

# Radical Pairs: Formation, Behavior, and Reactions

Podcast Learn & Fun \*

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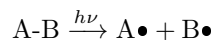
At the core, a *radical pair* is a pair of *radicals*—molecules or fragments that each possess one or more unpaired electrons. The unpaired electron is typically represented in molecular diagrams as a dot ( $\bullet$ ). For instance, a methyl radical would be written as  $\text{CH}_3\bullet$ . A radical pair forms when two radicals are generated in close proximity. They might result from homolytic bond cleavage (where a single bond is broken, and each fragment retains one electron) or through the interaction of an excited state molecule.

Radicals are highly reactive species because the unpaired electron makes them prone to interact with other molecules. When these radicals are in close proximity, their behavior can be significantly influenced by a variety of external factors such as magnetic fields, solvent environments, and thermal conditions.

## Formation of Radical Pairs

Radical pairs are typically formed through processes such as photochemical or electrochemical reactions, where a molecule undergoes homolytic bond cleavage. These processes result in the generation of two radicals, which are highly reactive species due to their unpaired electrons.

**Photolysis:** Photolysis refers to the dissociation of a molecule upon absorption of light. When a molecule absorbs a photon of light ( $h\nu$ ), the energy of the photon can cause the molecule to undergo homolytic bond cleavage, where each atom involved in the bond takes one of the shared electrons, forming two free radicals. For example, if a diatomic molecule, A-B, absorbs a photon, the bond between A and B might break, resulting in the formation of two radicals,  $\text{A}\bullet$  and  $\text{B}\bullet$ :

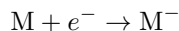


In this case, the bond is cleaved in such a way that each fragment retains one electron, leading to the creation of the radical pair.

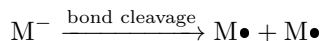
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**Electrolysis:** In electrochemical reactions, particularly during processes like electrolysis, an electron is transferred to a molecule at the cathode (reduction reaction). This electron transfer can induce homolytic bond cleavage in the molecule, resulting in the formation of two radicals. For instance, if a molecule (M) is reduced by gaining an electron:



This newly formed ion may undergo bond cleavage to produce two radicals:



The generated radical pair is important for subsequent electrochemical processes, such as charge transfer or further reactions with other species in the solution.

**Excited-State Intermediates:** Some radical pairs can also form through excited-state intermediates. In this case, a molecule is first excited to a higher energy state (often via absorption of light or interaction with another species). The molecule in this excited state may undergo bond cleavage, forming two radicals before it relaxes back to a lower energy state. The key feature of this process is that the radicals are often generated in *close proximity* to each other, typically on the scale of nanometers. The proximity of the radicals can have significant implications for their subsequent interactions, as they may recombine, undergo further reactions, or interact with other species.

The fact that these radical pairs are generated in such close proximity is crucial because it allows for the possibility of the radicals interacting with each other in specific ways, such as recombination (where the radicals may pair back together to form the original molecule) or other reactions.

## The Behavior of Radical Pairs

The behavior of radical pairs is dictated by several factors:

**Spin Correlation** Radical pairs consist of two radicals with unpaired electrons. These unpaired electrons can have specific spin configurations, which significantly affect the pair's reactivity and behavior. There are two main types of spin states for radical pairs: singlet and triplet.

(1) Singlet State ( $S = 0$ ): The singlet state occurs when the two radicals have antiparallel spins. That is, the spins of the two radicals are opposite, resulting in a total spin of zero. In this state, the electrons are paired in such a way that their total angular momentum cancels out. This can lead to different chemical reactivity than in the triplet state. Singlet radical pairs typically have lower reactivity compared to triplet pairs because the spins are paired and may not be as readily involved in subsequent reactions.

(2) Triplet State ( $S = 1$ ): The triplet state occurs when the two radicals have parallel spins. This results in a total spin of one. Radical pairs in the

triplet state generally exhibit higher reactivity compared to those in the singlet state, since the parallel spins can increase the likelihood of interactions with other species or molecules. This increased reactivity is often crucial in chemical and biological processes.

The transition between these two states, from singlet to triplet or vice versa, can occur through spin conversion processes. These transitions are typically governed by quantum mechanical effects, such as spin relaxation and spin exchange. In a solution or under the influence of external factors, the radical pair can experience these processes, which are crucial in determining the overall dynamics and reactivity of the system.

**Magnetic Effects** Radical pairs are particularly sensitive to magnetic fields, which can influence the dynamics of their spin states. This sensitivity is a key feature of radical pair chemistry and has applications in both quantum chemistry and biological systems, such as magnetoreception in animals.

(1) Zero-Field Splitting (ZFS): Zero-field splitting is a phenomenon that occurs due to the interaction between the spins of the two radicals within the radical pair. This interaction causes an energy splitting even in the absence of an external magnetic field. ZFS is an important effect because it indicates that the system's energy levels are influenced by the intrinsic properties of the radicals, and it provides insight into how the radicals interact with each other. This effect can influence the reactivity of radical pairs, particularly in the absence of external magnetic influences.

(2) Magnetoreception: One fascinating application of radical pairs is their role in magnetoreception, a process by which certain animals, such as birds, detect and navigate using Earth's geomagnetic field. In this context, radical pairs are believed to be involved in the biochemical processes that allow animals to sense magnetic fields. The reactivity of radical pairs can be influenced by the orientation and intensity of magnetic fields, enabling organisms to use this information for navigation. This ability to detect magnetic fields is thought to be based on the effects of Earth's geomagnetic field on the spin states of radical pairs, providing a remarkable example of quantum biology.

**Spin Relaxation and Quantum Coherence** Radical pairs exhibit quantum mechanical behavior that can lead to phenomena such as quantum entanglement. These effects are important in a variety of systems, including potential applications in quantum computing.

(1) Spin Relaxation: Spin relaxation refers to the process by which a radical pair transitions from a non-equilibrium state (e.g., an excited spin state) to a more stable configuration. This can occur due to various interactions, such as collisions with solvent molecules or external perturbations. Spin relaxation affects the population of singlet and triplet states and thus influences the chemical reactivity and dynamics of the radical pair.

(2) Quantum Coherence: Radical pairs can exhibit quantum coherence between their spin states, meaning that the spin states are in a superposition, with

the system maintaining coherence between the singlet and triplet states. This coherence is an essential feature of quantum systems and can lead to phenomena like quantum entanglement, where the states of the two radicals become interdependent. This property has potential applications in quantum computing and other areas of quantum technology, where control over quantum states is critical.

In summary, the behavior of radical pairs is shaped by their spin correlation, which determines their reactivity, their sensitivity to magnetic fields, and their potential for exhibiting quantum mechanical effects such as coherence and entanglement. Understanding these factors is crucial not only for the study of radical chemistry but also for the exploration of advanced quantum technologies and biological processes like magnetoreception.

## Reactions Involving Radical Pairs

The reactivity of radical pairs depends on their spin states, the surrounding environment, and various external factors, which can significantly influence the outcome of their interactions. Below, we explore the primary reaction types involving radical pairs:

**Recombination** Recombination is one of the most straightforward fates for a radical pair. In this process, the two radicals recombine to form a stable molecule by pairing their unpaired electrons. The likelihood and rate of recombination can depend on the spin states of the radicals. While recombination can occur in both singlet and triplet states, singlet state recombination is typically faster and more probable due to the lower energy barrier. The specific environment, such as solvent polarity and temperature, can also influence the efficiency of recombination.

**Interconversion Between Singlet and Triplet States (Intersystem Crossing, ISC)** Radical pairs are capable of undergoing intersystem crossing (ISC), which involves a transition between the singlet and triplet spin states. This process occurs when a radical pair moves from one spin state to another, often as a result of thermal fluctuations or other external factors. ISC is influenced by several factors:

(1) **Thermal Energy:** At higher temperatures, thermal energy can provide the necessary activation energy for the radical pair to transition between singlet and triplet states.

(2) **Solvent Interactions:** The solvent environment can affect the rates of ISC by altering the spin-orbit coupling or by influencing the stability of the radical pair in different spin states.

(3) **Magnetic Fields:** External magnetic fields can influence the relative energies of the singlet and triplet states and may thus enhance or inhibit ISC. This is due to the interaction between the radical pair's magnetic moment and the applied field.

ISC is a crucial process in many photochemical and biological systems because it determines the dynamics of radical pair evolution and can influence the efficiency of reactions that depend on specific spin states.

**Charge Transfer Reactions** Radical pairs can also engage in charge transfer reactions, in which one radical either donates or accepts an electron from another species. In these reactions, the radical pair’s reactivity is altered by interactions with nearby molecules or ions, leading to electron transfer. Charge transfer can occur when one radical has a strong tendency to donate an electron, while the other has a high affinity for accepting one.

These charge transfer processes are vital in a variety of biological and chemical contexts. For instance, in photosynthesis, radical pairs generated in light-driven reactions may facilitate electron transfer between cofactors in photosynthetic proteins, contributing to the generation of high-energy intermediates used to produce ATP and other essential molecules. Similarly, in certain enzymatic reactions, radical pairs can initiate electron transfer steps that drive biochemical processes.

**Chemical Reactions** In biological systems, radical pairs play a significant role in chemical reactions, particularly in the context of enzymatic catalysis and cellular signaling. These reactions often involve the formation and transformation of reactive intermediates, which can affect cellular processes, gene expression, and metabolic regulation.

(1) Photosynthesis: Radical pairs are central to the early stages of photosynthesis, particularly in the light reaction. When light is absorbed by chlorophyll, it excites electrons, which then form radical pairs. These pairs participate in a sequence of electron transfers that lead to the generation of high-energy compounds, such as ATP and NADPH, which are used in the Calvin cycle to produce sugars and other metabolic intermediates.

(2) Cellular Signaling: Radical pairs also play a role in cellular signaling pathways, where they can influence the activity of various biomolecules. For example, in some signaling pathways, radical pairs may trigger the production of reactive oxygen species (ROS), which are involved in regulating cell growth, stress responses, and other critical functions.

Additionally, radical pairs can be involved in enzyme catalysis, where the reactive radicals serve as intermediates that facilitate complex chemical transformations essential for life processes.

## Experimental Techniques to Study Radical Pairs

To study these transient species and their properties, chemists rely on a range of experimental techniques that provide detailed insights into the behavior and characteristics of radical pairs. Below is an expanded explanation of the key experimental techniques commonly used to study these species:

**Electron Paramagnetic Resonance (EPR) Spectroscopy** Electron Paramagnetic Resonance (EPR) spectroscopy, also known as Electron Spin Resonance (ESR), is a powerful analytical technique used to detect species with unpaired electrons, such as radicals. In this technique, a sample is exposed to a magnetic field, and the resulting absorption of electromagnetic radiation is measured. This absorption provides information about the electronic environment, spin states, and interactions between the radicals in the pair.

Key insights that can be obtained from EPR include: (1) *Spin state analysis*: EPR allows researchers to differentiate between singlet and triplet states in radical pairs, which are important for understanding the dynamics of recombination or other subsequent reactions. (2) *Hyperfine interactions*: EPR can reveal the interactions between the electron spins and nearby nuclei (hyperfine coupling), which is critical for understanding the spatial arrangement and reactivity of the radical pair. (3) *Electron-spin correlation*: EPR provides information on how the spins of the radicals are correlated, which helps in exploring the mechanisms that govern their recombination or separation.

**Time-Resolved Spectroscopy** Time-resolved spectroscopy involves the measurement of spectral changes over a short time scale, typically on the nanosecond to microsecond range. This technique is invaluable for studying the dynamics of radical pairs because it allows researchers to track how these species evolve over time. When radical pairs are generated, they undergo various processes such as recombination, spin conversion, or other reactions, which can be monitored through time-resolved methods.

Key applications of time-resolved spectroscopy for radical pairs include: (1) *Monitoring reaction kinetics*: By observing the evolution of the radical pairs over time, scientists can measure the rates of key processes like recombination (where the radicals pair together and form a stable molecule), spin conversion (transitioning from singlet to triplet states or vice versa), and separation. (2) *Time-dependent spectroscopic features*: Various techniques, such as transient absorption or fluorescence spectroscopy, are used to capture the fleeting presence of radical pairs and their intermediate states. This helps in determining the lifetimes of the radical pairs and their reactivity under different conditions. (3) *Mechanistic insights*: Time-resolved studies can reveal how external factors, such as temperature or solvent properties, influence the behavior of radical pairs.

**Magnetic Field Effects** The application of an external magnetic field offers a way to manipulate and probe the spin dynamics of radical pairs. Magnetic field effects are particularly important for studying the spin evolution and reaction rates of radical pairs. The strength and direction of the applied field can influence the transitions between different spin states (e.g., singlet to triplet), and by varying the magnetic field, researchers can gain insight into the magnetic interactions between the radicals.

Key aspects of studying magnetic field effects in radical pairs include: (1)

*Zeeman effect:* The application of a magnetic field splits the energy levels of the electron spins, leading to changes in the recombination rates or other reaction dynamics. These changes can be observed to understand the relationship between spin states and reaction kinetics. (2) *Spin-selective reactions:* Magnetic fields can induce selective changes in the rates at which radical pairs recombine or undergo other transformations, as certain spin states (singlet vs. triplet) may have different reactivity profiles. (3) *Radical pair mechanism:* By studying how the reaction rates change in response to magnetic fields, scientists can explore the mechanisms governing radical pair recombination and the factors that control spin-dependent reactions.

In combination, these techniques provide a comprehensive set of tools for studying radical pairs and offer deep insights into the fundamental processes that govern their behavior. Researchers can analyze not only the identities and properties of the radical species but also their interactions, reactivity, and the factors that influence their dynamics. This knowledge is crucial for understanding a wide range of chemical and biological processes, including those involved in photosynthesis, molecular magnets, and radical-based signaling pathways.