

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

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

where  $\lambda$  is the interaction radius, and  $\eta$  is the solvent viscosity. Equation (3) can be rewritten as

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

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

We propose the following simple model to calculate the probability  $\phi$ . 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  $\tau_c$  is short compared with  $\tau_{\text{enc}}$ . 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  $\theta$ , 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  $\theta$ . Although there may be several values of  $\theta$  at which  $J$  peaks, we here for the sake of discussion assume that there is only one such orientation  $\theta_0$ . The time which elapses after the formation of a "radical pair" before the optimum orientation  $\theta_0$  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,  $\tau_{\text{enc}}$ ,

whether an exchange "reaction" has taken place or not. The probability that the "radical pair" undergoes an exchange "reaction" after a time  $\tau$  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

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

With  $\phi$  given by Eq. (10), the limiting conditions for  $W_\alpha$  in Eq. (6) are

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

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

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

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,  $k_\alpha$  is the same for each of the hyperfine lines, and we obtain the following expression for the average linewidth from Eqs. (5) and (6):

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

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  $\phi$ . At low solvent viscosities, where the lowest values of  $\phi$  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  $\phi$ .

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