

Spin-selective reactions in three-spin systems in high-energy radiation experiments

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The spin-correlated radical pair is a basic object of spin chemistry that is thoroughly studied by many researchers. The next important step is to understand 3-, 4-, ...-spin systems. Constructing covalently bonded multi-spin structures is a promising strategy. This approach, however, is of interest primarily from a quantum computing perspective since the complexity of such structures takes away the possibility to study spin effects in elementary spin-selective chemical reactions involving free small paramagnetic particles, such as solvated electrons, radicals, oxygen molecule, etc. The purpose of this lecture is to draw community's attention to possibilities of studying 3-spin systems using the high-energy radiation, which, in a solution containing paramagnetic scavengers, creates an ensemble of three-spin systems "spin-correlated radical ion pair/ paramagnetic particle" composed of individual species.

The lecture focuses on a particular example of a very important spin-selective reaction of electron transfer to molecular oxygen in its triplet ground state

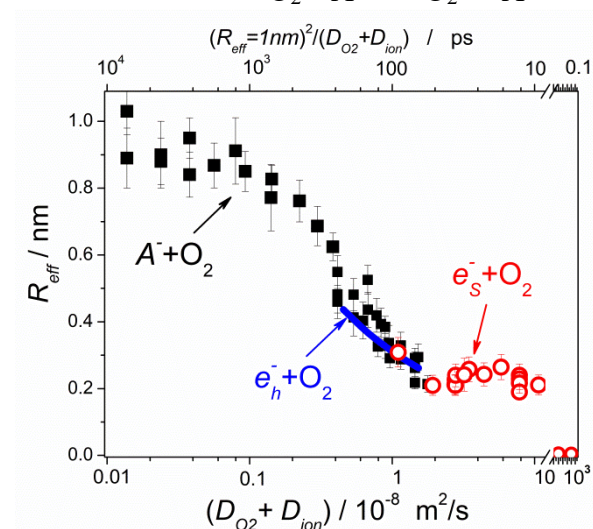


Figure 1. Effective radii R_{eff} of i) electron scavenging by O_2 in alkanes (circles) and water (line, data from [3]); ii) of electron transfer to O_2 from aromatic radical anions in various alkanes (squares) on the reactants' relative diffusion coefficient. The upper scale shows a typical time scale for the diffusion controlled encounters.

time for triplet O_2 , that is about of 8 ps [2]. As the factors reducing the intersystem crossing rate in the encounter complex, the Heisenberg spin exchange interaction and the quantum Zeno effect are discussed.

This reaction can be studied using luminophore solution, radiation-induced fluorescence of which is quenched due to reaction (1). Recording the fluorescence intensity decay from the solution in different magnetic fields allows one to determine both the rate constant k for reaction (1) and the spin dephasing rate for spin-correlated radical ion pairs, which avoid the decay due to the spin mismatch in the encounter complex [1].

Experiments showed that the spin selectivity in reaction (1) manifests itself as a significant decrease in the reaction effective radius $R_{eff} = k/4\pi D$ upon an increase in the relative diffusion coefficient D of the reactants, that is equivalent to the decrease in the reactants' encounter time (Figure 1). The spin statistical factor equal to 1/3 can be observed when the D value exceeds *ca.* 10^{-8} m^2/s . Surprisingly, corresponding encounter time is much longer than the spin-lattice paramagnetic relaxation

[1] V. I. Borovkov et al., J. Phys. Chem. A **117**, 1692(2013)

[2] C.-L. Teng et al., J. Magn. Reson. **148**, 31 (2001)

[3] A. J. Elliot, Radiat. Phys. Chem. **34**, 753 (1989)