SYNTHESES AND DEGRADATIONS OF FLUORINATED HETEROCYCLICS

III.   PERFLUOROALKYL AND PERFLUOROALKYLETHER-1,3,4-OXADIAZOLES

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SUMMARY

2,5-Bis(perfluoro-n-heptyl)-, 2-perfluoroalkylether-5-perfluoro-n-
heptyl-, and 2,5-bisperfluoroalkylether-1,3,4-oxadiazoles were synthesized
and characterized. 2,5-Bis(perfluoro-n-heptyl)-1,3,4-oxadiazole was
thermally and hydrolytically stable at 325°C; however, in the presence of
air, degradation took place at 235°C. The perfluoroalkylether analogue
exhibited thermal and hydrolytic stability at 325°C; it was found to be
unaffected by Jet-A fuel and air at 235°C. At 325°C in air some degradation
occurred as evidenced by volatiles production, oxygen consumption, and
96% starting material recovery.

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INTRODUCTION

Polyperfluoroalkylethers exhibit exceptionally good thermal stability in conjunction with low glass transition temperatures and fuel resistance. These properties render these compositions attractive as potential candidates for advanced sealants required to function under extreme environmental conditions in the presence of fuel. For such applications it is of utmost importance to avoid the introduction of weak links during curing and/or chain-extending operations. Furthermore, to develop a practical sealant system the crosslinking process should proceed readily, preferentially in a quantitative yield at relatively moderate temperatures.
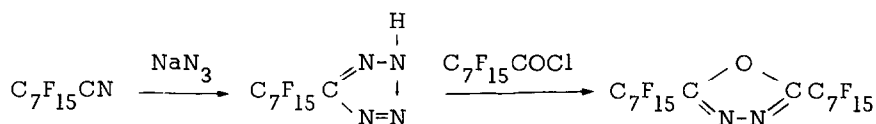
To determine which type of a heterocycle offers optimum properties for curing a perfluoroalkylether-based sealant system one of the approaches is to study models. The investigations performed on s-triazines and 1,2,4-oxadiazoles were described previously [1,2]. The current work is devoted entirely to perfluoroalkyl and perfluoroalkylether substituted 1,3,4-oxadiazoles.

RESULTS AND DISCUSSION

Model compound synthesis

It has been reported that the 1,3,4-oxadiazole ring system is inherently more thermally stable than the isomeric 1,2,4-arrangement [3]. In addition, the one step synthesis of 1,3,4-oxadiazoles utilizing the reaction of an acyl halide with a tetrazole [4] offers a definite advantage over the relatively tedious procedures required to produce the 1,2,4-materials. In view of the above considerations, investigation of the 1,3,4-oxadiazoles as potential crosslinking and/or chain extending "segments" appeared warranted.
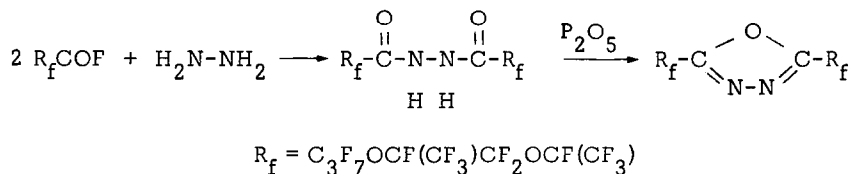
The first member of this series, 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole was synthesized by the following sequence:

$$C_7F_{15}CN \xrightarrow{\text{NaN}_3} C_7F_{15}C \underset{N=N}{\overset{N-N}{\diagup}} \overset{H}{\underset{|}{N}} \xrightarrow{C_7F_{15}COCl} C_7F_{15}C \underset{N-N}{\overset{O}{\diagdown}} CC_7F_{15}$$

in an overall 74% yield. The reaction of the analogous perfluoroalkylether-tetrazole with perfluoroalkyl and perfluoroalkylether acyl halides failed to result in the oxadiazole ring formation.

The desired 2-perfluoroalkyl-5-perfluoroalkylether-1,3,4-oxadiazole, however, was produced in ~47% yield when the above depicted perfluoro-n-heptyltetrazole was treated with a perfluoroalkylether acid chloride, e.g., $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl$.

Finally 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole was prepared in 31% yield, via bis(perfluoroalkyletheracyl) hydrazine followed by phosphorus pentoxide dehydration employing the method of Chambers and Coffman [5]:

$$2\ R_fCOF + H_2N-NH_2 \longrightarrow R_f-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-R_f \xrightarrow{P_2O_5} R_f-C\underset{N-N}{\overset{O}{\diagdown}}C-R_f$$

$$R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$$

Degradation studies

The results of the degradation studies performed on the 2,5-bis(per-fluoro-n-heptyl)-1,3,4-oxadiazole are summarized in Table 1. It can be seen that in the absence of oxygen the material exhibited good stability up to 325°C. This was true both in inert atmospheres and in the presence of water. These investigations were performed in argon to allow the detection of nitrogen, if liberated, since the latter was postulated as a breakdown product of 1,3,4-oxadiazoles under electron impact [6,7].

TABLE 1

Summary of degradation studies performed on 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole

Temp. °C	Atm.	Starting Material		Oxygen Consumed		Products	
		Used mg	Recov %[a]	mg	%[b]	mg	%[a]
235	Air-1	939.9	97.9	5.4	100	30.6	3.2
235	Air-2[c]	242.7	98.9	none	0	0.6	0.2
235	Argon/H_2O[d]	871.6	99.3	–	–	1.5[e]	0.2
325	Argon	834.1	99.5	–	–	1.2	0.1
325	Air[c]	1032.8	60.0[f]	54.2	99.6	348.0	33.7
325	Argon/H_2O[g]	930.5	99.8	–	–	2.6[e]	0.3

a) Percent of the weight of the starting material. b) Percent of oxygen available. c) This test was performed using large ampoule; oxygen available, 54.5 mg. d) In this test 84.1 mg of water was employed. e) In view of the water present this value is not very accurate. f) The involatile residue amounted to 69% of the oxadiazole originally taken; however, it contained 88% of the 1,3,4-oxadiazole admixed with material absorbing at 6.18 and 6.31 μ. g) In this test 80.6 mg of water was employed.

Thus it was of importance to determine whether this degradation path is also present under thermal or hydrolytic conditions. In none of the tests was nitrogen evolution observed, which is in agreement with thermal breakdown findings of others [7]. After subjecting the sample to argon/water environment at 235°C the only products found in the volatiles were small quantities of carbon dioxide and fluorohydrocarbons whereas in the involatile residue traces of R_fCONH_2 were present as shown by a weak infrared band at 5.9 μ. No amide was detected by gas chromatography. Under analogous conditions but at 325°C, the results were virtually identical. In the absence of water at 325°C perfluoro-n-octanonitrile was the only constituent of the volatiles. Thus it can be deduced that water as such has no degradative action upon 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole. The products formed are derived from the hydrolysis of the nitrile initially produced. This behavior is analogous to that observed for the 1,2,4-oxadiazole [2].

Contrary to the behavior of the 1,2,4-analogue the 1,3,4-oxadiazole was found to be oxidatively unstable. No reproducible results could be obtained in air at 235°C. Using identical samples of starting material one test resulted in complete oxygen consumption together with production of volatiles. In another test, employing a much larger relative quantity of oxygen, virtually no degradation took place. This would then indicate that a trace of impurity can catalyze the decomposition. The susceptibility of the 1,3,4-oxadiazoles to nucleophilic attack was demonstrated by Brown and Cheng [8]; on the other hand, this isomer is supposed to exhibit better thermal stability [3]. The low oxidative stability was clearly shown by the exposure to air at 325°C when all the available oxygen was consumed and only 60% of the starting material was recovered. The products formed are listed in Table 2. It should be noted that SiF_4, BF_3, and part of the CO_2 are derived most likely from the reaction of COF_2 and R_fCOF species with the walls of the ampoule. The unidentified products consisted of perfluoroalkyl carbonyls, R_fCOF (identified by infrared absorption at $5.27\,\mu$ and mass spectral abundances at m/e = 97, 47, and 66), perfluoro-alkyl acid anhydrides $(R_fCO)_2O$ (identified by infrared abosrptions at 5.38 and 5.52 μ) and an unidentified compound which exhibited strong absorptions in the infrared at 6.18 and 6.31 μ. The latter material was present also in the involatile residue. The relative quantity of nitrile $(C_7F_{15}CN)$ produced was much higher than in the argon test performed at the same temperature which shows clearly that oxygen-initiated ring opening is operative here. Inasmuch as all the oxygen was consumed, it is safe to assume that in the presence of sufficient air (oxygen) no oxadiazole would be recovered.

In view of the above findings it was concluded that 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole and related compositions are not suitable for the visualized sealant applications. Consequently no studies involving Jet-A fuel were carried out.

Although the oxidative stability of the 1,3,4-oxadiazole ring system, when substituted by perfluoroalkyl groups, was found to be poor, the tremendous difference in reactivity of the perfluoroalkyl- and perfluoro-

TABLE 2

Products formed on thermal oxidative degradation of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole in air

Product	$235°C$ $\%^{a,b}$	$325°C$ $\%^{a}$
CO	0.05	0.5
CO_2	0.49	9.9
SiF_4	0.36	10.3
COF_2	1.40	4.4
BF_3	?	0.7
$C_7F_{15}CN$	0.4	3.7
CF_4	T	T
Unidentified	0.5	10.1

a) Percent of starting material.
b) The data are for the Air-1 test listed in Table 1.

alkylether-substituted s-triazines [1] made it reasonable to assume that similar effects might also be operative here. It has been discussed previously and it is being reemphasized again that it is not the ether function which is responsible for this behavior but the steric hindrance of the $-CF(CF_3)-$ arrangement adjacent to the ring. Accordingly, 2,5-bis-(perfluoroalkylether)-1,3,4-oxadiazole was synthesized and subjected to degradative testing. The results of these investigations are compiled in Table 3 and the nature and relative proportion of the products formed under the different conditions are given in Table 4.

It is apparent from these data that at $235°C$ under oxidizing, hydrolytic, and fuel environments, very little decomposition took place as shown by starting material recovery and the degradation products found. Based on the latter value and due to the difficulty in separating the unchanged oxadiazole from Jet-A fuel it is most likely that the actual degree of degradation is lower than that reported in Table 3. Oxidatively, however,

TABLE 3

Summary of degradation studies performed on 2,5-bis(perfluoroalkylether)-
1,3,4-oxadiazole

Temp. °C	Atm.	Starting Material Used mg	Recov %[a]	Oxygen Consumed mg	%[b]	Products mg	%
235	Air	523.0	99.3	0.3	5.3	3.4	0.65
235	Ar/H$_2$O[c]	502.8	99.8	-	-	0.9	0.18
235	Air/Jet-A[d]	635.5	97.3	5.8	100	2.0	0.31
325	N$_2$	586.2	99.2	-	-	4.3	0.73
325	Air	300.9	96.1	1.2	20.6	11.8	3.92

a) Percent of the weight of the starting material. b) Percent of oxygen available. c) In this test 61.7 mg of water was employed and it was quantitatively recovered. d) In this test 667.3 mg of Jet-A fuel was used.
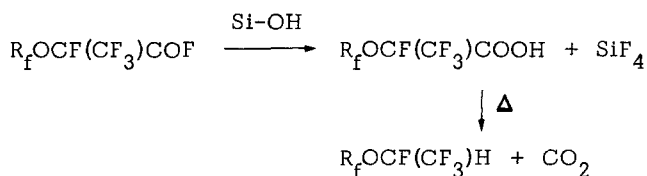
TABLE 4

Products formed on degradation of 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole

Compound	%[a] (235°C Air)	%[a] (325°C N$_2$)	%[a] (325°C Air)	%[a] (235°C Air/Jet-A)[b]
CO	0.02	0.02	0.06	0.05
CO$_2$	0.21	0.03	1.25	0.08
SiF$_4$	0.02	0.01	1.23	?
C$_3$F$_7$OCF(CF$_3$)CF$_2$OCF(CF$_3$)CONH$_2$	0.02	T[c]	0.02	T
C$_3$F$_7$OCF(CF$_3$)CF$_2$OCF(CF$_3$)CN	0.25	0.29	0.49	0.02
C$_3$F$_7$OCF(CF$_3$)CN	T	T	T	T
C$_3$F$_7$OCF(CF$_3$)CF$_2$OCF(CF$_3$)H	0.08	0.34	0.76	0.14
C$_3$F$_7$OCF(CF$_3$)H	T	T	0.06	0.15

a) Weight percent is based on weight of oxadiazole used. b) The typical products formed by the Jet-A itself when subjected to air at 235°C are not included. c) T= <0.0005% by weight.

the bis(perfluoroalkylether)-1,3,4-oxadiazole was not as stable as its
1,2,4-isomer [1,2], particularly at the higher temperature; yet, it was
definitely much more stable than the perfluoro-n-heptyl-substituted analogue.
Among the products listed (see Table 4) the nitrile, $C_3F_7OCF(CF_3)CF_2OCF$-
$(CF_3)CN$, originates most likely from dissociation of the oxadiazole. The
hydrogenated fluorocarbons are probably produced from further degradation
of the nitrile to acid fluorides and from the decomposition of the other
dissociation components. One of the possible operative processes is
presented below:

$$R_fOCF(CF_3)COF \xrightarrow{\text{Si-OH}} R_fOCF(CF_3)COOH + SiF_4$$

$$\downarrow \Delta$$

$$R_fOCF(CF_3)H + CO_2$$

The presence of silicon tetrafluoride and carbon dioxide supports this
scheme.

Conclusions

Based on the above findings it can be concluded that the 1,3,4-
oxadiazole ring system can be rendered relatively oxidatively stable by
suitable substitution. Apparently, materials with $-CF(CF_3)-$ arrangements
next to the 1,3,4-oxadiazole ring offer comparable, possibly better,
stability in the fuel environment than the 1,2,4- compounds. Since polyper-
fluoroalkylethers derived from perfluoropropene oxide are the current
candidates for the sealant applications, the employment of the 1,3,4-
oxadiazoles as crosslinking segments may thus be considered. On the
other hand, in view of the oxidative behavior at elevated temperatures,
these compositions might not be as desirable as the 1,2,4-ring arrangement.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under a nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared (IR) spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Molecular weights were determined in hexafluorobenzene solution using a Mechrolab Model 302 vapor pressure osmometer. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were performed using a CEC Model 21-620 mass spectrometer and a DuPont spectrometer 491-B coupled to a data acquisition and processing system. The latter instrument was employed both in GC-MS and batch modes.

Preparation of perfluoro-n-heptyltetrazole

A mixture of perfluoro-n-octanonitrile (24.94 g, 63.93 mmol), dimethylformamide (35 ml), ammonium chloride (3.76 g, 70.28 mmol), and sodium azide (4.53 g, 69.68 mmol) was heated under nitrogen by-pass at 100-103°C for 14 hr. The initially present two layers became a slightly orange single phase with a solid at the bottom of the flask. Dimethylformamide was then removed in vacuo to yield a pasty residue which was only partially soluble in water (75 ml), but dissolved on addition of 20% HCl (75 ml). The organic material was extracted with ether, washed with 20% HCl and water and dried over anhydrous $MgSO_4$. Evaporation of ether yielded 30.10 g (98.3% yield) of crude n-perfluoroheptyltetrazole. This material was crystallized from chloroform affording 15.63 g (51% yield) of product, mp 88-89°C. On evaporation of the mother liquor an additional 9.45 g of the tetrazole was obtained bringing the total yield to 81.9%.

Preparation of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole

A mixture of perfluoro-n-heptyltetrazole (10.01 g, 22.85 mmol) and perfluoro-n-octanoyl chloride (11.04 g, 25.52 mmol) was heated under a nitrogen by-pass at 89-93°C for 4.7 hr; at 104-112°C for 38.6 hr and finally at 121-125°C for 24 hr. The product was purified by dissolving it in ether followed by washing with sodium carbonate solution and water. The residue left on removal of ether was crystallized from ether-ethanol giving 16.55 g (89.9% yield) of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole, mp 33-34°C. Anal. Calcd. for $C_{16}F_{30}N_2O$: C, 23.84; F, 70.70; N, 3.48. Found: C, 23.98; F, 70.98; N, 2.82.

Preparation of 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole, n-$C_7F_{15}[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (n.c.)

A mixture of perfluoro-n-heptyltetrazole (3.03 g, 6.92 mmol) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl$ (3.69 g, 7.17 mmol) was heated under nitrogen by-pass at 115-118°C for 100 hr. The prolonged heating was required in view of the low reactivity of the perfluoroalkylether acid chloride. The product mixture was subsequently distilled at 25 mm Hg; the fraction bp 105-114°C was dissolved in Freon 113, washed with sodium bicarbonate, water and dried over magnesium sulfate. Vacuum distillation yielded pure n-$C_7F_{15}[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, bp 118-121°C, 25 mm Hg. Anal. Calcd. for $C_{17}H_{32}O_3N_2$: C, 22.99; F, 68.45; O, 5.40; N, 3.15; MW, 888.15. Found: C, 23.29; F, 68.36; N, 3.39; MW, 930.

Preparation of 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (n.c.)

Under nitrogen by-pass to a stirred solution of $C_3F_7OCF(CF_3)CF_2OCF$-$(CF_3)COF$ (7.17 g, 14.39 mmol) in benzene (15 ml) was added hydrazine hydrate (0.73 g, 14.58 mmol). After stirring for 1.5 hr the mixture was

refluxed for 4 hr with a water eliminator attached. Subsequently the
mixture was cooled and decanted; the product dissolved in Freon-113 and
filtered. To the solid residue, remaining after Freon-113 removal in vacuo,
was added phosphorus pentoxide (16.8 g, 118 mmol). The solid mixture was
then heated under nitrogen by-pass for 2 hr at 250°C. The product,
(3.54 g, 50.7% yield) bp 76-67°C/2.9-1 mm Hg, was dissolved in Freon-
113, washed with water, 5% sodium bicarbonate solution, and dried over
magnesium sulfate. Distillation gave pure 2,5-bis(perfluoroalkylether)-
1,3,4-oxadiazole (2.16 g, 31% yield) bp 102-104°C/9 mm Hg. Anal. Calcd.
for $C_{18}F_{34}N_2O_5$: C, 22.29; F, 66.58; N, 2.89; O, 8.25; MW, 970.16.
Found: C, 21.98; F, 66.89; N, 3.21; MW, 950.

Degradation studies

   The degradation investigations were performed in sealed ampoules
of ca 50 ml volume, unless otherwise specified, over a period of 48 hr at
235 and 325°C. The media studied were nitrogen or argon, air, nitrogen
or argon/water, and Jet A-fuel. The quantities of material employed were
between 0.5-1.0 g, whereas the gas pressures used were ca 350 mm Hg at
room temperature. In the experiments involving water and Jet-A fuel these
materials were weighed into the ampoules. At the conclusion of an
experiment the ampoules were cooled in liquid nitrogen and were opened
into the vacuum system. The liquid nitrogen noncondensibles were measured
with the aid of a Sprengel pump and determined by mass spectrometry. The
liquid nitrogen condensibles, which were volatile at room temperature,
were fractionated from a warming trap through -23, -78°C into a liquid
nitrogen cooled trap. Each fraction was measured, weighed and analyzed
by infrared spectroscopy, gas chromatography, and mass spectrometry. The
residue itself was weighed and subjected to gas chromatography, infrared
spectral analyses, and differential thermal analysis.

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