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Chemically induced magnetic isotope effect on tin nuclei

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A magnetic isotope effect on ^{117}Sn and ^{119}Sn nuclei was observed for the first time in the photolysis of (1-naphthylmethyl)-trimethyltin 1. The isotope effect is accompanied by the fractionation of magnetic and non-magnetic tin isotopes: the magnetic isotopes are accumulated in starting compound 1, whereas the non-magnetic isotopes predominate in the photolysis product, hexamethyldistannane 2.

Magnetic isotope effect is a dependence of the chemical reaction rate on the spin and magnetic moment of the nuclei of reactants. This phenomenon is manifested in spin-selective reactions of paramagnetic species (atoms, radicals, radical ions, metal ions, triplet and high-spin molecules) and results in the fractionation of isotopes over their magnetic moments. The effect was discovered in 1976 for carbon isotopes[1] and then found for many other isotope pairs and triads (^{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; ^{199,201}Hg/^{200,202}Hg; ^{24}Mg/^{25}Mg/^{26}Mg; ^{235}U/^{238}U).[2–4]

An attempt[5] to find the fractionation of tin isotopes has been made as early as in 1979 and, seemingly, was successful. However, in 1985, Podoplelov *et al.*[6] did not find this effect in more thorough experiments but determined a reason for failure and indicated ‘reefs’ in the way to nuclear-spin selectivity of reactions of organotin compounds. The purpose of this work was to declare the discovery of a magnetic isotope effect on tin nuclei in the photolysis of (1-naphthylmethyl)trimethyltin.

(1-Naphthylmethyl)trimethyltin **1** was synthesised and purified using a known procedure.[7] Photolysis of compound **1** in a concentration of 0.1 mol dm^{-3} in [^{2}H$_8$]THF was carried out in evacuated Pyrex NMR tubes 5 mm in diameter at room temperature with light from a DRSh-500 mercury lamp using a filter to isolate a line at 365 nm. An NMR tube was placed in a quartz

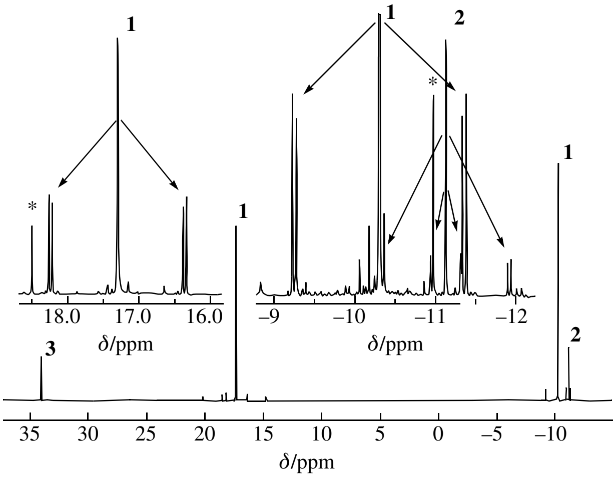

Figure 1 Fragments of the ^{13}C-{^1H} NMR spectra of compounds **1**, **2** and **3**. Arrows indicate the ^{119}Sn and ^{117}Sn satellites used in calculations, and * denotes signals from admixtures.

cell filled with water and revolved under irradiation with a rate of 2 rpm. Irradiation was monitored by absorption spectra. The solvent (Merck) enriched in deuterium (99.95%) was used as received. The reaction mixture was analysed in the course of photolysis by ^1H and ^{13}C NMR spectroscopy on a Bruker AVANCE-600 spectrometer using a procedure described previously.[8,9]

In the course of the reaction, the ^1H and ^{13}C NMR spectra exhibited the intensity of signals from starting compound **1**, additional signals of the photolysis products (hexamethyldistannane $Me_3SnSnMe_3$ **2** and 1,2-dinaphthyl **3**) appeared, and their intensity increased (equation 1). We detected no other products, whose concentration would exceed 5%, by the NMR spectra.

$$2C_{10}H_7CH_2SnMe_3 + h\nu \longrightarrow Me_3SnSnMe_3 + (C_{10}H_7CH_2)_2 \qquad (1)$$

The ^{13}C NMR spectrum with signal assignment in the high-field region (signals of the Me_3Sn groups) is presented in Figure 1. In this spectrum, the signal from **2** is easily identified from two pairs of ^{13}C–$^{117/119}Sn$ satellites. The degree of transformation of **1**, *i.e.*, chemical conversion *F*, was determined from the ratio of intensities of signals from **1** and **2**. The isotope composition of the products was determined by iteration analysis of the total line shape in the ^{13}C NMR spectral region containing signals of the Me_3Sn groups, taking into account the residual inhomogenity of the polarising magnetic field and phase distortions using the INTSPECT-2 program, as described elsewhere.[8,9] The spectra were integrated at irradiation time intervals of 0, 2200 and 7000 min.

The degree of isotope enrichment (or depletion) *S* is expressed through the correlation

$$S = A^*/A_0^*, \qquad (2)$$

where A^* is the concentration of the corresponding isotopomer at the time moment *t*, and A_0^* is the initial concentration of the respective isotope in stating compound **1**.

The main result of the study is presented in Figure 2 in the form of changes in the isotope compositions of **1** and **2** as functions of the chemical conversion *F*. It is clear from these data that, during photolysis, starting (1-naphthylmethyl)trimethyltin **1** is enriched in the ^{117}Sn and ^{119}Sn magnetic isotopes and for **1** $S > 1$, while hexamethyldistannane $Me_3SnSnMe_3$ **2** is depleted in these isotopes and, hence, for this compound, $S < 1$. Thus, we succeeded to obtain reliable evidence that the photolysis of compound **1** is accompanied by the fractionation of tin isotopes over the magnetic moment; *i.e.*, the magnetic isotope effect on the tin nuclei is observed.

Analysis of the chemical and isotope compositions of the reaction products shows that the photolysis of **1** results in the homolytic cleavage of the C–Sn bond and the generation of a triplet radical pair **4** (equation 3):

$$C_{10}H_7CH_2SnMe_3 \overset{h\nu}{\rightleftarrows} [C_{10}H_7\dot{C}H_2\ \dot{S}nMe_3]^T \longrightarrow C_{10}H_7\dot{C}H_2 + \dot{S}nMe_3. \qquad (3)$$

Further transformations of the radical pairs occur *via* two main routes. The radical pair dissociates partially with radical escape into the volume, where they further recombine pairwise to form **2** and **3**. However, the most significant channel of radical pair transformation is spin triplet–singlet intersystem crossing followed by radical recombination inside the pair, leading to the regeneration of compound **1**. In this case, the radical pair acts as a spin-selective nanoreactor in which the intersystem crossing is selective by both electron and nuclear spin: the pairs containing the magnetic ^{117}Sn and ^{119}Sn isotopes experience a fast triplet–singlet intersystem crossing and preferentially recombine. The intersystem crossing of pairs with the non-magnetic ^{116}Sn, ^{118}Sn and ^{120}Sn isotopes is late because it is induced by much weaker magnetic interactions with the protons of radicals. These pairs dissociate predominantly to afford **2** and **3**. As a result, starting compound **1** is enriched in magnetic isotopes, and **2**, being a recombination product of the $SnMe_3$ radicals that left the pair, is depleted in the latter. We experimentally observed this phenomenon of isotope fractionation over magnetic moments of their nuclei.

The fast triplet–singlet intersystem crossing of radical pair **4** is induced by strong magnetic interactions of an unpaired electron with the ^{117}Sn and ^{119}Sn tin nuclei. The energies of this interaction are 4.3×10^9 and 4.5×10^9 Hz for the ^{117}Sn and ^{119}Sn nuclei, respectively.[9] Because of this, ^{119}Sn fractionation should be more efficient than the fractionation of ^{117}Sn. Indeed, this was observed in experiments (Figure 2): **1** accumulates the ^{119}Sn nuclei, whereas **2** looses them to a greater extent than the ^{117}Sn nuclei. Since we have observed for the first time such a significant difference in magnetic effects on nuclei of the same isotope, we will study this phenomenon in more detail elsewhere.

For the partially reversible spin-selective reaction (equation 3), the concentration of an isotope (^{117}Sn or ^{119}Sn) *S* in the starting reactant as a function of chemical conversion *F* should satisfy the following correlation:[2]

$$\log S = (1 - \alpha) \log (1 - F), \qquad (4)$$

where α is the coefficient of isotope fractionation, determining the ratio of the reaction rate of molecules containing a magnetic isotope to that of molecules without magnetic isotopes, and is expressed by the correlation

$$\alpha = (1 - P)/(1 - P^*), \qquad (5)$$

where *P* is the probability of recombination of a pair with the non-magnetic isotopes, and P^* is the above probability for a pair with the ^{119}Sn and ^{117}Sn magnetic isotopes. The already

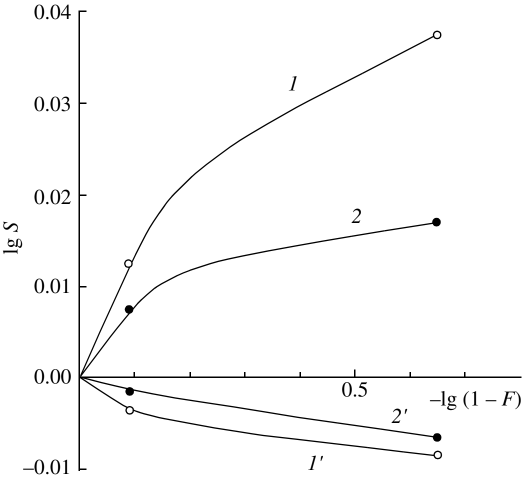

Figure 2 Dependence of the ^{117}Sn and ^{119}Sn isotope content in **1** (*1*, *2*) and **2** (*1′*, *2′*) on chemical conversion [in the coordinates of equation (4)]. Curves *1* and *1′* concern the ^{119}Sn isotope (open circles), and curves *2* and *2′* show the ^{117}Sn isotope (solid circles).

accumulated rich experience on the fractionation of magnetic and non-magnetic isotopes in these reactions[2] shows that correlation (4) is always fulfilled rather rigidly. For the photolysis of **1**, this dependence deviates strongly from linearity. Figure 2 shows that the enrichment of **1** and depletion of **2** in the magnetic tin isotopes tend, most likely, to some limiting values. This phenomenon is caused, most reasonably, by the exchange reaction

$$C_{10}H_7CH_2Sn^*Me_3 + {}^{\bullet}SnMe_3 \longrightarrow C_{10}H_7CH_2SnMe_3 + {}^{\bullet}Sn^*Me_3. \qquad (6)$$

The ${}^{\bullet}SnMe_3$ radicals, which escaped into the volume from the primary radical pair and were depleted in the magnetic isotopes, transfer the latter to **1** *via* reaction (6), thus compensating its isotope enrichment. On the contrary, the appearance of the ${}^{\bullet}Sn^*Me_3$ radicals (enriched in the magnetic tin isotopes) in the volume due to this exchange increases the content of the latter in hexamethyldistannane **2** that formed. This isotope exchange *via* the radical mechanism is additionally evidenced by the fact that the isotopomers containing ^{119}Sn and ^{117}Sn behave similarly, and their limiting values are achieved in parallel. The contribution of exchange reaction (6) increases with an increase in the chemical conversion because the fraction of regenerated (isotope-enriched) **1** increases. Undoubtedly, the second reaction of radical exchange in **2** also occurs (equation 7)

$$Me_3Sn^*SnMe_3 + {}^{\bullet}SnMe_3 \longrightarrow Me_3SnSnMe_3 + {}^{\bullet}Sn^*Me_3. \qquad (7)$$

Both of these exchange processes can cause the achievement of a stationary limit by fractionation and were the main reasons for failure of the authors of preceding works.[6,7]

The initial slope of the $\log S$ *vs.* $\log(1 - F)$ plot makes it possible to estimate $\alpha(^{119}\text{Sn}) \approx 1.15$. For comparison, note that in the classical photolysis reaction of dibenzyl ketone $\alpha(^{13}\text{C})$ is only 1.04.[2]

Thus, we found for the first time the magnetic effect on tin nuclei and obtained data on the mechanism of its appearance.

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References

1 A. L. Buchachenko, E. M. Galimov, V. V. Ershov, G. A. Nikiforov and A. D. Pershin, *Dokl. Akad. Nauk SSSR*, 1976, **228**, 379 (in Russian).

2 A. L. Buchachenko, *J. Phys. Chem.*, 2000, **A104**, 5660.

3 A. L. Buchachenko, D. A. Kouznetsov and A. V. Shishkov, *J. Phys. Chem.*, 2004, **A108**, 702.

4 A. L. Buchachenko, D. A. Kouznetsov, S. E. Arkhangel'skii, M. A. Orlova and A. A. Markaryan, *Dokl. Akad. Nauk*, 2005, in press.

5 A. V. Podoplelov, T. V. Leshina, R. Z. Sagdeev, Yu. N. Molin and V. I. Gol'danskii, *Pis'ma v ZhETF*, 1979, **29**, 419 (in Russian).

6 A. V. Podoplelov, Sen Chel Su, R. Z. Sagdeev, M. S. Shtein, V. M. Moralev, V. I. Gol'danskii and Yu. N. Molin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2207 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2041).

7 M. Builpitt, W. Kitching, W. Adcock and D. Doddrell, *J. Organomet. Chem.*, 1976, **116**, 187.

8 V. A. Roznyatovsky, Yu. A. Ustynyuk, A. Kh. Vorob'ev, N. N. Zemlyanskii and I. V. Borisova, *Zh. Fiz. Khim.*, 2004, **78**, 1281 (*Russ. J. Phys. Chem.*, 2004, **78**, 1277).

9 V. A. Roznyatovsky, V. V. Roznyatovsky and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2102 (in Russian).

10 Landolt-Börnstein, in *Magnetic Properties of Free Radicals*, ed. H. Fisch, Springer-Verlag, Berlin, 1990, vol. 17.

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