

encounters after each jump. If the time required to make a jump is much less than τ_{enc} , the average duration of an encounter, $n \approx \tau_{\text{enc}}^{-1}$. The quantity τ_{enc} may be approximated by

$$\tau_{\text{enc}} \approx \pi \lambda^3 \eta / kT, \quad (5)$$

where λ is the interaction radius, and η is the solvent viscosity. Equation (3) can be rewritten as

$$W_\alpha = k_\alpha z N_r p / N_s \tau_{\text{enc}} + R_\alpha, \quad (6)$$

which, when combined with Eq. (5), gives $W_\alpha \propto T/\eta$, provided $p=1$.

We propose the following simple model to calculate the probability p . During an encounter between radicals, we will assume that the distance between them remains effectively constant. The relative orientation of the radicals, which can be expressed by a set of Eulerian angles, $\theta(t)$, changes during an encounter, provided the rotational correlation time τ_c is short compared with τ_{enc} . If we assume that $\theta(t)$ is a random function of time, it follows that $J_{ij}(t)$, during an encounter, is also a random function of time. This assumes that J_{ij} is a function of θ , which is reasonable in this case, since the odd electron, being principally localized on the NO group, is anisotropically shielded from the environment by the bulky *t*-butyl groups. Let us, for convenience, say that the radicals encounter at $t = -\tau_{\text{enc}}/2$, and fly apart at $t = \tau_{\text{enc}}/2$. Dropping the subscripts i and j , the exchange integral in Eq. (2) becomes

$$J = J[\theta(t), r_0] = J(t), \quad |t| < \tau_{\text{enc}}/2, \quad (7)$$

where r_0 is the ensemble average of the distance between two radicals during an encounter. Our model implies that $J(\theta, r_0)$ is a peaked function of θ . Although there may be several values of θ at which J peaks, we here for the sake of discussion assume that there is only one such orientation θ_0 . The time which elapses after the formation of a "radical pair" before the optimum orientation θ_0 is attained is a random variable, because $\theta(t)$ is a random function.

Let us define J_0 as the average exchange frequency during an encounter. Since we assume that $J(t)$ has no explicit time dependence, J_0 is given by the ensemble average at any local time t in the interval $|t| < \tau_{\text{enc}}/2$, for instance, $t=0$, i.e.,

$$J_0 = \langle J(0) \rangle, \quad (8)$$

where the angle brackets indicate the ensemble average.

The problem, as a result of this model, is analogous to the principle of random lifetimes in unimolecular reactions. J_0 corresponds to the first-order kinetic rate constant. The difference is that in our case there is a limit to the duration of the "radical pair," namely, τ_{enc} ,

whether an exchange "reaction" has taken place or not. The probability that the "radical pair" undergoes an exchange "reaction" after a time τ is given by

$$f(\tau) = \exp(-J_0\tau). \quad (9)$$

Hence the probability that an exchange reaction takes place in the time $\tau = \tau_{\text{enc}}$ is simply

$$p = 1 - \exp(-J_0\tau_{\text{enc}}). \quad (10)$$

With p given by Eq. (10), the limiting conditions for W_α in Eq. (6) are

$$W_\alpha = k_\alpha z N_r / N_s \tau_{\text{enc}} + R_\alpha \quad \text{for } J_0\tau_{\text{enc}} \gg 1 \quad (11)$$

and

$$W_\alpha \rightarrow k_\alpha z J_0 N_r / N_s + R_\alpha \quad \text{for } J_0\tau_{\text{enc}} \rightarrow 0. \quad (12)$$

If there is a second paramagnetic species in solution, spin exchange between the radical and the second paramagnetic species may be important. This appears to be the case in oxygen-containing solutions. The observed exchange frequency is the sum of two contributions

$$\nu_{\text{ex}} = \frac{z}{N_s} \left(\frac{N_r p}{\tau_{\text{enc}}} + \frac{N_0 p'}{\tau'_{\text{enc}}} \right), \quad (13)$$

where N_0 is the number of oxygen molecules in solution and the primes signify oxygen-radical interactions.

DISCUSSION

Since the populations for the states $M_I = -1, 0$, and 1 are approximately equal, k_α is the same for each of the hyperfine lines, and we obtain the following expression for the average linewidth from Eqs. (5) and (6):

$$W = k' N_r T p / \eta N_s + 0.55 G, \quad (14)$$

where $R = 0.55 G$ is the residual linewidth discussed earlier. It is apparent from Figs. 1(a), 1(b), and 2(a) that all the extrapolated linewidths at $T/\eta = 0$ are greater than $0.55 G$. The largest discrepancy is approximately $0.5 G$ for the most concentrated solutions, and the discrepancy appears to depend upon concentration. The most likely mechanism giving rise to the additional linewidth is intermolecular dipole-dipole broadening. The diffusional motion of the radicals averages out this line broadening mechanism at lower viscosities, and we have consequently not taken this effect into account in calculating p . At low solvent viscosities, where the lowest values of p were obtained, the dipolar contribution to the linewidth must be only a small fraction of R , whereas the measured W are greater than $6 G$. We do not expect, therefore, that neglect of the dipole-dipole broadening mechanism leads to any significant error in the calculated values of p .

From Fig. 2(b) we find that the linewidth contributions due to radical-radical and radical-oxygen exchange are additive, thus justifying Eq. (13).