A mechanism is described which may explain the effects of magnetic field on the rate of recombination of two radicals (R + R) and on the rate of reactions between doublet and triplet electronic states (D + T). It is based on the influence of the magnetic field on the rate of singlet-triplet and doublet-quartet intersystem crossings within pairs of the reacting species.

The influence of magnetic field on chemical reactions is one of the most important and interesting problems of chemical physics. To date, however, no complete description of this effect has been given.

Recent developments in the theory of chemically induced dynamic nuclear polarization (CIDNP) /1-4/ predict a mechanism which may explain the effect of magnetic field on the rate of chemical reactions. This is based on intersystem crossing in radical pairs, induced by Zeeman and nuclear hyperfine interactions within the radicals of reacting species.

As an example to illustrate this mechanism, let us consider the recombination (or disproportionation) of two radicals. If the precursor of the recombination product is a radical pair in the singlet state, the probability of formation of a molecule in nuclear spin state ab is given by the equation /5/:\[ P_{ab} = \alpha + \left(1-\alpha\right) \int_0^\infty \left| C_{s,ab}(t) \right|^2 f(t) dt \] (1)
Here $\alpha$ is the probability of primary recombination, the second term is that of secondary recombination of the pair. Coefficient $1-\alpha$ gives the probability that the radical pair escapes primary recombination and dissociates. The radicals diffuse apart but may return into the original pair with probability $f(t)$, and recombine with probability $\alpha$.

Coefficient $|C_{s,ab}(t)|^2$ represents probability that the radical pair remains in the singlet state during the diffusional movement of the radicals. Integration in eq. (1) implies averaging over all diffusional trajectories.

For the singlet radical pair

$$|C_{s,ab}(t)|^2 = 1 - \left( \frac{H_{ab}}{D_{ab}} \right)^2 \sin^2 D_{ab} t$$

where $H_{ab}$ is the matrix element of singlet-triplet ($S-T_o$) mixing, i.e.

$$H_{ab} = \langle S | H | T_o \rangle = \frac{1}{2} \left( \Delta g \beta H + \sum_{i} a_i m_i^a - \sum_{j} a_j m_j^b \right)$$

$a_i$, $a_j$ and $m_i^a$, $m_j^b$ are the hyperfine coupling constants and nuclear spins of radicals in nuclear spin states $a$ and $b$, respectively.

$$D_{ab} = \left( H_{ab}^2 + J^2 \right)^{1/2}$$

$J$ is the average electron exchange energy in the pair. Equation 2 shows that the probability that the radical pair remains in the initial singlet state diminishes with time, owing to the singlet-triplet transitions induced by the difference in Zeeman energy between the radicals, $\Delta g \beta H$, and by hyperfine interactions.

The function

$$f(t) = nt - 3/2 \exp (-t/\tau)$$

takes into account the exponential distribution of the diffusional trajectories over the radical life-time $\tau$. 

158