Molecular Motion in Liquids and Solutions. II.

Dynamic Nuclear Polarization and Nuclear Magnetic Relaxation in Free Radical Solutions of Toluene

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Two methods are utilized to study the relaxation behaviour and molecular motion in solutions of free radicals in toluene: the investigation of longitudinal and transversal solvent proton relaxation at a properly chosen frequency (48 MHz), and the determination of enhancement factors of the dynamic proton polarization over a large frequency range. The temperature dependence of the quantities concerned is measured between $+70\ ^\circ$C and $-120\ ^\circ$C.

The results can be interpreted in terms of a pure dipole-dipole interaction between proton and electron spins whose time dependence is provided by translational random motions of the molecules and rotational tumbling of associated complexes. The activation energies for both processes are 3.1 kcal/mole and 7.8 kcal/mole, respectively. The solvation is only very weak. The relative contribution of rotational tumbling is $R=0.26$, from which the average co-ordination number is estimated to be less than one.

In the preceding paper magnetic nuclear-electron double resonance was used to study certain molecular properties of solutions and to compare them with other parameters such as the dielectric relaxation time and the viscosity of liquids [1]. Whilst the frequency- and temperature-dependence of the dynamic polarization of solvent nuclei in several organic solutions of free radicals could be described by a translational diffusion mechanism [2, 3], in solutions of toluene departures from this rule were observed at low temperatures [3, 4]. The re-investigation of toluene solutions over an extended frequency-range made it possible to distinguish between different processes of molecular motion. From measurements of the (solvent-)proton spin relaxation times at a high radio-frequency, conclusions could be drawn concerning the association or solvation of molecules.

An experimental investigation of "solvent effects" seems to be of general importance. The use of organic free radical solutions is favourable to magnetic resonance studies because the interactions are mainly reduced to the (solvent-) proton- (radical-) electron couplings. The proton spin relaxation can thus be treated in approximation as a two-spin system. Toluene has the advantage, for this kind of study, of possessing an extended temperature range in the liquid phase. Since, in general, different molecular processes have different activation energies a study of the temperature-dependence of the relaxation times makes it possible to distinguish between these processes, if the frequency is chosen properly. A measurement of the enhancement factor of the dynamic nuclear polarization by the OVER-HAUSER effect is, on the other hand, required to establish the nature of the interactions between the two spin species, to fix the absolute scale of the correlation times of motion and to check the validity of an exponential activation law. Moreover, a dynamic polarization study within a frequency range of several orders of magnitude and over a wide temperature range provides experimental information on the problem of dynamic nuclear polarization in liquids in general, which has been frequently discussed in the literature [2, 3, 5, 6].

1. Experimental Details and Results

Solutions of DPPH (Diphenyl picryl hydrazyl) and BPA (bis-diphenylene-p-chlor-phenyl allyl) in

[1] K. D. KRAMER, W. MÜLLER-WARMUTH, and N. ROTH, Z. Naturforschg. **20 a**, 1391 [1965].

[2] K. D. KRAMER and W. MÜLLER-WARMUTH, Z. Naturforschg. **19 a**, 375 [1964].

[3] K. D. KRAMER, W. MÜLLER-WARMUTH, and J. SCHINDLER, J. Chem. Phys. **43**, 31 [1965].

[4] K. H. HAUSSER, G. J. KRÜGER, and F. NOACK, Z. Naturforschg. **20 a**, 91 [1965].

[5] R. E. RICHARDS and J. W. WHITE, Proc. Roy. Soc. London A **279**, 481 [1964]. — R. A. DWEK, J. G. KENWORTHY, D. F. S. NATUSCH, R. E. RICHARDS, and D. J. SHIELDS, Proc. Roy. Soc. London A **291**, 487 [1966].

[6] K. H. HAUSSER, Z. Phys. **183**, 265 [1965].

toluene were used, but within the experimental error the results did not depend on the type of radical[7]. Due to its broad ESR-spectrum, however, DPPH was not suitable for dynamic polarization measurements.

The dependence on temperature of the proton spin relaxation times T_1 and T_2 of the solutions as well as T_{10} and T_{20} of the pure solvent was measured at 48 MHz. The values for T_1 were obtained by observing the recovery of the nuclear magnetization after saturation with $90°$ pulses. Short T_2's were measured with a $90° - 180°$-programme, longer ones by using CARR–PURCELL/MEIBOOM–GILL-sequences. The pulse separation was 1 ms in such cases, so that about 10 000 pulses were used for transverse relaxation times of the order of 10 s. The accuracy is estimated to be 5% for T_1 and 10% for T_2. Within the limits of error the recovery and decay of mag-

netization was in all cases exponential. – For the analysis of the data, only the relaxation rates belonging to the interaction with the electron spins, were required. Therefore, in Fig. 1 $1/T_1'$ and $1/T_2'$ are plotted vs. the inverse of the temperature, T_1' and T_2' being obtained using the relations

$$\frac{1}{T_1'} = \frac{1}{T_1} - \frac{1}{T_{10}} \quad \text{and} \quad \frac{1}{T_2'} = \frac{1}{T_2} - \frac{1}{T_{20}}. \quad (1)$$

The relaxation rates of pure toluene are on average one order of magnitude lower than those of the solution.

The enhancement factors of the dynamic proton polarization were measured for magnetic fields of 15 G, 175 G, 3410 G, and 13 200 G. The corresponding proton and electron magnetic resonance frequencies are respectively 65 kHz and 44 MHz, 750 kHz and 493 MHz, 14.5 MHz and 9.55 GHz, and 56.3 MHz and 37 GHz. – In addition earlier data for 1070 G (4.5 MHz and 3 GHz) were utilized[3]; the measurements at low temperatures, however, have proved to be incorrect. The reason was probably that the temperature control system could not compensate for the strong microwave heating in the sample.

With the exception of the 13 200 G apparatus the double resonance spectrometers used for these studies and the experimental techniques required have been described elsewhere[2, 3, 8−10]. The nuclear electron double resonance spectrometer operating at very strong magnetic fields has high resolution and its principle is similar to the one described by RICHARDS and WHITE[11].

Saturation of the electron resonance at 37 GHz was achieved by using a helical delay line[12] as proposed by HAUSSER[13]. The helix consists of a coil of 1.9 mm diameter with ten turns bronze wire; which couples to the microwave radiation via a small antenna of adjustable length entering into the broad side of the wave guide. Matching of the antenna is provided by a variable short. A klystron with 10 watt output (ELLIOTT 8FK1) is used to produce the 37 GHz radiation. The NMR coil (6 turns wound compactly) is placed outside the helix.
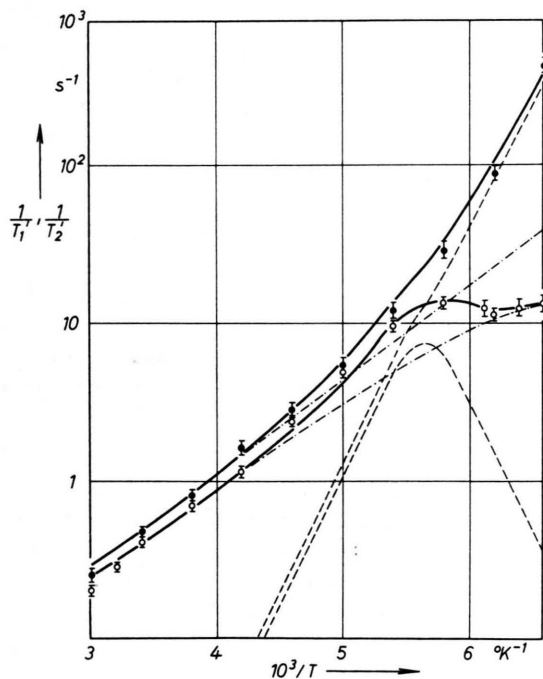

Fig. 1. The relaxation rates $1/T_1'$ (o) and $1/T_2'$ (●) of a $5.1 \cdot 10^{-3}$ molar solution of DPPH in toluene measured at a frequency of 48 MHz plotted vs. the inverse of the temperature; the meaning of the lines will be discussed in section 4.

[7] We are much obliged to Dr. H. SPIESECKE for having the samples prepared in his laboratory. Careful cleaning and degassing has proved to be of extreme importance, especially at low temperatures.
[8] W. MÜLLER-WARMUTH, Z. Naturforschg. 15 a, 927 [1960].
[9] H. GRÜTZEDIEK, K. D. KRAMER, and W. MÜLLER-WARMUTH, Rev. Sci. Instr. 36, 1418 [1965].

[10] J. HAUPT and W. MÜLLER-WARMUTH, Z. Naturforschg. 21 a, 158 [1966].
[11] R. E. RICHARDS and J. W. WHITE, Proc. Roy. Soc. London A 279, 474 [1964].
[12] R. H. WEBB, Rev. Sci. Instr. 33, 732 [1962].
[13] K. H. HAUSSER and F. REINBOLD, Z. Naturforschg. 16 a, 1114 [1961].

Superheterodyne detection with an intermediate frequency of 5 MHz is employed for the NMR signal. The spectrometer consists essentially of a very stable quartz oscillator, a radiofrequency bridge and a preamplifier all operating at 56 MHz, with a local oscillator, mixers, i. f. amplifiers and a phase sensitive detector working at 5 MHz. To improve the sensitivity a rapid modulation of the magnetic field at a frequency large compared with both linewidth and line separations (in our case 12 kHz) is provided. This procedure makes phase sensitive detection of the sideband possible if a second lock-in detector is used. Another advantage is that the matching of the NMR frequency to the fixed ESR frequency can easily be achieved by varying the modulation frequency. Fig. 2 shows a photograph of the unenhanced and enhanced proton resonance of toluene.
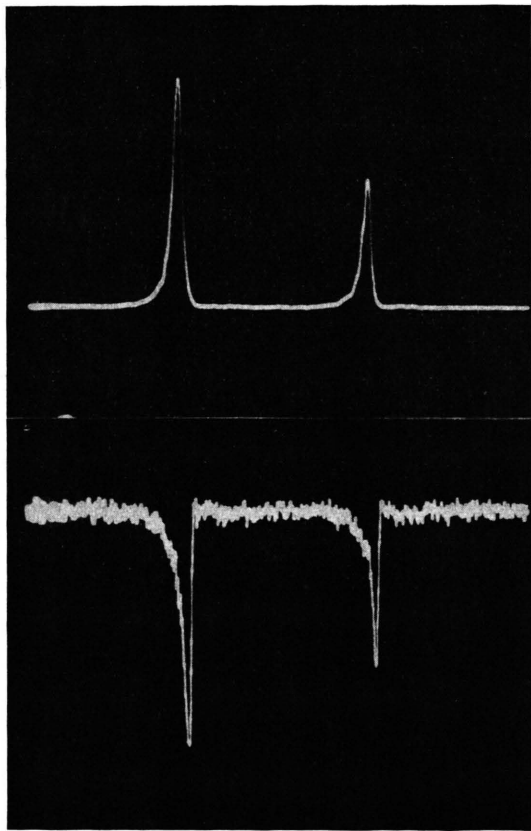

Fig. 2. Unenhanced and enhanced proton resonance spectrum of BPA/toluene solutions in a magnetic field of 13 200 G. In the lower photograph the gain is reduced by a factor 15. The scanning rate is 1 s/cm*, the frequency scale 82 Hz/cm*. The degree of saturation is about 70%.

* Scale of the figure: 0.75.

The procedure for obtaining the data is the same as that used before [1]. With P being the nuclear polarization and P_0 its thermal equilibrium value the enhancement factor is given by

$$P/P_0 = 1 - \varrho f s \cdot \gamma_S/\gamma_I . \qquad (2)$$

The leakage factor f was derived from T_1 and T_{10} in the usual way. P/P_0 is determined by the ratio of the proton resonance signal intensity with and without enhancement. By extrapolation to infinite power the enhancement for $s = 1$ is obtained. Thus the nuclear-electron coupling parameters ϱ were derived.

In Fig. 3, as an example, values for ϱ measured in the 13 200 G field are given as a function of the inverse of the temperature. With this spectrometer
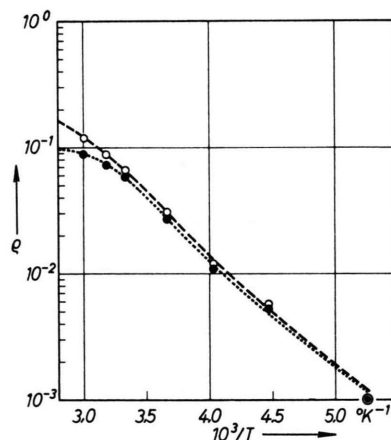

Fig. 3. Nuclear-electron coupling parameters ϱ_{Ring} (○) and ϱ_{Methyl} (●) measured at 13 200 G in solutions of BPA in toluene.

it was possible to determine the coupling parameters for the ring and the methyl protons separately. Since the differences between ϱ_{Ring} and ϱ_{Methyl} were found to be small, average values were taken for Fig. 4. The points indicated in Fig. 4 are the results of measurements in the different magnetic fields plotted against the electron resonance frequency. As it was particularly the decay of the polarization in strong magnetic fields which was to be studied, a logarithmic plot was chosen. For the evaluation of the high temperature data a linear plot is more suitable. The lines in the graph will be discussed later.

In all experiments the temperature of the samples had to be controlled very carefully. This was achieved by using servo systems to heat a strong flow of cold gaseous nitrogen. The temperatures could thus

be kept constant within a degree. The accuracy of absolute temperature measurement, however, is probably less.
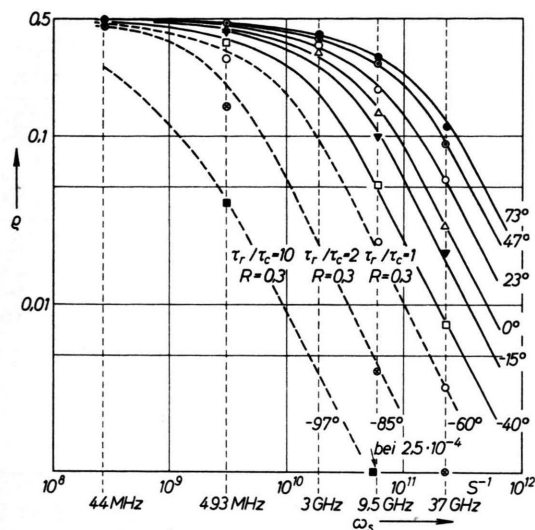

Fig. 4. Nuclear-electron coupling parameters measured in different magnetic fields and at different temperature in solutions of BPA in toluene. The lines will be discussed in section 3.

2. Translational and Rotational Motion of Molecules

The relaxation rates $1/T_1'$ and $1/T_2'$ as well as the coupling parameter ϱ can be related to the correlation functions of the different mechanism of motion in the usual manner. Fig. 4 shows that in the limit of extreme narrowing (low frequencies, high temperatures) a maximum value of $\varrho_{\max} = 0.5$ is obtained. This means that only dipole-dipole interactions between the proton spins (gyromagnetic ratio γ_l) and the electron spins (γ_S) need to be considered [14]. Since the minimum electronic relaxation times are of the order of 10^{-7} s, being larger than all the correlation times of motion, the electronic relaxation will be neglected when considering mechanisms causing fluctuations of the local fields, produced by the electrons, at the nuclei. We are left with dipolar interactions modulated in time by the molecular motion. Under certain assumptions, speci-

fied in preceding papers, the parameters ($1/T_1'$, $1/T_2'$ and ϱ) can be expressed in terms of spectral densities $J(\omega)$ of the correlation functions:

$$\frac{1}{T_1'} = \frac{\pi}{5} \gamma_S^2 \gamma_l^2 \hbar^2 \left[3 J(\omega_l) + 7 J(\omega_S) \right],$$

$$\frac{1}{T_2'} = \frac{\pi}{5} \gamma_S^2 \gamma_l^2 \hbar^2 \left[2 J(0) + \tfrac{3}{2} J(\omega_l) + \tfrac{13}{2} J(\omega_S) \right],$$

$$\varrho = \frac{0.5 \, J(\omega_S)}{0.7 \, J(\omega_S) + 0.3 \, J(\omega_l)}. \tag{3}$$

It is not possible to interpret the results of Fig. 1 and 4 by one single process of motion. Only the "high temperature" data could be explained by a translational diffusion mechanism [3, 4, 15]. We have tried, therefore to explain the results by assuming that relative translational and rotational motions of single molecules carrying proton and electron spins and rotational tumbling of complexes formed by two or more molecules are of equal influence. This is a reasonable model for the molecular motion, if solvation effects are postulated.

The relaxation in systems with spins belonging to different phases has been treated in the literature [16]. We suppose that there is a certain probability W_r of finding protons of solvent molecules closely associated with electron spins (e. g. in a particular solvation sphere of the dissolved radical), whilst the majority of relaxing protons belongs to molecules which are independently tumbling in the liquid (population probability $W_t \gg W_r$). If a fast exchange between the molecules in the two phases is assumed, the total relaxation rate is given by [16]

$$\frac{1}{T'_{(1, 2)}} = \frac{W_t}{T'_{(1, 2)t}} + \frac{W_r}{T'_{(1, 2)r}} \tag{4}$$

where $T'_{(1, 2)t}$ and $T'_{(1, 2)r}$ are the relaxation times derived from (3) with spectral density functions for the two processes of motion.

The magnetic dipolar interactions of nuclei in the associated phase are characterized by a fixed nuclear-electron distance b, with the azimuthal and polar angles of the separation vectors randomly changing in time. The motion is, therefore a rotational tumbling of complexes of molecules. The effective correlation time τ_r in the spectral density functions $J_r(\omega)$ belonging to $T_{(1, 2)r}$ may be determined chief-

[14] Dynamic nuclear polarization measurements in weak magnetic fields are very sensitive even to small contributions of scalar interaction, see e. g. W. MÜLLER-WARMUTH, Z. Naturforschg. **21 a**, 153 [1966].

[15] For the activation energy in ref. [4] a value of 1.1 kcal/Mol was erroneously given instead of 4.4 kcal/Mol. The theore-

tical curve of Fig. 5 is based on the correct value, which is an average for high and low temperatures assuming that there is only one mechanism of motion.

[16] J. R. ZIMMERMANN and W. E. BRITTIN, J. Phys. Chem. **61**, 1328 [1957]. — D. BECKERT and H. PFEIFER, Ann. Phys. Leipzig 7 (16), 262 [1965].

ly by the correlation time of this random rotation, or by the average residence time of a molecule in this phase, depending on which is the shorter. — For nuclei of solvent molecules, which move independently in the liquid, the interactions are also distinguished by random fluctuations of the nuclear-electron separations. The main contribution to relaxation is given by the translational diffusion of these molecules, characterized by a correlation time τ_t [17]

$$\tau_t = d^2/[3(D_I + D_S)] . \qquad (5)$$

Here, d is the minimum approach of solvent and radical molecules; D_I and D_S are their diffusion constants. The explicit forms of the spectral density functions $J_t(\omega)$ and $J_r(\omega)$ are given in the literature, see [1].

Using these functions in (3) and (4), finally the expressions

$$\frac{1}{T_1'} = K_t[7\,\tau_t\,f_t(\omega_S\,\tau_t) + 3\,\tau_t\,f_t(\omega_I\,\tau_t)] + K_r\left[\frac{7\,\tau_r}{1+\omega_S^2\,\tau_r^2} + \frac{3\,\tau_r}{1+\omega_I^2\,\tau_r^2}\right],$$

$$\frac{1}{T_2'} = K_t[\tfrac{13}{2}\tau_t\,f_t(\omega_S\,\tau_t) + \tfrac{3}{2}\tau_t\,f_t(\omega_I\,\tau_t) + 2\,\tau_t] + K_r\left[\frac{\tfrac{13}{2}\tau_r}{1+\omega_S^2\,\tau_r^2} + \frac{\tfrac{3}{2}\tau_r}{1+\omega_I^2\,\tau_r^2} + 2\,\tau_r\right], \qquad (6)$$

$$\varrho = \frac{0.5\left[K_t\,\tau_t\,f_t(\omega_S\,\tau_t) + \dfrac{K_r\,\tau_r}{1+\omega_S^2\,\tau_r^2}\right]}{0.7\left[K_t\,\tau_t\,f_t(\omega_S\,\tau_t) + \dfrac{K_r\,\tau_r}{1+\omega_S^2\,\tau_r^2}\right] + 0.3\left[K_t\,\tau_t\,f_t(\omega_I\,\tau_t) + \dfrac{K_r\,\tau_r}{1+\omega_I^2\,\tau_r^2}\right]}$$

are obtained [18], with

$$K_t = \frac{4\,\pi}{25}\,\frac{W_t\,\gamma_S^2\,\gamma_I^2\,\hbar^2\,N_S}{d^3} \quad \text{and} \quad K_r = \frac{1}{10}\,\frac{W_r\,\gamma_S^2\,\gamma_I^2\,\hbar^2}{b^6} .$$

The formula for ϱ has been given in the earlier paper [1]. The quotient

$$R = \frac{K_r}{K_t} = \frac{5\,W_r\,d^3}{8\,\pi\,W_t\,N_S\,b^6} \approx \frac{5\,m\,d^3}{8\,\pi\,N_I\,b^6}, \qquad (7)$$

where $W_t \approx 1$, $W_r \approx m\,N_S/N_I$ with N_S and N_I being the concentration of radical electrons and solvent nuclei, respectively and m the average number of nuclei co-ordinated to radical molecules, measures the relative contribution of "rotation" at equal correlation times.

3. Dynamic Polarization Data

In ref. [1] R was estimated to be of the order of 1 for weakly solvated radical solutions and 10 for strongly hydrated aqueous solutions of paramagnetic ions. With $R = 1$ the frequency-dependence curves show a slightly modified behaviour from that of pure translational diffusion. The effect is the more pronounced the larger the ratio τ_r/τ_t is, but less so when $R < 1$. Considering Fig. 4 within the limits of accuracy all the data between 73 °C and − 40 °C can be described by the translational relaxation

mechanism alone. The curves drawn for the best fit of the measured points, yield correlation times which follow an experimental activation law

$$\tau_t = \tau_{0t} \exp\{E_t/(R_{\mathrm{Gas}}\,T)\} . \qquad (8)$$

This is no longer true, however, at low temperatures. The dotted lines in Fig. 4 suppose that the same activation law should also be valid for the translational motion at lower temperatures, but here a rotational contribution is becoming important. An agreement with (6) could then be found with $0.2 \leqq R \leqq 0.4$ and increasing τ_r/τ_t-ratios with decreasing temperature. In Fig. 5 the τ_t values obtained with $R = 0.3$ and $\tau_r/\tau_t = 1\ (-60°)$, $2\ (-85°)$ and $10\ (-97°)$, respectively are plotted versus the inverse of the temperature. The solid lines for τ_r and τ_t will be explained in section 4.

Since the relative contribution of rotational motion is so small ($R \approx 0.3$) the decay of the dynamic polarization is only noticeably affected at very low temperatures, where the enhancement factors are smaller than expected without rotation. Therefore, the parameters can be only approximately determined. From the τ_r/τ_t ratios the activation energy for the rotation of complexes is estimated to be two or three times larger than E_t. The investigation shows on the other hand that small solvation effects may

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[17] Unfortunately different authors use τ_t-definitions that differ by some factor. Eq. (5) is in agreement with PFEIFER's definition (Ann. Phys. Leipzig **8**, 1 [1961] and ref. [1]; it is 1/3 of the τ_t in ref. [4], however.

[18] Because of normalization in the extreme narrowing case, $f_t(\omega\,\tau_t) = \tfrac{1}{5}\,f(\omega\,\tau_t)$ is used for the tabulated translational function instead of $f(\omega\,\tau_t)$ in the preceding papers.
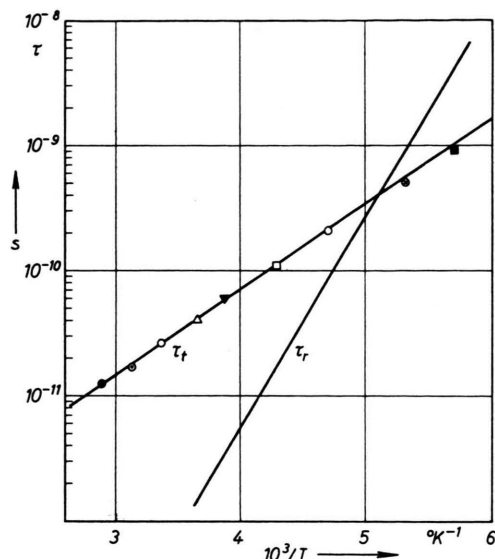
Fig. 5. Temperature-dependence of translational and rotational correlation times. The points correspond to the dynamic polarization data, the lines belong to the interpretation of relaxation data.

not be noticeable if the temperature range of the liquid phase of a solution is too small.

Another effect will only be discussed qualitatively since it is not very important in toluene solutions; namely the difference between the enhancement factors of non-equivalent nuclei. As Fig. 3 shows, the nuclear-electron coupling for the ring protons is slightly stronger than for the methyl protons. Such a behaviour may be more pronounced in other cases and may yield additional information.

4. Nuclear Relaxation Data

Once the value of τ_t for one temperature and the form of the temperature dependence (8) have been established, the experimental relaxation data of Fig. 1 yield more precise information on the quantities concerned. An analysis of the data by means of Eq. (6) resulted finally in the solid lines of Fig.1. The dash-dotted lines indicate that a pure translational mechanism with parameters derived from the high temperature limit describes the measured relaxation rates less well at lower temperatures. The dotted curves show a rotational contribution of such magnitude as to give the correct values for $1/T_1'$ and $1/T_2'$ if added to the translational contribution. This means that the measurements can be rather correctly interpreted using Eq. (6), if τ_r fol-

lows a similar activation law to that of τ_t in Eq. (8) with an activation energy E_r (see Fig. 5). The resulting parameters are:

$$E_t = 3.1 \text{ kcal/Mol}, \qquad E_r = 7.8 \text{ kcal/Mol},$$
$$\tau_{ot} = 1.4 \cdot 10^{-13} \text{ s}, \qquad \tau_{or} = 7.6 \cdot 10^{-19} \text{ s},$$
$$K_t = 4.7 \cdot 10^9 \text{ s}^{-2}, \qquad K_r = 1.2 \cdot 10^9 \text{ s}^{-2},$$
$$R = 0.26$$

and finally, if m is related to the number of molecules rather than to nuclei in the solvation sphere

$$d = 4.3 \text{ Å} \quad \text{and} \quad b = 4.7 \, m^{1/6} \text{ Å}.$$

Since b is probably not much larger than d a very small solvation follows; with $d \approx b$ one has $m \approx 0.6$.

Systematic departures of the data from the interpretation given above (see Fig. 1) occur at high temperatures (values of T_1 too great). These errors can be partially related to the existance of two inequivalent groups of protons in toluene. The pulse apparatus measures only certain averages [19]. This difficulty is removed if α,α,α-tri-deutero toluene is used which has protons only in ring positions. Fig. 6
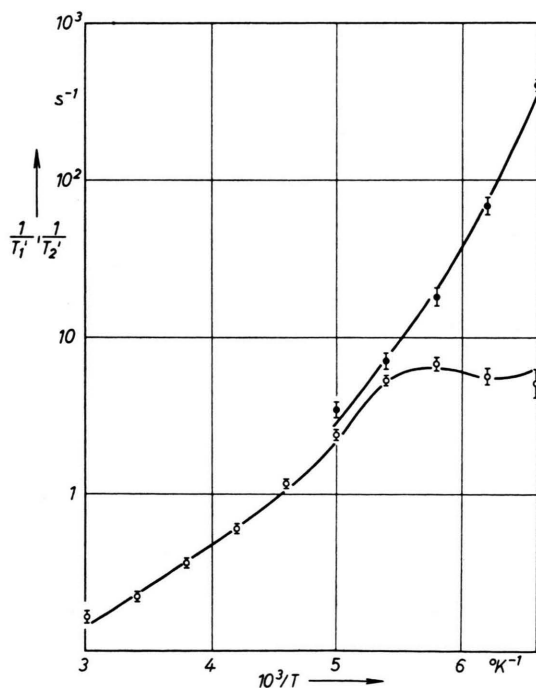
Fig. 6. Same as Fig. 1 for a $2.7 \cdot 10^{-3}$ molar solution of DPPH in α,α,α-tri-deutero toluene.

[19] The difference between methyl- and ring-proton relaxation times in pure toluene was measured by POWLES (Proc. Phys. Soc. London **85**, 87 [1965]). These values were also used for the calculation of ϱ in Fig. 3.

shows that the agreement is a little better. The investigation of toluene with all methyl protons replaced by deuterons was intended to check, whether the existence of two different sets of protons, one in a group which is already rotating within the molecule, would change the whole relaxation behaviour. Fig. 6 proves, however, that there are only very small differences.

Conclusions

In contrast to other organic solutions of free radicals so far investigated a weak solvation of radical molecules could be observed. On average not quite every radical molecule has one solvent molecule associated. Since the effect is so weak, it might have escaped notice in other solutions, if the conditions of experimental observation were less favourable.

Furthermore a detailed knowledge of the OVER-HAUSER effect in such solutions and on the relaxation was obtained. The absolute contribution of rotational tumbling to the relaxation rates is easily derived from the quantity R. Equation (6) shows immediately that it is $R \, \tau_r/\tau_t$ in the case of extreme narrowing when $\omega_S \tau_t$, $\omega_S \tau_r \ll 1$. Thus, at room temperatures, for instance, the rotational contribution is only about 0.4%. It increases strongly if τ_r/τ_t increases. Finally, in the limit $\omega_I \tau_t$, $\omega_I \tau_r \gg 1$ the rotational contribution to $1/T_2'$ is still given by $R \, \tau_r/\tau_t$, whilst it is $\frac{24}{5} \, (\sqrt{\tau_t/\tau_r})/\sqrt{6 \, \omega_I}$ for $1/T_1'$. This means that the rotational contribution to the spin-lattice relaxation decreases again at extremely low temperatures after having been of major importance near the maximum of the curve in Fig. 1.

It will be interesting to apply the methods used here to studies of other systems, especially to solutions of those free radicals which are generally supposed to cause much greater solvation effects.