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SHORT PAPER

Organotin wood preservatives: their compatibility with synthetic pyrethroid insecticides

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The stability of three synthetic pyrethroids (cypermethrin, deltamethrin and permethrin) to selected tributyltin compounds, Bu_3SnX [where $X = OSnBu_3$, Cl, $O_2CC_6H_5$, O_2C(naphthenyl), $OSO_2C_2H_5$], $(Bu_3SnO)_3PO$ and $(Bu_4N)(Bu_3SnCl_2)$, in toluene solution was investigated by infrared spectroscopy over a 24-week period. It was found that only $(Bu_3Sn)_2O$ reacted with the pyrethroids and that their order of reactivity was cypermethrin > deltamethrin > permethrin. An attempt was made to elucidate the reaction mechanism(s) occurring between $(Bu_3Sn)_2O$ and the pyrethroids by studying mixtures of this tributyltin fungicide with simple model compounds, $R^1CO_2R^2$ where $R^1 = CH_3$; $R^2 = CH_2C_6H_5$ and $R^1 =$ cyclo–C_3H_5 and $R^2 = CH_2C_6H_5$.

Keywords: Synthetic pyrethroids, cypermethrin, deltameltrin, permethrin, tributyltin fungicide, IR spectroscopy, NMR spectroscopy, compatibility

INTRODUCTION

In recent years tributyltin compounds have found extensive use as fungicides in organic solvent-based wood preservatives.[1] The organotin derivative most commonly used in this context is bis(tributyltin) oxide [$(Bu_3Sn)_2O$] although both tributyltin naphthenate [Bu_3SnO_2C(naphthenyl)], tris(tributyltin) phosphate [$(Bu_3SnO)_3PO$] and tributyltin benzoate ($Bu_3SnO_2CC_6H_5$) have achieved commercialization in certain countries. However, although these compounds are toxic to some forms of insects,[2] the results of tests carried out against species which attack timber, e.g. the common furniture beetle (*Anobium punctatum*), the deathwatch beetle (*Xestobium rufovillosum*) or the house longhorn beetle (*Hylotrupes bajulus*), indicate that their effectiveness as insecticides in timber is limited at the concentrations normally employed, i.e. 1–3%. Thus, in order to afford complete protection to constructional timber, the organotin is often combined with organic contact insecticides. The wood-preserving industry has shown increasing interest in the use of synthetic pyrethroids as insecticides in wood preservative formulations since they offer a reduced risk of environmental pollution compared with the existing organochlorines. In fact, cypermethrin, deltamethrin and permethrin (Fig. 1) have been approved for this application in some countries. One restriction in the use of these synthetic pyrethroids is the reported[3] incompatibility with the fungicide bis(tributyltin) oxide, which means that these two biocides may not be used together in dual-purpose formulations.

In this work wc investigate this incompatibility and extend the study to other tributyltin fungicides.

EXPERIMENTAL

Bis(tributyltin) oxide and tributyltin naphthenate were obtained from Schering AG and Pvba Corn. Van Loocke, respectively, and were used without further purification. The remaining tributyltin compounds were prepared according to published procedures.[4] Benzyl acetate was obtained from Aldrich Chemical Co. Benzyl cyclopropylcarboxylate was prepared by the azeotropic dehydration of equimolar quantities of cyclopropylcarboxylic acid and benzyl alcohol in boiling toluene using a Dean and Stark separator.

NMR spectra were recorded on a JEOL FX60Q spectrometer, with field frequency lock to external D_2O. ^{119}Sn spectra were recorded at 22.24 MHz under nuclear Overhauser suppressed conditions. ^{119}Sn chemical shifts ($\delta^{119}Sn$) are relative to $(CH_3)_4Sn$ and are accurate to ± 0.1 ppm. ^{13}C spectra were recorded at 15.0 MHz; ^{13}C chemical shifts ($\delta^{13}C$) are relative to $(CH_3)_4Si$ and are accurate to 0.05 ppm.

Infrared (IR) spectra were recorded on a Perkin-Elmer 1330 instrument.

RESULTS AND DISCUSSION

The synthetic pyrethroids used in this investigation, permethrin (**I**), cypermethrin (**II**) and deltamethrin (**III**), have structures shown in Fig. 1 in which both *cis* and *trans* isomers are possible.

I: X = Cl, R = H, 40% *cis*, 60% *trans*

II: X = Cl, R = CN, 40% *cis*, 60% *trans*

III: X = Br, R = CN, 100% *cis*

The compatibility of these three pyrethroids with selected tributyltin compounds was investigated by solution IR spectroscopy. Thus, IR spectra of toluene solutions of the pyrethrods (0.4 mmol) were first recorded over the range 2000–1400 cm^{-1} and the ketonic carbonyl stretching frequencies noted ($\nu(C{=}O)$ I = 1730, II = 1740, III = 1735 cm^{-1}). A 10-molar excess of the appropriate tributyltin compound (Table 1) was added to these solutions and the solution IR spectrum immediately recorded. Subsequent spectra were then recorded after 1, 7, 14, 28, 56, 84 and 168 days. In those solutions where reaction between the organotin and the pyrethroid had occurred, evidence was obtained by the appearance or disappearance of bands in the IR spectrum (and particularly by the disappearance of the $\nu(C{=}O)$ band pertaining to the pyrethroid). Table 1 indicates those solutions in which reaction had occurred after a period of 168 days. In fact, it was found that only $(Bu_2Sn)_2O$ reacted with the pyrethroids. This observation is in slight disagreement with that of Carter,[3] who suggested that mixtures of deltamethrin with $(Bu_3Sn)_2O$, with $(Bu_3SnO)_3PO$ or with $Bu_3SnOCOC_6H_5$ were unstable. We believe that this was due to the presence of a trace of $(Bu_3Sn)_2O$ in the samples of the latter two organotin compounds

Table 1 Reactivity of synthetic pyrethroids with tributyltin compounds[a]

Organotin	Synthetic pyrethroid[b] I	II	III
—	×	×	×
$(Bu_3Sn)_2O$	√	√	√
Bu_3SnCl	×	×	×
$(Bu_3SnO)_3PO$	×	×	×
$\{NBu_4\}\{Bu_3SnCl_2\}$	×	×	×
Bu_3Sn(naphthenate)[c]	×	×	×
$Bu_3SnOSO_2C_2H_5$	×	×	×
$Bu_3SnOCOC_6H_5$	×	×	×

[a] After 168 days in toluene solution. [b] ×, no reaction; √, reaction. [c] Naphthenic acid is a hydrocarbon fraction of general formula $HO_2C(CH_2)n\overline{CR(CR_2)_3C}R_2$ (where n = 1–5 and R = H or alkyl.

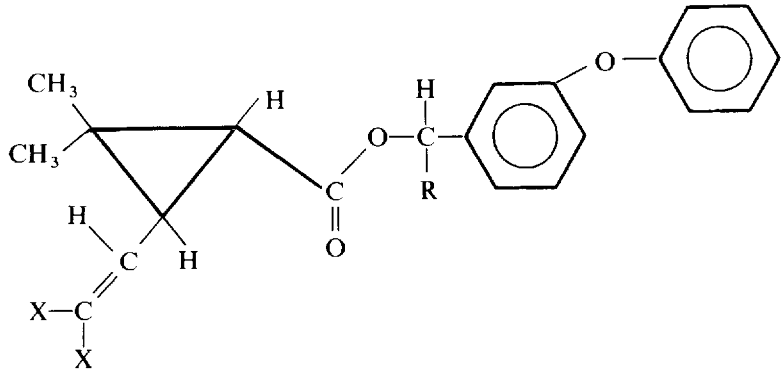

Figure 1

employed. In our own studies, initially, a sample of $(Bu_3SnO)_3PO$ was believed to react with cypermethrin, but on close inspection of the organotin by ^{119}Sn NMR,[5] the additional presence of $(Bu_3Sn)_2O$ was confirmed. Consequently, all organotin compounds used in this study were examined by ^{119}Sn NMR (Table 2) to check their purity.

Table 3 shows the order of reactivity of the pyrethroids with $(Bu_3Sn)_2O$, i.e. cypermethrin (**II**) > deltamethrin (**III**) ≫ permethrin (**I**).

In an attempt to elucidate the reaction mechanism(s) occurring between $(Bu_3Sn)_2O$ and the pyrethroids, we have studied mixtures of this organotin compound with simple model compounds, i.e. $R^1CO_2R^2$ where $R^1 = CH_3$; $R^2 = CH_2C_6H_5$ and $R^1 = cC_3H_5$; $R^2 = CH_2C_6H_5$ by NMR spectroscopy. For the purpose of recording the NMR spectra, CCl_4 was chosen as a suitable solvent, being non-coordinating and having only one ^{13}C resonance which is well separated from regions of interest. However, we have recently demonstrated[7] that tributyltin alkoxides react with CCl_4 under refluxing conditions. Therefore, investigations were carried out using petroleum ether (b.p. 60–80°C) as reaction solvent; after the reaction it was removed under reduced pressure and the products redissolved in CCl_4 in an atmosphere of nitrogen, prior to NMR analysis.

It has previously been reported[8] that the bis(trialkyltin) oxides [$(R_3Sn)_2O$ where alkyl = ethyl, butyl] react with ethyl acetate (**A**) to afford a mixture of the appropriate trialkyltin acetate and trialkyltin ethoxide. In our studies,

Table 2 ^{119}Sn NMR data

Compound	$\delta^{119}Sn$ (ppm)	Solvent (concentration, $g\,cm^{-3}$)
$(Bu_3Sn)_2O$	84.7	$CCl_4(0.1)$
Bu_3SnCl	143.5	$CCl_4(0.1)$
$(Bu_3SnO)_3PO$	88.2[a]	Toluene(1.0)
	−106.0[a]	
$(NBu_4)(Bu_3SnCl_2)$	−54.3	Toluene(0.25)
	−62.4	Toluene(1.0)
$Bu_3SnOSO_2C_2H_5$	49.5	$CCl_4(0.1)$
	46.2[b]	Neat liquid
$Bu_3SnOCOC_6H_5$	98.8	Neat liquid
$Bu_3SnOCOCH_3$ (**IV**)	90.9	$CCl_4(0.2)$
$Bu_3SnOCH_2C_6H_5$ (**V**)	101.4	$CCl_4(0.5)$
$Bu_3SnOCO\overline{CHCH_2C}H_2$ (**VI**)	89.0	$CCl_4(0.2)$
$(Bu_3Sn)_2O +$ $CH_3COOCH_2C_6H_5$	90.0 (**IV**)* 100.6 (**V**)*	CCl_4
$(Bu_3Sn)_2O +$ $\overline{CH_2CH_2C}HCOOCH_2C_6H_5$	87.7 (**VI**)* 100.5 (**V**)*	CCl_4

[a] Two resonances correspond to the four- and five-coordinate tin sites (Ref. 5). [b] Ref. 6.
*Assignment; see above in first column.

Table 3 Reaction of synthetic pyrethroids with bis(tributyltin) oxide $(Bu_3Sn)_2O$ [time in days]

Evidence for reaction[a]	Synthetic pyrethroid I	 II	 III
Evidence for commencement of reaction	28	<1	1
Evidence for approx 50% reaction	84	1	7
Evidence for complete reaction	>168	7	~28

[a] Using IR methods; by disappearance of $\nu(C{=}O)$ band of the pyrethroid.

we have attempted to investigate compounds more akin to the pyrethroids. Thus, $(Bu_3Sn)_2O$ was refluxed with an equimolar quantity of benzyl acetate (**B**) or benzyl cyclopropylcarboxylate (**C**) for 22 h in petroleum ether under an atmosphere of nitrogen (Fig. 2).

Inspection of the ^{119}Sn and ^{13}C NMR spectra of the CCl_4 solutions and comparison with NMR spectra of solutions containing authentic organotin compounds (Tables 2 and 4) showed that in the former case $Bu_3SnOCOCH_3$ and $Bu_3SnOCH_2C_6H_5$ were present and in the latter $Bu_3SnOCO\overline{CHCH_2CH_2}$ and $Bu_3SnOCH_2C_6H_5$ resulted.

As a result of these studies we believe that a general reaction mechanism can be written for

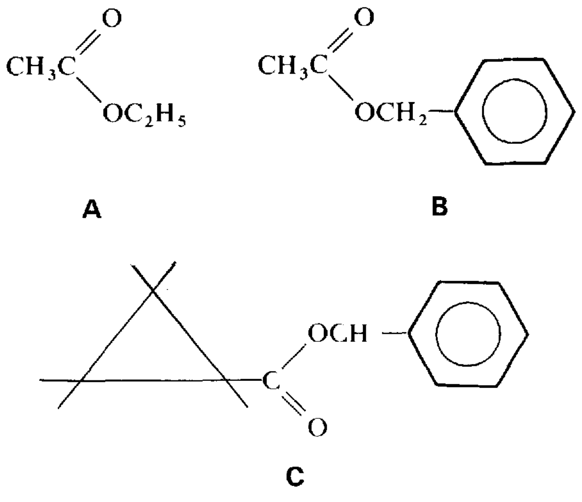

Figure 2

the reaction of $(Bu_3Sn)_2O$ with carboxylate esters (Eqn [1])

$$Bu_3SnOSnBu_3 + R^1COOR^2 \rightarrow [R^1C(OSnBu_3)_2OR^2] \downarrow R^1COOSnBu_3 + R^2OSnBu_3 \qquad [1]$$

Since the pyrethroids may be considered to be substituted benzyl cyclopropylcarboxylates, we believe that the above reaction provides an explanation of their incompatibility with $(Bu_3Sn)_2O$.

CONCLUSION

This work has demonstrated that of the seven organotin compounds investigated, only $(Bu_3Sn)_2O$ reacted with any of the synthetic pyrethroid insecticides under the conditions studied. Thus, it may be concluded that, of the compounds that are at present commercially used in combination with pyrethroids, $(Bu_3SnO)_3PO$, Bu_3Sn(naphthenate) and $Bu_3SnOCO.C_6H_5$ should not pose any stability problem, *provided* they do not contain traces of $(Bu_3Sn)_2O$. The reasons for the pronounced lack of reactivity of permethrin (**I**) with $(Bu_3Sn)_2O$ are not apparent; its lack of a CN group in contrast to cypermethrin (**II**) and deltamethrin (**III**) may be significant in this context.

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Table 4 ^{13}C NMR data[a]

$CH_3COOCH_2C_6H_5$	168.9 (C=O); 65.7(OCH_2); 20.4(CH_3); 136.3, 128.2, 128.1, 127.8 (C_6H_5)
$\overline{CH_2CH_2CH}COOCH_2C_6H_5$	179.7 (C=O); 64.3(OCH_2); 12.7($\overline{\underline{C}HCH_2CH_2}$); 8.6($\overline{CH\underline{C}H_2\underline{C}H_2}$); 140.6, 128.1, 127.1, 126.9 (C_6H_5)
$Bu_3SnOCOCH_3$(**IV**)	175.4 (C=O); 20.7(CH_3)
$Bu_3SnOCH_2C_6H_5$(**V**)	68.1 (OCH_2); 144.9, 127.6, 126.3, 126.2 (C_6H_5)
$Bu_3SnOCO\overline{CHCH_2CH_2}$(**VI**)	178.9 (C=O); 12.7 ($\overline{\underline{C}HCH_2CH_2}$; 7.7($\overline{CH\underline{C}H_2\underline{C}H_2}$)
$(Bu_3Sn)_2O + CH_3COOCH_2C_6H_5$	175.3 (C=O, **IV**); 20.6(CH_3, **IV**); 144.4, 127.7, 126.3, 126.2(C_6H_5, **V**); 67.5 (OCH_2, **V**)
$(Bu_3Sn)_2O + \overline{CH_2CH_2CH}COOCH_2C_6H_5$	178.9 (C=O, **VI**); 12.7($\overline{\underline{C}HCH_2CH_2}$, **VI**); 7.6($\overline{CH\underline{C}H_2\underline{C}H_2}$, **VI**); 144.2, 127.7, 126.3, 126.2(C_6H_5, **V**); 67.3(OCH_2, **V**)

[a] Excluding chemical shifts of the butyl-carbon atoms.

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