BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 495—496 (1974)

The Pyrolysis of Hexyl Phosphates and Their Salts

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(Received September 5, 1973)

Synopsis. The isomer distribution of hexene from the tri-*n*-hexyl phosphate changes gradually as the decomposition proceeded. However the formation of the isomers other than 1-hexene was appreciably depressed by the addition of anhydrous disodium hydrogen phosphate.

There have been several reports on the thermal decomposition of alkyl phosphates,[1] alkyl phosphorochloridates,[2] and alkyl phosphites.[3] The olefins obtained by these procedures were mixtures of the isomers. The isomer distributions of the olefin and the mechanism of the formation of the isomer on the thermal decomposition of phosphate had not yet been studied.

In the present paper, the isomer distributions of the *n*-hexene obtained from the pyrolysis of *n*-hexyl phosphates under several different conditions were determined, and the pyrolysis method of obtaining 1-hexene as the sole product has been investigated.

Mono-(I), di-(II), and tri-*n*-hexyl phosphate (III) were prepared in the usual way.[4]

The sodium dihexyl phosphate and the disodium hexyl phosphate were prepared by the addition of an equivalent of alcoholic sodium hydroxide to II and to I respectively; after the solvent had then been distilled off, the residues were dried *in vacuo*. The lithium salts were prepared in the same manner. The magnesium or calcium hexyl phosphate was prepared by the double decomposition in the aqueous solution of sodium hexyl phosphate and the corresponding metal halide respectively. The precipitate was filtered and, after several washing with water, dried *in vacuo*.

In every run of pyrolysis, 0.1 mol of the phosphate was decomposed in a 10-ml distilling flask heated by means of a metal bath at reduced pressure (30 mmHg). The decomposition of phosphate began in the range from 280° to 310 °C, and was over in a few minutes. The pyrolysis products were trapped in a tube cooled with liquid nitrogen in 90—95% yields. They were analyzed with glc on two columns: a 3 m×3 mmφ column (A), packed with PEG 1000 (10%) on Chromosorb W (60—80 mesh), at the column-temperature of 110 °C, and a 15 m×3 mmφ column (B), packed with ODPN (40%) on C-22 fire brick (60—80 mesh), at the column-temperature of 25 °C, using nitrogen gas as the carrier. The glc peaks were identified by comparing their retention times with those of authentic samples. The A column was used for the determination of the yields of *n*-hexene and *n*-hexanol. The B column was used for the determination of the relative ratio of the *n*-hexene isomers.

The isomer distribution of hexene from the pyrolysis of III changed gradually as the decomposition proceeded. (Fig. 1) At the beginning of the decomposition, only 1-hexene was produced, but the ratio of 1-hexene to the other isomers gradually decreased with the progress of the decomposition; finally it approached the ratio which was attained by refluxing 1-hexene with phosphoric acid for 24 hr. When a small amount of

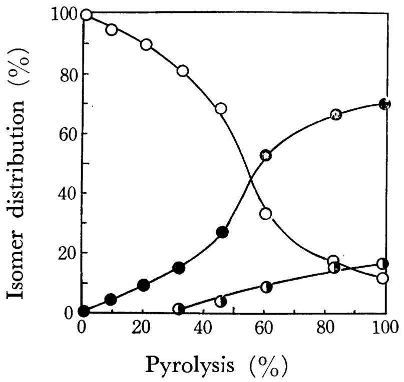

Fig. 1. Relationship between the isomer distribution of tri-*n*-hexyl phosphate. ○: 1-hexene, ●: 2-hexene, ◑: 3-hexene.

Table 1. The relative yields of hexene and hexanol obtained from pyrolysis of tri-*n*-hexyl phosphate and metal hexyl phosphates

Phosphate[a]	Product from the pyrolysis of phosphates (mol%)					
	Hexene isomer					Hexanol
	1-	*cis*-2-	*trans*-10-	*cis*-3-	*trans*-3-	
$PO(OR)_3$	68	16	10	2	4	t
$ROPO(ONa)_2$	50	t[b]	t	0	0	50
$ROPO(OLi)_2$	50	t	t	0	0	50
$ROPO(O_2Ca)$	65	14	14	3	4	t
$ROPO(O_2Mg)$	29	34	23	5	9	t
$(RO)_2PO(ONa)$	30	t	t	0	0	70
$(RO)_2PO(OLi)$	51	2	3	0	0	64
$[(RO)_2PO]_2Ca$	59	21	20	t	t	t

a) R; n-C_6H_{13}, b) t; trace

TABLE 2. THE EFFECTS OF THE ADDITION OF Na_2HPO_4 OR $Na_4P_2O_7$ ON THE PYROLYSIS OF TRI-*n*-HEXYL PHOSPHATE

Additive	Amount of Additive $\frac{[A]}{(RO)_3PO}$ [a]	Products from the pyrolysis of phosphate (mol%)					
		Hexene isomer					Hexanol
		1-	*cis*-2-	*trans*-2-	*cis*-3-	*trans*-3-	
Na_2HPO_4	14	72	t [b]	t	0	0	28
Na_2HPO_4	7	62	5	3	t	t	30
$Na_4P_2O_7$	14	73	t	t	0	0	27
$Na_4P_2O_7$	7	64	4	2	t	t	30

a) molar ratio, b) t; trace.

phosphoric acid was added to III, from the beginning of the decomposition the hexene isomers were produced.

The isomer distributions of the hexene obtained by the overall pyrolysis of III and the metal *n*-hexyl phosphates are shown in Table 1.

Although III gave a mixture of all the hexene isomers, disodium or dilithium hexyl phosphate gave 1-hexene and *n*-hexanol. The temperatures of the beginning of the decomposition of alkali metal hexyl phosphates were higher (300 °C) than that of III (280 °C), but that of calcium or magnesium hexyl phosphate was the same as that of III, according to the results of TGA analysis. Calcium or magnesium hexyl phosphate also gave a mixture of all the hexene isomers.

When a few tablets of sodium hydroxide were added to III, the formation of any isomer other than 1-hexene was inhibited, but a considerable amount of *n*-hexanol was produced (74%).

The formation of the isomers of hexene other than 1-hexene by means of the pyrolysis of III was appreciably depressed (at least the formation of *n*-hexanol was) by the addition of a large excess of anhydrous disodium phosphate or tetrasodium pyrophosphate. (Table 2)

The formation of the isomer of hexene by means of the pyrolysis of III may be autocatalyzed with the phosphoric acid resulting from its decomposition. The effect of the addition of sodium hydroxide or the salt may be explained on the basis of the neutralization of the acid. The differences in the behavior of the decompositions of sodium, lithium, calcium, and magnesium hexyl phosphates may be due to the differences in the valences and electronegativities of the metals.[5,6]

The hexanol may be produced by means of the hydrolysis of the hexyl phosphate by the alkali metal hydroxide resulting from the hydrolysis of the alkali metal hexyl phosphate.

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