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Pyrolysis of branched-chain perfluoroalkanes in the presence of halogens

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Abstract

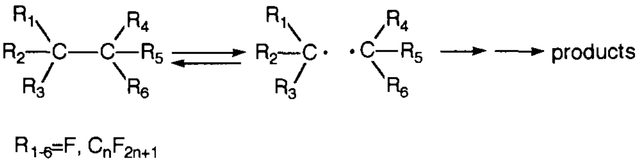
The thermal decomposition of some highly branched perfluoroalkanes in the presence of molecular halogens (Cl_2, Br_2, I_2) has been studied. The clear-cut cleavage of the most hindered carbon–carbon bond and the trapping by halogens of the intermediate radicals so formed account for the product distribution. Kinetic measurements support a mechanism based on homolytic rupture of the perfluoroalkanes as the rate-determining step, followed by the fast reaction of the intermediates with halogens.

Introduction

Perfluoroalkanes are very stable compounds because of the strength of the carbon–fluorine bond [1]. Their thermal stability is therefore limited by the carbon–carbon bond strengths. As the number of perfluoroalkyl substituents increases along the main chain, the decomposition temperature decreases, confirming that the bonds between the carbon atoms with the highest number of substituents are those most readily broken [1–4]. In our efforts to study highly branched perfluorocarbons capable of initiating the polymerization of vinylic monomers upon moderate heating [5, 6], we now describe some clean pyrolyses of perfluoroalkanes containing tertiary and quaternary centres in the presence of molecular halogens capable of trapping the intermediate radicals. This mechanistic study also provides a useful method for obtaining secondary and tertiary perfluoroalkylhalides which are otherwise difficult to synthesize.

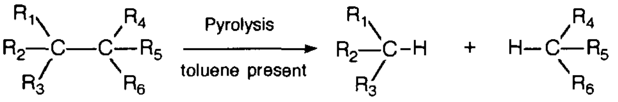
Results and discussion

We have reported previously [6] that the mechanism for the pyrolysis of crowded perfluoroalkanes involves, as a first step, an equilibrium between the starting reagent and the two radicals derived from the homolytic cleavage of the most hindered carbon–carbon bond, followed by rearrangements and recombination of the intermediate radicals [eqn. (1)].



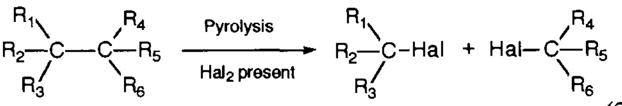
(1)

The activation energy for the whole process, calculated via the Arrhenius equation, is the sum of the energy contributions of the kinetically relevant steps. If a hydrogenated compound such as toluene is present during the thermolyses, it is easy to obtain the related hydrides [6] [eqn. (2)]



(2)

Toluene acts as an efficient radical trap: the rate-determining step corresponds simply to the cleavage of the most substituted carbon–carbon bond, because the trapping of radicals occurs very rapidly thus avoiding their rearrangement and/or coupling. To confirm these results, we have now used the molecular halogens Cl_2, Br_2 and I_2 as radical traps [eqn. (3)] [3, 7].



(3)

The kinetic progress of the reactions has been monitored by ^{19}F NMR spectroscopy (see Experimental

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TABLE 1. Rate constants (k) and activation energy (E_a) for the pyrolysis of perfluoroalkanes in the presence of halogens

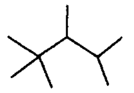
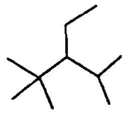
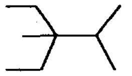
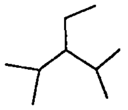
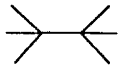
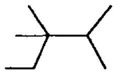
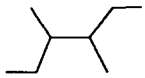
Compound No.	Perfluoro-alkane	Halogen	Temperature (°C)	k (s^{-1})×10^5	E_a (kcal mol^{-1})
1 [5]		I_2	141	0.67	42.5
			151	2.34	
			161	7.34	
		Br_2	141	0.70	
		Cl_2	151	2.00	
2 [5]		I_2	191	2.90	46.8
		Br_2	191	3.20	
		Cl_2	181	0.89	
			191	2.40	
			201	7.97	
3 [5]		I_2	181	1.40	
		Br_2	181	1.50	
4 [8]		I_2	201	5.40	39.9
		Br_2	201	5.00	
		Cl_2	181	0.77	
			191	1.99	
			201	4.96	
5 [8]		Br_2	251	4.04	55.7
			261	11.03	
			271	28.92	
6 [9]		Cl_2	181	0.74	
			201	4.20	
7 [5]		Br_2	241	1.25	44.4
			251	2.87	
			261	6.39	
8 [3]		Cl_2	251	0.73	49.3
			261	1.78	
			271	4.17	

TABLE 2. Rate constants for the pyrolysis of perfluoroalkanes at 181 °C in the presence of radical traps

Perfluoro-alkane	k (s^{-1})×10^5
1	65.02
2	0.89
3	1.40
4	0.77
5	0.001
6	0.74
7	0.004
8	0.0005

section for details). Kinetic data, as reported in Table 1*, correspond to first-order reactions. The activation energies for the pyrolyses of some perfluoroalkanes have been obtained by kinetic measurements at different temperatures. As can be seen from Table 1, the experimental values of the k constants for a given perfluoroalkane, at the same temperature, are independent (within experimental error) of the halogen used. Furthermore, the rate coefficients for the pyrolysis of compound **1** in the presence of toluene [6] and halogens compare very well. These results strongly support the contention that cleavage of the most substituted carbon–carbon bond is the rate-determining step in these pyrolyses, whilst trapping of the intermediate radicals occurs in a subsequent fast step. The relative reactivities of these perfluorocarbons towards thermolysis in the presence of halogen are listed in Table 2, where the first-order rate constants tabulated are at 181 °C.

These data show that (i) in perfluoroalkanes, carbon–carbon bonds between quaternary and tertiary centres are more readily broken than those containing only tertiary centres (compounds **1**–**4**, **6** and **7** versus compound **5** and **8**); (ii) one or two isopropyl groups as substituents in the molecule introduce an extra strain

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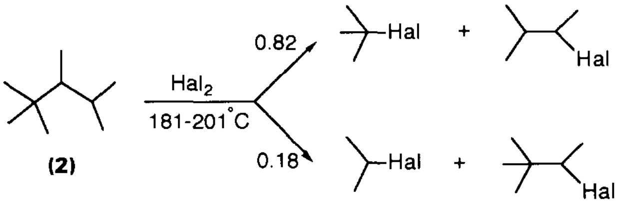
*All unmarked bonds in this paper are to fluorine.

which consequently decreases the thermal stability (compound **1** versus **7**, compound **2** versus **6**); (iii) the total number of carbons is important: molecules containing a bond between a quaternary and a tertiary carbon atom show a marked decrease in their stability when a methyl group has been replaced by an ethyl one thus suggesting that the arrangement of one more difluoromethylene unit on similarly substituted C–C bonds increases their strain energy content (compound **4** versus **7**, compound **2** versus **3**). The number of carbons can even be more important than the degree of substitution. In fact, compound **6** has a carbon–carbon bond between the quaternary centres, but its thermal stability is slightly higher than compound **2** which possesses only a tertiary–quaternary carbon bond but one more carbon atom; (iv) the presence of a fluorine atom as a substituent on the C–C bond drastically decreases the steric hindrance whilst increasing the thermal stability (compound **1** versus **5**).

As far as the products are concerned, we have always obtained the two perfluoroalkyl halides arising from the homolysis of the most crowded carbon–carbon bond. There is a notable exception for compound **2**: here two competing decomposition pathways are involved [eqn. (4)].

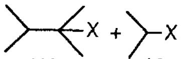
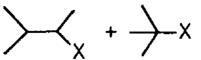
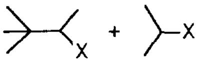
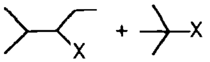
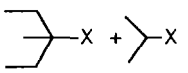
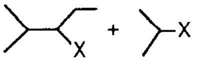
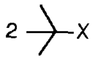
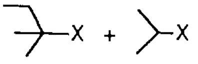
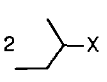


(4)

We have observed previously similar behaviour during the neat thermolysis of compound **2** [6]: in this case, even if the intermediate radicals are readily trapped by molecular halogens, competition again occurs between cleavage of the quaternary–tertiary carbon bond and the tertiary–tertiary bond, i.e. the energy supplied to the system is sufficient to break either bond. To avoid or minimize this effect, we decreased the reaction temperature: at 171 °C the rate of the reaction is quite low but we still found the same product distribution and the same product ratio as previously.

The thermal decomposition of perfluoroalkanes **1–8** in the presence of molecular halogens provides a useful way of obtaining secondary and tertiary perfluoroalkyl halides [10] (Table 3). Some of these compounds were previously unknown. The compounds concerned could be used as starting materials for a variety of chemical transformations such as perfluoroalkylations, telomerizations or organometallic reactions [11].

TABLE 3. Thermolysis of perfluoroalkanes in the presence of halogens

Perfluoro-alkane	Temperature (°C)	Products	
1	161	 **(9)** **(10)**	(X=Cl, Br, I)[a]
2	201	 **(11)** **(12)**  **(13)**	(X=Cl, Br, I)
3	181	 **(14)**	(X=Cl, Br)
4	201	 **(15)**	X=Cl, Br, I)
5	261		(X=Cl, Br, I)
6	201		(X=Cl)
7	261	 **(16)**	(C=Cl, Br, I)
8	271	 **(17)**	(X=Cl)

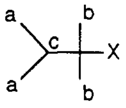
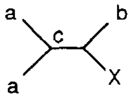
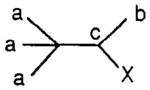
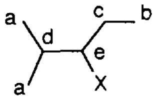
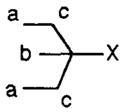
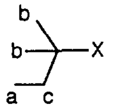
[a] X=Cl, compound a; X=Br, compound b; X=I, compound c.

In conclusion, what we have indicated in this paper and in our previous one [6] is that perfluorocarbon thermal stability can be diminished progressively by replacing fluorine atoms with perfluoroalkyl substituents along the main chain; pyrolysis occurs under mild conditions (at least when compared with more linear compounds) and quite selectively, affecting the most substituted carbon–carbon bond in the rate-determining step of the reaction. This allows a simple product distribution both in presence or absence of radical traps.

Experimental

^{19}F NMR spectra were recorded on a Varian 200 MHz spectrometer with $CHCl_3$ as the solvent and $CFCl_3$ as the internal standard. GLC analyses were performed using an 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)]. Mass spectra were obtained on a Varian-Mat CH7A mass spectrometer equipped with a magnetic analyzer.

TABLE 4. ^{19}F NMR chemical shift of new perfluoroalkyl halides[a]

Halide	X	a	b	c	d	e
	Cl I	70.9 67.9	67.5 59.8	168.2 147.4		
	Br	71	77	173	138	
	Cl Br I	62.0 62.0 62.0	75.7 73.6 69	125.6 127.5 133		
	Cl Br	70.0 68.8	79.2 77.2	115.4[b] 122.3[b] 111.2[c] 119.4[c]	174.8 170.0	133.0 136.5
	Cl I	79.7 75.0	67.0 57.5	111.5 108.5		
	Cl Br I	80.7 79.2 78.6	69.1 65.7 62.6	114.2 109.3 102.5		

[a] All signals are actually complex multiplets due to through-bond and through-space scalar couplings.

[b] AB system, J(F–F) = 268 Hz.

[c] AB system, J(F–F) = 270 Hz.

Warning: The high toxicity of several compounds, particularly tertiary iodides and bromides [12], requires great care and appropriate experimental devices (well vented fume cupboard, protective gloves).

Kinetic measurements. General procedure

The starting perfluoroalkane (1.0 g) was charged together with a twofold molar excess of halogen into an NMR tube. This was sealed and fully immersed in a thermostatted oil bath at the temperatures indicated in Table 1. The course of the reaction was monitored using ^{19}F NMR spectroscopy to 40%–50% conversion of the starting perfluoroalkanes.

Synthesis of perfluoroalkyl halides. General procedure

In a 5 ml glass tube fitted with a Rotaflo stopcock, 1.0 g of starting perfluoroalkane was charged together with a twofold molar excess of halogen. The tube was fully immersed in a thermostatted oil bath for 48 h at the temperatures indicated in Table 3 to allow complete conversion to products. Using a vacuum line, the crude mixture was subjected to trap-to-trap distillation: the highest boiling perfluoroalkyl halide was isolated in the traps held at −35 °C for iodides, −60 °C for bromides and −75 °C for chlorides. Spectroscopic data for known compounds agree with literature reports: perfluoro-2-bromo-2,3-dimethylbutane (**9b**) [13], heptafluoro-2-halopropanes (**10a–c**) [14], perfluoro-2-chloro-3-methylbutane (**11a**) [15], perfluoro-2-iodo-3-methylbutane (**11c**) [16], perfluoro-butyl halides (**12a–c**) [14, 17], perfluoro-3-bromo-3-methylpentane (**15b**) [3] and perfluoro-2-chlorobutane (**17**) [15]. All the new perfluoroalkyl halides were characterized via their ^{19}F NMR spectra (Table 4). GLC/electron impact mass spectra was only used to confirm the molecular weight of the products via the presence of the parent ion peak: the fragmentation pattern was not sufficiently diagnostic to clarify the structure.

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