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AN ^{17}O NMR STUDY OF SOME DI- AND TRI-n-BUTYLTIN(IV) CARBOXYLATES

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Summary

The ^{17}O NMR spectra of tri-n-butyl and di-n-butyl-tin(IV) carboxylates exhibit only one signal. This effect is interpreted as due to a fast exchange (on the NMR time scale) of the oxygen atoms of the carboxyl group bonded to the central tin atom. The implications of the observations for the structures of organotin(IV) carboxylates in solutions of non-coordinating solvents are discussed.

Introduction

The application of multinuclear NMR spectroscopy to the study of the structure of organotin(IV) compounds in solutions has increased markedly in recent years. Valuable results have been obtained, especially in those cases when in addition to NMR data for nuclei in the organotin(IV) part of the molecule (^{1}H, ^{13}C and ^{119}Sn), data for nuclei from other parts of the molecule were also recorded, e.g. the ^{31}P NMR spectra of the tri-n-butyltin(IV) phosphates and phenylphosphates [1], and the ^{15}N NMR spectra of triorganotin(IV) oxinates [2]. The use of ^{17}O NMR spectroscopy for such studies has not previously been reported.

We present below the results of a ^{17}O NMR spectroscopic study of tri- and di-n-butyltin(IV) carboxylates, of the types $Bu_3SnOOCR$ (compounds **1**) and $Bu_2Sn(OOCR)_2$ (compounds **2**), respectively, where, Bu = n-butyl and R = CH_3, C_6H_5, $C_6H_5OCH_2$, or $C_6H_5SCH_2$ (see Table 1). We studied these carboxylates previously [3–6] by ^{13}C and ^{119}Sn NMR spectroscopy and infrared spectroscopy. The results from those studies showed that triorganotin(IV) carboxylates in non-coordinating solvents contain simple molecules with a quasitetrahedral geometry around a four-coordinate tin atom. Under the same conditions the diorganotin(IV) carboxylates contain five-coordinate tin atoms. In the solutions of coordinating solvents the coordination number of the tin increases to five in triorganotin(IV) compounds and to six in diorganotin(IV) compounds, owing to the formation of complexes with molecules of solvents (1/1 and 1/2).

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TABLE 1

^{17}O NMR PARAMETERS OF COMPOUND 1 AND 2

No.	Compound	$\delta(^{17}O)$ [a] (ppm)	$w_{1/2}$ [b] (Hz)	Temperature (K)	Note
1a	$Bu_3SnOOCC_6H_5$	261	500	360	neat liquid
1a		241	550	330	25% (v/v) solution in $CHCl_3$
1b	$Bu_3SnOOCCH_2SC_6H_5$	276	500	330	saturated solution in $CHCl_3$
2a	$Bu_2Sn(OOCC_6H_5)_2$	275	1200	330	70% (v/v) solution in $CHCl_3$
2a		280	1000	330	50% (v/v) solution in $CHCl_3$
2b	$Bu_2Sn(OOCCH_2SC_6H_5)_2$	272	1000	330	saturated solution in $CHCl_3$
2c	$Bu_2Sn(OOCCH_3)_2$	291	550	360	neat liquid
2c		291	900	340	neat liquid
2d	$Bu_2Sn(OOCCH_2OC_6H_5)_2$	249	900	330	saturated solution in $CHCl_3$

[a] ±3 ppm. [b] ±10%.

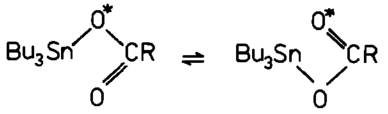
Experimental

The compounds were prepared by published methods [3,4,7,8]. The ^{17}O NMR spectra were measured on the JNM-FX 100 spectrometer (JEOL, Japan) equipped with a 10 mm broad band probe operating at 13.5 MHz. The typical instrument settings were as follows; spectral width 10 kHz, 1k data points (zero filling to 2k), 90° pulse angle, acquisition delay 200 μs, pulse repetition 60 ms. The signal-to-noise ratio was improved by applying a 100 Hz exponential factor to the FID prior to Fourier transformation. Neat deuterium oxide in a coaxial capillary was used as lock and external reference ($\delta = 0$).

The recording of ^{17}O NMR spectra is difficult, owing to a low natural abundance of the ^{17}O isotope (0.037%) and a spin number I 5/2, especially at low values of the magnetic field strength and in viscous solutions [9]. The measurements were thus carried out either with neat liquids or in saturated solutions at higher temperatures (see Table 1). To obtain the spectra it was necessary to accummulate 60000–600000 pulses. The preservation of the structure of compounds upon temperature variation was confirmed by simultaneous determination of the ^{119}Sn chemical shifts the changes in these parameters were within the limits typical of the structural configuration at the room temperature [3,4].

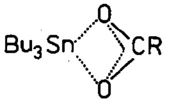
Results and discussion

The $\delta(^{17}O)$ values of the studied compounds at the natural abundance level of the ^{17}O isotope, the half-height widths of signals $w_{1/2}$, and the temperatures of measurements are given in Table 1. The ^{17}O NMR spectra of the compounds studied are characterized by the presence of one NMR signal only (the ^{17}O NMR signal of $C_6H_5OCH_2$ in compound **2d** was not observed, probably because of a large linewidth), whereas organic esters exhibit two well resolved signals [9–11]; thus carboxyl groups of substituted methyl benzoates have chemical shifts $\delta(^{17}O)$ in acetone solutions of 125–132 ppm (OCH_3) and 350–355 ppm (C=O) [11]. In the ^{17}O NMR spectra of methyl phenoxyacetate we observed NMR signals at 359 (C=O), 137 (OCH_3) and 58 ppm ($C_6H_5OCH_2$) measured at 360 K as neat liquid. In contrast, in the NMR spectra of carboxylic acids only one ^{17}O NMR signal was observed [9–11], the C=O and C–O–H positions being averaged by rapid intermolecular proton transfer. Furthermore only one signal was observed in the alkali metal salts of the acids [9]. It is necessary to suggest an explanation for the presence of only one signal in the ^{17}O NMR spectra of the compounds **1** and **2**, with δ (^{17}O) values lying between those for the two oxygen atoms of the carboxyl group of organic esters and close to those for carboxylic acids and their alkali metal salts, respectively. The infrared spectra of compounds **1** and **2** in CCl_4 solutions measured under comparable conditions reveal the presence of the monodentate carboxyl group ($\nu_{as} \sim 1660$ cm^{-1}, $\nu_s \sim 1340$ cm^{-1}) in compounds **1** and the bidentate chelate carboxyl group (ν_{as} 1600–1630 cm^{-1}, ν_s 1370–1400 cm^{-1}) in compounds **2** [12]. These results unambigously rule out an ionic structure for compounds **1** and **2**, and reduce the probability of the fast intermolecular exchange of oxygen atoms due to the formation of associated species with bridging carboxyl groups (with compound **1a** such association was not observed even in the neat liquid [13]). A further feature also argues against an ionic structure for the compounds; namely that compounds **1a** and **1b** have δ (^{119}Sn) values of 113.4 and 125.5 ppm, respectively ($CDCl_3$, 300 K, tetramethylstannane as the standard) and coupling constants $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C})$ 352.8 and 357.7 Hz, respectively; such parameters are typical of four-coordinate tri-n-butyltin(IV) compounds [3]. The corresponding values for compounds **2** are in the range -117.4 to -161.1 ppm and 549.3 to 618.3 Hz [4], those being typical of five-coordinate di-n-butyltin(IV) compounds [14,15]; the Bu_3Sn^+ cation with planar geometry or Bu_2Sn^{2+} cation with linear geometry should have substantially higher values of $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C})$ owing to a greater contribution of *s* electron density in bonding orbitals of central tin atoms caused by a change in hybridization ($sp^3 \rightarrow sp^2$ in compounds **1** and $sp^3 \rightarrow sp$ or $sp^2 \rightarrow sp$ in compounds **2**). A more likely explanation involves a fast intramolecular exchange (on the NMR time scale) between the two oxygen atoms of the carboxyl group bonded to the tin atom by the process shown in eq. 1 for compounds **1**.

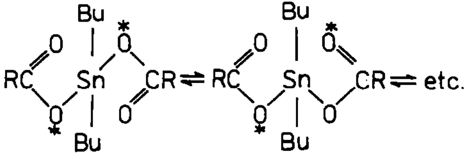


(1)

On the NMR time scale this exchange corresponds to the structure:

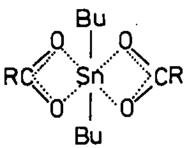


For compounds **2** the corresponding process shown in eq. 2 would apply.



(2)

or



The fast intramolecular exchange shown in these equations assumes that there is chelate bonding of the carboxyl group not only in compounds **2** but also in compounds **1**. Such a structure has been demonstrated for crystals of triorganotin(IV) carboxylates [16,17]. (It should be noted that the bridging nature of the carboxyl group in associated species does not exclude a parallel chelate function [18].) However, the bidentate chelate coordination of the carboxyl group around the tin atom in the organotin(IV) carboxylates has a very asymmetric geometry. Such asymmetry is greater in compounds **1** than in compounds **2** and this accounts for the difficulties of determinating the coordination number of tin in these compounds. In compounds **1** the coordination of oxygen atoms of the carboxyl group to the central tin atom is relatively weak and the geometry differs only slightly from the tetrahedral arrangement of compounds of four-coordinate tin atom [16,17]. The substantially higher Lewis acidity of the di-n-butyltin(IV) group results in a stronger coordination bond Sn...O–C, and so compounds **2**, as shown by the ^{13}C and ^{119}Sn NMR spectra parameters, have structures involving five-coordinate tin. The fast exchange of oxygen atoms in organotin(IV) carboxylates can be regarded as an example of fluxional non-rigidity of a chelate ligand in coordination compounds.

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