

Application of the magnetic isotope effect in the separation of heavy isotopes based on the example of tin

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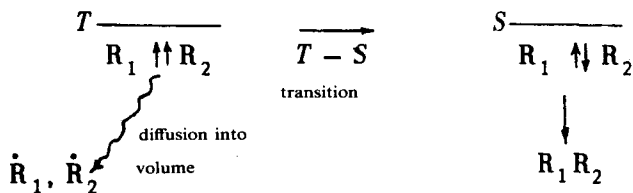
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The first experimental confirmation was obtained for the possibility of heavy isotope separation based on the use of the magnetic isotope effect.

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The isotope effects which are known to chemical physics and the existing methods of isotope separation (also including laser methods) are based, ultimately, on the difference of isotopic masses. Recently, a fundamentally new isotope effect was reported^{1,2} (the so called magnetic isotope effect) in radical chemical reactions in solutions which is based on the difference of the magnetic moments of isotopes.

Magnetic isotope effects (MIE) occur in a pair of two free radicals with uncompensated electron spins. Such a pair may exist in two electronic states: singlet and triplet. The most likely to exhibit MIE are the following triplet pairs:



Recombination of a radical pair (RP) in the triplet state is forbidden by the spin. The hyperfine interaction (HFI) $A\vec{I}\cdot\vec{S}$ with the magnetic nuclei in the radicals violates this spin selection rule as it mixes the singlet and triplet RP terms. The probability of T - S -conversion induced by HFI is defined, in the simplest case, by the following expression:³

$$P_{T-S} = \frac{1}{2} \frac{I(I+1)A^2 r_m^2}{1 + (I + 1/2)^2 A^2 r_m^2}$$

(τ_m is a mean RP lifetime). It follows from (1)* that in the case of short-lived RPs ($A\tau_m < 1$) the difference of the HFI constants or nuclear spins of isotopes leads to their selection. Moreover, the product of radical recombination R_1R_2 will be the enrichment of magnetic isotopes and the conversion products of radicals diffused into the volume will be depleted.

The literature heretofore describes MIEs for hydrogen, carbon, nitrogen and oxygen.^{1,2,4,5} In this letter we report on the first experimental results concerning isotope effects of a magnetic nature observed for heavy elements. We investigated the radical reaction of dissociation of trimethylolhydride $(\text{CH}_3)_3\text{SnH}$ in the absence of a radical starter—nitrodiisobutyronitrile. The role of a starter in the given reaction consists, basically, of the generation of radicals $\cdot\text{Sn}(\text{CH}_3)_3$. It is notable that, HFI constants of magnetic nuclei of Sn^{117} (7.6% content) and Sn^{119} (8.58% content) in these radicals attain very high values (-1530 Oe for Sn^{117} and -1611 Oe for Sn^{119}).⁶ This allows one to expect appreciable effects of separation of the magnetic and nonmagnetic tin isotopes.

In the reaction in question the magnetic effects occur in the pair $(\text{CH}_3)_3\text{Sn} + \text{Sn}(\text{CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ (A). In this case the electron spins of a RP are uncorrelated and the initial spin states are determined by the statistical weight of *S*- and *T*-states ($\frac{1}{4}$ and $\frac{3}{4}$, respectively). The general rules for magnetic effects in such a case agree qualitatively with the case of the initial RPs in a triplet state.⁷ The radical recombination product (A) and the product of radical yield into the volume, $(\text{CH}_3)_3\text{SnH}$ (B), which in this case coincide with the initial reagent, have both demonstrated the isotope selection. The total content of the Sn^{117} and Sn^{119} isotopes in the product (A) measured by the proton magnetic resonance method was 17.8%, and in the product (B), 13.5%¹¹ (at a 50%-degree of reaction). Variation of reagent concentrations has produced up to 19.2% enrichment of the magnetic isotopes in product (A).

We should note that the high values of HFI constants are characteristic for hetero-organic radicals containing silicon, lead and other elements. The radical reactions involving hetero-organic compounds are, therefore, highly perspective for the separation of magnetic and nonmagnetic isotopes.

In conclusion we wish to point to the unique possibility presented by the discovery of the magnetic isotope effect for the separation of nuclear isomers. As we know, nuclear isomers may differ with respect to both spin and HFI energies. This difference may be very substantial. Thus, for example, spins of the tin isotope Sn^{119} and its isomer Sn^{119m} (used as a absorber and emitter in the Mossbauer spectroscopy) are $\frac{1}{2}$ and $\frac{1}{2}$, respectively. Admittedly, according to the shell model, the magnetic moments of Sn^{119m} and Sn^{119} are expected to be quite close to each other—as well as in the cases of two remaining known Mössbauer isomer sources ($\text{Kr}^{83m} - \text{Kr}^{83}$, $\text{Pt}^{195m} - \text{Pt}^{195}$). Nevertheless, in many cases not only the spins but also the magnetic moments of ground and excited isomer nuclear states can strongly differ. Thus, according to (1)*, one would expect a selection of nuclear isomers with respect to different products in the radical reactions. On the other hand, experimental studies of the effectiveness of nuclear isomer separation in these reactions may, evidently, provide additional means for determining the magnetic moments of nuclei in excited states.

¹The same method was used to measure magnetic isotope content in the initial compound before the reaction—16.0%.

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