CHF}$  group; accordingly the excited radical  $\cdot\text{CF}_2-\text{CHTF}$  is mainly formed. Since the C-F bond is stronger than the C-H and C-T bonds, the major tritium-labelled product formed from the radical by elimination should be  $\text{CF}_2=\text{CFT}$ , and  $\text{CF}_2=\text{CHT}$  should be a minor product. However, an unexpectedly large amount of  $\text{CF}_2=\text{CHT}$  was obtained experimentally. This apparent contradiction may be explained by the following mechanism involving a 1,2-fluorine atom migration. The excited  $\cdot\text{CF}_2-\text{CHTF}$  radical is converted into the alternative excited radical  $\text{CF}_3-\dot{\text{C}}\text{HT}$  by 1,2-fluorine migration, in which a fluorine-bridged complex may be formed as an intermediate. The tritium-labelled 1,1-difluoroethylene may then be readily formed by the expulsion of a fluorine atom from the  $-\text{CF}_3$  group of the excited  $\text{CF}_3-\dot{\text{C}}\text{HT}$  radical. In this system, it is difficult for the  $\cdot\text{CF}_2-\text{CHTF}$  radical to form a hydrogen-bridged complex to facilitate 1,2-hydrogen migration. If the radical were capable of this migration, the tritium-labelled parent compound  $\text{CF}_2=\text{CFT}$  would be produced in high yield.

Scott and Jennings investigated the addition of thermal hydrogen atoms to trifluoroethylene.<sup>8</sup> They irradiated hydrogen containing a small amount of 1,1,2-trifluoroethylene with a drop of mercury with a low-pressure mercury lamp, and the products were analysed by gas chromatography and mass spectrometry. An unexpected product,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ , was obtained in high yield, but the mechanism for its formation was not discussed. We may now provide an explanation by the following mechanism, involving 1,2-fluorine migration. The excited  $\cdot\text{CF}_2-\text{CH}_2\text{F}$  radical, formed by the addition of hydrogen to  $\text{CF}_2=\text{CHF}$ , is converted into the excited  $\text{CF}_3-\dot{\text{C}}\text{H}_2$  radical by 1,2-fluorine migration. The unexpected  $\text{C}_4$ -product  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$  can be formed from the  $\text{CF}_3-\dot{\text{C}}\text{H}_2$  radicals by an association process after collisional deactivation.

In the case of the 1,1-difluoroethylene system, the tritium atom adds almost exclusively to the  $=\text{CH}_2$  group, and so the excited  $\cdot\text{CF}_2-\text{CH}_2\text{T}$  radical is mainly formed. This radical is not capable of 1,2-fluorine migration, since both fluorine atoms are bound to a radical carbon. As a result, the tritium-labelled parent compound  $\text{CF}_2=\text{CHT}$  is formed on elimination of hydrogen from the radical. No *cis*- or *trans*-1,2-difluoroethylene was found, demonstrating that such a 1,2-fluorine migration does not easily occur in this system.

The activation energies of the 1,2-fluorine and 1,2-hydrogen migration reactions in 1,1,2-trifluoroethyl and 1,2-difluoroethyl radicals were estimated by INDO calculations. The results suggest that the excited  $\cdot\text{CF}_2-\text{CHTF}$  and  $\cdot\text{CFH}-\text{CFHT}$  radicals are energetically capable of 1,2-fluorine, but not 1,2-hydrogen, migration.

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