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Radio Induced $^{12}C/^{13}C$ Magnetic Isotope Effect

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The separation of carbon isotopes ^{12}C and ^{13}C induced by magnetic electron–nuclear interaction in radical pairs is increased by selective microwave pumping at the frequency of EPR transitions in ^{13}C-containing radicals; the pumping accelerates the triplet–singlet conversion of ^{13}C radical pairs and therefore increases the nuclear spin selectivity of chemical reactions; this new effect has been called the radio induced magnetic isotope effect (RIMIE).

The chemical reactivity of radicals depends not only on the mass of the isotopic nuclei but also on their magnetic properties: spin, magnetic moment and magnetic electron–nuclear hyperfine interaction. The former is well known as the classical isotope effect, the latter has become known recently and is called the magnetic isotope effect (MIE).[1]

MIE results in the separation of magnetic and nonmagnetic isotopes in coupling reactions of radicals and to the redistribution of these isotopes between the products of coupling reactions and those of other radical reactions. For example, photolysis of the dibenzylketone molecule $PhCH_2COCH_2Ph$ (DBK) occurs *via* the triplet state and is accompanied by dissociation and generation of the triplet pair ($Ph(\dot{C}H_2\,\dot{C}OCH_2Ph$). In order for this geminate radical pair to recombine and regenerate the starting ketone it must undergo the triplet–singlet spin conversion that transforms an unreactive triplet pair into a singlet one capable of recombination.

In radical pairs with magnetic ^{13}C nuclei (in particular, in the CO group of the $\dot{C}OCH_2Ph$ radical) hyperfine interaction induces fast triplet–singlet spin conversion and these magnetic pairs are able to recombine. Triplet–singlet conversion of nonmagnetic pairs (with ^{12}C nuclei in the CO group) is delayed and $PhCH_2\dot{C}O$ radicals which escape recombination mostly decompose with formation of carbon monoxide. As a result the magnetic ^{13}C nuclei return in the regenerated starting ketone while the nonmagnetic ^{12}C nuclei move into other products (first of all into carbon monoxide).

The efficiency of isotope separation due to MIE depends on the molecular dynamics of the radicals, on their lifetime and on the radical pair spin dynamics governed by the magnetic interactions.[2] A new way of increasing the efficiency of MIE is radio frequency pumping of the electron paramagnetic resonance (EPR) transitions, which induces an additional channel for triplet–singlet conversion of magnetic radical pairs and stimulates their geminate recombination.

This effect was predicted in 1981[3] and was observed experimentally for H/D isotope pairs in the photoreduction of menadione in dodecylsulphate (DDS) micelles.[4] In this communication we report the first experimental observation of radio induced MIE (RIMIE) for $^{12}C/^{13}C$ nuclei in the DBK photolysis in DDS micelles.

The laser pulses used for DBK photolysis (λ = 388 nm, 15 ns pulse duration, 50 mJ in pulse) were synchronized with radio frequency pulses (2 μs duration), so that the short laser pulse was covered by a long radio pulse.† The time interval between each synchronized pair of laser and radio pulses was 100 ms. The frequency of the radio wave irradiation was 1530 MHz. This corresponds to pumping the high field component ^{13}C spin projection $m = -1/2$ in the EPR spectrum of the $PhCH_2\dot{C}O$ radical in a magnetic field of B_0 = 60.3 mT, the amplitude of the radio frequency pumping being B_1 = 0.48 mT.

The DBK conversion and the isotope contents were measured by HPLC and mass spectrometry (MAT 90, Finnigan). The starting ketone was enriched in the magnetic isotope ^{13}C, its proportion δ_0 being 52.4%.

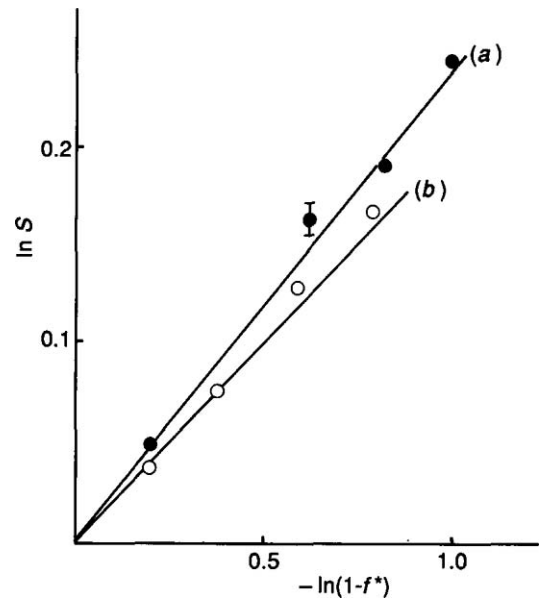

Fig. 1 Isotopic enrichment S of DBK as a function of ^{13}C-DBK conversion f^*: (*a*) radio frequency pumping, B_1 = 0.48 mT; (*b*) no radio frequency pumping, $B_1 = 0$

Due to MIE ^{12}C-DBK decomposes faster than ^{13}C-DBK and the relation between isotopic enrichment and chemical conversion is given by eqn. (1) where $S = \delta/\delta_0$, δ is the proportion of

$$S = (1 - f^*)^{\epsilon} \qquad (1)$$

the ^{13}C isotope in the ketone after photolysis and f^* is the ^{13}C-DBK chemical conversion.[2] The coefficient ϵ shows the efficiency of the isotopic separation.

The experimentally measured enrichment S is shown in Fig. 1 as a function of $(1 - f^*)$ and fits eqn. (1): the higher the ketone conversion the higher the magnetic isotope enrichment of its remaining part. The separation coefficients ϵ are different: for radio pumping photolysis $\epsilon_{rf} = -0.25 \pm 0.01$, without pumping $\epsilon_0 = -0.21 \pm 0.01$, in fact, radio pumping increases the isotopic selectivity in the radical pairs and the isotopic enrichment of the ketone.

The estimated value of the effect is not large. One factor, however, should be kept in mind, that radio frequency pumping induces micellar solution heating which could not be avoided, at least in these experiments. The values of the MIE and the isotopic separation in solution drop sharply as the temperature rises and therefore the difference in isotopic separation, shown in Fig. 1, with and without radio frequency pumping is certainly reduced. This is the lowest value of the effect, whilst its real value is greater and its existence is irrefutable. There are, of course, problems in avoiding the heating induced by radio frequency pumping and also in evaluating the full extent of the effect. These can be solved but they are outside the frame of reference of the present communication.

† The length of the radio frequency pulse was chosen to exceed by at least an order of magnitude the lifetime of the radical pair in the micelle.

Mendeleev Commun., 1991, 1(3), 85–86

It is known[2] that the coefficient ϵ can be expressed in terms of the recombination probabilities of the magnetic and nonmagnetic radical pairs, P^* and P, as in eqn. (2).

$$\epsilon = (P - P^*)/(1 - P^*) \quad (2)$$

For photolysis without radio pumping

$$1 - \epsilon_0 = (1 - P)/(1 - P_0^*) \quad (3)$$

with radio pumping

$$1 - \epsilon_{rf} = (1 - P)/[1 - (P_0^* + P_{rf})] \quad (4)$$

The only difference between eqns. (3) and (4) is that with radio pumping the recombination probability of the magnetic radical pair P_0^* is replaced by the value $(P_0^* + P_{rf})$, where P_{rf} is the additional contribution to the recombination induced by radio frequency pumping.

By combining (3) and (4) we obtain the ratio

$$(1 - \epsilon_0)/(1 - \epsilon_{rf}) = 1 - [P_{rf}/(1 - P_0^*)] \quad (5)$$

The probability P_0^* for the benzylacyl–benzyl radical pair in a 60 mT magnetic field (under photolysis conditions) is unknown but it is known in zero field.[2] Comparison of this value with the recombination probabilities and with their magnetic field dependence[5] for similar radical pairs shows that P_0^* can be taken to be equal to 0.40. Hence, from eqn. (5) we find that the ratio $P_{rf}/P_0^* = 0.05$, *i.e.* radio frequency pumping just one high field EPR transition increases the magnetic radical pair recombination probability by 5%. This radio induced contribution to the recombination probability increases when the pumping amplitude B_1 is larger.

RIMIE is a new type of isotopic phenomena which is based upon selective radio frequency radical pumping, the latter inducing selective chemical reactions of radicals with nuclei of magnetic isotopes. This effect has been successfully used for isotopic separation.

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