# INVESTIGATIONS ON ORGANOTIN COMPOUNDS

## XX*. THE EXISTENCE OF COMPLEXES WITH FIVE-CO-ORDINATED TIN IN SOLUTIONS

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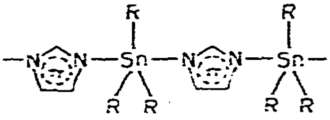
### INTRODUCTION

In an earlier paper[1] we described the exceptional stability of a new class of triorganotin compounds containing a tin-nitrogen linkage. Characteristic of this group were a number of trialkyl- and triaryltin derivatives of heterocyclic bases such as imidazole, 1,2,4-triazole, benzimidazole and benzotriazole. However, similar derivates of pyrrole or pyrazole are quite unstable. It appeared that the group of stable compounds invariably contains a heterocyclic five-membered ring with at least two nitrogen atoms in a 1,3 position. This led to the supposition that the stability might be due to the complexing ability of the second nitrogen atom with formation of a co-ordination polymer with five-co-ordinated tin atoms (I).



(I)

IR spectroscopy and X-ray analysis[2] confirm the main issue of this conception. Five-co-ordination in trialkyltin salts has been recognized with increasing frequency during the last few years, but mostly in the solid state. It was first suggested by Beattie and Gilson[3] that the spectral evidence for an ionic structure of trimethyltin fluoride and acetate[4] could also point to a structure in which fluorine or acetate groups bridge two (pentacovalent) trimethyltin groups. In the course of our studies the latter structure was even preferred for trialkylstannylimidazole and hence also for the acetates[5]. Similar observations were made by Kriegsmann[6] who also postulated some association in trimethyltin chloride and bromide. The latest evidence[7] points to the existence of a co-ordination polymer even when such strongly anionic groups as the perchlorate or tetrafluoroborate ions are present, so that the ionic model seems to be abandoned altogether.

In contrast to the large amount of information in the solid state, the occurrence of five-co-ordinated tin in solution is much less studied. The trimethyltin dibromide

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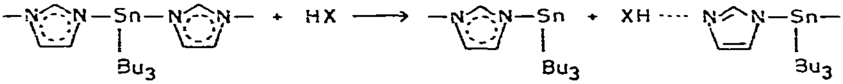
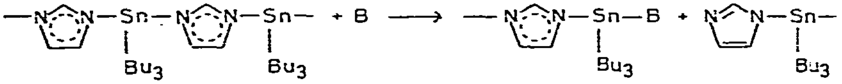
anion was shown to exist[8], also it was found that in concentrated solutions trialkyltin acylates associate appreciably to oligomers, which again contain five-co-ordinated tin atoms[9,10]. Nasielski[11] found that in acetonic solutions complexes of the type $(CH_3)_3SnBrI^-$ or $(CH_3)_3SnI_2^-$ are formed from the trialkyltin halide with excess of iodide.

The present study was undertaken with a twofold aim. First our efforts were directed towards the possible occurrence of associated *N*-tributylstannylimidazole in an inert solvent. Since this compound exists as the polymer (I) in the solid state, it was expected that also in concentrated solutions the formation of polymers might be detected. Secondly, the action of competing complexing agents upon the tin–nitrogen bond could be evaluated by a study of concentrated solutions. These agents will break down the polymer chain either by complexing with the second nitrogen atom of *N*-tributylstannylimidazole according to reaction (1) if they are of acidic nature:



(1)

or by complexing with the tin atom if they are basic [reaction (2)]:



(2)

(II)

Reagents of the former class are only of limited interest because they leave normal tetra-co-ordinated tin atoms behind upon reaction, but basic ligands form new complexes (II) with the general formula $Bu_3SnImB$. From a study of the effectiveness of a number of basic ligands in breaking down the polymer (I) *i.e.* in forming complexes with tributylstannylimidazole a more general picture is obtained of the complexing ability of tributylstannylimidazole and, by extrapolation, of molecules of the type $R_3SnX$.

The technique used consisted of measurements of the viscosity of toluene solutions which allowed a rapid, though only qualitative scanning of many ligands. Attempts at measuring the molecular weight of solutions of tributylstannylimidazole in the same solvent and at the same temperature were made in order to put the results on a more quantitative level. However, we were unsuccessful because of insufficient sensitivity of the method used.

## EXPERIMENTAL

The preparation of the organotin compounds will be described in a separate publication[12]. Toluene was carefully dried on sodium before use. The complexing agents were all purchased except dimethylacetamide and dimethylthioacetamide which were prepared and purified by standard methods. All compounds were carefully dried and checked by IR spectroscopy for the absence of OH vibrations.

Viscosity was measured with an Ubbelohde[13] viscometer* at 20.0°C ± 0.1°C. The kinematic viscosity $\nu$ was calculated by means of the equation

$$\nu = \eta/\rho = At - B/t$$

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* The viscosimeters were manufactured at the Centraal Laboratorium T.N.O., Delft.

in which $A$ and $B$ are constants obtained from measurements of liquids of known viscosity, and $t$ the measured time of flow. From the set of viscometers available, for each measurement one was chosen for which the time of flow was between 3 and 10 minutes.

## RESULTS AND DISCUSSION

### *A. Polymeric tributylstannylimidazole in solution*

The viscosity of solutions of *N*-tributylstannylimidazole and *N*-tributylstannyl-1,2,4-triazole in toluene was found to be highly dependent on the concentration (Fig. 1).

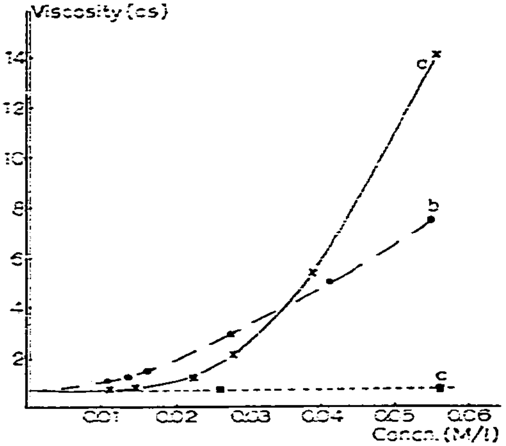

Fig. 1. The viscosity of solutions of organotin derivatives in toluene at 20.0° C. a) *N*-tributylstannylimidazole; b) *N*-tributylstannyl-1,2,4-triazole; c) *N*-tributylstannylpyrrole and *N*-tributylstannylpyrazole.

No viscosity increase, on the contrary, was found for *N*-tributylstannylpyrrole and -pyrazole. Obviously the co-ordination polymer (I) is formed in not too dilute solutions of the former organotin derivatives. In this respect the imidazoles behave in the same way as the acetates, for which association was also found in concentrated solutions[9]. An independent check on the occurrence of polymers of the type (I) was obtained from NMR measurements. Concentrated solutions of trimethylstannylimidazole in $CHCl_3$ or $CDCl_3$ yield high values for the Sn–H coupling constants, which points to the presence of $sp^2$-hybridized tin[14].

Rather than by the phenomenon itself, we were struck by the fact, that the viscosity increase starts at concentrations of about 0.5 % (or 0.01 $M$). It seems a safe estimate that dimeric molecules do not yet increase the viscosity (at least this is not found for the acetate in solutions which by IR analysis contain over half of the trialkyltin acetate molecules associated). Consequently an appreciable amount of at least trimeric species has to be present in solutions containing a few hundredth of a mole of tributylstannylimidazole per litre. In the absence of molecular weight determinations, nothing more definite can be said, but we may compare the result of Fig. 1 with the viscosity increase found for 4(5)-methylimidazole in benzene by Hückel and coworkers[15]. A few results are compared in Table 1 and although both sets of measurements have been done at different conditions (temperature and solvent), the viscosity of solutions of tributylstannylimidazole is so much larger than that of 4-methylimidazole, that these differences are of minor importance.

TABLE 1

COMPARISON OF VISCOSITY OF SOLUTIONS OF *N*-TRIBUTYLSTANNYLIMIDAZOLE AND 4(5)-METHYLIMIDAZOLE

| *N-tributylstannylimidazole* | | *4(5)-methylimidazole*[a] | | |
|---|---|---|---|---|
| *Conc. (Mol/l)* | $\nu = \eta/\rho$ *(cs) 20° in toluene* | *Conc. (Mol/l)* | $\nu = \eta/\rho$ *(cs)* | |
| | | | *30°C in benzene* | *50°C in benzene* |
| 0 | 0.686 | 0 | 0.646 | 0.506 |
| 0.0112 | 0.697 | 0.080 | 0.664 | |
| 0.0280 | 2.04 | 0.242 | 0.717 | 0.545 |
| 0.0392 | 5.30 | 0.475 | 0.828 | 0.606 |
| 0.0560 | 13.9 | 0.607 | 0.905 | 0.652 |
| | | 2.068 | 1.700 | |
| | | 3.738 | 2.665 | |

[a] Taken from ref. 15.

Rejecting the rather remote possibility that the viscosity of a solution of polymer (I) is very much larger than that of a solution of a polymer of 4-methylimidazole of the same degree of polymerization, we conclude that imidazole units are bridged by trialkyltin groups more effectively than by hydrogen atoms. This is a rather surprising result which indicates that the co-ordinate bonds between the tin atom and both nitrogen atoms have appreciable strength.

### *B. The rupture of the co-ordinate tin–nitrogen bond by complexing agents*

The second part of this study concerns the breaking down of the co-ordination polymer by means of complexing agents that compete for the tin-imidazole co-ordinate bond. The results are presented graphically in Fig. 2.

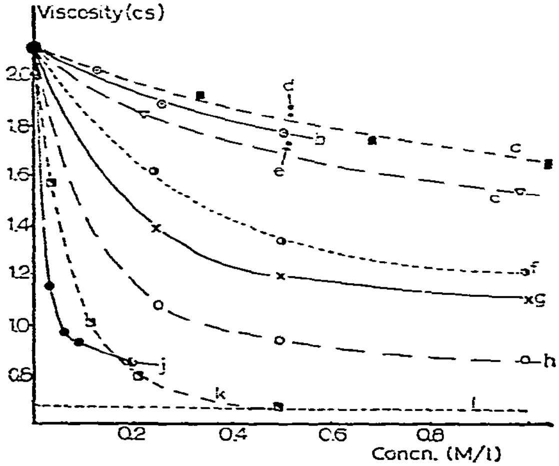

Fig. 2. The viscosity of 0.028 *M* solutions of *N*-tributylstannylimidazole in toluene in the presence of various amounts of complexing agents. a) tetrahydrofuran, b) tributylamine, c) tetrahydrothiophene, d) butyl bromide, e) butyl chloride, f) pyridine, g) *N*,*N*-dimethylthioacetamide, h) *N*,*N*-dimethylacetamide, j) tributylphosphine, k) ethanol, l) vicosity of toluene.

Only one acidic compound (ethanol) is included in this study. Obviously this is a very effective agent and the first one to reduce the viscosity to that of the pure solvent. But the molar ratio of ethanol over imidazole has to be about 20 before this point is reached (and even then the main species might be an oligomer). When it is realized that this reaction is essentially a competition between tin and hydrogen atoms for the basic nitrogen atom of imidazole [*cf.* reaction (1)], it becomes clear that the "tributyltin bridge" is formed in preference to the hydrogen bridge in these structures. This result confirms the conclusions drawn in the previous subsection.

The remainder of the complexing agents are of the basic type, they degrade the polymer according to reaction (2) with maintenance of the five-co-ordination around the tin atom. From the results given in Fig. 2 it is clear that next to a group of ligands of low activity (containing tetrahydrofuran, tetrahydrothiophene, butyl chloride, butyl bromide and tributylamine) four compounds strongly decrease the viscosity namely (in order of activity) pyridine, *N,N*-dimethylthioacetamide, *N,N*-dimethylacetamide and tributylphosphine. Striking is the very high activity of the last compound especially in the lower concentrations.

Among the saturated compounds clearly the derivatives of second-row elements (P, S, Cl) are stronger complexing agents than those of either first-row (N, O) or third-row (Br) elements. This maximum of activity indicates that the tin atom in the compound studied ($Bu_3SnIm$) behaves as a metal of class B according to the classification given by Ahrland *et al.*[16,17]. This sequence is reversed in the unsaturated ligands, where the amide complexes stronger than the thioamide. In this respect tributylstannylimidazole shows a behaviour similar to that of $SnCl_4$, which is complexed by tetrahydrothiophene better than by tetrahydrofuran, but by dimethylthioacetamide and dimethylacetamide equally well[18]. If, as seems probable, steric factors are not assumed to play a decisive role in fixing the sequences found, the most attractive explanation of our results may be based on the principle evoked by Ahrland *et al.*[17] to explain the difference between A-type and B-type metals. The latter, which form the most stable complexes with ligand atoms of the second period of the periodic table, would be able to donate electrons from their $d$-orbitals into empty $d$-orbitals of the ligand with formation of a $d\pi$–$d\pi$ bond. This possibility is fundamentally lacking when ligand atoms of the first period are bound, but a similar back donation is feasible with unsaturated ligands, where back donation might involve a relatively low-lying empty $\pi$-orbital of the ligand. These $\pi$-orbitals are antibonding in the ligand molecules, but energetically probably are even better available than the $d\pi$-orbitals of elements like phosphorus and sulphur. Consequently, although metals of class B form more stable complexes with second-row elements when *saturated* ligands are concerned, no prediction can be made of the relative stability of unsaturated ligands, since all depends on the energies of the empty $p\pi$-orbitals here.

The picture just given is attractive from still another point of view. Since the charged alkylated tin ions already show definite class B character (stable sulphides), this is all the more expected for uncharged molecules like trialkylstannylimidazole, where the metal bears no appreciable positive charge and thus should be ideally suited for donating electrons. In fact this mechanism may also be an important factor in the stabilization of the polymeric tributylstannylimidazole itself; it could be a logical explanation of the above-mentioned fact, that imidazole forms stronger tributyltin bridges than hydrogen bridges.

The formation of stabilizing $d\pi$ bonds in our compounds is in principle the same but in direction opposite to the $p\pi$–$d\pi$ bond formation between silicon and nitrogen in silylamines[19], silicon and oxygen[20] and between silicon and germanium and aromatic systems[21]. In these systems the $p_z$ or $\pi$-electrons of the light atoms are donated into the empty $3d$ orbitals of silicon. Many studies (of which only a few can be cited) have been devoted to this phenomenon and, though there is still some conflicting evidence, it seems as if the $\pi$-electron-withdrawing power of the elements rapidly decreases in the order silicon, germanium, (and is probably absent in) tin and lead. The results of this study imply that with tin donation of $d\pi$ electrons from the filled $4d$ orbital occurs instead of (or perhaps in addition to) acceptation into the empty $5d$ orbital. With lead it is to be expected that this trend is continued.

## ACKNOWLEDGEMENTS

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## SUMMARY

N-Tributylstannylimidazole forms complexes with basic ligands (B) in which the tin atom becomes pentacovalently bound. In the general structure $Bu_3SnImB$, B may be another molecule of $Bu_3SnIm$, which gives rise to the formation of a co-ordination polymer. In inert solvents this polymer causes the viscosity to rise sharply with increasing concentration. The efficiency of competing complexing agents can be evaluated by following the decrease of the viscosity of solutions of $Bu_3SnIm$ upon addition of these agents. Results are (i) that association of $Bu_3SnIm$ occurs more readily than association of imidazole over hydrogen bridges, (ii) that $Bu_3SnIm$ is complexed preferentially by either second row atoms (P, S) or by unsaturated ligands. A possible explanation, involving stabilization of the complexes by back donation of $d\pi$-electrons from the tin atom towards the ligands, is discussed.

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