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The coupling $^2J(^{119}Sn-O-^{13}CO)$ in tributyltin acetate

Hung-Viet Pham, Bruno Rusterholz, Ernö Pretsch and Wilhelm Simon
Department of Organic Chemistry, Swiss Federal Institute of Technology, CH-8092 Zürich (Switzerland)

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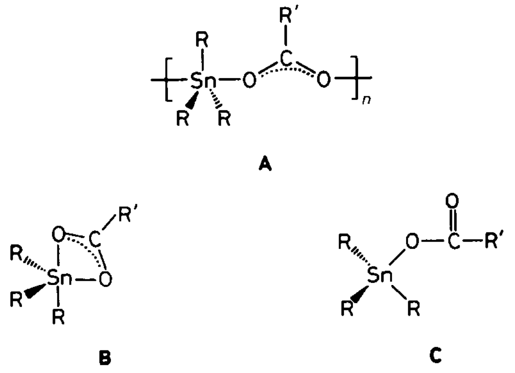
Abstract

The observation of a single coupling between the carbonyl carbon atom and the tin center in tributyltin acetate proves that monomeric structures predominate in diluted $CDCl_3$ solution at low temperatures (< 38 ° C). At higher temperatures (above 38 ° C) no coupling can be observed due to a fast intermolecular exchange of the acetate groups.

Introduction

It is well established that triorganyltin carboxylates form polymeric structures in solid phase as well as in concentrated solutions in organic solvents [1]. However, upon dilution usually oligomeric, and finally, monomeric species containing tetrahedral tin atoms and free carbonyl groups are produced [2]. The crystal structures of many triorganyltin carboxylates have been determinated by X-ray diffraction analysis [2]. These carboxylates in the solid state have two forms, a chain polymeric form (**A**) and monomeric form (**B** or **C**) where R and R′ are alkyl groups (Scheme 1).



Scheme 1.

The most common forms with ligands containing no other coordinating sites than carboxylic groups involve association through carboxylate bridging (type **A**) [2–5]. Typical examples of structure **A** are provided by trimethyltin acetate, $Me_3SnOCOMe$, and trimethyltin trifluoroacetate, $Me_3SnOCOCF_3$ [6]. The geometry at the tin atom is trigonal-bipyramidal. The carbons bonded to the tin atom occupy the equatorial positions with the electronegative oxygen atoms in the axial sites [7].

The monomeric form is one of two structures, the trigonal-bipyramidal (**B**) or the tetrahedral (**C**) one. Usually, bulky R or R′ groups prevent polymer formation. X-ray studies show that triaryltin benzoate derivates are monomers with structure **B** [8,9]. Although both oxygen atoms of the carboxylate were claimed to be coordinating, they were found to be inequivalent, and their distances from the tin atom significantly different [8,9]. The IR spectra of some triaryltin benzoates in KBr pellets and in CCl_4 showed very similar carbonyl stretching frequencies, which were found to be shifted to lower frequencies relative to those of the uncomplexed acid [8,9]. Therefore, this penta-coordinated structure **B** was postulated not only for the solid state triaryltin benzoates, but also for solutions in non-coordinating solvents (e.g. CCl_4) [8,9]. In contrast, NMR studies indicated that triorganyltin carboxylates in non-coordinating solvents such as deuterochloroform contain monomeric molecules with a quasitetrahedral geometry (structure **C**) for the four-coordinated tin atom. Only in coordinating solvents D (e.g. pyridine, dimethylsulfoxide or hexamethylphosphoramide) was a five-coordinated tin species observed, with one coordinating solvent molecule ($R_3SnOCOR' \cdot D$) [10,11]. In these interpretations, the usual NMR parameters e.g. the chemical shifts $\delta(^{119}Sn)$, $\delta(^{13}C)$ and the one-bond coupling constant $^1J(^{119}Sn-^{13}C)$ were used.

We show below that a further NMR parameter, the two-bond coupling constant $^2J(^{119}Sn-O-^{13}C)$ via an oxygen atom, is useful, especially in the determination of the coordination number and the geometry at the tin center in the case of triorganyltin carboxylates.

Experimental

Preparation of $Bu_3Sn-O-^{13}COCH_3$

The carbon-13-enriched tributyltin acetate (TBTA) was prepared by a known method [3,14] from bis(tributyltin)-oxide (TBTO) and carbon-13-enriched acetic acid (90 atom %) (AA). A mixture of TBTO (954 mg, 1.6 mmol) and AA (195 mg, 3.2 mmol) was stirred for 30 min at 120 ° C then cooled to about 50 ° C and 20 ml of hexane was added. The solution was then filtered immediately to remove any unchanged acid. Further cooling led to precipitation of the crude product, which was filtered off by suction and recrystallized twice from hexane: 235 mg (21%) of the product, m.p. 84.8–85.2 ° C were obtained. Anal. found: C 48.13, H. 8.67. TBTA (90% enriched with carbon-13) calc.: C 48.30, H 8.64%.

NMR Measurements

The ^{13}C and ^{119}Sn FT NMR spectra were recorded at 50.32 MHz and 74.63 MHz, respectively, on a 4.70-T Bruker WP 200 SY spectrometer. A 10 mm o.d. tube containing 2.5 ml of 0.2 *M* carbon-13-enriched tributyltin acetate TBTA in deuterochloroform was used at probe temperatures of -50 ° C to $+50$ ° C.

Details of ^{13}C measurements: spectral width, 2525.25 Hz (approximately 50 ppm); acquisition time, 6.488 s; data table size, 32K of 24 bit words; pulse duration, 6 μs (approximately 15°); number of transients, generally 400 to 600; digital resolution, 0.154 Hz/data-point. Broad-band proton decoupling of approximately 2 W with 250 1/h ambient temperature air cooling was applied during the acquisition period. $(CH_3)_4Si$ was used as an internal standard.

Details of ^{119}Sn measurements: spectral width, 3731.34 Hz (approximately 50 ppm); acquisition time, 2.195 s; data table size, 16K; pulse duration, 17 μs (approximately 60°); digital resolution, 0.455 Hz/data-point; number of transients, 1000 to 10000. In order to reduce potentially unfavorable NOE, a broad-band proton decoupling of 2 W was switched off for 4.0 s between the end of the acquisition period and the next pulse. A coaxial 1.2 mm o.d. capillary containing tetramethyltin was used as an external standard.

Reagents

Deuterochloroform (99.8 atom% D) was obtained from Ciba-Geigy AG, Basle, Switzerland and bis(tributyltin)-oxide (purum) from Aldrich GmbH, D-Steinheim. Carbon-13-enriched acetic acid (90 atom %) was obtained from Stohler isotope chemicals (SIC), Azusa, California, USA.

Results and discussion

Although ^{13}C–^{119}Sn-couplings between the carbon atoms of the three organic substituents and the tin atom in trialkyltin carboxylates have been reported in many cases, coupling between the carboxylate carbon and the tin atom has not yet been reported. This might be due either to the fact that the corresponding coupling constant is too small to be observed or to a fast intermolecular exchange. The suggestion of a fast intermolecular exchange is supported by the observation of an anion catalyzed exchange in mixtures of different tributyltin derivatives R_3SnX [12,13]. It has indeed recently been postulated that the predominant species in solution are independent of the nature of X in the dissolved triorganotin compound [14].

In contrast to the above-mentioned fast intermolecular exchange of trialkyltin derivates, a fast intramolecular exchange was suggested for tributyltin acetate in chloroform at temperatures above 57°C [15]. In the ^{17}O NMR spectrum of tributyltin carboxylates only one signal was observed at these temperatures. Its chemical shift (240–276 ppm) lies between those observed for C=O (350–355 ppm) and C-O (125–132 ppm) oxygen atoms in esters [15]. A fast intramolecular exchange was postulated to account for this observation since infrared spectroscopic evidence (no ionic structures observed) was believed to be against an intermolecular exchange [15] (see Fig. 1). This fast exchange of oxygen atoms in triorganyltin carboxylates

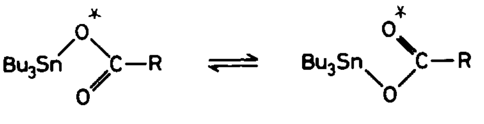


Fig. 1. Postulated intramolecular exchange of $Bu_3SnOCOR$ (according to ref. 15).

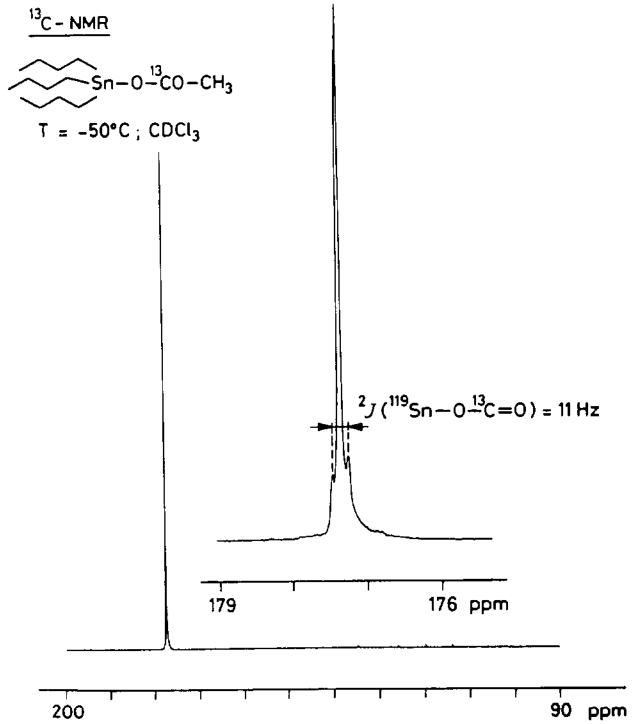


Fig. 2. Determination of the two-bond coupling constant $^{2}J(^{119}Sn\text{-}O\text{-}^{13}C)$ of the compound $Bu_3SnO^{13}COCH_3$ in $CDCl_3$ at −50 °C in the ^{13}C NMR spectrum.

can be regarded as an example of fluxional non-rigidity of a chelate ligand in coordination compounds.

To decide between the conflicting proposals, carbon-13 enriched tributyltin acetate was prepared and investigated at different temperatures by NMR. Figures 2 and 3 show the relevant parts of the ^{13}C NMR spectrum and ^{119}Sn NMR spectrum recorded at −50 °C. A ^{13}C–^{119}Sn coupling constant of 11 Hz was clearly observed. Thus there is no fast intermolecular exchange. The observed splittings (doublet in both spectra) provide direct proof that only monomers are present in the deuterochloroform solution even at this low temperature.

These results confirm clearly that triorganyltin carboxylates exist as monomers in dilute solutions [10]. For a polymeric structure such as A the C=O signal would have a more complex multiplicity in the ^{13}C NMR spectrum, and the ^{119}Sn NMR spectrum would show a coupling to two carbonyl carbon atoms. It was additionally found that the coupling constant $^{1}J(^{119}Sn\text{-}^{13}C)$ between the tin atom and the α-carbon atom of the butyl chains has a value of 360 Hz, which is consistent with a tetrahedral configuration of the tin atom of the type C [3,10,11].

A comparison of the coupling constant $^{2}J(^{119}Sn\text{-}O\text{-}^{13}C)$ ($|J| = 11$ Hz) with those $^{2}J(^{119}Sn\text{-}C\text{-}^{13}C)$ between the tin atom and β-carbon atom of the butyl chains ($|J| = 21$ Hz) shows that coupling between ^{119}Sn and ^{13}C through an oxygen atom is relatively weak. This bond is readily broken if the temperature is raised. Thus no coupling can be detected above 40 °C, in contrast to the situation at low tempera-

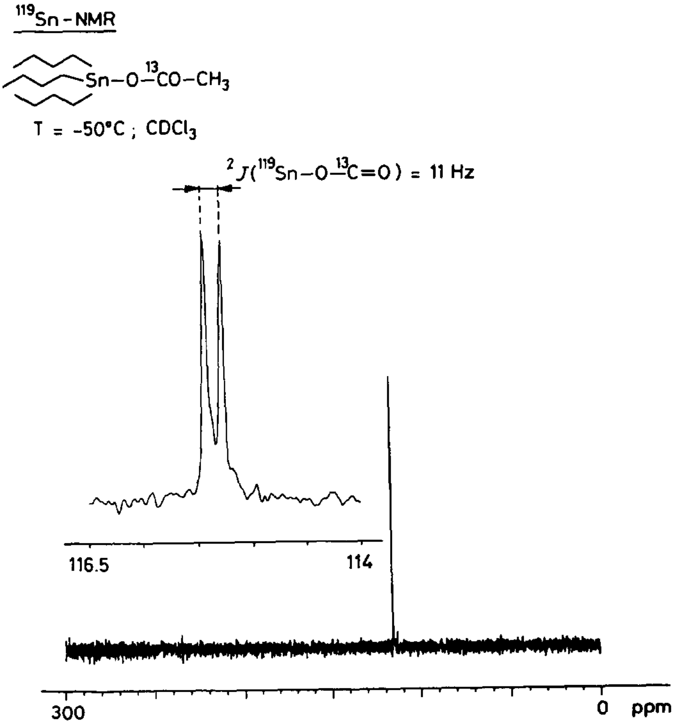


Fig. 3. Determination of the two-bond coupling constant $^2J(^{119}Sn\text{-}O\text{-}^{13}C)$ of the compound $Bu_3SnO^{13}COCH_3$ in $CDCl_3$ at −50 °C in the ^{119}Sn-NMR spectrum.

ture (see Fig. 2 and Fig. 3), because intermolecular exchange becomes fast on the NMR time scale (mean life time < 0.1 s).

Acknowledgement

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