J. Am. Chem. Soc. **2001,** *123,* 6767−6772 6767

Pyrolyses of Chlorodifluoromethane and Trifluoromethane in the Presence of Hydrogen. Mechanism and Optimization of Reaction Conditions

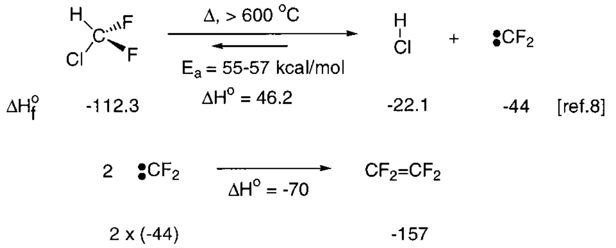
Raphaele Romelaer, Virginie Kruger, J. Marshall Baker, and William R. Dolbier, Jr.*

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

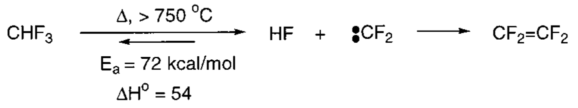
Received June 29, 2000

Abstract: When $CHClF_2$ and CHF_3 are subjected to high-temperature, gas-phase flow pyrolysis in the presence of H_2, they are converted, via a free radical chain mechanism, to CH_2F_2, CHF_2CHF_2, and CF_3CH_2F in good yield. Optimal conditions for pyrolysis of $CHClF_2$ involve a high conversion (92%) at 650 °C with an observed yield of products = 18, 17, and 28%, respectively, whereas optimal conditions for CHF_3 involve a low conversion (24%) at 775 °C, but a higher yield of products (26, 6, and 39%, respectively).

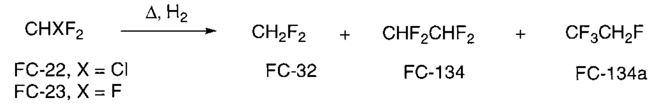
The high-temperature (>600 °C) pyrolysis of chlorodifluoromethane (FC-22) comprises the major industrial source of tetrafluoroethylene (TFE).[1,2] The mechanism of this process has been demonstrated to involve unimolecular extrusion of molecular HCl to form difluorocarbene [CF_2:], which then dimerizes to form TFE.[3] The kinetic and thermodynamic parameters associated with this reaction have been studied extensively, both experimentally and theoretically,[4−8] and although there remains ambiguity in some of the values, particularly with respect to the heat of formation of CF_2: (recommended value, −44 kcal/mol),[9] the reaction is considered chemically and thermochemically very well defined, with reversible formation of CF_2: competing with its dimerization to form TFE.



The pyrolysis of CHF_3 (FC-23), although much less studied and requiring considerably higher temperatures (>750 °C), follows essentially the same mechanistic course, and it therefore also comprises a potentially useful source of TFE.[7,10−12]



In an effort to develop broader use of these ready sources of CF_2:, studies of copyrolysis of $CHClF_2$ with hydrogen were carried out independently by Elf Atochem[13] and DuPont,[14] and it was discovered that under appropriate conditions this process leads to effective quenching of TFE formation with resultant formation of CH_2F_2 (FC-32), CHF_2CHF_2 (FC-134), and CF_3CH_2F (FC-134a).



Brief mention of a pyrolytic reaction of $CHClF_2$ with H_2 to form CH_2F_2 had been made by DiFelice and Ritter in 1994.[15] These authors interpreted the CH_2F_2 formation as deriving from competitive insertion of CF_2: into H_2, and no mention was made of either CHF_2CHF_2 or CF_3CH_2F being formed.

Co-pyrolysis of CHF_3 (FC-23) with H_2 led to similar results.[16]

In view of the commercial interest in hydrofluorocarbons (HFC's) such as CH_2F_2 and CF_3CH_2F, a study of the mechanisms of these reactions was initiated in order to determine how modification of reaction conditions might affect product yields and selectivities.

---

(1) Park, J. D.; Benning, A. F.; Downing, F. B.; Lancery, J. F.; McHarness, R. C. *Ind. Eng. Chem.* **1947**, *39*, 354.

(2) Hamilton, J. M., Jr. In *Advances in Fluorine Chemistry*; Stacey, M., Tatlow, J. C., Sharpe, A. G., Eds.; Butterworth: Washington, 1963; Vol. 3, pp 117−180.

(3) Hudlicky, M. *Chemie der Organischen Fluoroverbindungen*; Veb Deutscher Verlag der Wissenschaften: Berlin, 1960.

(4) Gozzo, F.; Patrick, C. R. *Tetrahedron* **1966**, *22*, 3329−3336.

(5) Edwards, J. W.; Small, P. A. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 396−400.

(6) Barnes, G. R.; Cox, R. A.; Simmons, R. F. *J. Chem. Soc. B* **1971**, 1176−1180.

(7) Schug, K. P.; Wagner, H. G.; Zabel, F. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 167−175.

(8) Su, M.-C.; Kumaran, S. S.; Lim, K. P.; Michael, J. V.; Wagner, A. F.; Dixon, D. A.; Kiefer, J. H.; DiFelice, J. *J. Phys. Chem.* **1996**, *100*, 15827−15833.

(9) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5573−5580.

(10) Tschuikow-Roux, E.; Marte, J. E. *J. Chem. Phys.* **1965**, *42*, 2049−2056.

(11) Tschuikow-Roux, E. *J. Chem. Phys.* **1965**, *42*, 3639−3642.

(12) Politanskii, S. F.; Shevchuk, V. U. *Kinet. Catal.* **1968**, *9*, 411−417.

(13) Schirmann, J.-P.; Hub, S.; Lantz, A. Patent WO 96/25377, 1996.

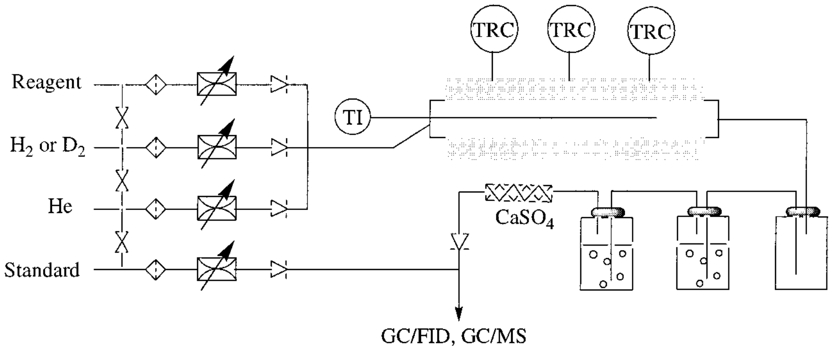
(14) Manogue, W. H.; Noelke, C. J.; Swearingen, S. H. Patent WO 95/24369, 1995.

(15) DiFelice, J. J.; Ritter, E. R. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, Spring 1994, San Diego, CA; American Chemical Society: Washington, DC, 1994; 24-Fuel, pp 158−162.

(16) Private communication, E. Lacroix and S. Hub.

10.1021/ja0023581 CCC: $20.00

Chart 1



Experimental Section

Pyrolysis. The pyrolyses of $CHClF_2$ or CHF_3 in the presence of H_2 were carried out at atmospheric pressure and isothermally in a continuous-flow reactor (Chart 1).

All gas inlets were controlled by the four mass flow meters (Brooks). Sources of the chemicals were as follows: $CHClF_2$ (Elf Atochem), CHF_3 (Elf Atochem, 95%), D_2 (Strate Welding Supply Co., 99.7%), and H_2 and He (Strate Welding Supply Co., 95−97% and 99.995%).

The gas mixtures passed through the quartz reactor ($CHClF_2$ pyrolysis) or the Inconel 600 reactor (CHF_3 pyrolysis), which is heated by a furnace (Applied Test Systems, Series 3210) with three thermocouples. Three Omega controllers (CN 76000) (indicated as TRC in Chart 1) control the temperature of the three-heating-zone furnace. The temperature inside the reactor is indicated by a thermocouple (Omega, Type K) with three junctions (indicated as TI in Chart 1).

At the outlet, the gases are passed through a KOH solution (1 M) in order to neutralize HCl and HF and are dried by anhydrous calcium sulfate (Drierite). An internal standard, CH_4 ($CHClF_2$ pyrolysis) or $CHClF_2$ (CHF_3 pyrolysis), is then introduced in order to determine conversion, yields, and carbon balance after reaction and GC analysis. The reaction time (t) represents the ratio between the reactor volume (quartz, $V = 150$ cm^3; Inconel reactor, $V = 100$ cm^3) and the total flow rate at the reaction temperature (cm^3·s^{-1}).

The GC analysis of the gas mixture was performed on a HP chromatograph using the following operating conditions: column, Plot Al_2O_3/KCl (Chrompack), 50 m × 0.53 mm, film 10 μm; carrier gas, N_2 (11 mL/min); temperature, 40 °C (5 min) to 200 °C (at 4 °C/min); detector, FID, 250 °C; injector temperature, 250 °C. The products were identified by comparison of their GC retention times and mass spectra with those of pure samples. Quantitative analyses of the product/standard ratios were obtained by comparison with mixtures prepared for calibration purposes. The relative response coefficients (k_i/k_{std}) of each compound are given in Table 1.

After the determination of the inlet flow of $CHXF_2$ and the outlet flow rates of $CHXF_2$ and each product, the results given in the tables and represented graphically in the figures were calculated as indicated below (X = Cl or F):

$$\text{conversion of } CHXF_2 = \frac{n(CHXF_2)_i - n(CHXF_2)_o}{n(CHXF_2)_i} \times 100 = \frac{\Delta n(CHXF_2)}{n(CHXF_2)_i} \times 100$$

where $n(CHXF_2)_i$ is the inlet molar flow rate (mmol·h^{-1}) and $n(CHXF_2)_o$ is the outlet molar flow rate (mmol·h^{-1}).

$$\begin{array}{c}\text{yield (\%)}\\ \text{(from consumed } CHXF_2)\end{array} = \frac{x[\text{product flow rate (mmol·h}^{-1})]}{\Delta n(CHXF_2)} \times 100$$

where $x = 2$ for C_2 products and $x = 1$ for C_1 products.

$$\text{carbon balance (of consumed } CHXF_2) = \sum \text{yields of products}$$

Table 1. Relative Response Coefficients (k_i/k_{std}) Determined by GC-FID

I	k_i/k_{std}	
	std = CH_4	std = $CHClF_2$
$CHClF_2$ (FC-22)	3.83	1
CHF_3 (FC-23)	n/a	2.32
CHF_2CHF_2 (FC-134)	0.73	0.19
CF_3CH_2F (FC-134a)	0.73	0.19
CH_2F_2 (FC-32)	2.22	0.58
$CF_2{=}CF_2$ (TFE)	0.73	0.19
CH_4	1	0.26

Computational Methodology. Density functional theory calculations were performed using the Gaussian 98 program package.[17] Reactants, products, intermediates, and transition structures were optimized using Becke's hybrid three-parameter functional (B3LYP)[18] and the 6-31G(d) basis set.[19] 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 identity transition structures and determine thermal/zero-point energies. Transition structures were characterized by a single imaginary frequency. Thermochemical information at temperature T and $P = 1.00$ atm was obtained using frequencies scaled by 0.9804.[20] An intrinsic reaction coordinate (IRC) calculation was performed for each transition structure to examine the reaction pathway for each elementary step. Single-point energies were calculated for each structure and transition state using the B3LYP level of theory, using the 6-311+G(2df,2p) basis set.[21]

Results and Discussion

The pyrolysis of $CHClF_2$, either alone or in the presence of He, leads to formation of TFE as the major product. When the reaction is run at 1 atm, at 700 °C, with a contact time of 0.3 s, conversion of $CHClF_2$ is 25%, with TFE being formed in 90% yield along with 10% of other products, the major ones being cyclo-C_4F_8, HCF_2CF_2Cl, and $H(CF_2)_3Cl$.[1] In no case were

---

[17] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

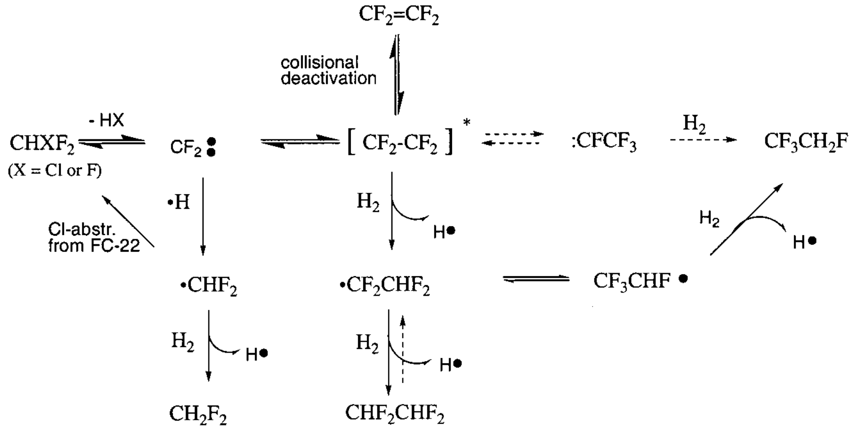
[18] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[19] Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acta* **1973**, *28*, 213−222.

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

[21] Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062−1065.

Scheme 1. Proposed Free Radical Chain Mechanism for the Thermal Reaction of $CHXF_2$ (X = Cl or F) with H_2



the compounds of interest, CH_2F_2, HCF_2CHF_2, or CF_3CH_2F, reported as being present in significant amounts in the pyrolysate when $CHClF_2$ was pyrolyzed *in the absence* of H_2. Likewise, all studies of the pyrolysis of CHF_3 (FC-23) reported a similarly clean formation of TFE.

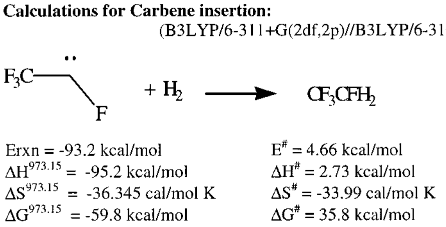
In contrast, the co-pyrolysis of $CHClF_2$ and H_2 led to quenching of the formation of TFE, with concomitant formation of hydrofluorocarbons (HFC's) CH_2F_2, HCF_2CHF_2, and CF_3CH_2F as major products.

Mechanistic Hypothesis and Computational Work. Although it is tempting to attribute the formation of CH_2F_2 to the simple insertion of CF_2: into the H−H bond, it is unlikely that such an insertion process contributes significantly to CH_2F_2 formation. Unlike CH_2: and even CHF: (which have calculated barrier heights of 2 and 7 kcal/mol, respectively, for insertion into H_2),[22,23] with a calculated barrier of 34 kcal/mol, the process of H_2 insertion by CF_2: does not, in practice, appear able to compete kinetically with its dimerization to TFE,[24] the barrier for which has been estimated to be 2.8 kcal/mol.[8]

Instead, the formation of all three HFC products, CH_2F_2, CHF_2CHF_2, and CF_3CH_2F, is attributed to a free radical chain process (Scheme 1) that becomes mechanistically accessible only when the pyrolyses of $CHClF_2$ or CHF_3 are carried out in the presence of H_2.

Free radical processes have previously been proposed to intervene during the pyrolysis of $CHClF_2$, particularly when long contact times are used, with such processes being proposed to lead not only to TFE, but also to most of the observed oligomeric hydrochlorofluorocarbon side products.[25]

We propose that initiation of the productive free radical chain process described in Scheme 1 derives primarily from the reaction of H_2 with "activated" [TFE]*, which is created with about 70 kcal/mol of excess energy when it is formed by the combination of two CF_2's. With more excess energy than the calculated π-bond energy of TFE,[26] this [TFE]* species should act much like a perfluoroalkyl "diradical" when it collides with an H_2 molecule, and it should thus abstract H quite readily. Activated TFE "diradicals" have previously been proposed as reactive intermediates in TFE dissociation and CF_2: carbene recombination reactions.[27,28]



Once radicals are produced in the presence of CF_2:, TFE, and H_2, reasonable propagating steps can be proposed that will allow formation of all three of the observed products. Both CH_2F_2 and CHF_2CHF_2 can be formed via the sequential addition of two hydrogen atoms shown in Scheme 1, but explaining CF_3CH_2F (FC-134a) is another matter. Formation of CF_3CH_2F requires a shift of fluorine at some point in the mechanism. Again, it is tempting to propose that formation of CF_3CH_2F derives from insertion of H_2 into fluorotrifluoromethylcarbene, CF_3CF:, which could be formed by F-shift rearrangement of the activated [TFE]*. If formed, CF_3CF: should indeed readily undergo insertion into H_2 (activation barrier ∼ 4.7 kcal/mol), as indicated by our DFT calculations. However, the very large calculated barrier for rearrangement of TFE to CF_3CF: (∼68.8 kcal/mol activation barrier)[29] makes it unlikely that such a process can be responsible for the significant amount of CF_3CH_2F formed in the reaction. Instead, we propose that the F-shift most likely occurs after TFE has picked up its first H atom, at the $CHF_2CF_2^{\cdot}$ radical stage:

$$CHF_2CF_2\bullet \rightleftharpoons \bullet CHFCF_3$$

$$E^{\ddagger}(\text{calcd}) = 29.2\ \text{kcal/mol}$$

Reports of fluorine atom shifts in carbon radical systems are rare, but such rearrangements are apparently feasible.[30−35] In

---

(22) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5847−5852.

(23) Ignatyev, I. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1997**, *119*, 12306−12310.

(24) Battin-Leclerc, F.; Smith, A. P.; Hayman, G. D.; Murrells, T. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3305−3313.

(25) Zhang, Z.; Pollard, R. *Int. J. Chem. Kinet.* **1995**, *27*, 1151−1164.

(26) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282−7283.

(27) Buravtsev, N. N.; Kolbanovsky, Y. A. *J. Fluorine Chem.* **1999**, *96*, 35−42.

(28) Buravtsev, N. N.; Kolbanovsky, Y. A.; Ovsyannikov, A. A. *Mendeleev Commun.* **1994**, 190−191.

(29) Cramer, C. J.; Hillmyer, M. A. *J. Org. Chem.* **1999**, *64*, 4850−4859.

(30) Kotaka, M.; Sato, S.; Shimokoshi, K. *J. Fluorine Chem.* **1988**, *41*, 371−382.

(31) Kotaka, M.; Sato, S.; Shimokoshi, K. *J. Fluorine Chem.* **1987**, *37*, 387−396.

(32) Kotaka, M.; Kohida, T.; Sato, S. *Z. Naturforsch.* **1990**, *45b*, 721−722.

(33) Sung, K.; Tidwell, T. T. *J. Org. Chem.* **1998**, *63*, 9690−9697.

(34) Kovtonyuk, V. N.; Kobrina, L. S.; Volodin, A. M. *Russ. Chem. Bull.* **1995**, *44*, 95−98.

(35) Dolbier, W. R.; Palmer, K.; Koroniak, H.; Zhang, H. Q.; Goedkin, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 1059−1060.

Table 2. Pyrolysis of $CHClF_2$ in He and in H_2 at 650 °C

conditions			yield (%)				carbon balance (%)
$He/H_2/CHClF_2$	t (s)	conv (%)	CH_2F_2	$CF_2{=}CF_2$	CF_3CH_2F	CHF_2CHF_2	
32/5/1	3	90	4	43	6	2	55
0/5/1	6	91	19	1	25	16	61
0/10/1	5	92	18	1	28	17	64

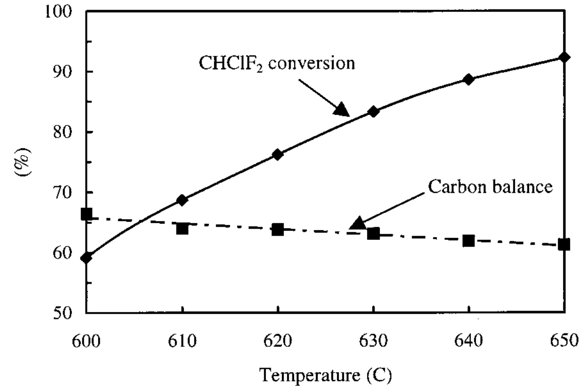


Figure 1. Conversion and carbon balance vs temperature during the pyrolysis of $CHClF_2$ in H_2 ($H_2/CHClF_2$ = 10, t = 5 s).

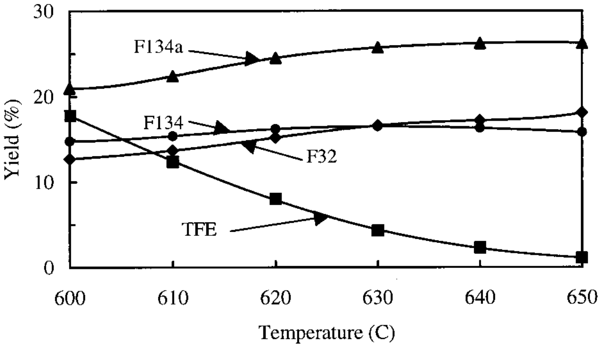


Figure 2. Yields vs temperature during the pyrolysis of $CHClF_2$ in H_2 ($H_2/CHClF_2$ = 19, t = 5 s).

the accompanying paper, UB3LYP/6-311+G(2df,2p)//UB3LYP/6-31G(d) calculations provided an estimated barrier ($E^{\ddagger}$) of 29.2 kcal/mol for this rearrangement.[36] On the basis of these calculations, we believe that the unimolecular 1,2-fluorine atom shift of $CHF_2CF_2^{\cdot}$ should be competitive with its second, bimolecular H atom abstraction.

Therefore, the free radical chain mechanism, initiated and facilitated by the presence of H_2 as depicted in Scheme 1, appears to explain the formation of all three product HFC's.

Pyrolysis of $CHClF_2$ in the Presence of H_2. All pyrolyses of $CHClF_2$ were carried out at atmospheric pressure and isothermally in a continuous-flow reactor constructed of quartz, with the goal of determining the effect of temperature, time of reaction, ratio of $H_2/CHClF_2$, and the presence of He diluant on the yields of the three product HFC's and on the conversion of $CHClF_2$. These results were then compared with those obtained with CHF_3.

(i) Effect of the Reaction Temperature. The pyrolysis of $CHClF_2$ was carried out between 600 and 650 °C in the presence of an excess of hydrogen ($H_2/CHClF_2$ = 10, t = 5 s). The conversion of $CHClF_2$ as a function of temperature and the carbon balance, as well as the observed yields of product formation, are presented in Figures 1 and 2.

The data represented in these figures indicate that, over the 50 °C range of temperature studied, there is both a dramatic increase in the conversion of $CHClF_2$ (from 60% at 600 to 95% at 650 °C) and a significant inhibition of formation of tetrafluoroethylene (from 18% at 600 °C to 1% at 650 °C). HFC yields rise slightly over this range, remaining just about optimal at 650 °C (CH_2F_2, 18%; CHF_2CHF_2, 16%; and CF_3CH_2F, 26% yield), whereas the carbon balance drops slightly. No coking is observed under these conditions, and most of the unaccounted mass is believed to correspond to the formation of hydrochlorofluorocarbon C_3 and C_4 byproducts that were not quantified by our GC analytical process. With 95% conversion and 60% overall yield of the hydrofluorocarbons of interest, *a temperature of 650* °C *is consequently considered optimal for selective preparation of HFC's CH_2F_2, CHF_2CHF_2, and CF_3CH_2F via the pyrolysis of $CHClF_2$ in the presence of H_2.*

(ii) Impact of Dilution with Helium. The effect of changing the ratio of $H_2/CHClF_2$ at optimal temperature, 650 °C, was examined, as was the impact of diluting the reactants with He.

The data in Table 2 indicate that halving the $H_2/CHClF_2$ ratio from 10 to 5 (only modest lowering of the H_2 partial pressure from 0.9 to 0.83 atm) concentration has little impact on either the conversion of $CHClF_2$ or the efficiency of product formation. However, diluting the mixture with a large amount of helium, while not affecting conversion of $CHClF_2$, modifies drastically the distribution of the products, diminishing HFC formation and strongly favoring TFE formation (43% yield). This result undoubtedly derives from a combination of two factors: (a) the significant lowering of the partial pressure of H_2 (from 0.83 to 0.13 atm), and (b) the collisional deactivation (by He) of the activated $CF_2{=}CF_2^*$ formed from combination of two CF_2:'s, both of which would kinetically inhibit the free radical chain process.

(iii) Effect of a Radical Initiator. Since a free radical chain process is proposed as the mechanism of HFC formation, the effect of adding a free radical initiator to the reaction flow was examined. Perfluoroneooctane (BDE ≈ 40 kcal/mol) was chosen as initiator,[37] since it should dissociate rapidly into two perfluoro-*tert*-butyl radicals at the temperatures being used in the $CHClF_2$ pyrolyses. Such t-$C_4F_9^{\cdot}$ radicals should react rapidly with H_2 to initiate the free radical chain process.

Table 3 compares the results of $CHClF_2/H_2$ pyrolysis with and without such initiation. Use of an initiator is seen to enhance conversion and carbon balance slightly, while enhancing CH_2F_2 formation, partially at the expense of the C_2 HFC products. This can be understood, within the context of our free radical chain mechanism, as deriving from generation of $H^{\cdot}$ *earlier* in the mechanism, when the CF_2: moiety should be more prevalent. (Under the normal $CHClF_2/H_2$ pyrolysis conditions, H• would not be formed until $[CF_2{=}CF_2]^*$ is formed by dimerization of CF_2:, according to the postulated mechanism.)

(iv) Use of Other Difluorocarbene Sources. To gain further insight into the CF_2: → HFC process from $CHClF_2$, which is complicated by cogeneration of HCl, three different thermal CF_2: sources that do not generate HCl were used under

---

[36] Romelaer, R.; Baker, J. M.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6773–6777.

[37] Tonelli, C.; Tortelli, V. *J. Fluorine Chem.* **1994**, *67*, 125–128.

Table 3. Pyrolysis of $CHClF_2$ in H_2 at 650 °C in the Presence of Initiator, Perfluoroneooctane (5% Molar vs $CHClF_2$)

conditions				yield (%)				carbon balance (%)
$H_2/CHClF_2$	init	*t* (s)	conv (%)	CH_2F_2	$CF_2{=}CF_2$	CF_3CH_2F	CHF_2CHF_2	
10/1	no	4	92	19	1	26	14	60
10/1	yes	4	96	27	0	24	11	62

Table 4. Production of HFC's Using Varied Sources of Difluorocarbene: $CHClF_2$, Hexafluorocyclopropane (HFCP), Hexafluoropropylene Oxide (HFPO), and Tetrafluoroethylene (TFE) (H_2/:CF_2 Source = 10)

conditions			yield (%)				carbon balance (%)
:CF_2 source	*t* (s)	conv (%)	CH_2F_2	$CF_2{=}CF_2$	CF_3CH_2F	CHF_2CHF_2	
$CHClF_2$	5	92	18	1	28	17	64
HFCP	5	100	35	1	26	15	77
HFPO	5	100	28	3	26	16	73
TFE	5	99	14	n/a	28	16	58

Table 5. Pyrolysis of $CHClF_2$ in D_2 versus H_2 at 650 °C

conditions			yield (%)				carbon balance (%)
$H_2/D_2/CHClF_2$	*t* (s)	conv (%)	CH_2F_2	$CF_2{=}CF_2$	CF_3CH_2F	CHF_2CHF_2	
10/0/1	5	92	18	1	28	17	64
0/10/1	5	87	17[a]	11[a]	21[a]	11[a]	60

[a] Partially deuterated products are obtained (see Table 6).

copyrolysis conditions with H_2 at 650 °C. Hexafluorocyclopropane (HFCP) and hexafluoropropylene oxide (HFPO) are traditional, lower temperature sources of CF_2:, with HFCP decomposition starting at 190 °C[38] and HFPO decomposition at 150 °C.[39,40] At 650 °C, complete conversion of these CF_2: sources is likely. Although TFE is not ordinarily considered a source of CF_2:, it is recognized that TFE formation is *reversible* under the conditions (>650 °C) of $CHClF_2$ pyrolysis, so it was tested as a potential source of CF_2: and HFC's. Table 4 gives the results of these experiments.

Although enhanced carbon balance and CH_2F_2 yield are observed for the "pure" CF_2:-forming reagents (HFCP and HFPO), nevertheless all four CF_2: sources give remarkably similar product mixtures. Most notably, the yields of CHF_2CHF_2 and CF_3CH_2F in each run are virtually identical! HCl does not, therefore, seem to be playing a determining role in the free radical chain process. Because $CHClF_2$ does not undergo thermal conversion to HFC's in the absence of H_2, HCl cannot be capable of donating an H atom to initiate a free radical chain process analogous to Scheme 1. This may be because HCl will preferably undergo a four-center addition reaction to activated TFE to form CHF_2CF_2Cl (the reverse of the unimolecular β-elimination process).[41] Of course, that is not to say that HCl cannot be a source of H atoms once the free radical process has been initiated by the intervention of H_2.

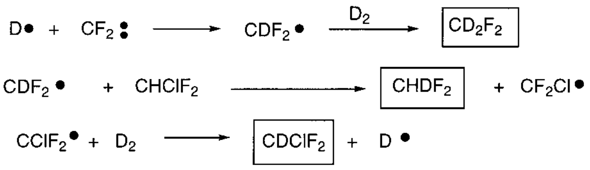
(v) Use of D_2 in Place of H_2. When D_2 was used in place of H_2, the results in terms of $CHClF_2$ conversion and HFC production (as shown in Table 5) were remarkably similar to those obtained with H_2. Diminished conversion and C_2–HFC formation are perhaps indicative of an isotope effect in the propagation steps generating these products,[42,43] whereas production of difluoromethane, which is determined by $D^\cdot$ addition to CF_2:, is not significantly affected. The observed increase in TFE yield is another indication of the diminished efficiency of the chain process in D_2.

Table 6. D/H Distribution in Products, As Determined by GC/MS and Yields Obtained from the $CHClF_2$ Pyrolysis in D_2 (650 °C, $D_2/CHClF_2$ = 10, *t* = 5 s)

compounds	GC/MS distribution (%)	molecule deuteration (%)	yield (%)
$CHClF_2$	20	80	2.6
$CDClF_2$	80		10.4
CH_2F_2	9	69	1.5
$CHDF_2$	45		7.75
CD_2F_2	46		7.8
CF_3CH_2F	4	83	0.8
CF_3CHDF	27		5.7
CF_3CD_2F	69		14.5
CHF_2CHF_2	5	80	0.6
CHF_2CDF_2	31		3.4
CDF_2CDF_2	64		7.0

The observed distribution of deuterium in the compounds of interest, which was determined by GC/MS analysis for each compound, is given in Table 6.

Deuterium incorporation into the products as well as into recovered chlorodifluoromethane is significant. The significant incorporation of deuterium into recovered chlorodifluoromethane and the approximately equal amounts of $CHDF_2$ and CD_2F_2 can be rationalized by the sequence below:



Formation of mainly dideuterated C_2-HFC's, CDF_2CDF_2 and CF_3CD_2F (64% and 69%, respectively), is consistent with the sequential deuterium atom abstractions shown in Scheme 1.

---

[38] Birchall, J. M.; Fields, R.; Hazeldine, R. N.; McLean, R. J. *J. Fluorine Chem.* **1980**, *15*, 487–495.

[39] Millauer, H.; Schwertfeger, W.; Siegemund, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 161–179.

[40] Krusic, P. J.; Roe, D. C.; Smart, B. E. *Isr. J. Chem.* **1999**, *39*, 117–123.

[41] Volkov, G. V.; Barabanov, V. G.; V'yunov, K. A.; Maksimov, B. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1990**, *60*, 1029–1032.

[42] At these temperatures, isotope effects should be relatively small. The primary isotope effect, k_H/k_D, for CF_3 radical reacting with H_2 versus D_2 can be calculated to have a value of ~2.1 at 650 °C.[43]

[43] Arthur, N. L.; Donchi, K. F.; McDonell, J. A. *J. Chem. Soc., Faraday Trans. 1* **1975**, 71, 2431.

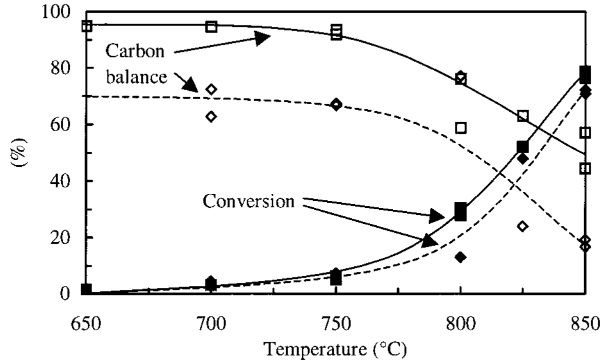


Figure 3. Conversion and carbon balance vs temperature during pyrolysis of CHF_3 in H_2 (—) and in He (- - -) between 650 and 850 °C (He or $H_2/CHF_3 = 10$, $t = 3$ s, Inconel reactor).

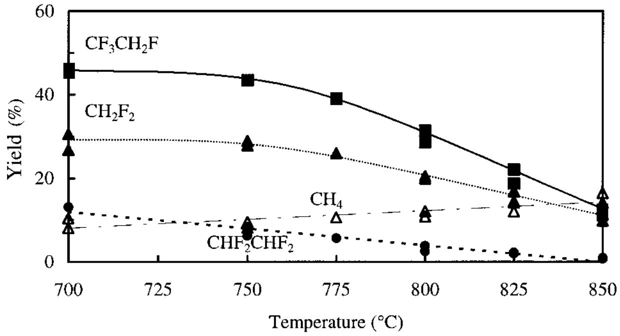


Figure 4. Yield vs reaction temperature during the pyrolysis of CHF_3 in H_2 ($T = 700-850$ °C, $H_2/CHF_3 = 3$, $t = 4$ s, Inconel reactor).

Pyrolysis of CHF_3 in the Presence of H_2. Although requiring significantly higher temperatures than the pyrolyses of $CHClF_2$, the pyrolysis of CHF_3 (FC-23) constitutes an equally good source of difluorocarbene and TFE, and it should therefore also produce HFC's when the pyrolysis is carried out in the presence of H_2. Our investigation of the pyrolysis of CHF_3 was carried out in an Inconel 600 reactor, at atmospheric pressure and at temperatures between 650 and 850 °C.

Initial experiments compared the thermal behavior of CHF_3 in the presence of He versus that in the presence of H_2 (He or $H_2/CHF_3 = 10$, reaction time of 3 s). Comparisons of the total conversion and the carbon balance as a function of the reaction temperature are presented in Figure 3. Conversion of CHF_3 is the same in He and H_2, which suggests a common primary decomposition pathway for the two processes.

However, the carbon balance is much higher in H_2, and the nature of the products is drastically different in the two media. TFE is the major (almost exclusive) product (60−70% yield) in He at temperatures between 650 and 800 °C, whereas a mixture of the usual HFC's (60−65% total yield) is formed when CHF_3 is pyrolyzed at temperatures from 650 to 775 °C in a flow of H_2. A large amount of methane (∼30% yield) is also observed in the presence of H_2, as a result of wall-catalyzed hydrogenolysis processes in the Inconel 600 reactor. Figure 4 shows the nature of the product mixtures as a function of temperature.

Further experiments showed that low ratios of H_2/CHF_3 (∼3:1) and short reaction times (∼4−5 s) provided optimal results, in terms of carbon balance and HFC yields. Higher temperatures favor the formation of increasing amounts of byproducts, such as methane in the Inconel 600 reactor, but also of ethane and mono- and difluorobenzene (detected by GC/MS). Figures depicting these and other optimization experiments can be found in the Supporting Information.

Table 7. Pyrolysis of CHF_3 and of $CHClF_2$ in H_2

reagent		CHF_3	$CHClF_2$
reactor		Inconel	quartz
temperature	(°C)	775	650
pressure	(atm)	1	1
H_2/reagent		3	10
reaction time	(s)	4	5
conversion	(%)	21	92
CF_3CH_2F yield	(%)	39	28
CH_2F_2 yield	(%)	26	18
CHF_2CHF_2 yield	(%)	6	17
CH_4 yield	(%)	11	0
carbon balance	(%)	82	63

Thus, at 775 °C, using a ratio of H_2/CHF_3 equal to 3 and a contact time of 4 s, the total conversion is 21%, with the yields of CF_3CH_2F, CH_2F_2, and CHF_2CHF_2 being 39%, 26%, and 5% respectively, and the carbon balance being an acceptable 82%. This compares to the optimal results for $CHClF_2$ at 650 °C, where the observed yields were 25%, 19%, and 16%, respectively, with 92% conversion.

An interesting difference in the CHF_3 pyrolysis results as compared to the results obtained using $CHClF_2$ is the relative lack of CHF_2CHF_2 as a product in the CHF_3 pyrolysis. This lack of observation of CHF_2CHF_2 in the CHF_3 pyrolyses is undoubtedly the result of its H_2-promoted isomerization to CF_3CH_2F at these high temperatures. This isomerization, which does not occur thermally in the absence of H_2, is the subject of the accompanying paper.[36]

Table 7 presents a comparison of the "optimal" results for both $CHClF_2$ and CHF_3 pyrolysis.

It can be seen that the pyrolysis of CHF_3 presents some advantages, i.e., smaller requirement for hydrogen, improved carbon balance, and improved yields of CH_2F_2 and CF_3CH_2F.

Conclusions

In conclusion, strong evidence, both experimental and theoretical, has been obtained that allows probable definition of the mechanism of HFC formation during the pyrolysis of $CHClF_2$ and CHF_3 in the presence of hydrogen. The data that have been presented are consistent with the free radical chain process depicted in Scheme 1. It is proposed that unimolecular formation of CF_2: from either $CHClF_2$ or CHF_3 is followed by dimerization of CF_2: to form "hot" TFE, which abstracts H from H_2 to initiate a free radical chain process that results in formation of CH_2F_2, CHF_2CHF_2, and CF_3CH_2F.

Although optimization studies did not result in finding conditions that favor a *single* product, it was found that, under the high-temperature conditions of pyrolysis of CHF_3, the selective formation of two HFC's, CH_2CF_2 and CF_3CH_2F, was possible.

Acknowledgment. Preliminary work by S. Hub and D. Guillet, and helpful discussions with S. Hub, E. Lacroix, and J. P. Schirmann, all of Elf Atochem, are acknowledged with thanks. Support of this research by Elf Aquitaine, Inc. through funding of postdoctoral appointments for V.K. and R.R. and for funding construction of the flow reactor is gratefully acknowledged.

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

JA0023581