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THE EFFECT OF SOLVENT UPON THE RATES AND MECHANISMS OF ORGANOMETALLIC REACTIONS.

II*. MOLECULAR COMPLEXES OF METHYLTIN HALIDES AND TIN TETRAHALIDES

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SUMMARY

Methyltin halides give solid molecular complexes with the organic solvents normally employed in organometallic chemistry. Me_3SnBr gives complexes of the type $Me_3SnBr \cdot L$ with monodentate ligands (Py, DMSO, DMF, HMPT) and complexes of the type $2Me_3SnBr \cdot L$ with bidentate ligands (dioxane, TMED).

Me_2SnHal_2, $MeSnHal_3$ and $SnHal_4$ give complexes containing either two monodentate ligands or one bidentate ligand.

INTRODUCTION

It is well known[1] that the rates and mechanisms of reactions of organotin compounds depend to a significant extent on the solvent in which the reactions occur. The effect of the solvent upon the kinetics and mechanisms of reactions of organotin compounds has been explained by assuming that nucleophilic solvent molecules form complexes with organotin molecules during the transition state of the reaction[2]. At present, however, it is not possible to extend this explanation of solvent effects to include all organotin compounds since quantitative studies in this field are quite rare.

An investigation of the effect of the solvent upon the reactivity of organotin compounds is at present being made in our laboratory and we have shown that organotin compounds can form solid molecular complexes with organic solvents of the type employed for organometallic reactions in a similar manner to that known for other electron donors[3]. This paper deals with the synthesis and identification of solid molecular complexes of methyltin halides or tin tetrahalides with a number of organic solvents. Nuclear quadrupole resonance and Mössbauer spectroscopic studies of the electronic structure and the geometry of the complexes will be the subject of the ensuing papers of this series[4,5].

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* For Part I see ref. 1.

RESULTS AND DISCUSSION

I. Molecular complexes of the type $Me_3SnBr \cdot L$ and $2Me_3SnBr \cdot L$

Complexes of Me_3SnBr with monodentate ligands such as pyridine, HMPT, DMSO and DMF were synthesised by the addition of the necessary amount of the donor to the organometallic compound dissolved in ligroin. An exothermal reaction occurred in each case. After 2–3 h white crystals were formed which were filtered, washed with pentane and dried *in vacuo*.

Complexes containing bidentate ligands (dioxane, TMED) were synthesised in a similar manner. Their composition was 2/1, in other words one bidentate ligand was bound to two molecules of Me_3SnBr, irrespective of the ratio (2/1 or 1/1) of the initial components. Elemental analyses and melting points of the compounds are listed in Table 1.

TABLE 1

MOLECULAR COMPLEXES OF Me_3SnBr

Complexes	*M.p. (°C)*	*Analysis, found (calcd.) (%)*		
		C	*H*	*N*
$Me_3SnBr \cdot Py$	66–68	29.9(29.7)	4.4(4.4)	4.1(4.3)
$Me_3SnBr \cdot HMPT$	72–75 (dec.)	26.1(25.5)	6.6(6.4)	10.1(9.9)
$Me_3SnBr \cdot DMSO$	63–64	19.3(18.6)	4.7(4.7)	
$Me_3SnBr \cdot DMF$	30–31	22.8(22.7)	5.4(5.1)	4.2(4.4)
$2Me_3SnBr \cdot dioxane$	37–38	20.7(20.8)	4.5(4.5)	
$2Me_3SnBr \cdot TMED$	77–78 (dec.)	23.4(23.8)	5.4(5.6)	4.5(4.6)

II. Molecular complexes of the type $Me_2SnHal_2 \cdot 2L$ ($Hal = Cl, Br$)

These were obtained by adding the calculated (1/2) amount of the donor to dimethyltin dihalides dissolved in hot benzene. The mixture was cooled to room temperature, left for 8–10 h when white crystals were formed which were filtered, washed with benzene, then with hexane and dried *in vacuo*. Melting points and elemental analyses of the complexes are listed in Table 2. All these complexes are readily crystallised from benzene.

A similar procedure gave the dioxane complexes whose composition was close to 1/1 irrespective of the ratio of the initial components (1/1 or 1/2). Complexes prepared in this way were $Me_2SnCl_2 \cdot$dioxane (Found: C, 23.4; H, 4.3. $C_6H_{14}Cl_2O_2Sn$ calcd.: C, 23.4, H, 4.6%) and $Me_2SnBr_2 \cdot 0.8$ dioxane (Found: C, 16.5; H, 3.4. Calcd.: C, 16.5; H, 3.3%). The bidentate nature of dioxane suggests that complexes containing this ligand might form oligomeric chains, a difference in the terminal units being responsible for the uncertain stoichiometry and diffuse melting points (92–100° for $Me_2SnCl_2 \cdot$dioxane, 70–74° for $Me_2SnBr_2 \cdot 0.8$ dioxane) observed.

III. Molecular complexes of the type $MeSnHal_3 \cdot 2L$ ($Hal = Cl, Br$)

Solid complexes of methyltin trihalides with pyridine, HMPT, DMSO and DMF have been synthesised. The elemental analyses and melting points are listed in Table 3.

TABLE 2

MOLECULAR COMPLEXES OF Me_2SnHal_2 (Hal=Cl, Br)

Complexes	*M.p.* (°C)	*Analysis, found (calcd.) (%)*			
		C	*H*	*N*	*Hal*
$Me_2SnCl_2 \cdot 2Py^a$	158–160 (dec.)	37.9(38.1)	4.4(4.3)	7.1(7.4)	18.6(18.5)
$Me_2SnBr_2 \cdot 2Py^b$	164–166 (dec.)	30.9(30.9)	3.4(3.4)	6.0(6.0)	34.2(34.2)
$Me_2SnCl_2 \cdot 2HMPT$	122–123	29.1(29.1)	7.5(7.8)	14.8(14.5)	12.2(12.3)
$Me_2SnBr_2 \cdot 2HMPT$	142–143	25.2(25.2)	6.2(6.3)	12.3(12.6)	23.3(24.0)
$Me_2SnCl_2 \cdot 2DMSO^c$	112–113	19.3(19.2)	4.8(4.8)		18.5(18.8)
$Me_2SnBr_2 \cdot 2DMSO^d$	121–122	15.4(15.5)	4.0(3.9)		34.1(34.4)
$Me_2SnCl_2 \cdot 2DMF^e$	85–86	26.2(26.3)	5.6(5.5)	7.2(7.6)	18.9(19.3)
$Me_2SnBr_2 \cdot 2DMF^f$	69–71	21.2(21.3)	4.3(4.4)	6.1(6.2)	35.1(35.1)

[a] Ref. 6, m.p. 163°, [b] Ref. 6, m.p. 173°. [c] Ref. 7, m.p. 113°. [d] Ref. 9, m.p. 119–120°. [e] Ref. 8, m.p. 84–85.5°. [f] Ref. 8, m.p. 68.0–70.5°.

TABLE 3

MOLECULAR COMPLEXES OF $MeSnHal_3$ (Hal=Cl, Br)

Complexes	*M.p.* (°C)	*Analysis, found (calcd.) (%)*			
		C	*H*	*N*	*Hal*
$MeSnCl_3 \cdot 2Py$	150 (subl.)	34.0(34.0)	3.6(3.4)	7.2(7.2)	27.0(27.4)
$MeSnBr_3 \cdot 2Py^a$	200 (subl.)	24.6(24.8)	2.4(2.5)	5.3(5.3)	45.4(45.1)
$MeSnCl_3 \cdot 2HMPT$	> 160 (dec.)	26.4(26.5)	6.8(6.7)	14.5(14.3)	17.8(18.1)
$MeSnBr_3 \cdot 2HMPT$	> 160(dec.)	21.3(21.3)	5.0(5.4)	12.2(11.6)	32.4(32.7)
$MeSnCl_3 \cdot 2DMSO^b$	> 150(dec.)	15.5(15.5)	3.9(3.9)		27.1(27.6)
$MeSnBr_3 \cdot 2DMSO$	> 156 (dec.)	11.4(11.3)	2.9(2.8)		45.3(45.2)
$MeSnCl_3 \cdot 2DMF$	> 110 (dec.)	22.3(22.3)	4.5(4.6)	7.2(7.4)	27.8(28.3)
$MeSnBr_3 \cdot 2DMF$	70–72 (dec.)	16.2(16.2)	3.4(3.3)	5.3(5.4)	46.3(46.1)

[a] Ref. 6, m.p. 203°. [b] Ref. 7, m.p. 175°.

For volatile complexes containing Py, HMPT, and DMSO, melting points were measured in sealed capillaries.

The complexes $MeSnHal_3 \cdot 2Py$ were synthesised by mixing $MeSnHal_3$ dissolved in benzene with the calculated amounts of pyridine. A white amorphous precipitate was formed instantaneously, the reaction being exothermal (as demonstrated by the effervescence of the solvent). The precipitate was filtered, washed with benzene, then with hexane and dried *in vacuo*. These complexes could not be crystallised, however, but were readily sublimed *in vacuo* at 100–110°.

The complexes $MeSnHal_3 \cdot 2HMPT$ and $MeSnHal_3 \cdot 2DMSO$ were obtained in a similar manner, the former complex being recrystallised from benzene, while the the latter was recrystallised from ethanol. Recrystallisation from ethanol was cumbersome.

The complexes $MeSnHal_3 \cdot 2DMF$ were synthesised by mixing a cooled (0°) solution of $MeSnHal_3$ in hexane with the calculated amount of DMF. A transparent oil was formed which, after some time, gave a white difficultly crystallisable solid.

In addition, complexes of $MeSnHal_3$ with dioxane were also obtained, their compositions (elemental analyses) being: $2MeSnBr_3 \cdot$dioxane (Found: C, 8.3; H, 1.7; Br, 57.0. $C_6H_{14}Br_6O_2Sn_2$ calcd.: C, 8.6; H, 1.7; Br, 57.4%) and $MeSnCl_3 \cdot 0.9$ dioxane (Found: C, 17.9; H, 3.6. Calcd.: C, 17.8; H, 3.3%).

IV. Molecular complexes of the type $SnHal_4 \cdot 2L$ and $SnHal_4 \cdot L$ (Hal=Br, I)

The tin bromide complexes were synthesised by mixing a solution of $SnBr_4$ in CCl_4 with the calculated amount of the Lewis base. The observed ratio of metal to ligand in the resulting complexes was 1/2 for monodentate ligands and 1/1 for bidentate.

The resulting white crystalline compounds were washed with excess CCl_4 and then with hexane and were sublimed by moderate heating.

Elemental analyses and melting points (measured in sealed capillaries, due to the considerable volatilities of the respective compounds) are listed in Table 4.

The tin iodide complexes were synthesised in a similar manner using benzene as the solvent. The resulting dark-red $SnI_4 \cdot 2HMPT$ and brown $SnI_4 \cdot 2Py$ were washed with benzene and dried *in vacuo*. The analyses are listed in Table 4.

TABLE 4

MOLECULAR COMPLEXES OF $SnHal_4$ (Hal=Br, I)

Complexes	*M.p. (dec.) (°C)*	*Analysis, found (calcd.) (%)*		
		C	*H*	*N*
$SnBr_4 \cdot 2Py$	>270	20.1 (20.1)	1.9 (1.7)	4.6 (4.7)
$SnBr_4 \cdot 2HMPT$	>185	18.2 (18.1)	4.5 (4.6)	11.2 (10.5)
$SnBr_4 \cdot 2DMSO$[a]	172–173	8.1 (8.1)	2.0 (2.1)	
$SnBr_4 \cdot 2THF$	130–132	16.3 (16.3)	3.0 (2.8)	
$SnBr_4 \cdot$dioxane	140–143	9.1 (9.1)	1.7 (1.7)	
$SnBr_4 \cdot DME$	150–152	9.4 (9.1)	1.8 (1.9)	
$SnI_4 \cdot 2HMPT$	> 85	14.7 (14.6)	3.7 (3.7)	8.0 (8.5)
$SnI_4 \cdot 2Py$	>180	15.5 (15.3)	1.5 (1.3)	3.1 (3.6)

[a] Ref. 9, melts above 215° (dec.).

Syntheses of methyltin halides. Purification of solvents

Methyltin halides were synthesised using known procedures: Me_3SnBr[10], m.p. 26–27° (lit.[11] 27°); Me_2SnBr_2[12], m.p. 76–77° (lit. 74°); Me_2SnCl_2, *cf.* the synthesis of Me_2SnBr_2[12], m.p. 106–108° (lit.[13] 107°); $MeSnBr_3$ and $MeSnCl_3$[14], m.p. 53–54 and 50–52°, respectively (lit. 54–55 and 51–52°). A commercial sample of $SnBr_4$ was purified by distillation, b.p. 202°, while a commercial sample of SnI_4 ("pure for analysis" purity grade) was used unchanged.

The solvents were purified using standard techniques[15]. Pyridine was purified through the formation of pyridinium perchlorate, b.p. 115.5°; *N,N,N',N'*-tetramethylethylenediamine (TMED) was refluxed with CaH_2 for 12 h and distilled over $LiAlH_4$, b.p. 120°; hexamethylphosphoric triamide (HMPT) was dried over molecular sieves of 4 Å diameter and twice distilled over CaH_2, b.p. 65°/1 mmHg; dimethyl sulphoxide (DMSO) was kept over BaO and distilled over CaH_2, b.p. 60°/1 mmHg, m.p. 16°; *N,N*-dimethylformamide (DMF) was shaken with anhydrous K_2CO_3 for 6h and then distilled *in vacuo* over P_2O_5, b.p. 38–40°/10 mmHg; tetrahydrofuran (THF) and dimethoxyethane (DME) were refluxed with alkali (sodium metal) then distilled over sodium metal, and, just before use, over $LiAlH_4$, b.p. 64 and 81°, respectively; dioxane was purified according to the method previously described[15] and distilled over $LiAlH_4$ before use, b.p. 101.5°.

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