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DIPHOSPHATETRAAZACYCLOOCTATETRAENES. II. PROPERTIES AND DEGRADATIONS

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SUMMARY

1,5-Bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene and 1,3-bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene were found to decompose at 316°C to phospha-s-triazines. The symmetrical arrangement liberated perfluoroalkylether nitrile with concommitant formation of the corresponding diphospha-s-triazine; the unsymmetrical isomer eliminated the $(C_6H_5)_2PN$ unit to give the monophospha-s-triazine. The thermal and oxidative stabilities of the two compounds differed widely with the unsymmetrical isomer being significantly more stable than the symmetrical arrangement. Spectral data pertinent to these results are discussed. Both materials were found to be effective in arresting perfluoroalkylether fluid degradation in oxidizing atmospheres in the presence of metal alloys.

INTRODUCTION

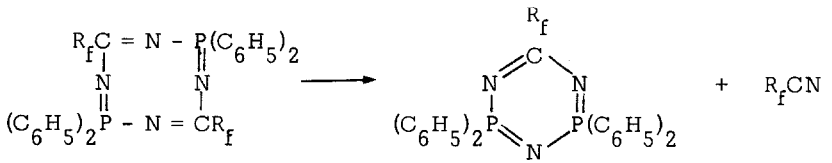
Past investigations [1] have shown monophospha-s-triazines and diphospha-s-triazines to exhibit thermal and oxidative stabilities comparable to the parent triazines and phosphazenes, in conjunction with the ability to arrest degradation of perfluoroalkylether fluids [2,3]. If one considers

phospha-s-triazines to be equivalent to phosphazene trimers, then diphospha-tetraazacyclooctatetraenes [4] should be equivalent to phosphazene tetramers. Following this reasoning further, then heterocyclic octatetraenes should thus exhibit thermal and oxidative stabilities at least equal to those of the six-membered phospha-s-triazines [5]. The current studies were undertaken to prove the validity of these postulations.

RESULTS AND DISCUSSION

Diphosphatetraazacyclooctatetraenes

Based on the degradation data presented in Table 1, the eight-membered rings are markedly less thermally stable than the six-membered analogues. Furthermore, contrary to expectations, the symmetrical isomer, 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, was found to exhibit significantly lower thermal stability than the unsymmetrical cyclooctatetraene. Both of the isomers decomposed into phospha-s-triazines, as can be seen from the product listing given in Table 2. The symmetrical cyclooctatetraene breaks down with elimination of the nitrile and formation of diphospha-s-triazine, i.e.,



whereas the unsymmetrical compound liberates the $[(C_6H_5)_2PN]$ moiety, i.e.,

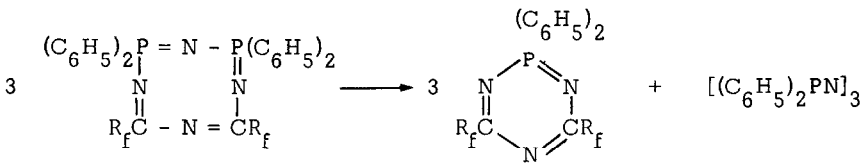


TABLE 1

Degradations of symmetrical and unsymmetrical diphosphatetraazacyclooctatetraenes

Test No.	Compound[a]	Temp °C	Atm	Starting Materials Used mg	Starting Materials Recovered %[b]	Oxygen Consumed mg	Oxygen Consumed %[c]	Volatile Products %[b]
1	s-$[R_f'CN]_2[\Phi_2PN]_2$	235	Air	458.5	79	0.1	1.8	4.2
2	s-$[R_f'CN]_2[\Phi_2PN]_2$	316	N_2	333.7	0.3	-	-	30.5
3	s-$[R_f'CN]_2[\Phi_2PN]_2$	316	Air	377.6	0	1.7	26.7	48
4	u-$[R_f"CN]_2[\Phi_2PN]_2$	235	Air	357.5	87	0.1	2.1	1.0
5	u-$[R_f"CN]_2[\Phi_2PN]_2$	316	N_2	364.1	13	-	-	5.5
6	u-$[R_f"CN]_2[\Phi_2PN]_2$	316	Air	249.1	25	2.5	8.2	4.5

a) $R_f' = C_3F_7OCF(CF_3)$; $R_f" = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

b) Weight percent of starting material.

c) Percent of oxygen available.

TABLE 2

Degradations of symmetrical and unsymmetrical diphosphatetraazacyclooctatetraenes: major products formed

Test No.	Compound[a]	Cond.	$[R_f"CN]_2[\Phi_2PN]$ %[b]	$[R_f'CN][\Phi_2PN]_2$ %	$[\Phi_2PN]_3$ %	$\Phi_2P(O)F$ %	R_fCN[c] %	R_fH[c] %	C_6H_6 %
1	s-$[R_f'CN]_2[\Phi_2PN]_2$	235, Air	-	15	-	-	4.2	T	-
2	s-$[R_f'CN]_2[\Phi_2PN]_2$	316, N_2	-	69	-	T	30	0.3	0.2
3	s-$[R_f'CN]_2[\Phi_2PN]_2$	316, Air	-	12	17	22	39	0.3	9
4	u-$[R_f"CN]_2[\Phi_2PN]_2$	235, Air	13	-	?	-	0.1	T	-
5	u-$[R_f"CN]_2[\Phi_2PN]_2$	316, N_2	63	-	11	?	4.1	0.5	0.1
6	u-$[R_f"CN]_2[\Phi_2PN]_2$	316, Air	59	-	12	?	3.7	0.3	0.1

a) $R_f' = C_3F_7OCF(CF_3)$; $R_f" = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

b) Weight percent of starting material.

c) R_f is any perfluoroaliphatic or perfluoroalkylether group; in all the tests, the nitrile corresponding to the original R_fCN unit amounted to > 95% of the perfluorinated nitriles identified and quantitated.

It cannot be ignored that the ease of degradation of the symmetrical cyclooctatetraene is possibly facilitated by the volatility of the liberated nitrile. However, the formation of diphenylphosphinyl fluoride and diphenylphosphazene trimer in the presence of oxygen (air), together with the decreased production of diphospha-s-triazine, would tend to indicate that the mechanism is not as simple as would appear from the thermal results alone. Past studies have shown the corresponding diphospha-s-triazine to be oxidatively relatively stable [1], thus either the cyclooctatetraene itself or the dissociation intermediate must be very susceptible to oxygen attack. The observed oxygen depletion is in agreement with the products found.

Oxygen does not seem to affect the extent of degradation of the unsymmetrical cyclooctatetraene; actually more starting material was recovered under oxidizing than purely thermal conditions.

Electron delocalization provides for strong overall bonding in compounds such as benzenes, triazines, and phosphazenes. Yet, in the case of the latter compounds, the observed stability is not believed to be due to the d_{π}-p_{π} bonding but rather to a discontinuous "island" type π orbital arrangement [6,7]. In view of the observed differences in the thermal behavior of the symmetrical and unsymmetrical cyclooctatetraenes, it could be deduced that different types of bonding are present in the two isomers.

[redacted]

the cyclooctatetraenes were reported previously [2-4]; the ultraviolet absorptions are listed in Table 3.

The presence in the infrared spectrum of the unsymmetrical cyclooctatetraenes of bands at 6.35μ and 6.45μ as compared to a single band in s-triazines, monophospha-s-triazines, diphospha-s-triazines, and the symmetrical cyclooctatetraenes, points to the existence in this compound of two distinct arrangements, N=C-N=C and P=N-P=N. This is further confirmed by the ultraviolet data wherein the N=C-N=C presence is supported by the absorption at 324 nm. The increase in the extinction coefficient as

TABLE 3

Ultraviolet absorption characteristics and intensities (log ε) of six- and eight-membered heterocycles

Compound	Wavelength (nm)				
	232	267	275	280	324
$[C_7F_{15}CN]_3$	-	-	-	2.87	-
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$	4.10	3.35	3.24	-	3.41
$[C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN][(C_6H_5)_2PN]_2$	4.39	3.51	3.39	-	-
s-$[C_3F_7OCF(CF_3)CN]_2[(C_6H_5)_2PN]_2$	4.63	4.18	4.14	-	-
u-$[C_3F_7OCF(CF_3)CN]_2[(C_6H_5)_2PN]_2$	4.48	3.69	3.58	-	3.93

compared to the monophospha-s-triazine tends to indicate increased contribution from an arrangement involving two phosphorus atoms as compared to the single phosphorus present in the monophosphatriazine system. Based on the thermal degradation data, the presence of the two carbons must impart strain to the eight-membered ring arrangement, reflecting the apparent instability of tetraazacyclooctatetraenes, $[RCN]_4$, of which no member has so far been prepared to our knowledge. However, the conjugation of the N=C-N=C chain apparently provides more stability than the P=N-P=N grouping. Consequently, the monophospha-s-triazine ring is formed accompanied by $[(C_6H_5)_2PN]$ elimination. The determination of bond lengths and angles in these two isomers and comparison with tetrameric phosphazene structures may thus be quite interesting.

In the case of the symmetrical cyclooctatetraene, neither the N=C-N=C conjugation nor the stabilizing effect of the P=N-P=N grouping are present. The absence of π character in the ring is indicated by the shift of the infrared C=N absorption to 6.0μ and lack of absorption beyond 275 nm in the ultraviolet region. Apparently in this environment the loss of the nitrile occurs more readily than $[(C_6H_5)_2PN]$ elimination yielding the stable diphospha-s-triazine

One of the potential applications for the diphosphatetraazacyclooctatetraenes is as fluid additives. In analogy to phospha-s-triazines, diphosphatetraazacyclooctatetraenes were found to effectively inhibit oxidation of Krytox fluids (duPont trade name, $F\text{-}[CF(CF_3)CF_2O]_n\text{-}C_2F_5$) and to prevent corrosion of M-50 ball bearing alloy by these fluids. This is illustrated by the data given in Table 4.

TABLE 4

Degradation of Krytox fluid in the presence of M-50 alloy coupon at 600°F in oxygen for 24 hr[a]

Fluid Used g	Additive	Oxygen Consumed Total mg	Oxygen Consumed % [b]	Oxygen Consumed mg/g [c]	Total Products Formed mg	Total Products Formed mg/g [d]
12.13	none	70.8	24.6	5.84	576.7	47.54
12.16	1% [e] s-$[R_fCN]_2[\Phi_2PN]_2$ [f]	0.0	0.0	0.0	34.9	2.87
13.33	1% u-$[R_f'CN]_2[\Phi_2PN]_2$ [g]	0.0	0.0	0.0	1.8	0.14

a) The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the oxygen was measured and the products were collected and measured.

b) Percent of oxygen available.

c) Oxygen consumed in mg/g Krytox employed.

d) Products formed in mg/g Krytox employed.

e) The percent is weight percent of additive per weight of Krytox fluid.

f) $R_f = C_3F_7OCF(CF_3)$.

g) $R_f' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

It should be noted that the volatile condensibles produced were not the Krytox degradation products [8,9], but were derived entirely from the cyclooctatetraenes as is evident from the listing presented in Table 5.

TABLE 5

Composition of volatiles produced on heat treatment of Krytox fluid in the presence of 1% of unsymmetrical and symmetrical diphosphatetraazacyclooctatetraenes[a]

Product	s-$[R_fCN]_2[\Phi_2PN]_2$[b] (%)[d]	u-$[R_f'CN]_2[\Phi_2PN]_2$[c] (%)
CF_3CN	0.2	5.6
CF_3CF_2CN	0.2	1.1
$C_3F_7OCF{=}CF_2$	0.1	1.7
$C_3F_7OCF(CF_3)H$	0.3	6.1
$C_3F_7OCF(CF_3)CN$	93.2	11.1
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$	-	1.7
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$	-	50.0
C_6H_6	6.4	15.0
$(C_6H_5)P(O)F_2$	?	3.9

a) For details of the degradation conditions, see Table 1.

b) $R_f = C_3F_7OCF(CF_3)$.

c) $R_f' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

d) This is weight percent of the given compound in the volatiles collected.

EXPERIMENTAL

The degradation investigations were performed in sealed ampoules of ca 50 ml volume over a period of 24 hr at the specified temperatures. The media studied were nitrogen and air; the gas pressures used were ca 350 mm Hg at room temperature. 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 and determined by gas chromatography and 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, batch mass spectrometry, and GC-MS. The involatile residues were handled in an inert

atmosphere enclosure to avoid any interferences from subsequent hydrolysis or oxidations in the case of purely thermal degradations. The residue itself was weighed and subjected to batch mass spectrometry, gas chromatography, and infrared spectral analysis. The ultraviolet spectra were taken in Freon-113 solution using a Beckman Model 35 spectrophotometer.

CONCLUSIONS

The diphosphatetraazacyclooctatetraenes, contrary to expectations, were found to be thermally significantly less stable than phospha-s-triazines. It is believed that in the eight-membered ring stresses are put on bond angles at the carbon atoms (in analogy to the apparently unstable tetraaza-cyclooctatetraene ring system) resulting in the driving force to form the six-membered ring analogues. Lack of conjugation in the C=N-P=N structure is most likely responsible for the lowered thermal stability of the symmetrical isomer as compared to unsymmetrical isomer.

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