

DIPHOSPHITES OF BIVALENT METALS*

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Accurate data were determined for preparing diphosphites $MH_2P_2O_5$ ($M = Mg, Ca, Sr$) by thermal decomposition of dihydrogen-bis(orthophosphites). For the first time, magnesium diphosphite was prepared in a pure state. The infrared spectra of magnesium, calcium, strontium, and zinc diphosphites were determined and analysed; it was found that the absorption bands in the region $660-680\text{ cm}^{-1}$ and $910-935\text{ cm}^{-1}$ were characteristic of the bond POP; the bond is angular, the angle value being $156-161^\circ$.

Diphosphites of a general formula $M(II)H_2P_2O_5$ are the products of thermal condensation of dihydrogenbis(orthophosphites) $M(II)H_4P_2O_6$ ($M(II)$ is a bivalent metal). The preparation of Ca and Ba diphosphites by this procedure was the subject of a paper by Amat¹, that of Mg, Ca, Sr, and Ba diphosphites was reported by Grant, Payne, and Skledar². Amat describes only $CaH_2P_2O_5$ and Grant and coworkers only $SrH_2P_2O_5$ as pure substances. In recent years, the diphosphites $ZnH_2P_2O_5$ (ref.³), $PbH_2P_2O_5$ (ref.⁴) and $FeH_2P_2O_5$ (ref.⁵) have been prepared. In an effort to obtain more information on the characteristic bonding feature of diphosphites, the absorption spectra of the latter two compounds were studied.

The present paper aims, in the first place, at studying systematically thermal decomposition of dihydrogenbis(orthophosphites) with respect to the preparation of Mg, Ca, Sr, Ba and Zn diphosphites and, in the second place, at studying their infrared spectra to obtain information on bonding relations in diphosphites.

EXPERIMENTAL

Phosphorous acids H_3PO_3 and D_3PO_3 were prepared by the reaction of phosphorous chloride with H_2O and D_2O , respectively. The hydrogenbis(orthophosphites) of the metals under study were prepared by a procedure described previously^{3,6-10}. Deuterated dihydrogenbis(orthophosphites) were prepared by neutralising the solution of D_3PO_3 in D_2O with anhydrous carbonate MCO_3 ($M = Mg, Ca, Sr, Zn$). Carbon dioxide was removed from the reaction mixture by boiling under reduced pressure and by saturating the solution with nitrogen. The concentration of the reactants in the solution obtained was pre-determined from solubility diagrams⁶⁻⁹.

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Phosphorus was determined gravimetrically as $Mg_2P_2O_7$ after oxidation with 65% nitric acid; magnesium was determined in the same way¹¹. When determining phosphite, bivalent ions were masked by a complexone¹². Calcium, strontium, and barium were determined gravimetrically as sulfates¹¹. Zinc was determined electrogravimetrically¹³.

Physico-Chemical Measurements

Thermal decomposition at an increasing temperature was studied both in an inert nitrogen atmosphere and in air by a Derivatograph (MOM, Budapest). The course of isothermal heating was studied using a special oven of our own design³. During the thermal decomposition, not

TABLE I

Thermographic Study of Dihydrogenbis(orthophosphites)

A Condensation onset; B condensation end; C redox decomposition; D dehydration onset; E dehydration end.

Temperature °C	DTA GTA	Isothermal heating	Temperature °C	DTA GTA	Isothermal heating
$MgH_4P_2O_6$			$SrH_4P_2O_6$		
110	—	A	180	—	A
140	A	B	210	—	B
230	—	C	290	A	C
480	B	—	310	B	—
620	C(exo)	—	460	C	—
$CaH_4P_2O_6 \cdot H_2O$			$BaH_4P_2O_6 \cdot 0.5 H_2O$		
40	D	D	70	—	D
50	—	E	100	—	E
70	E	—	120	D	—
120	—	A	170	E, A ^a	—
130	A	B	180	—	A ^a
170	—	C	190	—	C
230	B	—	310	C(exo)	—
290	C(exo)	—	$ZnH_4P_2O_6$		
			110	—	A
			150	A	—
			160	—	B
			260	—	C
			300	B	—
			310	C	—

^a Condensation is not finished.

only the mass decrease but also the analytical composition of the products were followed to determine the onset of the redox decomposition of the anion. The products of thermal decomposition were currently analysed for phosphites (by cerimetry^{14,15}) and for calcium, magnesium, strontium, barium, and zinc (by complexometry¹⁶⁻¹⁸).

X-ray studies were made by the Debye-Scherrer method on a Mikrometa II (Chirana) apparatus, radiation CuK α . The diffraction lines were evaluated visually by comparison to a standard with an accuracy of 0.05 mm and in a relative four-grade scale of intensities.

The infrared molecular spectra were obtained with a UR-20 (Zeiss) apparatus in the region 400–4000 cm⁻¹ in a Nujol suspension and, in addition, in tablets of potassium bromide.

RESULTS AND DISCUSSION

Thermogravimetry and Roentgenography

The results of the study of dihydrogenbis(orthophosphites) at a constant and varying temperatures are compiled in Table I. The course of GTA curves in an air atmosphere and at a temperature programme 3.5°C/min was discussed under the assumption that it obeys the equation¹⁹

$$-dm/dt = A \exp(-E/RT) m^n,$$

where m is the mass of the sample, T is the temperature, E is the activation energy, R is the gas constant, and n is the reaction order. The determination of the values of E and n was made graphically²⁰; the results obtained for calcium and strontium dihydrogen bis(orthophosphite) are given in Table II. The dehydration of the other phosphites studied is probably more complicated since GTA curves do not satisfy the conditions of Carroll and Freeman¹⁹. The value of the activation energy obtained for dehydration of SrH₄P₂O₆ is comparable with that observed for the transfer of a proton during dehydration of kaolinite²¹. Lower values of the activation energy of the dehydration of CaH₄P₂O₆·H₂O correlate with the lower dehydration temperature; also, a spontaneous cooling of the sample caused by a higher content of water may have influenced the results.

TABLE II

Kinetic Parameters of Dehydration Reactions

E Activation energy, n bonding order.

Reaction	E , kJ . mol ⁻¹	n
CaH ₄ P ₂ O ₆ ·H ₂ O → CaH ₄ P ₂ O ₆ + H ₂ O	70	2/3
CaH ₄ P ₂ O ₆ → CaH ₂ P ₂ O ₅ + H ₂ O	120	1
SrH ₄ P ₂ O ₆ → SrH ₂ P ₂ O ₅ + H ₂ O	260	1

On the basis of the data given in Table I, Mg diphosphite was prepared by drying dihydrogenbis(orthophosphite) to constant weight at 190°C. Analogically, calcium, strontium, zinc and deuterated magnesium, calcium, strontium and zinc diphosphites were prepared at 140, 220, 180 and 200, 160, 250 and 210°C, respectively. As compared to the literature¹⁻⁵, we succeeded in adding a pure $\text{MgH}_2\text{P}_2\text{O}_5$ to the series of diphosphites. In the case of the barium salt, it was confirmed that the condensation is connected with an overall redox decomposition. A systematic study of the thermal decomposition, especially under isothermal conditions, supplied accurate data on the suitable temperature for drying dihydrogenbis(orthophosphite) when preparing diphosphites. It was shown that the values 230°C and 200°C reported by Grant and coworkers² for Mg and Ca, respectively, were influenced by the redox decomposition of the diphosphites; that also was the reason why only pure $\text{SrH}_2\text{P}_2\text{O}_5$ was obtained by these authors.

When studying the temperature of the onset of condensation of dihydrogenbis(orthophosphites) of Mg, Ca, Sr, Ba and Zn, an increase with the increase of the polarisation force of the cation may be seen. A relation is thus suggested between the firmness of the system of hydrogen bonds in dihydrogenbis(orthophosphite) and between the action of the cation, as has already been observed by the former two authors of the present paper, when studying binary phosphites of alkaline metals and chromium²². This also accounts for the instability of $\text{BaH}_2\text{P}_2\text{O}_5$ where the dispro-

TABLE III

X-Ray Powder Diffraction Patterns of the Diphosphites Prepared (interplanar distance values are given in pm; intensities in brackets)

$\text{MgH}_2\text{P}_2\text{O}_5$	590(2)	510(2)	420(1)	380(4)	360(4)
	336(3)	321(3)	305(3)	281(1)	253(1)
	239(1)	232(3)	222(1)	207(1)	167(2)
	154(2)	145(1)	141(1)	137(1)	
$\text{CaH}_2\text{P}_2\text{O}_5$	620(3)	590(3)	370(3)	345(2)	321(3)
	300(2)	273(1)	261(1)	248(1)	220(1)
$\text{SrH}_2\text{P}_2\text{O}_5$	730(4)	680(4)	380(1)	360(3)	328(4)
	311(4)	291(1)	259(1)	233(1)	229(1)
	200(1)	194(1)	174(1)	157(1)	120(1)
$\text{ZnH}_2\text{P}_2\text{O}_5$	560(3)	480(4)	380(1)	340(1)	310(3)
	292(2)	270(2)	269(4)	258(1)	246(2)
	224(1)	212(1)	204(2)	186(2)	178(1)
	170(1)	161(1)	155(1)	148(1)	145(1)
	140(1)	138(1)			

portionation temperature of the anion is comparable to the high temperature of condensation of barium dihydrogenbis(orthophosphite).

The diphosphites obtained were characterised by X-ray powder diffraction patterns; the interplanar distances are brought together in Table III.

Infrared Absorption Spectroscopy

The infrared absorption spectra of the phosphites under study are given in Tables IV and V. The absorption bands in the regions $660-680\text{ cm}^{-1}$ and $910-935\text{ cm}^{-1}$ are, when compared to molecular spectra of phosphites $\text{M}^{\text{II}}\text{HPO}_3 \cdot n\text{H}_2\text{O}$, characteristic of diphosphites. Analogically to diphosphates and polyphosphates, the bands were assigned to the symmetrical and antisymmetrical valence vibrations of the group POP (ref.²³⁻³²). In accordance with the conclusions of other authors²³, the values of ν_s and ν_{as} obtained do not obey the linear correlation dependence as in the case of diphosphates. Besides, in diphosphites, the linear regression of the values of the fre-

TABLE IV
Infrared Absorption Spectra

σ_{H} Wavenumber of the absorption band of $\text{MH}_2\text{P}_2\text{O}_5$; σ_{D} wavenumber of the absorption band of $\text{MD}_2\text{P}_2\text{O}_5$. m middle, s strong, sh shoulder, vs very strong, w weak.

$\text{MgH}_2\text{P}_2\text{O}_5$		$\text{CaH}_2\text{P}_2\text{O}_5$		Assignment
$\sigma_{\text{H}}, \text{cm}^{-1}$	$\sigma_{\text{H}}/\sigma_{\text{D}}$	$\sigma_{\text{H}}, \text{cm}^{-1}$	$\sigma_{\text{H}}/\sigma_{\text{D}}$	
415 m	1.012	440 s	0.989	} δ OPO
490 vs	0.990	495 m	0.990	
570 vs	0.991	535 m	1.019	
		565 s	1.010	
680 m	1.015	665 m	0.992	} ν_s POP
935 vs	0.984	920 vs	0.995	
1 055 vs	0.995	1 065 s	0.995	} ν PO
1 075 vs	0.995	1 095 s	0.995	
1 095 vs	1.004	1 130 s	0.991	
1 220 vs	1.008	1 210 vs	1.000	
1 275 s	0.996			} δ OPH
1 010 sh	1.347	1 030 w	1.373	
1 040 m	1.333	1 040 m	1.351	
2 480 sh	1.370	2 450 m	1.372	} ν PH
2 490 m	1.372	2 490	1.368	

quencies ν_s and ν_{as} of POP calculated by the least squares method is fraught with a very large error due, evidently, to a narrow range in the frequency values. On the basis of the assignment of valency vibrations POP, similarly as in the studies of other

TABLE V

Infrared Absorption Spectra

σ_H : Wavenumber of the absorption band of $MH_2P_2O_5$; σ_D : wavenumber of the absorption band of $MD_2P_2O_5$. For symbols see Table IV.

$SrH_2P_2O_5$		$ZnH_2P_2O_5$		Assignment
σ_H, cm^{-1}	σ_H/σ_D	σ_H, cm^{-1}	σ_H/σ_D	
445 s	1.000	465 m	1.000	} δ OPO
500 m	1.000	565 s	1.009	
520 m	1.010			
565 s	1.000			
660 m	1.023	665 m	1.000	ν_s POP
915 vs	0.984	910 vs	0.984	ν_{as} POP
1 070 s	1.005	1 050 vs	1.010	} ν PO
1 085 w	1.000	1 150 sh	1.018	
1 125 vs	1.000	1 190 vs	1.000	
1 210 vs	0.992	1 230 vs	1.008	
1 010 m	1.374	1 030 s	1.411	} δ OPH
1 030 m	1.338	1 075 s	1.414	
2 445 m	1.374	2 550	1.371	ν PH

TABLE VI

Valence Vibrations and Valence Angle of the Group POP

Compound	ν_s POP, cm^{-1}	ν_{as} POP, cm^{-1}	Angle POP, $^\circ$
$MgH_2P_2O_5$	680	935	158
$CaH_2P_2O_5$	665	920	160
$SrH_2P_2O_5$	660	915	161
$ZnH_2P_2O_5$	665	910	156
$PbH_2P_2O_5$	670 ^a	915 ^a	155
$FeH_2P_2O_5$	670 ^b	930 ^b	162

From the literature: ^a ref. 4; ^b ref. 5.

authors²⁴⁻³³, the valence angle POP may be determined. The values obtained are given in Table VI.

The values of the wavenumbers of absorption bands of valence vibrations POP increase with an increase in the polarisation force of the cation. This rule is disobeyed by the wavenumber of the absorption bands ν_s POP of $\text{PbH}_2\text{P}_2\text{O}_5$ and ν_{as} POP of $\text{ZnH}_2\text{P}_2\text{O}_5$ which may be due to the difference in the configuration of the electron shell of the respective cation. This dependence of the wavenumbers on the polarisation force of the cation is also characteristic for diphosphates where it was discussed as the result of polarisation of the bonds metal-oxygen and of the increase of the effective charge on phosphorus for the d_π -interaction²⁴. According to the values of the POP valence angles it may be concluded that the POP bond in diphosphites has a somewhat larger angle than that in diphosphates. This comparison does, however, not consider some of the diphosphates of three- and fourvalent metals whose POP bond is linear, and the completely symmetrical vibration ν_s POP is inactive in an amorphous state (A_{1g} , D_{3d}) in the infrared spectrum³².

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