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Synthesis and Characterization of Substitution Complexes of Dialkyl-Phosphonates with Tin(II) Chloride

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Abstract: ***The substitution products of tin(II) dialkylphosphites in (1:2 molar ratio) have been synthesized by reacting benzene solution of sodium dialkylphosphite with ethanolic solution of anhydrous tin(II) chloride. The reaction seems to be endothermic in nature and carried out in refluxing benzene (8-9 hrs). The Sodium chloride formed was filtered off and excess of solvent was removed under reduced pressure. The complexes synthesized were yellow brown colored viscous liquids soluble in common organic solvent and characterized by elemental analysis as well as spectroscopic (IR, NMR, ^{1}H, ^{31}P & C) measurements. On the basis of above studies the formations of Sn-O-P chemical linkage have been established.***

Keywords: Tin(II) Chloride, Sodium dialkylphosphite, substitution complex

1. Introduction

The derivatives of organophosphorus ligands[1-5], which have long history, were described for the first time in 1956[6]. Their metal organometal and organic derivatives had attracted the attention of chemists due to their interesting chemical bonding patterns as well as their insecticidal properties[7]. The derivatives of organophosphorus ligands are widely used as active pesticides[8], fungicides, herbicides, anti AIDS agents, antibacterial agents[9, 10], fireproofing agents, antifriction agents in automobile industries, and are being used in biological activities[11]. Recent survey of literature reveals that a lot of work has been reported in the recent years[12]. It had been reported in earlier publication[13] that dialkylphosphonate form addition complexes with tin(IV) and organotin (IV) chlorides[14] when mixed together, while in the presence or triethylamine of by taking sodium dialkylphosphites, these form substitution products (organotin(IV) dialkyl-phosphites) with tin-oxygen-phosphorus (Sn-O-P) chemical linkage.[13] The chemistry of metal and organometalloidal phosphites and phosphonates had been reviewed by P.N. Nagar[6] in 1993. In view of the interesting results obtained in our laboratory on the chemistry of dialkylphosphonates, dialkyldithiophosphates, alkylene dithiophosphates.[15-19] It was considered of interest to study the addition and substitution reactions of dialkylphosphonates with stannous chloride. The present paper deals with substitution reactions of dialkylphosphonates with tin(II) chloride.

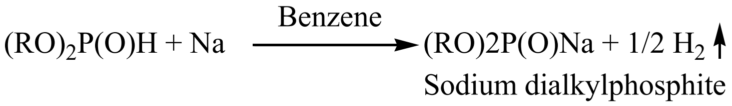
2. Materials and Methods

Solvents were dried by standard methods; Dialkylphsophonates were synthesized by method reported in the literature[20]. A.R. grade tin(II) chloride was used Tin was estimated as SnO_2[21]. The IR spectra were recorded on FTIR 8400, S SHIMADZU JAPAN in the range 4000-225 cm^{-1} and ^{1}H NMR, ^{31}P NMR, ^{13}C NMR spectra were recorded on JEOL 300MHZ FTNMR system in $CDCl_3$ solvent. Elemental analysis was performed on a Perkin Elmer carbon hydrogen analyzer. Analytical results were summarized in table (I).

Preparation of Substitution complexes [$(RO)_2P(O)_2Sn.xH_2O$]: The substitution complexes were synthesized in 1:2 molar ratio. Sodium (0.46g) was dissolved in 20-30 ml anhydrous benzene. Dimethylphosphonate (2.20g) was added slowly in front of oven into sodium metal taken in anhydrous benzene. The content was refluxed for (5-6) hours. When sodium metal get completely dissolved, the sodium salt of dialkylphosphonate (sodiumdialkylphosphite) was prepared to (sodiumdialkylphosphite), anhydrous ethanolic solution of stannous (II) chloride (2.25g) was added drop wise with constant stirring on magnetic stirrer within 1 hour at room temperature. After complete addition, the content was refluxed for 6-7 hours. The sodium chloride formed was filtered off and excess of solvent was removed under reduced pressure. A yellow brown viscous liquid was obtained. Similarly other substitution complexes were also synthesized by same method. Estimation of tin was carried out by decomposing the compound in a mixture of HNO_3/H_2SO_4 (A.R) and precipitating it as $Sn(OH)_2$ by gradual addition of liquid ammonia followed finally by igniting it as SnO_2[20]

3. Result and Discussion

The substitution products of the type $[(RO)_2P(O)_2]Sn.xH_2O$ where R=(Me, Et, ^{n}Pr, ^{i}Pr, ^{i}Bu, Ph] have been synthesized by reacting sodium metal using anhydrous benzene as solvent, with benzene solution of dialkylphosphonates, on refluxing for 5-6 hours when sodium dialkylphosphites was prepared. To it ethanolic solution of anhydrous tin(II) chloride was slowly added at room temperature with stirring. After complete addition, the content was refluxed for 6-7 hours. A yellow brown coloured viscous liquid was obtained after removing NaCl and solvent under reduced pressure.



$$(RO)_2P(O)H + Na \xrightarrow{\text{Benzene}} (RO)2P(O)Na + 1/2\ H_2\uparrow$$

Sodium dialkylphosphite

$$SnCl_2.xH_2O + 2(RO)_2P(O)Na \xrightarrow{\text{Benzene}} (RO)_2P(O)Sn.xH_2O] + 2NaCl\downarrow$$

tin(II) dialkylphosphite

The above complexes are soluble in common organic solvent. All the complexes have been characterized by elemental analysis and spectroscopic analysis (IR, ^{1}H NMR, ^{31}P, ^{13}C) which are discussed below:

IR spectra

The infrared spectra of the products have been recorded in the region 400-4000 cm^{-1}. The IR spectrum of these newly synthesized products shows the following characteristics changes (Table II).

1. The $\nu_{P\text{–}H}$ absorption band present at ~2350 cm^{-1} in ligands had been completely disappeared in all the products.
2. The $\nu_{P=O}$ absorption band present at 1250 cm^{-1} as sharp and strong absorption band was shifted strongly towards lower wave number (~100 cm^{-1}) and partially mixed to P-O-C absorption band. The P=O frequency is sensitive to substitution.
3. The ν(P)-O-(C) linkage appears to have two strong frequencies one due to stretching of P-O bond and other due to O-C stretching. These two frequencies are found to be characteristics of P-O-(C) linkage. The (P)-O-C (alkyl) group shows an intense absorption band around 1030 cm^{-1}. The frequency range 1055-950 cm^{-1} has been assigned to the P-O-C (alkyl) stretching vibration shifted to lower wave number ~1020-930 cm^{-1} in the substituted product. In addition to the P-O-C (alkyl) strong band, compound containing P-O-CH_3 group also show a characteristic weak band at 1180±10 cm^{-1}. Similarly compound containing P-O-C_2H_5 linkage show a weak band at 1160±10 cm^{-1}.

   The P-O-phenyl group shows an intense band in region 1250-1190 cm^{-1} due to O-Phenyl linkage. In pentavalentphosphorus compound the P-O stretching frequency of the P-O phenyl linkage occurs at a higher frequency (4-21 cm^{-1}) than trivalent phosphorus compounds. However in the substituted complexes, the P-O phenyl linkage shows downfield shift.
4. A new absorption band had been observed at 690-630 cm^{-1} which was tentatively assigned to Sn-O-P absorption band which indicate the formation of new Sn-O chemical band.

^{1}H NMR spectra

The ^{1}H NMR spectra of substituted complexes are ligands were recorded in $CDCl_3$ solution using TMS as an internal standard (Table III). The signal due to P-H proton present at δ 685 ppm in the spectra of dialkylphosphonate are absent in the corresponding substituted complexes showing the formation of (RO-P-O-C<) linkage be deprotonation. The proton attached to carbon atoms of alkyl or alkoxy group gives multiplet due to coupling with phosphorus atom (Table III).

^{31}P NMR spectra

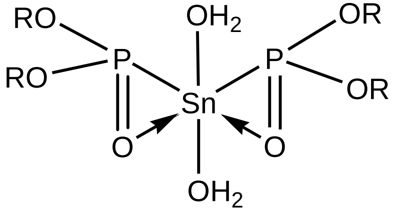
The ^{31}P NMR signals for complexes appears in the region (7.03-3 ppm) which seems to be due to oxidation of P^{III} to P^V by consuming atmospheric oxygen $P^{III} \xrightarrow{1/2O_2} >P^V=O$ which is in the region of petavalentphosphorus atom phosphonate ester. Whereas in $[(^iC_4H_9O)_2PO]_2Sn$ the ^{31}P signals observed in –δ 2.12 ppm which is indicative of the presence of phosphoryl (P=O) group in the products. In comparison to dialkylphosphonate ^{31}P (0-10 ppm), the ^{31}P signals has been slightly deshielded and thus appeared in the higher ppm range which is due to the formation of complexes on one hand and on the other hand due to chemical bonding of phosphorus with Sn(II). The detailed are listed in Table (III).

^{13}C NMR spectra

The ^{13}C NMR spectral data of the complexes are recorded in $CDCl_3$ and are summarized in Table(IV). A comparison of ^{13}C NMR spectra of the ligands with substituted products furnished relevant information about the mode of chemical bonding between the ligands and tin metal atom. A slight downfield shifting has been observed which also supports phosphoryl coordination to tin(II).

4. Conclusion

Based upon the above study and spectroscopic data of the compounds under consideration, the plausible structure of synthesized complex $(RO)_2PO)_2Sn.x2H_2O$ has been tentatively assigned as under;



References

[1] Organophosphorus ligands: Recent developments in design, synthesis, and application in environmentally benign catalysis; Demchuk O. M. and Jesinski R. *Phosphorus, Sulfur, and Silicon*; 199, 2 (2016). (DOI:10.1080/10426507.2015.1064921)

[2] Synthesis and characterization of 2-mercapto-2-thion-1,3,2-dioxaphospho-lanes and dioxaphosphorinanes; H.P.S. Chauhan, C.P. Bhasin, G. Srivastava and R.C. Mehrotra; *Phosphorus and sulfur and silicon*; 15, 99 (1983).

[3] Dialkyl (Alkylene) Dithiophosphate Adducts of Anhydrous Stannous Chloride: Synthesis,

Characterization, and Biological Activities; Mohsin M., Nagar M. and Chaudhary A. *Phosphorus and sulfur and silicon*; 187(11): 1331-1338 (2012).

[4] Chemistry of diorganodithiophosphate derivatives of arsenic, antimony and bismuth; H.P.S. Chauhan. *Coord. Chem. Revs*., 173, 30 (1998).

[5] Tetraorganodichalcogenoimidodiphosphorus acid and their main group metal derivatives; C. Silverstru, and J.E. Drake; *Coord. Chem. Revs*.; 223, 177 (2001).

[6] P.N. Nagar, *Phosphorus sulfur and silicon*, 79, 207-237 (1993).

[7] C. Fest and K.J. Scmidt, The chemistry of organophosphorous pesticides (Springer Verlag) New York, II edition (1982).

[8] "The chemistry of organjophosphorous pesticides" C. Fest and K.S. Schmudt, Springverlag; IInd edition (1982).

[9] Metal and organometalloidal phosphites and phosphonates; P.N. Nagar, *Phosphorous, Sulfur and Silicon*; 207-237, 79 (1993) A Review.

[10] Dialkyl dithiophosphates derivatives of non-transition elements; R.C. Mehrotra, G. Srivastava and B.P. Singh; *Coord. Chem. Revs*., 55, 207 (1984).

[11] P. Sauigai and B. Lorga. *J. Am. Chem. Soc*. 1261 (16), 5338 (2004).

[12] D.K. Cao, Y.F. Liu, Yousong, L. Zheng. *New J. of Chemistry*, 29, 721 (2005).

[13] P.N. Nagar. *J. Ind. Chem. Soc*. 81, 417 (2004).

[14] P.N. Nagar, *J. Ind. Chem. Soc*. 67, 703 (1990).

[15] Neelam Harkut, B.K. Jha and P.N. Nagar. *Phosphorus sulfur and silicon*, 182, 2801 (2007).

[16] Syntheses and characterization of citronelloloxy dichloro phosphine

[17] derivatives of dialkyl ammonium dithiophosphates and dialkyl

[18] phosphonates: Gupta B., bansal A. K., Sharma A. and Nagar M. *J. Indian Chem. Soc*., Vol. 87, pp. 621-625 (2010).

[19] H.P.S. Chauhan, C.P. Bhasin, G. Srivastava and R.C. Mehrotra, *Phosphorus sulfur and silicon*, 15, 99 (1983).

[20] R.C. Mehrotra, G. Srivastava and B.P.S. Chauhan. *Coord. Chem. Rev*. 55, 207 (1984).

[21] H.P.S. Chauhan. *Coord. Chem. Rev*. 1, 173 (1998).

[22] J.C. Bailer Jr. Inorganic synthesis (MC Graw Hill New York 1953). Vol. IV P 61.

[23] A.I. Vogal "A text book of quantitative inorganic analysis" ELBS and Longmans (1980).

Table I: Analytical data for the substitution complexes of $[(RO)_2PO]_2Sn$ dialkylphosphonate with Stannous

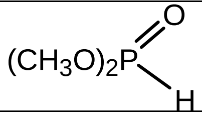
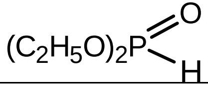
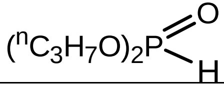
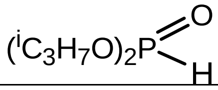
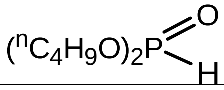
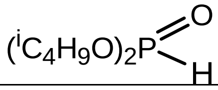
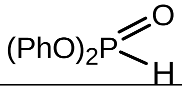
S. No.	Reactants				Product F/c	NaCl F/c	% Yield	% C	% H	% Sn
	Dialkylphosphonates		Na	$SnCl_2.2H_2O$						
1.	 $(CH_3O)_2P(O)H$	2.20 g	0.46g	2.25 g	$[(CH_3O)_2PO]_2Sn$ 2.62/3.36	0.99/1.17	77.97	14.28	3.57	35.32
2.	 $(C_2H_5O)_2P(O)H$	2.76 g	0.46g	2.25 g	$[(C_2H_5O)_2PO]_2Sn$ 2.90/3.93	0.23/1.17	73.79	24.48	5.10	30.27
3.	 $(^nC_3H_7O)_2P(O)H$	3.32 g	0.46g	2.25 g	$[(C_3H_7O)_2PO]_2Sn$ 3.75/4.40	0.93/1.17	78.12	32.14	6.25	26.49
4.	 $(^iC_3H_7O)_2P(O)H$	3.32 g	0.46g	2.25 g	$[(^nC_3H_7O)_2PO]_2Sn$ 3.70/4.80	1.10/1.17	77.08	32.14	6.25	26.49
5.	 $(^nC_4H_9O)_2P(O)H$	3.80 g	0.46g	2.25 g	$[(^iC_4H_9O)_2PO]_2Sn$ 3.98/5.04	1.06/1.17	78.96	38.09	7.14	23.54
6.	 $(^iC_4H_9O)_2P(O)H$	3.80 g	0.46g	2.25 g	$[(^iC_4H_9O)_2PO]_2Sn$ 4.10/5.04	1.03/1.17	81.34	38.09	7.14	23.54
7.	 $(PhO)_2P(O)H$	4.68 g	0.46g	2.25 g	$[(PhO)_2PO]_2Sn$ 4.90/5.24	1.02/1.17	83.90	49.31	3.42	20.32

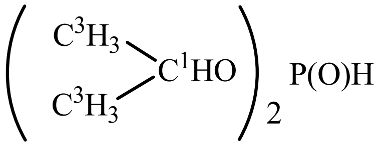
Table II: Characteristic IR spectral data of the substituted complexes of dialkylphosphonates with stannous (II) chloride.

S. No.	Compound	Substituted complexes v cm^{-1}				$(RO)_2P(O)H$ $v$cm^{-1}
		$v_{(P)=O-C}$	v_{P-O-C}	$v_{P=O}$	v_{Sn-O}	$v_{P=O}$
1.	$[(CH_3O)_2PO]_2Sn$	1050-920	850	1150	680	1268
2.	$[(C_2H_5O)_2PO]_2Sn$	1015-900	800	1162	633	1275
3.	$[^n(C_3H_7O)_2PO]_2Sn$	1020-950	810	1150	635	1265
4.	$[^i(C_3H_7O)_2PO]_2Sn$	1010-950	815	1165	650	1275
5.	$[^n(C_4H_9O)_2PO]_2Sn$	1040-900	825	1200	685	1275
6.	$[^i(C_4H_9O)_2PO]_2Sn$	1030-920	830	1190	670	1266
7.	$[(C_6H_5)_2PO]_2Sn$	1050-990	825	1225	690	1250

Table III: NMR (^{1}H, ^{31}P) spectral data of the substituted complexes of dialkylphosphate with stannous (II) chloride

S. No.	Structure of product	^{1}H NMR (δ ppm)	^{31}P NMR ppm sub. complex	^{31}P NMR ppm (RO)$_2$P(O)H
1.	$[(CH_3O)_2PO]_2Sn$	3.7-4.3 (d, OMe) 7.3 (P-H)	+34.2	12.86
2.	$[(C_2H_5O)_2PO]_2Sn$	1.8-2.1 (sext, Me), 4.1 (q, CH_2O), 7.4 (P-H)	+7.03	9.63
3.	$[^n(C_3H_7O)_2PO]_2Sn$	0.9 (t, Me), 2.1 (q, CH_2), 4.0 (q, CH_2O), 7.2 (P-H)	+7.29	8.53
4.	$[^i(C_3H_7O)_2PO]_2Sn$	1.2 (t, Me), 2.4 (q, CH_2), 3.9 (q, CH_2O), 7.5 (P-H)	-8.01	6.25
5.	$[^n(C_4H_9O)_2PO]_2Sn$	0.8 (t, Me), 1.5 (m, CH_2), 2.1 (m, CH_2), 3.9 (q, CH_2O), 7.4 (P-H)	+7.72	8.0
6.	$[^i(C_4H_9O)_2PO]_2Sn$	0.9 (t, Me), 1.9 (m, CH_2), 2.1 (m, Me), 3.8 (q, CH_2O), 7.3 (P-H)	-2.12	9.9
7.	$[(PhO)_2PO]_2Sn$	7.0-7.2 (m, Ph), 7.3-7.4 (m, Ph), 7.5 (P-H)	+8.53	0.9

Table IV: ^{13}C NMR spectras data (δ) of the substituted complexes of dialkylphosphonates with stannous(II) chloride

S.No.	Ligands and substituted complexes	C_1	C_2	C_3	C_4
1.	$(CH_3O)_2P(O)H$ $[(CH_3O)_2PO]Sn$	54.3 58.8	- -	- -	- -
2.	$(C_2H_5O)_2P(O)H$ $[(C_2H_5O)_2PO]_2Sn$	60.51 65.40	15.34 17.30	- -	- -
3.	$(C_3H_7O)_2P(O)H$ $[(^nC_3H_7O)_2PO]_2Sn$	65.0 68.90	21.1 30.09	8.12 10.12	- -
4.	 $(iC_3H_7O)_2PO)_2Sn$	68.43 70.50	22.56 29.20	- -	- -
5.	$C_4H_3C^3H_2C^2H_2C^1H_2P(O)H$ $[(^nC_4H_9O)_2PO]_2Sn$	75.30 78.20	30.15 33.25	13.20 15.10	8.25 10.15
6.	$[(PhO)_2P(O)]H$ $[(PhO)_2PO]_2Sn$	110 (o) 115 (o)	120 (m) 123 (m)	125 (p) 128 (p)	- -