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Magnetic Isotope Effect in the Photolysis of Organotin Compounds

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Photolysis of organotin molecules $RSnMe_3$ is shown to be a spin selective radical reaction accompanied by fractionation of magnetic, $^{117,119}Sn$, and nonmagnetic, $^{118,120}Sn$, isotopes between starting reagents and products. A primary photolysis process is a homolytic cleavage of the C−Sn bond and generation of a triplet radical pair as a spin-selective nanoreactor. Nuclear spin dependent triplet−singlet conversion of the pair results in the tin isotope fractionation. Experimentally detected isotope distribution unambiguously demonstrates that the classical, mass-dependent isotope effect is negligible in comparison with magnetic, spin-dependent isotope effect.

Introduction

Fractionation of isotopes in chemical and biochemical reactions is induced by two isotope effects; their origin and physical nature are shown in Figure 1. A birth of molecule, as a central event in chemistry, is controlled by two physical factors—energy and angular momentum. The two interactions, different in nature and scale—Coulomb and magnetic, stand behind these factors. The former creates classical, mass-dependent isotope effect; the latter is a source of magnetic, nuclear spin-dependent isotope effect. After the first isotope effect stands an old, widely recognized and deserved mass-selective isotopy; the magnetic isotope effect as a fundamental phenomenon introduces in chemistry and related sciences a new, nuclear spin-dependent isotopy.

The physics of these two isotopies are completely different: the former is based on the difference in energy of isotopic molecules; the latter appeals to the difference in nuclear spins and nuclear magnetic moments of reagents. The classical isotope effect (CIE) sorts isotopic nuclei on their masses; the magnetic isotope effect (MIE) demonstrates nuclear spin selectivity of reactions and separates isotopic nuclei according to their magnetic moments.[1]

Since the discovery in 1976,[2] MIE was detected in many chemical reactions, for many isotopic pairs and triads (H−D, $^{12}C-^{13}C$, $^{16}O-^{17}O-^{18}O$, $^{28}Si-^{29}Si-^{30}Si$, $^{32}S-^{33}S-^{34}S$, $^{72}Ge-^{73}Ge-^{74}Ge$, $^{235}U-^{238}U$, $^{198,200}Hg-^{199,201}Hg$, $^{24}Mg-^{25}Mg-^{26}Mg$). In all these cases chemical reactivity of reagents with magnetic nuclei is strongly different from that of reagents with nonmagnetic, spinless nuclei.[3] An attempt to detect MIE-induced fractionation of tin isotopes was made in 1979 and seemed to be successful;[4] however, in 1985 the same authors in more careful experiments did not confirm the results of previous publication.[5] The purpose of this paper is to declare reliably detected MIE on the tin nuclei in the photolysis of tin organic compounds.

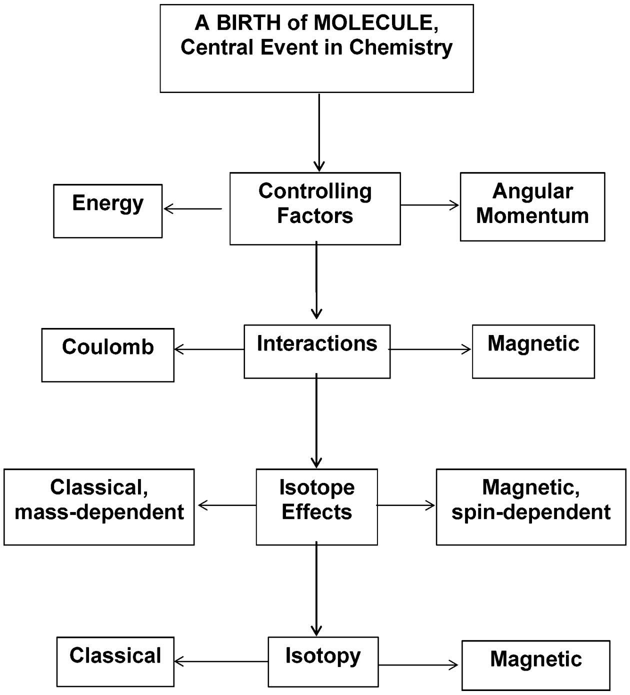

Figure 1. Scheme illustrating the origin and physical nature of classical and magnetic isotopies.

Experimental Section

(1-Naphthylmethyl)trimethyltin (**1**) and (9-fluorenyl)trimethyltin (**2**) were synthesized and purified according to a known procedure.[6,7] Photolysis of both starting compounds **1** and **2** was carried out in tetrahydrofurane-d_8 solutions, 0.1 M, in Pyrex NMR tubes 5 mm in diameter, sealed under vacuum. NMR tube with solution was placed in a quartz vessel filled with water at 25 °C and was rotated with a rate of 2 rpm. Irradiation was performed with a light from a high-pressure mercury lamp using a filter to select spectral line at 365 nm.

Both chemical and isotope composition of the reaction mixture were analyzed by ^{1}H and ^{13}C NMR spectroscopy on

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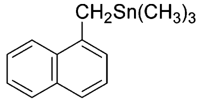
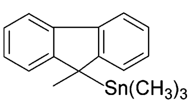
the Bruker AVANCE−600 spectrometer using procedure described previously.[8,9]

Results and Discussion

Photolysis Products and NMR Spectra. ^{1}H and ^{13}C NMR spectra of the starting compounds **1** and **2** were monitored during the photolysis as well as reaction products **3** and **4** from **1** and **3**, **5**, and **6** from **2**. In the latter case the yields of **5** and **6** were nearly equal. No other products whose concentration would exceed more than 5% of the starting compounds were detected at the conversion 60−70%.



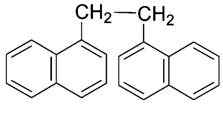
1



2

$(CH_3)_3Sn\text{-}Sn(CH_3)_3$

3



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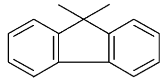

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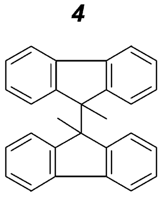

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As an example, the ^{13}C NMR spectrum with signal assignment in the high-field region is shown in Figure 2. The signal from **1** and **2** is easily identified as the two pairs of $^{13}C-^{117,119}Sn$ satellites (nuclear spins of both tin isotopes are identical, $^1/_2$; magnetic moments are only slightly different, −1.0 and −1.046 μB for ^{117}Sn and ^{119}Sn respectively, so that spin−spin coupling constants $J(^{13}C-^{117}Sn)$ and $J(^{13}C-^{119}Sn)$ differ by 5% only). Some pairs belong to the $^{13}CH_2Sn(CH_3)_3$ fragment of **1** (at 18.5−16.0 ppm) and $^{13}CHSn(CH_3)_3$ fragment of **2** (at 38.5−40.5 ppm); other pairs refer to $^{13}CH_3Sn(CH_3)_2$ fragments in **1** and **2**, and they fall in the region from −9 to −12 ppm (see Figure 2a,b).

The ^{13}C NMR signal of **3** consists of four pairs of satellites: the two inner pairs belong to fragment $^{13}CH_3-Sn-^{117,119}Sn-$; the outer pairs refer to the $^{13}CH_3-^{117,119}Sn-Sn-$ fragment (Figure 2). Central NMR lines of satellites belong to the same fragments with nonmagnetic, spinless tin nuclei, mainly to ^{116,118,120}Sn. Some lines in the spectra of **1**−**3** and **2** and **3** are superimposed or overlapped.

Chemical conversion F was determined from the ratio of signal intensities of **1** and **3** (for **1**) and of **2** and **3** (for **2**) under the assumption that the $Sn(CH_3)_3$ group is transferred from the starting reagents into the products as a whole. Isotope composition was determined by iteration analysis of the total line shape in the ^{13}C NMR spectral region containing signals of the Me$_3$-Sn groups, taking into account the residual inhomogenity of the polarizing magnetic field and phase distortions using the INTSPECT-2 program, as described elsewhere.[8,9]

Isotope Fractionation. Isotope enrichment (or depletion) S is determined as the ratio

$$S = (A^*)/(A_0^*) \tag{1}$$

where (A^*) is the concentration of certain isotopomer during the reaction and (A_0^*) is that in the starting compounds **1** and **2** initially. Figure 3a exhibits the isotope fractionation between the starting reagent **1** and product **3**; it shows the dependence of S on the chemical conversion F in terms of eq 2 (see later). As the starting reagent **1** decomposes, its remaining fraction is enriched with ^{117,119}Sn magnetic isotopes ($S > 1$), whereas the reaction product **3** is depleted with these isotopes ($S < 1$) and, respectively, enriched with nonmagnetic ^{118,119}Sn nuclei.

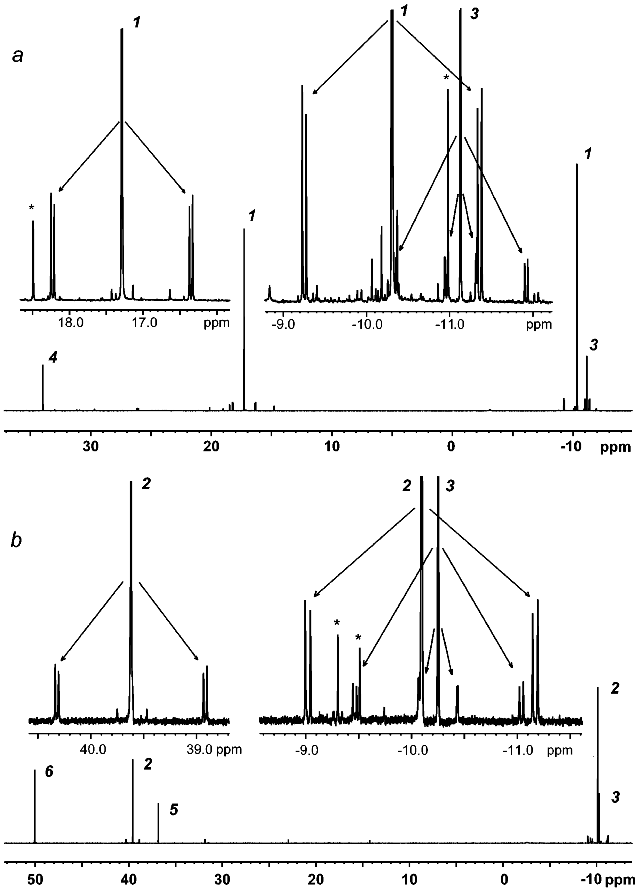
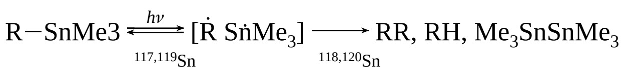


Figure 2. Fragments of the $^{13}C-\{^1H\}$ NMR spectra of compounds **1**, **3**, and **4** (a) and **2**, **3**, **5**, and **6** (b). Arrows indicate the ^{119}Sn and ^{117}Sn satellites, a star denotes signals from admixtures.

A similar fractionation of magnetic and nonmagnetic isotopes was detected in the photolysis of **2** (Figure 3b). The only difference is that for **2** the measurement of isotopic contents of ^{117}Sn at the conversions more than 30% was not successful because of NMR lines overlapping.

Isotope fractionation unambiguously demonstrates that the photolysis of organotin compounds is a spin-selective reaction in which magnetic isotope effect functions. The reaction scheme for both compounds **1** and **2** can be presented in generalized form as follows:



$$R-SnMe3 \underset{^{117,119}Sn}{\overset{h\nu}{\rightleftharpoons}} [\dot{R}\ \dot{S}nMe_3] \underset{^{118,120}Sn}{\longrightarrow} RR, RH, Me_3SnSnMe_3$$

where R denotes the organic radical in **1** and **2**, RR corresponds to **4** and **6**, and RH is **5**.

The spin-selective monoreactor is a radical pair in the triplet spin state,[10] generated by homolytic cleavage of the C−Sn bond. Recombination of radicals in this nanoreactor is spin forbidden; however, the pairs with magnetic nuclei ^{117,119}Sn undergo very fast triplet−singlet spin conversion and recombine in the singlet spin state, regenerating starting reagents enriched with magnetic

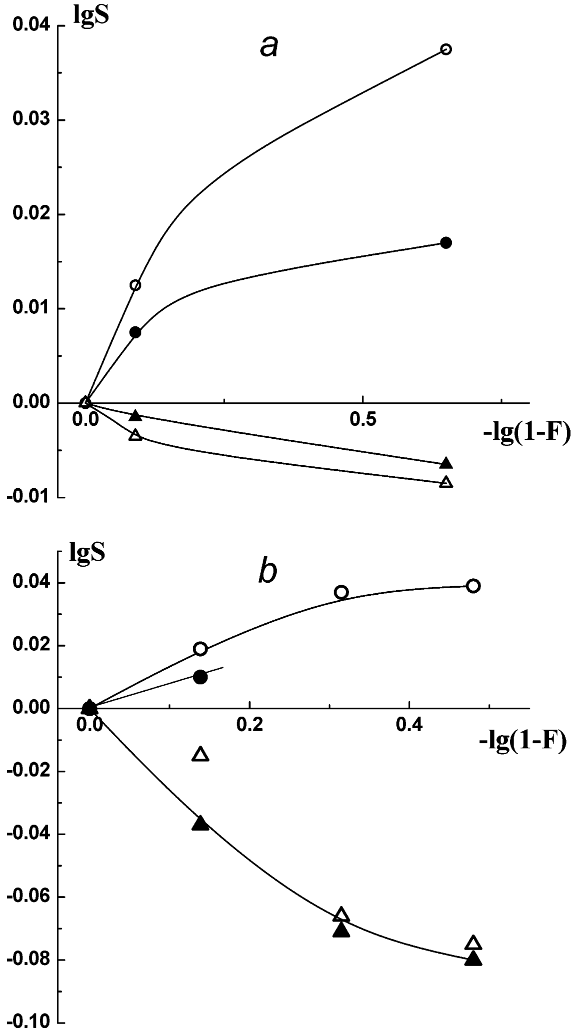


Figure 3. Isotopic composition as a function of chemical conversion F at the photolysis of **1** (a) and **2** (b). Open circles refer to ^{119}Sn, filled circles to ^{117}Sn in **1** and **2**; triangles refer to **3**: open ones to ^{119}Sn, filled ones to ^{117}Sn.

isotopes. Triplet−singlet spin conversion is induced by strong magnetic electron−nuclear interaction (hyperfine coupling) between an unpaired electron and the ^{117,119}Sn nuclei in the $SnMe_3$ radical; its magnitude is 4.3×10^9 and 4.5×10^9 Hz for ^{117}Sn and ^{119}Sn nuclei, respectively.[11] These frequencies are adequate to the rate of triplet−singlet spin conversion of the pairs with magnetic tin nuclei.

The rate of spin conversion of the pairs with nonmagnetic tin nuclei is by 2 orders of magnitude slower than that of the pairs with magnetic nuclei, so that these pairs mostly dissociate and result in reaction products of escaped radicals and one of them, $SnMe_3$, carries an excess of nonmagnetic tin nuclei. As a result, magnetic tin nuclei are accumulated in the starting molecules **1** and **2**.

The theory of magnetic isotope effect[1] predicts a linear relation between S and F in coordinates log S and $\log(1 - F)$:

$$\log S = \left(\frac{1 - \alpha}{\alpha}\right) \log(1 - F) \tag{2}$$

where α is a one-step enrichment coefficient:

$$\alpha = (1 - P)/(1 - P^*) \tag{3}$$

Here P and P^* are recombination probabilities of the pairs with nonmagnetic and magnetic nuclei; because $P^* > P$, $\alpha > 1$. Equation 2 is known to be rigorously fulfilled for magnetic isotope effects of all elements, wiht the exception of tin (Figure 3), for which this dependence strongly deviates from the linear one. The reason of exception is a reaction of exchange by $SnMe_3$ groups:

$$\mathrm{R\mathbf{Sn}Me_3} + \dot{\mathrm{S}}\mathrm{nMe_3} \rightarrow \mathrm{RSnMe_3} + \dot{\mathbf{S}}\mathbf{n}\mathrm{Me_3}$$

which produces also isotope exchange and tends to equalize isotope composition of starting reagents and products. A competition between these two processes, isotope fractionation in the primary reaction and isotope scrambling in the secondary reactions, decreases the of efficiency of isotope separation already at rather low chemical conversion, about 20−30%.

Another problem, as seen from Figure 3, is that at first sight there is no isotope balance between starting reagents and products. The reason for this apparent imbalance is a limitation of isotope analysis by NMR because of differences in nuclear relaxation times and partial NMR lines overlapping. The same limitation results in an apparent difference in fractionation of ^{117}Sn and ^{119}Sn despite the fact that both these nuclei have almost identical magnetic moments (the difference is about 5%), so that the difference in fractionation is expected to be not more than 5%.

Conclusion

For the first time we observed the magnetic isotope effect on the tin nuclei in the photolytic reactions of (1-naphthylmethyl)trimethyltin and (9-fluorenyl)trimethyltin. The reactions are nuclear spin selective and fractionate magnetic and nonmagnetic tin isotopes (^{117,119}Sn and ^{118,120}Sn, respectively): the former are accumulated in the starting molecules, the latter are concentrated in the reaction product hexamethyldistannane. One-step enrichment coefficients, estimated at low chemical conversions, are 1.16 and 1.15 for the two organotin compounds; however, at higher conversions the exchange reaction reduces the efficiency of isotope separation and tends to equalize the isotope composition of starting reagents and products.

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