chloride, and bringing the solution with sodium hydroxide to pH 9. The precipitate was washed, dissolved in hydrochloric acid, reprecipitated with sodium hydroxide, dissolved by shaking with the protonated form of Dowex 50W × 12 ion exchanger, brought to pH 4 with 3 *N* potassium hydroxide, and precipitated as KH_2PO_4 by addition of acetone and cooling overnight in a deep freeze. The potassium dihydrogen phosphate was washed with acetone, dried at 60° under reduced pressure, and analyzed for ^{18}O by the method of Boyer, *et al.*[18]

Registry No.—Ethyl dihydrogen phosphate, 1623-14-9; isopropyl dihydrogen phosphate, 1623-24-1; methyl dihydrogen phosphate, 812-00-0; dicyclohexylammonium salt of isopropyl dihydrogenphosphate, 7695-58-1; *t*-Butyl dihydrogen phosphate, 2382-75-4; *n*-propyl dihydrogen phosphate, 1623-06-9.

Acknowledgment.—This investigation was supported in part by a Research Grant GM-05842 from the U. S. Public Health Service.

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[18] P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

The Thermal Decomposition of Metal O,O-Dialkylphosphorodithioates[1]

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The thermal decomposition of metal O,O-dialkylphosphorodithioates has been shown to be an autocatalytic reaction yielding olefins, mercaptans, hydrogen sulfide, and polymeric residue. The reaction is dependent on the structure of the alkyl groups and, for a series of divalent metals, on the size of the metal cation. Specifically, the rate of decomposition increases with increasing number of hydrogens on the β-carbon atoms in the alkyl groups and with decreasing metal cation size. These results, plus information on the sequence of product formation, product distribution, effect of added reagents, and deuteration of the alkyl groups, form the basis for a proposed reaction mechanism. The mechanism includes an isomerization followed by an intramolecular (*cis*) elimination as key steps to the formation of olefins.

The thermal decomposition of metal O,O-dialkylphosphorodithioates has been the subject of a number of investigations[2–7] but the detailed mechanism has not been clearly understood.

Hanneman and Porter[5] have recently examined the volatile olefins formed during the pyrolysis of zinc O,O-dialkylphosphorodithioates at 215 to 302°, and concluded that the decomposition proceeded through a carbonium ion mechanism. Luther and Sinha[6] have compared the formation of olefins, mercaptans, and hydrogen sulfide from 25 to 250° for zinc di-*n*-butyl and diisobutyl phosphorodithioates, and reached the conclusion that the thermal decomposition proceeded by a free-radical mechanism. Ashford, Bretherick, and Gould[7] examined the thermal decomposition of zinc di(4-methylpentyl-2)phosphorodithioate between 130 and 190°, and concluded that the mechanism of decomposition includes the partial isomerization of thiono- to thiolosulfur with subsequent decomposition of both isomers by one or more routes involving carbonium ions and free radicals. Several studies[2–4] have been concerned with the determination of the thermal decomposition temperature for gas evolution and for solid residue formation. From a chemical analysis of the gases and the residue, Feng[2] proposed a reaction involving release of an olefin, an isomerization to form a =P(SH)= group, and, finally, the formation of an interthioanhydride, which upon occurring for two or more alkyl groups in a given molecule leads to a polymeric structure.

Heretofore, none of the reported work involved a study with pure materials to determine both the effect of the cation and the structure of the alkyl group on the rate of thermal decomposition. This paper reports the results of such an investigation at 155°, and proposes a mechanism involving an isomerization and an intramolecular (*cis*) elimination of olefin from the thiolosulfur isomer as key steps in the decomposition scheme.

Experimental Section

Preparation of Metal O,O-Dialkylphosphorodithioates.—The O,O-dialkylphosphorodithioic acids and their ammonium salts were prepared essentially by the procedure of Wystrach, *et al.*[8] The ammonium salts were purified by recrystallization from isooctane or isooctane–ethyl alcohol mixtures.

The zinc (or other metal) salts were prepared by metathetic reactions using aqueous solutions of the ammonium salts and filtered aqueous solutions of $ZnCl_2$ (or the chloride, nitrate, or sulfate of the other metals) in stoichiometric amounts. Solid, insoluble metal salts were isolated by filtration and purified by recrystallization. Liquid products were extracted from the aqueous mixture with pentane, washed with water, and dried and the pentane was removed by evaporation under vacuum.

Table I lists the metal O,O-dialkylphosphorodithioates prepared. Zinc O,O-diisopropylphosphorodithioate was chosen initially as a representative compound for extensive investigation, since it is readily purified by recrystallization and hence well suited to our purpose. The deuterated zinc O,O-diisopropylphosphorodithioate was prepared from 2-propyl-1,1,1,3,3,3-d_6 alcohol.

Apparatus and Procedure.—The apparatus used for the thermal decomposition of the metal O,O-dialkylphosphorodithioates is sketched in Figure 1. Liquids of proper boiling point (*o*-xylene, bp 144°; bromobenzene, bp 155°; decane, bp 174°) were refluxed in the jacket to obtain the desired, constant, reproducible reaction temperature. D is a water absorber containing a starch indicator in which the hydrogen sulfide was titrated continuously with standard potassium iodide–iodine solution. The manostat (F) maintains the system at about 1 atm by releasing water from the gas holder as gas is formed.

After purging the apparatus with nitrogen, a weighed sample of about 0.004 mole of the phosphorodithioate was placed in

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[1] Presented in part before the Division of Petroleum Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[2] I.-M. Feng, *Wear*, **3**, 309 (1960).

[3] I.-M. Feng, W. L. Perilstein, and M. R. Adams, *ASLE Trans.*, **6**, 60 (1963).

[4] N. E. Gallopoulos, *ibid.*, **7**, 55 (1964).

[5] W. W. Hanneman and R. S. Porter, *J. Org. Chem.*, **29**, 2996 (1964).

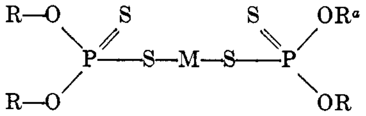
[6] H. Luther and S. K. Sinha, *Erdoel Kohle*, **17**, 91 (1964).

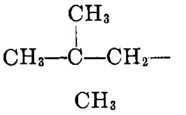
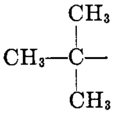
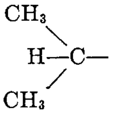
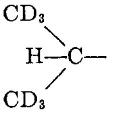
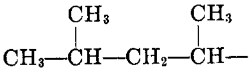
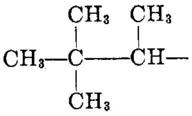
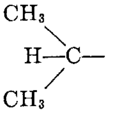
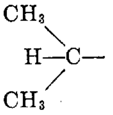
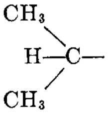
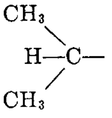
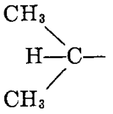
[7] J. S. Ashford, L. Bretherick, and P. Gould, *J. Appl. Chem.*, **15**, 170 (1965).

[8] V. P. Wystrach, E. O. Hook, and G. L. M. Christopher, *J. Org. Chem.*, **21**, 707 (1956).

Table I

Metal O,O-Dialkylphosphorodithioates



Alkyl group (R)	Metal (M)	Registry no.	Mp, °C	% P Calcd	% P Found	% S Calcd	% S Found	% M Calcd	% M Found
 $CH_3-C(CH_3)_2-CH_2-$	Zn	7540-54-7	223.5–224.5	9.96	10.1	20.6	20.4	10.5	11.0
 $CH_3-C(CH_3)_2-$	Zn		Unstable at room temperature	...	...	...	...	...	...
$CH_3CH_2CH_2-$	Zn	6248-51-7	Liquid	12.2	12.7	25.2	26.7	12.8	13.5
 $(CH_3)_2C(H)-$	Zn	2929-95-5	144.0–144.5	12.2	12.2	25.5	26.5	12.8	13.1
 $(CD_3)_2C(H)-$	Zn	7491-63-6	144.0–145.0	...	...	...	...	...	...
 $CH_3-CH(CH_3)-CH_2-CH(CH_3)-$	Zn	2215-35-2	Liquid	9.13	8.83	18.9	19.2	9.64	9.82
 $CH_3-C(CH_3)_2-CH(CH_3)-$	Zn	7491-65-8	136.5–137.5	9.13	9.12	18.9	20.3	9.64	8.5
CH_3CH_2-	Zn	7268-60-2	180.0–181.0	...	...	...	...	...	...
 $(CH_3)_2C(H)-$	Pb	7481-28-9	131.5–132.0	9.50	9.89	19.7	20.3	31.8	30.8
 $(CH_3)_2C(H)-$	Cu	7481-27-8	78.5–79.5	12.6	13.4	26.2	25.5	13.0	13.3
 $(CH_3)_2C(H)-$	Cd	7481-26-7	138.0–139.0	11.1	13.0	23.0	23.8	20.2	19.1
 $(CH_3)_2C(H)-$	Ag[b]	7481-25-6	161.0–162.5	9.13	9.95	18.9	18.1	31.8	34.2
 $(CH_3)_2C(H)-$	H	107-56-2	Colorless liquid	14.5	13.8	29.9	29.3	...	...

[a] All of the compounds contained 1 mole of water per mole except the completely anhydrous copper salt and the free acid. [b] Only monovalent metal.

the sample tube (B) and brought to reaction temperature. The amounts of hydrogen sulfide and other noncondensable gases were recorded as a function of time. When the gas evolution essentially stopped (slight gas evolution continues indefinitely), the reactor was cooled to room temperature. Gas volume measurements were corrected for system expansion owing to heating and for changes in system volume owing to the addition of the potassium iodide–iodine solution.

The gases were analyzed by mass spectroscopy and/or vapor phase chromatography. The liquid product was analyzed by mass spectroscopy and/or infrared absorption spectroscopy. Quantitative elemental analyses were obtained in some cases to check material balances. The residual solid was analyzed by infrared absorption spectroscopy and quantitative elemental analyses.

Figure 2 shows a plot of the formation of hydrogen sulfide and propylene as a function of time for zinc O,O-diisopropylphosphorodithioate at 155°. The shape of the curves is typical for all the compounds studied. The induction period given in subsequent tables is defined as the intercept of the abscissa

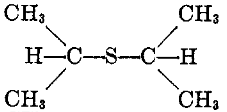
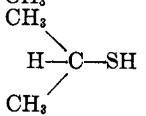
Table II

Decomposition of Zinc O,O-Diisopropylphosphorodithioate at 155°

A. Material balance

	Wt, g[a]	Mole
Charge	2.082	4.08×10^{-3}
Residue	1.531	Unknown
Liquid	0.317	3.30×10^{-3}
H_2S	0.00886	0.261×10^{-3}
Olefin	0.183	4.35×10^{-3}

B. Yield of C_3H_7 groups

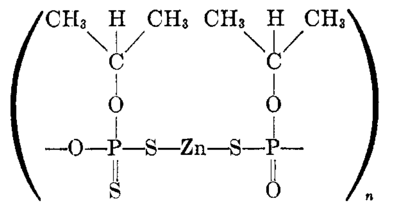
Product	Component	Mole %	C_3H_7/mole charge
Liquid[b]		12	0.19
		67	0.54
	$CH_3CH_2CH_2SH$	3.5	0.03
	Unidentified	17.5[c]	0.14
Gas	$CH_3CH{=}CH$	...	1.03
Total			1.93

[a] Recovery, 2.040 g, 98.0% (wt). [b] Average mol wt, 96; 0.317 g, 0.81 mole/mole charge. [c] By difference.

upon extrapolating the linear part of the curves. The rates of hydrogen sulfide and olefin formation are the slopes of these lines.

Results and Discussion

Composition of Reaction Products.—The products of the thermal decomposition of metal O,O-dialkylphosphorodithioates at 155° fall into two general categories. The residual material was a glass-like, insoluble solid which is difficult to characterize. Infrared absorption spectra showed bands at 8.2 to 8.3 and at about 15 μ, which agree with P=O and P=S, respectively.[9a] Quantitative elemental analyses[9b] and a melting point above 400° suggest the following structure for the residue of zinc O,O-diisopropylphosphorodithioate. Although the analyses are the same, this



structure differs from that proposed by Feng[2] in the P—O—P and P=S bonds; Feng proposed P—S—P and only P=O (no P=S). Attempts to determine the molecular weight of the residual material were unsuccessful; the material was either soluble in or reacted with all available solvents.

The volatile products were separated into (a) materials condensable in the ice–water bath, (b) hydrogen sulfide, and (c) noncondensable gases other than hydrogen sulfide. The noncondensable gases other than hydrogen sulfide were olefins; for the large alkyl groups the olefins were found in the cold trap. Results from the typical run shown in Figure 2 are given in Table II. From Figure 2 it is evident that the decomposition is autocatalytic.

If the unidentified material in Table IIB is assumed to have one alkyl group per mole, 1 mole of the zinc O,O-diisopropylphosphorodithioate yields about 2 moles of alkyl groups as volatile products. Calculations from the analyses of the residue also show about 2 moles of alkyl groups per mole of charge remaining.

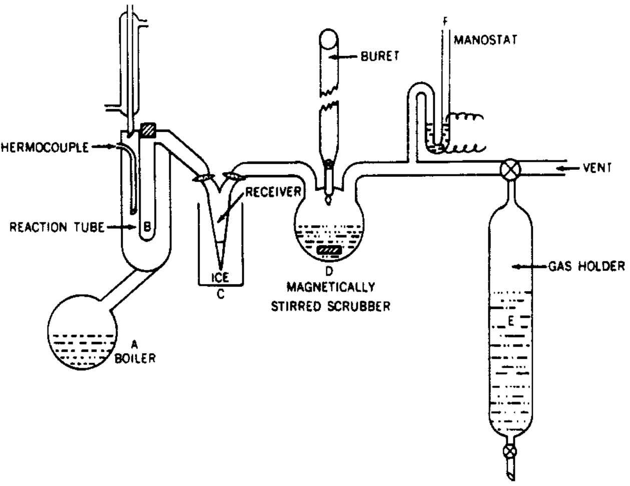


Figure 1.—Thermal decomposition apparatus.

Sequence of Product Formation.—The sequence of product formation was determined by sampling the vapor phase periodically during the induction period with a syringe at a point just above the surface of the zinc O,O-diisopropylphosphorodithioate. The results showed that the sequence of the appearance of products was (1) propylene, (2) isopropyl mercaptan, and (3) hydrogen sulfide.

In an experiment in which zinc O,O-di-*n*-propylphosphorodithioate was charged to the reactor, only *n*-propyl mercaptan was found. If the mercaptan was the product of addition of hydrogen sulfide to the olefin in an acid environment,[7] such as exists in this system, isopropyl mercaptan would be expected. This observation is supported by those of Luther and Sinha[6] who found only *n*-butyl mercaptan and isobutyl mercaptan in the decomposition of the corresponding zinc salts. This is additional evidence that the formation of mercaptan precedes the formation of hydrogen sulfide, and evidence that a rearrangement of the alkyl group from oxygen to sulfur is involved in the reaction sequence. Additional experimental evidence for such a rearrangement was observed in the infrared spectrum of zinc O,O-diisopropylphosphorodithioate which had been heated at 144 and 155° for periods shorter than the induction period for rapid decomposition. A band appeared at 8.2 to 8.3 μ which agrees with that of the phosphoryl group.[9a]

Effect of Added Materials on the Decomposition Reaction. Acids.—The addition of acids to the zinc

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(9) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 311. (b) *Anal.* Calcd for $C_6H_{14}O_4P_2S_3Zn$: C, 19.3; H, 3.75; P, 16.6; S, 25.8; Zn, 17.5. Found: C, 16.5; H, 3.40; P, 17.1; S, 25.7; Zn, 17.4.

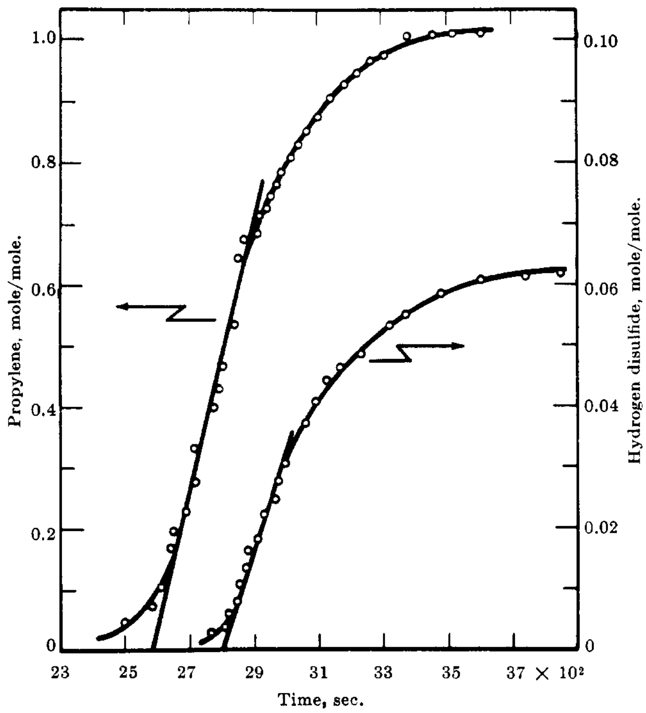

Figure 2.—Olefin and hydrogen sulfide formation for decomposition of zinc O,O-diisopropylphosphorodithioate at 155°.

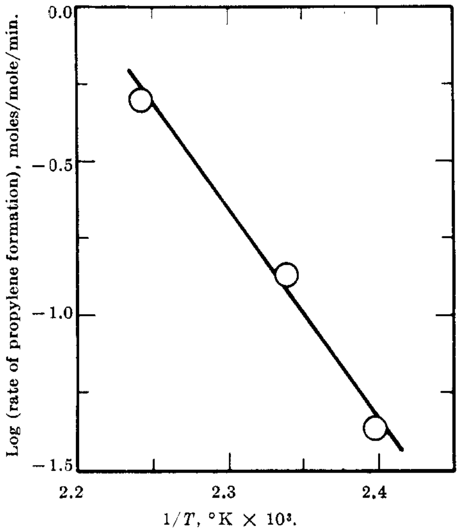

Figure 3.—Effect of temperature on the rate of olefin formation.

O,O-diisopropylphosphorodithioate decomposition system decreased the induction period. With 15 mole % stearic acid, the induction period to olefin formation at 155° decreased from 43 to 38 min, a repeatable difference. With 50 mole % *p*-toluenesulfonic acid the induction period was 14 min. These results suggest that in the decomposition of the phosphorodithioate alone a =P(OH)= or other acid group is forming during the induction period and is responsible for the autocatalytic character of the decomposition. However, free O,O-diisopropylphosphorodithioic acid had an induction period of about 28 min. This is understandable if the above-mentioned rearrangement takes place during the induction period.

Bases.—When a base, *n*-octylamine, was added to the dialkylphosphorodithioate, no apparent decomposition took place up to 165 min. Hence, it is concluded that basic materials inhibit the decomposition.

Peroxides.—O,O-Dialkylphosphorodithioates are known to act as peroxide decomposers and the mechanism is considered to be ionic.[10] When a 10% solution of benzoyl peroxide in benzene was added slowly to the zinc salt at 155°, no decomposition occurred. As soon as the peroxide addition was discontinued, the reaction followed its usual induction period and rate of decomposition. However, the relation between the antioxidant activity and the thermal stability of O,O-dialkylphosphorodithioates has not been established, nor is it apparent here.

The addition of phenyl-α-naphthylamine, a free-radical scavenger, to the reaction mixture had no apparent effect. These data are not in agreement with the conclusion of Luther and Sinha[6] that the decomposition proceeds by a free-radical mechanism.

Hydrocarbon Dilution.—Solutions of zinc O,O-diisopropylphosphorodithioate in *n*-hexadecane were heated at 155° in a nitrogen atmosphere. The data in Table III show the induction period to be relatively unaffected by dilution, but show that the rates of propylene and hydrogen sulfide evolution after the induction period are dependent on the concentration.

TABLE III

EFFECT OF CONCENTRATION ON DECOMPOSITION OF ZINC O,O-DIISOPROPYLPHOSPHORODITHIOATE AT 155°

Additive concn, mole %	Induction period, min Hydrogen sulfide	Olefin	Rates of formation, mole/mole/min Hydrogen sulfide	Olefin
8.9	. . .	42.5	2.11×10^{-4}	0.0079
30.3	53.3	42.1	7.79×10^{-4}	0.0343
100.0	46.5	43.0	83.4×10^{-4}	0.133

Temperature.—Figure 3 shows an Arrhenius plot of the rate of olefin formation for the thermal decomposition of zinc O,O-diisopropylphosphorodithioate. The calculated activation energy is about 31 kcal/mole. The induction period also decreased with increasing temperature.

Alkyl Group Structure.—The effect of alkyl group structure on the thermal decomposition of zinc O,O-dialkylphosphorodithioates at 155° is shown in Figures 4 and 5. The systematic variation of both the induction period and the rate of hydrogen sulfide formation with the number of hydrogen atoms attached to the β-carbon atom of the alkyl group is apparent; the lower the number of β-hydrogen atoms, the greater the thermal stability. The limiting case where R is neopentyl is not included in the figures because an induction period was not defined after heating for 50 hr. The data for the *t*-butyl derivative are less precise than the other data because of poor stability. The results for two compounds having six β-hydrogen atoms per phosphorus atom are not identical; the difference in the structure of these groups suggests varying contributions owing to inductive or steric effects of the alkyl groups.

Isotope Effects.—The foregoing data on alkyl group structure suggest that the hydrogens on the β-carbon atoms are *directly* involved in a critical step of the decomposition. To further establish this, the thermal decomposition of zinc O,O-diisopropylphosphorodi-

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[10] G. W. Kennerly and W. L. Patterson, Jr., *Ind. Eng. Chem.*, **48**, 1917 (1956).

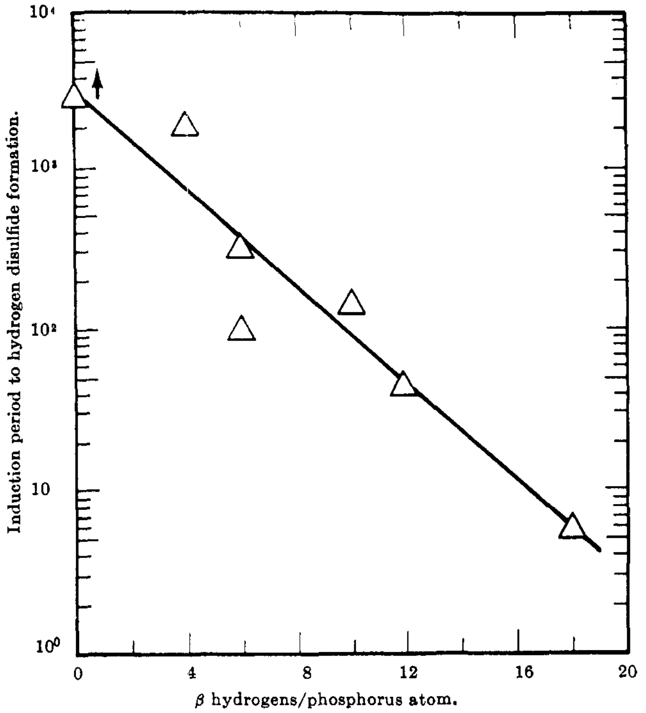

Figure 4.—Effect of number of β hydrogens per phosphorus atom on induction period.

thioate with deuterium replacing all the hydrogens on β-carbon atoms was determined at 155°. The results in Table IV show that deuterium leads to longer induction times and to lower rates of decomposition.

TABLE IV

EFFECT OF DEUTERIUM ON THE RATE OF THERMAL DECOMPOSITION OF ZINC DIISOPROPYLPHOSPHORODITHIOATE

	Induction time, min		Rate of formation, mole/mole/min		k_H/k_D	
Product	I_H	I_D	k_H	k_D	Exptl	Calcd[a]
Propylene	43.0	64.3	0.133	0.0372	3.6	3.5
H_2S (or D_2S)	46.5	75.2	8.34×10^{-3}	0.84×10^{-3}	10	...

[a] See L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p 20.

An estimate of the k_H/k_D ratio can be obtained from differences in the zero-point energy of the carbon-hydrogen and carbon-deuterium bonds. Using the equation of Mylander[11] and the observed wave numbers ($\bar{\nu}$) of 2276 and 2930 cm^{-1} for carbon-hydrogen and carbon-deuterium, respectively, the estimated value at 155° is 3.5, which is in good agreement with the observed value of 3.6. At 500°, the estimated value is 2.0, which agrees with the reported k_H/k_D for the pyrolysis of esters at 500°.[12] The essential check of experimental and estimated values of k_H/k_D is further evidence that the scission of the β-carbon-hydrogen bond is directly involved in the olefin formation.

Metal Cation Size.—The effect of the metal cation on the thermal stability of five metal O,O-diisopropylphosphorodithioates is shown in Table V along with the crystal radii of the metal cations. Figure 6 shows the rate of olefin formation as a function of the crystal radii. Hydrogen sulfide evolution shows a similar correlation. With the exception of silver, the indicated correlations are significant in that they demonstrate the importance of either thiophosphoryl or phosphoryl group in the decomposition reactions. Evidently, the metal possesses a coordination-type influence on the electron-rich double bond sulfur and/or oxygen. Thus, it is reasoned that the larger the size of the metal the greater its influence with consequent increase in resistance to isomerization and subsequent decomposition. This supports the previous finding that the decomposition in the initial stages involves the double

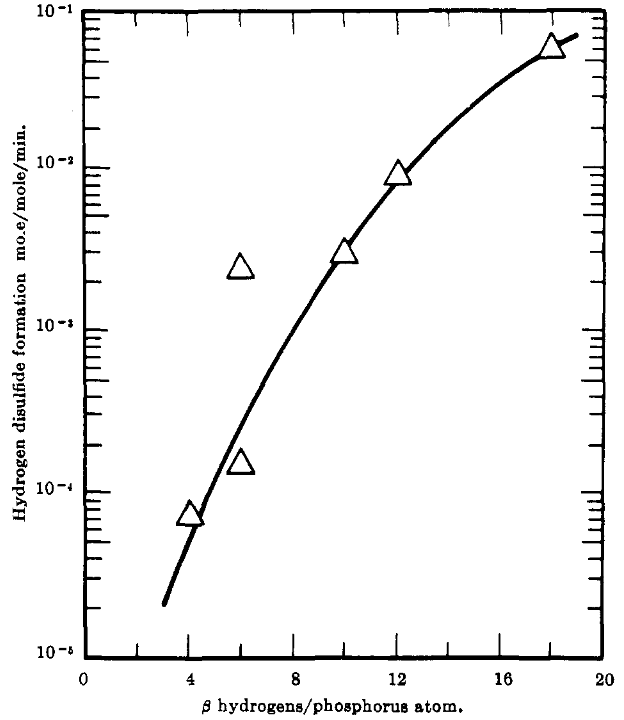

Figure 5.—Effect of number of β hydrogens per phosphorus atom on rate of decomposition.

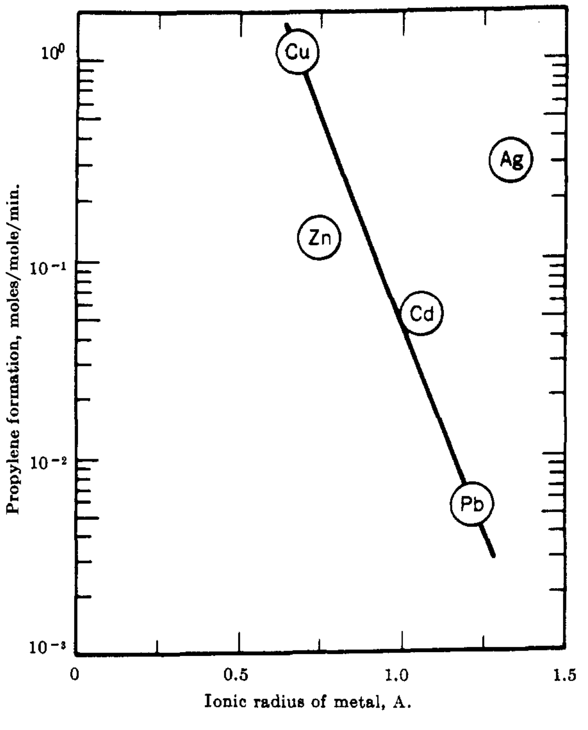

Figure 6.—Effect of size of cation on rate of propylene formation.

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(11) See Table IV, footnote *a*.

(12) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

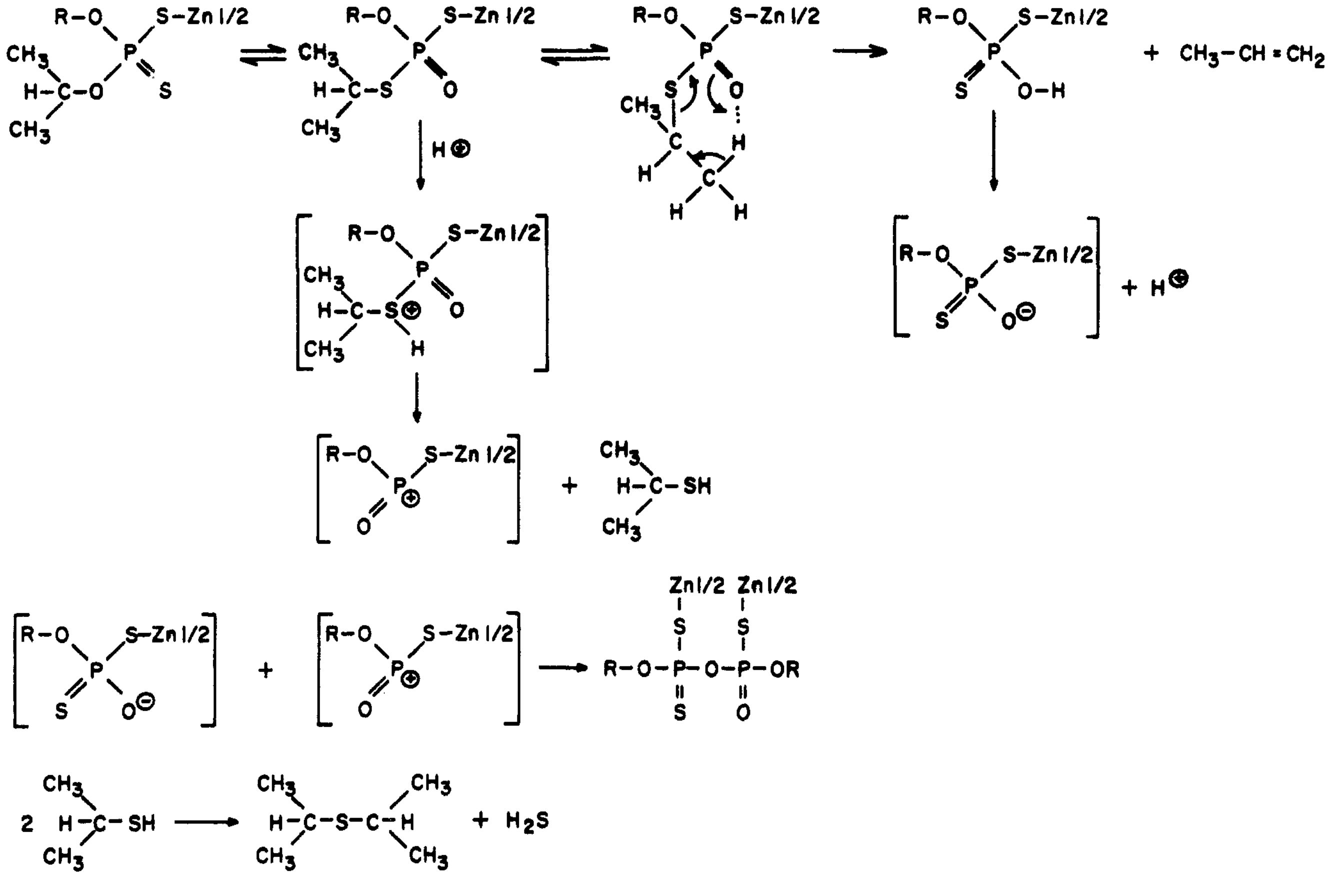

Figure 7.—Mechanism of the thermal decomposition of zinc O,O-diisopropylphosphorodithioate.

TABLE V

EFFECT OF METAL CATION ON DECOMPOSITION OF METAL O,O-DIISOPROPYLPHOSPHORODITHIOATES AT 155°

Additive	Ionic radius of metal, A[a]	Induction period, min Olefin	Induction period, min H_2S	Rate after induction period, mole/mole/min Olefin	Rate after induction period, mole/mole/min H_2S
Cupric	0.69	13	14	1.09	12.8×10^{-3}
Zinc	0.74	43	47	0.133	8.33×10^{-3}
Cadmium	0.97	20	25	0.090	4.58×10^{-3}
Lead	1.21	53	93	0.0054	0.257×10^{-3}
Silver	1.26	16	21	0.312[b]	5.92×10^{-3} [b]
$(i\text{-}C_3H_7O)_2$-P(S)SH	...	28	30	0.836[b]	79.0×10^{-3} [b]

[a] These radii represent the relative sizes of the outer electron shells of the ions, compared to those for alkali and halogen ions; they do not have absolute values such that their sums are equal to equilibrium interionic distances: L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514. [b] Mole/2 moles/min.

bond sulfur and/or oxygen and a hydrogen on the β-carbon atom.

Relative to the size of the silver ion (1.26 A), the rates of both propylene and hydrogen sulfide formation appear to be too high. However, the coordination bonds of silver are fixed at approximately 180° from its valence bond[13] and, hence, it was predicted and found that the influence of the metal on the electron-rich sulfur and/or oxygen atoms should be less than expected from the correlation obtained with the lead, cadmium, copper, and zinc salts. Thus, both the size of the metal and its coordination characteristics appear to be critical to the thermal stability of metal O,O-dialkylphosphorodithioates.

Proposed Mechanism for the Thermal Decomposition of Metal O,O-Dialkylphosphorodithioates.—Based on the preceding evidence, the mechanism scheme shown in Figure 7 is proposed. The isomerization step is responsible for the induction period and is considered to be acid catalyzed. Infrared analysis of the melt during the induction period shows the development of the P=O. The formation of straight- or branched-chain mercaptans from phosphorodithioates with the corresponding alkyl groups prior to hydrogen sulfide elimination supports this step. The over-all mechanism accounts for the sequence in which the gaseous products are formed.

The intramolecular (*cis*) elimination reaction for the formation of the olefin, analogous to that for the pyrolysis of esters and xanthates,[12] is supported collectively by the correlation of the rate of decomposition with the number of hydrogens on the β-carbon atom, the size of the metal cation, and the value of 3.6 for k_H/k_D. The observed k_H/k_D ratio would not be expected for a typical carbonium ion process (E1) in which the formation of the carbonium ion is the slow step and the loss of a proton is the fast step. Supporting quantitative evidence for this conclusion is found in a comparison of the calculated $\Delta\Delta F$, 183 cal/mole per deuterium, with those reported for secondary isotope effects in acid-catalyzed reactions; a $\Delta\Delta F$ of 183 at 155° is considerably higher than those observed.[14]

The formation of mixed olefin isomers cited by Hanneman and Porter[5] and Ashford, *et al.*,[7] as evidence for olefin formation *via* the carbonium ion mechanism is not considered to be in conflict with the proposed

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(13) J. C. Bailar, Jr., University of Illinois, Urbana, Ill., private communication, 1962.

(14) R. E. Weston, Jr., *Ann. Rev. Nucl. Sci.*, **11**, 439 (1961).

mechanism, since the acidic nature of the system at elevated temperatures can catalyze olefin isomerization. Data indicating that olefin isomerization does occur are shown in Table VI. These experiments were made by passing a known olefin sample at a high space velocity over decomposing zinc O,O-diisopropylphosphorodithioate at 155° and analyzing the product by gas chromatography. These results are in contrast with those of Ashford, *et al.*,[7] who contacted 99.1% 4-methyl-1-pentene with the decomposition residue at 60° for 3 hr without olefin isomerization. The difference in rate of isomerization at this unrealistically low decomposition temperature, 95° below the decomposition temperature employed by them, could account for their observation. However, carbonium ion stability may have an influence on the rate of the isomerization step. Also, the alkyl group could undergo rearrangement at this step. It is significant, however, that predominantly *n*-propyl mercaptan was formed from the decomposition of the corresponding zinc *n*-propyl salt in this work, and *n*-butyl mercaptan was formed from the zinc *n*-butyl salt in the work of Luther and Sinha.[6] Finally, it is also significant that Perry[15] found from the decomposition of zinc O,O-di(4-methyl-2-pentyl)phosphorodithioate, 96% of 4-methyl-1-pentene and 4-methyl-2-pentene, the products expected from *cis* elimination, and only 4% of 2-methyl-1-pentene and 2-methyl-2-pentene, the products expected *via* a rearrangement of a carbonium ion.

TABLE VI

OLEFIN ISOMERIZATION

Component	Reagent, %	Product, %
4-Methyl-1-pentene	98.3	95.0
4-Methyl-*cis*-2-pentene	1.7	2.4
4-Methyl-*trans*-2-pentene	...	<0.1
Unidentified (not C_6)[a]	...	2.5

[a] Probably from decomposing zinc salt.

Conclusions

The dependence of the thermal stability of metal O,O-dialkylphosphorodithioates on variations of both the alkyl group structure and the size of the metal ion suggests that the initial reaction involves an isomerization followed by an intramolecular (*cis*) elimination of olefin.

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Bis(phenoxy)phosphinyl as *N*-Blocking Group in Amino Sugar Nucleoside Synthesis[1]

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3,4,6-Tri-*O*-acetyl-2-deoxy-2-*N*-[bis(phenoxy)phosphinyl]amino-α-D-glucosyl bromide (1) was condensed with 6-benzamido-9-chloromercuripurine to give the substituted nucleoside (2a) and this on *N*-debenzoylation and treatment with ammoniacal benzyl alcohol yielded 9-{2-*N*-[bis(benzyloxy)phosphinyl]amino-2-deoxy-β-D-glucopyranosyl}adenine (2c) which was hydrogenated, under mild conditions, to 9-(2-amino-2-deoxy-β-D-glucopyranosyl)adenine (3). Condensation of 1 with bis(trimethylsilyl)cytosine gave the substituted nucleoside (4b), which upon treatment with ammoniacal benzyl alcohol and mild hydrogenation yielded 1-(2-amino-2-deoxy-β-D-glucopyranosyl)cytosine (5).

The nucleosides of amino sugars are usually synthesized by condensing a blocked amino sugar halide with a derivative of a purine or pyrimidine according to the Fischer–Helferich[2] method, as modified by Davoll and Lowy,[3] or Hilbert and Johnson.[4] In the synthesis of nucleosides of 2-amino-2-deoxyaldoses considerable difficulty has been experienced in the selection of an *N*-blocking group which can be easily removed, especially if the neighboring hydroxyl group is configurationally *trans*. In addition, the *N*-blocking group on C-2 should not be strongly participating as otherwise it may interfere with the reactivity of the glycosyl halide in nucleoside formation. In some few cases the *N*-acetyl has been used successfully[5-7] for such syntheses but has not always been removed from the reaction product. Other blocking groups employed have been the *N*-benzyloxycarbonyl,[7] *N*-methoxycarbonyl,[7] and from this laboratory, the *N*-2,4-dinitrophenyl,[8] *N*-benzylsulfonyl,[9] and the *N*-trifluoroacetyl[10] groups have been used for this purpose. The 2,4-dinitrophenyl[8] group gave both anomeric forms of a purine nucleoside, since it shows no tendency to participate at C-1.

We now wish to report the use of bis(phenoxy)-phosphinyl, $PO(OC_6H_5)_2$, as an *N*-blocking group in the synthesis of a purine nucleoside, 9-(2-amino-2-deoxy-β-D-glucopyranosyl)adenine (3), and of a pyrimidine nucleoside, 1-(2-amino-2-deoxy-β-D-glucopyranosyl)cytosine (5).

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