

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, ¹H, ³¹P & 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 ligands¹⁻⁵, which have long history, were described for the first time in 1956⁶. Their metal organometal and organic derivatives had attracted the attention of chemists due to their interesting chemical bonding patterns as well as their insecticidal properties⁷. The derivatives of organophosphorus ligands are widely used as active pesticides⁸, fungicides, herbicides, anti AIDS agents, antibacterial agents^{9, 10}, fireproofing agents, antifriction agents in automobile industries, and are being used in biological activities¹¹. Recent survey of literature reveals that a lot of work has been reported in the recent years¹². It had been reported in earlier publication¹³ that dialkylphosphonate form addition complexes with tin(IV) and organotin (IV) chlorides¹⁴ when mixed together, while in the presence or triethylamine or 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. Nagar⁶ 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

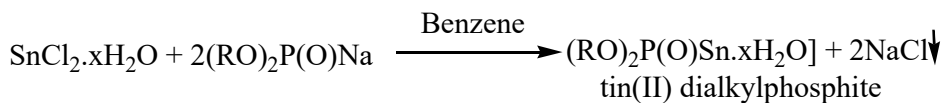
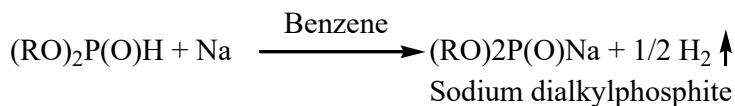
Solvents were dried by standard methods; Dialkylphosphonates were synthesized by method reported in the literature²⁰. A.R. grade tin(II) chloride was used Tin was estimated as SnO₂²¹. The IR spectra were recorded on FTIR 8400, S SHIMADZU JAPAN in the range 4000-225 cm⁻¹ and ¹H NMR, ³¹P NMR, ¹³C NMR spectra were recorded on JEOL 300MHZ FTNMR system in CDCl₃

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.xH₂O]: 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 HNO₃/H₂SO₄ (A.R) and precipitating it as Sn(OH)₂ by gradual addition of liquid ammonia followed finally by igniting it as SnO₂²⁰

3. Result and Discussion

The substitution products of the type [(RO)₂P(O)₂Sn.xH₂O where R=(Me, Et, ⁿPr, ⁱPr, ⁱBu, 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.



The above complexes are soluble in common organic solvent. All the complexes have been characterized by elemental analysis and spectroscopic analysis (IR, 1H 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 ν_{P-H} absorption band present at $\sim 2350\text{ cm}^{-1}$ 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 ($\sim 100\text{ cm}^{-1}$) and partially mixed to P-O-C absorption band. The P=O frequency is sensitive to substitution.
3. The $\nu(P-O-C)$ 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 $1055-950\text{ cm}^{-1}$ has been assigned to the P-O-C (alkyl) stretching vibration shifted to lower wave number $\sim 1020-930\text{ cm}^{-1}$ in the substituted product. In addition to the P-O-C (alkyl) strong band, compound containing P-O-CH₃ group also show a characteristic weak band at $1180 \pm 10\text{ cm}^{-1}$. Similarly compound containing P-O-C₂H₅ linkage show a weak band at $1160 \pm 10\text{ cm}^{-1}$. The P-O-phenyl group shows an intense band in region $1250-1190\text{ cm}^{-1}$ due to O-Phenyl linkage. In pentavalentphosphorus compound the P-O stretching frequency of the P-O phenyl linkage occurs at a higher frequency ($4-21\text{ cm}^{-1}$) 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 $690-630\text{ cm}^{-1}$ which was tentatively assigned to Sn-O-P absorption band which indicate the formation of new Sn-O-P chemical band.

1H NMR spectra

The 1H 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 $\delta 685\text{ ppm}$ 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

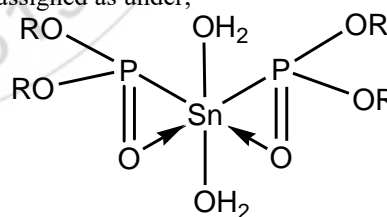
$P^{III} \xrightarrow{1/2O_2} >P^V=O$ which is in the region of pentavalentphosphorus atom phosphonate ester. Whereas in $[(C_4H_9O)_2PO]_2Sn$ the ^{31}P signals observed in $-\delta 2.12\text{ ppm}$ which is indicative of the presence of phosphoryl (P=O) group in the products. In comparison to dialkylphosphonate ^{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 $(RO)_2PO)_2Sn \cdot xH_2O$ has been tentatively assigned as under;



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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 ₂ O							
1.		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.		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.		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.		3.32 g	0.46g	2.25 g	$[(iC_3H_7O)_2PO]_2Sn$ 3.70/4.80	1.10/1.17	77.08	32.14	6.25	26.49
5.		3.80 g	0.46g	2.25 g	$[(C_4H_9O)_2PO]_2Sn$ 3.98/5.04	1.06/1.17	78.96	38.09	7.14	23.54
6.		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.		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 ν cm ⁻¹				(RO) ₂ P(O)H ν cm ⁻¹
		$\nu_{P=O-C}$	ν_{P-O-C}	$\nu_{P=O}$	ν_{Sn-O}	$\nu_{P=O}$
1.	$[(CH_3O)_2PO]_2Sn$	1050-920	850	1150	680	1268
2.	$[(C_2H_5O)_2PO]_2Sn$	1015-900	800	1162	633	1275
3.	$[(nC_3H_7O)_2PO]_2Sn$	1020-950	810	1150	635	1265
4.	$[(iC_3H_7O)_2PO]_2Sn$	1010-950	815	1165	650	1275
5.	$[(nC_4H_9O)_2PO]_2Sn$	1040-900	825	1200	685	1275
6.	$[(iC_4H_9O)_2PO]_2Sn$	1030-920	830	1190	670	1266
7.	$[(C_6H_5)_2PO]_2Sn$	1050-990	825	1225	690	1250

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

S. No.	Structure of product	^1H NMR (δ ppm)	^{31}P NMR ppm sub. complex	^{31}P NMR ppm (RO) $_2$ P(O)H
1.	$[(\text{CH}_3\text{O})_2\text{PO}]_2\text{Sn}$	3.7-4.3 (d, OMe) 7.3 (P-H)	+34.2	12.86
2.	$[(\text{C}_2\text{H}_5\text{O})_2\text{PO}]_2\text{Sn}$	1.8-2.1 (sext, Me), 4.1 (q, CH $_2$ O), 7.4 (P-H)	+7.03	9.63
3.	$[(^n\text{C}_3\text{H}_7\text{O})_2\text{PO}]_2\text{Sn}$	0.9 (t, Me), 2.1 (q, CH $_2$), 4.0 (q, CH $_2$ O), 7.2 (P-H)	+7.29	8.53
4.	$[(^i\text{C}_3\text{H}_7\text{O})_2\text{PO}]_2\text{Sn}$	1.2 (t, Me), 2.4 (q, CH $_2$), 3.9 (q, CH $_2$ O), 7.5 (P-H)	-8.01	6.25
5.	$[(^n\text{C}_4\text{H}_9\text{O})_2\text{PO}]_2\text{Sn}$	0.8 (t, Me), 1.5 (m, CH $_2$), 2.1 (m, CH $_2$), 3.9 (q, CH $_2$ O), 7.4 (P-H)	+7.72	8.0
6.	$[(^i\text{C}_4\text{H}_9\text{O})_2\text{PO}]_2\text{Sn}$	0.9 (t, Me), 1.9 (m, CH $_2$), 2.1 (m, Me), 3.8 (q, CH $_2$ O), 7.3 (P-H)	-2.12	9.9
7.	$[(\text{PhO})_2\text{PO}]_2\text{Sn}$	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.	$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$	54.3	-	-	-
	$[(\text{CH}_3\text{O})_2\text{PO}]_2\text{Sn}$	58.8	-	-	-
2.	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$	60.51	15.34	-	-
	$[(\text{C}_2\text{H}_5\text{O})_2\text{PO}]_2\text{Sn}$	65.40	17.30	-	-
3.	$(\text{C}_3\text{H}_7\text{O})_2\text{P}(\text{O})\text{H}$	65.0	21.1	8.12	-
	$[(^n\text{C}_3\text{H}_7\text{O})_2\text{PO}]_2\text{Sn}$	68.90	30.09	10.12	-
4.	$\left(\begin{array}{c} \text{C}^3\text{H}_3 \\ \text{C}^3\text{H}_3 \end{array} \right) \text{C}^1\text{HO} \bigg)_2 \text{P}(\text{O})\text{H}$ $(i\text{C}_3\text{H}_7\text{O})_2\text{PO})_2\text{Sn}$	68.43	22.56	-	-
		70.50	29.20	-	-
5.	$\text{C}_4\text{H}_3\text{C}^3\text{H}_2\text{C}^2\text{H}_2\text{C}^1\text{H}_2\text{P}(\text{O})\text{H}$	75.30	30.15	13.20	8.25
	$[(^n\text{C}_4\text{H}_9\text{O})_2\text{PO}]_2\text{Sn}$	78.20	33.25	15.10	10.15
6.	$[(\text{PhO})_2\text{P}(\text{O})]\text{H}$	110 (o)	120 (m)	125 (p)	-
	$[(\text{PhO})_2\text{PO}]_2\text{Sn}$	115 (o)	123 (m)	128 (p)	-