Anomalous elimination of HCl from 2-chloro-1,1-difluoroethane. Likely involvement of a 1,2-FCl interchange mechanism

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Abstract—A novel 1,2-FCl interchange mechanism is proposed to be involved in the unexpected thermal conversion of CH_2ClCHF_2 to 1,2-difluoroethylene. © 2002 Elsevier Science Ltd. All rights reserved.

The quantitative thermal behavior of haloethanes has been a subject of consistent interest over the last half century.[1,2] More recently, there has been an increased interest in chlorine- and fluorine-substituted hydrochlorofluorocarbons (HCFC's) and chlorofluoroethanes in particular, because of their potential as replacements for ozone-depleting Freon refrigerants. When chlorofluoroethanes are heated in the gas phase, although free radical chain processes can occasionally intervene,[2] they generally preferentially undergo a unimolecular, four-center, β-elimination of HX,[3] the barriers to which are for the most part determined by whether HCl or HF is eliminated as well as by the total number and relative positions of the halogens in the molecules. The relative reactivities of these C_2-HCFC's and their products of elimination have generally been quite predictable. For example, when both HCl and HF eliminations are possible, and polar factors similar, the HCl eliminations generally dominate, as in the pyrolysis of 1-chloro-1-fluoroethane, where HCl elimination was found to be virtually exclusive.[4] β-Eliminations usually dominate α-eliminations, and rearrangements have never previously been known to play a significant role in the 1,2-elimination reactions of haloethanes.

Therefore, it was with some amazement that in the course of a recent study of the thermal behavior of C_1 and C_2 HCFC's we observed 1,2-difluoroethylene to be the major product from the flow thermolysis of 1-chloro-2,2-difluoroethane (**F142**) (along with the expected β-HCl elimination product, 1,1-difluoroethylene).
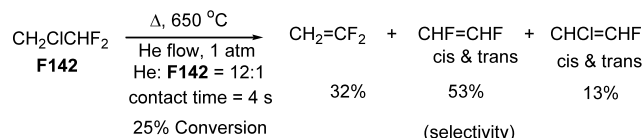
The reaction was studied over a temperature range 500–650°C, with no reaction being observed at 500°C, less than 1% at 550°C, and a 3% conversion at 600°C. Product ratios exhibited little variation with respect to temperature or He:**F142** ratio.

What can be the source of the unexpected, rearranged 1,2-difluoroethylene product? In this preliminary letter we propose that the above reaction comprises what is perhaps the clearest example of a novel unimolecular 1,2-FCl interchange mechanism that was recently proposed by Holmes and co-workers in their computational and experimental study of the 1,3-HCl elimination reaction of $CF_2ClCF_2CH_3$.[5,6]

Proposed mechanism:
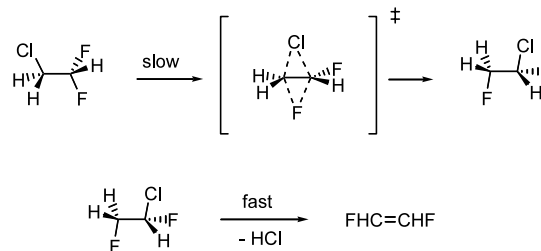
Readily available 1-chloro-1,1-difluoroethane (**F142b**) is a good, clean thermal source of 1,1-difluoroethylene.[4,7–9] However, the pyrolysis of its less accessible isomer, 2-chloro-1,1-difluoroethane (**F142**) has not previously been reported.[10]

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Table 1. Activation parameters for HCl elimination from fluorinated monochloroethanes

Chloroethane	Log A	E_a (kcal/mol)	Ref.	Calcd barrier[a] (kcal/mol)
CH_3CH_2Cl	13.7	57.8	12	51.9
CH_3CHFCl	13.9	57.0	4	49.5
CH_3CF_2Cl (**142b**)	13.0	55.3	13	–
CH_2FCH_2Cl	13.5	63.8	14	56.5
CHF_2CH_2Cl (**142**)	–	–		67.2
$CHFCHFCl$	–	–		56.3

[a] Density functional theory calculations were performed using the Gaussian 98 suite of programs.[11,15,16]

As the available kinetic data in Table 1 indicates, the **F142b** isomer, with α-fluorines is relatively reactive, actually even more reactive than ethyl chloride towards thermal β-elimination of HCl. This is probably because the α-fluorines of **F142b** can stabilize the build up of positive charge at the α-position that occurs within the highly asymmetric and polarized elimination transition state. In contrast, the presence of the β-fluorines in **F142** strongly inhibits such elimination, because of their detrimental inductive effect on the transition state (depicted in Fig. 1).

Lacking experimental kinetic data for **F142**, calculations were carried out on the related series of HCFC's, and it was found, as expected, that the β-elimination of HCl from **F142** should have the greatest barrier of the series (67.2 kcal/mol). This apparently opens the door for the 1,2-FCl interchange mechanism to become energetically accessible and competitive with the normal β-elimination mechanism. Once this interchange occurs, loss of HCl from the resulting CHFCHFCl to form the *cis*- and *trans*-1,2-difluoroethylenes should be very fast, as indicated by its relatively low calculated barrier (56.3 kcal/mol) for β-elimination.

We propose the intervention of the 1,2-FCl interchange mechanism primarily because there is no logical alternative that can explain the formation of significant amounts of 1,2-difluoroethylene in this reaction. Calculations indicate that the barrier to the interchange process ($E_a = 61.9$ kcal/mol, with $\Delta H° = 6.4$ kcal/mol)[17] should be competitive with HCl elimination ($E_a = 67.2$ kcal/mol).[11] Once formed $CH_2FCHFCl$ should undergo rapid β-HCl elimination ($E_a = 56.3$ kcal/mol)[11] to form CHF=CHF. There is no evidence of significant intervention of a free radical chain process in this reaction. α-Elimination of HCl from **F142** (calcd barrier of 88
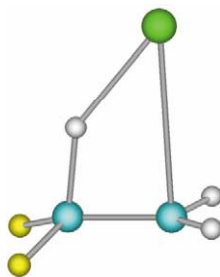
kcal/mol)[11] would not be competitive, and even if it did occur, the required subsequent 1,2-F shift would not compete with the almost barrierless 1,2-H-shift.

Additional corroborating computational and experimental evidence for the intervention of the 1,2-FCl interchange mechanism in the thermal decomposition of **F142** will soon be forthcoming from the Holmes group, and parallel work that will be reported in due course continues in our group.

References

1. Maccoll, A. *Chem. Rev.* **1969**, *69*, 33–60.
2. Barton, D. H. R.; Onyon, P. F. *Trans. Faraday Soc.* **1949**, *45*, 725–735.
3. Hiberty, P. C. *J. Am. Chem. Soc.* **1975**, *97*, 5975–5979.
4. Martens, G. J.; Godfroid, M.; Decelle, R.; Verbeyst, J. *Internat. J. Chem. Kinet.* **1972**, *4*, 645–655.
5. Heard, G. L.; Holmes, B. E. *J. Phys. Chem. A* **2001**, *105*, 1622–1625.
6. Burgin, M. O.; Heard, G. L.; Martell, J. M.; Holmes, B. E. *J. Phys. Chem.* **2001**, *105*, 1615–1621.
7. Huybrechts, G.; Van Assche, G. *Internat. J. Chem. Kinet.* **1999**, *31*, 283–289.
8. Jones, Y.; Holmes, B. E.; Duke, D. W.; Tipton, D. L. *J. Phys. Chem.* **1990**, *94*, 4957–4963.
9. McDaniel, J. B.; Holmes, B. E. *J. Phys. Chem.* **1996**, *100*, 3044–3050.
10. Our studies of **F142** were prompted by discussions with Dr. J. P. Schirmann of Elf Atochem in which a number of unusual observations made by Elf Atochem in their studies of HCFC's were mentioned.
11. Reactants, products, intermediates, and transition structures were optimized using Becke's hybrid three parameter functional (B3LYP)[16] and the 6-31G(d) basis set. Single-point energies were calculated using B3LYP level of theory using the 6-311+G(2df,2p) basis set.

Figure 1. Calculated transition state for HCl elimination from **F142**.[11]

12. Evans, P. J.; Ichimura, T.; Tschuikow-Roux, E. *Internat. J. Chem. Kinet.* **1978**, *10*, 855.

13. Huybrechts, G.; Van Assche, G.; Van Der Auwera, S. *Internat. J. Chem. Kinet.* **1998**, *30*, 359–366.

14. Cadman, P.; Day, M.; Trotman-Dickenson, A. F. *J. Chem. Soc. A* **1971**, 1356–1360.

15. Frisch, M. J. T. G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. J. A.; 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.; Baboul, A. G.; 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

16. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

17. Holmes, B. E.; Heard, G. L.; Beaton, P. T., unpublished B3PW91/6-311+G(2d,p) calculations.