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MASS SPECTRA OF SOME PERFLUOROALKYL AND PERFLUOROALKYLETHER SUBSTITUTED 1,3,4-OXADIAZOLES

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SUMMARY

Electron impact fragmentation patterns were obtained for 2,5-bis-(perfluoroalkyl)-, 2,5-bis(perfluoroalkylether)-, and 2-perfluoroalkylether-5-perfluoroalkyl-1,3,4-oxadiazoles. All the compounds gave parent ions. Cleavage β to the oxadiazole ring occurred preferentially; however, cleavage α to the ring also took place. Fragmentation of the ring was accompanied by the loss of a fragment of mass 28; this was most evident in the case of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole.

INTRODUCTION

Investigations of the 1,2,4-oxadiazoles have revealed correlations between the electron impact breakdown patterns and the products formed upon thermal degradation [1-5]. Furthermore, the ring substituents were found to have a profound effect both on the fragmentation patterns and ring stability. The 1,3,4-oxadiazole ring system offers another potential candidate to chain extend fluorinated polymers; thus a comparison of its breakdown patterns with that of the 1,2,4-isomers and the effect of substituents on ring stability had to be evaluated.

TABLE 1

Ion fragments and intensities relative to base peak[a]

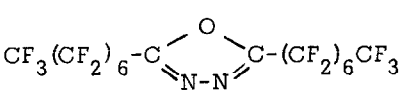
m/e	I	II	III	m/e	I	II	III
69	100.0	97.6	81.9	437	17.8	3.8	
71	3.3			459	5.8		
76	7.5	3.0	3.0	487	95.2		
78	5.1			488	13.1		
81	3.6			519		3.0	3.0
90	5.1			537		21.4	
92	10.4	4.0	3.0	538		3.2	
93	10.7	4.5		569		27.1	
97		6.9	8.0	570		4.3	
100	23.6	14.3	12.9	619			19.7
109	36.7	5.6	1.2	703		9.1	
112	3.8			709	4.3		
119	74.6	37.9	34.8	769		6.0	
126		4.9	6.7	785			10.1
128		2.0	3.5	787	39.3		
131	56.3	15.7	3.5	788	8.0		
143	3.6			806	3.2 (M^+)		
147		16.6	13.9	819		25.3	
150		6.1	7.4	820		5.6	
159	4.5	7.2		851			7.0
169	61.9	100.0	100.0	869		32.4	
170		5.7	4.8	870		6.2	
181	15.0	6.3		888		1.1 (M^+)	
219	11.0	3.4		901			31.9
231	6.5			902			7.0
281	8.7	3.2		951			15.1
335		22.0	27.6	952			3.3
369	19.8	10.6		970			0.1 (M^+)
403		7.4					

a) Peaks having intensities less than 3% of the base peak (with the exception of m/e 109, 128 and parent ions) and lower than m/e 69 are not reported.

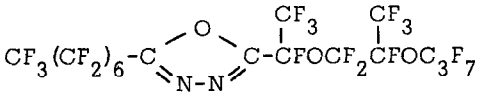
Cotter, et al. [1,6] stipulated that 1,3,4-oxadiazoles liberate molecular nitrogen when subjected to electron impact. Since all the compounds studied contained at least one phenyl substituent, it was of interest to determine whether such a breakdown mechanism is characteristic for this ring system or whether it is substituent dependent.

RESULTS AND DISCUSSION

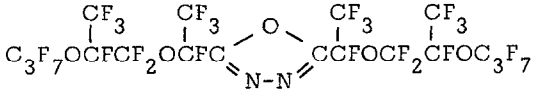
The syntheses and the thermal properties of the three 1,3,4-oxadiazoles, compounds I-III, have been reported elsewhere [7]; their mass spectral breakdown patterns are given in Table 1.



I (MW=806)



II (MW=888)

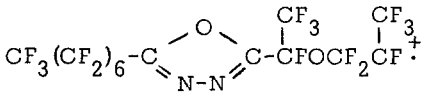


III (MW=970)

Each of the oxadiazoles gave a parent ion although of relatively low intensity. In all three compounds, in agreement with the findings published for the phenyl-free members of the 1,2,4-oxadiazole series [3], cleavage β to the ring was the major fragmentation process as shown in compound I by m/e 487 [M-319(C_6F_{13})], in compound II by m/e 569 [M-319(C_6F_{13})] and also m/e 537 [M-351($C_3F_7OCF(CF_3)CF_2O$)], and in compound III by m/e 619 [M-351].

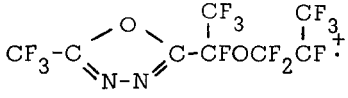
No evidence of cleavage α to the ring was detected in the 3-perfluoroalkylether-5-perfluoroalkyl-1,2,4-oxadiazole, whereas in 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole, and the 3,5-bisperfluoroalkylether analogue, it occurred to a very low degree ($\sim$1% of the base peak) [3]. However, in the

1,3,4-oxadiazole series the fragmentation α to the ring was significant as shown by the relatively high abundances in compound I at m/e 437 [M-369 (C_7F_{15})], in compound II by the ions 519 [M-369] and 437 [M-451($CF(CF_3)$-$OCF_2CF(CF_3)OC_3F_7$)] and in compound III by 519 [M-451]. This mode of breakdown was unexpected especially in the perfluoroalkylether substituted compounds wherein the cleavage β to the ring is favored by the presence of the oxygen atom [3,8]. This effect of the oxygen function is illustrated by the 169^+ base peak (C_3F_7) in both of the oxadiazoles which contain the perfluoroalkylether chain (compounds II and III). In compound II the alternate ion associated with the fragmentation governed by the oxygen atom, e.g. the ion 703^+ resulting from the loss of the C_3F_7O group, apparently undergoes rearrangement involving fluorine transfer giving the ion 403^+ and perfluorohexene, i.e.,



m/e=703

$-C_6F_{12}$



m/e=403

Unfortunately, the metastable for this process was not detected, although similar rearrangements were observed in the 1,2,4-oxadiazole series [3]. In the case of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole (I) a metastable at m/e ~280 indicated that the 369^+ ion (C_7F_{15}) is derived from the 487^+ ion leaving a fragment of mass 118 which corresponds to the five ring atoms with one CF_2 group attached. This same ion (487^+), which constitutes the second most intense peak in the mass spectrum of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole, apparently undergoes a second type of transformation producing the 459^+ ion and a fragment of mass 28 as shown by the metastable at m/e ~432.

The question which arises is the nature of the fragment of mass 28, namely is it CO or N_2. In view of the studies of Cotter, et al. [1,6], who did postulate the liberation of molecular nitrogen from the 1,3,4-oxadiazole ring system and since no mass 28 fragments appeared to be liberated by 1,2,4-oxadiazoles [3], it is most likely that the mass 28 loss observed here is due to N_2. This also applies to the other ions present in the mass spectra of the three 1,3,4-oxadiazoles in which a unit of mass 28 must be present but where again it is unknown whether that unit is composed of two nitrogens or a carbon and an oxygen atom. A specific ion in question is the 109^+ ion which is one of the most prominent peaks in the mass spectrum of compound I and which is also present in the mass spectra of the other two analogues, but is not a fragment formed by perfluoroalkyl and perfluoropropene oxide derived perfluoroalkylether chains [8]. This ion can be either $C_2F_3N_2$ or C_3F_3O; the isotopic ratio of the peaks 110/109 of 3.31% supports the C_3F_3O assignment in agreement with Cotter, et al. [1,6]. Thus, based on this data it can be concluded that the 1,3,4-oxadiazole ring system under electron impact liberates molecular nitrogen and that this process is independent of the nature of the substituents. This type of fragmentation cannot readily occur and was therefore not observed in the analogously substituted 1,2,4-oxadiazoles [3]. Otherwise, there is a strong resemblance between the breakdown patterns of the two series of compounds.

Examining the relative abundances of ions which are associated with the oxadiazole ring breakdown, i.e. ions at m/e 76, 92, 109, 126, 128, and 159, it is evident that these are significantly more prevalent in 2,5-bis-(perfluoro-n-heptyl)-1,3,4-oxadiazole than in the perfluoroalkylether substituted analogues, in particular compound III. This finding is in good agreement with the results of thermal studies which showed the latter to exhibit significantly better stability than compound I [7].

EXPERIMENTAL

A DuPont 21-491B double focusing mass spectrometer was employed to obtain the mass spectra using an ionizing voltage of 70 eV and an ion accelerating voltage of 1400 V. The mass spectra were recorded with the aid of

a DuPont 21-094 data acquisition/processing system and a CEC 5-124A oscillograph, the latter to detect metastables and to obtain isotopic ratios. The solid samples and liquids exhibiting low vapor pressures were introduced via the direct introduction probe, which was not heated; other compounds were injected as liquids into a reservoir-molecular leak inlet system. The temperature of the source was 220-240^{o}C.

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