MAGNETIC FIELD DEPENDENCE OF 'H CIDNP IN THE REACTION OF TRIMETHYLTIN HYDRIDE WITH DIBENZYL KETONE

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The magnetic field dependence of ¹H CIDNP in the photochemical reaction of trimethyltin hydride enriched by the stable isotope ¹¹⁷Sn in the presence of dibenzyl ketone as initiator has been analysed. Comparing the experimental and simulated ¹H CIDNP spectra of benzyltrimethyltin shows that the radical pair mechanism can account for the observed CIDNP effects. The absence of a magnetic isotope effect in reactions of tin-containing compounds is discussed with reference to the obtained ¹H CIDNP data.

1. Introduction

Chemically induced dynamic nuclear polarization (CIDNP) has been studied in some reactions of tincontaining radicals [1-3]. Polarized ¹H and ¹¹⁷Sn resonances have been observed in the thermal decomposition of 2,2'-azobis(2-methyl-propionitrile) with trimethyltin hydride [2], in the photochemical decomposition of distannane [3] and 3-oxobutyltrimethyltin [4] and in the photochemical reactions of trimethyltin hydride with di-t-butyl peroxide or dibenzyl ketone [1,2]. These experiments have been explained qualitatively by the radical pair mechanism and also quantitatively in the case of the photochemical decomposition of polystannanes [5]. Because of the large hyperfine coupling constants, tincontaining radicals should be good models for studying the magnetic isotope effect (MIE) of tin [6,7]. This effect could be potentially very important in relation to the separation of isotopes of heavy elements. However, a number of reactions involving tin

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radicals did not demonstrate any noticeable MIE [8,9]. Two possible reasons were given to explain these negative results [8,9]: (i) the existence of a nuclear-spin-independent spin-orbit mechanism of singlet-triplet (S-T) conversion due to the heavy atom effect or (ii) chemical exchange by tin-containing fragments between initial compounds and reaction products [9]. Moreover, Maillard et al. [10] have shown that reaction of tributyltin radicals with oxygen is unusually fast. They suggest that this is due to the heavy atom effect on recombination. However, heavy atom spin-orbit coupling would tend to suppress CIDNP effects, while in fact quite strong ¹¹⁹Sn CIDNP has been observed [5]. Thus, a discrepancy exists between the CIDNP effects observed and the absence of magnetic isotope effects. The present ¹H CIDNP study on tin-containing radicals has been undertaken to gain more insight into this matter. The magnetic field dependence of the 'H CIDNP effect of the reaction between trimethyltin hydride (containing both the magnetic ¹¹⁷Sn and nonmagnetic ¹¹⁸Sn isotopes) and dibenzyl ketone has been obtained and is compared with ¹H CIDNP simulations. Low field CIDNP has been used to test whether CIDNP effects on the reaction considered can be explained using the radical pair mechanism [11].

2. Experimental

The photochemical experiments were carried out with a FT-NMR spectrometer (Varian XL-100) operating at 100 MHz which is equipped with a NMR light probe with external 'H lock. For the field-dependent CIDNP measurements the following system was used: The unfiltered light of a mercury lamp (Philips SP-1000WQ) was focused with quartz optics on a rotating quartz NMR tube located in an auxiliary magnet above the magnet of the spectrometer. After a 2s light pulse and 1s delay during which the sample tube moves from the auxiliary magnet to the probe by gravitation, a detection pulse was set off. The spectral width was 1000 Hz. A more detailed description of the falling tube system for sample transfer between magnets is given in ref. [12].

Solutions of dibenzyl ketone (Aldrich) 0.05M and trimethyltin hydride 0.08M in benzene- d_6 were degassed by dry nitrogen (300s) in a NMR tube. Trimethyltin hydride and benzyltrimethyltin with isotope ¹¹⁷Sn were prepared from metallic tin (92% ¹¹⁷Sn, 8% ¹¹⁸Sn) as reported earlier [9]. A computer program [11] was used to simulate the field dependence of the polarized resonances of interest.

3. Results and discussion

In accordance with Lehnig [2] the mechanism for the photochemical reaction of trimethyltin hydride, enriched by ¹¹⁷Sn, with dibenzyl ketone is taken to be the following:

?hCH₂COCH₂Ph ╤╧	$PhCH_2 +$	$OCCH_2Ph$,	(1)
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t. . .

$$PhCH_2CO \rightarrow PhCH_2 + CO, \qquad (2)$$

$$2 \operatorname{PhCH}_{2} \rightarrow \operatorname{PhCH}_{2} \operatorname{CH}_{2} \operatorname{Ph}, \qquad (3)$$

$$PhCH_{2} + Me_{3}SnH \rightarrow PhCH_{3} + Me_{3}Sn^{2}, \qquad (4)$$

$$PhCH_2 + Me_3Sn \rightarrow PhCH_2SnMe_3, \qquad (5)$$

$$2 \operatorname{Me}_{3} \operatorname{Sn}^{*} \to \operatorname{Me}_{6} \operatorname{Sn}_{2}.$$
(6)

A typical ¹H CIDNP spectrum is shown in fig. 1B. The most interesting tin-containing products in this reaction, from the point of view of CIDNP, is the recombination product of benzyl and trimethyltin radicals: benzyltrimethyltin (5). We measured the field dependence of ¹H CIDNP generated in fields from 5 to 800 mT (fig.2). In the benzyltrimethyltin molecules with ¹¹⁷Sn the multiplet effect changes sign between 5 and 15 mT (figs. 2a-2c) and the maximum intensity of the net effect occurs at 7 mT (fig. 2b), a sing reversal of the net effect occurs in a field



Fig. 1. ¹H NMR spectrum of the reaction mixture of trimethyltin hydride (0.08M) and dibenzyl ketone (0.05M). (A) before and (B) Is after illumination. CIDNP was generated in a magnetic field of 200 mT.



Fig. 2. 'H CIDNP field dependence spectra of the methylene protons of benzyltrimethyltin. Top row: observed 'H CIDNP spectra. Bottom row: corresponding simulated 'H CIDNP spectra at the indicated field values of the auxiliary magnet. The singlet at 2.15 ppm (q) is due to the methylene protons in the compound containing the ¹¹⁸Sn isotope. The doublet at 2.24 and 2.06 ppm is due to the coupling of these methylene protons with the ¹¹⁷Sn isotope.

of 100 to 150 mT (figs. 2e–2f). For molecules containing ¹¹⁸Sn the CIDNP in low field is very weak (fig. 2a–2d); it changes sign and becomes stronger than the doublet components of PhCH₂¹¹⁷SnMe₃ in high field. In the calculations we took into account all the nuclei of trimethyltin and benzyl radicals possessing magnetic moments, but substituted the hyperfine coupling constants of the aromatic ring protons of the benzyl radical by $A_{eff} = \sqrt{\sum_i A_i^2}$. The polarization of the methylene protons of benzyltrimethyltin may be built up not only in the radical pair

PhCH₂ 'SnMe₃

(encounter pairs of uncorrelated free radicals) but also in the pair

PhCH₂ OCCH₂Ph

(triplet pairs). Therefore we calculated CIDNP for both radical pairs separately and added the spectra with weighting factors determined at a magnetic field of 800 mT. Parameters used in the calculation are presented in table 1.

The agreement between experimental and simulated ¹H CIDNP effects is quite good at all field values of the auxiliary magnet (fig. 2). The radical pair

Table 1

g-values and hyperfine coupling constants of the radicals to calculate CIDNP intensities of the methylene group is polarised benzyltrimethyl¹¹⁷Sn and benzyltrimethyl¹¹⁸Sn

Radical	g-value	Hyperfine coupling constant (mT)
Me ₃ Sn	2.0163 [13]	$a({}^{117}Sn) = -153.0 [13]$ $a_{H}^{CH_3} = 0.25 [13]$
PhCH ₂	2.0026 [14]	$a_{\rm H}^{\rm CH_2} = -1.63 [14]$ $a_{\rm H}^{o} = -0.52 [14]$ $a_{\rm H}^{m} = 0.18 [14]$ $a_{\rm H}^{m} = -0.62 [14]$
PhCH ₂ CO	2.0007 [15]	$a_{\rm H}^{\rm CH} = 0.04$ [15]

mechanism is therefore sufficient to explain the experimental 'H CIDNP results.

The presence of strong spin-orbit coupling to explain the absence of a MIE for tin is not only unlikely from the theoretical point of view [16], but also is not supported by the present experiments. A spinorbit coupling interaction of the same order as the large hyperfine coupling interaction of ¹¹⁷Sn in the trimethyltin radical (see table 1) is necessary to suppress the MIE. ¹H CIDNP effects will then not be present in the case of the trimethyltin radical with nonmagnetic tin due to the small hyperfine coupling constant of 'H in this radical (see table 1), contrary to what is observed for benzyltrimethyl ¹¹⁸Sn (fig. **IB**). The spin-orbit coupling interaction thus plays only a minor role in the radical pair intersystem crossing. Therefore, we suggest that the absence of a MIE of tin [8,9] has a chemical reason. As shown experimentally [9] rapid exchange between radical pair products and starting compounds leading to isotope scrambling occurs in many tin-containing compounds and would tend to mask the primary magnetic isotope effects.

The present observations of CIDNP in magnetic and nonmagnetic tin-containing products can be completely accounted for by the radical pair mechanism and show that even for these heavy-metal-centered radicals spin-orbit coupling is not important in radical pair reactions. Therefore, for successful detection of MIE in these systems the chemical exchange reactions should be suppressed.

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