The Thermal Decomposition of Dialkyl Phosphates and O,O-Dialkyl Dithiophosphates[1]

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The thermal decomposition of several dialkyl phosphates and O,O-dialkyl dithiophosphates was studied and and included the free acids, zinc salts, and S-bornyl esters. Pyrolysis was performed at $\geqslant$215° in a flowing helium stream in the injection port of a gas chromatograph. The volatile products formed rapidly and were easily gas chromatographed. Analysis indicated that pyrolysis leads to volatile olefins which are structurally related to the alkyl group in the original phosphate derivative. Skeletal rearrangement of alkyl groups during pyrolysis generally was not significant. The decompositions were shown to proceed by a carbonium ion mechanism. Pyrolysis was also shown to be acid catalyzed.

The pyrolysis of zinc dialkyl dithiophosphates was conducted in the heated injection block of a gas chromatographic unit.[2a] The volatile pyrolysate consisted of olefins structurally related to the alcohol used originally in preparation of the esters.[2b] As part of the study of the thermal stability of zinc dialkyl dithiophosphates, an investigation was made to determine the mechanism by which these compounds undergo pyrolysis.

Decomposition of dialkyl dithiophosphates can possibly occur either by an E1 (unimolecular) or an intramolecular (*cis*) elimination.[3]

The unimolecular (E1) reaction involves the initial formation of a carbonium ion followed by elimination of a proton from the β-carbon atom. This is the route by which the acid-catalyzed dehydrations of many alcohols proceed.[3] Rearrangement of a primary carbonium ion to a more stable secondary or tertiary carbonium ion is to be expected. Skeletal rearrangements are also possible.

The intramolecular (*cis*) elimination is the accepted mechanism for the thermal decomposition of carboxylic acid esters and xanthates. Products obtained from this decomposition are those resulting from elimination without rearrangement. Esters of primary alcohols decompose to form 1-olefins exclusively. Esters of secondary and tertiary alcohols form olefins whose structures can be predicted from the structure of the alcohol. No skeletal rearrangements occur.

In order to differentiate between the two possible decomposition mechanisms, a series of dithiophosphates was prepared. These model compounds were then thermally decomposed in the heated injection block of a gas chromatographic unit. The volatile pyrolysis products were identified and measured.

Experimental

Standard preparative methods were utilized for all the model compounds studied. All alcohols used in preparations were examined by gas chromatography and shown to be better than 99% pure. Dialkyl dithiophosphoric acids were prepared by the reaction of the specific alcohol with phosphorus pentasulfide. Zinc dialkyl dithiophosphates were prepared from the corresponding acids by reaction with zinc oxide. S-Bornyl esters were prepared from the dithiophosphoric acids by reaction with α-pinene. Phosphate esters were prepared by the reaction of the specific alcohol with phosphorus pentoxide. The model phosphates and dithiophosphates were examined by nuclear magnetic resonance. No evidence for alkyl carbon skeletal rearrangement was found.

The unique pyrolysis chamber used in these experiments has been previously described.[2a] The gas chromatographic column utilized was $^1/_8$-in. o.d. copper refrigeration tubing, 30 ft. long, and packed with 28.6 wt. % propylene carbonate on 42–60-mesh firebrick. Pyrolysates were chromatographed at ambient temperature. Table I lists the relative retention times of the olefin products which were identified by retention times, using standards. The pyrolysis, as well as the chromatography, was conducted in a flowing helium stream, flow rate 35 ml./min. The pyrolysis temperatures ranged from 215 to 302°. Under these conditions volatilization of the esters did not occur. Decomposition is a liquid phase rather than vapor phase reaction.

TABLE I

RELATIVE CORRECTED GAS CHROMATOGRAPHIC RETENTION TIMES OF OLEFINS[a]

Pentenes		Propylene and butenes	
1-Pentene	0.75	Propylene	0.39
cis-2-Pentene	0.87	1-Butene	0.90
trans-2-Pentene[b]	1.00	Isobutene[b]	1.00
2-Methyl-2-butene	1.13	*trans*-2-Butene	1.11
3-Methyl-1-butene	0.53	*cis*-2-Butene	1.36
2-Methyl-1-butene	0.89		

[a] All compounds were identified by retention time. [b] Each group of compounds was internally referenced.

Results

Decomposition Products.—The decomposition products derived from zinc di-*n*-amyl dithiophosphate are listed in Table II. Products from other straight-chain alcohol derivatives are also given. Volatile products from zinc dialkyl dithiophosphates synthesized from branched amyl alcohols are given in Table III.

TABLE II

OLEFINS FORMED FROM PYROLYSIS OF ZINC O,O-DIALKYL DITHIOPHOSPHATES PREPARED FROM STRAIGHT-CHAIN AMYL ALCOHOLS[a]

Alcohol	1-Pentene	*cis*-2-Pentene	*trans*-2-Pentene	2-Methyl-2-butene	Other
n-Amyl	39	24	33	2	2
2-Pentyl	19	33	45	1	2
3-Pentyl	5	36	57	1	1

[a] Values are given as weight per cent concentration.

The most stable carbonium ion formed without skeletal rearrangement from straight-chain amyl alcohols is $CH_3CH_2\overset{+}{C}HCH_2CH_3$ and from branched chain amyl alcohols is $CH_3\overset{+}{C}(CH_3)CH_2CH_3$.

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[1] Presented in part before the Division of Petroleum Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[2] (a) R. S. Porter, A. S. Hoffman, and J. F. Johnson, *Anal. Chem.*, **34**, 1179 (1962); (b) C. E. Legate and H. D. Burnham, *ibid.*, **32**, 1042 (1960).

[3] Edwin S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959.

TABLE III

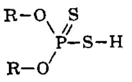
OLEFINS FORMED FROM PYROLYSIS OF ZINC O,O-DIALKYL DITHIOPHOSPHATES PREPARED FROM BRANCHED-CHAIN AMYL ALCOHOLS[a]

Alcohol	3-Methyl-1-butene	2-Methyl-2-butene	2-Methyl-1-butene	Others[b]
3-Methyl-1-butyl	12	53	27	8
3-Methyl-2-butyl	6	64	22	8
2-Methyl-1-butyl	1	56	32	11
Neopentyl	. . .	71	28	1

[a] Values are given as weight per cent concentration. [b] Primarily straight-chain pentenes.

TABLE IV

PYROLYSIS PRODUCTS OF O,O-DIISOAMYL DITHIOPHOSPHORIC ACID DERIVATIVES[a]



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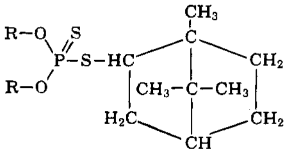

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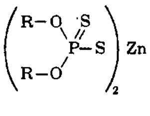

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Volatile pyrolysis products	O,O-Diisoamyl dithiophosphoric acid (A)	S-Bornyl-O,O-diisoamyl dithiophosphate (B)	Zinc O,O-diisoamyl dithiophosphate (C)
Butenes	1	4	2
3-Methyl-1-butene	13	15	12
2-Methyl-1-butene	23	24	27
1-Pentene	1	1	2
cis-2-Pentene	3	2	4
2-Methyl-2-butene	59	54	53

[a] Values are given as weight per cent concentration.

TABLE V

PYROLYSIS PRODUCTS OF DIBUTYL ACID PHOSPHATES AND S-BORNYL-O,O-DIBUTYL DITHIOPHOSPHATES

	Volatile Products, wt. %				
	1-Butene	Isobutene	*cis*-2-Butene	*trans*-2-Butene	Propylene
Di-*n*-butyl acid phosphate	28	. . .	32	40	. . .
Di-sec-butyl acid phosphate	12	. . .	42	46	. . .
S-Bornyl-O,O-di-*sec*-butyl dithiophosphate	17	. . .	38	45	. . .
Isobutyl acid phosphate	5	69	12	14	. . .
S-Bornyl-O,O-diisobutyl dithiophosphate	5	71	9	12	3

The principal product predicted from the straight-chain carbonium ion is a mixture of *cis*- and *trans*-2-pentene with the *trans* isomer predominating. The branched-chain carbonium ion leads to the formation of predominantly 2-methyl-2-butene with a lesser quantity of 2-methyl-1-butene.

The intramolecular *cis*-elimination mechanism would produce 1-pentene as the only product from esters of *n*-amyl alcohol. Secondary, straight-chain amyl alcohols would be expected to form 1-pentene and *cis*- and *trans*-2-pentene. Esters of the branched-chain, primary amyl alcohols should produce only methyl-1-butenes.

In every case, the products approach those predicted as forming from the most thermodynamically stable carbonium ion. Thus, from the *n*-amyl ester there were produced *cis*- and *trans*-2-pentene in addition to 1-pentene. The ester of neopentyl alcohol having no β-hydrogen atoms cannot undergo *cis* elimination. The formation of 2-methyl-2-butene and 2-methyl-1-butene from this ester is indicative of a carbonium-ion mechanism involving skeletal rearrangement.

The pyrolysis products of diisoamyl dithiophosphoric acid, zinc diisoamyl dithiophosphate, and S-bornyl diisoamyl dithiophosphate are shown in Table IV. These data show no significant differences in the product distribution. It is thus concluded that the mechanism of pyrolysis is the same for all these compounds. Perry noted the similarity of olefin distributions produced from the pyrolysis of zinc and lead dimethyl pentyl dithiophosphates.[4]

The products obtained from the pyrolysis of dibutyl acid phosphates and S-bornyldibutyl dithiophosphates are shown in Table V. The yields of 1-butene and *trans*-2-butene, along with the skeletal rearrangements of the isobutyl esters, strongly suggest a carbonium ion mechanism.

Effect of pH.—The effect of pH upon the decomposition point of zinc diisoamyl dithiophosphate is shown in Fig. 1. The thermal decomposition point was defined as the point at which a visible cloud appeared in a 5% solution of the thiophosphate in mineral oil when heated at a rate of 1–2°/min. The pH of the oil was changed by the addition of diisoamyl dithiophosphoric acid, oleic acid, and alkylbenzene sulfonic acid to it. The greater effect of pH on the decomposition point due to addition of oleic acid may be attributed to the increased polarity of the test oil due to the large amount of oleic acid required to lower the pH.

Effect of Pyrolysis Temperature.—Table VI shows the effect of the pyrolysis chamber temperature and the presence of added base upon the decomposition products of zinc di(3-methyl-2-butyl) dithiophosphate. Pyrolysis at either 215 or 302° leads to virtually identical product distribution. A sample of the thiophosphate was dissolved in quinaldine (2-methylquinoline) in order to neutralize any free acid which might act as a catalyst for the decomposition. Pyrolysis under these two conditions yielded essentially the same product distribution.

TABLE VI

PYROLYSIS PRODUCTS OF ZINC O,O-DI(3-METHYL-2-BUTYL) DITHIOPHOSPHATE[a]

	Pyrolysis temp.		
Volatile products	302°	215°	215°, sample dissolved in 2-methylquinoline
Propylene	5	4	1
3-Methyl-1-butene	6	5	6
2-Methyl-1-butene	22	21	20
2-Methyl-2-butene	64	68	73
Unidentified	3	2	. . .

[a] Values are given as weight per cent concentration.

Table VII shows the products obtained from the pyrolysis of zinc di-*n*-amyl dithiophosphate and di-*n*-amyl acid phosphate. In this case, the rearrange-

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(4) S. G. Perry, *J. Gas Chromatog.*, **2**, 93 (1964).

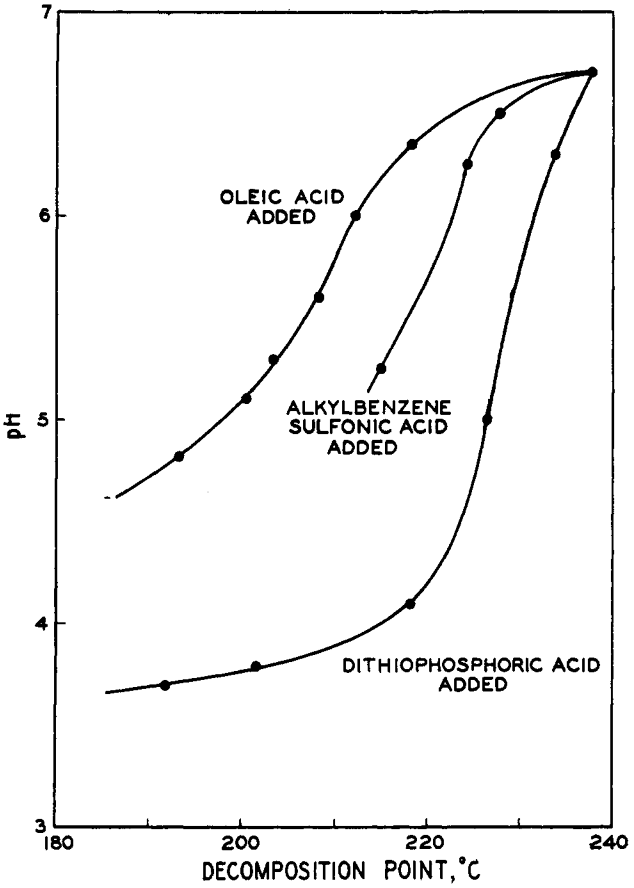

Fig. 1.—Effect of pH on decomposition of zinc O,O-diisoamyl dithiophosphate.

ment of the initially formed, straight-chain carbonium ion is enhanced under acidic conditions and retarded by base as shown by the yield of 1-pentene.

Olefin Rearrangement.—In order to determine the possibility of skeletal rearrangements of the initially formed olefins in the pyrolysis chamber, the following experiment was performed. Small samples of zinc O,O-di-*n*-amyl dithiophosphate were placed in sealed stainless steel tubes of the same material as the pyrolysis chamber. These tubes were immersed in a bath heated to 315°. Individual tubes were withdrawn at 0.25, 0.5, 1, 2, 4, 8, and 16 min., and the volatile pyrolysis products were analyzed. The products in each case were the same. No evidence of skeletal rearrangement of the initially formed olefins was noted on prolonged heating in the presence of the solid decomposition products.

TABLE VII

THERMAL DECOMPOSITION PRODUCTS OF ZINC O,O-DI-*n*-AMYL DITHIOPHOSPHATE AND DI-*n*-AMYL ACID PHOSPHATE AT 302°[a]

Product	Zinc O,O-di-*n*-amyl dithiophosphate		Di-*n*-amyl acid phosphate
		Quinaldine added	
1-Pentene	39	48	25
trans-2-Pentene	33	29	46
cis-2-Pentene	24	11	26
2-Methyl-2-butene	2	7	3
Unidentified	2	5	...

[a] Values are given as weight per cent concentration.

Discussion

The results of this study show that dialkyl phosphates and dialkyl dithiophosphates thermally decompose by a carbonium ion mechanism. These materials are not vaporized under the conditions so that the decomposition is a liquid rather than vapor phase reaction. Evidence is also presented to support the fact that the reaction is acid catalyzed.

These results are in general accord with data obtained on two of these compounds using related decomposition techniques.[4] In contrast with these results, however, *cis*-2-olefins were reported to predominate over the more thermodynamically stable *trans* isomer. The contradictory nature of this earlier result has been recognized.[4]

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