

Experimental Evidence for 1,2-Fluorine Atom Migration in Tritiated 1,1,2-Trifluoroethyl Radical

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Tritiated compounds containing 2,2,2-trifluoroethyl groups were formed by the reaction of tritium atoms with trifluoroethylene. The result can be accepted as definitive evidence for a 1,2-fluorine atom migration occurring in the reaction intermediate, tritiated 1,1,2-trifluoroethyl radical.

Introduction

Although there are a number of studies on the reactions of recoil tritium atoms with organic compounds, similar studies with fluorinated olefines are rare [1–4]. We therefore have investigated the reactions of recoil tritium atoms with vinyl fluoride, 1,1-difluoroethylene, and trifluoroethylene [5]. We suggested that the 1,2-migration of a fluorine atom occurred in the tritiated 1,1,2-trifluoroethyl radical (CHTF–CF₂) which was formed by the addition reaction of a tritium atom to trifluoroethylene.

The objective of the present work is to experimentally obtain definitive evidence that the CHTF–CF₂ radical undergoes 1,2-fluorine atom migration, through a more detailed analysis of the products of the reaction of tritium atoms with trifluoroethylene.

Experimental

Trifluoroethylene and 1,1-difluoroethylene were supplied by Professor Ishikawa of Tokyo Institute of Technology. Other fluorinated compounds used for the identification of products were CH₂FCHF₂ (PCR) and CF₃CH₃ supplied by Central Glass Co., Japan. ³He and ⁴He were supplied by CEA (France) and Japan Helium Center, respectively. Tritium atoms were formed by the ³He(n,p)T nu-

clear reaction. Each gas was used without any further purification except for several cycles of degassing for the condensable compounds. Sample mixtures containing trifluoroethylene, ³He, and ⁴He were prepared by standard vacuum line techniques and sealed in reaction vessels of about 20 ml in volume. The compositions of the sample mixtures are summarized in Table I.

The sample mixtures were irradiated at the TRIGA Mark II reactor of the Musashi Institute of Technology for 1 h with a thermal neutron flux of $8.0 \times 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.

The tritiated products in the irradiated samples, with or without the products of the reaction of trifluoroethylene with hydrogen atoms which were formed by the mercury photosensitized decomposition of hydrogen [6], were analyzed by a Shimadzu GC-7A gas chromatograph equipped with a conventional thermal conductivity detector and a Packard Model 894 gas proportional counter. The He carrier gas was adjusted to 40 ml/min. A 4 m × 3 mm stainless steel column packed with Porapak-N (80–100 mesh, Waters Associates Inc., Milford, MA) and a 50–170 °C temperature programmed operation was well suited for separation of the products. There also were the products that could not be identified only through their retention times. Some of them could be determined on the basis of the identification of the corresponding products of hydrogen atom reactions with trifluoro-

Table I. Helium effect on reactions of tritium atoms with trifluoroethylene at constant parent pressure.

	Gas pressure [Torr]				
	15	15	15	15	15
Trifluoroethylene	15	15	15	15	15
Helium-3	60	60	60	60	60
Helium-4	0	39	138	336	465
Tritiated products	Relative yields ^a				
1,1-Difluoroethylene	192	826	1063	2108	1575
Acetylene	95	238	837	1891	595
Trifluoroethylene	1000	1000	1000	1000	1000
1,1,1-Trifluoroethane	1	51	126	304	185
1,1,1,4,4,4-Hexafluorobutane	145	n.d. ^b	1571	2513	5425
1,1,1,3,3,4-Hexafluorobutane	96	n.d. ^b	1243	2055	2395
1,1,1,3,4,4-Hexafluorobutane	178	n.d. ^b	1551	3023	4046
1,1,2,3,3,4-Hexafluorobutane	82	n.d. ^b	572	1285	1310

^a Trifluoroethylene yield is normalized to 1000; ^b not determined.

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roethylene by mass spectrometry and ^1H - and ^{19}F -NMR spectroscopy [6].

Results and Discussion

The observed yields (relative to that of $\text{CF}_2=\text{CTF}$ as 1000) of the tritiated products are summarized in Table I.

The tritiated products identified were acetylene, fluoroacetylene, ethylene, 1,1-difluoroethylene, trifluoroethylene, 1,1,2,3,3,4-hexafluorobutane, and 1,1,1-trifluoroethane, 1,1,1,4,4,4-, 1,1,1,3,3,4-, and 1,1,1,3,4,4-hexafluorobutane which contained one or two 2,2,2-trifluoroethyl groups. The peaks of fluoroacetylene and ethylene on the chromatogram were too close and too small to determine the yields of these products.

The observed relative yields of 1,1-difluoroethylene, acetylene, and 1,1,1-trifluoroethane, as shown in Table I, increased with increasing ^4He pressures up to 336 Torr, decreased with further increasing pressure. The maximum relative yields of these products were 2108, 1891, 304, respectively. The observed relative yields of 1,1,1,4,4,4-, 1,1,1,3,3,4-, 1,1,1,3,4,4-, and 1,1,2,3,3,4-hexafluorobutane monotonously increased with increasing ^4He pressures, and were 5425, 2395, 4046, 1310, respectively, at the ^4He pressure of 465 Torr.

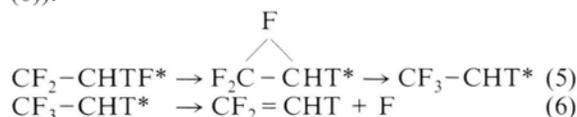
The tritiated parent compound $\text{CF}_2=\text{CTF}$ can be formed through two processes: direct substitution (shown in reaction (1)) and addition elimination (reactions (2) and (4)).



Tritiated fluoroacetylene should be formed by the elimination of HF from excited $\text{CF}_2=\text{CHT}$. It is obvious that tritiated acetylene and ethylene are decomposition products, although their formation processes are not clear yet.

The observed amount of tritiated 1,1-difluoroethylene has suggested that the excited $\text{CHTF}-\text{CF}_2$ radicals undergo a fluorine atom migration, in which a fluorine bridging complex may be formed

as the intermediate prior to decomposition as mentioned in the previous work [5] (reactions (5) and (6)).



However, the formation of $\text{CF}_2=\text{CHT}$ does not give clear-cut evidence of the fluorine atom migration, because there are possibilities for $\text{CF}_2=\text{CHT}$ to be formed by the direct T for F substitution reaction (7) and the addition-elimination sequence (reactions (2) and (8)).



The fact that tritiated 1,1,1-trifluoroethane, and three hexafluorobutanes containing one or two 2,2,2-trifluoroethyl groups were identified can be accepted as definitive evidence for the 1,2-fluorine atom migration in tritiated 1,1,2-trifluoroethyl radical. The radicals primarily formed in the reaction between tritium atom and trifluoroethylene are CF_2-CHTF and CTF_2-CHF (reactions (2) and (3)). The compounds containing 2,2,2-trifluoroethyl groups cannot be produced from these radicals. However, provided that CF_3-CHT radicals are formed from CF_2-CHTF through the 1,2-fluorine-atom process (reaction (5)), the compounds containing 2,2,2-trifluoroethyl groups can be formed by some reactions between CF_3-CHT radicals and other coexisting chemical species.

The hexafluorobutanes containing one or two 2,2,2-trifluoroethyl groups were observed as major products in the pressure range 138–465 Torr of the ^4He moderator, as shown in Table I. The results suggest that a large number of CF_3-CHT radicals were produced from $\text{CHTF}-\text{CF}_2$ radicals through the 1,2-migration process, and then were stabilized through the collision with the ^4He moderator prior to decomposition.

A 1,2-fluorine atom migration as described above has also been suggested by a theoretical study on this migration in the 1,1,2-trifluoroethyl radical [7].

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