

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

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

Work is continuing in other compounds of the  $\text{UCl}_3$  structure, and at lower temperatures.

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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  $T/\eta$ , where  $\eta$  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  $\eta/T$ . 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  $\eta$  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.<sup>1</sup> 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 Tuttle<sup>2</sup> have developed a theory which gives the dependence of the spin exchange frequency  $\nu_{\text{ex}}$  on temperature and the viscosity of the solvent. They assume

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

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

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

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