Spin statistical factor in the reaction of distant electron transfer

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The rate of a bimolecular reaction between paramagnetic particles generally depends on the total electron spin of the reactants. Such asymmetric reactivity of organic radicals is the origin for many of the spin polarization phenomena in chemistry.

In chemical kinetics, the spin dependence is usually described by introducing the so-called spin statistical factor $\sigma < 1$, which, to a first approximation, is equal to the statistical weight of reactive states of the pair of the reactants among all possible spin states. For diffusion-controlled reactions, the observed reaction rate constant k is expressed in this case as $k = \sigma \times K_D = \sigma \times 4\pi RD$, where D is the sum of the reagents' diffusion coefficients, K_D and R are *hypothetical* rate constant and effective reaction radius that would be if the spin dependence *disappeared*. The σ value can be used to estimate the intersystem crossing rate within the encounter complex of the reactants.

To develop a quantitative kinetic model of a spin-selective reaction, it is important to have information about corresponding spin factor and its dependence on the conditions under which the studied reaction takes place. For reactions between neutral organic radicals, in which short-ranged covalent bonds are formed, the expected value of K_D can be estimated more or less accurately. For electron transfer between particular donor and acceptor, the effective radius R can be significantly larger than the sum of the van der Waals radii of the reactants. Thus, careful measurements to determine both the parameter K_D and the spin statistical factor σ are required.

This presentation discusses the problem of determining the spin factor in reactions between triplet oxygen molecules and solvated electrons or radical anions in liquids:

$$e^- + {}^3O_2 \rightarrow {}^2O_2^{-\bullet} \qquad \text{and} \qquad A^{-\bullet} + {}^3O_2 \rightarrow A + {}^2O_2^{-\bullet}$$

The expected value of the spin factor would be $\sigma = 1/3$. In the experiments, however, the σ value increases with slowing down the diffusion of reactants. This effect originates from the dipole-dipole interaction of the spins of unpaired electrons in ${}^3O_2$ molecule since this interaction causes mixing between reactive doublet and non-reactive quartet spin states. It was found that although this dipole-dipole interaction results in a very rapid paramagnetic relaxation of oxygen molecules with a characteristic time of $T_1 \approx 8$ ps [1], the doublet-quartet mixing in the reaction encounter complex involving the ${}^3O_2$ molecule proceeds on a much longer timescale. The possible reasons for that are discussed.

[1] C.-L. Teng, H. Hong, S. Kiihne, R.G. Bryant. *J. Magn. Reson*. **2001**, *148*, pp.

31–34.