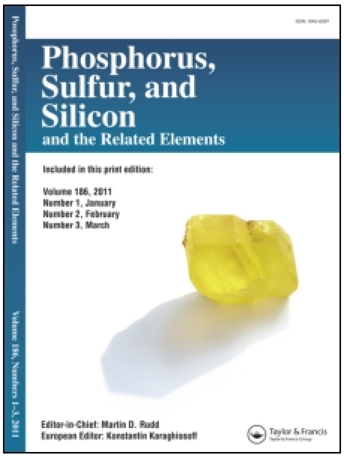

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ON THE INTERACTION BETWEEN DIALKYL PHOSPHITES AND METAL SALTS

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ON THE INTERACTION BETWEEN DIALKYL PHOSPHITES AND METAL SALTS

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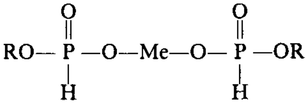
The interaction between dialkyl phosphites $(RO)_2P(O)H$ where $R = CH_3$, C_2H_5, C_4H_9 and metal salts MeX_2 where Me = Zn, Ca, Co, Mn, Cd and X = Cl, NO_3 and CH_3COO was studied. It was found that the reaction depends on the substitutes in the dialkyl phosphites as well as on the nucleophilicity of the metal salts. The monoalkyl phosphorous acid esters of the following general formula were obtained:



$$RO-\underset{H}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-O-Me-O-\underset{H}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-OR$$

INTRODUCTION

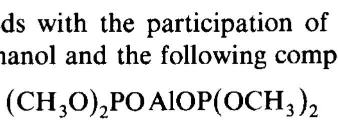
Studies on the interaction of triesters of phosphorous acid and metal salts have been conducted by Schutzenberger,[1] Pomey[2] and Risler.[3] It is reported that in the interaction between trialkyl phosphites and $PtCl_2$ or $AuCl_2$ complexes of general formula $(RO)_3P \cdot nPtCl_2$ are formed. A. E. Arbuzov[4] studied later the interaction between trialkyl phosphites and copper chloride. In this case two complexes have been isolated. Arbuzov also found that on heating above 150°C a low boiling compound is evolved which he assumed to be either hydrogen chloride or methyl chloride.

A complex was also isolated[5] on treating diisobutyl phosphite and copper acetate:

$$|(i\text{-}BuO)_2PH(O)|_4 \cdot Cu(CH_3COO)_2$$

According to the authors of the US Patent 3,201,348[6] the interaction between dialkyl phosphites and $MoCl_5$ results in the evolution of hydrogen chloride and leads to the formation of products of the following structure: $(RO)_2P(O)MoCl_4$.

It is established that the reaction between dimethyl phosphite and trimethoxyaluminium[7] proceeds with the participation of the hydrogen atom of the P—H group affording methanol and the following compound:



$$(CH_3O)_2PO\underset{\underset{OCH_3}{|}}{Al}OP(OCH_3)_2$$

Studying the complex-formation between dialkyl phosphites and boron chloride Bedell and co-workers[8] for the first time find that these complexes decompose forming alkyl halides:

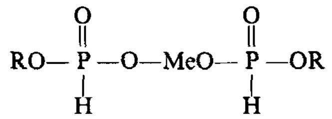
$$(RO)_2PH(O) \cdot BCl_3 \xrightarrow[-RCl]{} ROPH(O)OBCl_2$$

The same investigators have also demonstrated that diphenyl phosphite does not form a complex with boron chloride but reacts with it to evolve hydrogen chloride:

$$(PhO)_2P(O)H + BCl_3 \xrightarrow[-HCl]{} (PhO)_2P(O)BCl_2$$

The reactions between dialkyl phosphites and metal salts were studied also by V. V. Orlovskii *et al.*[9] They obtained metal salts of the monoalkyl phosphorous acid esters. Orlovskii *et al.* also examined the influence of anions and cations of the salts on the reaction rates.

The aim of the present investigation was to examine the interaction between dialkyl phosphite and metal salts and to determine the conditions leading to synthesis of compounds of the following general formula:



$$RO-\overset{\overset{O}{\|}}{\underset{H}{\underset{|}{P}}}-O-MeO-\overset{\overset{O}{\|}}{\underset{H}{\underset{|}{P}}}-OR$$

RESULTS AND DISCUSSION

The interaction between dialkyl phosphite and amine hydrochlorides[10] accompanied by the evolution of alkyl halides and the study of its mechanism[11] indicated that a reaction between dialkyl phosphites and metal salts of the type MeX_n where $n = 1, 2, 3$ is also possible.

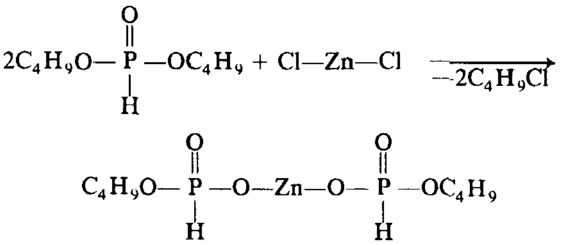
The interaction between dialkyl phosphites and metal salts of the type MeX_2 was examined since in this case various end products, such as monomers, oligomers and polymers containing metal in their main chain can be prepared.

The reaction between dibutyl phosphite and zinc chloride at a mole ratio of 1 : 4 proceeds at 125°C with the evolution of a liquid with a b.p. of 78–79°C and $n_D^{20°} = 1.4007$ which was shown by infrared spectroscopy and gas chromatography to be butyl chloride.

In the infrared spectrum of the end products (Figure 1) are present the following absorption bands: 2410 cm^{-1} (P—H group), 1185 cm^{-1} (P=O) group), 1080 cm^{-1} (P—O—C function), 2880–2960 cm^{-1} characteristic for the CH_2CH_3 groups. The band at 575 cm^{-1} can be ascribed to the Zn—O group.[12] The elemental analysis (see Table I) agrees with the following general formula:

$$C_8H_{20}O_6ZnP_2$$

On the basis of these data it can be assumed that the following reaction takes place:



$$2C_4H_9O-\overset{\overset{O}{\|}}{\underset{H}{\underset{|}{P}}}-OC_4H_9 + Cl-Zn-Cl \xrightarrow[-2C_4H_9Cl]{} C_4H_9O-\overset{\overset{O}{\|}}{\underset{H}{\underset{|}{P}}}-O-Zn-O-\overset{\overset{O}{\|}}{\underset{H}{\underset{|}{P}}}-OC_4H_9$$

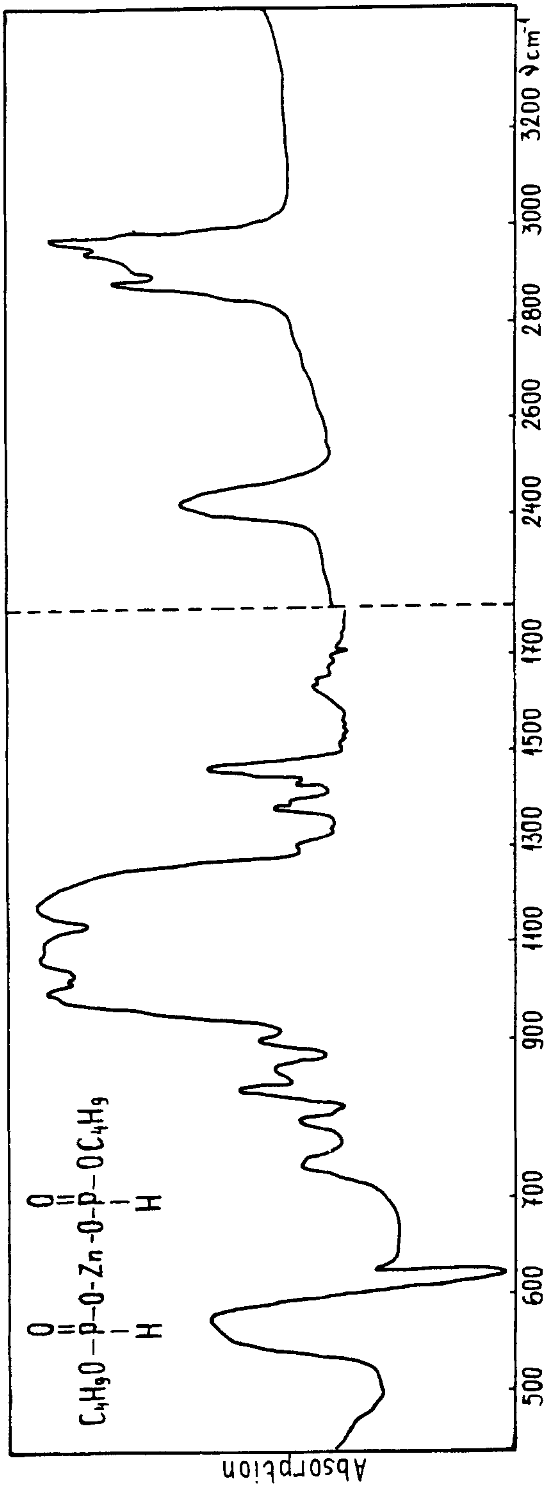
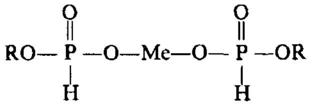


FIGURE 1 Infrared spectra of the zinc salt of the monobutyl ester of the phosphorous acid.

TABLE I

Metal salts of the monoalkyl esters of phosphorous acid

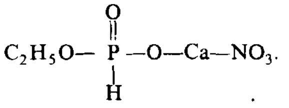


$$RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-Me-O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OR$$

R	Me	Yield %	Me (%) Calc.	Me (%) Found	P (%) Calc.	P (%) Found
C_4H_9	Ca	81	12.73	12.70	19.74	20.34
C_4H_9	Zn	85	19.26	18.90	18.26	19.24
C_2H_5[a]	Ca	93	15.50	15.20	24.03	23.76
C_2H_5	CO	98	21.27	21.00	22.39	22.72
C_2H_5	Mn	93	20.12	—	22.72	23.76
C_2H_5[b]	Ca	91	18.95	19.00	14.69	13.48
CH_3	Cd	90	37.16	36.00	20.50	19.43

[a] For the first time obtained by V. V. Orlovskii *et al.*[9]

[b] The salt has the following structure:



$$C_2H_5O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-Ca-NO_3.$$

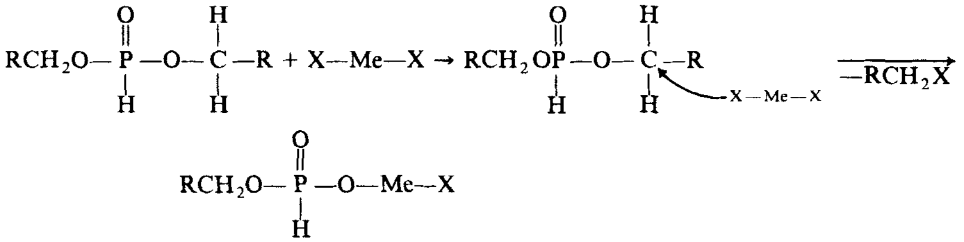
From the time dependence of the reaction (Figure 2, curve 1) it can be seen that the chloride atoms are replaced at the same rate.

The reaction between dibutyl phosphite and calcium chloride was also studied. In this case evolution of butyl chloride at 122°C was observed. The calcium salt of the monobutyl phosphorous acid ester was also isolated and analyzed (see Table I).

The experimental data indicate that the interaction between dibutyl phosphite and zinc chloride proceeds kinetically as a second order nucleophilic substitution (see Table II):

$$W = k(DBP)(ZnCl_2)$$

The results from the kinetic studies indicate that the interaction between dialkyl phosphites and metal salts probably follows the following mechanism:



$$RCH_2O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-R + X-Me-X \rightarrow RCH_2O\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-R \;\; X-Me-X \xrightarrow[-RCH_2X]{} RCH_2O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-Me-X$$

It is known that diisobutyl phosphite forms with copper acetate a complex.[5] It can be assumed that the currently studied interaction also proceeds via the formation of similar complexes. Mixtures of diethyl phosphite and metal salts were examined by infrared spectroscopy. The P=O absorption band for these mixtures with zinc chloride, cobaltous chloride, cadmium acetate and manganese acetate is 1258–1260 cm^{-1} i.e. there is no shift in this absorption band when compared to that of diethyl

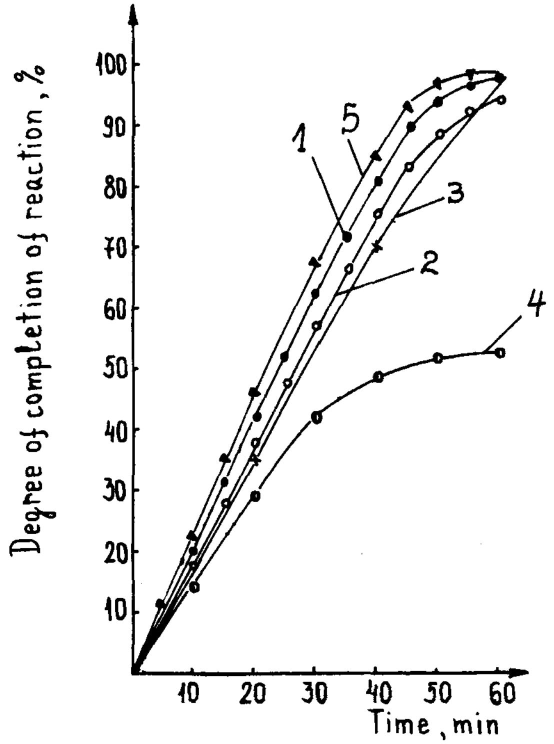


FIGURE 2 Degree of completion of the interaction between dialkyl phosphorous and metal salts: curve 1—dibutyl phosphite : $ZnCl_2$ = 4 : 1 (at 125°C); curve 2—dibutyl phosphite : $CaCl_2$ = 4 : 1 (at 122°C); curve 3—diethyl phosphite : $CaCl_2$ = 4 : 1 (at 70°C); curve 4—diethyl phosphite : $Ca(NO_3)_2$ = 4 : 1 (at 115°C); curve 5—diethyl phosphite : $Mn(OOCCH_3)_2$ = 4 : 1 (at 112°C).

TABLE II

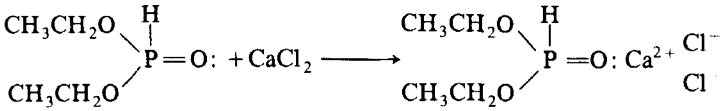
Kinetics data of the dibutyl phosphite-zinc chloride reaction[a]

(DBP) mole/l	($ZnCl_2$) mole/l	$W_0^H \cdot 10^2$ mole/l · min	$k \cdot 10^3$ $mole^{-1}/l \cdot min^{-1}$	n_t	
				DBP	$ZnCl_2$
4.8	1.2	1.77	3.07	—	1
4.62	2.27	3.28	3.14	1	—
4.06	4.06	5.29	3.21	—	—

[a] DBP—dibutyl phosphite.

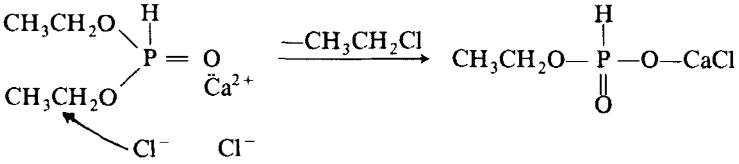
phosphite. The infrared spectrum of the diethyl phosphite–calcium chloride mixture shows an absorption band due to the P=O group at 1235 cm^{-1} i.e. this band is shifted by 25 cm^{-1} with respect to the pure diethyl phosphite. This shift in the absorption of the P=O function is retained at 80°C, a temperature at which the reaction proceeds. The ^1H-NMR spectrum of the same mixture shows the P—H proton signal strongly shifted with respect to that of the pure diethyl phosphite.

On the basis of the data from infrared and ^1H-NMR spectroscopy it can be assumed that the interaction between diethyl phosphite and calcium chloride proceeds first through the formation of a complex i.e.



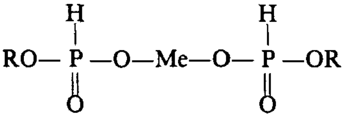
in which case the evolution of ethyl chloride can take place as:

(a) an intramolecular interaction:



The results obtained indicated that ethyl chloride is evolved as a result of a bimolecular interaction. This does not contradict the conclusion that first the reaction proceeds through the formation of a complex between diethyl phosphite and calcium chloride since the latter process takes place at considerably lower temperatures i.e. 25–30°C. Under the conditions at which ethyl chloride is evolved the starting compounds are completely bonded in a complex.

The infrared spectra of the end products show that P=O absorption band for the zinc, calcium and manganese salt to be at 1185 cm^{-1} for the cobaltous salt at 1220 cm^{-1} and for the cadmium salt at 1150 cm^{-1}. This strong shift in the absorption of the P=O function in the end products can be ascribed to the presence of structures with coordinative bonds between the metal and the oxygen atom of the phosphoryl group or to the existence of conjugation between the phosphoryl oxygen and the metal:



$$RO-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-Me-O-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-OR$$

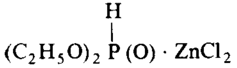
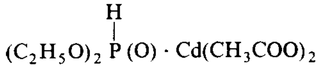
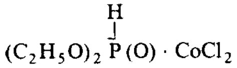
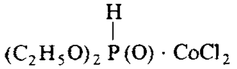
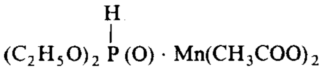
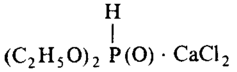
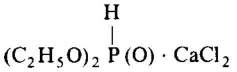
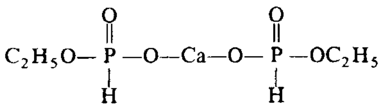
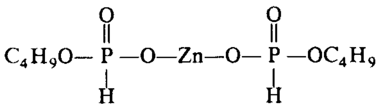
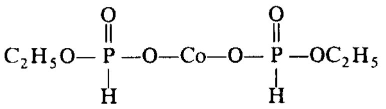
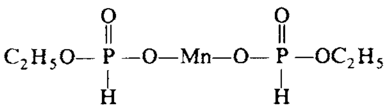
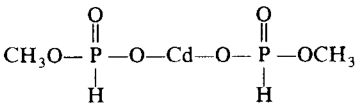
The suggested scheme of the interaction between dialkyl phosphites and metal salts proceeding directly or via a complex indicates that the interaction rate will be a function of the strength of the nucleophile as well as of the positive charge on the cation center: the greater the strength of the nucleophile and the size of the positive charge, the higher the reaction rate.

A discussion on the effect of the size of the positive charge on the rate of the reaction will be perhaps useful.

The reaction between diethyl phosphite and calcium chloride proceeds at 70°C, a temperature at which no reaction between dibutyl phosphite and calcium chloride takes place. A comparison between the reaction completion as a function of time for the process between diethyl phosphite and calcium chloride (curve 3) and dibutyl phosphite and calcium chloride (curve 2) indicates that both reactions are approxi-

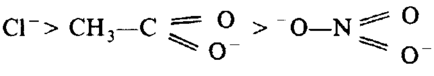
TABLE III

Infrared spectral data from mixtures of diethyl phosphite and metal salts in 1 : 4 mole ratio and metal salts of monoalkyl phosphorous acid esters

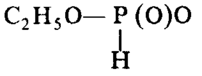
Starting Compounds	P=O cm^{-1}	Highest temperature to which mixture is heated, °C	Temperature at which spectrum is recorded, °C
$(C_2H_5O)_2P(O)H$	1260	22	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot ZnCl_2$	1258	60	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot Cd(CH_3COO)_2$	1258	60	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot CoCl_2$	1258	25	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot CoCl_2$	1259	110	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot Mn(CH_3COO)_2$	1260	30	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot CaCl_2$	1235	65	22
 $(C_2H_5O)_2\overset{\overset{H}{\vert}}{P}(O)\cdot CaCl_2$	1235	65	80
 $C_2H_5O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}O{-}Ca{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}OC_2H_5$	1185	—	22
 $C_4H_9O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}O{-}Zn{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}OC_4H_9$	1185	—	22
 $C_2H_5O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}O{-}Co{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}OC_2H_5$	1220	—	22
 $C_2H_5O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}O{-}Mn{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}OC_2H_5$	1220	—	22
 $CH_3O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}O{-}Cd{-}O{-}\overset{\overset{O}{\Vert}}{\underset{\underset{H}{\vert}}{P}}{-}OCH_3$	1150	—	22

mately similar in spite of the fact that the reaction with diethyl phosphite takes place at 70°C while that with dibutyl phosphite proceeds at 122°C; both reactions were conducted at the same mole ratios. Having in mind that in both cases the nucleophile is the same, the difference can come from the different size of the positive charge on the alpha-carbons in diethyl and dibutyl phosphite.

The difference in the reaction temperatures in the interaction between diethyl phosphite and the various salts ($Ca(NO_3)_2$ at 115°C; Mn $(O_2CCH_3)_2$ at 112°C; $CaCl_2$ at 70°C) can be explained with the different nucleophilic strength of the anions. The increase in temperature corresponds to the decrease in nucleophilicity:[13]

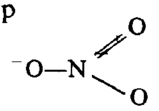


From the curve 4 depicted in Figure 2 giving the reaction completion vs. reaction time relationship for the interaction between diethyl phosphite and calcium nitrate it can be seen that the rate of the reaction slows down considerably after the replacement of one of the nitrate groups. This could be due to the effect of the new substituent

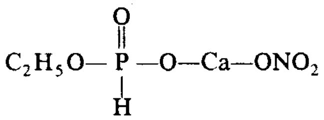


$$C_2H_5O-\underset{H}{\underset{|}{P}}(O)O$$

on the nucleophilicity of the group



in the salt formed:



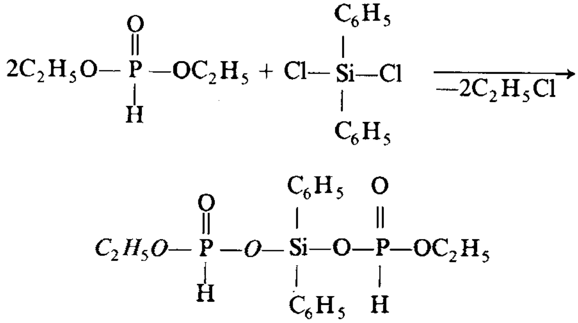
$$C_2H_5O-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-O-Ca-ONO_2$$

The effect of the new substituent on the strength of the nucleophile will be present in all cases presently studied but it will be most pronounced in the weakest nucleophile, i.e. the nitrate ion.

A similar effect of the substituents on the strength of the nucleophile is also corroborated by the interaction between diethyl phosphite and calcium chloride and diethyl phosphite and cobaltous chloride. The reaction with cobaltous chloride takes place at 105°C, a temperature 35°C higher than that at which the interaction between diethyl phosphite and calcium chloride proceeds. Since in the two cases the same alpha-carbon atom and the same nucleophile participate in the reaction, the temperature difference can be ascribed to the different electronegativities of calcium and cobalt. The latter being more electronegative probably decreases the strength of the nucleophile attached to it.

The results obtained indicated that any electron pair donor acting as a nucleophile can interact with dialkyl phosphites according to the suggested scheme.

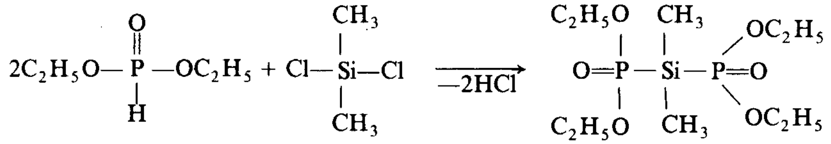
The interaction between diethyl phosphite and dichlorodiphenyl silane supports this assumption. It was established that at 105°C a reaction proceeds accompanied by the evolution of ethyl chloride:



$$2C_2H_5O-P(=O)(H)-OC_2H_5 + Cl-Si(C_6H_5)_2-Cl \xrightarrow[-2C_2H_5Cl]{} C_2H_5O-P(=O)(H)-O-Si(C_6H_5)_2-O-P(=O)(H)-OC_2H_5$$

In this case too the process is rapid i.e. completion is 98.2% in one hour. The end product was isolated and determined.

Dichlorodimethylsilane, in contrast to dichlorodiphenylsilane, reacts with diethyl phosphite with the evolution of hydrogen chloride.[14] The experiments carried out confirm this course of the reaction:



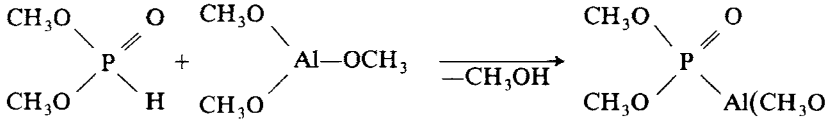
$$2C_2H_5O-P(=O)(H)-OC_2H_5 + Cl-Si(CH_3)_2-Cl \xrightarrow[-2HCl]{} (C_2H_5O)_2P(=O)-Si(CH_3)_2-P(=O)(OC_2H_5)_2$$

How can this difference be explained?

The two chlorosilanes differ in the type of substituents bonded to silicon. The phenyls will decrease the electron density at the silicon atom which in turn will lower the electron density at the chlorine. Conversely, the methyl groups tend to shift electron density toward the positive center. This should increase additionally the electron density at the chlorine atom.

The increase in electron density at the chlorine atom in dichlorodimethylsilane is reflected in the acid-base interaction between dichlorodimethylsilane and diethyl phosphite.

These results allow the assumption that in the cases where the nucleophile is strong an acid-base reaction will take place i.e. the hydrogen of the P—H group will be affected. In support of this conclusion is the established participation of the P—H hydrogen atom in the reaction between dimethyl phosphite and trimethoxyaluminium:[7]



The nucleophile CH_3O^- bonded to the aluminium is the strongest in comparison with the ones employed in the interaction between metal salts and dialkyl phosphites.[13] This is perhaps the cause determining the reaction course.

It was found that the reaction between diethyl phosphite and calcium chloride in the presence of pyridine at a mole ratio of 1 : 1 : 1 proceeds at 93°C, a temperature

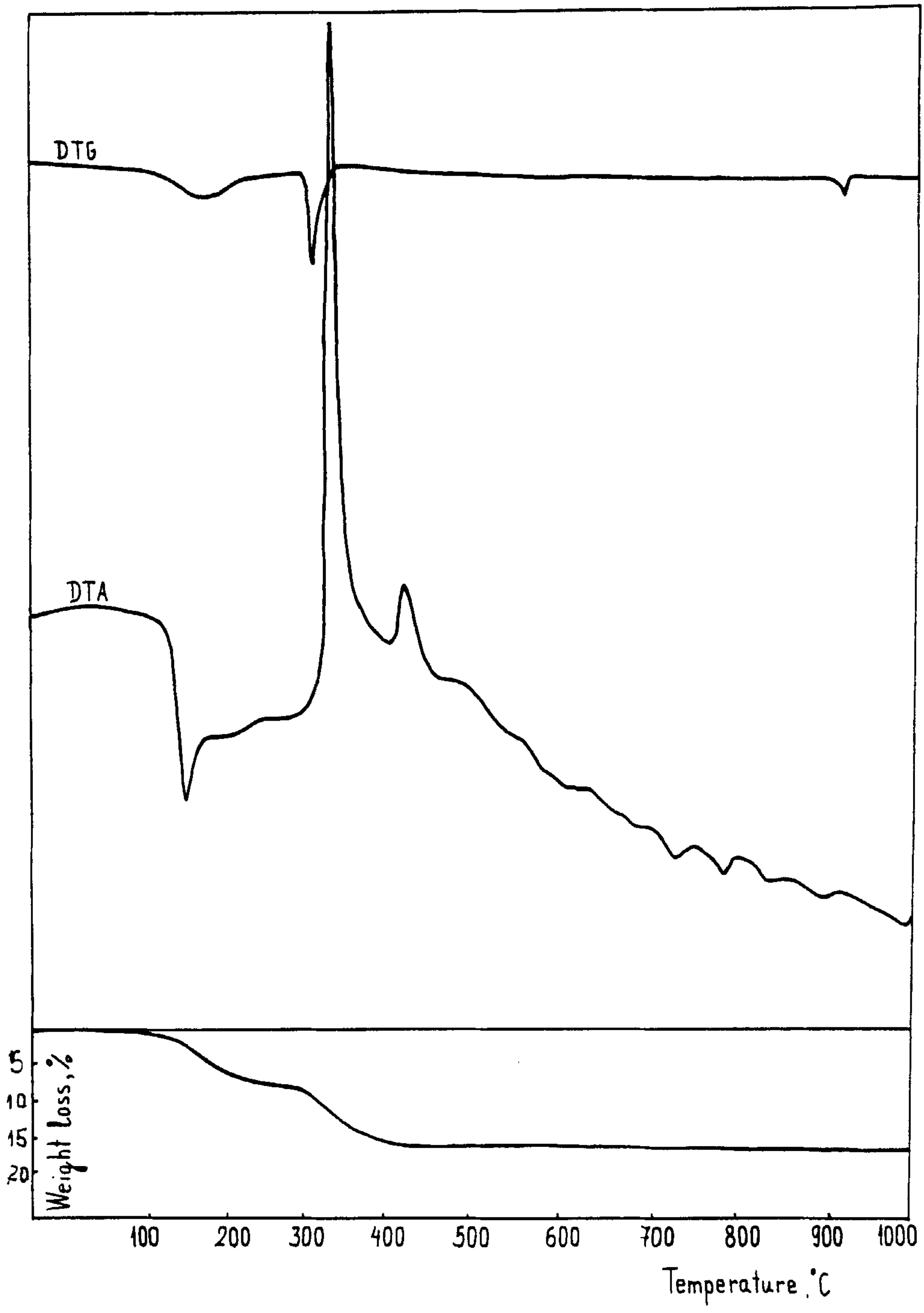


FIGURE 3 DTG, DTA and TG curves of the zinc salt of the monobutyl ester of the phosphorous acid.

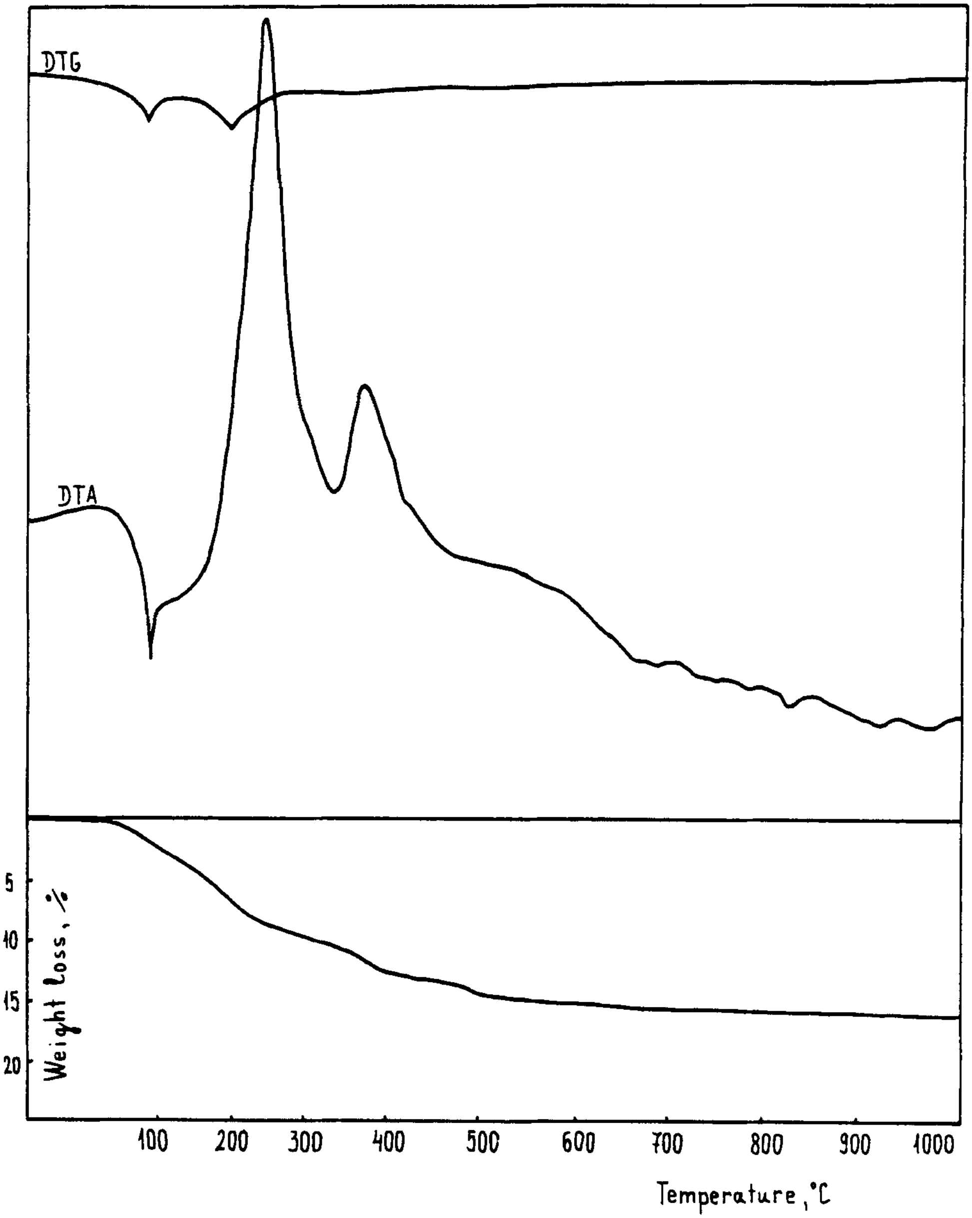


FIGURE 4 DTG, DTA and TG curves of the manganese salt of the monoethyl ester of the phosphorous acid.

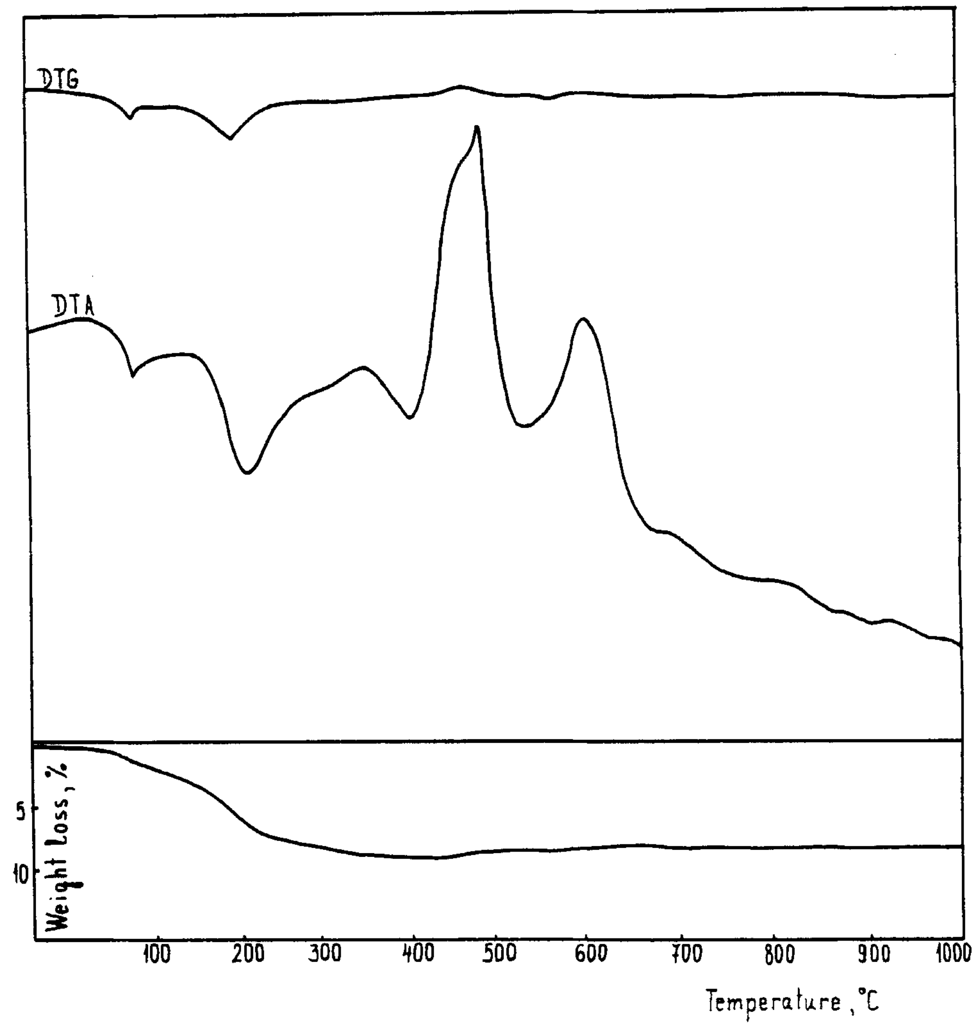
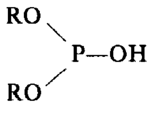


FIGURE 5 DTG, DTA and TG curves of the cobaltous salt of the monoethyl ester of the phosphorous acid.

by 23°C higher than the one required when the interaction is conducted in the absence of pyridine.

It is well known[15] that in the presence of bases the 3-coordinate form of dialkyl phosphites markedly increases. In it the partial positive charge at the cationic center will be different from that in the 4-coordinate isomer.



The reaction carried out in the presence of pyridine shows that the partial positive charge in the 3-coordinate form is lower.

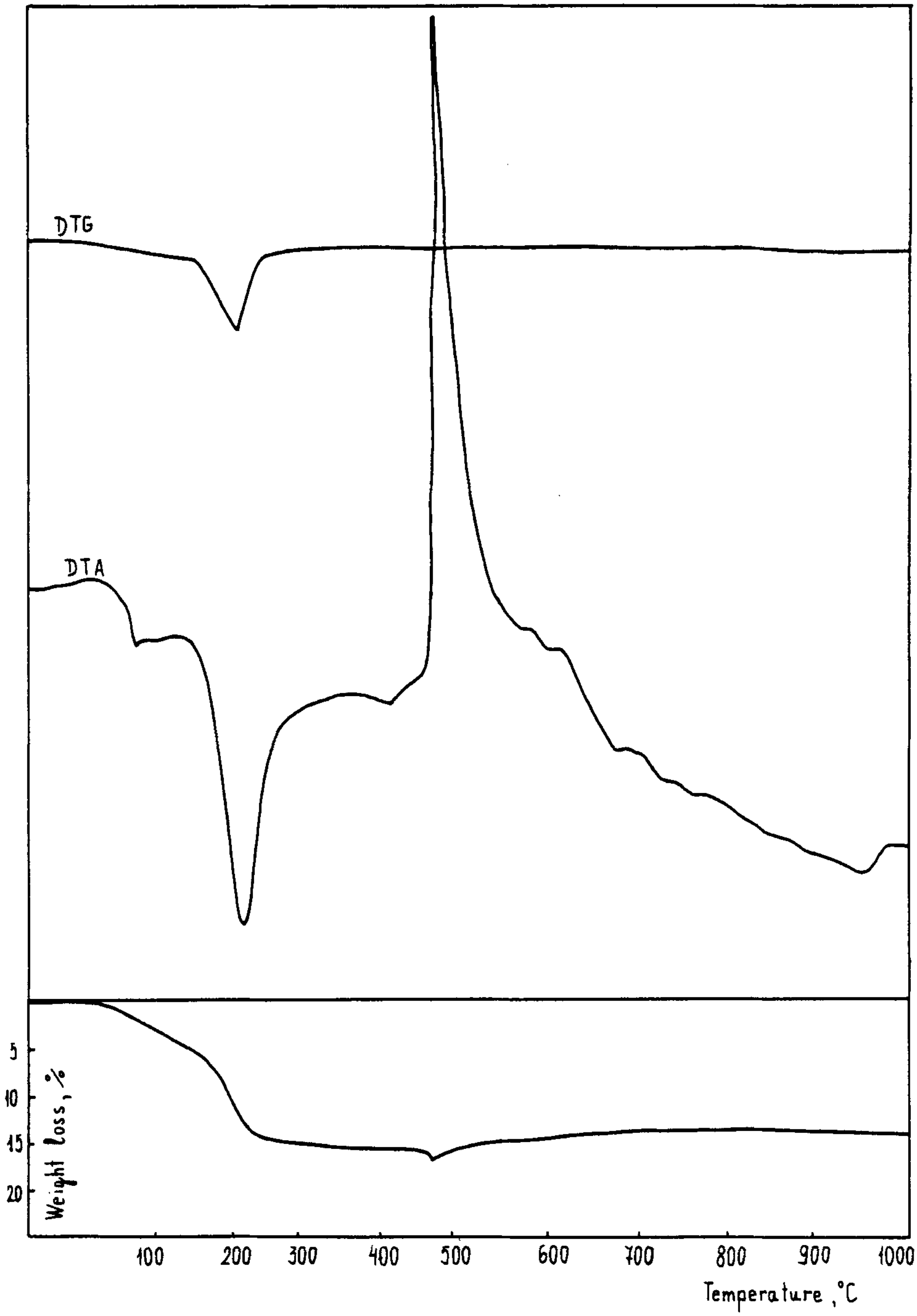


FIGURE 6 DTG, DTA and TG curves of the calcium salt of the monoethyl ester of the phosphorous acid.

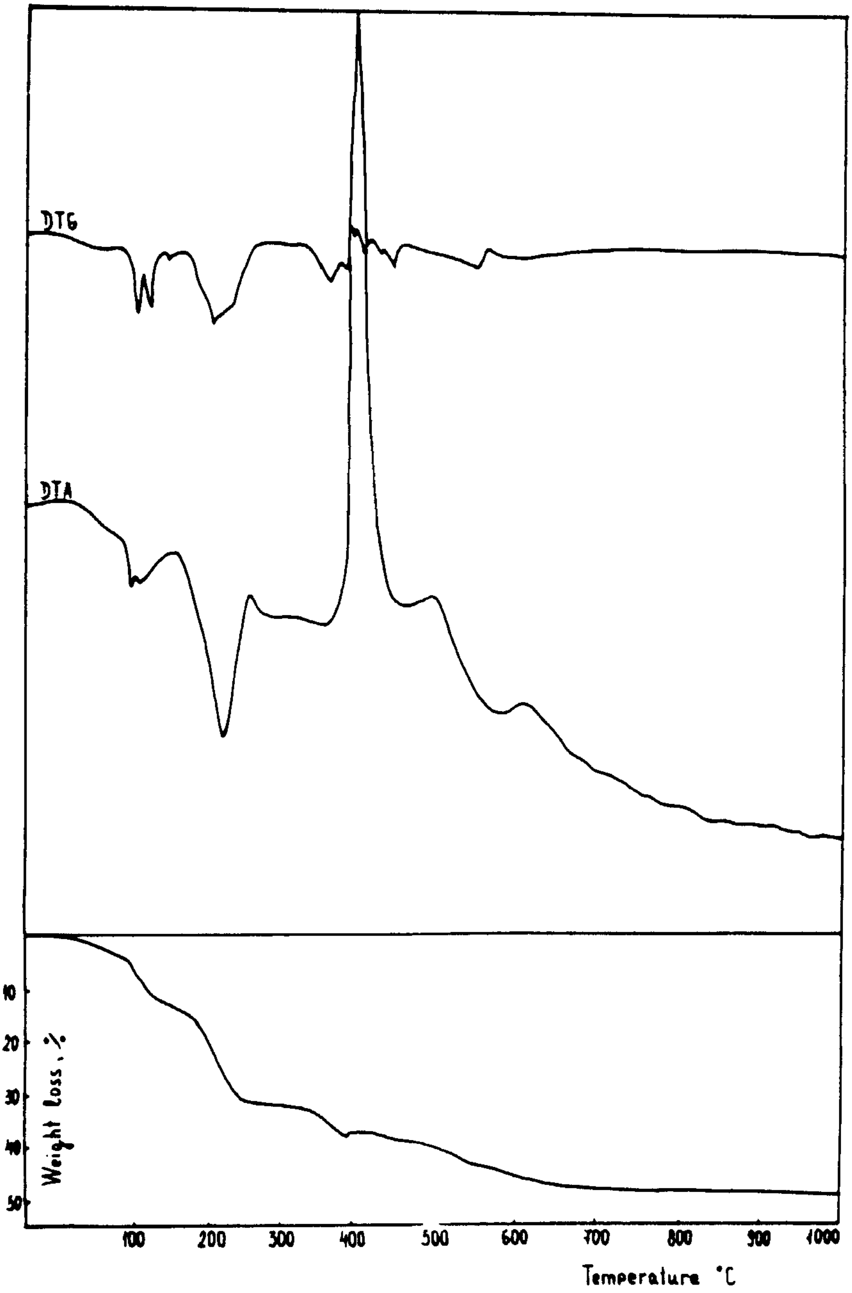


FIGURE 7 DTG, DTA and TG curves of the cadmium salt of the monomethyl ester of the phosphorous acid.

The thermal stability of the salts obtained was examined. The zinc salt of the phosphorous acid monobutyl ester (Figure 3) loses about 5% of its weight on heating at 200°C; at 400°C it loses 16%. In the interval between 400°C and 1000°C losses in weight are not noticed. A study of the DTA curve beyond 400°C shows that a series of exothermal effects take place which are not accompanied by weight losses. These are probably due to structural changes in the studied salt. Similar is also the behaviour of the maganese salt of the phosphorous acid monoethyl ester (Figure 4). The cobaltous salt of the phosphorous acid monoethyl ester loses about 8% of its weight till 1000°C (Figure 5). In contrast to the other two salts this one is not only thermally more stable, but its TG curve is different. Thus the exothermal effects at 490°C and 610°C are accompanied by an increase in the weight of the sample which can be solely the result of oxidative processes taking place.

The study of the calcium salt of the phosphorous acid monoethyl ester indicated an increase also in the weight of the sample accompanied by an exothermal effect at 580°C; the mass increase in the interval between 500°C and 800°C being approximately 2.5% (Figure 6).

The lowest thermal stability was shown by the cadmium salt of the phosphorous acid monomethyl ester (Figure 7). Till 1000°C it loses about 50% of its mass.

The demonstrated interaction between dialkyl phosphites and metal salts is a convenient method for the synthesis of new phosphorous- and metal-containing monomers, oligomers, and polymers. Depending on the functionality of the salt one can prepare linear and cross-linked products.

EXPERIMENTAL

Starting compounds: dimethyl phosphite, diethyl phosphite and dibutyl phosphite (Fluka) were purified by vacuum distillation under nitrogen. Triethyl phosphite (Fluka); zinc chloride, calcium chloride cobaltous chloride, calcium nitrate, manganese acetate and cadmium acetate, dichlorodiphenylsilane (Fluka), dichlorodium ethylsilane (Fluka).

Interaction between dibutyl phosphite and zinc chloride. In a three-necked flask provided with stirrer, thermometer and a condenser are placed zinc chloride (39.95 g, 0.28 mole) and dibutyl phosphite (215.6 g, 1.12 mole) with continuous stirring. The temperature of the reaction mixture reaches 70–80°C on the addition of the dibutyl phosphite and has to be maintained at 45–50°C during its addition. After that the temperature is increased to 125°C and the liquid evolved collected in a flask. The time dependance of the amount of liquid evolved is monitored.

The same dependence was followed during an experiment conducted under the same conditions and in the same apparatus between zinc chloride and dibutyl phosphite at 1 : 1 mole ratio.

Interaction between dibutyl phosphite and calcium chloride. Calcium chloride (22.25 g, 0.20 mole) and dibutyl phosphite (158.8 g, 0.82 mole) react at 122°C. After the evolution of butyl chloride ceases (36.6 ml, 98.8% conversion) the excess of dibutyl phosphite is removed under reduced pressure (2 mm Hg/120°C) and the residue recrystallized from methanol–*n*-hexane to give 50.3 g of material, 81% yield.

Interaction between diethyl phosphite and calcium nitrate. Calcium nitrate (36.5 g, 0.22 mole) and diethyl phosphite (121.0 g, 0.88 mole) react at 115°C. The reaction stops after 52% of the theoretical amount of ethyl nitrate is evolved. The excess of diethyl phosphite is removed under reduced pressure (2 mm Hg/80°C) and the residue recrystallized from methanol–ether to give 48 g of material, 91% yield.

Interaction between diethyl phosphite and calcium chloride. Calcium chloride (24.85 g, 0.22 mole) and diethyl phosphite (121.0 g, 0.88 mole) react at 70°C. The evolution of ethyl chloride is monitored by bubbling it through a liquid and after it ceases the excess diethyl phosphite is removed by distillation (2 mm Hg/80°C) to give a residue which on recrystallization from methanol–ether affords 53 g of material, 93.4% yield.

Interaction between diethyl phosphite and cobaltous chloride. Cobaltous chloride (45.6 g, 0.36 mole) and diethyl phosphite (193.4 g, 1.40 mole) react at 120°C. After evolution of ethyl chloride ceases the excess of diethyl phosphite is removed by distillation (2 mm Hg/80°C) to give a residue which on recrystallization from methanol-ether afforded 95 g (98% yield) of material.

Interaction between diethyl phosphite and manganese acetate. Manganese acetate (37.45 g, 0.23 mole) and diethyl phosphite (121.9 g, 0.88 mole) react at 112°C. The excess diethyl phosphite is removed after evolution of ethyl acetate ceases (2 mm Hg/80°C). The residue is recrystallized from methanol–ether to give 58.5 g (93% yield) of material.

Interaction between dimethyl phosphite and cadmium acetate. Cadmium acetate (157.4 g, 0.68 mole) and dimethyl phosphite (331 g, 3.0 mole) react at 120°C. The excess dimethyl phosphite is removed (2 mm Hg/80°C) after the evolution of methyl acetate ceases. The residue is recrystallized from methanol–ether to give 185.6 g (90.2%) of material.

Interaction between dichlorodiphenylsilane and diethyl phosphite. Dichlorodiphenylsilane (30.22 g, 0.12 mole) and diethyl phosphite (68.12 g, 0.49 mole) react at 102°C. The excess diethyl phosphite is removed (2 mm Hg/80°C) after the evolution of ethyl chloride ceases. The residue is recrystallized repeatedly from methanol–ether to give 45.2 g (94.1% yield) of material.

Interaction between dichlorodimethylsilane and diethyl phosphite. Dichlorodimethylsilane (73.6 g, 0.57 mole) and diethyl phosphite (160 g, 1.16 mole) react at 40°C to evolving hydrogen chloride.

Interaction between triethyl phosphite and calcium chloride. Calcium chloride (11.7 g, 0.11 mole) and triethyl phosphite (73.0 g, 0.44 mole) are heated at 135°C. No reaction with evolution of ethyl chloride is observed to proceed. The thermal studies are carried out on a MOM derivatograph in an air atmosphere till 1000°C at a heating rate of 10°/minute.

Interaction between diethyl phosphite and calcium chloride in the presence of pyridine. Calcium chloride (24.9 g, 0.196 mole), diethyl phosphite (27.0 g, 0.196 mole) and pyridine (16.48 g, 0.196 mole) react at 93°C.

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