SYNTHESES AND DEGRADATIONS OF FLUORINATED HETEROCYCLICS

II.   PERFLUOROALKYL AND PERFLUOROALKYLETHER-1,2,4-OXADIAZOLES

K.J.L. PACIOREK, R.H. KRATZER, J. KAUFMAN, J.H. NAKAHARA,
R.W. ROSSER,[*] and J.A. PARKER[*]

Ultrasystems, Inc., 2400 Michelson Drive

Irvine, California 92715   (U.S.A.)

SUMMARY

   3-Perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole and
3,5-bis(perfluoroalkylether)-1,2,4-oxadiazole were synthesized and charac-
terized. The 3,5-bis(perfluoroalkylether)-1,2,4-oxadiazole was subjected
to thermal, thermal oxidative, and hydrolytic degradations at 235 and 325°C
and was found to be stable under these conditions as evidenced by
practically quantitative recovery of the test samples. In the presence of
Jet-A fuel at 235°C a low degree of degradation, ~4%, was observed.
3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was found to be stable to
attack by water at 325°C; however in air in the presence of Jet-A at 235°C
the extent of degradation was in excess of 10%.

INTRODUCTION

   Previous studies [1] were concerned primarily with perfluoroalkyl and
perfluoroalkylether substituted s-triazines and 1,2,4-oxadiazoles derived
from the interaction of terephthalonitrile-bis-N-oxide with perfluoroalkyl

[*]National Aeronautics & Space Administration, Ames Research Center,
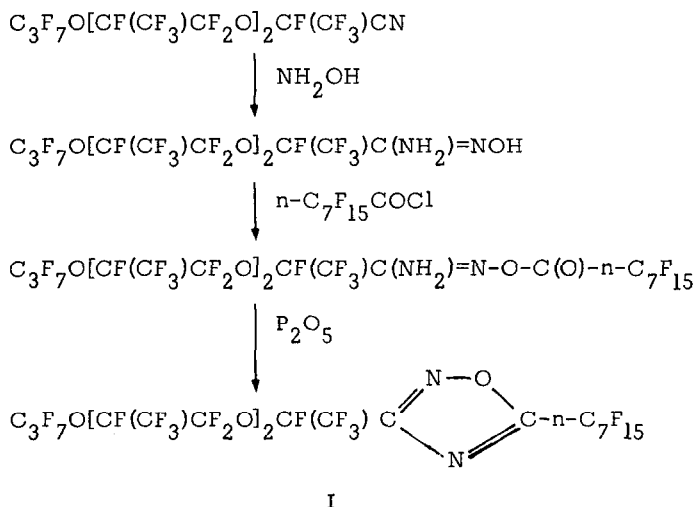Moffett Field, California 94035

and perfluoroalkylether nitriles. Only limited investigations were performed at that time on 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole. As stated before, the objective of these investigations is to determine on specific model compounds the relative thermal, thermal oxidative, and hydrolytic stability of potential crosslinks useful for curing perfluoroalkylether-based elastomers and to evaluate the effect of Jet-A fuel on the most promising candidates. The perfluoroalkylether-substituted triazine was shown to exhibit a markedly better hydrolytic stability than its perfluoroalkyl analogue, which was ascribed to the tertiary nature of the carbon atoms attached to the triazine ring. Thus, it was of importance to determine whether similar effects are operative in the 1,2,4-oxadiazole series.

RESULTS AND DISCUSSION

Model compound synthesis

It has been established that the 1,2,4-oxadiazole ring, when substituted by perfluoroalkyl groups, possesses very good thermal, thermal oxidative and hydrolytic stability comparable to that of the perfluoroalkylether substituted s-triazines [1]. One would expect these desirable properties to be even further enhanced by the presence of perfluoroalkylether substituents. Accordingly, the feasibility and ease of formation of these compounds needed to be explored, especially since the ultimate objective of these studies is to utilize the most promising ring arrangements and the most direct processes leading to their formation in chain extending or crosslinking perfluoroalkylether polymers. In conjunction with the above requirement it was also of importance to determine how readily the "mixed" perfluoroalkyl, perfluoroalkylether-1,2,4-oxadiazole can be formed. These types of compositions represent potential polymer systems utilizing both perfluoroalkyl and perfluoroalkylether segments.

3-Perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole, I, was prepared in an overall 64% yield by the general procedure of Brown and Wetzel [2]:

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN$$

$$\downarrow \quad NH_2OH$$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$$

$$\downarrow \quad n\text{-}C_7F_{15}COCl$$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N\text{-}O\text{-}C(O)\text{-}n\text{-}C_7F_{15}$$

$$\downarrow \quad P_2O_5$$

I

The analogous bis-perfluoroalkylether-1,2,4-oxadiazole, II, was obtained in an overall 40% yield employing the above procedure and substituting a perfluoroalkylether acid chloride for the octanoyl acid chloride
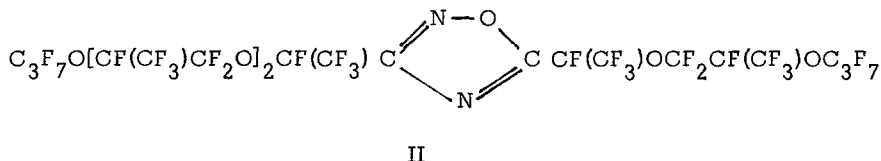
II

Degradation studies

The degradations were performed in sealed ampoules of ca 50 ml volume over a period of 48 h at 235 and 325°C. The atmospheres studied were nitrogen, air, nitrogen/water, argon/water, and air/Jet-A fuel. The results of these experiments are summarized in Tables 1 and 2.

3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was previously subjected to nitrogen and air at 325°C as well as to nitrogen/water atmospheres at 235°C [1]. It was of interest to determine the effect of higher temperatures on its stability in the presence of water, especially since the absence of hydrolysis at 235°C in water was surprising in view of the $-CF_2-C{\underset{\textstyle N}{\overset{\textstyle N}{\big\langle}}}$

TABLE 1

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

Temp	Atmosphere	Starting Material		Oxygen		Products Formed				
°C		Used	Recovered	Consumed		CO_2	CO	R_fCONH_2	R_fCN	R_fH
		mg	%(a)	mg	%(b)	%(a)	%(a)	%(a)	%(a)	%(a)
325	N_2/H_2O(c)	532.1	98.4	-	-	0.12	0.17	0.42	-	+(e)
235	Air/Jet-A(d)	832.2	72.9	5.9	100	0.27	0.04	6.63	1.01	1.71

(a) Weight percent of starting material.

(b) Percent of available oxygen.

(c) The quantity of water employed was 53.2 mg.

(d) The quantity of Jet-A fuel employed was 847.0 mg.

(e) Could not be quantitatively determined due to large amount of water present.

TABLE 2

Summary of degradation studies performed on $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)-C$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)-C \begin{array}{c} N-O \\ \diagdown \\ \diagup \\ N \end{array} C-CF(CF_3)OCF_2CF(CF_3)OC_3F_7$$

Temp °C	Atmosphere	Starting Material		Oxygen		Products Formed					
		Used	Recovered	Consumed		SiF_4	CO_2	CO	$R_fOR_fCONH_2$	R_fOR_fCN	R_fOR_fH
		mg	%(a)	mg	%(b)	%(a)	%(a)	%(a)	%(a)	%(a)	%(a)
235	Air	813.1	98.8	0.5	10	0.20	0.41	-	-	0.2	0.2
235	Ar/H_2O(c)	708.9	98.8	-	-	-	0.31	-	Trace	+(f)	+(f)
235	Air/Jet-A(d)	896.1	92.3	5.6	100	-	0.20	0.04	0.39	1.13	0.73
325	N_2	693.0	99.4	-	-	0.02	0.07	-	-	Trace	Trace
325	Air	679.5	98.7	0.8	16	0.23	0.44	0.26	-	0.2	0.2
325	N_2/H_2O(e)	469.1	98.5	-	-	-	0.11	0.01	Trace	+(f)	+(f)

(a) Weight percent of starting material.

(b) Percent of available oxygen.

(c) The quantity of water employed was 101.3 mg.

(d) The quantity of Jet-A employed was 920.2 mg.

(e) The quantity of water employed was 49.0 mg.

(f) Could not be quantitatively determined due to large amount of water present.

arrangement present in the 1,2,4-oxadiazole ring. This same grouping is a component of the s-triazine ring and must be in this combination responsible for the hydrolytic instability of tris(perfluoro-n-heptyl)-s-triazine [1]. It is obvious from the data presented in Table 1 that even at 325°C, the extent of degradation of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was very minor. This unexpected finding is so far unexplained.

The ultimate application visualized for these systems is as fuel tank sealants; consequently, the effect of Jet-A fuel on these compounds at elevated temperatures had to be evaluated. Prior to discussing the data given in Table 1, certain aspects need to be clarified. Subjecting Jet-A alone to 235°C in an air atmosphere resulted in complete oxygen depletion. However, since the quantity of oxygen available was very small (5.9 mg) as compared to the quantity of Jet-A employed ($\sim$ 1 g), the extent of oxidation as evidenced by carbon dioxide, carbon monoxide, and carbonyls formation was also very low. The Jet-A itself was virtually unchanged by this treatment as shown by comparison of the GC-MS analysis of this treated fuel with that of an original sample. The oxygen-containing volatiles formed accounted for $\sim$ 10% of the oxygen consumed. It is quite plausible that at least 50% of the oxygen consumed was transformed into water (which would correspond to $\sim$ 0.15 mmol). From Table I it can be seen that the quantity of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole employed was 1.03 mmol; consequently, the quantity of the amide theoretically possible is in reasonable agreement with the 6.6% of n-$C_7F_{15}CONH_2$ produced. Based on these findings it is apparent that the oxadiazole is susceptible to hydrolysis provided a solubilizing medium is present. This is in agreement with Dr. Tamborski's investigations [3] which showed that in the presence of tetrahydrofuran and water, 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole undergoes extensive hydrolysis at 100°C. These results would indicate that if the polymer system containing the perfluoroalkyl-1,2,4-oxadiazole linkage is essentially insoluble in Jet-A or any other fuel or solvent, no hydrolytic degradation should occur since water alone is ineffective.

The results of the studies performed on the perfluoroalkylether substituted 1,2,4-oxadiazole are summarized in Table 2. Under all the

conditions, with the exception of the air-Jet-A treatment, ~ 99% of the starting material was recovered unchanged. The effect of air at 235 and 325°C was virtually the same, based on starting material recovery and oxygen consumption. This is unexpected and may be attributable to the presence of a small quantity of an impurity. From the air-Jet-A exposure at 235°C, 92.3% of the starting material was recovered intact; the detected and quantitated products, however, accounted for only ~ 4% of the material loss. In view of the experimental difficulties associated with physically separating the Jet-A fuel from the (liquid) test sample, it is quite plausible that the actual extent of degradation is better represented by the amount of products formed than by the quantity of starting material recovered since no other indication of degradation such as discoloration could be observed. In the case of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole, this argument cannot be made because the starting material is a solid which could be fairly readily separated from Jet-A fuel. In addition, the dark brown discoloration observed in this test indicated that degradation was more extensive.

Conclusions

The stabilities of the perfluoroalkyl and perfluoroalkylether substituted 1,2,4-oxadiazoles seem to follow the trend observed for the analogously substituted triazines in particular with respect to hydrolytic stability [1]. However, it has to be noted that neither of the 1,2,4-oxadiazoles can be hydrolyzed by water alone whereas 1,3,5-tris(n-perfluoro-n-heptyl)-s-triazine does not need a solvent to undergo hydrolysis. Under the conditions employed, the thermal and thermal oxidative stabilities of 1,2,4-oxadiazoles and 1,3,5-triazines appear to be comparable with the perfluoroalkylether-substituted materials exhibiting better properties especially in hydrolytic environments. These conclusions take under consideration the results of investigations conducted on perfluoroalkylether-substituted s-triazines in nitrogen/water at 325°C and air/Jet-A at 235°C [4]. Based on the above it can be predicted that either of the ring arrangements can be incorporated

into a perfluoroalkylether polymer system without an adverse effect on the overall stability.

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. The perfluoroalkylether nitrile and acid fluoride obtained from the Air Force Materials Laboratory were employed without purification due to the relatively small samples available and the likelihood of material loss on purification.

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 3-perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]$-n-$C_7F_{15}$ (n.c.)

Under nitrogen by-pass to a stirred solution of hydroxylamine hydrochloride (0.59 g, 8.49 mmol) in dry methanol (10 ml) was added at 22-25°C sodium methoxide (8.26 mmol in 5 ml methanol). Into this solution was then introduced $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN$ (5.02 g, 7.81 mmol), again at 22-25°C. After stirring for 2 hr at room temperature, methanol was

taken off under reduced pressure and the resulting mixture (white solid suspended in a clear liquid) was taken up in Freon 113, filtered and evaporated under reduced pressure. The remaining involatile, clear liquid, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$, 4.32 g (81.8% yield) was employed without further purification in the next step.

Under nitrogen by-pass to a stirred solution of the amidoxime (4.07 g, 6.02 mmol) in tetrahydrofuran (20 ml) was added slowly at $0°C$ perfluoro-n-octanoyl chloride (2.61 g, 6.03 mmol) in tetrahydrofuran (7 ml). After completing the addition the reaction mixture was stirred for 1 hr at $0°C$, then 2 hr at room temperature. Subsequently, tetrahydrofuran was removed under reduced pressure leaving a viscous liquid (5.82 g, 90.2% yield); this material exhibited an infrared spectrum containing bands characteristic for the expected structural arrangement, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N-O-C(O)-n-C_7F_{15}$.

A mixture of this O-perfluoroalkylether-perfluoro-n-octanoylamidoxime (5.82 g, 5.43 mmol) and phosphorus pentoxide (7.10 g, 50.0 mmol) was heated under nitrogen by-pass for 10.3 hr at $230°C$. Subsequently, the oxadiazole was distilled from the reaction mixture under reduced pressure. Redistillation gave the pure product (4.99 g, 64% overall yield) bp $84-88°C/1$ mmHg.
Anal. Calcd. for: $C_{20}F_{38}O_4N_2$: C, 22.79; F, 68.48; N, 2.66; O, 6.07; MW, 1054.17.
Found: C, 22.97; F, 67.85; N, 2.72; MW, 1072.
The mass spectral breakdown pattern was in agreement with the assigned structure [5].

Preparation of 3,5-bis-perfluoroalkylether-1,2,4-oxadiazole,
$\underline{C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7}$ (n.c.)

Under nitrogen by-pass to a stirred solution of the amidoxime, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$, (9.20 g, 13.61 mmol) in tetrahydrofuran (25 ml) was added slowly at $0°C$ $C_3F_7OCF(CF_3)CF_2OCF-(CF_3)COCl$ (7.01 g, 13.62 mmol) in tetrahydrofuran (8 ml). After completing the addition, the reaction mixture was stirred for 1 hr at $0°C$, then 2 hr at room temperature. Subsequently, tetrahydrofuran was removed under

reduced pressure giving the O-perfluoroalkylether-perfluoroalkylether-acyl-amidoxime, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N-O-C(O)CF(CF_3)-OCF_2CF(CF_3)OC_3F_7$, as a viscous liquid (14.32 g, 91.2% yield).
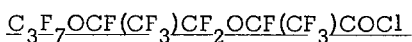
A mixture of the thus obtained O-perfluoroalkylether-perfluoroalkylether-acyl-amidoxime (14.32 g, 12.41 mmol) and phosphorus pentoxide (16.0 g, 112.7 mmol) was heated under nitrogen by-pass for 12 hr at 210-216°C. Subsequently, the oxadiazole was distilled from the reaction mixture under reduced pressure. Redistillation gave the pure product (6.13 g, 40% overall yield), bp 120-122°C/7.2 mmHg.

Anal. Calcd. for $C_{21}F_{40}O_6N_2$: C, 22.20; F, 66.89; N, 2.47; O, 8.45; MW, 1136.18.

Found: C, 22.59; F, 66.98; N, 2.90; MW, 1220.

The mass spectral breakdown pattern was in agreement with the assigned structure [5].

Preparation of perfluoroalkylether acid chloride,

$\underline{C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl}$

A mixture of perfluoroalkylether acid, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)-CO_2H$, (12.98 g, 26.16 mmol, obtained by water hydrolysis of the corresponding acid fluoride) and 11.73 g (54.67 mmol) of isopthaloyl chloride was heated under nitrogen by-pass at 110-120°C for 8 hr. Distillation under reduced pressure gave 11.39 g (84.6% yield) of a water clear distillate, bp 82-84°C/129 mmHg.

Degradation studies

The degradations were performed in sealed ampoules of ca 50 ml volume over a period of 48 h at 235 and 325°C. The media studied were nitrogen, air, N_2 or Ar/water, and air/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 were weighed into the ampoules. At the conclusion of an experiment the ampoules were cooled in liquid nitrogen and opened to

the high vacuum system. The liquid nitrogen noncondensibles were measured and quantitatively analyzed by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through traps kept at -23 and $-78^{\circ}C$ into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and GC-MS. The residues were weighed and subjected to GC-MS analysis, infrared spectral analysis, and differential thermal analysis.

ACKNOWLEDGEMENTS

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