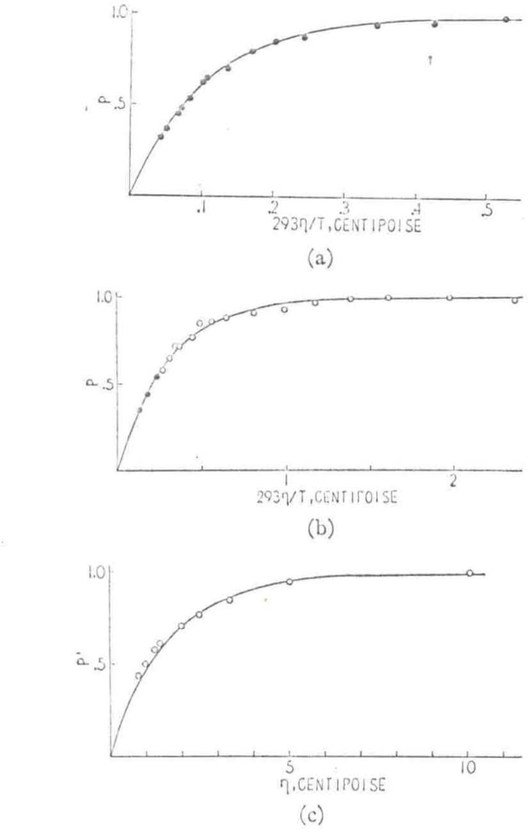

FIG. 3. (a) Probability of exchange during a single radical encounter, p, vs $293\eta/T$ for DTBN in propane. Solid line is a plot of $p=1-\exp(-2.81\times10^3\eta/T)$. (b) Probability of exchange during radical encounter, p, vs $293\eta/T$ for DTBN in n-pentane. Solid line is a plot of $p=1-\exp(-1.01\times10^3\eta/T)$. (c) Probability of spin exchange during radical–oxygen encounter, p', vs η in methylcyclohexane. $T=293$°K for all points. Solid line is a plot of $p'=1-\exp(-0.19\times10^3\eta/T)$.

due to the reduction of p, the exchange probability per radical–radical encounter. The values of $p(\eta, T)$ were obtained by the following procedure. The linear portion of the W vs T/η curve was extrapolated, and $p(\eta, T)$ was calculated from the ratio

$$(W_{\mathrm{obs}}-0.55)/(W_{\mathrm{ext}}-0.55),$$

where 0.55 G is the residual linewidth of the lines in the absence of exchange. In Figs. 3(a) and 3(b) we plot $p(\eta, T)$ vs $293\ \eta/T$ for radical–radical exchange in propane and pentane, respectively. The open circles are data from pressure measurements; the filled circles are the data from the variable temperature measurements. Figure 3(c) is a plot of the probability of a radical–oxygen exchange reaction during an encounter vs the viscosity of methyl cyclohexane. It should be recalled that in methyl cyclohexane, $p=1$ for radical–radical exchange in the entire range of measurements. The solid lines in Figs. 3(a)–3(c) are plots of $p=1-\exp(-2.81\times10^3\ \eta/T)$, $p=1-\exp(-1.01\times10^3\ \eta/T)$, and $p=1-\exp(-0.193\times10^3\ \eta/T)$, respectively. These results are discussed in the next section.

THEORY

The influence of intermolecular spin exchange on paramagnetic resonance spectra in liquids is well understood. As the exchange rate ν_{ex} increases, each hyperfine component of the resonance spectrum is broadened at a rate which depends upon the degeneracy of its nuclear spin state. The lines also shift toward the center of the spectrum. When the hyperfine lines are still well separated, so that the linewidths can be measured accurately, the relationship

$$W_\alpha=k_\alpha\nu_{\mathrm{ex}}+R_\alpha \tag{1}$$

offers an excellent means of evaluating the exchange frequency. In Eq. (1) W_α is the peak–peak linewidth of the absorption derivative of the αth hyperfine component, k_α is a proportionality constant, and R_α represents other contributions to the linewidth. The exchange Hamiltonian is represented by

$$\mathcal{H}_{\mathrm{ex}}=-\sum_{i<j}J_{ij}\mathbf{S}_i\mathbf{S}_j$$

with the exchange integral J_{ij} given by

$$J_{ij}=e^2\iint\psi_{\mathrm{A}}^*(\mathbf{r}_i)\psi_{\mathrm{B}}^*(\mathbf{r}_j)(\mathbf{r}_{ij})^{-1}\psi_{\mathrm{B}}(\mathbf{r}_i)\psi_{\mathrm{A}}(\mathbf{r}_j)\,d\tau_i d\tau_j, \tag{2}$$

where i and j refer to the unpaired electrons experiencing mutual spin precession, and A and B denote the two radicals. Since J_{ij} depends strongly on the overlap of the wavefunctions, $\int\psi_{\mathrm{A}}^*(\mathbf{r}_i)\psi_{\mathrm{B}}(\mathbf{r}_i)d\tau_i$, it is in general a function not only of the distance between A and B but of their relative orientation as well.

If we assume that the potential energies between radicals are small compared with thermal energies, the theory of random flights applies to their motions. We shall assume that the exchange interaction is important only for nearest neighbors and $J_{ij}\sim0$ after one of the radicals has made a diffusional jump. If the exchange probability during an encounter p is unity ν_{ex} is simply equal to the encounter rate between radicals, ν_{enc}. If on the other hand p is less than 1, both ν_{enc} and p are important in determining ν_{ex}. Accordingly, Eq. (1) becomes

$$W_\alpha=k_\alpha\nu_{\mathrm{enc}}p+R_\alpha. \tag{3}$$

As pointed out by Pake and Tuttle,[2] ν_{enc} is given by

$$\nu_{\mathrm{enc}}=nN_rz/N_s, \tag{4}$$

where n is the frequency of diffusional jumps of the radicals, N_r and N_s are the number of radical molecules, and solvent molecules in solution, respectively, and z is the averge number of new neighbors a radical