Electron Spin Relaxation of (Diphenyl)⁻ in Dimethoxyethane*

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The electron relaxation times T_1 and T_2 have been measured by ESR pulse techniques in solutions of normal and perdeuterated (diphenyl)⁻ in dimethoxyethane at various radical concentrations and temperatures. The results are discussed in terms of different relaxation mechanisms. The most important contribution to spin-lattice relaxation at high concentration is dipolar interaction with other radical electrons modulated by translational diffusion. Spin-spin relaxation has in addition contributions from electron exchange and ion pairing.

1. Introduction

The investigation of relaxation phenomena in electron spin resonance (ESR) of organic free radicals in organic solutions has been greatly improved by the use of ESR pulse spectrometers operating at X-band frequency. It has been shown that at high radical concentrations the most important spin-lattice relaxation process is dipole-dipole interaction between the electrons modulated by the translational diffusion motion of the radicals [1,2], as was already assumed earlier from Overhauser effect studies [3]. For the spin-spin relaxation however the results were more complicated. It could only be stated that several relaxation mechanisms were contributing to it. These were assumed to be dipole-dipole interaction modulated by diffusional motions, and scalar interaction modulated by electron exchange (and in this case often called exchange interaction) or by the lifetime of ion pairs (and hence called ion pairing) [2]. Milow et al. studied 2,4,6-tri-t-butyl phenoxyl and found contributions from exchange and dipole-dipole interaction [4]. In order to clarify the contributions of different relaxation processes quantitatively in a special case we have used fairly high concentrated solutions of the (diphenyl)⁻ radical both normal and perdeuterated in dimethoxyethane (DME). Due to the smaller magnetic moment of the deuteron as compared to the proton the dipolar and the scalar hyperfine interaction with the free electron are different in these two molecules. To-gether with the temperature and concentration dependence of the relaxation rates a rather complete analysis of the data is thus possible.

2. Experimental

The samples of normal and perdeuterated (diphenyl)⁻ in DME have been prepared by reduction with sodium. It has not been possible to obtain such high radical concentrations using potassium. This was probably due to the formation of biradicals. The concentrations were determined by measurements of the spin-lattice relaxation time of the solvent protons under the assumption that this does not depend much on the type of the radical. The calibration was done with test samples of DPPH in DME of known concentration [1]. Consequently the relative concentrations were quite well known, whereas the absolute values may have a systematic error. The temperature was measured to ±1 °C by a thermocouple at the cavity.

The relaxation time measurements were carried out with an X-band pulse spectrometer described elsewhere [1]. T_1 was measured by two 90° pulses, T_2 by the 90°−180° electron spin echo. The results are shown in Figs. 2 to 4. The measuring accuracy depends on the radical concentration, due to the sensitivity, and on the T_2 value, due to the dead time of the spectrometer [1]. The accuracy of T_1 is typically ±10%, except for low concentration or short T_2, where the limits of error are given in Figure 4. The limits of error of $1/T_2$ are indicated in Figure 3. They are similar in Fig. 4 where only

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a few of them are shown. The hatched area in Fig. 3 indicates that range of concentration and $1/T_2$, where, due to sensitivity and dead time, no signal is observable. The shortest T_2 which can be measured is 3×10^{-8} s.

3. Relaxation Mechanisms and their Modulation by Motional Effects

The possible relaxation mechanisms and their modulation by motional processes have long been known. Therefore, we make here only a short list together with some remarks which we need for the interpretation of the experimental data.

A) Dipolar Interaction

a) Dipolar Interaction with other Electrons

This is an intermolecular interaction modulated by the translational motion of the radicals. The theory has been developed by Torrey [5] and the result for our case has been given in an earlier paper [6]. The contributions to the spin-lattice relaxation rate $1/T_1$ and to the spin-spin relaxation rate $1/T_2$ are

$$\frac{1}{T_{1,2\,t}} = \frac{2\,\pi\,\gamma_S^4\,\hbar^2\,N_S}{5\,d^3\,\omega_S}\,g_{1,2\,t}(a,\omega_S\,\tau_t)\,; \quad (1)$$

γ_S is the gyromagnetic ratio and ω_S the larmor frequency of the electrons, τ_t the correlation time of the translational motion [6], d the distance of closest approach of two interacting electrons, and N_S the number of radicals per cm³. Torrey's parameter

Fig. 1. Normalized relaxation rates caused by dipole-dipole interaction with other electrons vs. $\omega_S\,\tau_t$.

$a = \langle r^2 \rangle / 12\,d^2$, where $\langle r^2 \rangle$ is the mean square jump distance, characterizes the diffusion process [5, 6]. The normalized relaxation rates $g_{1,2\,t}(a,\omega_S\,\tau_t)$ are plotted in Figure 1. The parameter was chosen to be $a = 10^{-3}$ rather than $a = 0$ because that seems more realistic, and the difference in the relaxation rates of these two cases lies within our measuring accuracy in the region of interest. $a \approx 0$ had been found in an earlier investigation of radical diffusion in DME [6]. At X-band frequency, where $\omega_S\,\tau_t > 1$, $g_2(a,\omega_S\,\tau_t)$ depends only slightly on a and is practically proportional to $\omega_S\,\tau_t$. The temperature dependence is contained in τ_t, for which an Arrhenius activation law is assumed. At constant temperature this contribution to the relaxation rates is proportional to the radical concentration.

b) Dipolar Interaction with Nuclei

Since dipolar interaction decreases rapidly for increasing distance of the interacting spins we do not regard interaction of the electrons with nuclei in other molecules. We take into account only the intramolecular interaction with nuclei in the radical which is modulated by the rotational tumbling of the radicals. This contribution to the electron relaxation rates is [2]:

$$\frac{1}{T_{1r}} = \frac{4\,\gamma_S^2\,\gamma_I^2\,\hbar^2\,I(I+1)}{15\,b_{SI}^6}\,\frac{5\,\tau_r}{1+\omega_S^2\,\tau_r^2} \quad (2\,\mathrm{a})$$

$$\frac{1}{T_{2r}} = \frac{4\,\gamma_S^2\,\gamma_I^2\,\hbar^2\,I(I+1)}{15\,b_{SI}^6}$$
$$\cdot \tfrac{1}{2}\,\tau_r\left\{2 + \frac{3}{1+\omega_I^2\,\tau_r^2} + \frac{5}{1+\omega_S^2\,\tau_r^2}\right\}. \quad (2\,\mathrm{b})$$

γ_I is the gyromagnetic ratio, I the spin and ω_I the larmor frequency of the nuclei, τ_r the correlation time of the rotational motion and b_{SI} the average distance of the electron and the nuclei (i. e. the distance which one nucleus would have if it had the same interaction with the electron as have all the interacting nuclei together). This contribution does not depend on the radical concentration. It is, however, proportional to $\gamma_I^2\,I(I+1)$ which, for protons, is 15.91 times larger than for deuterons.

B) Scalar Interaction

a) Scalar Interaction Modulated by Electron Exchange (Exchange Interaction)

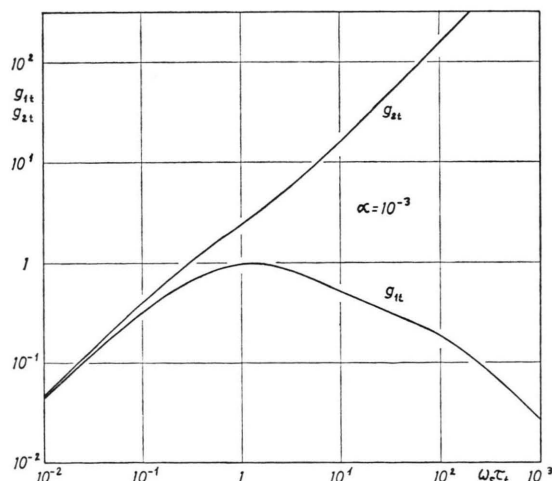This corresponds to "scalar relaxation of the first kind" in the terminology of Abragam [7]. The theory

for this interaction was treated by Kivelson [8]. For high radical concentration we get:

$$\frac{1}{T_{1e}} = \frac{1}{3}\gamma_S^2 \sum_\lambda n_\lambda a_\lambda^2 I_\lambda(I_\lambda+1) \frac{2\tau_e}{1+\omega_S^2 \tau_e^2}, \quad (3\,a)$$

$$\frac{1}{T_{2e}} = \frac{1}{3}\gamma_S^2 \sum_\lambda n_\lambda a_\lambda^2 I_\lambda(I_\lambda+1)\tau_e \left\{1 + \frac{1}{1+\omega_S^2 \tau_e^2}\right\}$$
$$(3\,b)$$

τ_e is the exchange time which is some times called τ_2 in literature [9], a_λ is the hyperfine coupling constandt in Oe of the λth group of n_λ equivalent nuclei with spin I_λ. This is exactly the same result as that of Currin [10] which can, at least for the central line of the spectrum, easily be extended to low radical concentrations (see Annex). In normal or perdeuterated diphenyl all the I_λ are equal and it is seen that

$$I(I+1)\sum_\lambda n_\lambda a_\lambda^2 \sim \gamma_I^2 I(I+1). \quad (4)$$

Taking the result of Pake and Tuttle [11] in combination with the theory of Torrey [5] we obtain

$$\tau_e = \frac{10\,a}{1+5\,a}\frac{\tau_t N_L}{Z\,p\,N_S} = \frac{c}{N_S}. \quad (5)$$

N_L is the volume concentration of solvent molecules, Z the number of molecular neighbours encountered by a radical during one diffusion step and p the probability for electron exchange during one encounter of two radicals. Since $\omega_S \tau_e \gg 1$ we find at constant temperature

$$1/T_{1e} \sim \gamma_I^2 I(I+1) N_S, \quad (6\,a)$$

$$1/T_{2e} \sim \gamma_I^2 I(I+1) N_S^{-1}. \quad (6\,b)$$

b) Scalar Interaction in an Ion Pair

Due to the reduction process Na^+ was present in the samples giving rise to an ion pair together with the (diphenyl)⁻. In such an ion pair the scalar interaction of the electron with the ^{23}Na nucleus is modulated by the lifetime of the ion pair τ_1 or by the exchange time of the electrons τ_e whichever is shorter. The contributions to the relaxation are given by [12]:

$$\frac{1}{T_{1i}} = \frac{1}{3}\gamma_S^2 a_{Na}^2 I_{Na}(I_{Na}+1)\frac{2\tau_i}{1+\omega_S^2 \tau_i^2}, \quad (7\,a)$$

$$\frac{1}{T_{2i}} = \frac{1}{3}\gamma_S^2 a_{Na}^2 I_{Na}(I_{Na}+1)\tau_i\left\{1+\frac{1}{1+\omega_S^2 \tau_i^2}\right\}$$
$$(7\,b)$$

where

$$\tau_i^{-1} = \tau_1^{-1} + \tau_e^{-1}. \quad (8)$$

For τ_i we get:

$$\tau_i = c/(N_S + c/\tau_1) \quad (9)$$

where c has the same meaning as in Eq. (5) and does not depend on the concentration. Also here we have $\omega_S \tau_i \gg 1$ and at constant temperature

$$1/T_{1i} \sim N_S + c/\tau_1, \quad (10\,a)$$

$$1/T_{2i} \sim (N_S + c/\tau_1)^{-1}. \quad (10\,b)$$

4. Concentration Dependence of the Relaxation Rates

Figures 2 and 3 show the concentration dependence of $1/T_1$ and $1/T_2$ respectively at 22 °C. The spin-lattice relaxation rate can be put in the form:

$$1/T_1 = 1/T_{10} + 1/T_{1t}. \quad (11)$$

$1/T_{1t}$ is the contribution of dipolar interaction with other radical electrons according to Equation (1). $1/T_{10}$ is the extrapolated value for low concentration (not necessarily zero). The fitted curve in Fig. 2 was drawn with $1/T_{1t} = 4.1 \times 10^{-15} N_S$ and $1/T_{10} = 6.7 \times 10^4$. The latter may have contributions from
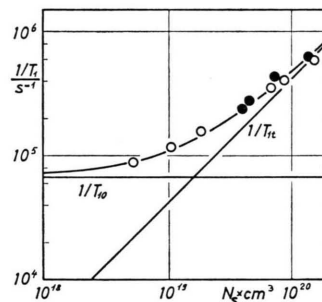

Fig. 2. Concentration dependence of spin-lattice relaxation rates of normal (●) and perdeuterated (○) (diphenyl)⁻ in DME at 22 °C. For $1/T_{10}$ and $1/T_{1t}$ see text.

spin-rotational interaction and, via electron exchange, from spin-orbit coupling [2]. These are both very rapidly modulated, so that their contributions to $1/T_1$ and to $1/T_2$ are equal. Hence they have no measurable contribution to the total $1/T_2$, which is at least two orders of magnitude larger than $1/T_{10}$.

The behaviour of the spin-spin relaxation rate is more complicated. If we sum up all the contributions listed in Sect. 3 we get the following concentration dependence:

$$1/T_2 = A N_S + \gamma_I^2 I(I+1)(B + C N_S^{-1}) + D(E + N_S)^{-1}. \quad (12)$$

The constants A to E are the same for normal and perdeuterated radicals. Due to the use of Eqs. (3) and (7), Eq. (12) is only valid for high radical concentrations. In a more general way the relaxation
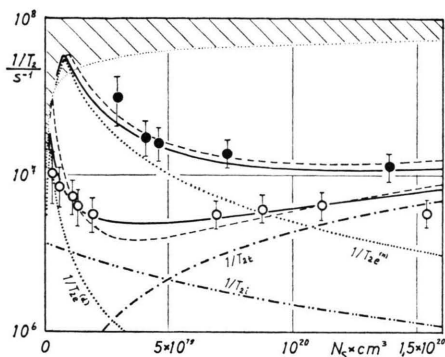

Fig. 3. Concentration dependence of spin-spin relaxation rates of normal (●) and perdeuterated (○) (diphenyl)⁻ in DME at 22 °C. Theoretical curves: — — — first fit, ———— second fit (see text). Contributions to the second fit: normal (diphenyl)⁻: $1/T_{2t}$, $1/T_{2i}$ and $1/T_{2e}^{(n)}$, perdeuterated (diphenyl)⁻: $1/T_{2t}$, $1/T_{2i}$ and $1/T_{2e}^{(d)}$.

rates for exchange and ion pairing can be obtained by the theory of Currin [10]. This is shown in the annex. Equation (3) must then be replaced by the curves of Fig. A 2 for normal and perdeuterated (diphenyl)⁻ and Eq. (7) by the relaxation behaviour of the central lines in Fig. A 1 E ($\nu = \pm 1$ and $\nu = 0$).

By fitting the constants A to E the theoretical curves of Fig. 3 were obtained. At low concentration the modification described in the annex was used. The constants of two different fits are given in Table 1. For the first fit (broken curves) we as-

Table 1. Constants used for fitting the concentration dependence of $1/T_2$.

	A	B	C	D	E
1st fit	5.3×10^{-14}	0	1.2×10^{18}	3.1×10^{25}	0
2nd fit	4.4×10^{-14}	0	9.5×10^{17}	2.6×10^{26}	7.0×10^{19}

sumed that the lifetime of the ion pair is much longer than the exchange time and hence ion pairing is only modulated by the electron exchange. The second fit (solid curves) was obtained by assuming a concentration independent τ_1 which is contained in E.

Two unsuccessful measurements were tried with normal (diphenyl)⁻ at concentrations of 4.4×10^{18} cm⁻³ and 1.0×10^{19} cm⁻³. In both cases no signal

could be observed. This is in agreement with our interpretation, since at these concentrations the theoretical curves for normal (diphenyl)⁻ both fall into that region of Fig. 3 where, due to dead time and sensitivity, no signal is observable.

The second fit (solid curves) describes the experimental results better. The different relaxation contributions to this fit are therefore plotted in Figure 3. For the deuterated radical $1/T_{2e}$ is most important at low and $1/T_{2t}$ at high concentration. For the normal radical $1/T_{2e}$ is even more important at low but still quite important at high concentration. This was already assumed in the earlier study [1], but could not be stated quantitatively, since the deuterated radical had not been studied.

The constants of the second fit can now be used for the evaluation of the molecular and motional parameters:

Aa) Dipolar interaction with other electrons

From our fits of $1/T_1$ and $1/T_2$ we get $T_{1t}/T_{2t} = g_{2t}/g_{1t} = 10.7$. With this value we obtain from Fig. 1: $\omega_S \tau_t = 4.57$ and $\tau_t = 7.8 \times 10^{-11}$ s, which agrees well with τ_t of BDPA in TME [6]. Further we get the distance of closest approach $d = 7.2$ Å, which seems somewhat large but still reasonable.

Ab) Dipolar interaction with nuclei

Since $B = 0$ we can only state that this relaxation contribution to $1/T_2$ is much smaller than all the others. It may contribute to $1/T_{10}$, but it must be so rapidly modulated, that, as in the cases of spin-rotational interaction and spin-orbit coupling, it has no measurable contribution to $1/T_2$.

Ba) Scalar interaction modulated by electron exchange

From C we get $\tau_e = 7.72 \times 10^{10} N_S^{-1}$ (in s if N_S is given in radicals per cm³). For the evaluation we used the coupling constants of normal (diphenyl)⁻ given in Reference [13]. We thus have τ_e ranging from about 3×10^{-8} s to 6×10^{-10} s in our concentration range. We have $\omega_S \tau_e \geq 28$, $1/T_{1e} \leq 10^4$ s⁻¹ and hence the contribution to $1/T_1$ is negligible.

Bb) Scalar interaction modulated by ion pairing

Our E value leads to $\tau_1 = 1.1 \times 10^{-9}$ s. The smallest value of τ_i then becomes about 3×10^{-10} s and we have $\omega_S \tau_i \geq 20$, $1/T_{1i} \leq 6 \times 10^3$ s⁻¹ and hence no measurable contribution to $1/T_1$. Finally we obtain from D the coupling constant of ²³Na: $a_{Na} = 2.95$ Oe. These values are again reasonable.

5. Temperature Dependence of the Relaxation Rates

Figure 4 shows $1/T_1$ and $1/T_2$ at different radical concentrations plotted against reciprocal temperature. The extrapolated values $1/T_{10}$ according to Eq. (11) have also been plotted. After subtraction of these from $1/T_1$ we assume that the remaining relaxation rate is $1/T_{1t}$, due to dipolar interaction with other electrons. This assumption is confirmed
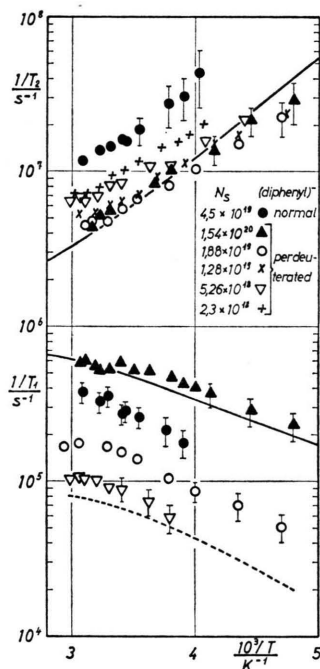

Fig. 4. Spin-spin and spin-lattice relaxation rates of normal and perdeuterated (diphenyl)⁻ in DME at different concentrations vs. reciprocal temperature, ——— relaxation rates according to Torrey's theory for perdeuterated (diphenyl)⁻ at $N_S = 1.54 \times 10^{20}$ cm⁻³, ····· extrapolated $1/T_{10}$ values (see text).

by former measurements of different radicals dissolved in DME [1,2,6]. Figure 4 includes theoretical curves for both $1/T_{1t}$ and $1/T_{2t}$. These were calculated by Torrey's theory assuming $a = 10^{-3}$ (Fig. 1) using the τ_t value at 22 °C obtained in the previous section and an activation energy of 3.0 kcal/mole for τ_t, which was obtained by former investigations of electronic and nuclear relaxation in DME [1,6]. Since $1/T_{10}$ amounts to 12% of our highest concentration of deuterated (diphenyl)⁻ $1/T_1$ values, the $1/T_{1t}$ curve was drawn about 12% lower than these.

The corresponding theoretical $1/T_{2t}$ curve fits approximately the $1/T_2$ values of the same sample.

This agrees with our interpretation of the concentration dependence of $1/T_2$ in Figure 3. The difference of $1/T_{2t}$ in Figs. 3 and 4 at $10^3/T = 3.39$ K⁻¹ and $N_S = 1.54 \times 10^{20}$ cm⁻³ lies within the uncertainty of the concentration determination. Obviously our highest concentration of deuterated (diphenyl)⁻ sample had a somewhat lower concentration than assumed.

For the further interpretation $1/T_{10}$ was subtracted from all $1/T_1$ values. Thus $1/T_{1t}$ was obtained and, by Torrey's theory, also $1/T_{2t}$. This was then subtracted from all $1/T_2$ values giving

$$1/T_2'' = 1/T_2 - 1/T_{2t} \qquad (13)$$

which is plotted in Figure 5. Now the concentration dependence of $1/T_2''$ is systematic: lower radical concentrations have higher relaxation rates. The highest rate has, of course, the normal (diphenyl)⁻
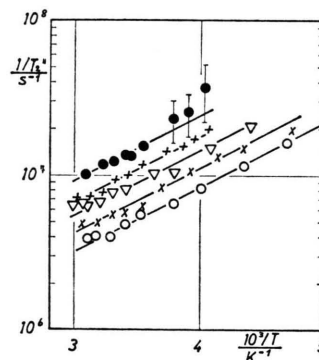

Fig. 5. Spin-spin relaxation rates of Fig. 4 after subtraction of $1/T_{2t}$ (see text).

due to the stronger interaction with protons. The relaxation mechanisms contributing to $1/T_2''$ (i.e. electron exchange and ion pairing) can contribute to $1/T_1$ only in the order of $1/T_{10}$ which is at least two orders of magnitude smaller than $1/T_2''$. This again confirms our interpretation of Sect. 4, which implied $\omega_S \tau_e \gg 1$ and $\omega_S \tau_i \gg 1$. Therefore, as concerns the temperature dependence of the two contributions to $1/T_2''$, we can state that they are proportional to their respective correlation times and hence exhibit the same activation energies. The average activation energy of $1/T_2''$ is (1.9 ± 0.1) kcal/mole. The lines in Fig. 5 are drawn with this value. This is then the activation energy of the mixed contribution of electron exchange and ion pairing. It may be close to the activation energy of τ_e since the influence of τ_1 is not so large.

6. Conclusion

As a conclusion we can state that dipolar interaction with other electrons and scalar interaction with radical nuclei and with ^{23}Na in ion pairs do contribute to the electron spin-spin relaxation of (diphenyl)⁻ in DME whereas no contribution from dipolar interaction with radical nuclei could be found. The latter may contribute together with spin-rotational interaction and spin-orbit coupling to spin-lattice relaxation where, at fairly high concentration, dipolar interaction with other electrons is predominant.

Annex

Application of Currin's Theory to the Evaluation of Spin-Spin Relaxation Rates due to Electron Exchange

All the relaxation rates considered in this section are those which we have called $1/T_{2e}$ so far. We start from Currin's equation (2.23)[10]:

$$\overline{\psi}(S) = N \frac{\sum_{\beta} \varrho_{\beta}/(S - i\,\Omega_{\beta} + q)}{1 - q \sum_{\beta} \varrho_{\beta}/(S - i\,\Omega_{\beta} + q)}. \quad (A1)$$

$\overline{\psi}(S)$ is the Laplace transform of the free induction decay or the echo envelope (in the case of external inhomogeneities). S is the Laplace parameter, which corresponds to a type of complex frequency and contains a relaxation rate. Ω_{β} is practically the frequency and ϱ_{β} the relative intensity of hfs component β with negligible electron exchange. N is the total number of electron spins and the exchange frequency $q = 1/\tau_e$ is proportional to the radical concentration N_S, as stated in Equation (5).

Currin has shown[10] that for very slow exchange Eq. (A1) represents a spectrum with lines positioned at Ω_{β} having relaxation rates $1/T_2^{(\beta)} = q(1 - \varrho_{\beta})$. Whereas for rapid exchange the spectrum consists of one single Lorentzian line centered at the mean frequency of the unperturbed spectrum having the relaxation rate Eq. (3 b) of Kivelson[8] which is proportional to $\tau_e = 1/q$.

We are thus left with an increasing relaxation rate at small q and a decreasing rate at large q. In between must be a maximum and we want to know the relaxation rate near that maximum. For this purpose we must do the back transformation of Equation (A1). For this back transformation we have to find the residues of $\overline{\psi}(S)\exp(St)$. We first

need the roots of the denominator of Eq. (A1) which are given by:

$$1/q = \sum_{\beta} \varrho_{\beta}/(S - i\,\Omega_{\beta} + q). \quad (A2)$$

For the sake of simplicity we assume from now on that our unperturbed spectrum is symmetric about the centre frequency ω_0, which is the case for both the normal and the perdeuterated (diphenyl)⁻ radical. Thus we can rewrite (A2) in the form

$$1/q = \tau_e = \varrho_0/x + 2\,x \sum_{\beta \geq 1} \varrho_{\beta}/(x^2 + \delta\omega_{\beta}^2). \quad (A3)$$

Here we have introduced the new variable

$$x = S - i\,\omega_0 + q; \quad (A4)$$

$\delta\omega_{\beta}$ is the frequency distance of the unperturbed hfs component β from the centre.

If we now consider the spectrum under the influence of exchange, the centre line will remain at its position and the line β will shift to a new position $\delta\omega_{\nu}$ and will have a new relaxation rate $1/T_2^{(\nu)}$ given by:

$$\delta\omega_{\nu} = \mathrm{Im}\{x_{\nu}\}, \quad (A5)$$

$$1/T_2^{(\nu)} = q - \mathrm{Re}\{x_{\nu}\}. \quad (A6)$$

The roots x_{ν} of (A3) in combination with (A5) and (A6) solve our problem.

This will be illustrated by a few examples:

1) Doublet caused by interaction with one proton. We have without exchange two lines at $\pm\delta\omega$, $\varrho_0 = 0$, $\varrho_1 = 1/2$. (A3) reduces to

$$\tau_e = x/(x^2 + \delta\omega^2). \quad (A7)$$

This case has been already evaluated by Currin[10] and Anderson[14]. The result is shown in Fig. A1 A (we measure all frequencies and relaxation rates by $\delta\omega$). For $1/\tau_e\,\delta\omega < 2$ we have two symmetric lines with frequency shift $\pm\delta\omega_1$ from the centre and the same relaxation rate $1/T_2^{(1)}$. For $1/\tau_e\,\delta\omega \geq 2$ we have one single line at the centre with two relaxation rates. In practice, only the smaller of these can be observed experimentally.

2) Triplet caused by two protons or one deuteron. The unperturbed spectrum has a centre line plus two lines at $\pm\delta\omega$. (A3) becomes

$$\tau_e = \varrho_0/x + 2\,\varrho_1\,x/(x^2 + \delta\omega^2). \quad (A8)$$

The situation is shown in Figs. A1 B (for two protons) and A1 C (one deuteron). For the centre line we have $x = x_0$ always real. It stays in the centre and has relaxation rate $1/T_2^{(0)}$. With increasing
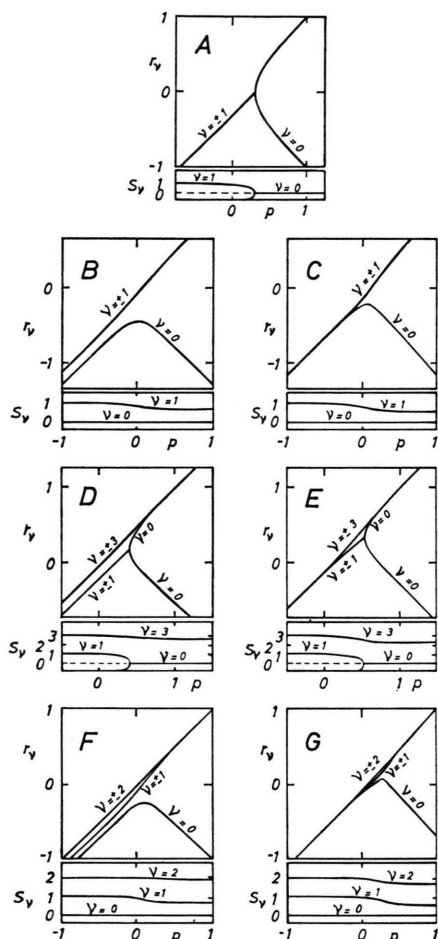
Fig. A1. Electron exchange. Frequency shifts $s_\nu = \delta\omega_\nu/\delta\omega$ and logarithms of spin-spin relaxation rates $r_\nu = \log(1/T_2^{(\nu)}\,\delta\omega)$ of hfs components vs. logarithm of reciprocal exchange time $p = \log(1/\tau_e\,\delta\omega)$. The different multiplets are caused by the following nuclear spins: A one spin 1/2, B two spins 1/2, C one spin 1, D three spins 1/2, E one spin 3/2, F four spins 1/2 and G one spin 2.
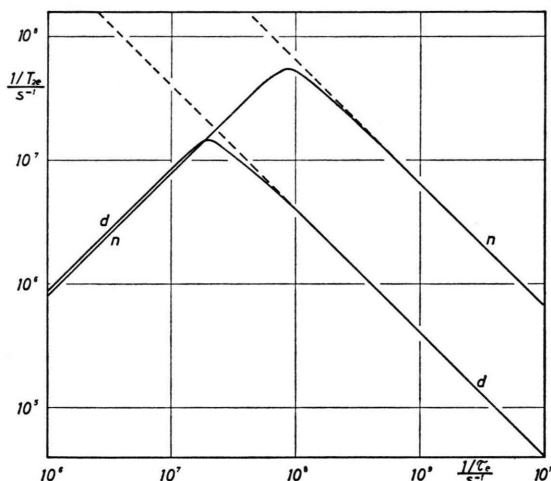

Fig. A 2. Spin-spin relaxation rates of the central line in the ESR spectra of normal (n) and perdeuterated (d) (diphenyl)⁻ caused by electron exchange vs. reciprocal exchange time. The broken lines correspond to Kivelson's theory.

$1/\tau_e$ the two outer lines are shifted towards the centre but they never collapse completely. Their relaxation rate is $1/T_2^{(1)}$ and this soon becomes so large that the two lines are no longer observable leaving only the centre line which then narrows with further increasing $1/\tau_e$.

3) Quartet caused by three protons or by one ^{23}Na (which we have in the ion pairing). The unperturbed spectrum has two lines with intensity ϱ_1 at $\pm\delta\omega$ and two lines with intensity ϱ_3 at $\pm 3\,\delta\omega$. We have

$$\tau_e = 2\,x\,\{\varrho_1/(x^2 + \delta\omega^2) + \varrho_3/(x^2 + 9\,\delta\omega^2)\}\,. \quad (A9)$$

Figures A 1 D and A 1 E show the results for three spins 1/2 or one spin 3/2 respectively. The two

inner lines collapse at $1/\tau_e\,\delta\omega = 2.4966$ and 3.2961 respectively. They behave exactly as the doublet in the first example. The two outer lines never collapse completely but soon become so wide that they can no longer be observed. They behave, therefore, as the outer lines of the triplet.

4) Quintet caused by four protons or by one nuclear spin $I = 2$. The situation is similar to the triplet and is illustrated in Figs. A 1 F and A 1 G.

We could now procede in the same way but the calculations though not difficult get more and more cumbersome with increasing numbers of hfs components. Only the relaxation rate of the centre line can be calculated easily from the real root of (A 3). Fortunately, both (diphenyl)⁻ radicals possess a centre line and their relaxation rates are given in Figure A 2. These relaxation rates have been used in the interpretation of our experimental results in Figure 3. The relaxation rates of Kivelson's formula are plotted by broken lines in Fig. A 2 for comparison.

[1] R. Brändle, G. J. Krüger, and W. Müller-Warmuth, Z. Naturforsch. **25 a**, 1 [1970].

[2] G. J. Krüger, Advan. Mol. Relaxation Processes **3**, 235 [1972].

[3] J. Haupt and W. Müller-Warmuth, Z. Naturforsch. **17 a**, 1011 [1962].

[4] A. D. Milov, K. M. Salikov, and Yu. D. Tsvetkov. Chem. Phys. Lett. **8**, 523 [1971].

[5] H. C. Torrey, Phys. Rev. **92**, 962 [1953].

[6] G. J. Krüger, Z. Naturforsch. **24 a**, 560 [1969].

[7] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.

[8] D. Kivelson, J. Chem. Phys. **33**, 1094 [1960].

[9] M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, J. Chem. Phys. **51**, 2690 [1969].

[10] J. D. Currin, Phys. Rev. **126**, 1995 [1962].

[11] G. E. Pake and T. R. Tuttle, Phys. Rev. Lett. **3**, 423 [1959].

[12] M. R. Das, S. B. Wagner, and J. H. Freed, J. Chem. Phys. **52**, 5404 [1970].

[13] Landolt Börnstein, Numerical Data and Functional Relationships in Science and Technology, Group II, Vol. 1, Magnetic Properties of Free Radicals, by H. Fischer, p. 107, Springer-Verlag, Berlin 1965.

[14] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 [1954].