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COMMUNICATION

Encapsulation of organotin compounds in metal acetate glasses

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Triorganotin halides, oxides and sulphides can be dissolved in molten, mixed-metal acetates at *ca* 140–160°C without decomposition; quenching provides glasses into which are encapsulated the organotin species. Halide/acetate and oxide/acetate, but not sulphide/acetate, exchanges occur in the melt. Only partial exchange was found for hindered trineophyl tin chloride [$(PhCMe_2CH_2)_3SnCl$], in contrast to the complete exchanges observed for the butyl (Bu), phenyl (Ph) and cyclohexyl (Cy) analogues. Complete oxide/acetate exchange was found for $(Bu_3Sn)_2O$, partial exchange occurred for $(Cy_3Sn)_2O$, whilst no exchange resulted with bis(trineophyltin) oxide or $(Ph_3Sn)_2O$. Tin–tin bonds (e.g. as in $Ph_3SnSnPh_3$) and carbon–tin bonds (even the allyl–Sn bond in $Bu_3SnCH_2CH{=}CH_2$) are not affected. The acetate glasses dissolve in aqueous media with release of the organotin species and they have potential as slow-release systems which is currently being investigated.

Keywords: Organotin compounds, glasses, encapsulation, slow release

INTRODUCTION

Organotin compounds are considered to be among the more thermally stable of organometallic compounds. Although few detailed studies on the thermolysis of organotins have been reported,[1] various compounds are known to be stable to above 200°C (for example, see the decomposition temperatures T_D in Table 1). In general, organotins may be used in a wide range of solvents up to reflux temperatures. In contrast, study of organotin compounds in molten salt media or in glass matrices has attracted no attention. There are several potential applications for organotin compounds hosted in a glass matrix, and whilst the temperatures required for silicate glass formation are too high, there are other materials which form melts and glasses at sufficiently low temperatures for safe use with organotin species. One such group of materials are metal acetates. In this communication, we wish to report preliminary findings on the use of acetate melts and glasses as solvents for triorganotin, tetraorganotin and ditin compounds.

RESULTS AND DISCUSSION

Metal acetates, either as mixtures or occasionally singly, were initially reported (in 1969) to form glasses on cooling from the melt.[2,3] These glasses have softening points T_s (which are the temperatures at which the glasses are sufficiently fluid to act as solvents) frequently less than 200°C (see Table 1). We have found that a variety of organotin compounds can be dissolved in molten acetates, practically without decomposition. However, anion/acetate exchange can result. Table 2 lists compounds successfully dissolved in the sodium acetate:potassium acetate:calcium acetate [$AcONa:AcOK:(AcO)_2Ca$ (1:1:1)] melt at *ca* 140–160°C. The metals can be subsequently quenched to provide glasses; solutions of up to 5% (w/w) concentrations have been prepared without any adverse effect on the glass formation.

The acetate glasses dissolve in water; subsequent extraction of the organotins into an organic solvent, e.g. dichloromethane (CH_2Cl_2), provides a simple and effective method of collecting the encapsulated

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Table 1 Organotin compounds extracted from the AcONa:AcOK:$(AcO)_2Ca$ (1:1:1) glass[a]

Dissolved material			Extracted material		
Compound	$\delta(^{119}Sn)^b$	$T_D(°C)^c$	Compound	$\delta(^{119}Sn)^b$	
Bu_3SnF	–	285	Bu_3SnOAc	$+104.7$ $[+96]^{d,e}$	
Bu_3SnCl	$+150.3$	180	Bu_3SnOAc	$+104.0$ $[+96]^{d,c}$	
$(Bu_3Sn)_2O$	$+77.8^d$	95	Bu_3SnOAc	$+93.0$ $[+96]^{d,e}$	
$Bu_3SnCH_2CH{=}CH_2$	-17.3^f	–	$Bu_3SnCH_2CH{=}CH_2$	-16.8	
$Bu_3SnSC_{12}H_{25}$	-75.0	–	$Bu_3SnSC_{12}H_{25}$	-75.8	
Cy_3SnCl	$+72.3$	280	Cy_3SnOAc	$+9.0$ $[8.4]^g$	
$(Cy_3Sn)_2O$	-6.6	300	$(Cy_3Sn)_2O$	-6.6 (2)	
			Cy_3SnOAc	$+8.8$ (1)	Integration ratios
			unknown	$+9.9$ (4)	
$(PhCMe_2CH_2)_3SnCl$	$+118^d$	220	$(PhCMe_2CH_2)_3SnCl$	$+117.5$ (1)	Integration ratio
			$(PhCMe_2CH_2)_3SnOAc$	$+81.8$ (2)	$[81.8]^g$
$[(PhCMe_2CH_2)_3Sn]_2O$	$+50.2$	315	$[(PhCMe_2CH_2)_3Sn]_2O$	$+56.3$	
Ph_3SnCl	-45.3	280	Ph_3SnOAc	-114.2 $[-113.0]^j$	
$(Ph_3Sn)_2O$	-83.8	140^h	$(Ph_3Sn)_2O$	-83.7	
		290^i	Ph_4Sn?	-129.2 minor	
Ph_4Sn	-120.0	–	Ph_4Sn	-120.0	
$(Ph_3Sn)_2$	-143.0	285	$(Ph_3Sn)_2$	-143.0	
$(Ph_3Sn)_2S$	-52.6	–	$(Ph_3Sn)_2S$	-52.6	
Ph_3SnOH	-86.6^d	75^j	$(Ph_3Sn)_2O$	-83.7	

– Not measured. [a]Compounds obtained by CH_2Cl_2 extraction of the ground glass. [b]In $CDCl_3$ solution, relative to Me_4Sn; unless otherwise indicated, values were obtained in this study. [c]Decomposition temperature; obtained in this study. [d]Ref. 5. [e]Values attained in CD_2Cl_2. [f]Ref. 6. [g]Values for authentic samples, obtained in this study in $CDCl_3$. [h]Ref. 4. [i]Ref. 1 and this study. [j]Decomposition to $(Ph_3Sn)_2O$: Ref. 1.

Table 2 Glass transition (T_g°C) and glass softening (T_s°C) temperatures of acetate glasses

Glass components materials (ratio)	$T_g(°C)^a$	$T_s(°C)^b$
AcOLi:AcONa (4:3)	60	160
AcOK:$(AcO)_2Ca$ (1:1)	110	270
AcONa:$(AcO)_2Ca$ (1:1)	–	310
(2:1)	110	–
AcONa:$(AcO)_2Zn$ (1:1)	–	180
AcONa:AcOK:$(AcO)_2Ca$ (1:1:1)	–	140
AcOK:$(AcO)_2Pb$ (1:3)	42	<80

[a]Refs 2, 3. [b]Data obtained in this study.

organotin compounds. However, as an analytical method it could suffer if reactions with water or acetate occurred on the glass's dissolution in water. Nevertheless this procedure did indicate that recovery of total organotins was always very high and that little decomposition occurred: however, products in amounts less than 5% could remain undetected. Use of thin layer chromatography (TLC) (using 1% acetic acid in chloroform ($CHCl_3$) as eluent and spraying with dithizone) clearly showed that the amounts of diorganotin obtained from the dissolved triorganotin species were, at the very most, only present in small amounts.

Alternatively, the encapsulated tin compounds could be Soxhlet-extracted from the finely ground glass using dichloromethane as solvent. This method has the advantage of releasing the organotin compounds actually held in the glass but has the potential disadvantage of leaving behind any poorly soluble organotins (such as Bu_3SnF or decomposition products). The data in Table 1 are for extractions by this second method. Organotin compounds were identified by $\delta(^{119}Sn)$ values.

As can be seen in Table 1, anion/acetate exchanges occurred with triorganotin halides (including Bu_3SnF) and one bis(trialkyltin) oxide $[(Bu_3Sn)_2O]$. No $\delta(^{119}Sn)$ value has been reported for insoluble Bu_3SnF. While it remains a possibility that Bu_3SnF could have a $\delta(^{119}Sn)$ value in the region of 95–100, we are confident that the extracted material from the Bu_3SnF experient, with $\delta(^{119}Sn) = 104.7$, is Bu_3SnOAc from comparison with values for authentic Bu_3SnOAc. Only partial exchange results with the sterically hindered trineophyltin chloride $[(PhCMe_2CH_2)_3SnCl]$, in contrast to the complete exchanges found for Bu_3SnCl, Ph_3SnCl or Cy_3SnCl.

Merely blending, at room temperature, the powdered acetate glass with these trialkyltin chlorides and extracting the organotin compounds with refluxing dichloromethane resulted in recovery of the trialkyltin *chloride* only. Thus the anion exchanges, which are essentially solvolytic reactions, are occurring in the short period (<5 min) that the tin compounds are held at the melt temperature – 140–160°C – before quenching the melt. Longer times in the melt should lead to more extensive exchanges. More limited exchanges occurred for oxides. Partial exchange results with $(Cy_3Sn)_2O$; for both $[PhCMe_2CH_2)_3Sn]_2O$ and $(Ph_3Sn)_2O$, no acetate exchange was realized. The easier substitution of chlorides than oxides follows the general reactivity trend towards nucleophiles.

No anion exchanges occurred with the tin–sulphur (Sn–S) bonded compounds, $(Ph_3Sn)_2S$ or $Bu_3SnSC_{12}H_{25}$, and no acetate-induced cleavage of Sn–Sn bonds (as in $Ph_3SnSnPh_3$) or carbon–tin bonds (in tetraorganotin compounds) resulted. The recovery of allyltributyltin, in particular, suggests the acetate melts are far from severe media.

The conversion of Ph_3SnOH to $(Ph_3Sn)_2O$ has been previously recognized as a thermal change, occurring at 75°C.[1]

As mentioned earlier, the acetate glasses dissolve in aqueous media. The rate of dissolution of a particular glass – and hence the release of the encapsulated organotin species – varies with the moisture content of the medium with which it is in contact. The acetate glasses have some potential as vehicles for the slow release of biocidal triorganotin compounds. The anion/acetate exchanges realized for some triorganotin species are of little consequence since the bioactivity is essentially independent of the anion in aqueous media. The acetate glass systems can be used as such or in combination with other media, e.g. phosphate glasses, for particularly long-term slow release into aqueous environments. We are currently investigating their potential as slow-release systems as well as studying the structures and reactivities of the organotins within the melt and the glass.

EXPERIMENTAL

The acetate glasses were made by fusing the components at the minimum possible temperature, *ca* 140–160°C for the AcONa:AcOK:$(AcO)_2Ca$ glass. Two methods were used to encapsulate the organotin material within the glass. In some cases, the tin compound was simply stirred into the melt and the resulting solution quickly quenched. Alternatively the tin species was added at room temperature to the powdered pre-formed glass and the mixture heated to the liquid state and then quenched as before. The concentration of the organotin compound was in the range 1–5% (w/w).

Tin compounds

These were all samples either from previous studies or obtained in this study by standard procedures. All had the expected spectral and analytical data.

Extractions

The recovery of the organotin compounds from the glass could be achieved on dissolving the glass in water and extracting the resulting mixture several times with CH_2Cl_2. Alternatively, the ground-up glass was Soxhlet-extracted using CH_2Cl_2 as solvent. In both cases, removal of the solvent from the sodium sulphate-dried CH_2Cl_2 extracts provided the tin species, which were identified by ^{119}Sn NMR spectroscopy, using a JEOL FX90 spectrometer.

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