

# Thermal Isomerization of 1,1,2,2-Tetrafluoroethane (FC-134) to 1,1,1,2-Tetrafluoroethane (FC-134a) in the Presence of Hydrogen

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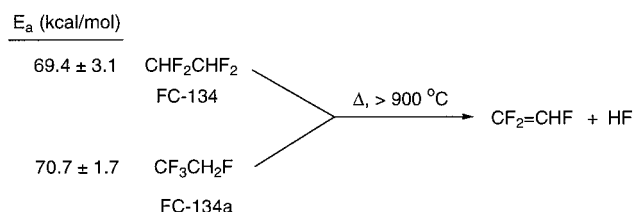
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**Abstract:** The mechanism of the high-temperature, gas-phase isomerization of 1,1,2,2-tetrafluoroethane (FC-134) to 1,1,1,2-tetrafluoroethane (FC-134a) in the presence of H<sub>2</sub> has been explored both experimentally and computationally. Studies of the impact of temperature, H<sub>2</sub>/FC-134 ratio, and contact time on conversion and yield, as well as a study of deuterium incorporation when D<sub>2</sub> was used in place of H<sub>2</sub>, led to the conclusion that a free radical chain mechanism involving rearrangement of CHF<sub>2</sub>CHF<sub>2</sub> to CF<sub>3</sub>CHF is involved.

In the accompanying paper, it is reported that the high-temperature gas-phase pyrolysis of CHClF<sub>2</sub> (FC-22) and CHF<sub>3</sub> (FC-23) in the presence of hydrogen leads to selective formation, mainly via a free radical chain process, of CH<sub>2</sub>F<sub>2</sub> (FC-32), CHF<sub>2</sub>CHF<sub>2</sub> (FC-134), and CF<sub>3</sub>CH<sub>2</sub>F (FC-134a).<sup>1</sup> In the course of this study it became apparent that, particularly at the higher temperatures studied, FC-134 was isomerizing to FC-134a under the pyrolysis conditions. Because the non-Lewis-acid-catalyzed isomerization of FC-134 to FC-134a is unprecedented, it was decided to take a closer look at this apparent H<sub>2</sub>-induced process in order to define its mechanism.

The thermal reactivities of FC-134 and FC-134a have been previously examined, with both undergoing virtually exclusive elimination of HF to form CF<sub>2</sub>=CHF at temperatures >900 °C.<sup>2,3</sup> Although small amounts of CH<sub>2</sub>F<sub>2</sub> (FC-32) and CF<sub>2</sub>=CF<sub>2</sub> (TFE) were detected, particularly at higher temperatures, no mention was made of isomerization of FC-134 to FC-134a in these early investigations.



Within the past decade, work by Kemnitz demonstrated that FC-134 will isomerize to FC-134a when it is passed over a conditioned chromia catalyst at 320–445 °C.<sup>4,5</sup> Such reactions are considered to proceed via Lewis-acid-catalyzed elimination of HF, followed by recombination of the absorbed CF<sub>2</sub>=CHF/HF to give the more thermodynamically stable CF<sub>3</sub>CH<sub>2</sub>F isomer.

Until the present work, however, there had been no reports of non-Lewis-acid-catalyzed, gas-phase thermal conversion of

FC-134 to FC-134a.<sup>6,7</sup> This is understandable in view of the unfavorable thermodynamics of this two-step reaction at the temperatures necessary to establish equilibrium between FC-134 and FC-134a, via the logical and precedented unimolecular HF elimination–bimolecular HF addition mechanism depicted by eqs 2 and 3 in Table 1, which provides all relevant experimental<sup>8</sup> and calculated (DFT) thermodynamic data.

Although the thermodynamics of the HF elimination/addition sequence (eqs 2 and 3) are quite acceptable at 25 °C (where the process is not kinetically feasible), and even at 350 °C (where the chromia-catalyzed equilibration is observed to occur), at the temperatures that are required to induce the thermal unimolecular first step (eq 2) of the sequence (>700 °C), the second, addition step (eq 3) has become a highly unfavorable reaction in terms of free energy (at 700 °C, the  $T\Delta S$  component of  $\Delta G^\circ$  is +35.4 kcal/mol, more than enough to outweigh the exothermic  $\Delta H^\circ$  of the reaction.)

The forbidding thermodynamics of the equilibria in Table 1, combined with the high activation energy of the first step (eq 2), virtually exclude this elimination–addition two-step process as a possible mechanism for the high-temperature conversion of FC-134 to FC-134a.

The present study was therefore initiated, first to demonstrate that the thermal conversion of FC-134 to FC-134a in the presence of H<sub>2</sub> actually occurs, and, if so, to determine the mechanism of this process. Indeed, it was found that, under conditions (700 °C) where FC-134 in the presence of inert gas (He) undergoes but 3.4% conversion to form 1.4% FC-134a (plus 1.2% CF<sub>2</sub>=CHF), a 29% conversion of FC-134 is observed in the presence of H<sub>2</sub> to form 25% FC-134a (plus only 0.6% CF<sub>2</sub>=CHF). A free radical chain mechanism is proposed to rationalize the results.

## Experimental Section

The CHF<sub>2</sub>CHF<sub>2</sub> isomerization reaction was carried out at atmospheric pressure and isothermally in a continuous-flow reactor, which is depicted in the accompanying paper, and using a procedure analogous to that described there.<sup>1</sup>

(6) While this work was in progress, patents from Elf Atochem appeared which provided the first mention of the H<sub>2</sub>-induced isomerization of FC-134 to FC134a.<sup>7</sup>

(7) Hub, S.; Guillet, D., FR2758556; WO983165; EP975567

(8) Burgess, D. R., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R. *Prog. Energy Combust. Sci.* **1996**, *21*, 453–529.

(1) Romelaer, R.; Kruger, V.; Baker, J. M.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6767–6772.

(2) Millward, G. E.; Hartig, R.; Tschuikow-Roux, E. *J. Phys. Chem.* **1971**, *75*, 3195–3201.

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(4) Kemnitz, E.; Niedersen, K.-U. *J. Catal.* **1995**, *155*, 283–289.

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**Table 1.** Calculated (and Experimental) Thermodynamic Data (B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d))

eq	reaction	<i>T</i> , °C	$\Delta H^\circ$ (exptl) <sup>a</sup>	$\Delta S^\circ$ (exptl) <sup>a</sup>	$\Delta G^\circ$ (exptl) <sup>a</sup>
1	CHF <sub>2</sub> CHF <sub>2</sub> ⇌ CF <sub>3</sub> CH <sub>2</sub> F	25	-5.9 (-4.3)	-0.75 (-1.3)	-5.7 (-3.9)
		350	-5.8	-0.53	-5.5
		700	-5.7	-0.44	-5.3
2	CHF <sub>2</sub> CHF <sub>2</sub> ⇌ CF <sub>2</sub> =CHF + HF	25	23.5 (27.7)	35 (34.6)	13.1 (17.4)
		350	24.7	36	2.0
		700	23.8	36	-11.2
3	CF <sub>2</sub> =CHF + HF ⇌ CF <sub>3</sub> CH <sub>2</sub> F	25	-29.4 (-31.6)	-35.7 (-35.9)	-18.8 (-20.9)
		350	-30.5	-36.9	-7.5
		700	-29.5	-36.4	6.0

<sup>a</sup> Experimental data, in parentheses, are from ref 6.

The reagents are as follow: CHF<sub>2</sub>CHF<sub>2</sub> (SynQuest Laboratories Inc., 99% minimum), CHClF<sub>2</sub> (Elf-Atochem), CH<sub>4</sub> (Matheson Gas Products Inc.), and H<sub>2</sub> and He (Strate Welding Supply Co., 95–97% and 99.995%).

The gas mixtures are passed through either a quartz or an Inconel 600 reactor, which is heated by a furnace (Applied Test Systems, Series 3210) with a temperature range from 650 to 850 °C (maximum temperature 700 °C in the case of the quartz reactor).

At the outlet, the gases are passed through a KOH solution (1 M) in order to neutralize HF and are dried by anhydrous calcium sulfate (Drierite). An internal standard, CH<sub>4</sub> for the quartz reactor or CHClF<sub>2</sub> for the Inconel reactor, is then introduced in order to determine the carbon balance and the yields after reaction and GC analysis.

The GC analysis of the gas mixture was performed on an HP chromatograph using the following operating conditions: column, 1% SP 1000, 60/40 carboxpack, 4 m × 1/8 in. stainless steel; carrier gas, N<sub>2</sub> (8 mL/min); temperature, 40 °C (10 min) to 180 °C (at 4 °C/min); detector, FID, 250 °C; injector temperature, 250 °C. The products were identified by comparison of GC retention times and mass spectra of pure samples.<sup>1</sup> Quantitative analysis of the product/standard ratios was obtained by comparison with mixtures prepared for calibration purposes. The relative response coefficients (*k<sub>i</sub>/k<sub>std</sub>*) of each compound were determined by GC-FID and are reported in the accompanying paper.<sup>1</sup>

After the determination of the inlet flow of FC-134 and the outlet flow rates of FC-134 and each product, the results given in the tables and/or represented graphically in the figures were calculated as indicated below:

$$\text{conversion of FC-134} = \frac{n(\text{CHF}_2\text{CHF}_2)_i - n(\text{CHF}_2\text{CHF}_2)_o}{n(\text{CHF}_2\text{CHF}_2)_i} \times 100$$

$$= \frac{\Delta n(\text{CHF}_2\text{CHF}_2)}{n(\text{CHF}_2\text{CHF}_2)_i} \times 100$$

where  $n(\text{CHF}_2\text{CHF}_2)_i$  is the inlet molar flow rate (mmol·h<sup>-1</sup>) and  $n(\text{CHF}_2\text{CHF}_2)_o$  is the outlet molar flow rate (mmol·h<sup>-1</sup>).

$$\text{yield (\%)} = \frac{x(\text{product flow rate}) (\text{mmol} \cdot \text{h}^{-1})}{\Delta n(\text{CHF}_2\text{CHF}_2)} \times 100$$

(from consumed FC-134)

where  $x = 1$  for C<sub>2</sub> products and  $x = 0.5$  for C<sub>1</sub> products.

carbon balance (from consumed FC-134) =  $\sum$  yields of products

overall production of FC-134a = conversion × yield of FC-134a

Reaction time:

$$t \text{ (s)} = \frac{\text{volume of the reactor (cm}^3\text{)}}{\text{total flow rate at the reaction temperature (cm}^3\text{·s}^{-1}\text{)}}$$

For the quartz reactor,  $V = 150 \text{ cm}^3$ ; for the Inconel reactor,  $V = 100 \text{ cm}^3$ .

**Computational Methodology.** Density functional theory calculations were performed using the Gaussian 98 program package. Reactants, products, intermediates, and transition structures were optimized using Becke's hybrid three-parameter functional (B3LYP) and the 6-31G(d) basis set. Restricted and unrestricted wave functions were used for closed- and open-shell species, respectively. Using the same level of theory, vibrational frequency calculations were performed on all stationary points to identify transition structures and determine thermal/zero-point energies. Transition structures were characterized by a single imaginary frequency. Thermochemical information at temperature  $T$  and  $P = 1.00 \text{ atm}$  was obtained using frequencies scaled by 0.9804.<sup>9</sup> An intrinsic reaction coordinate (IRC) calculation was performed for each transition structure to examine the reaction pathway for each elementary step. Single-point energies for each structure and transition state were calculated using the B3LYP level of theory, using the 6-311+G(2df,2p) basis set, with restricted and unrestricted wave functions being again used for closed- and open-shell species, respectively.

## Results and Discussion

The experimental investigation of the thermal behavior of CHF<sub>2</sub>CHF<sub>2</sub> (FC-134) with and without the presence of H<sub>2</sub> was carried out at atmospheric pressure and isothermally in the above-described continuous-flow reactor: from 650 to 700 °C in a quartz reactor, and from 700 to 850 °C in an Inconel 600 reactor.

The intent of the investigation was to determine the effect of the presence of hydrogen (H<sub>2</sub>) on the outcome and dynamic behavior of the reaction as compared to the results when the pyrolysis is carried out in the presence of inert gas (He), and to determine the mechanism of the observed reactions.

**Studies in the Quartz Reactor. (i) Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> (FC-134) in the Presence of He.** The pyrolysis of FC-134 in He was carried out at 700 °C, with ratios of He/CHF<sub>2</sub>CHF<sub>2</sub> ranging from 9 to 20 and the times of reaction ranging from 5 to 9 s. The FC-134 conversion and the yields of products are given in Table 2. These data indicate that, in the presence of He, FC-134 undergoes but a low conversion (2–3%), with small amounts of CF<sub>2</sub>=CHF and FC-134a being formed under these conditions.

**(ii) Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> (FC-134) in the Presence of H<sub>2</sub>.** In contrast to its inertness in He, FC-134 exhibited a significantly enhanced reactivity when pyrolyzed in the presence of H<sub>2</sub>. As seen in Table 3, although giving only a modest 3–4% conversion at 650 °C, FC-134 experienced a dramatic increase in both the degree of its conversion (14–29%) and the yield of product FC-134a (82–88%), along with an excellent carbon balance (90–95%), when the temperature of the reactor was increased to 700 °C. Contrasting these results with the mere traces of FC-134a produced in the absence of H<sub>2</sub>, they demonstrate conclusively that the presence of hydrogen during FC-134 pyrolysis promotes its isomerization to FC-134a.

**(iii) Pyrolysis of FC-134a in He and H<sub>2</sub>.** In contrast to the dramatic reactivity exhibited by FC-134 in the presence of H<sub>2</sub>, FC-134a remained virtually inert when subjected to identical reaction conditions, undergoing <1% conversion in either H<sub>2</sub> or He. Although traces of FC-134 were observed in the presence of H<sub>2</sub>, none was detected when the pyrolyses were carried out in He.<sup>10</sup>

**Studies in the Inconel Reactor.** Corroborative results were obtained when the pyrolyses of FC-134 were carried out in the Inconel 600 reactor. Use of the Inconel 600 allowed pyrolyses

(9) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(10) See Supporting Information for detailed data.

**Table 2.** Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> in Helium at 700 °C (Quartz Reactor)

conditions			yield (%)			carbon balance (%)	overall formation of CF <sub>3</sub> CH <sub>2</sub> F (%)
He/CHF <sub>2</sub> CHF <sub>2</sub>	t (s)	conv (%)	CH <sub>2</sub> F <sub>2</sub>	CF <sub>2</sub> =CHF	CF <sub>3</sub> CH <sub>2</sub> F		
9/1	5	1.9	5.7	30.1	43.1	78.9	0.8
17/1	5	1.8	> 0	36.2	36.4	72.6	0.7
12/1	8	3.5	6.2	29.7	46.3	82.2	1.6
20/1	9	3.4	6.7	34.1	41.0	81.8	1.4

**Table 3.** Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> in Hydrogen at 650 and 700 °C for Reaction Times of 5 and 9 s (Quartz Reactor)

conditions			yield (%)			carbon balance (%)	overall formation of FC-134a (%)
T (°C)	H <sub>2</sub> /CHF <sub>2</sub> CHF <sub>2</sub>	t (s)	conv (%)	CH <sub>2</sub> F <sub>2</sub>	CF <sub>2</sub> =CHF		
650	11/1	5	2.1	0	0	97.3	2.0
650	21/1	5	2.7	0	0	96.1	2.6
650	11/1	9	3.9	0	0	95.8	3.7
650	21/1	9	4.4	0	0	97.8	4.3
700	11/1	5	14.3	3.3	2.0	88.4	12.7
700	19/1	5	14.7	3.2	2.9	88.0	12.9
700	12/1	9	26.0	3.2	2.2	81.5	21.2
700	22/1	9	29.3	3.2	2.2	84.8	24.8

**Table 4.** Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> in He at 700 °C (Inconel Reactor)

conditions			yield (%)					carbon balance (%)	overall formation of CF <sub>3</sub> CH <sub>2</sub> F (%)
He/CHF <sub>2</sub> CHF <sub>2</sub>	t (s)	conv (%)	CH <sub>4</sub>	CH <sub>2</sub> F <sub>2</sub>	CF <sub>2</sub> =CF <sub>2</sub>	CF <sub>2</sub> =CHF	CF <sub>3</sub> CH <sub>2</sub> F		
23/1	4	12.7	0	1.2	36.4	10.8	5.8	54.2	0.7
14/1	4	25.7	0	1.8	20.9	6.8	4.5	34.0	1.1
4/1	12	34.8	0	2.6	7.1	5.6	6.6	21.9	2.3

**Table 5.** Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> in H<sub>2</sub> at 700 °C (Inconel Reactor)

conditions			yield (%)					carbon balance (%)	overall formation of CF <sub>3</sub> CH <sub>2</sub> F (%)
H <sub>2</sub> /CHF <sub>2</sub> CHF <sub>2</sub>	t (s)	conv (%)	CH <sub>4</sub>	CH <sub>2</sub> F <sub>2</sub>	CF <sub>2</sub> =CF <sub>2</sub>	CF <sub>2</sub> =CHF	CF <sub>3</sub> CH <sub>2</sub> F		
18/1	6	33.2	1.2	12.6	0.6	2.5	62.5	79.4	20.8
11/1	6	32.2	1.1	12.4	0.8	2.8	60.5	77.6	19.5
8/1	6	28.5	1.3	11.8	1.1	3.2	57.6	75.0	16.4
6/1	22	39.7	1.9	10.9	0	3.0	69.6	85.4	27.6
3/1	29	38.4	1.6	10.3	0	3.1	66.3	81.3	25.5
1/1	32	34.3	0.8	9.3	0	0.8	55.3	66.2	19.0

**Table 6.** Pyrolysis of CHF<sub>2</sub>CHF<sub>2</sub> in H<sub>2</sub> between 650 and 850 °C (Inconel Reactor)

conditions			yield (%)					carbon balance (%)	overall formation of CF <sub>3</sub> CH <sub>2</sub> F (%)	
T (°C)	H <sub>2</sub> /CHF <sub>2</sub> CHF <sub>2</sub>	t (s)	conv (%)	CH <sub>4</sub>	CH <sub>2</sub> F <sub>2</sub>	CF <sub>2</sub> =CF <sub>2</sub>	CF <sub>2</sub> =CHF			CF <sub>3</sub> CH <sub>2</sub> F
650	17/1	6	14.7	1.2	3.5	2.0	1.8	25.1	33.5	3.7
700	18/1	6	33.2	1.2	12.6	0.6	2.5	62.5	79.4	20.8
750	15/1	6	65.3	2.2	11.3	0	1.4	74.9	89.8	48.9
800	15/1	5	92.0	6.5	12.2	0	1.0	59.6	79.3	54.8
850	18/1	5	100	28.9	11.9	0	0	20.3	61.1	20.3

to be carried out at considerably higher temperatures (up to 850 °C, where up to 100% conversion of FC-134 could be observed), but disadvantageously, the metal reactor gave rise to competitive, reactor-induced dehydrogenative/hydrogenative processes, which lowered the yield of FC-134a formation.

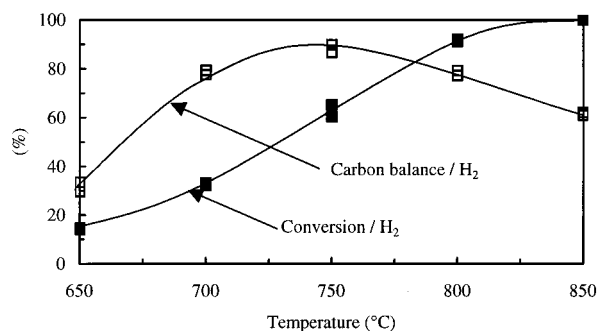
The results given in Tables 2, 3, 4 and 5 allow a direct comparison of results in quartz and Inconel at 700 °C. It can be seen that, whereas conversion of FC-134 in the presence of He (Table 4) increases in the Inconel reactor, the yields of FC-134a do not, and carbon balances are low (mostly due to formation of "heavy products", such as CF<sub>2</sub>=CHCF<sub>3</sub> and CF<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>, which were detected by GC/MS, but not quantified). The increased conversions derive largely from the emergence of a new product, C<sub>2</sub>F<sub>4</sub> (TFE), the formation of which was undoubtedly catalyzed by the reactor wall (since it was not observed during the studies in the quartz reactor).

In the presence of H<sub>2</sub>, conversions increased significantly (Table 5) compared to those in He, but mass balances suffer

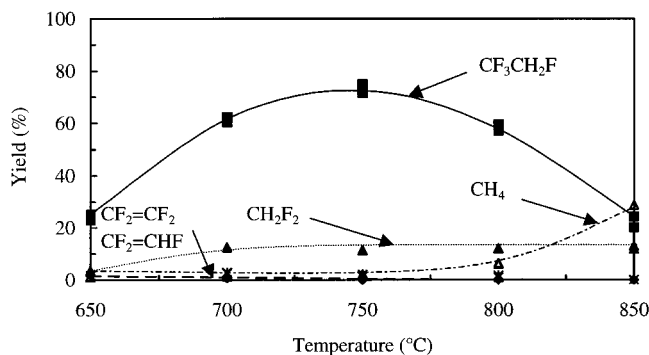
and the yields of FC-134a are not so high as those observed in quartz (65% vs 88%). Nevertheless, H<sub>2</sub> promotion of the isomerization of FC-134 to FC-134a is clearly demonstrated by the contrasting data in Tables 4 and 5.

Methane appears as a new product in the presence of H<sub>2</sub>, formed by wall catalysis, with little TFE being observed. The lack of TFE is not surprising, since it has already been demonstrated that, at such temperatures, H<sub>2</sub> promotes the efficient conversion of TFE to the trio of products, CH<sub>2</sub>F<sub>2</sub>, FC-134, and FC-134a.<sup>1</sup>

**(i) Temperature Dependence.** Pyrolysis of FC-134 in the absence of H<sub>2</sub>, even at temperatures as high as 850 °C, leads to little formation of FC-134a (no more than 5.8%), despite an increase in conversion of FC-134 from 12% (at 650 °C) to 93% (at 850 °C).<sup>10</sup> In contrast, as seen in Table 6 and graphically depicted in Figures 1 and 2, when H<sub>2</sub> is present, conversions of FC-134 increase sharply with temperature (65% at 750 °C, 92% at 800 °C, and 100% at 850 °C), as do yields and overall



**Figure 1.** Conversion and carbon balance vs temperature during pyrolysis of  $\text{CHF}_2\text{CHF}_2$  in  $\text{H}_2$  (Inconel 600 reactor).



**Figure 2.** Product yields vs temperature during pyrolysis of  $\text{CHF}_2\text{CHF}_2$  in  $\text{H}_2$  (Inconel 600 reactor).

productions of FC-134a, with these reaching a maximum at about 750 °C, where values of 75% and 49%, respectively, are observed.

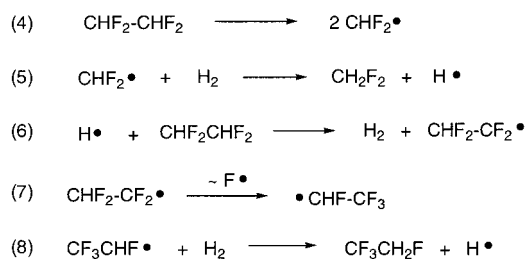
From these results, the optimal conditions for conversion of FC-134 to FC-134a can be stated as follows:

(a) For Inconel 600 reactor: 750 °C,  $\text{H}_2/\text{FC-134} = 10$ , contact time = 5 s; to obtain 60% conversion, 75% yield, and thus 49% overall production.

(b) For quartz reactor: 700 °C,  $\text{H}_2/\text{FC-134} = 12$ , contact time = 9 s; to obtain 26% conversion, 81% yield, and 21% overall production.

**Mechanistic Hypothesis.** Although there can be no doubt that the presence of  $\text{H}_2$  promotes the specific conversion of FC-134 to FC-134a, the question of the mechanism of this isomerization remained unsettled at this point in the study. One can be certain, however, based on our knowledge of the thermodynamics of the potential two-step elimination–addition mechanism (Table 1) and confirmed by results of FC-134 pyrolyses in He, that this mechanism cannot be operative.

The formation of small but significant amounts of  $\text{CH}_2\text{F}_2$  (FC-32) in the reaction, and the lack of viable mechanistic alternatives, induced us to consider a free radical chain mechanism for the process. As a hypothesis, it was proposed that carbon–carbon bond homolysis of FC-134 could lead to initiation of the free radical chain mechanism depicted below:



**Table 7.** Calculations on 1,2-F and 1,2-H Radical Rearrangements

equation	calcd $E^\ddagger$ <sup>a</sup>		reaction enthalpies <sup>a</sup>		
	INDO <sup>b</sup>	DFT <sup>c</sup>	INDO <sup>b</sup>	DFT <sup>c</sup>	expt <sup>d</sup>
F-shift $\text{CF}_2\text{CHF}_2 \rightarrow \text{CF}_3\text{CHF}\bullet$	25.9	29.2	-6.1	-6.6	-3.8
H-shift $\text{CF}_2\text{CHF}_2 \rightarrow \text{CHF}_2\text{CF}_2\bullet$	56.1	56.1	0	0	0

<sup>a</sup> In kcal/mol. <sup>b</sup> Reference 13. <sup>c</sup> This work (UB3LYP/6-311+G-(2df,2p)//UB3LYP/6-31G(d)). <sup>d</sup> Reference 8.

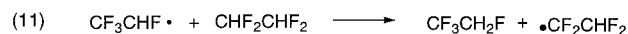
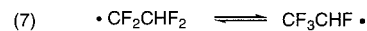
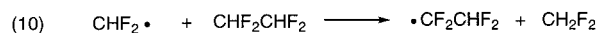
Although the homolysis step (4) has an  $E_a$  of ~91–93 kcal/mol (BDE of FC-134),<sup>8</sup> since this is an *initiation* step, few such radicals are required to get the free radical chain process started. The essential role of hydrogen, as a promoter of the free radical chain mechanism, derives from the relative facility of steps (5) and (6), which apparently serve as an efficient pathway to radical  $\text{CHF}_2\text{CF}_2\bullet$ . Values of 9.8 and 10.6 kcal/mol are reported as the  $E_a$ 's for the H-atom-transfer steps (5)<sup>11,12</sup> and (6),<sup>8</sup> respectively. Although bimolecular, with such low activation barriers these steps should be kinetically viable.

Perhaps the most interesting if not controversial step in the proposed mechanism is the fluorine radical shift in step 7. Reports of fluorine atom shifts in carbon radical systems are rare, but such rearrangements nevertheless appear to be relatively facile, much more so than the analogous H atom shifts.<sup>13–18</sup> In 1988, Kotaka examined the specific F-shift of eq 7 by semi-empirical calculations,<sup>13</sup> with his results being given in Table 7. Our own DFT calculations, also given in Table 7, were consistent with Kotaka's INDO calculations, and they indicated an  $E^\ddagger$  of only 29.2 kcal/mol for this unimolecular 1,2-F atom shift.

Using the DFT activation parameters for the F-shift in Table 7, a rate constant of  $3 \times 10^6 \text{ s}^{-1}$  at 700 °C was calculated. Although there are no reported kinetic parameters for the reverse of eq 6, using the experimental rate parameters<sup>8</sup> for the reaction of  $\text{CF}_3\bullet$  with  $\text{H}_2$  (and assuming an  $[\text{H}_2]$  of 0.012 M) to estimate that process, it appears that the F-shift should be kinetically competitive.

It is interesting that the calculated activation energy for the degenerate 1,2-H atom shift is much higher (56.1 kcal/mol), thus indicating that a 1,2-F radical shift is significantly more facile than an analogous 1,2-H shift.

It is necessary to comment on why the radical chain rearrangement process should be significantly less efficient in the absence of  $\text{H}_2$ . Although an analogous free radical chain mechanism, depicted by eqs 10, 7, and 11, below, is potentially



available when FC-134 is pyrolyzed either alone or in the presence of He, such a process is observed to be much less

(11) This is actually a mean value for the reaction of  $\text{CF}_3\bullet$  with  $\text{H}_2$ .

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**Table 8.** Conversion, Yield, and Carbon Balance Obtained during the CHF<sub>2</sub>CHF<sub>2</sub> Thermal Activation in H<sub>2</sub> and in D<sub>2</sub> at 700 °C (Quartz Reactor)

conditions		conv (%)	yield (%)		carbon balance (%)
H <sub>2</sub> /D <sub>2</sub> /CHF <sub>2</sub> CHF <sub>2</sub>	t (s)		CH <sub>2</sub> F <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> F	
15/0/1	5	21	6	88	94
0/15/1	5	20	5 <sup>a</sup>	86 <sup>a</sup>	91

<sup>a</sup> Partially deuterated products are obtained (see Table 9).

efficient than that which occurs in the presence of H<sub>2</sub>. Its relative inefficiency must derive from the smaller rate constants of the propagation steps (10) and (11),<sup>8</sup> when compared with those of the alternative, better propagation steps (5), (6), and (8) that are available in the presence of H<sub>2</sub>.

**D<sub>2</sub> Experiments.** To determine the degree of involvement of H<sub>2</sub> in the rearrangement mechanism, as well as to probe the nature of that involvement, the reaction was carried out using D<sub>2</sub> in place of H<sub>2</sub>. The quartz reactor was used in order to avoid complications due to reactor-induced, catalytic H<sub>2</sub> processes. The results are given in Tables 8 and 9, which allow direct comparison of H<sub>2</sub> and D<sub>2</sub> results.

From the data in Table 8, it can be seen that conversion of FC-134 is not significantly affected by substitution of D<sub>2</sub> for H<sub>2</sub>, and that there is no apparent kinetic isotope effect in the rate-determining process of isomerization. There is also no effect upon the yield of FC-134a.

Looking at the deuterium distribution in the product mixture (Table 9), it is seen that deuterium incorporation is significant, thus ruling out any purely intramolecular mechanism, or the simple elimination–addition mechanism (eqs 2 and 3). The results almost certainly confirm the free radical nature of the rearrangement process. The major isotopomer of product FC-134a formed is the monodeuterio product, with little undeuterated product being observed.

Recovered, nonconverted FC-134 also exhibits significant deuterium incorporation. Indeed, looking at the total deuterium

**Table 9.** Deuterated Compounds Distribution Determined by GC/MS and Yields Obtained during the CHF<sub>2</sub>CHF<sub>2</sub> Pyrolysis in D<sub>2</sub> (700 °C, D<sub>2</sub>/CHF<sub>2</sub>CHF<sub>2</sub> = 15, t = 5 s, New Quartz Reactor)

compounds	GC/MS distribution (%)	overall production (%)
CF <sub>3</sub> CH <sub>2</sub> F	4	1
CF <sub>3</sub> CHDF	84	14
CF <sub>3</sub> CD <sub>2</sub> F	12	2
CHF <sub>2</sub> CHF <sub>2</sub>	76	61
CHF <sub>2</sub> CDF <sub>2</sub>	22	18
CDF <sub>2</sub> CDF <sub>2</sub>	2	1

content of the product mixture, an almost equal amount of deuterium has been incorporated into recovered FC-134 (20% deuterium “yield”) as into product FC-134a (18% deuterium “yield”). The incorporation of deuterium into both starting FC-134 and product FC-134a is readily explained within the context of the proposed radical chain mechanism, but not by other, nonradical mechanisms.

## Conclusions

On the basis of the sum of the evidence, and in the absence of a reasonable alternative, it is concluded that the mechanism for the H<sub>2</sub>-induced isomerization of FC-134 to its more thermodynamically stable isomer, FC-134a, proceeds via the proposed free radical chain mechanism.

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**Supporting Information Available:** Computational data tables and supplementary tables and figures that describe thermolysis data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. <

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