Oligomerization of nitrogen-containing perfluoroacyl fluorides with hexafluoropropene oxide

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Abstract

The ionic oligomerization of eight nitrogen-containing perfluoroacyl fluorides {perfluoro(3-dimethylaminopropionyl fluoride) (**1a**), perfluoro(dimethylaminoacetyl fluoride) (**1b**), perfluoro(morpholinoacetyl fluoride) (**1c**), perfluoro(3-pyrrolidinopropionyl fluoride) (**1d**), perfluoro(3-morpholinopropionyl fluoride) (**1e**), perfluoro(2-morpholinopropionyl fluoride) (**1f**), perfluoro(2-methyl-3-morpholinopropionyl fluoride) (**1g**) and perfluoro(3-morpholinobutyryl fluoride) (**1h**)} with hexafluoropropene oxide (HFPO) has been investigated. The 1:1 adducts of the acyl fluorides and HFPO were obtained in good yield except for the cases of **1f**, **1g** and **1h**. The difference in the reactivity of two isomers (**1e** and **1f**) is discussed in terms of the nucleophilicity of the alkoxide formed from them on the basis of the molecular orbital calculations.

Introduction

Poly(tetrafluoroethylene) (PTFE) is widely used because of its unusual properties such as a high thermal stability, an inertness towards chemical attack, a low coefficient of friction, non-adhesiveness and a low dielectric constant [1]. However, conventional melt processing cannot be applied to PTFE because of a high melting point, a lack of flow above melting points and insolubility. Thus, the use of a comonomer is required in order to make fabrication easier by lowering the crystallinity of PTFE. Perfluorovinyl ethers are commonly used as a comonomer for the modification of PTFE.

By contrast, the oligomerization of acyl fluorides with hexafluoropropene oxide (HFPO) is an important reaction, because the oligomers thus obtained are key intermediates for making perfluorovinyl ethers [2]. We describe the oligomerization of some nitrogen-containing perfluoroacyl fluorides with HFPO in order to obtain new perfluorinated monomers having an dialkylamino group as the side-chain**. Our final goal was to make a high-performance fluoropolymer for gas separation, using these monomers for the modification of PTFE and taking advantage of the bulkiness of the pendant perfluorodialkylamino group [4].

Results and discussion

It is known that many parameters including the kind of catalyst, the temperature and the ratio of reactants, as well as the type of perfluoroacyl fluoride employed, influence both the yield and degree of the oligomerization of HFPO [2]. In order to optimize the reaction conditions for the formation of 1:1 oligomers, the reaction using perfluoro(3-dimethylaminopropionyl fluoride) (**1a**) has been investigated. Table 1 lists the results for the oligomerization of **1a** with HFPO under various reaction conditions. When 0.2–0.3 equiv. of catalyst (KF or CsF) and 1.0–1.5 equiv. of HFPO were used, the desired oligomer **4** was obtained in good yield (Runs 2, 3, 4 and 7). Because this reaction is a competitive one involving alkoxide anions derived both from the acyl fluoride (**2**) and HFPO (**6**) (Scheme 1), the use of excess F^- and HFPO increases the formation of **6**, which results in lowering the yield of **4**. It was also found that the use of spray-dried potassium fluoride afforded higher yields of **4** compared with the case using cesium fluoride (Runs 7 and 8). However, the selectivity of **4** to **5** (the oligomer with $n=2$) was

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**During the course of our studies of this oligomerization, a patent dealing with the oligomerization of perfluoro(3-diethylaminopropionyl fluoride) with HFPO was filed [3].

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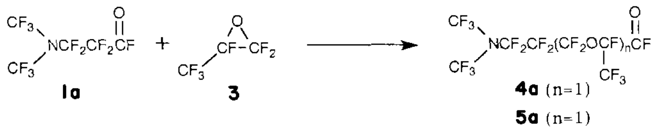
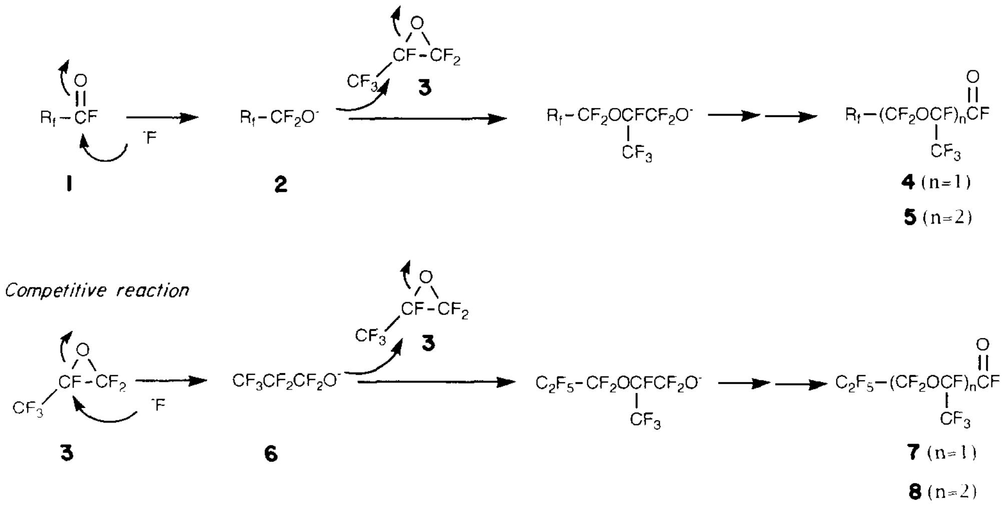
TABLE 1. Results of the oligomerization of perfluoro(3-dimethylaminopropionyl fluoride) (**1a**) with HFPO



Run No.	Acyl fluoride (mmol)	Catalyst[a] (mmol) [equiv.]			HFPO[a] (mmol) [equiv.]		Yields[b] (%)	
							4a	5a
1	9.25	CsF	2.2	[0.23]	27.4	[2.97]	33	0.5
2	9.04	CsF	2.3	[0.25]	15.1	[1.67]	53	0.4
3	9.15	CsF	2.2	[0.24]	14.5	[1.58]	41	0.4
4	8.92	CsF	2.2	[0.25]	10.2	[1.14]	53	0.2
5	8.89	CsF	9.4	[1.05]	9.36	[1.05]	27	–
6	8.89	CsF	0.72	[0.08]	6.98	[0.79]	13	0.4
7	9.01	KF	2.2	[0.25]	12.9	[1.43]	71	5.5
8	9.01	KF	9.1	[1.01]	10.7	[1.18]	48	3.6

[a]Values in brackets are equiv. per acyl fluoride.
[b]Yields based on acyl fluoride.



Scheme 1. Reaction mechanism.

decreased as a result of the increase of the formation of **5**.

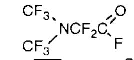
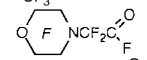
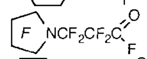
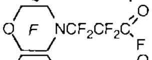
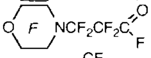
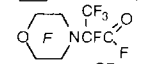
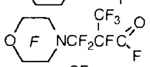
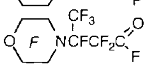
For other nitrogen-containing perfluoroacyl fluorides (**1b–h**), reaction conditions which were almost similar to those for Run 7 in Table 1 were applied. The 1:1 adducts of the acyl fluorides and HFPO (**4**) were obtained in good yield except for the cases of **1f**, **1g** and **1h** (Table 2). From the reaction using **1f** (which is an isomer of **1e**), only a trace of **4f** was formed and most of the starting material was recovered. Instead, considerable amounts of oligomers (**7**) derived from HFPO were produced. No appreciable amounts of the expected oligomers were formed in the case of **1g** and **1h**.

We have investigated why the yield of **4f** was very low compared with that of its isomer **4e**. This reaction consists of two steps, i.e. the reaction of **1** + F^- and that of **2** + **3** (Scheme 1). In order to clarify which step influenced the apparent difference between **1e** and **1f** most, ^{19}F NMR spectroscopy and molecular orbital calculations have been performed on the acyl fluorides (**1e** and **1f**) and on the alkoxides (**2e** and **2f**).

The ^{19}F NMR spectra of **1e** and **1f** were measured by adding an excess amount of potassium fluoride or cesium fluoride in tetraglyme at room temperature (Figs. 1 and 2).

In the spectrum of **1e**, the absorption peak appearing at 25.5 ppm is due to the fluorine of the acyl fluoride [e-fluorine in Fig. 1(a)]. However, this peak disappeared when cesium fluoride was added to the system and a new peak appeared concomitantly at −26.5 ppm, indicating the generation of an alkoxide [Fig. 1(b)].

TABLE 2. Results of the oligomerization of N-containing perfluoroacyl fluorides with HFPO

Acyl fluoride		(mmol)	KF[a] (mmol)	[equiv.]	HFPO[a] (mmol)	[equiv.]	Yields[b] (%) 4	5
	(1b)	9.18	2.2	[0.24]	36.0	[3.91]	45	9.6
	(1c)	13.7	2.2	[0.16]	32.1	[2.35]	72	1.0
	(1d)	9.72	2.2	[0.23]	19.3	[1.99]	40	0.7
	(1e)	9.58	2.2	[0.23]	14.1	[1.47]	39	–
	(1e)	9.40	2.0[c]	[0.21]	18.2	[1.94]	47	0.9
	(1f)	11.2	2.2	[0.20]	14.9	[1.33]	1.5	–
	(1g)	9.12	2.4	[0.26]	18.8	[2.06]	–	–
	(1h)	6.76	2.2	[0.33]	22.4	[3.31]	–	–

[a]Values in brackets are equiv. per acyl fluoride.
[b]Yields based on acyl fluoride.
[c]Cesium salt used instead of potassium salt.

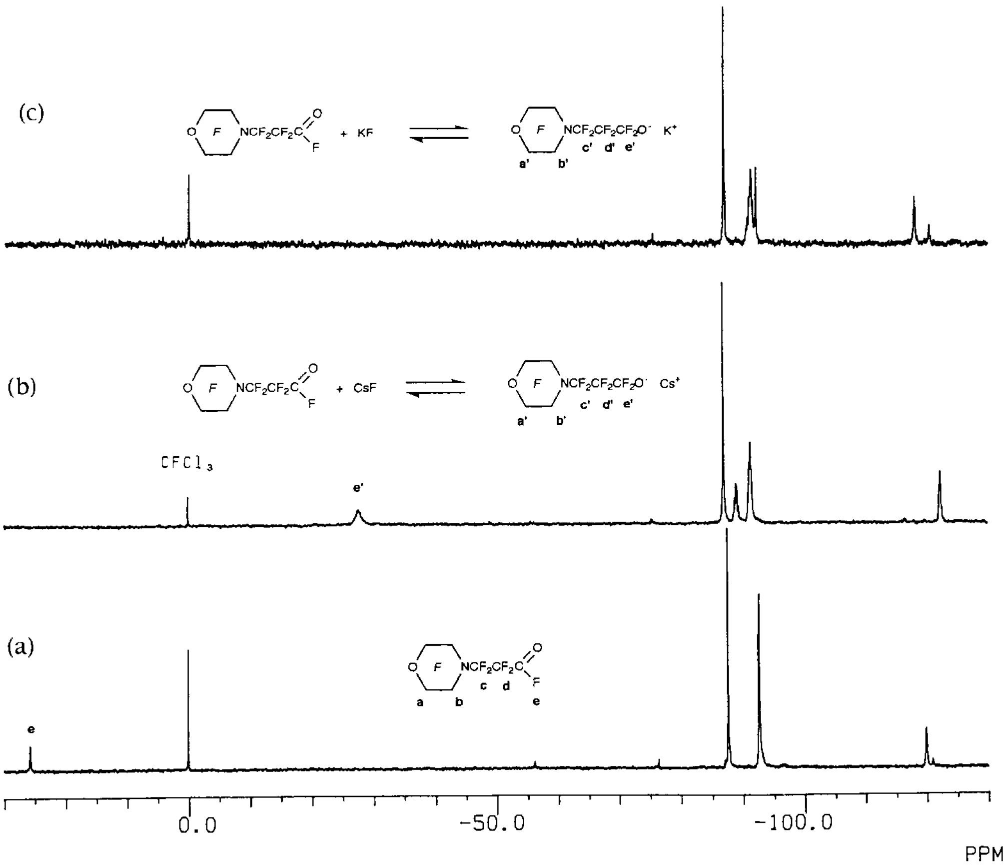


Fig. 1. ^{19}F NMR spectra of perfluoro-3-morpholinopropoxide salts.

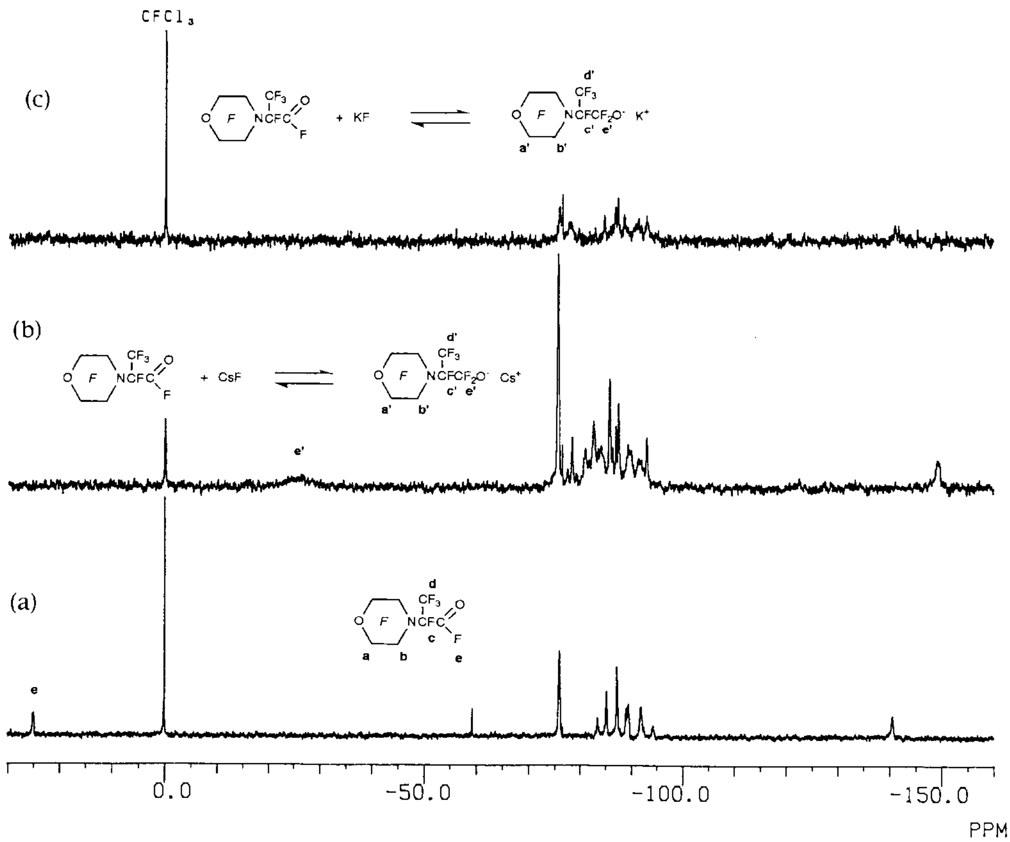


Fig. 2. ^{19}F NMR spectra of perfluoro-2-morpholinopropoxide salts.

Consequently, this new peak was assigned to the α-CF_2 group of cesium alkoxide (e′-fluorine). However, in the potassium fluoride system, the presence of an absorption peak corresponding to the α-CF_2 group of the alkoxide could not be confirmed [Fig. 1(c)], which may be ascribed to rapid fluoride-ion exchange.

Similarly, in the ^{19}F NMR spectrum of **1f**, which was obtained by adding cesium fluoride as a fluoride-ion source, the generation of an alkoxide was confirmed by the presence of an absorption peak at −25 ppm [Fig. 2(b)], but not in the case of the potassium fluoride system [Fig. 2(c)].

Molecular orbital calculations of the acyl fluorides (**1e** and **1f**) and of the alkoxides (**2e** and **2f**) were carried out by MOPAC using the PM3 Hamiltonian [5] (Tables 3 and 4). Both reactions **1e**→**2e** and **1f**→**2f** were endothermic ($\Delta H_f = -126$ and -131 kcal mol^{-1}, respectively). The atomic charges on the carbonyl carbon (^{9}C) of the two acyl fluorides (**1e** and **1f**) were similar in magnitude. The activation energies were also calculated for the formation of the alkoxides by nucleophilic attack of a fluoride anion on the carbonyl carbon of **1e** and **1f**, respectively (Fig. 3). It was found that the activation energy for **1e** was 19.1 kcal mol^{-1} and that for **1f** was 3.3 kcal mol^{-1}. These results support the fact that the alkoxide **2** is easily formed both from **1e** and **1f**, and that its formation should be more facile from **1f** than from **1e**. There was no difference between **1e** and **1f** in terms of the reaction which produces alkoxide (**1**+F^-).

Next, we investigated another reaction step (the reaction of **2**+**3**) by calculating the net atomic charges of the alkoxides (**2e** and **2f**). The net atomic charge of the alkoxide-O atom of **2e** was more negative than that of **2f** (^{10}O in Table 4). This demonstrates that **2e** is more reactive as a nucleophile than **2f**.

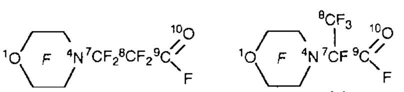
In conclusion, it is reasonable to assume that the poor nucleophilicity of **2f** relative to **2e** is responsible for the low yield of **4f**. Because this reaction is competitive between the alkoxide anions produced from the acyl fluoride (**2e** and **2f**) and that from HFPO (**6**) (Scheme 1), it is considered that small difference in the reactivity of the alkoxide has a considerable influence on the reaction pathway. Thus, in the case of **1f**, the side-reaction rather than the desired one occurs predominantly.

Experimental

Reagents

All nitrogen-containing perfluoroacyl fluorides used were synthesized by electrochemical fluorination of the

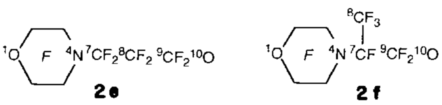
TABLE 3. Net atomic charges associated with perfluoro(morpholinopropionyl fluorides)



1e 1f

Acyl fluoride	Net atomic charges						Heat of formation (kcal mol^{-1})
	^{1}O	^{4}N	^{7}C	^{8}C	^{9}C	^{10}O	
1e	−0.2712	−0.2237	0.2644	0.2018	0.3325	−0.2216	−710.00024
1f	−0.2685	−0.1898	0.0913	0.3544	0.3239	−0.2085	−713.30112

TABLE 4. Net atomic charges associated with perfluoro(morpholinopropoxide) anions



2e 2f

Alkoxide anion	Net atomic charges						Heat of formation (kcal mol^{-1})
	^{1}O	^{4}N	^{7}C	^{8}C	^{9}C	^{10}O	
2e	−0.2906	−0.2267	0.2525	−0.0447	0.5085	−0.5706	−836.32015
2f	−0.2985	−0.0916	−0.3254	0.3496	0.5467	−0.4563	−844.40328

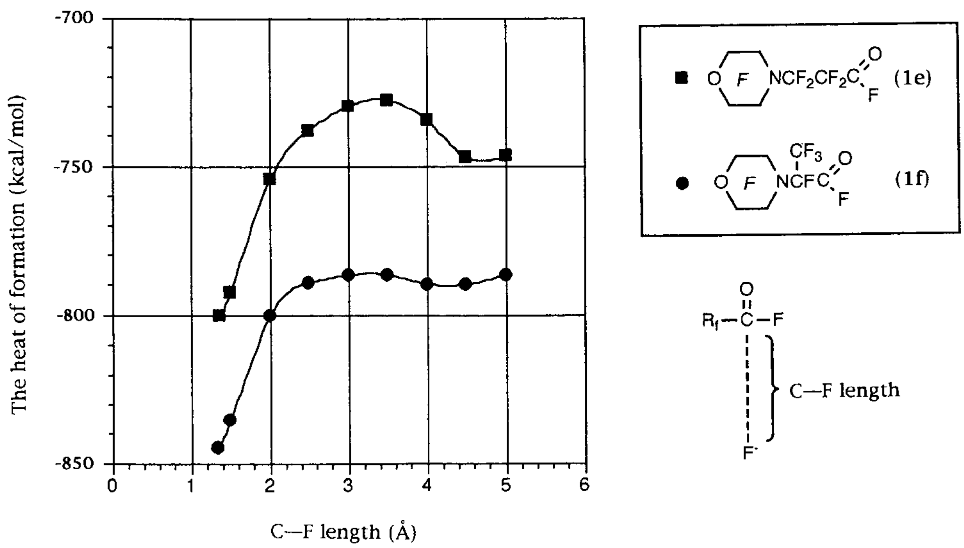


Fig. 3. The heat of formation of perfluoro(morpholinopropionyl fluoride) + F^{-}.

corresponding methyl esters of alkylamino-substituted acetic, propionic or butyric acids [6], and were fractionally distilled with dry sodium fluoride prior to use. Anhydrous cesium fluoride (Aldrich) was dried by heating overnight at 300 °C and finely ground in a dry box. Spray-dried potassium fluoride (Morita Chemical Co.) was used as received. Tetraethylene glycol dimethyl ether (tetraglyme) was dried over molecular sieves (0.3 nm, Merck). Hexafluoropropene oxide (Daikin, purity 73.0%), which contained unreacted hexafluoropropene, was used without further purification.

Instruments

Analytical GLC work was carried out with a Shimadzu GC-6A gas chromatograph using stainless-steel columns packed with Thermol-3 on Uniport B. For semi-preparative work, a Gasukuro LL-75 modified gas chromatograph was used employing a stainless column (10-mm diameter) packed with 30% Silicone QF-1 on Chromosorb PAW. The carrier gas was helium in all cases.

^{19}F NMR spectra were measured, using $CFCl_3$ as an internal standard in $CDCl_3$ solvent, on a Hitachi R-90F (84.68 MHz) spectrometer. Mass spectra were measured on a Shimadzu GC–MS 7000 instrument at 70 eV.

As typical examples of oligomerization reactions, those using **1a, 1e** and **1h** will be described.

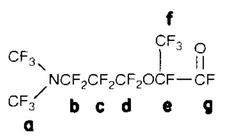
Oligomerization of perfluoro(3-dimethylaminopropionyl fluoride) (1a) with HFPO

In a 50-ml autoclave, potassium fluoride (2.2 mmol), tetraglyme (15 ml) and acyl fluoride **1a** (9.01 mmol) were added under dry nitrogen. After degassing by cooling at −196 °C, the mixture was slowly heated up to room temperature and stirred for 30 min. The mixture was then frozen by immersion in a liquid nitrogen bath and the calculated amount of hexafluoropropene oxide (HFPO) (12.9 mmol) was introduced by vacuum transfer. After the mixture had been stirred at 0 °C for 2 h and overnight at room temperature, the volatile compounds were separated from potassium fluoride and tetraglyme under dynamic vacuum into consecutive cold traps cooled at −78 °C and −196 °C. The oligomer with $n=1$ (**4a**) was collected in the −78 °C trap and its ^{19}F NMR spectral data are listed in Table 5. Further characterization was performed by formation of the methyl ester. Thus, 1 ml of methanol was added to a capped Pyrex vessel (10 ml) containing the reaction mixture (4.46 g) freed from potassium fluoride and tetraglyme, and the vessel was shaken for several minutes. Fluorocarbons (lower phase) were separated from the unreacted methanol (upper phase) and were analyzed by GLC, IR and ^{19}F NMR methods. The following compounds were identified: methyl perfluoropropionate (0.40 g), methyl perfluoro(2-methyl-3-oxahexanoate) (the methyl ester of **7**) (0.38 g), methyl perfluoro-(3-dimethylaminopropionate) (0.36 g), methyl perfluoro(6-dimethylamino-2-methyl-3-oxahexanoate) (the methyl ester of **4a**) (2.97 g) and unidentified material (0.35 g). The yield of **4a** was 71% based on the acyl fluoride employed. Methyl perfluoro(3-dimethylaminopropionate) and the methyl esters of oligomers with $n=1$ (**4a**) and $n=2$ (**5a**) were purified for further characterization by semi-preparative GLC methods.

Methyl perfluoro(3-dimethylaminopropionate) (nc): B.p. 106.0–107.0 °C, n_D^{20} 1.3015, d_4^{20} 1.6169. IR (capillary film) (cm^{-1}): 1789 (s) [ν(C=O)]. MS *m/z*: 252 [$(CF_3)_2NCF_2CF_2^+$, 2.2]; 202 ($C_3F_8N^+$, 34.9); 164 ($C_3F_6N^+$, 11.4); 159 ($CF_2CF_2CO_2Me^+$, 10.8); 131 ($C_3F_5^+$, 26.3); 119 ($C_2F_5^+$, 15.5); 114 ($C_2F_4N^+$, 53.9); 100 ($C_2F_4^+$, 18.8); 81 ($C_2F_3^+$, 15.1); 69 (CF_3^+, 100); 59 (CO_2Me^+, 98.1). ^{19}F NMR δ: −118.2 (α-CF_2); −92.2 (β-CF_2); −52.2 (CF_3−); 3.93 (Me, $J(\alpha\text{-}CF_2-CF_3)=7.9$ Hz, $J(\beta\text{-}CF_2-CF_3)=16.1$ Hz) ppm.

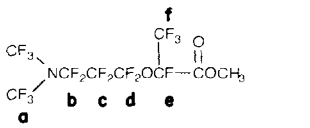
Methyl perfluoro-(6-dimethylamino-2-methyl-3-oxahexanoate) (the methyl ester of **4a**) (nc) had b.p. 155.0–156.0 °C. Its NMR and mass data are listed in Tables 6 and 8, respectively. The NMR data of methyl ester of **5a** (the oligomer with $n=2$) are listed in Table 7.

TABLE 5. Chemical shifts (ppm) in the ^{19}F NMR spectrum of **4a**



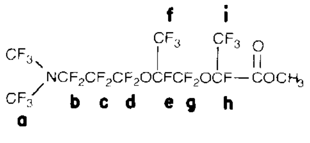
a	b	c	d	e	f	g
−53.1	−91.5	−125.2	−78 to −88	−131.0	−82.4	26.4

TABLE 6. Chemical shifts (ppm) in the ^{19}F NMR spectrum of the methyl ester of **4a**



a	b	c	d	e	f
−53.1	−91.4	−125.3	−79.5 to −86.3	−132.0	−82.9

TABLE 7. Chemical shifts (ppm) in the ^{19}F NMR spectrum of the methyl ester of **5a**

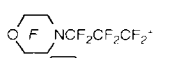


a	b	c	d, g	e	f	h	i
−53.0	−91.4	−125.0	−76 to −88	−145.6	−80.6	−132.1	−82.9

TABLE 8. Mass data for the methyl ester of **4a**

m/e	Relative intensity	Fragment
458	0.5	$M^+ - F$
325	8.2	$M^+ - (CF_3)_2N$
302	2.7	$(CF_3)_2NCF_2CF_2CF_2^+$
214	16.4	$C_4F_8N^+$
202	26.4	$(CF_3)_2NCF_2^+$
169	16.0	$C_3F_7^+$
159	8.7	$CF_3CFCO_2CH_3^+$
131	31.1	$C_3F_5^+$
114	44.9	$C_2F_4N^+$
100	22.9	$C_2F_4^+$
69	100	CF_3^+

TABLE 9. Mass data for the methyl ester of **4e**

m/e	Relative intensity	Fragment
380	3.2	
280	24.4	
214	6.0	$C_4F_8N^+$
169	47.8	$C_3F_7^+$
164	12.1	$C_2F_4N^+$
147	7.9	$C_3F_5O^+$
119	100	$C_2F_5^+$
114	32.5	$C_2F_4N^+$
100	47.3	$C_2F_2^+$
69	44.6	CF_3^+

Oligomerization of perfluoro(3-morpholinopropionyl fluoride) (1e) with HFPO

The oligomerization and work-up of the products were conducted in a similar manner to that described above for **1a**. The reaction of acyl fluoride **1e** (9.58 mmol) and HFPO (14.1 mmol) in the presence of potassium fluoride (2.2 mmol) in tetraglyme (15 ml) resulted in the formation of a mixture of volatile products (7.24 g) in the cold traps. The products (6.23 g) condensing at −78 °C were treated with methanol to give methyl esters and were analyzed. The following compounds were identified: methyl perfluoro(2-methyl-3-oxahexanoate) (the methyl ester of **7**) (1.14 g), methyl perfluoro(2,5-dimethyl-3,6-dioxanonanate) (0.12 g), methyl perfluoro(3-morpholinopropionate) (1.66 g) [6c], methyl perfluoro-(2-methyl-6-morpholino-3-oxahexanoate) (the methyl ester of **4e**) (2.04 g), methyl perfluoro(2,5-dimethyl-9-morpholino-3,6-dioxanonanate) (the methyl ester of **5e**) (0.02 g) and unidentified material (1.25 g). The yield of **4e** was 39% based on the acyl fluoride employed. This material was a liquid having a high boiling point. Its mass spectra data are listed in Table 9.

Oligomerization of perfluoro(3-morpholinobutyryl fluoride) (1h) with HFPO

The oligomerization and work-up of the products were conducted in a similar manner. The reaction of acyl fluoride **1h** (6.76 mmol) and HFPO (22.4 mmol) in the presence of potassium fluoride (2.2 mmol) in tetraglyme (15 ml) afforded a mixture of volatile products (9.50 g) in the cold traps. The products (6.40 g) condensing at −78 °C were treated with methanol to give methyl esters and were analyzed similarly. The following compounds were obtained: methyl perfluoro(2-propoxypropionate) (1.74 g), methyl perfluoro(2,5-dimethyl-3,6-dioxanonate) (0.03 g), methyl perfluoro(3-morpholinobutyrate) (2.52 g) [6d] and unidentified material (2.09 g). The formation of the expected oligomer with $n = 1$ was not confirmed in this case.

Calculations

Molecular orbital calculations were carried out using MOPAC Version 6 [5] employing PM3 hamiltonian. Calculation of the activation energy was started from the alkoxide anion, and the heats of formation were obtained by extended calculations of the C−F bond of the α-CF_2 group at 0.5 Å steps.

Acknowledgments

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