BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(5), 1299—1300 (1974)

Pyrolysis of Tris(2,3-dibromopropyl) Phosphate and Its Related Compounds

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(Received Junuary 18, 1974)

Synopsis. The main product obtained by the pyrolysis of halogenated alkyl phosphate was found to be alkyl halide. The phosphoryl group was substituted for the halogen atom, olefins being minor products.

In a previous paper, we reported that the products obtained by the pyrolysis of *n*-hexyl phosphates were the mixtures of hexene isomers, the acid having a conspicuous influence on the isomer distribution.[1]

Tris(2,3-dibromopropyl) phosphate (I) is wellknown as an effective fire retardant for synthetic polymers, but its behavior in pyrolysis has not yet been studied.

We have investigated the pyrolysis of I and its related compounds as regards the behavior of halogen atom.

Tris(2,3-dichloropropyl) phosphate (II)[2] and trihexyl phosphate (III) were prepared by the reaction of phosphorus oxychloride with 2,3-dichloropropyl alcohol and hexyl alcohol, respectively.

Tris(2-chloroethyl) phosphate (IV),[2] tris(1-methyl-2-chloroethyl) phosphate (V)[2] and tris(1-chloromethyl-2-chloroethyl) phosphate (VI)[2] were prepared by the addition of phosphorus oxychloride to ethylene oxide, propylene oxide and epichlorohydrin, respectively.

I and diethyl 2,3-dibromopropyl phosphate (VII)[2] were prepared by the addition of bromine to the corresponding allyl phosphates at −15 °C. After they had been treated with a cation exchange resin column chromatography to remove trace of free acid, they were dried *in vacuo*.

In each run of pyrolysis, 0.1 mol of the phosphate was decomposed in a 20 ml-distilling flask heated (250—260 °C) with a metal bath at reduced pressure (3 mmHg). The decomposition was over in a few minutes. The pyrolysis products were trapped in a tube cooled with liquid nitrogen. They were analyzed with glc on a 3 m × 3 mmϕ column, packed with Ucon LB 550X on Chromosorb W (60—80 mesh) at column temperature of 160 °C, using nitrogen gas as the carrier. The glc peaks were identified by comparing their retention times with those of authentic samples, or by analysis of NMR and mass spectra of the fractions obtained by preparative glc.

The results of the pyrolysis of several halogenated alkyl phosphates are given in Table 1.

In the pyrolysis of I, 1,2,3-tribromopropane as the main product, *cis*- and *trans*-1,3-dibromopropene, 2,3-dibromopropene-1 and 3-bromopropene-1 were given as distillable products. No free bromine and a trace amount of hydrogen bromide could be detected. The residue was halogen-containing polymerized alkyl phosphate, the structure of which is still unidentified. II gave a mixture of 1,2,3-trichloropropane as a major product, 2,3-dichloropropene-1, 1,3-dichloropropene and a trace amount of 3-chloropropene-1. IV gave 1,2-dichloroethane as a major product and a small amount of vinyl chloride. In the pyrolysis of VII, 87% ethyl bromide was obtained but only a trace amount of 1,2,3-tribromopropane. In the case of the equimolar mixture of I and III, 50% hexyl bromide was obtained but only a trace amount of 1,2,3-bromopropane. In the case of the equimolar mixture of II and III, 21% hexyl chloride was obtained, which was less than the corresponding hexyl bromide from the mixture of I and III. In the case of the equimolar mixture of I and II, 49% of 1-bromo-2,3-dichloropropane and 35% of 1,2,3-tribromopropane, formed

Table 1. Yields and compoments of the products obtained by the pyrolysis of tris(2,3-dibromopropyl) phosphate and its related compounds

Phosphate	Yield (wt%)	Components (relative ratio, mol%)
I	55	$CH_2{=}CHCH_2Br$ (12), $CH_2BrCH{=}CHBr$ (*trans*-: 5.7, *cis*-: 13), $CH_2BrCBr{=}CH_2$ (2.3), $CH_2BrCHBrCH_2Br$ (67)
II	30	$CH_2{=}CHCH_2Cl$ (t), $CH_2ClCH{=}CHCl$ (*trans*-: 5, *cis*-: 8), $CH_2ClCCl{=}CH_2$ (12), $CH_2ClCHClCH_2Cl$ (75)
IV	23	$CH_2{=}CHCl$ (5), CH_2ClCH_2Cl (95)
VII	41	C_2H_5Br (84.7), $CH_2{=}CHCH_2Br$ (10.3), $CH_2{=}CBrCH_2Br$ (4.2), $CH_2BrCH{=}CHBr$ (*trans*-: t, *cis*: 0.8), $CH_2BrCHBrCH_2Br$ (t)
I+III	45	$CH_2{=}CHCH_2Br$ (t), $CH_2BrCH{=}CHBr$ (t), $CH_2BrCBr{=}CH_2$ (t), $CH_2BrCHBrCH_2Br$ (t), C_6H_{12} (50), $C_6H_{13}Br$ (50)
II+III	44	$CH_2{=}CHCH_2Cl$ (t), $CH_2ClCH{=}CHCl$ (*trans*-: 1.3, *cis*-: 0.7), $CH_2ClCCl{=}CH_2$ (t), $CH_2ClCHClCH_2Cl$ (3), C_6H_{12} (77), $C_6H_{13}Cl$ (18)
V	43	$CH_2{=}CHCH_2Cl$ (45.5), $CH_3CH{=}CHCl$ (45.5), $CH_3CHClCH_2Cl$ (9)
VI	60	$C_2HClCH{=}CHCl$ (*trans*-: 26.7, *cis*-: 36.0), $CH_2ClCHClCH_2Cl$ (34.4), $CH_2{=}CH\text{-}CH_2Cl$ (2.9)

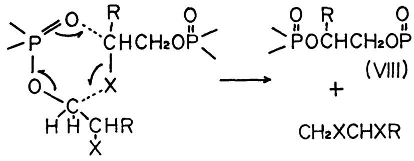
Table 2. Effects of additives on the pyrolysis of I

Additive[a]	Yield (wt%)	Component (relative ratio, mol%)				
		$CH_2{=}CHCH_2Br$	$CH_2{=}CBrCH_2Br$	$CHBr{=}CHCH_2Br$		$CH_2BrCHBrCH_2Br$
				cis	*trans*	
$H_4P_2O_7$	53	23	1	21	3	52
NaH_2PO_4	55	12	14	10	4	60
Na_2HPO_4	58	17	23	6	5	49
$Na_4P_2O_7$	56	12	23	5	4	56
$Ca_3(PO_4)_2$	59	22	15	8	3	52
CH_3COONa	60	9	68	16	2	5
Sb_2O_3	55	83	1	1	1	14

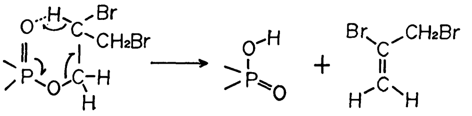
a) 25 wt%

by the transfer of bromine, and 5% of 1,2,3-trichloropropane and 4% of 1,2-dibromo-3-chloropropane, formed by the transfer of chlorine, were obtained.

The main products obtained by the pyrolysis of the halogenated alkyl phosphates were alkyl halides (95—67%), and olefins were minor products, different from the behaviors of unsubstituted alkyl phosphates in the pyrolysis.[1] This suggests that the formation process of alkyl halide involves intermolecular transfer of halogen atom, and the transfer of bromine atom occurred more easily than that of chlorine atom. The halogen substitution occurred more readily at the carbon atom having no halogen atom in the neighboring position. The following mechanism is suggested to account for the behavior.

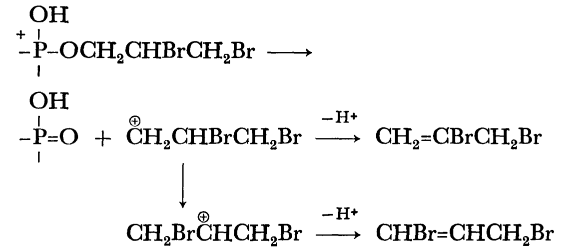


The formation of 2,3-dibromopropene-1 or 2,3-dichloropropene-1 might proceed through a six-membered ring transition intermediate as in the pyrolysis of alkyl carboxylate.[3]



1,3-Dibromopropene or 1,3-dichloropropene might be given through the isomerization of 2,3-dihalopropyl cation which was formed by acid catalyzed pyrolysis, into 1-halomethyl-2-haloethyl cation, followed by the elimination of a proton as follows.

3-Bromopropene-1 can be obtained from further decomposition of VIII.



$$\overset{\text{OH}}{\underset{|}{\overset{+|}{-\text{P}}}}\text{-OCH}_2\text{CHBrCH}_2\text{Br} \longrightarrow \overset{\text{OH}}{\underset{|}{\overset{|}{-\text{P}}}}{=}\text{O} + \overset{\oplus}{\text{C}}\text{H}_2\text{CHBrCH}_2\text{Br} \xrightarrow{-\text{H}^+} \text{CH}_2{=}\text{CBrCH}_2\text{Br}$$

$$\downarrow$$

$$\text{CH}_2\text{Br}\overset{\oplus}{\text{C}}\text{HCH}_2\text{Br} \xrightarrow{-\text{H}^+} \text{CHBr}{=}\text{CHCH}_2\text{Br} \quad (3)$$

Secondary alkyl phosphates V and VI gave more olefinic products than the halogen substituted products. This decomposition may proceed preferentially through reaction (2) or (3).

The effects of additives on the pyrolysis of I were studied. The results are given in Table 2.

Addition of sodium phosphates to I induced the substantial change in the yields of 2,3-dibromopropene-1 and *cis*-1,3-dibromopropene, which might be formed *via* reaction (2) or (3), in the same manner as the case of the pyrolysis of III.[1] However, the formation of alcohol could not be observed. Addition of phosphoric acid increased 3-bromopropene-1 and 1,3-dibromopropene, but decreased 1,2,3-tribromopropane. It was observed that by the addition of sodium acetate 2,3-dibromopropane markedly increased, whereas 1,2,3-tribromopropane decreased. Antimonous trioxide is also known to be an effective fire retardant when it is used with halogen-containing material. It was found that its addition caused serious changes of the composition of the products.

References

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