is given in Pake and Tuttle's paper.[2] Kivelson[3] has also discussed the problem of spin exchange in free radical solutions, and has presented a more quantitative theory.

In the next section, we give some of the experimental details, followed by the experimental results, from which are deduced the exchange probability p and its dependence on the viscosity η and temperature T. A simple model is then presented which gives the observed form of $p(\eta, T)$.

EXPERIMENTAL

A. Pressure Runs

The X-band paramagnetic resonance spectrometer, the high-pressure cavity bomb, and pressure generating and measuring equipment were the same as those described previously.[1b] The temperature of all runs was $20°\pm2°$C. Solvent viscosities were calculated from Bridgman's[4] data by a logarithmic temperature extrapolation at each pressure. The effect of the small fraction of solute on the solvent viscosity was assumed negligible. The following samples of the radical were measured in methyl cyclohexane (Eastman, spectro grade) as solvent in the pressure range 1–6000 kg/cm² ($\eta\cong0.74$–45 cP): (1) $0.012M$ deoxygenated solution, (2) $0.012M$ solution saturated with air at 1 atm, and (3) $0.0024M$ solution saturated with air at 1 atm. A sample of the radical in n-pentane (Phillips, 99 mole %) was also measured in the pressure range 1–10 200 kg/cm² (0.27–11 cP). The concentration was $0.012M$ and the solution was deoxygenated.

B. Temperature Runs

Two solvents were used, n-pentane (Phillips, 99 mole %), and propane (Phillips, 99.99 mole %). The radical was diluted with pentane, placed in a Pyrex capillary tube (5 mm o.d., 2 mm i.d.), degassed on a vacuum line and sealed off under vacuum. The concentration was about $0.004M$ and measurements were made between $20°$ and $60°$C. The propane solution was made by distilling the solvent from a n-pentane solution in a capillary at dry-ice temperature. Propane, previously condensed in a trap was distilled into the capillary, and the tube sealed under vacuum. The concentration was about $0.01M$ at $20°$C. Paramagnetic resonance measurements were made between $-137°$ and $81°$C. Viscosities of propane were obtained from the data of Lipkin et al.[5] and Sage and Lacey.[6] An extrapolation was necessary between $-137°$ and

$-73.3°$C. Corrections were made for the change in concentration of the radical due to changes in the liquid and vapor densities with temperature. The densities of the saturated liquid and vapor at various temperatures were obtained from the *International Critical Tables* for pentane, and from the data of Deschner,[7] Sage et al.,[8] and Thodos[9] for propane. We have assumed that the solute remains entirely in the liquid phase at all temperatures. The temperature of the measurement was maintained by passing a cooled or heated stream of nitrogen gas through a quartz Dewar in the microwave cavity containing the sample. The temperature was monitored by thermocouples placed above and below the sample. The accuracy of all temperature measurements is estimated as at least $\pm3°$C.

C. Treatment of Data

The paramagnetic resonance spectrum of DTBN in dilute fluid solution consists of three equally intense hyperfine lines of equal width, with $\langle g \rangle = 2.0064$, and $\langle a_N \rangle = 15.4$ G. In dilute solutions, when exchange is unimportant, each line has a peak-to-peak width of 0.55 G[10] due principally to unresolved hyperfine interactions with the t-butyl protons, $\langle a_H \rangle \sim 0.1$ G; this splitting may be resolved under stringent experimental conditions. As the exchange rate increases, the individual lines broaden, and the outer lines move toward the center of the spectrum. At high exchange rates the hyperfine structure collapses into a single "exchange-narrowed" line which becomes narrower as the exchange rate increases. All samples were sufficiently dilute that even at the highest exchange rates reached, the individual hyperfine lines were still resolved. The linewidths measured and referred to throughout this paper are the peak–peak linewidths of the first-derivative spectra. All three lines were measured, and the average was taken as the linewidth under the particular experimental conditions. Generally, two complete spectra were measured and averaged. The estimated accuracy of linewidth measurements between 2 and 4 G is $\pm2\%$, while the accuracy of measurements out of that range approaches 5%.

EXPERIMENTAL RESULTS

In Figs. 1(a) and 1(b) we have plotted the average linewidth of DTBN in propane and in n-pentane, respectively, vs the quantity $T/293\eta$ (cP⁻¹). The pentane measurements include points from the variable temperature measurements (filled circles), and from the variable pressure measurements (open circles).

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