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Thermal decomposition of branched-chain perfluoroalkanes

V. Tortelli*, C. Tonelli
Ausimont, Research and Development Centre, Via S. Pietro, 50-Bollate Milan (Italy)
C. Corvaja
Department of Physical Chemistry, University of Padova, via Loredan, 2-35131 Padova (Italy)

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Abstract

The pyrolysis of some branched perfluoroalkanes has been studied. Homolytic cleavage of the most hindered carbon–carbon bond occurs, followed by coupling and rearrangement of the radicals so formed. This mechanism accounts for all the reaction products. Some kinetic and thermodynamic data are presented.

Introduction

It is well known that perfluoroalkanes are very stable molecules because of the strength of the carbon–fluorine bond [1]. However, the thermal stabilities of perfluorocarbons are limited by carbon–carbon bond strengths which are lower than those of carbon–fluorine bonds. Homolytic cleavage of linear perfluorocarbons occurs at temperatures as high as 500 °C, but the presence of branching along the main chain, i.e. the presence of perfluoroalkyl-substituted carbon atoms, decreases the decomposition temperatures substantially [1–3]; strain factors which decrease the carbon–carbon bond strength are involved.

Previous literature reports on the pyrolysis of saturated perfluorocarbons, obtained by the fluorination over CoF_3 of tetrafluoroethylene oligomers [3], confirm that the bonds that break most easily are those between carbon atoms having maximum substitution by other carbons. A more recent contribution has appeared [4] but no full paper has been published as yet. A theoretical study of fluorocarbons containing secondary, tertiary and quaternary centres [5] suggested that the CF_3 group can be considered as less electron-withdrawing than a fluorine atom and that quaternary sites exhibit a significative negative Mulliken charge. However, further spectroscopic studies are necessary to support this interesting prediction.

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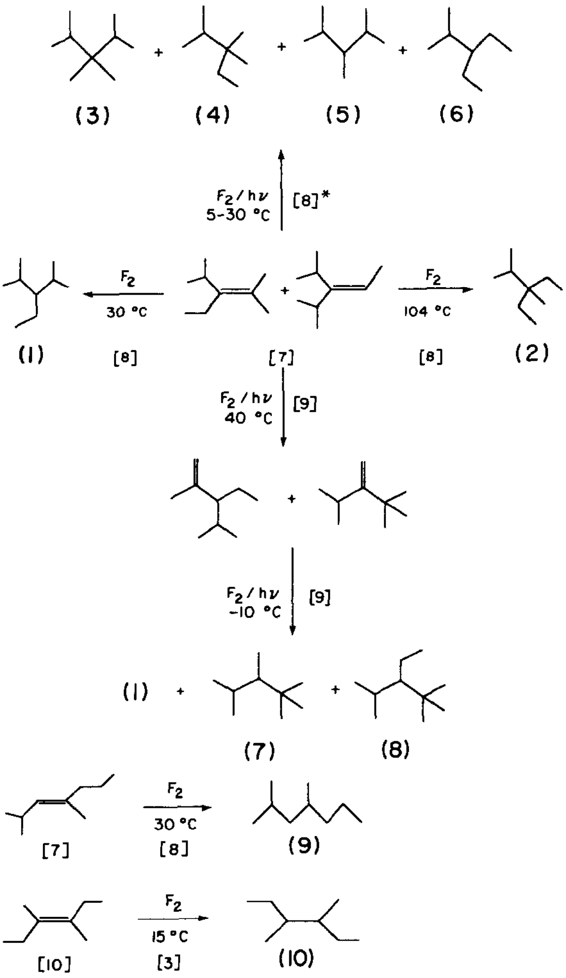
*Author to whom correspondence should be addressed.

As a part of a study to generate perfluoroalkyl radicals capable of initiating vinylic polymerization [6], we now present a contribution regarding the clean pyrolyses of some highly branched perfluoroalkanes.

Results and discussion

The synthesis of the starting materials was performed by the use of fluorination with elemental fluorine (usually in the presence of UV light) of some readily available branched perfluoro-olefins (see Scheme 1 for details).*



Scheme 1.

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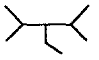
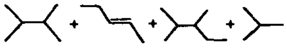
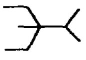
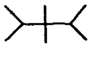
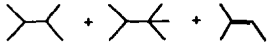
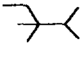
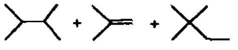
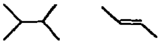
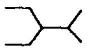
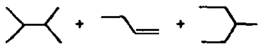
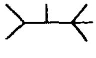
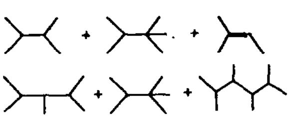
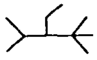
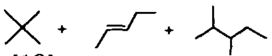
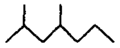
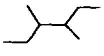
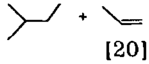
*All unmarked bonds in this paper are those to fluorine.

Perfluoroalkanes **1–10** were purified (to 95%) by fractional distillation of reaction mixtures. The pyrolysis products were analyzed directly as mixtures (when possible) or after fractional distillation by GLC/mass, IR and ^{19}F NMR spectroscopy. The results obtained are summarized in Table 1.

A mechanism which accounts for all of the products of decomposition is as follows: (i) homolytic cleavage of the most substituted carbon–carbon bond(s), leading to two intermediate radicals; (ii) elimination of CF_3 radicals from the most stable intermediate radical (C_nF_{2n+1}) with the formation of $C_{n-1}F_{2n-2}$ alkenes; and (iii) recombination of perfluoroalkyl radicals. As can be seen from Table 1, the temperatures needed for decomposition are not particularly high because of the presence of adjacent tertiary and quaternary

TABLE 1

Thermal decomposition of branched-chain fluorocarbons

Compound No.	Fluorocarbon	Temperature (°C)	Products[a]
1		240	 [11] [12] [9] [13]
2		200	 [3] [3]
3		150	 [9] [14]
4		240	 [15] [11]
5		320	 [16]
6		320	 [17] [11]
7		210	 [18] [19]
8		160	 [18]
9		400	no decomposition
10		320	 [20]

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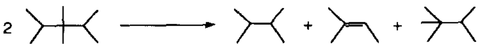
[a] Numerals in square brackets refer to references listed at end of text.

centres [cf. ref. 3]. Hence the products of the reaction, usually arising from only one specific cleavage, are few and it was not possible to detect, even as traces, any volatile by-products such as CF_4, C_2F_6, etc., typical of thermolysis at higher temperatures.

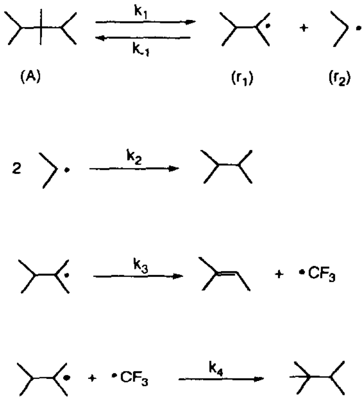
The mechanism is well illustrated by the pyrolysis of **3** (Scheme 2). The stoichiometry of the reaction (2 mol starting and 1 mol each of final products) was strictly confirmed:



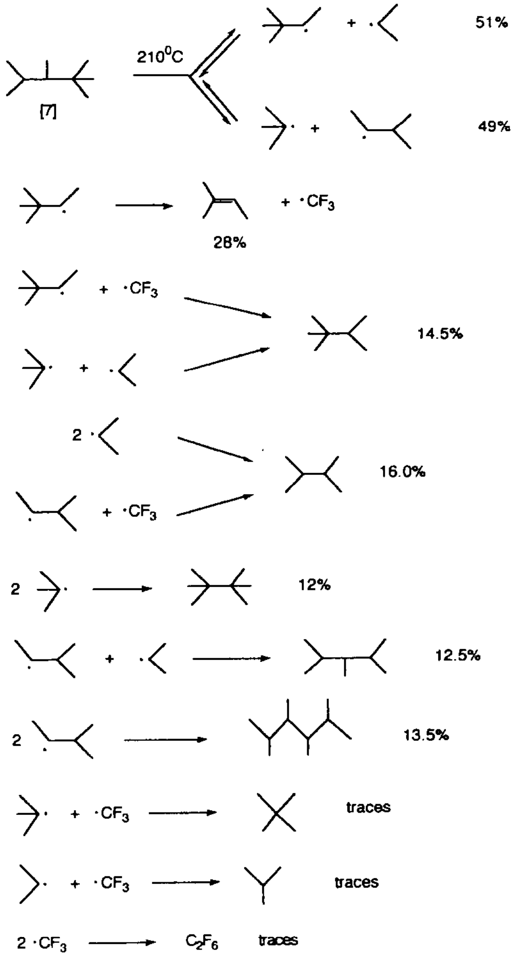
The pyrolysis of compound **7** was the only case in which we noticed competition between the cleavage of different carbon–carbon bonds (Scheme 3). This was probably due to the fact that the most favourable rupture leads to the perfluoro t-butyl radical which is fairly stable and does not readily undergo homocoupling nor β-elimination of another radical and so tends to recombine to the starting alkane. The other cleavage, even if not favourable, involves the isopropyl radical which reacts immediately. The balance between such competition gives the observed product ratio.

Compound **8**, on the other hand, even if very similar to **7** (the difference consists of an ethyl group instead of a methyl one), followed a normal behaviour pattern, with a unique cleavage between the quaternary and tertiary carbons leading to products. The explanation for such a difference is, in our opinion, the lower temperature required for pyrolysis; the energy supplied to the system allows only the most favourable breakage.

From Table 1 it is evident that C–C bonds become progressively susceptible towards rupture by heat as the carbon atoms involved became more highly substituted with perfluoroalkyl groups. When the number of substituents is the same, the key factor which explains the relative weakness of C–C bonds is the total number of carbon atoms in the perfluoroalkyl substituents. For example, compounds **1** and **5**, **2** and **4** and **7** and **8** each contain a bond between a quaternary and a tertiary carbon atom. However the replacement of a methyl group with an ethyl group results in a marked



Scheme 2.



Scheme 3.

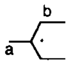
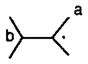
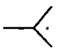
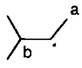
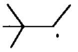
decrease in the thermal stability of the C—C bond, suggesting that the attachment of one more CF_2 group to similarly substituted C—C bonds increases the energy content of the latter, probably by steric compression.

EPR spectroscopy provides valuable support for the proposed mechanism. In fact, when the pyrolysis of a 10% solution of a perfluoroalkane in a perfluoropolyether solvent was performed in a degassed sealed tube inside the microwave cavity of the EPR spectrometer, it was possible to detect and fully characterize some intermediate radicals. The hyperfine coupling constants, which provide unequivocal evidence for the chemical structures, are summarized in Table 2.

Since our reactions were performed in a closed system (i.e. in sealed tubes, see Experimental section for details) at temperatures higher than the

TABLE 2

Hyperfine coupling constants (G) of perfluorinated radicals[a]

Radical No.	Radical type		$a_{F(\alpha)}$	$a_{F(\beta)}$	$a_{F(\gamma)}$
R_1		(ref. 21a)	67.4	19.2	–
R_2			–	18.3(a) 21.1(b)	3.1
R_3		(ref. 21c)	–	18.74(a) 2.77(b)	2.77
R_4		(ref. 21b)	–	18.7	–
R_5			68.4	18.1(a) 20.5(b)	2.4
R_6			66.8	20.7	1.9

[a]Radicals R_2 and R_3 were observed during the pyrolysis of perfluoroalkanes **2** and **3** respectively, while R_4, R_5 and R_6 were observed during pyrolysis of **7**. Radical R_1 was not observed under our experimental conditions. Literature data are provided for comparison.

boiling point of the starting perfluoroalkanes, it is not possible to exclude the possibility that they occurred in both the gaseous and liquid phases, even if it is more than likely that all took place in condensed phases. In fact, it should be noted that (i) the reaction temperatures are well below the critical temperatures of the reagents; and (ii) the selectivity of the pyrolyses can hardly be explained in terms of purely gas-phase reactions (only traces of self-coupling of CF_3 groups and cross-coupling of CF_3 groups with i-C_3F_7 and t-C_4F_9 groups were detected).

On this basis, some general calculations regarding the mechanism of thermolysis may now be undertaken. Coupling reactions between simple perfluoroalkyl radicals usually have activation energies close to zero with rate constants ranging from 10^{12} to 10^{13} cm^3 mol^{-1} s^{-1} [22]. Moreover β-elimination of CF_3 and further coupling usually occur, as previously noted, without any detectable 'leakage' from the cage (no C_2F_6 nor $(CF_3)_3CF$ was detected) and hence the rate of these reactions must be close to that of diffusion [23].

Thus, as far as Scheme 2 is concerned, the rate law may be written

$$-\frac{d[A]}{dt}=k_1[A]-k_1[r_1][r_2]$$

From a typical [concentration] versus time plot it is possible to calculate the rate constant and hence, via the Arrhenius equation, the activation energy for the decomposition (Table 3).

If compound **3** was pyrolyzed in the presence of a hydrogen-donor solvent such as toluene, which works as radical trap (cf. ref. 3), it was possible to obtain the 1-hydroperfluoro alkanes via a clean reaction (Scheme 4). No products typical of reactions not involving a radical trap (Scheme 2) were detected. The observed kinetic constants k_{obs} (first-order) were not dependent on the radical trap concentration [R] over the range $0.02 < [R]/[A] < 10$ (Table 4).

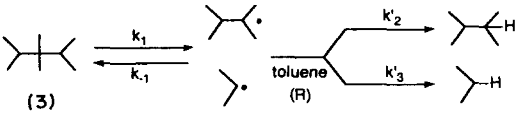
This means that (i) intermediate radicals extract hydrogen very rapidly, i.e. their stationary-state concentrations become very low; and (ii) $k'_2[R][r_1]$ and $k'_3[R][r_2] \gg k_{-1}[r_1][r_2]$ and $k'_1[A] \gg k'_{-1}[r_1][r_2]$, so that $k'_{obs} = k'_1$. In other words, homolytic cleavage becomes the rate-determining step. By comparison between the kinetic results obtained for the pyrolysis of compound **3** in the presence and absence of a radical trap, it is possible to state:

1. The first step in the process [eqn. (1) in Scheme 2] is actually an equilibrium and recombination of radicals in the cage plays an important role particularly at lower temperatures (cf. k_{obs}/k'_{obs} which approaches

TABLE 3

Rate constants (k_{obs}) and activation energy (E_a) for the pyrolysis of compound **3**

Temp. (°C)	$k_{obs} \times 10^5$ (s^{-1})	E_a (kcal mol^{-1})
141	0.29	46.5
151	1.23	
161	4.30	
171	15.00	

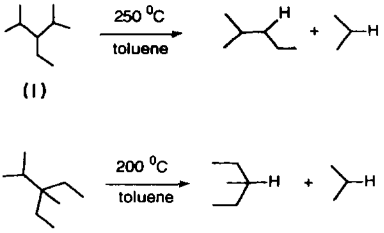


Scheme 4.

TABLE 4

Rate constants (k_{obs}) and activation energy (E'_a) for the pyrolysis of compound **3** in the presence of toluene

Temp. (°C)	$k'_{obs} \times 10^5$ (s^{-1})	k_{obs}/k'_{obs}	E'_a (kcal mol^{-1})
141	0.56	0.52	42.3
151	1.83	0.67	
161	6.02	0.71	



(1)

(2)

Scheme 5.

unity as the temperature increases (see Table 4), indicating that equilibrium at higher temperatures is shifted towards the right).

2. The use of a radical trap makes the reaction 'cleaner' kinetically; the rate-determining step is now the homolysis of the most substituted C—C bond, the recombination of intermediate radicals being negligible.
3. The lower value of the activation energy (E'_a) in the presence of the radical trap arises from the cleavage of the most substituted C—C bond; in the absence of the trap the calculated activation energy E_a represents the sum of the energy contributions of kinetically comparable steps.

As in the case of compound **3** we have studied the decomposition of alkanes **1** and **2** in the presence of toluene (Scheme 5). The activation energy values (kcal mol^{-1}) calculated using the Arrhenius equation were 55.7 and 40.0 for **1** and **2**, respectively. The activation energy for the decomposition of **2** was lowered by the presence of toluene, following the same trend as for compound **3**, whereas the activation energy value for **1** was the same (within experimental error) both in the presence and absence of toluene. This result can be explained in terms of the higher temperature necessary for the pyrolysis of compound **1**. This temperature is so high that the initial equilibrium is completely shifted to the right even in the absence of the radical trap which is now not necessary. In both cases, the rate-determining step is clearly the homolysis of a carbon–carbon bond and the similar values of the activation energies reflect this situation.

Experimental

NMR spectra were recorded on a Varian 200 MHz spectrometer with $CDCl_3$ as the solvent or neat and employing $CFCl_3$ or TMS as the internal standard. GLC analyses were performed with a HRGC 5300 Carlo Erba instrument equipped with thermoconductivity detectors [4.5 m columns packed with 10% Fomblin YR on Chromosorb W HP (60–80 mesh)]. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR instrument and EPR spectra on a Bruker ER 200 DX-band spectrometer.

General procedure for the pyrolysis of perfluoroalkanes

Into a high-pressure 10 ml glass tube equipped with a Rotaflo stopcock was condensed, via a vacuum line, 10 mmol of the starting perfluoroalkane. The reactor was then fully immersed in a thermostatted oil bath (if possible) or in a tubular oven at the temperature indicated in Table 1 and left there for several hours (usually 8–15 h) until reaction was complete. After cooling, the crude mixture was directly analyzed by GLC/MS, IR and ^{19}F NMR methods or sometimes distilled before analysis (in this case a 100 mmol scale reaction was used); products were identified usually by comparison with authentic samples and reported spectra (see references cited in Table 1).

Kinetic measurements were undertaken by ^{19}F NMR monitoring of the percentage decrease (to 40–50% conversion) of the starting perfluoroalkane (0.4 ml) directly placed in sealed NMR tubes. When toluene was used as a radical trap, only the expected hydrides were obtained. Heptafluoro-2-hydropropane and perfluoro-3-methyl-3-hydro-pentane were identified by comparison with literature data [3, 24].

Perfluoro-2,3-dimethyl-3-hydrobutane, $(C\overset{a}{F}_3)_2C\overset{b}{F}C(C\overset{c}{F}_3)_2H$ (b.p., 62 °C): ^{19}F NMR ($CFCl_3$, $CDCl_3$) δ: -73.9 (F_a, multiplet); -175.1 (F_b, multiplet); -59.7 (F_c, multiplet) ppm. ^{1}H NMR (TMS, $CDCl_3$) δ: -4.04 [septet of doublet, $J(F_c\text{–}H) = 8$ Hz, $J(F_b\text{–}H) = 4$ Hz] ppm. MS *m/e*: 301 ($M^+ - F$, 100); 281 (19); 231 (16); 213 (84); 181 (30); 163 (77); 113 (59); 69 (96). Ir (gas) (cm^{-1}): 2985, 2937.

Perfluoro-2-methyl-3-hydropentane, $(C\overset{a/a'}{F}_3)_2C\overset{b}{F}C\overset{c}{F}HC\overset{d}{F}_2C\overset{e}{F}_3$ (b.p., 53 °C): ^{19}F NMR ($CFCl_3$, acetone-d_6): -73.1 (F_a multiplet); -75.5 ($F_{a'}$, multiplet); -187.2 (F_b, multiplet); -213.1 (F_c, multiplet); -123.6 and -129.5 [F_d, AB system, $J(F\text{–}F) = 289$ Hz]; -83.5 (F_e, broad singlet) ppm. ^{1}H NMR (TMS, acetone-d_6): -3.5 [doublet of multiplet, $J(F_c\text{–}H) = 46$ Hz] ppm. MS *m/e*: 301 ($M^+ - F$, 25); 251 ($M^+ - CF_3$, 100); 213 (75); 163 (63); 151 (82); 119 (76); 113 (73); 69 (63). IR (gas) (cm^{-1}): 3032.

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