

function,¹⁶ we find that a shift of the observed magnitude would be produced by 0.03% $3p$ character on the Cl^- ion. This is surprisingly small and its elucidation must await further data.

¹⁶ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

Work is continuing in other compounds of the UCl_3 structure, and at lower temperatures.

ACKNOWLEDGMENT

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Effects of Hydrostatic Pressure and Temperature on Spin Exchange between Free Radicals in Solution

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The paramagnetic resonance linewidths of the di-*tert*-butyl nitroxide free radical have been measured as a function of hydrostatic pressure and of temperature in the pure hydrocarbon solvents methylcyclohexane, *n*-pentane, and propane. These data are reported at conditions under which intermolecular spin exchange gives the principal contribution to the linewidth. Deviations of the linewidth from a linear dependence on T/η , where η is the liquid viscosity, are attributed to a dropping off of p , the average exchange probability per radical-radical encounter, from unity at low values of η/T . The viscosity and temperature dependence of p is found to be $p = 1 - \exp(-a\eta/T)$, where a is a positive constant which depends upon the solvent. This form of $p(\eta, T)$ is shown to arise from a theory which treats the exchange reaction as a unimolecular kinetic process which may occur, however, only during a radical-radical encounter in the liquid. Radical-oxygen exchange rates were also measured in methyl cyclohexane and the same theory explains the η and T dependence.

INTRODUCTION

THE widths of individual hyperfine lines of free radicals in liquids are observed to broaden with increasing radical concentration and with decreasing solvent viscosity. This phenomenon is due to spin-exchange interactions which cause the magnetic environment of an electron spin undergoing magnetic resonance to fluctuate. At high solvent viscosities, the widths of the hyperfine lines increase anisotropically with viscosity as the radical tumbling becomes too slow to average the anisotropies in the spin Hamiltonian.¹ We are concerned in this paper with the study of radical-solvent systems in which spin exchange is the dominant line broadening process. We have done two types of experiments on the paramagnetic resonance linewidths of the free radical di-*t*-butyl nitroxide (DTBN) in solutions of simple saturated hydrocarbons in order to study these exchange interactions. In the first type of experiments, the paramagnetic

resonance linewidths were measured at constant temperature as a function of solvent viscosity. The solvent viscosity was varied by the application of hydrostatic pressure. Radical-oxygen exchange, as well as radical-radical exchange was studied in samples which were not deoxygenated. The second type of experiment was done by varying the temperature of solutions of the radical dissolved in liquid pentane and in liquid propane in sealed tubes. In this type of experiment the radical-radical exchange rates were correlated with the temperature, as well as with the viscosity of the liquid.

Pake and Tuttle² have developed a theory which gives the dependence of the spin exchange frequency ν_{ex} on temperature and the viscosity of the solvent. They assume

$$\nu_{\text{ex}} = \nu_{\text{enc}} p,$$

where ν_{enc} is the encounter rate of paramagnetic molecules in the liquid, and p is the probability of spin exchange during an encounter. Both ν_{enc} and p depend upon viscosity and temperature; an expression for ν_{enc}

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¹ (a) H. M. McConnell, *J. Chem. Phys.* **25**, 709 (1956). (b) N. Edelstein, A. Kwok, and A. H. Maki, *ibid.* **41**, 179 (1964).

² G. E. Pake and T. R. Tuttle, Jr. *Phys. Rev. Letters* **3**, 423 (1959).

is given in Pake and Tuttle's paper.² Kivelson³ 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 $20^\circ \pm 2^\circ\text{C}$. Solvent viscosities were calculated from Bridgman's⁴ 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 ($\eta \cong 0.74$ –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 Thodos⁹ 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 $\pm 3^\circ\text{C}$.

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 $\pm 2\%$, 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).

³ D. Kivelson, *J. Chem. Phys.* **33**, 1094 (1960).

⁴ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Son, Ltd., London, 1952).

⁵ M. R. Lipkin, J. A. Davison, and S. S. Kurtz, Jr., *Ind. Eng. Chem.* **34**, 976 (1942).

⁶ B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **30**, 829 (1938).

⁷ W. W. Deschner, *Ind. Eng. Chem.* **32**, 836 (1940).

⁸ B. H. Sage, J. G. Schaafsma, and W. N. Lacey, *Ind. Eng. Chem.* **26**, 1218 (1934).

⁹ G. Thodos, *Ind. Eng. Chem.* **42**, 1514 (1950).

¹⁰ J. Gendell (private communication).

Since the concentration of the radical was different in the two measurements, the linewidths observed at variable temperature were multiplied by the linewidth ratio of the two solutions at a common set of conditions (20°C , $P=1$ atm). This procedure is justified since in this range of concentration it was independently verified that the linewidth is linear with concentration.¹¹ The same linearity of linewidth with concentration was assumed in correcting the data for changes in liquid and vapor density with temperature.

The results of the variable pressure measurements in methyl cyclohexane at 20°C are presented in Fig. 2(a). It should be noted that for the deoxygenated solution, the linewidth is linear with η^{-1} , whereas a definite curvature is noticed for the two solutions containing oxygen. The dashed line in Fig. 2(a) is the theoretical plot of a $0.0024M$ deoxygenated solution, the slope of which is one-fifth that of the $0.012M$ deoxygenated solution. This relationship is also established by the linearity of W with concentration in the region of exchange rates covered by these experiments. The line was located to give the same difference in intercepts

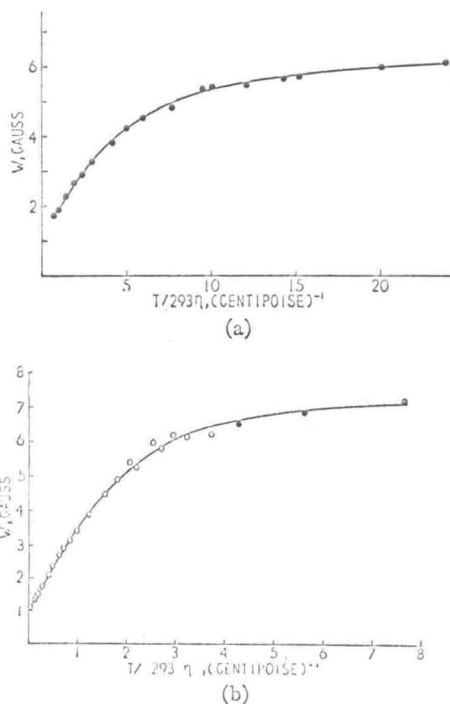


FIG. 1. (a) Linewidths of DTBN in liquid propane, $c \sim 0.01M$ at 20°C . Data obtained in sealed tube at variable temperature. (b). Linewidth of DTBN in liquid *n*-pentane. Open circles represent data at variable pressure with $T=293^{\circ}\text{K}$, while filled circles are data at variable temperature and $P=1$ atm. Liquids are deoxygenated. $c=0.012M$ for variable pressure data, and $c \sim 0.004M$ for variable temperature data. Linewidths were normalized for the concentration difference.

¹¹ A. Kwok, thesis, Harvard University, See also M. T. Jones, *J. Chem. Phys.* **38**, 2892 (1963); and J. Danner and T. R. Tuttle, Jr., *J. Am. Chem. Soc.* **85**, 4052 (1963).

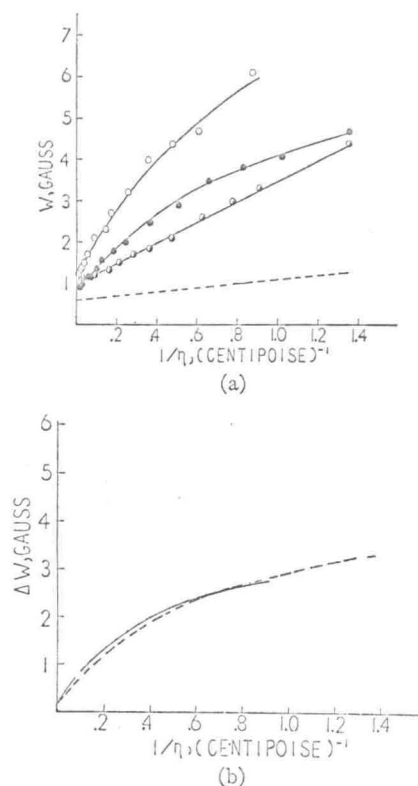


FIG. 2 (a) Linewidths of DTBN in liquid methylcyclohexane. All data are at variable pressure at $T=293^{\circ}\text{K}$. Open circles are $c=0.012M$, air saturated at $P=1$ atm, filled circles are $c=0.0024M$, air saturated at $P=1$ atm, and half-filled circles are $c=0.012M$, deoxygenated solution. The dashed line represents the expected behavior of a $c=0.0024M$ deoxygenated solution. (b) Linewidth differences ΔW between oxygen containing and deoxygenated solutions of DTBN in methylcyclohexane. Solid line is for a radical concentration of $c=0.012M$, while dashed line is for $c=0.0024M$.

between deoxygenated solutions as that observed between the oxygen containing solutions at these concentrations.

Figure 2(b) illustrates the effect of dissolved oxygen on the free radical linewidths. The solid line is the difference in linewidth (ΔW) between oxygen containing and deoxygenated solutions, at $c=0.012M$, whereas the dashed line is the difference in linewidth between the oxygen containing $0.0024M$ solution and that of the theoretical deoxygenated solution of the same concentration. It is observed that the nonlinearity of the curves in Fig. 2(a) is due to the presence of dissolved oxygen at both radical concentrations, and that the effect of oxygen is the same at both radical concentrations.

It is found that at high viscosities, the linewidth is approximately linear with T/η , which is the predicted behavior according to the theory of Pake and Tuttle² for $p=1$, whereas the slope falls off at lower viscosities. It is assumed that in the linear region $p=1$, and that the falling off of the linewidth at reduced viscosities is

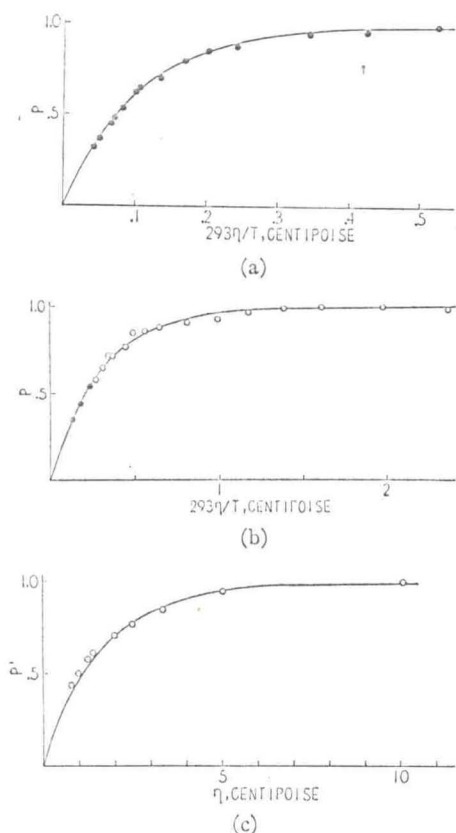


FIG. 3. (a) Probability of exchange during a single radical encounter, p , vs $293\eta/T$ for DTBN in propane. Solid line is a plot of $p=1-\exp(-2.81 \times 10^3 \eta/T)$. (b) Probability of exchange during radical encounter, p , vs $293\eta/T$ for DTBN in *n*-pentane. Solid line is a plot of $p=1-\exp(-1.01 \times 10^3 \eta/T)$. (c) Probability of spin exchange during radical-oxygen encounter, p' , vs η in methylcyclohexane. $T=293^\circ\text{K}$ for all points. Solid line is a plot of $p'=1-\exp(-0.19 \times 10^3 \eta/T)$.

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

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

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 $p=1-\exp(-2.81 \times 10^3 \eta/T)$, $p=1-\exp(-1.01 \times 10^3 \eta/T)$,

and $p=1-\exp(-0.193 \times 10^3 \eta/T)$, 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

$$W_\alpha = k_\alpha \nu_{\text{ex}} + R_\alpha \quad (1)$$

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 α th hyperfine component, k_α is a proportionality constant, and R_α represents other contributions to the linewidth. The exchange Hamiltonian is represented by

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

with the exchange integral J_{ij} given by

$$J_{ij} = e^2 \iint \psi_A^*(\mathbf{r}_i) \psi_B^*(\mathbf{r}_j) (\mathbf{r}_{ij})^{-1} \psi_B(\mathbf{r}_i) \psi_A(\mathbf{r}_j) d\tau_i d\tau_j \quad (2)$$

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, $\int \psi_A^*(\mathbf{r}_i) \psi_B(\mathbf{r}_i) d\tau_i$, 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 $J_{ij} \sim 0$ 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

$$W_\alpha = k_\alpha \nu_{\text{enc}} p + R_\alpha \quad (3)$$

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

$$\nu_{\text{enc}} = n N_r z / N_s \quad (4)$$

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 average number of new neighbors a radical

encounters and make a jump. The probability of an encounter being approximated

where λ is the viscosity. Equation

which, when provided $p=1$

We propose the probability calculations, we will remains effective of the radical Eulerian angles provided the compared with function of the encounter, is assumes that in this case, localized on the from the environment, for conversion $t = -\tau_{\text{enc}}/2$, and subscripts i and j becomes

where r_0 is the two radicals. that $J(\theta, r_0)$ may be several for the sake one such orientation the formation orientation θ_0 $\theta(t)$ is a random

Let us define during an encounter no explicit time average at all for instance,

where the angle

The problem to the principal reactions. J_0 constant. The limit to the d

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).

The form of $p(\eta, T)$ obtained in the previous section [Eq. (10)] is verified by the plots in Figs. 3(a)–3(c). The validity of Eq. (5) for τ_{enc} is assumed. The simple unimolecular reaction model is thus seen to account in a satisfactory way for the exchange probability parameter $p(\eta, T)$. Interestingly enough, it is empirically found that $J_0\tau_{\text{enc}}$ for radical–radical exchange is strongly solvent-dependent, and that for the same solvent (methyl cyclohexane) $J_0\tau_{\text{enc}} \gg J_0'\tau'_{\text{enc}}$. The values of $J_0\tau_{\text{enc}}$ are found to be $1.01 \times 10^3 \eta/T$ (*n*-pentane), $2.81 \times 10^3 \eta/T$ (propane), $\gtrsim 1 \times 10^3 \eta/T$ (methylcyclohexane), while $J_0'\tau'_{\text{enc}} = 0.19 \times 10^3 \eta/T$ (methylcyclohexane). Viscosities are expressed in centipoise.

From the empirical values of $J_0\tau_{\text{enc}}$ and Eq. (5) with $\lambda = 3 \times 10^{-8}$ cm, J_0 was calculated to be 1.6×10^{11} sec⁻¹ in *n*-pentane, 4.5×10^{11} sec⁻¹ in propane and $\gtrsim 1.6 \times 10^{11}$ sec⁻¹ in methylcyclohexane. $J_0'\tau'_{\text{enc}}$ is

about an order of magnitude smaller than the corresponding quantity for radical–radical exchange. It is expected, however, that λ' , the interaction radius for the oxygen molecule, is also appreciably smaller. These values of J_0 are about an order of magnitude larger than the value estimated by Pake and Tuttle² for polycrystalline DPPH (10^{10} – 10^{11} sec⁻¹).

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Crystal Structure of $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ †

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The crystal structure of $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ has been determined by x-ray diffraction. The tetragonal unit cell, having $a = 6.57$, $c = 18.62$ Å, contains four formula weights; the space group is $D_{4h}^{19} - I4_1amd$. Discrete BeF_4^{2-} and ZrF_8^{4-} ions are connected by shared Li^+ ions. The BeF_4^{2-} tetrahedron is quite regular with a Be–F distance of 1.57 ± 0.01 Å; the ZrF_8^{4-} dodecahedron has two independent Zr–F bonds of 2.05 ± 0.01 Å and 2.16 ± 0.01 Å, and deviates considerably from the shape predicted by theory.

INTRODUCTION

ZIRCONIUM is known to occur as the central atom of a variety of complex coordination polyhedra, often bearing eight ligands arranged in dodecahedral or square-antiprismatic symmetry.^{1,2} Racah³ and Duffey⁴ have derived orbital strengths for these configurations using $d^4s^1p^3$ hybridization. Their calculations established no significant energy difference between the configurations, if isolated complexes are considered.

The configuration adopted in a particular crystal is therefore determined in part by external influences, such as ligand–ligand repulsions, constraints due to

bonding between ligands, and packing requirements. Thus it is interesting to examine MX_8 -type configurations in which, as in the well known $\text{Mo}(\text{CN})_8^{4-}$ ion,⁵ the central metal atom is bonded to eight apparently equivalent monodentate ligands.

In an investigation of the phase diagram of the ternary system $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$, Thoma *et al.*⁶ discovered a primary phase of composition $6\text{LiF} \cdot \text{BeF}_2 \cdot \text{ZrF}_4$. The stoichiometry and preliminary x-ray studies suggested the possible occurrence of complex octafluorozirconate and tetrafluoroberyllate ions in the crystal.

The coexistence of two discrete complex anions in a crystal is not common. But since it seemed likely in this compound, a crystal-structure analysis was carried out to examine in detail the configuration of the discrete

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² R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *Nature* **199**, 559 (1963).

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⁴ G. H. Duffey, *J. Chem. Phys.* **18**, 746, 1444 (1950).

⁵ J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.* **61**, 2853 (1939).

⁶ R. E. Thoma *et al.*, U.S. Atomic Energy Commission Report ORNL-3591 (1964), pp. 3 ff.

ZrF_8^{4-} ion and bond distances

A single crystal melt of stoichiometric $\text{Li}_6\text{BeF}_4\text{ZrF}_8$ at 471°C. Neutron diffraction analyses indicate the ZrF_8^{4-} ion and this $\text{Li}^+:\text{Zr}^{4+}$ ratio.

X-ray precession method yielded a tetragonal unit cell with $a = 0.02$, $c = 18.62$ Å, space group $I4_1/amd$. An electron density map was obtained by a Fourier method. However, an electron density map of the compound was obtained by the method of volumes of the unit cell from which $\rho = 3.06$ g cm⁻³.

Photograph of the hkl reflections from radiation and spot densities by visual comparison with strips. Of the comparison with the range of the values.

The $\text{CuK}\alpha_1$ radiation is 139 cm⁻¹. The 0.01 cm parameter is larger than that in the errors were estimated for them was applied to the relative structural scale was four

STRUCTURE

The beryllium ion has tetrahedral symmetry to the Group $I4_1/amd$ space group, not wholly in the method, together with atomic contributions to the electron density from electron

⁷ A. J. C. Wilkins

⁸ International Union of Pure and Applied Chemistry, Birmingham

⁹ All Fourier transforms were done with the program FORDAP-2 written by R. D. Ellis