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The pyrolysis of perfluoroolefin oxides has been studied by gas chromatography/mass spectrometry at 400-700°C, in a current of He (1:10 dilution, contact time 1 sec). For oxides containing a terminal CF_2 group, the sole degradation route is through the elimination of difluorocarbene. Pyrolysis of symmetrical disubstituted oxides results in the elimination of a perfluoroalkylfluorocarbene, which subsequently isomerizes to the corresponding perfluoroolefin. In the pyrolysis of unsymmetric disubstituted oxides the elimination of perfluoroalkylfluorocarbenes occurs by both of the possible routes. Trisubstituted oxides eliminate bis-perfluoroalkylcarbenes. The decomposition of tetrasubstituted oxides proceeds along several directions concurrently.

Hexafluoropropylene oxide is used extensively in thermal reactions as a source of difluorocarbene [1, 2]. Kinetic studies [3, 4] show that even at 160-250°C this compound dissociates monomolecularly into difluorocarbene and $CF_3C(0)F$. For the thermal decomposition of 1,2-epoxyperfluoro-2-methylpropane a significantly higher temperature (320°C) and a contact time of 24 h are necessary, forming in this case difluorocarbene and hexafluoro-acetone [5]. It appears that until recently the only work devoted to the pyrolysis of other more complex perfluoroolefin oxides consisted of a study of the pyrolysis of epoxides of the pentamer and hexamer of tetrafluoroethylene [6]. However, the rather long contact time employed in the experiments favored the initiation of secondary reactions, and as a result the expected carbene-olefin isomerization product was detected only in the case of the pyrolysis of the pentamer of tetrafluoroethylene.

Resulting from the development of the hypohalogenite method for the epoxidation of fluoroolefins [7], various polyfluorosubstituted oxiranes have become available in recent years, and in this related work, designed to investigate their ability to eliminate per-fluoroalkylcarbenes, we have used a gas chromatography/mass spectrometry technique to study the products of pyrolysis, at atmospheric pressure, of the following oxides: 1,2-epoxy-perfluoropropane (I), 2,3-epoxyperfluorobutane (II), 1,2-epoxyperfluoropentane (III), 2,3-epoxyperfluorobexane (V), 2,3-epoxyperfluoro-2-methylpentane (VI), 2,3-epoxyperfluorobexane (VI), 1,2-epoxyperfluorobexane (VII), 2,3-epoxyperfluoro-4-methylpentane (IX), 1,2-epoxyperfluoroctane (X), 2,3-epoxyperfluoroctane (XI), 3,4-epoxyperfluoro-2,4-dimethylheptane (XII), 2,3-epoxyperfluoro-3-isopropyl-4-methylpentane (XIII), and 2,3-epoxyperfluoro-2,4-dimethyl-3-ethylpentane (XIV).

In a number of cases detection of the initial products of vacuum pyrolysis was achieved using the low-energy mass spectrometry technique.

EXPERIMENTAL

The perfluorooxirane samples in (I)-(XIV) were synthesized by epoxidation of fluoroolefins using the hypohalogenite method [7], and their purity was checked by gas chromatography/mass spectrometry.

The mass spectrometry units for studying the initial products of vacuum pyrolysis [8] and the final products of pyrolysis in the stream have been described previously [9]. Pyrolysis of the oxides at atmospheric pressure was carried out at 10 times dilution in helium in a heated quartz reactor, 200×3 mm, with a contact time of 1 sec. The pyrolysis

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Parent compound	Pyrol- ysis temper- ature,	Pyrolysis products
	°C	
F-C-CF-CF-	400	31% CaF, 69% CFaCFO
	100	
0 (I)		· · · · · · · · · · · · · · · · · · ·
CFCF-CF-CF	670	10% C ₂ F ₄ , 49% CF ₃ CF=CF ₂ , 39% CF ₃ CFO
	0.0	
(U)		
$\mathbf{F}_{\bullet}\mathbf{C}$ CF (n -C, \mathbf{F}_{\bullet})	650	27% C ₂ F ₄ , 1% CF ₃ CF=CF ₂ ,
	000	57% (<i>n</i> -C ₃ F ₇)CFO
an		
CFCF-CF-C-F	700	9% C_2F_4 , 26% C_2F_5CFO , 48% $CF_3CF=CF_2$,
		12% CF ₃ CFO
(IV)		
C.FCF-CF-C2F.	660	60% CF ₃ CF=CF ₂ , $36%$ C ₂ F ₅ CFO
(\mathbf{V})		
(CFa)-C-CF-CFFa	· 660	60% CF ₃ CF=CF ₂ , $40%$ C ₂ F ₅ CFO
(VI)		
$CF_{\bullet}CF_{\bullet}CF_{\bullet}(n-C_{\bullet}F_{\bullet})$	660	$11\% C_2F_4$, 8% CF ₃ CF=CF ₂ .
		40% (<i>n</i> -C ₃ F ₇)CFO, 32% CF ₂ =CFC ₂ F ₅ ,
(VIII)		8% CF3CFO
$\mathbf{F}_{2}\mathbf{C}$ $-\mathbf{C}\mathbf{F}$ $(n-\mathbf{C}_{4}\mathbf{F}_{4})$	760	$33\% C_2F_4, 5\% CF_3CF = CF_2,$
		62% (<i>n</i> -C ₄ F ₉)CFO
(VIII)		
$CF_1CF_{}CF(i-C_1F_1)$	760	$7\% C_2F_4$. 17% CF_3CF=CF.
		13% (<i>i</i> -C ₃ F ₇)CFO, 44% CF ₃ CF=CFCF ₃ ,
(IX)		10% CF ₃ CFO
F_2C CF (<i>n</i> -C ₆ F ₁₃)	630	$66\% C_2F_4$, 1% CF ₃ CF=CF ₂ ,
\sim		$33\% (n-C_{6}F_{13})CFO$
(X)		
CF3CF-CF (n-C4F11)	630	$10\% C_2 F_4, 3\% CF_3 CF = CF_2,$
\sim		$(n-C_5F_{11})CFO = 00\% CF_2 = CF(n-C_4F_9),$
(XĪ)		3% UF3UFU, $3%$ parent (AI)
$(i-C_3F_7)$ CF ₃	630	55% C ₅ F ₁₀ , 40% (<i>i</i> -C ₃ F ₇)CFO
	1	
$\vec{\mathbf{F}} = \mathbf{O}^{\mathbf{F}_1} \mathbf{O}^{\mathbf{F}_2}$		
(X11)	620	[C.E.O] 50/ C.E. 70/ C.E. 50/ C.E.
(i-C,F;)	000	23% (CFa) CF 2% (<i>i</i> -C-Fa)
CCFCF.		7% CF2=CFCF=CFCF, $4%$ (<i>i</i> -C2F-).CO
(i-C ₁ F ₁)	T i	3% C2F4. 41% C7F14. [CF3CF0]
(XIII)		
$(i-C_3F_7)$ CF ₃	630	$[C_8F_{10}O], 1\% n-C_4F_{10}, 12.5\% i-C_3F_7-C_2F_5,$
		$10,0\%$ $C_2F_6, 1\%$ $C_2F_4; 5\%$ $C_3F_8, 9\%$ $-C_4F_{10},$
C ₂ F ₆		$1 37.0 - 0.3 r_{7} - 0.0 - 0.2 r_{5}, 19.0 - 0.3 r_{6}, 10.0 - 0.6 r_{12}, 17.0 - 0.0 - $
(XIV)	1	[(013)200]

TABLE 1. Composition of the Pyrolysis Products of the Perfluoroolefin Oxides (I)-(XIV)

temperature was chosen such that at the contact time of 1 sec 100% conversion would be achieved. The pyrolysis products, collected in a trap cooled with liquid nitrogen, were heated to 20°C, and the trap was then opened to a previously evacuated sample vessel, of volume 150 ml, the pressure of which was then brought up to atmospheric by admission of He. The sample vessel had a rubber septum through which gas could be withdrawn using a sampling syringe. Because of high chemical reactivity, causing "cathode poisoning," the acid fluorides of perfluorocarboxylic acids present in the pyrolysis products were analyzed as the corresponding ethyl esters. Esterification was carried out by taking the gas sample into a syringe which had been previously rinsed with ethanol.

The mass spectra of the thermal decomposition products were recorded on a Finnigan MAT INCOS 50 gas chromatograph/mass spectrometer (1 m column CARBOPACK, 36°C, 5 min, followed by heating to 220°C, heating rate 15°C/min, carrier gas He).

RESULTS AND DISCUSSION

Typical compositions of the pyrolysis products of the oxides (I)-(XIV), obtained from relative areas of GC/MS peaks, are given in Table 1.

In contrast to the acid fluorides of perfluorocarboxylic acids, from whose mass spectra molecular ions are usually absent [10], the corresponding ethyl esters of

m/z	<i>I.</i> %					
	CF3CO2Et	C₂F₅CO₂Et	(<i>n</i> -C ₃ F ₁)CO ₂ Et	(i-C ₃ F ₇)CO ₂ Et	(n-C4F9)CO2Et	
31 43 45 50 51 69 73 78 81 93 95 97	3,1 5,6 3,0 6,1 9,1 6,2 100 4,3 3,1 0,9 6,1	13,1 7,7 5,6 6,2 9,2 2,0 55,8 3,0 2,0 2,3 3,7 3,5	10,0 8,2 5,4 3,4 5,8 1,7 100 1,9 2,4 3,4 2,1	$\begin{array}{c} 8.3\\ 8.7\\ 10,4\\ 1,2\\ 2,0\\ 0.6\\ 100\\ 1,0\\ 2,9\\ 1,5\\ 0,6\\ 16\\ \end{array}$	6,0 6,4 7,2 1,6 2,6 1,8 100 2,2 1,1 1,6 2,7 0,4 0,8	
99 100 109 113	21.7	15,1 0,7	38,9 7,4	21,8 2,1	22,8 4,4	
119 127 131 141	5,4 1,9	100	22,3 2,7	8,9 3,9	10,3 29,2	
142 147 149 150 163	0,2	20,9 14,0 0,6 4,3	4,1	4,6	1,7	
169 175 177 191 192		7,4 3,3 0,3	85,9	50,7 5,7	5,4	
195 197 199 213			5,5 21,5 6,4 4,1	0,9 82,6	1,5	
219 227 241 242			6,3 3,5	5,7 3,3 0,7	39,3	
245 247 249 263 277 291 292					3,3 6,3 2,7 2,9 1,9 1,5 0.2	

TABLE 2. Mass Spectra of the Ethyl Esters of Perfluorocarboxylic Acids (60 eV)

perfluorocarboxylic acids can be identified by their molecular ions, and also by the characteristic ions $[M - COOC_2H_5]^+$, $[M - C_2H_5]^+$, $[M - CH_3]^+$, and $[M - H]^+$ (Table 2).

In a number of experiments esters were not observed by mass spectrometry, although the corresponding products of carbene-olefin isomerization were detected (in these cases the formulas of the esters are given in square brackets) (see Table 1).

The sole route for the thermal dissociation of the oxides (I), (III), (VIII), and (X), which contain a terminal CF_2 group, was by the elimination of difluorocarbene, which is confirmed by the method of low-energy mass spectrometry. In atmospheric pyrolysis conditions, secondary products of the degradation of compounds (I), (III), (VIII), and (X) are tetrafluorethylene (TFE) and hexafluoropropylene (HFP), the quantity of HFP increasing somewhat at higher temperatures, but not exceeding 5%, which is in agreement with the data in [11]. It seems probable that HFP is formed through the recombination of difluorocarbene and trifluoromethylfluorocarbene, the latter being the product of the olefin-carbene isomerization of TFE [12].

In experiments on the pyrolysis of the symmetrical disubstituted oxides (II) and (V) (Table 1), esters of the corresponding perfluorocarboxylic acids and perfluoroolefins were detected. The pyrolyzate of (II) contains 50% HFP. Low-energy mass spectrometry confirms that together with TFE (the product of carbene-olefin isomerization of trifluoromethyl-fluorocarbene), difluorocarbene is also formed under vacuum pyrolysis conditions from (II),

Ton	m/z	I. %			
		$(\mathbf{CF}_3)_2\mathbf{CFC}(\mathbf{O})\mathbf{C}_2\mathbf{F}_5$	$(\mathbf{CF}_3)_2\mathbf{CFC}(\mathbf{O})\mathbf{CF}(\mathbf{CF}_3)_2$		
CF^+ CF_2^+ $C_2F_2^+$	31 50 62	10.4 4,2 0.6	4,5 1,1		
$\overrightarrow{CF_3^+}$ OC ₃ F ⁺ OC ₂ F ₂ ⁺	69 71 78	100,0 1,3 1,6	100,0		
${ \begin{array}{c} {{ m C}_2}{{ m F}_3}^+ \ { m O}{{ m C}_3}{{ m F}_2}^+ \ {{ m C}_3}{{ m F}_3}^+ \end{array} }$	81 90 93	3.2 0.4 2.6	2,0		
$OC_2F_3^+$ $C_2F_4^+$ $OC_3F_3^+$ $C_5F_5^+$	97 100 109	0.5 17.7 3.4 93.7	12.8 3.9		
$C_2 F_5$ $C_4 F_4$ + $O C_3 F_4$ + $C_3 F_5$ +	119 124 128 . 131	92,7 0,4 1,9 2.0	1,9		
$OC_3F_5^+$ $C_3F_6^+$ $OC_4F_5^+$	147 150 159	24,6 3,1 0,9	$\frac{2,9}{1,6}$		
$C_3F_7^+$ OC ₄ F ₇ +	169 197	28,1 32,9	$40.8 \\ 62.8$		

TABLE 3. Mass Spectra of Perfluoro-2,4-dimethylpentanone-3 and Perfluoro-2-methylpentanone-3 (60 eV)

apparently as a result of the dissociation of the vibrationally excited C_2F_4 * molecule. In addition, HFP is produced from the recombination of difluorocarbene and trifluoromethyl-fluorocarbene. It is significant that on pyrolysis of (V) (Table 1), only HFP is formed, probably because of the much greater thermal stability of the HFP* molecule compared with TFE* [13].

The pyrolysis of the unsymmetrical disubstituted perfluoroolefin oxides (IV), (VII), (IX), and (XI) proceeds by both possible routes, which was confirmed by the detection in each case of two ethyl esters of perfluorocarboxylic acids and two perfluoroolefins (Table 1).

The fact that the pyrolyzate of oxide (VI) (Table 1) contains 60% HFP, and that the pyrolyzate of oxide (XII) contains up to 55% isomeric C_5F_{10} perfluoroolefins (of which figure 15% represents perfluoropentene-2), leads to the conclusion that the trisubstituted oxides (VI) and (XII) are selective sources of $(CF_3)_2C$: and $(n-C_3F_7)(CF_3)C$: respectively.

The trisubstituted (XIII) and tetrasubstituted (XIV) oxides dissociate less selectively. Their pyrolysis products are found to contain ketones perfluoro-2,4-dimethylpentanone-3 (4%) and perfluoro-2-methylpentanone-3 (37%), respectively, which have characteristic mass spectra (Table 3).

Another thermal dissociation route, characteristic only for the oxides (XIII) and (XIV), and also for the oligomers of HFP [9], containing perfluoroisopropyl groups, is the separation of a pair of radicals at the position of maximum steric stress, arising from the presence of two branched substituents at a carbon atom. These processes can explain the formation of the products of recombination of the radicals (i-'C₃F₇ and 'CF₃) in the case of compound (XIII) and (i-'C₃F₇, 'C₂F₅, and 'CF₃) in the case of compound (XIV) (Table 1). The presence in the pyrolysis products of (XIII) of 41% of an unidentified compound having the composition C_7F_{14} (probably perfluoro-3,4-dimethylpentene-2), and in the pyrolysis products of (XIV) of 15% of perfluoro-2,4-dimethylpentene-2, is in accordance with a carbene mechanism for the rupture of the oxirane rings and subsequent carbene-olefin isomerization of the carbenes (i-C₃F₇)₂C: and (i-C₃F₇)(C₂F₅)C:.

From the results of this study, the compounds (V), (VI), and (XII) can be recommended as selective sources of the carbones $(C_2F_5)FC$; $(CF_3)_2C$; and $(n-C_3F_7)(CF_3)C$; respectively.

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MOLECULAR ASSOCIATION IN MIXTURES OF ACETONITRILE WITH AMIDES

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The equilibrium constants of molecular association were calculated on the basis of the data from the PMR spectra in binary nonaqueous mixtures of acetonitrile with amides. The systems with formamide and N-methylformamide are comparatively strongly associated, whereas the association in mixtures of acetonitrile with DMF and HMPA is weak. The excess heat capacity of the systems was calculated by models of the associative equilibria and was compared with experiment. The developed approach to the description of molecular association makes it possible to obtain qualitative and quantitative data on the association processes in the investigated systems.

The proton-accepting molecules of acetonitrile (AN) provide a convenient model for the study of molecular association in liquid mixtures [1-3]. Mixtures of acetonitrile with amides, which have been investigated very little, are of considerable theoretical and practical interest [4, 5].

EXPERIMENTAL

The PMR spectra of the binary systems were obtained on a Bruker AC200 spectrometer at 200 MHz. The spectra of the mixtures of acetonitrile with DMF and HMPA contain signals from the methyl protons of the acetonitrile and the amides (AM) and a signal from the formyl proton in the case of DMF. The spectra of the mixtures of acetonitrile with formamide (FA) and N-methylformamide (MFA) are much more complicated; the signals from the protons of the $-NH_2$ (-NH) group were most sensitive to change in the composition of the mixture. In the PMR spectrum these signals are broad bands (on account of coupling with ¹⁴N) and can be separated into several components (between two and four) depending on the nature of the amide (formamide or methylformamide) and the concentration of the mixture. (A

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