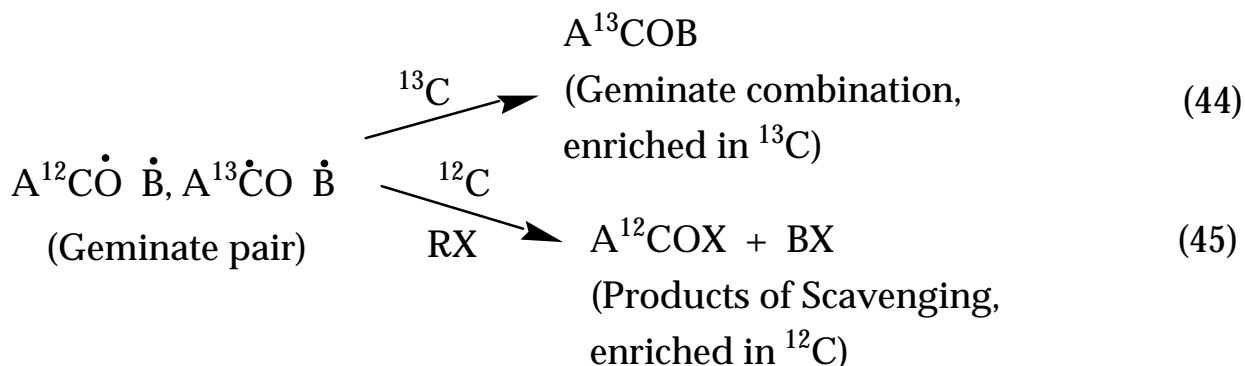


18. The Magnetic Isotope Effect on Radical Pair Reactions

In the same manner that the orientation of a nuclear spin can influence the rate of ISC of two nuclear spinomers in the presence of a strong (spin orienting) magnetic field, the rate of ISC of two isotopomers will depend on the magnetic properties of isotopomers even in the absence of a magnetic field. Using the example of a $\text{ACO} \cdot \cdot \text{B}$ pair, we consider the geminate pair reactivity of $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$ and $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$ in the absence of an applied field. Under the usual assumption that the isotopomers pairs are produced as a triplet state, the dynamic radical pairs undergo similar diffusional trajectories in physical space, but different trajectories in spin space. The situation with respect to ISC of the isotopomeric pairs is analogous to that for nuclear spinomers in the case of CIDNP (Figure 38). In particular, the $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$ pair is analogous to the $\text{A}^{13}\text{C}_\beta\text{O} \cdot \cdot \text{B}$ pair which undergoes rapid intersystem crossing and forms a cage combination product, and the $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$ pair is analogous to the $\text{A}^{13}\text{C}_\beta\text{O} \cdot \cdot \text{B}$ pair, which undergoes escape from the cage and forms scavenged products. The net result is that the $\text{A}^{13}\text{CO} \cdot \cdot \text{B}$ pairs selectively form cage products, and the $\text{A}^{12}\text{CO} \cdot \cdot \text{B}$ pairs selectively form escape or scavenged products (Eq. 44 and 45).



The ketone that is regenerated by cage reactions is enriched in ^{13}C , and the escape product (or scavenging products) are enriched in ^{12}C compared to isotopic content of the starting ketone. The overall process serves to **separate the magnetic isotope (^{13}C) from the non-magnetic isotope (^{12}C), with the magnetic isotope directing the geminate triplet pair towards geminate combination reactions, and the non-magnetic isotope directing the pair toward free radical reactions.**

Since the fraction of geminate reactions is very small in non-viscous solutions because of the small fraction of reencounters, the magnetic isotope effect is not significant in ordinary solvents. Reencounters are strongly encouraged in constrained space provided by certain supramolecular systems

such as micelles. Under these conditions the magnetic isotope effect becomes quite efficient and readily measurable.

Some other remarkable expectations of the above model have been confirmed experimentally: (a) the quantum yield for disappearance of the magnetic isotope ^{13}C ketone is lower (because of the more efficient recombination of the magnetic pairs) than the quantum yield of disappearance of the non-magnetic isotope ^{12}C ketone; (b) the rate of disappearance of the magnetic isotope ^{13}C ketone is faster (because of the faster rate limiting ISC for recombination reactions) than the rate of disappearance of the non-magnetic ^{12}C ketone. It has also been shown that the extent of ^{13}C enrichment at various positions starting from a natural abundance ketone is directly related to the magnitude of the hyperfine coupling at that position.

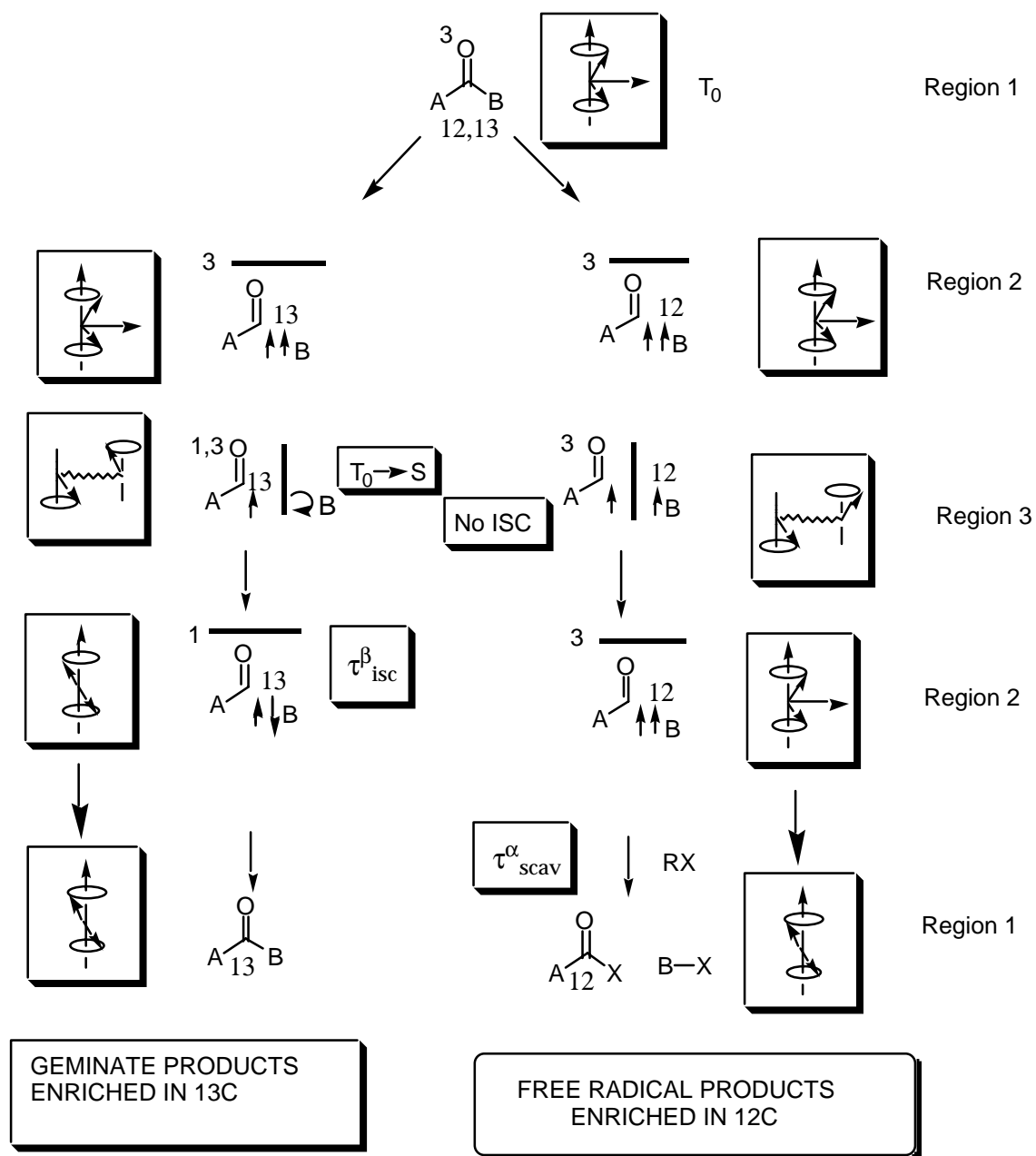


Figure 44. Vector model of the sorting of magnetic from non-magnetic nuclei that occurs in the dynamic radical pair. See text for discussion.