

ELECTRON SPIN-LATTICE RELAXATION IN ORGANIC FREE RADICALS IN SOLUTIONS

S. K. RENGAN, M. P. KHAKHAR, B. S. PRABHANANDA AND B. VENKATARAMAN

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay-5

ABSTRACT

The electron spin-lattice relaxation times of several semiquinones have been measured as a function of free radical concentration, temperature, solvent, and viscosity, using the pulsed saturation recovery technique. It is found that the recovery of the signal can be fitted to an exponential in all cases within the limits of experimental error. It is also found that the relaxation time T_1 is independent of the hyperfine component for a given free radical. Three different models for the liquid state have been employed to analyze the data and it has been postulated that the data, both in liquids and frozen liquids can be explained on the basis of a hindered motion, in hydrogen bonding solvents. A brief review of the earlier theoretical and experimental studies on electron spin-lattice relaxation of free radicals in solutions is also presented.

I. INTRODUCTION

Recently, the study of spin-lattice relaxation in free radicals has been drawing greater interest from the workers in the field of electron spin resonance (esr). Since the paper of Lloyd and Pake¹ on the saturation behaviour of the esr spectra of peroxyamine disulphonate ions in solution, at low magnetic fields, a number of papers, both experimental and theoretical, have been published about the spin-lattice relaxation of free radicals in solution. It is well known that a study of the detailed properties of the unsaturated line shapes of esr spectra of free radicals in solution can yield useful information about dynamical molecular processes such as internal rotations, molecular tumbling, solvent-radical interactions, radical-radical interactions, ion-pairing, etc. The very same processes which modulate the spin systems and lead to spin relaxation effects that decide the line shape, also determine the spin-lattice relaxation which is reflected in the saturation behaviour of the esr spectra. A study of the spin-lattice relaxation can therefore be used to get information about the dynamical molecular processes in solution. An understanding of the processes involved in the spin-lattice relaxation of free radicals in solutions has been made possible by the papers of Lloyd and Pake¹, Fiaenkel², Stephen³, Kivelson⁴, Freed⁵, McConnell⁶, Carrington⁷, Johnson⁸, Hyde⁹, Jones¹⁰ and their coworkers. It is fair to say, however, that there are still many unanswered questions, and the experimental methods for the determination of electron spin-lattice relaxation times of free radicals in solutions have not reached the accuracy and sim-

plicity that have been obtained in the measurement of nuclear spin-lattice relaxation times.

In this paper we shall first survey, in Section II, the various techniques used to study the spin-lattice relaxation. In Section III, we shall discuss the theoretical and experimental work carried out so far. In Section IV, the spin-lattice relaxation times of semiquinones measured by us by the saturation-recovery technique will be discussed. The measurements have been carried out as a function of the nature of the radical, nature of the solvent, temperature and concentration of the radical.

II. REVIEW OF THE METHODS FOR STUDYING THE SPIN-LATTICE RELAXATION OF FREE RADICALS IN SOLUTIONS

(a) Pulse methods.

Perhaps the most direct way of measuring spin-lattice relaxation is the saturation-recovery method¹¹. In this method the magnetic field is fixed corresponding to a paramagnetic absorption. A large saturating microwave field pulse perpendicular to the steady magnetic field is applied and the return of the complex portion of the susceptibility (χ'') to its equilibrium value is observed using conventional detection techniques operating at low microwave powers. The recovery curve of absorption is traced on an oscilloscope. This decay curve is then analyzed assuming it to be a superposition of several exponentials. In our laboratory we have employed a superheterodyne detection system at X-band with broad band isolators inserted at necessary points to prevent the AFC lock-in of the local oscillator from being affected by the pulsing. A Philco L-4146 switch has been used for the switching of the microwave power and both the pulse width and repetition rate can be varied. The main high power (500 mW) klystron V-53 C is locked to an external cavity and this branch of the microwave line is also isolated adequately to prevent the klystron from being unlocked during pulsing. *Figure 1* is a block diagram of the spectrometer which can be used for observing both resonance and relaxation. We are limited to the measurement of times greater than 3 μ s, which however can be achieved for many organic free radicals at temperatures near 0°C where most solutions still retain low viscosity. The two parts of the system that limit the response time are the IF amplifier with its characteristic recovery time and the microwave cavity whose decay time depends on its Q . Brown and Sloop¹² have recently described a pulsed X-band superheterodyne spectrometer with a response time of 40 ns. They have incorporated in the detector arm of the bridge a switch in a sense opposed to that of the main pulsing switch to blank out the amplifier during the high power period. They have also used a low Q cavity.

Besides the limitation on the relaxation times that can be measured by this method, such spectrometers suffer usually from lack of sensitivity. In our case, for example, most of the measurements have been made on concentrated solutions, though in certain favourable systems, with a very small number of hyperfine components we have been able to make measurements at radical concentrations as low as 10^{-3} M. The sensitivity of the system can be im-

ELECTRON SPIN-LATTICE RELAXATION IN FREE RADICALS

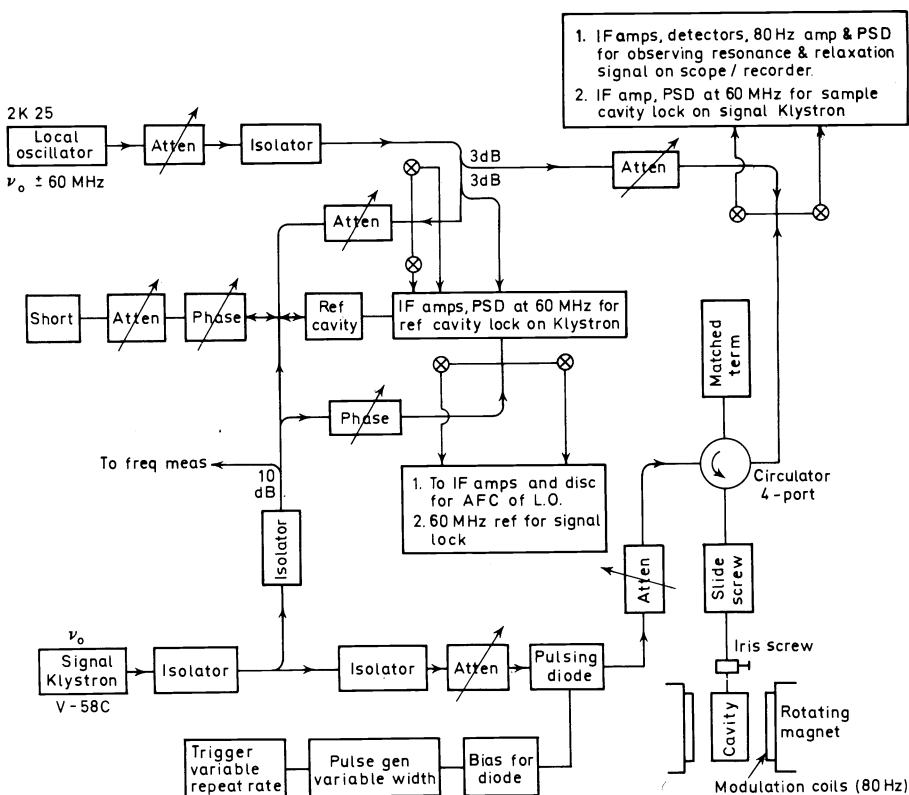


Figure 1. Block diagram of the X-band esr superheterodyne spectrometer used in spin-lattice relaxation measurements.

proved by increasing the ON/OFF power ratio of the pulsing switch. In this method, when the relaxation times are larger than one second, it becomes difficult to avoid saturation effects at the monitor power level necessary to obtain reasonable S/N ratio.

In the inversion recovery method¹³ one uses fast magnetic field sweeps and the recovery of the entire esr line at different stages after an adiabatic fast passage is studied. This method is convenient for relaxation times greater than one second.

Another method for measuring the relaxation time by observing the component of magnetization parallel to the steady magnetic field (using pick-up coils) under the influence of pulsing field perpendicular to the steady field has been described by Blombergen and Wang¹⁴. This system has a response time of about 10^{-7} s but is not yet made sensitive enough for work on dilute solutions of free radicals.

(b) Method of Hervé and Pescia.

The method recently developed by Hervé and Pescia¹⁵ under certain conditions offers an accuracy almost as good as the pulsed method in the 10^{-6} to 10^{-8} s range. In this method the microwave field is amplitude modulated and an analysis is made on the basis of Bloch's equations for an amplitude modulated microwave field H_1 . The in-phase and out-of-phase components of dM_z/dt are measured as a function of modulating frequency and a comparison is made with curves generated from the Bloch equations for cases $T_1 \gg T_2$ and $T_1 = T_2$ to determine T_1 . In this method there are still many unanswered questions: the interpretation of data in the range between $T_1 \gg T_2$ and $T_1 = T_2$, the minimum sensitivity, the effect of lossy solvents, etc.

(c) Dynamic nuclear polarization

Landesman¹⁶ has shown that in the case of dynamic nuclear polarization experiments where one of the spins is the unpaired electron of the free radical and the other is the solvent-nuclear spin, the enhancement of the nuclear resonance of the solvent-nuclear spin on saturation of the electron-spin transition is related to the electron spin-lattice relaxation time T_1 . T_1 can be extracted from a knowledge of the nature of the electron-nuclear coupling.

(d) The continuous saturation method¹⁷

The continuous saturation method is the simplest in terms of additional equipment needed. Its range of application is broad (i.e. from 10^{-2} to 10^{-9} s). The sensitivity of this technique is better than that of the pulse methods and is suited to the study of radicals at low concentrations.

In this method one defines a saturation factor $Z_{\alpha\beta}$ for the esr transition between levels α and β having degeneracy D_α by the relation

$$Z_{\alpha\beta} = \frac{n_{\alpha\beta}}{n_{\alpha\beta}^0} \quad (1)$$

where $n_{\alpha\beta}$ and $n_{\alpha\beta}^0$ refer to the equilibrium population difference between the two levels α and β in the presence and in the absence of rf field respectively. As shown by Lloyd and Pake¹ $Z_{\alpha\beta}$ can be written in the form

$$Z_{\alpha\beta} = (1 + 2V_{\alpha\beta}\Omega_{\alpha\beta})^{-1} \quad (2)$$

where $V_{\alpha\beta}$ is the probability of transition induced by the radiation and contains the factor D_α . $\Omega_{\alpha\beta}$ is the saturation parameter determined by the spin-lattice relaxation processes.

In the case of a homogeneous Lorentzian resonance line, we can express the linewidth as a function of the microwave magnetic field H_1 as

$$(\Delta H_{\alpha\beta})^2 = \frac{4}{3\gamma^2 T_2^2} + \frac{4H_1^2 D_\alpha \Omega_{\alpha\beta}}{3T_2} \quad (3)$$

where $\Delta H_{\alpha\beta}$ is the linewidth measured between points of extreme slope of the absorption line and T_2 is the inverse of linewidth in units of angular frequency measured at low microwave powers. A plot of $(\Delta H_{\alpha\beta})^2$ vs. H_1^2 yields a straight line with a slope equal to $(4D_\alpha \Omega_{\alpha\beta})/3T_2$ and an intercept at $4/(3\gamma^2 T_2^2)$.

H_1^2 can be measured by several methods discussed by Freed⁵ⁱ, Kooser¹⁷ and Jones^{10c}.

The error in the estimation of $\Omega_{\alpha\beta}$ comes from the error in the estimation of H_1 and the error in the determination of T_2 . It should be pointed out that in the case of lines having unresolved hyperfine structure it is difficult to estimate T_2 and the results obtained by this method are likely to lead to erroneous conclusions.

If the return to the equilibrium in the saturation-recovery method is exponential with a single relaxation time $T_{1\alpha\beta}$ then it can be readily shown that $T_{1\alpha\beta}$ obtained by this method is related to the $\Omega_{\alpha\beta}$ determined by the continuous saturation method

$$T_{1\alpha\beta} = D_{\alpha}\Omega_{\alpha\beta} \quad (4)$$

It is interesting to compare the spin-lattice relaxation time T_1 for the $M = 0$ line of $\text{TCNE}^- \text{K}^+$ in DME at 15°C , determined by the two techniques, at high concentrations. Eastman *et al.*^{5f} estimate $T_1 \sim 1.0 \mu\text{s}$ whereas the measurements by the saturation-recovery method carried out in our laboratory give a value of $T_1 \sim 5 \mu\text{s}$ in the concentration range where T_1 is shown by these authors to be independent of concentration. We believe, the difference in the two determinations comes mainly from the inaccuracies involved in the estimation of H_1 and T_2 in the continuous saturation method.

An excellent review of the various techniques available up to 1965 for the measurement of electron spin-lattice relaxation times has been made by Pescia^{15a}.

III. REVIEW OF THE EARLIER WORK ON RELAXATION OF FREE RADICALS IN SOLUTION

It was pointed out in Section I that the saturation behaviour of the esr spectra of free radicals in solution throws light on dynamical molecular processes such as internal rotations, molecular tumbling, solvent-radical interactions, ion-pairing, etc. From the theoretical treatments of the relaxation mechanisms and their influence on the saturation parameter, Ω and T_1 by Stephen³, Fraenkel^{2a, 2c}, Kivelson^{4a, 4d} and Freed^{5b, 5f, 5g} one can derive the dependence of T_1 (and Ω) on several parameters such as the nuclear spin quantum number of the esr transition, concentration of free radicals, nature of solvent, and temperature, and these are summarized below. It should be mentioned that electron-nuclear double resonance (ENDOR)^{5b} and electron-electron double resonance^{5e, 5g} (ELDOR) studies on free radicals in solutions also provide information on these dynamical processes.

(a) Hyperfine component dependence in dilute solutions

The linewidth variations among the hyperfine components observed in the esr spectra of paramagnetic molecules tumbling in solutions was first explained by McConnell⁶. The linewidth of a hyperfine component $(\Delta H)_{m_j}$ corresponding to an esr transition between two levels with nuclear spin state given by the quantum number m_j is expressed as^{2a, 2c, 4a, 6}

$$(\Delta H)_{m_j} = Km_j^2 + Lm_j + M \quad (5)$$

The term K arises from the modulation of the intramolecular electron-nuclear dipolar interaction (END), M arises from the modulation of the g -tensor term and other mechanisms, such as spin-rotation interaction which do not depend on m , L is a cross term arising from the simultaneous modulation of the END term and the g -tensor.

Based on similar considerations, Stephen and Fraenkel^{2a} predicted different saturation parameters also for different hyperfine components. However, the experiments of Schreurs and Fraenkel^{2c} on dilute solutions of *p*-benzosemiquinone ion and peroxyamine disulphonate ion proved inconclusive in establishing the nuclear state dependence of $\Omega_{\alpha\beta}$. It has been shown recently by Lingam, Nair and Venkataraman¹⁸, by the saturation recovery technique that the different hyperfine components in 2,5-ditertiary-butyl-*p*-benzosemiquinone ion (DTBSQ⁻) have the same spin-lattice relaxation time T_1 within the limits of the experimental error ($\pm 5\%$) and a similar tentative conclusion was arrived at for the case of *p*-benzosemiquinone ion (PBSQ⁻) also. Similar observations have been made by other workers also^{2e, 2f, 4c, 4d, 5b, 5d, 5i, 9, 19}. The obvious conclusion is that, in these free radicals the modulation of the END term is not the dominant process causing the spin-lattice relaxation.

It also follows that if the END term is not dominant and the electron spin-lattice relaxation times are independent of the nuclear spin quantum number of the hyperfine component one should expect an exponential recovery in the pulsed saturation recovery technique and the T_1 is related to the saturation parameter, $\Omega_{\alpha\beta}$, by equation 4.

It should be mentioned that nuclear electric quadrupole relaxation and the modulation of the isotropic part of the hyperfine interaction are also expected to relax different hyperfine components differently²⁰. The authors are not aware of any experimental confirmation of such effects.

(b) Concentration dependence

When the concentration of the radicals is increased the modulation of the radical-radical interactions becomes significant in determining the spin-lattice relaxation time. Freed and coworkers^{5f} have estimated the relative importance of dipole-dipole and exchange interactions. According to them the dominant process responsible for the concentration dependence of the relaxation, is the modulation of the Heisenberg exchange term. In the presence of strong exchange, the spin-lattice relaxation probability is increased, and the spin-lattice relaxation time in the presence of exchange $T_{1\bar{M}}$, is related to the spin-lattice relaxation time in the absence of exchange $T_1(O)$ by the expression

$$\left[1 - \frac{T_{1\bar{M}}}{T_1(O)}\right]^{-1} = m_{\bar{M}} b''^{-1} + a_{\bar{M}} \quad (6)$$

where

$$b'' = \omega_{\text{HE}}/NW_e$$

$$a_{\bar{M}} = f_{\bar{M}} = (N - 2D_{\bar{M}})/N$$

$$m_{\bar{M}} = 2f_{\bar{M}}/N$$

$D_{\bar{M}}$ = degeneracy of state with spectral index \bar{M}

N = total number of spin eigenstates

W_e = relaxation probability due to lattice-induced pure electron spin flips
 $= [2T_1(O)]^{-1}$

ω_{HE} = Heisenberg exchange frequency (7)

The Heisenberg exchange frequency is given by^{5c, 5f, 8, 21}

$$\omega_{\text{HE}} = \tau_2^{-1} [1 + J^{-2} \tau_1^{-2}]^{-1} \quad (8)$$

where τ_2 is the mean lifetime between the successive bimolecular encounter of identical radicals, τ_1 is the mean lifetime of an exchanging radical pair and J is twice the exchange integral. Strong exchange requires $(J\tau_1)^2 \gg 1$. The expression (6) has been obtained for the case when only Heisenberg exchange and lattice-induced pure electron spin flips are important. b'' can be determined as a function of concentration and spectral index \bar{M} by a study of linewidths^{5f}. The experimental results of Freed and coworkers^{5f} on TCNE⁻K⁺ in DME are in agreement with their expressions. Chemical exchange is also expected to give similar results.

The exchange interaction will become less significant when the size of the radical is big or when the radical is solvated. The strong exchange is expected to become significant when the viscosity of the solvent is increased leading to an increase in τ_1 . Since τ_2^{-1} is proportional to T/η , an increase in temperature leads to increase in ω_{HE} under strong exchange conditions.

It has also been shown by these workers^{5f} that the spin-lattice relaxation time T_1 , under strong exchange, approaches an asymptotic value with increasing concentration and the linewidths increase with temperature and concentration.

(c) Solvent and temperature dependence.

As stated above, the Heisenberg exchange term depends on the viscosity of the solvent and temperature and the ratio, $T_{1\bar{M}}/T_1(O)$ will vary when the viscosity, temperature or both are varied. However, in dilute solutions where the exchange is not dominant, this variation can be neglected.

In Section III(a), the spin-lattice relaxation of free radicals in dilute solutions in absence of exchange is shown to be predominantly independent of the particular hyperfine transition, and in such a situation, the major contribution to the spin-lattice relaxation comes from the modulation of the g -tensor term and spin-rotational interaction. The associated transition probabilities are given by^{2a, 4d, 4e}

$$W_e^g = \sum_{i=1}^3 [(g_i - g_s)^2/40] [\omega_e^2 \tau_R / (1 + \omega_e^2 \tau_R^2)] \quad (9)$$

and

$$W_e^{\text{SR}} = \sum_{i=1}^3 (g_i - g_e)^2 / 18 \tau_R \quad (10)$$

where g_1, g_2, g_3 are the components of the g -tensor, $g_s = \frac{1}{3} \sum_1^3 g_b$, $g_e = 2.0023$

and τ_R is the rotational correlation time associated with the tumbling free radical. The temperature and solvent dependence of the relaxation probability in these processes comes from the dependence of τ_R on these parameters. Many attempts have been made to predict τ_R , based on different models of the liquid state. Of these, the viscosity model, the conditional inertial rotation model and the quasilattice random flight model are of interest to us.

The viscosity model is a small step isotropic rotational diffusion model, the diffusion coefficient occurring in the diffusion equation being expressed in terms of the viscosity of the solvent η . Using the Debye–Stokes–Einstein relationship one gets

$$\tau_R = \frac{V_M \eta}{kT} \quad (11)$$

where V_M is the molecular volume. Gierer and Wirtz²³ have taken into account the discontinuous nature of the liquid which reduces the value of τ_R by a factor of six. The temperature dependence of the τ_R in this model can be expressed as

$$\tau_R = AT^{-1} \exp(E_\eta/RT) \quad (12)$$

In the above expression it has been assumed that $\eta = \eta_0 \exp(E_\eta/RT)$ which is true for most of the liquids. Anisotropy in the rotation modifies the expressions slightly^{24, 25}.

Atkins²⁶ developed a model in which the molecular rotation in liquids strongly resembles that which occurs in the gas phase. Atkins, Loewenstein and Margalit²⁷ modified this and proposed the conditional inertial rotation model in which it is assumed that the inertial rotation occurs only when the environment of the molecule attains an expanded lattice configuration. The concentration of such expanded lattice sites P_D is given by $P_D = P \exp(-E/RT)$. This assumption leads to an expression for τ_R :

$$\tau_R = AT^{-\frac{1}{2}} \exp(E/RT) \quad (13)$$

In this model the value of A increases as the moment of inertia of the molecule increases²⁷.

The quasilattice random flight model used by O'Reilly and Schacher²⁸ is based on the large step random walk theory of rotational diffusion, outlined by Ivanov²⁹. The model assumes that the liquid structure up to the first coordination shell may be approximated by a lattice. It is assumed that the molecule undergoes little reorientation at the normal lattice sites. It is further assumed that when the molecule is excited to a vacant interstitial site due to drastic changes in the intermolecular forces, the molecule will undergo large-amplitude reorientation. The correlation time in this model can be given as

$$\tau_R = A \exp(E/RT) \quad (14)$$

where A depends on molecular volume.

It should be mentioned that when one has a 'barrier' motion the rotational correlation time has a similar expression.

In all these models τ_R increases as the temperature is decreased. If g -modulation is important in determining the spin–lattice relaxation time

T_1 , $T_1 \propto 1/\tau_R$ for $(\omega_e \tau_R \ll 1)$ and $T_1 \propto \tau_R$ for $(\omega_e \tau_R \gg 1)$. On the other hand, if the spin-rotational interaction is important $T_1 \propto \tau_R$ always. Studying the spin-lattice relaxation at different microwave frequencies helps in determining which term is important. In situations where $T_1 \propto \tau_R$ we can write $T_1 = BT^n \exp(E/RT)$ or

$$\ln T_1 - n \ln T = C + E/RT \quad (15)$$

$n = -1$, $-\frac{1}{2}$ and 0 will correspond to the different models discussed above. The experimental results on semiquinone ions will be discussed in the light of the above mentioned models in Section IV.

(d) Spin-lattice relaxation for radicals with orbitally degenerate ground states

Free radicals with orbitally degenerate ground states have anomalously small relaxation times and it has been found by Das, Wagner and Freed^{5j} that their linewidths and saturation behaviour are independent of solvent, counterion and temperature. This is most clearly demonstrated for coronene and triphenylene anion radicals. However, in the cases of benzene and cyclooctatetraene anions (which are alkali metal prepared) there is an additional contribution to T_2^{-1} which increases with temperature. This contribution is correlated with counter-ion and solvent-dependent ion-pairing effects. Rataiczak and Jones^{10c} have observed recently that for benzene anion the linewidths are independent of concentration for concentrations less than 0.1 M. T_2 exhibits a maximum at 173 K and T_1 at approximately 188 K. T_1 is also found to be independent of concentration. These authors also found evidence for ion-pairing effects. Das, Wagner and Freed^{5j} have suggested that the independence of relaxation times from temperature, solvent and counter-ion where ion-pairing effects are negligible, arise from intramolecular relaxation mechanisms via the anomalous spin-orbit interactions. However, the range of $T_1(10^{-7}$ s) for the orbitally degenerate radicals is outside the scope of our present experimental capability of pulsed techniques and we have not, therefore, attempted to measure these.

IV. SPIN-LATTICE RELAXATION IN SEMIQUINONES

In this section we discuss our measurements of T_1 by the saturation recovery technique on a number of semiquinones. The saturation recovery trace was displayed on the dual-beam oscilloscope and compared with the output from an exponential generator. In all the cases studied so far, the saturation recovery was exponential and could be characterized by a single relaxation time T_1 within the limits of experimental error.

The relaxation times measured for the different hyperfine components showed that the spin-lattice relaxation in semiquinones is predominantly independent of nuclear spin state. This is in agreement with the observations of Lingam, Nair and Venkataraman¹⁸. Since T_1 was found to increase on decreasing the temperature, we have a situation where $T_1 \propto \tau_R$. We have analyzed our results according to equation 15. By a least squares analysis of the data the activation energies E and intercepts 'C' have been obtained for the cases $n = -1$, $-\frac{1}{2}$ and 0 , corresponding to the different models of the liquid state. The details of our results are given below:

(a) Samples and materials*(i) Chemicals used for relaxation studies.*

p-benzohydroquinone from May and Baker Ltd. was used without further purification whereas monochloro, monobromo, tolu, mono-*t*-butyl, 2,5-di-*t*-butyl, and 2,5-di-*t*-amyl hydroquinones from Eastman Organic Chemicals were purified by recrystallization from ethanol. 2,5-dichloro, 2,5-dimethyl and 2,6-dimethyl *p*-benzoquinones were also obtained from Eastman Organic Chemicals. The chloro compound was reduced with Zn dust in glacial acetic acid³⁰. The methyl quinones were reduced with 85% hydrazine hydrate solution³¹. Duroquinone was prepared from durene (Fluka, Switzerland, used without further purification) by the method of Smith and Dobrovlny³² and was recrystallized from 95% ethanol. It was reduced to durohydroquinone with Zn dust and glacial acetic acid³⁰.

The potassium salt of tetracyanoethylene anion (TCNE⁻) was obtained from the Department of Chemistry, Cornell University, USA.

(ii) Solvents and other inorganic chemicals:

Absolute ethyl alcohol (96%) from local suppliers was used without further purification. Isopropanol was obtained from Fluka, Switzerland, ethyleneglycol from NAARDEN, Holland and amyl alcohol from Allied Chemical and Dye Corporation. Methanol, *n*-butanol, *n*-decanol, glycerol and acetone used were ANALAR grade BDH products and were used without further purification. 1,2-dimethoxyethane (DME) from Aldrich Chemical Co. Inc. and tetrahydrofuran (THF) from L. Light & Co. Ltd. were purified³³ and stored under vacuum.

All the inorganic chemicals used were of reagent grade.

(iii) Preparation of semiquinones in alcohols, acetone.

The hydroquinones and potassium hydroxide were dissolved in appropriate solvents in different tubes. They were mixed in the esr sample tube itself just before the relaxation studies to get the corresponding semiquinone by the air oxidation of the hydroquinone. If the mixing is done in the esr sample tube the samples had a longer life time than if they were mixed outside and then transferred into the esr sample tube. The solubility of hydroquinones in viscous alcohols—*n*-butanol, *n*-decanol, glycerol, ethyleneglycol—was quite poor and almost saturated solutions were used.

(iv) Preparation of semiquinones in other solvents.

The semiquinones were prepared by method (iii) in ethanol as described above in the sample tube. The sample tube was then connected to the vacuum line and all the ethanol was removed under vacuum. Into the dry semiquinone sample was distilled previously purified, dry solvents, stored on the vacuum line. The sample tube was then sealed under vacuum.

(v) TCNE⁻ K⁺ samples.

The potassium salt of tetracyanoethylene was dissolved in DME in a sample tube under vacuum by distillation of DME from a reservoir of purified DME kept in vacuum.

(b) 2,5 ditertiarybutyl-*p*-benzosemiquinone ion (DTBSQ⁻)

The esr spectrum of this ion consists of a triplet with the intensity ratio 1:2:1. Each hyperfine line is further split by the interaction of the unpaired electron with the tertiary-butyl protons. However, at the concentrations used by us these fine hyperfine structures are unresolved. Thus, it becomes difficult to estimate T_1 for DTBSQ⁻ by the continuous saturation technique. The saturation-recovery method is ideally suited to study the spin-lattice relaxation behaviour of this radical. DTBSQ⁻ is quite stable and a sufficiently high concentration of this radical can be obtained in a number of solvents.

The measured spin-lattice relaxation times T_1 at different concentrations of DTBSQ⁻ in ethanol are plotted in *Figure 2*. It is seen that T_1 is independent

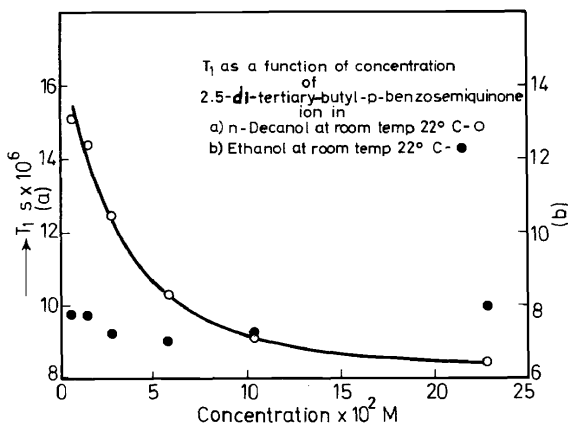


Figure 2. Spin-lattice relaxation times (T_1) as a function of concentration of DTBSQ⁻ in *n*-decanol and ethanol at 22°C.

of the concentration of DTBSQ⁻, in ethanol, within the limits of experimental error ($\pm 10\%$). However, T_1 shows concentration dependence in the highly viscous solvent *n*-decanol.

We feel that the concentration independent behaviour of T_1 for DTBSQ⁻ in ethanol shows that the exchange effects are not important in this system at concentration $\sim 10^{-2}$ M. The observed increase of linewidth on lowering the temperature below -40°C also confirms the above statement. (Exchange effects cause the linewidth to decrease with decrease in temperature). The observed increase in linewidth on increasing the temperature at higher temperatures ($> -40^\circ\text{C}$) can be explained on the basis of spin-rotational effects. Further, exchange effects are expected to become important as the viscosity of the solvent is increased. Thus, the observed dependence of T_1 on concentration in *n*-decanol is not surprising and can be attributed to the exchange term. The linewidth behaviour of DTBSQ⁻ in solvents other than THF and *n*-decanol (solvents are listed in *Table 1*) suggest that the Heisenberg exchange term is not important in these solvents. However, the dependence of T_1 on concentration has not been studied except for ethanol and *n*-decanol.

Figure 3 gives the plot of T_1 for DTBSQ⁻ in the mixed solvent ethanol-glycerol vs. $\ln \eta$ where η is the viscosity of the mixed solvent. (The viscosity

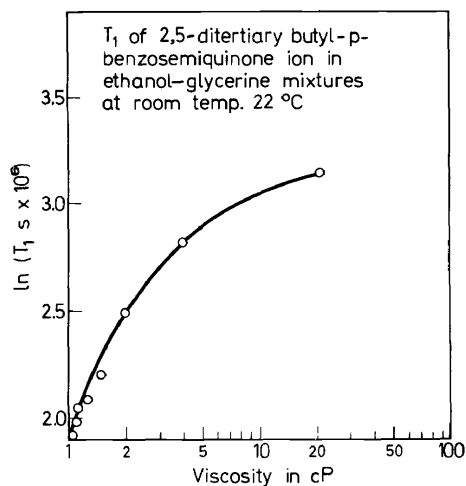


Figure 3. The logarithm of the spin-lattice relaxation times (T_1) plotted against $\ln \eta$ for $DTBSQ^-$ in ethanol-glycerine mixtures of different compositions at 22°C.

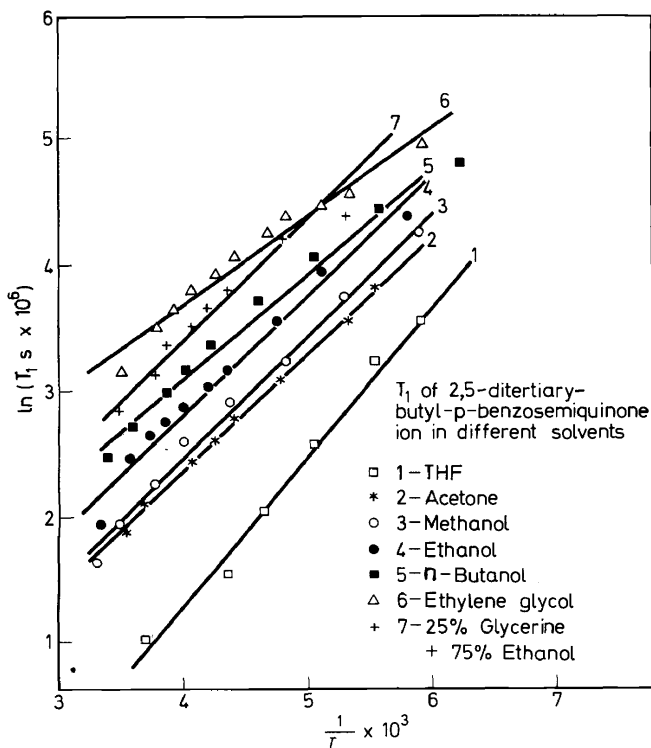


Figure 4. The plot of $\ln T_1$ against the reciprocal of temperature in kelvin for $DTBSQ^-$ in different solvents.

ELECTRON SPIN-LATTICE RELAXATION IN FREE RADICALS

is varied by changing the composition of the solvent). From the plot it is clear that T_1 is not proportional to the viscosity. Thus the viscosity model can be ruled out at least in the case of this mixed solvent.

T_1 has also been measured as a function of temperature T in a number of solvents. ($\ln T_1 - n \ln T$) has been plotted against $1/T$ in Figure 4 (for $n = 0$), Figure 5 (for $n = -\frac{1}{2}$) and Figure 6 (for $n = -1$). The activation energies E and the intercept 'C' obtained from this data are tabulated in Table 1. (Measurements of T_1 of DTBSQ⁻ in *n*-decanol have been carried out between 10 and 60°C. Since there was a possibility of concentration change due to decay of the radicals at high temperatures, the data points for this system are not plotted in Figures 4, 5 and 6).

If the viscosity model is the correct one, then the activation energy E for the case $n = -1$, must be equal to E_η obtained by fitting the viscosity data to the relation

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \tag{16}$$

The values of E_η for the solvents for which viscosities at various temperatures are known are also listed in Table 1.

The activation energies E are very different from E_η for the solvents

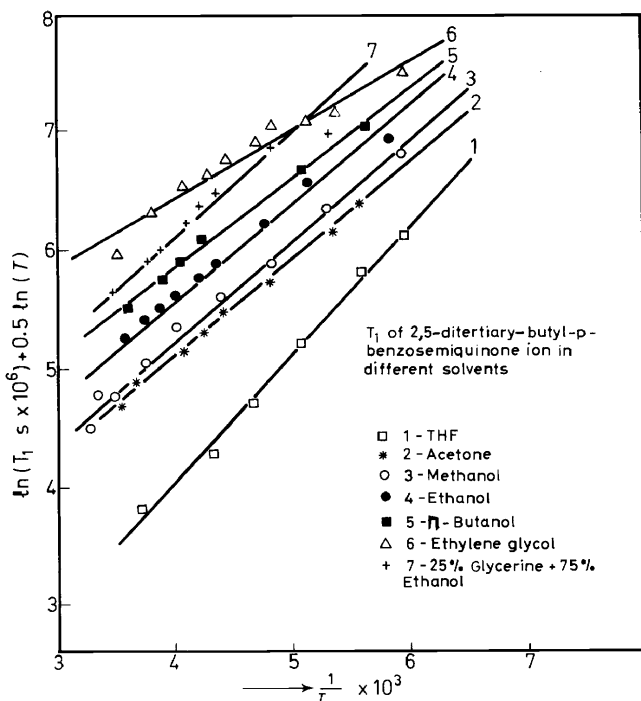


Figure 5. The plot of $\ln T_1 + 0.5 \ln T$ against the reciprocal of temperature in kelvin for DTBSQ⁻ in different solvents.

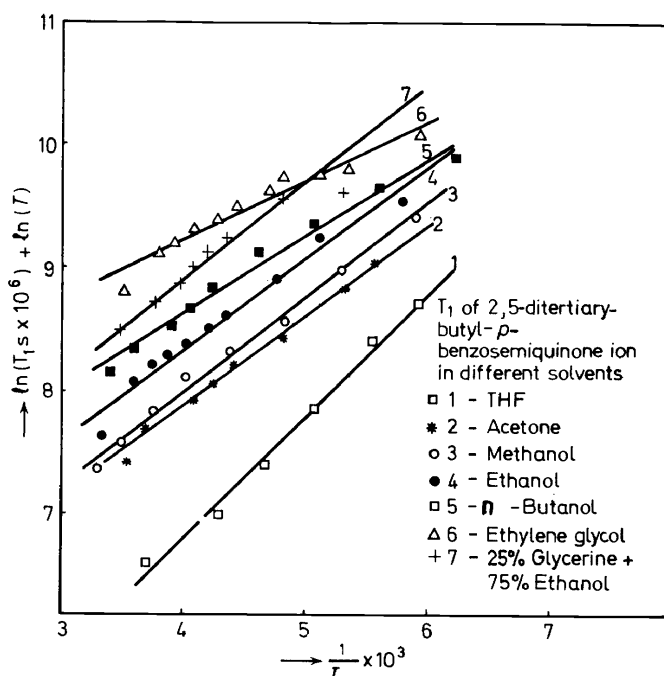


Figure 6. The plot of $\ln T_1 + \ln T$ against the reciprocal of temperature in kelvin for DTBSQ⁻ in different solvents.

Table 1. Comparison of the energies of activation (E) and intercepts (C) obtained from the equations: $\ln T_1 - n \ln T = C + (E/RT)$ for relaxation time T_1 of 2,5-ditert-butyl-*p*-benzosemiquinone in different solvents. Also tabulated for comparison are the energies of activation (E_η) obtained from the equation $\ln \eta = \ln \eta_0 + (E_\eta/RT)$

Solvent ^c	E_η (kcal mol ⁻¹) (± 1%)	E (kcal mole ⁻¹) (± 7%)			C^a (± 10%)		
		$n = 0^b$	$n = -0.5^b$	$n = -1.0^b$	$n = 0^b$	$n = -0.5^b$	$n = -1.0^b$
		Methanol	2.64	1.94	1.74	1.50	-1.46
Ethanol	3.14	1.90	1.68	1.46	-1.00	2.21	5.42
<i>n</i> -Butanol	4.60	1.66	1.44	1.24	-0.24	2.95	6.14
25% Glycerene- 75% ethanol	—	2.90	1.78	1.56	-0.52	2.50	6.06
Ethylene glycol	—	1.40	1.18	0.98	0.86	4.05	7.25
Acetone	1.72	1.86	1.64	1.42	-1.39	1.81	5.02
THF	1.82	2.38	2.16	1.96	-3.48	-0.30	2.88
<i>n</i> -Decanol	—	3.48	3.18	2.88	-3.43	-0.08	3.27

^a Units of C depend on the equation used.

^b n is varied to test different models; see text.

^c Concentration of the radical is about 10^{-12} M.

methanol, ethanol and *n*-butanol. Actually E shows a small decreasing trend when E_η is increased by changing the solvent. We can safely rule out the viscosity model in these solvents also.

In the case of ethylene glycol (m.p. -17°C) and *n*-butanol (m.p. -90°C), the temperature variation of T_1 has been observed to fit with the proposed equations even below the freezing point.

The observation of temperature-dependent spin-lattice relaxation in frozen solutions suggests the possibility of hindered rotation, the activation energy being determined by the barrier to the motion similar to that proposed in solid benzene³⁴. Since the straight line plot (*Figure 4*) extends from the liquid region to the solid region with perhaps a small change in slope, we are led to believe that the agency causing the barrier to the motion is the same in both liquid and solid solutions. Moreover, the activation energies are $\sim 1.7 \text{ kcal mol}^{-1}$ for the above mentioned solvents. It should be mentioned that these solvents have hydrogen-bonding properties and the radical could be inside a solvent cage. Hydrogen-bonding effects have been observed in the esr spectra of semiquinones in such solvents^{35, 36, 37}. We feel that the activation energy can be associated with hydrogen-bonding. Our claim that the semiquinone rotates even in the frozen solution is supported by the temperature-dependent linewidth studies of *p*-benzosemiquinone ion in solid hydroquinone matrix and solid biphenyl matrix by Krishnamurthy and Venkataraman³⁸. However, hydrogen-bonding is not expected in solvents like acetone and THF. The activation energies E obtained from the spin-lattice relaxation time measurements (for $n = -1$) are not much different from the E_η obtained from the viscosity data (*Table 1*). Thus in the case of these solvents the viscosity model may be applicable. However, we cannot rule out the other models. It is interesting to note that the activation energy E associated with the rotational correlation time, obtained from nuclear spin-lattice relaxation studies using the quasilattice random flight model in acetone is $1.5 \pm 0.2 \text{ kcal mol}^{-1}$ which agrees reasonably with the E measured in acetone solutions of DTBSQ⁻ in this work.

We cannot rule out the possibility of temperature-dependent transition probability due to Heisenberg exchange in THF and *n*-decanol. Since the viscosity of THF is small, probably this effect is small in THF. However, the highly viscous *n*-decanol is expected to show the effect of exchange. The large temperature dependence of T_1 is probably due to the additional contribution from the exchange term to the temperature dependence.

(c) Other substituted semiquinones in ethanol.

The effect of substituents in the ring of the semiquinone ion on T_1 has been investigated for methyl, *t*-butyl, *t*-amyl and halogen substitutions. *Table 2* gives the activation energies E and intercept 'C' in equation 15 determined for these semiquinones in ethanol. *Figures 7, 8 and 9* give the plot of $\ln T_1$ vs $1/T$ (i.e. $n = 0$) for these cases. It is seen that the activation energies change with substituents showing, in general, a tendency to decrease with increasing size of the substituent. This may be due to decreased solvent interactions in substituted semiquinones. 2,5-Dichlorosemiquinone, however, does not show any dependence of T_1 on temperature within the limits of experimental error; a behaviour we do not understand yet. Probably quad-

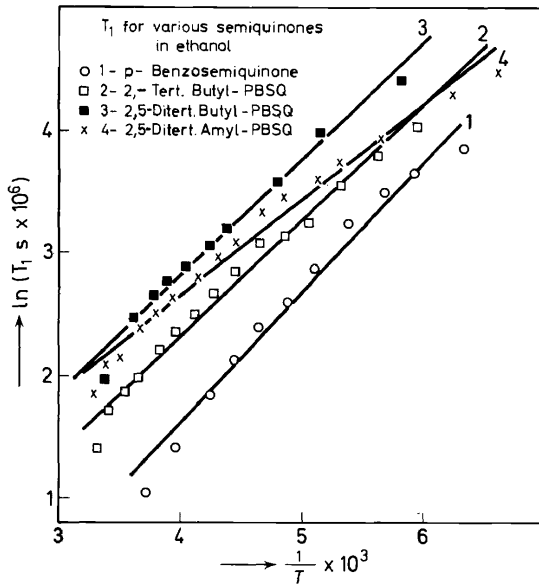


Figure 7. The plot of $\ln T_1$ against the reciprocal of T for ethanol solutions of tert-butyl and tert-amyl substituted p -benzosemiquinones. A similar plot for the unsubstituted semiquinone is given for comparison.

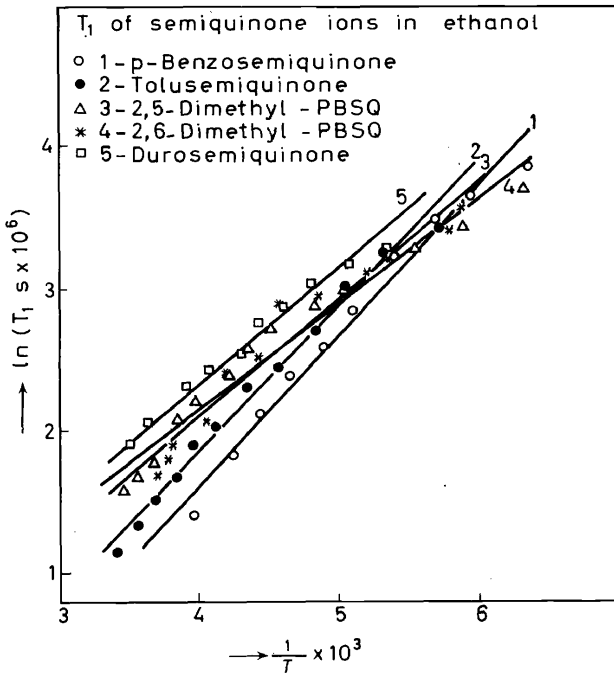


Figure 8. The plot of $\ln T_1$ against T^{-1} for ethanol solutions of methyl-substituted and the unsubstituted p -benzosemiquinone ions.

ELECTRON SPIN-LATTICE RELAXATION IN FREE RADICALS

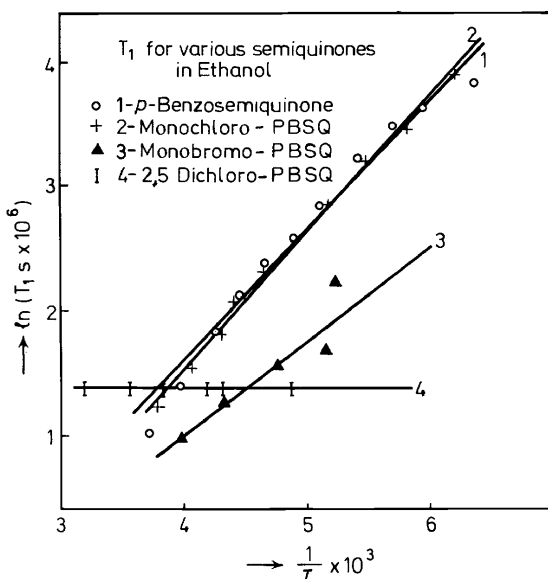


Figure 9. The plot of $\ln T_1$ against T^{-1} for ethanol solutions of halogen-substituted and the unsubstituted *p*-benzosemiquinone ions.

rupular interactions play an important role in this case and a detailed study of other halogen-substituted semiquinone is warranted.

Increase in the molecular volume and moment of inertia is expected to increase the intercepts 'C' according to all the models discussed in Section III. The intercepts 'C' given in Table 2 show such a behaviour, within the limits of experimental error.

Table 2. Comparison of the energies of activation (E) and intercepts (C) obtained from the equation: $\ln T_1 - n \ln T = C + (E/RT)$ for relaxation time T_1 of several semiquinones in ethanol.

Semiquinone ^c	E (kcal mol ⁻¹) ($\pm 7\%$)			C^a ($\pm 10\%$)		
	$n=0^b$	$n=-0.5^b$	$n=-1.0^b$	$n=0^b$	$n=-0.5^b$	$n=-1.0^b$
PBSQ	2.10	1.90	1.70	-2.60	0.57	3.72
Tolusemiquinone	2.04	1.80	1.58	-2.20	1.00	4.21
2,5-dimethyl PBSQ	1.48	1.28	1.06	-0.83	2.36	5.54
2,6-dimethyl PBSQ	1.58	1.42	1.22	-1.06	2.01	5.19
Durosemiquinone	1.64	1.40	1.18	-0.98	2.25	5.48
2-tert-butyl PBSQ	1.88	1.64	1.42	-1.40	1.76	4.98
2,5-ditert-butyl PBSQ	1.90	1.68	1.46	-1.00	2.21	5.42
2,5-ditert-amyl PBSQ	1.56	1.34	1.14	-0.49	2.69	5.88
Monochloro PBSQ	2.20	2.02	1.82	-2.90	0.21	3.37
2,5-dichloro PBSQ	0.00	—	—	1.38	—	—
Monobromo PBSQ	1.56	1.34	1.12	-2.10	1.07	4.27

^a Units depend on the equation used.

^b n is varied to test different models (see text).

^c Concentration of radical is about 10_{M}^{-2} .

(d) Rotational correlation time τ_R .

One can estimate the rotational correlation times from a knowledge of the g -tensors and spin-lattice relaxation times using equations 9 and 10 assuming an isotropic rotational motion. Using Schreurs and Fraenkel's^{2c} values for the g -tensor components of p -benzosemiquinone ion ($g_1 = 2.0091, g_2 = 2.0024, g_3 = 2.0023, g_S = 2.0047$), we get

$$\frac{W_e^g}{W_e^{SR}} = \frac{3041 \times 10^{-8} \omega^2 \tau_R}{40(1 + \omega^2 \tau_R^2)} \times \frac{18\tau_R}{4625 \times 10^{-8}} \quad (17)$$

It can be seen that W_e^g is always less than W_e^{SR} . The ratio W_e^g/W_e^{SR} will attain an asymptotic maximum value of 0.296, when $\omega\tau_R \gg 1$. Thus at the most the g -tensor modulation will contribute 25 per cent to the relaxation probability and the dominant mechanism causing spin-lattice relaxation will be the spin-rotational interaction. Using $T_1 = \frac{1}{2}(W_e^g + W_e^{SR})^{-1}$ for $T_1 = 50 \mu\text{s}$, the rotational correlation time $\tau_R \approx 3.3 \times 10^{-10}$ s and this is in the region $\omega\tau_R \gg 1$. However, when $T_1 = 1 \mu\text{s}$, $\tau_R \approx 5 \times 10^{-12}$ s and this corresponds to a region $\omega\tau_R < 1$. The observed increase in relaxation time with the decrease in temperature is because of the dominance of spin-rotational effect over the g -tensor modulation effect even in the $\omega\tau_R < 1$ region.

(e) Conclusions

The observed temperature dependence of T_1 of semiquinones in dilute solutions is mainly due to spin-rotational interaction. The observed temperature dependence in frozen solutions, requires the semiquinone to undergo hindered rotations in the frozen solutions also. In hydrogen-bonding solvents like the alcohols the activation energy E associated with the rotational correlation time seems to have no relation with the viscosity of the solvent. The activation energy E is probably associated with the hydrogen-bonding of the semiquinones with the solvent.

It is also observed that the contributions to the relaxation mechanisms from the modulation of the electron-nuclear dipolar interaction is not dominant in these semiquinones. Exchange effects have been definitely observed only in viscous solvents like n -decanol.

REFERENCES

- ¹ J. P. Lloyd and G. E. Pake, *Phys. Rev.* **94**, 579 (1954).
- ² (a) M. J. Stephen and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1435 (1960).
 (b) J. W. H. Schreurs, G. E. Blomgren and G. K. Fraenkel, *J. Chem. Phys.* **32**, 1861 (1960).
 (c) J. W. H. Schreurs and G. K. Fraenkel, *J. Chem. Phys.* **34**, 756 (1961).
 (d) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 1156 (1962).
 (e) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).
 (f) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **40**, 1815 (1964); **41**, 699 (1964).
 (g) J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **41**, 949 (1964).
 (h) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **41**, 3623 (1964).
 (i) J. H. Freed and G. K. Fraenkel, *J. Amer. Chem. Soc.* **86**, 3477 (1964).
 (j) G. K. Fraenkel, *J. Chem. Phys.* **42**, 4275 (1965); *J. Phys. Chem.* **71**, 139 (1967).
- ³ M. J. Stephen, *J. Chem. Phys.* **34**, 484 (1961).
- ⁴ (a) D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960).
 (b) D. Kivelson and G. Collins, *Proc. of the 1st International Conference on Magnetic Resonance, Jerusalem, Israel, 1961* p. 496, J. Wiley and Sons, New York (1962).
 (c) R. Wilson and D. Kivelson, *J. Chem. Phys.* **44**, 154 (1966).

ELECTRON SPIN-LATTICE RELAXATION IN FREE RADICALS

- (d) P. W. Atkins and D. Kivelson, *J. Chem. Phys.* **44**, 169 (1966).
 (e) D. Kivelson, *J. Chem. Phys.* **45**, 1324 (1966).
 (f) W. Plachy and D. Kivelson, *J. Chem. Phys.* **47**, 3312 (1967).
- ⁵ (a) J. H. Freed, *J. Chem. Phys.* **41**, 2077 (1964).
 (b) J. H. Freed, *J. Chem. Phys.* **43**, 2312 (1965).
 (c) J. H. Freed, *J. Chem. Phys.* **45**, 3452 (1966).
 (d) J. H. Freed, *J. Phys. Chem.* **71**, 38 (1967).
 (e) J. S. Hyde, J. C. W. Chien and J. H. Freed, *J. Chem. Phys.* **48**, 4211 (1968).
 (f) M. P. Eastman, R. G. Kooser, M. R. Das and J. H. Freed, *J. Chem. Phys.* **51**, 2690 (1969).
 (g) M. P. Eastman, G. V. Bruno and J. H. Freed, *J. Chem. Phys.* **52**, 2511 (1970); **52**, 321 (1970).
 (h) J. H. Freed and R. G. Kooser, *J. Chem. Phys.* **49**, 4715 (1968).
 (i) R. G. Kooser, W. V. Volland and J. H. Freed, *J. Chem. Phys.* **50**, 5243 (1969).
 (j) M. R. Das, S. B. Wagner and J. H. Freed, *J. Chem. Phys.* **52**, 5404 (1970).
- ⁶ H. M. McConnell, *J. Chem. Phys.* **25**, 709 (1956).
⁷ A. Carrington and H. C. Longuet-Higgins, *Mol. Phys.* **5**, 447 (1962).
⁸ C. S. Johnson, *Mol. Phys.* **12**, 25 (1967).
⁹ J. S. Hyde and H. W. Brown, *J. Chem. Phys.* **37**, 368 (1962).
¹⁰ (a) M. T. Jones, *J. Chem. Phys.* **40**, 1837 (1964); **42**, 4054 (1965).
 (b) R. D. Rataiczak and M. T. Jones, *J. Chem. Phys.* 1971 (in press)
- ¹¹ (a) C. F. Davis, M. W. P. Strandberg and R. L. Kyhl, *Phys. Rev.* **111**, 1268 (1958).
 (b) P. L. Scott and C. D. Jeffries, *Phys. Rev.* **127**, 32 (1962).
- ¹² J. M. Brown and D. J. Sloop, *Rev. Sci. Instr.* **41**, 1774 (1970).
¹³ J. G. Castle, P. F. Chester and P. E. Wagner, *Phys. Rev.* **119**, 953 (1960).
¹⁴ N. Bloembergen and S. Wang, *Phys. Rev.* **93**, 72 (1954).
¹⁵ (a) J. Pescia, *J. Phys.* **27**, 782 (1966); *Ann. Phys.* **10**, 389 (1965).
 (b) J. Herve and J. Pescia, *C.R. Acad. Sci. Paris* **256**, 5079 (1963).
- ¹⁶ A. Landesman, *J. Phys. Radium* **20**, 937 (1959).
¹⁷ R. G. Kooser, Thesis, Cornell University, and references cited therein (1968).
¹⁸ K. V. Lingam, P. G. Nair and B. Venkataraman. Reported at the International Symposium on Electron and Nuclear Magnetic Resonance, Clayton, Victoria, Australia (August 1969).
¹⁹ J. H. Freed, D. S. Leniart and J. S. Hyde, *J. Chem. Phys.* **47**, 2762 (1967).
²⁰ A. Abragam and J. Combrisson, *Nuovo Cimento*, **6**, Suppl. No. 3, 1197 (1957).
²¹ J. D. Currin, *Phys. Rev.* **126**, 1995 (1962).
²² N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
²³ A. Gierer and K. Wirtz, *Z. Naturforsch.* **8a**, 532 (1953).
²⁴ L. D. Favro, *Phys. Rev.* **119**, 53 (1960).
²⁵ W. T. Huntress, *J. Chem. Phys.* **48**, 3524 (1968).
²⁶ P. W. Atkins, *Mol. Phys.* **17**, 321 (1969).
²⁷ P. W. Atkins, A. Loewenstein and Y. Margalit, *Mol. Phys.* **17**, 329 (1969).
²⁸ D. E. O'Reilly and G. E. Schacher, *J. Chem. Phys.* **39**, 1768 (1963); D. E. O'Reilly, *J. Chem. Phys.* **49**, 5416 (1968).
²⁹ E. N. Ivanov, *Soviet Physics—JETP*, **18**, 1041 (1964).
³⁰ T. H. James and A. Weissberger, *J. Amer. Chem. Soc.* **60**, 98 (1938).
³¹ J. E. LuValle and A. Weissberger, *J. Amer. Chem. Soc.* **69**, 1576 (1947).
³² L. I. Smith and F. J. Dobrovolny, *J. Amer. Chem. Soc.*, **48**, 1420 (1926).
³³ M. P. Khakhar, Thesis, Bombay University (1966).
³⁴ E. R. Andrew and R. E. Eades, *Proc. Roy. Soc.* **A218**, 537 (1953).
³⁵ P. J. Zandstra, *J. Chem. Phys.* **41**, 3655 (1964).
³⁶ D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.* **82**, 2671 (1960).
³⁷ J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.* **37**, 2832 (1962).
³⁸ M. V. Krishnamurthy and B. Venkataraman, *Indian J. Pure and Appl. Phys.* **9**, 325 (1967).