THE MASS SPECTRA OF SOME 1,3,2-OXAZAPHOSPHOLANES

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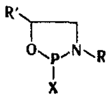
The mass spectra of six 1,3,2-oxazaphospholanes have been obtained. The compounds studied give strong m/e = M lines; the relative stability of the molecular ion correlates with the structure of the molecule. During the process of dissociative ionization, cleavage of the C—C and the P—O bonds in the ring takes place, with the molecular ion losing a R'CHO molecule. It has been shown that the molecule of an olefin is formed from the molecular ion mainly through an alkoxy group. A probable process of dissociative ionization is the loss by the molecular ion of an alkoxy group or, in the case of the 2-chloro derivative, the loss of a Cl atom.

In the present work, we have obtained the mass spectra of the 1,3,2-oxazaphospholanes (I-IV) in order to study further the dissociative ionization of cyclic phosphites and their derivatives. The mass spectrometry of a number of five-membered cyclic phosphites has been studied previously [1], and so have those of a number of acyclic phosphites [2].

The relative intensities of the lines necessary to discuss the probable pathways of dissociative ionization are given in Table 1. Table 2 shows the m/e values of the diffuse lines and the decompositions of metastable ions corresponding to them. As an example, Fig. 1 gives the spectrum of compound (I).

For the compounds studied, extremely strong lines corresponding to the formation of a stable molecular ion are observed. As was to be expected [3], the intensity of the line with m/e = M decreases with an increase in the number of carbon atoms in the alkoxy radical (Table 1).

TABLE 1. Relative Intensities of Some Lines for the 1,3,2-Oxazaphospholanes



m/e of the ion	$\frac{I}{\Sigma I}\cdot 100$					
	I $R=CH_3$, $R'=H$, $X=OCH_3$	II $R=CH_3$, $R'=H$, $X=OC_2H_5$	III $R=CH_3$, $R'=H$, $X=OC_3H_7$-*i*	IV $R=C_6H_5$, $R'=H$, $X=OC_2H_5$	V $R=R'=CH_3$, $X=OCH_3$	VI $R=R'=CH_3$, $X=Cl$
$M^{+\cdot}$	9,1	5,4	3,5	11	6,0	7,7
$(M-28)^{+\cdot}$	0,12	3,2	0,19	1,7	0,47	0,11
$(M-42)^{+\cdot}$	0,27	0,07	8,8	—	—	—
$[M-X]^+$	7,8	6,6	8,1	3,0	4,7	18
$(M-30)^{+\cdot}$	6,5	1,6	—	0,31	—	0,44
$(M-44)^{+\cdot}$	0,3	2,6	0,12	0,68	8,6	8,4
91	0,3	3.7	11,0	7,6	2,5	0,78
90	6,1	5,3	1,4	0,52	7,9	0,94
77	—	—	—	7,1	—	—
42	12	7,1	8,1	1,0	9,0	13,0

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TABLE 2. Decompositions of Metastable Ions

Compound	m/e of the diffuse line	Reaction	Compound	m/e of the diffuse line	Reaction
I M 135	81,7	$135 \xrightarrow[-(30)]{-(CH_2O)} 105$	IV M 211	158,7	$211 \xrightarrow[-(28)]{-(C_2H_4)} 183$
	77,1	$105 \xrightarrow[-(15)]{-(CH_3)} 90$		69,6	$119 \xrightarrow[-(28)]{-(C_2H_4)} 91$
	34,6	$104 \xrightarrow[-(44)]{-(C_2H_4O)} 60$		85,4	$166 \xrightarrow[-(47)]{} 119$
II M 149	98,3	$149 \xrightarrow[-(28)]{-(C_2H_4)} 121$		61,4	$183 \xrightarrow[-(77)]{-(C_6H_5)} 106$
	74,0	$149 \xrightarrow[-(44)]{-(C_2H_4O)} 105$	V M 149	74,0	$149 \xrightarrow[-(44)]{-(CH_3CHO)} 105$
	68,4	$121 \xrightarrow[-(30)]{-(CH_2O)} 91$		77,1	$105 \xrightarrow[-(15)]{-(CH_3)} 90$
	68,0	$119 \xrightarrow[-(29)]{-(C_2H_5)} 90$		84,8	$118 \xrightarrow[-(18)]{-(H_2O)} 100$
III M 163	68,4	$121 \xrightarrow[-(30)]{-(CH_2O)} 91$	VI M (Cl^{35}) 153 M (Cl^{37}) 155	91	$153 \xrightarrow{-(Cl^{35})} 118$
	34,6	$104 \xrightarrow[-(44)]{-(C_2H_4O)} 60$		89,8	$155 \xrightarrow{-(Cl^{37})} 118$
				84,8	$118 \xrightarrow[-(18)]{-(H_2O)} 100$

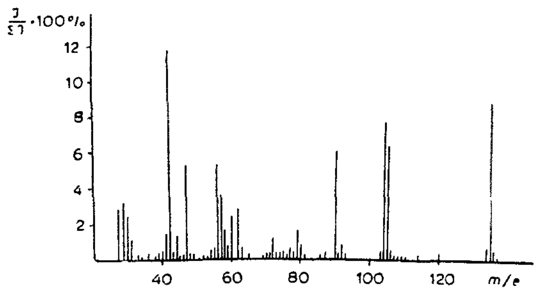

Fig. 1. Mass spectrum of 2-methoxy-3-methyl-1,3,2-oxazaphospholane.

Of interest from the point of view of the structure of the cyclic phosphites and their derivatives is dissociative ionization with cleavage of the P−O bond and the C−C bond in the β position with respect to the C−O bond in the ring with the formation of the ion $M^{+\cdot}-CH_2O$ (or $M^{+\cdot}-CH_3CHO$ when the H atom is replaced by CH_3). This pathway of dissociative ionization has been reported for cyclic phosphites [1, 4]. The lines corresponding to this pathway of dissociative ionization are also observed for the compounds studied in the present work (see Table 1). An exception is compound (III) in the mass spectrum of which the line for m/e = $M-CH_2O$ is scarcely observed. However, the molecular ion of this compound readily loses a propylene molecule. Consequently the appearance of a strong line with m/e = $M-(C_3H_6 + CH_2O)$ was to be observed, since the ion formed has a structure similar to that of the molecular ion (the radical $CH_3-CH-CH_3$ replaced by H). In fact, this line is very pronounced in the mass spectrum of compound (III).

The intensity of the line with m/e = $M-CH_2O$ for compounds (I-III), as in the case of the line with m/e = M, is determined by the structure of the alkyl radical of the alkoxy group: a decrease in its intensity is observed on passing from (I) to (II) and (III). This experimental result is easy to understand, since the ions formed differ just in the structure of the alkyl radical. For compound (III) it is the largest and is branched, which explains the fact that this compound is less stable than compounds (I) and (II).

As in the case of the cyclic phosphites [1], the probable process of dissociative ionization is the loss by the molecular ion of a molecule of the olefin arising from the alkyl radical of the alkoxy group. In this process, a H atom migrates to the charged fragment. As was to be expected, exceptions are formed by molecules containing an OCH_3 group as the alkoxy radical, the formation of a molecule of olefin from this being impossible. The splitting off of a CH_2 biradical is unlikely because of the energetics of the process, which is confirmed experimentally by the mass spectra of the compounds studied. It must be noted that in the mass spectra the lines with m/e = $M-C_2H_4$ are due to the decomposition of the molecular ion and not to thermal decomposition in the inlet system. Evidence for this conclusion is presented by the figures of Table 2. For compounds (II) and (IV) diffuse lines are observed which are due to the decomposition of the metastable molecular ions in the following way:

$$\overset{+\cdot}{M} \longrightarrow M^{+\cdot}-28.$$

The loss of an alkoxy radical by the molecular ion is a probable process for all the compounds studied, while the splitting out of an alkyl radical from the alkoxy group of the molecular ion is less probable than the process mentioned above, particularly when the radical is a methyl group. However, the loss by the molecular ion of a molecule of formaldehyde leads to the formation of an ion which subsequently loses an alkyl radical with great probability precisely when the radical is a methyl group. The mass spectra of compounds (I) and (V) show diffuse lines corresponding to this process. It must be noted that the formation of the ion $M^{+\cdot}-15$ is not characteristic for the compounds studied even though, as well as the methyl group of the alkoxyl radical, there are methyl groups attached to the five-membered ring. In the case of an acyclic phosphite, an extremely intense line with m/e = M−15 is observed, according to the literature [2].

The line with m/e = 42 is due largely to the ions $CH\equiv\overset{+}{N}-CH_3$, since the replacement of the CH_3 radical on the nitrogen atom by C_6H_5 (IV) sharply decreases its intensity, while for compound (IV) an intense line with m/e = 104 is due to the ion $CH\equiv\overset{+}{N}-C_6H_5$ of identical structure.

EXPERIMENTAL

The mass spectra were obtained in an MI-1305 mass spectrometer fitted with a glass inlet system and an electron energy of 50 eV and a temperature of the inlet system of 100°C.

The physical constants of the compounds studied corresponded to those given in the literature [5-7].

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