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Proton spin relaxation and methyl and hydroxy group motion

Peter Beckmann

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Abstract: Proton spin-lattice relaxation rates $R = T_1^{-1}$ have been measured in powdered samples of 4-methyl-2,6-di-tertiarybutyl phenol between 77 and 170 K. Deuteration of the hydroxy proton leads to a large change in R in the vicinity of the 120-K R maximum and in the high-temperature region. The data are successfully, although probably not uniquely, fitted and the interpretation suggests that in addition to the motion of the hydroxy proton playing a significant role in the relaxation, the two pairs of t-butyl methyl groups also contributing are inequivalent. The departure, at low temperatures, from an ω^{-2} dependence of R where ω is the nuclear Larmor angular frequency is also investigated.

Introduction

Proton spin-lattice relaxation measurements have yielded a great deal of information concerning methyl group motion in 4-methyl-2,6-di-tertiarybutyl phenol (MDBP). A schematic diagram of the molecule is shown in Fig. 1. At temperatures below 50 K, quantum mechanical tunnelling of the 4-methyl group dominates the relaxation process (1) whereas at temperatures above 80 K the relaxation is dominated by the motions of the t-butyl groups (2). The complicated motions of the t-butyl groups and their constituent methyl groups give rise to two maxima in R , the spin-lattice relaxation rate. The quantity R is the inverse of T_1 the spin-lattice relaxation time. At 31 MHz, these maxima occur at 125 and 300 K. A consistent and simultaneous analysis of the value of R at the two maxima leads to the model whereby the 300-K maximum arises from the rotation of two of the six t-butyl methyls and the entire t-butyl groups and the 125-K maximum arises from the rotation of the other four t-butyl methyls (2). This analysis leads to a good fit of the data at 31 MHz between 125 and 340 K, the melting point. However, the temperature dependence of the relaxation in the vicinity of and below the 125-K maximum displays some interesting features (discussed below), and a quantitative fit was not obtained. It was assumed in this analysis that the hydroxy proton plays a negligible role in the relaxation process. In this paper, we focus our attention on the relaxation in the vicinity of the 125-K maximum and in particular on the role of the hydroxyl proton. We have measured the spin-lattice relaxation rate at 21 MHz between 77 and 170 K in fully protonated MDBP and a sample in which the hydroxy proton has been replaced with a deuteron. The experimental values of R , shown in Fig. 2, indicate the effect of deuteration and suggest that the motion of the hydroxy proton plays a significant role in the relaxation process. We also investigate the role of the methyls in the relaxation and the interesting frequency dependence of R at low temperatures.

Experimental

Proton spin-lattice relaxation rates $R = T_1^{-1}$ were measured using the conventional $\pi-t-\pi/2$ pulse sequence with a Spin-Lock 21-MHz spectrometer. The temperature was controlled by placing the sample chamber inside a copper can, the outside of which was in thermal contact with a heater. This copper can was placed inside another copper can the outside of which was in

thermal contact with a liquid nitrogen bath. By appropriately adjusting the densities of the helium exchange gas in the two cans and the current in the heater, the temperature could be varied from 77 to about 180 K. Temperature was measured by placing a thermocouple in good thermal contact with the inner copper can well away from the heater. The cryostat is the same as the one employed in the low-temperature studies (1) where the nitrogen bath was replaced with a helium bath.

Two powder samples were used: the first a commercially obtained sample of fully protonated MDBP and the second a sample grown from a deuterated solvent (ethyl alcohol) resulting in the deuteration of the hydroxy proton. This procedure was repeated several times. The author has performed R measurements on three different commercial samples of MDBP in three different countries using three different spectrometers, and if impurities are present, they do not affect the R measurements. This has been confirmed by using the commercial samples as they are and by recrystallizing several times from isopropyl alcohol and degassing.

Analysis and Discussion

Although our prime concern is investigating the effects on the relaxation of the hydroxy proton we will also discuss other interesting properties of the relaxation. The hydroxy group is in position 1 of the benzene ring and the *n*-butyl groups are adjacent to it in positions 2 and 6 as shown in Fig. 1. The 4-methyl group plays no role in the relaxation at these temperatures. We refer to the fully protonated sample as sample H and the deuterated sample as sample D. Thus, R_H and R_D refer to the relaxation rates of the two samples.

Nuclear spin-lattice relaxation caused by molecular motion modulation of the dipolar interaction between protons is described by the BPP function (3).

$$R = C \left[\frac{\tau}{1 + \omega^2 \tau^2} + \frac{4\tau}{1 + 4\omega^2 \tau^2} \right], \quad [1]$$

$$\tau = \tau_0 e^{E_a/kT}.$$

The parameter C depends on the details of the molecular motion and the geometry, τ is the correlation time for molecular reorientation, E_a is an appropriate activation energy, and ω is the nuclear Larmor angular frequency which, in the present study, is 2π (21 MHz). Often, sums of BPP functions are employed and the reader is referred to Ref. (2) and the references cited therein for the details.

Although the value of R at the maximum is adequately explained by the model summarized in the Introduction, the data at 16, 31, and 59 MHz (2) as well as the present data (sample H) at 21 MHz cannot be fitted by a single BPP function. This is clear from the broad asymmetric nature of the maximum. A single BPP function fit at high and low temperatures leads to an $R \sim 75 \text{ sec}^{-1}$ at the maximum whereas the observed value is 32 sec^{-1} . More surprisingly, the data cannot be fit very successfully by a sum of two BPP functions. This suggests that either all four methyls assumed responsible for the relaxation are inequivalent and/or the motion of the hydroxyl group is contributing. The data in Fig. 2 show a marked difference in R for the two samples, which suggests that the hydroxy proton plays a significant role in the relaxing process. If the only role of deuteration was that of the proton dilution factor, one would expect R to decrease by 23/24, the ratio of the number of protons in the two samples. This clearly does not account for the observed difference.

We present a consistent and logical although certainly not unique fit of the temperature dependence of R_H and R_D . We must look for more than two BPP functions to fit the R_H data and use the R_D data as a guide. In the low-temperature or long correlation time limit ($\omega\tau \gg 1$), Eq. [1] predicts

$$R = \frac{2C}{\omega^2 \tau_0} e^{-E_a/kT}. \quad [2]$$

It is clear from the data that $\ln(R) \propto -T^{-1}$. This implies that if sums of BPP functions are contributing then they have, to within experimental uncertainty, the same activation energy E_a . In this case, Eq. [2] is still valid and the ratio C/τ_0 is replaced by the sum of such ratios. The data for R_H and R_D , for $T < 90 \text{ K}$ ($10^3 T^{-1} > 11 \text{ K}^{-1}$) are indistinguishable and a linear least-squares fit to Eq. [2] yields $EJk = 1280 \text{ K}$ or $E_a = 10.6 \text{ kJ/mole} = 2.54 \text{ kcal/mole}$. The fit gives a correlation coefficient of 0.997, which implies a small uncertainty in the slope, E_a/k . Realistic uncertainties were obtained by drawing straight lines through the data ($T < 90 \text{ K}$) to obtain upper and lower limits to the slope. The resulting uncertainty of $E_a \pm 12\%$ is certainly larger than would be obtained by a more complicated fitting procedure. This result of $2.54 \pm 0.30 \text{ kcal/mole}$ at 21 MHz is to be compared with $2.48 \pm 0.42 \text{ kcal/mole}$ at 59 MHz, $2.36 \pm 0.07 \text{ kcal/mole}$ at 31 MHz, and $2.25 \pm 0.08 \text{ kcal/mole}$ at 16 MHz (2). Taking into account the uncertainties, there is no strong indication that the activation-energy is frequency dependent.

In the high-temperature or short correlation time limit ($\omega\tau \ll 1$), Eq. [1] predicts

$$R = 5 C \tau_0 e^{E_a/kT}. \quad [3]$$

Although the data are less precise at the higher temperatures, both the R_H and R_D data are consistent with Eq. [3] with the same activation energy obtained from the low-temperature data and we assume a unique value of $E_a = 2.54 \pm 0.30 \text{ kcal/mole}$ throughout the remainder of the analysis. The high-temperature R_H at 31 MHz was found to be $2.38 \pm 0.04 \text{ kcal/mole}$, which is the same as the low-temperature value at this frequency (2). The high-temperature value of E_a for 16 and 59 MHz is consistent with that for 31 MHz (2). Within the experimental uncertainties from this and the previous (2) work, there is no strong indication that the activation energies are different at temperatures above and below the temperature of the R maximum.

The experimental values of R_D can be fit quite reasonably to the sum of two BPP functions as indicated in Fig. 2a. We note, however, that the region at the maximum still appears flatter than the fitted curve. We shall return to this point. We write

$$R_D = R_A + R_B \quad [4]$$

and the parameters τ_0 and C for R_A and R_B are given in Table 1. The next step is very simple. A freehand curve is drawn through the observed R_H values. The difference $R_\Delta = R_H - R_D$ is well approximated by a single BPP function. Thus we write

$$R_H = R_D + R_\Delta = R_A + R_B + R_\Delta. \quad [5]$$

Plots of R_Δ and R_H (the latter agreeing with the observed values by construction) are shown in Fig. 2b and C and τ_0 for R_Δ are given in Table 1. Also given in Table 1 is the value of R at its maximum and the temperature at which that maximum occurs for R_A , R_B , and R_Δ .

We can associate R_Δ with the relaxation caused by the motion of the hydroxyl proton. Steric potential calculations (2) indicate that the hydroxy proton should see a considerably higher barrier and therefore should not contribute to the relaxation in this temperature range. We note,

however, that for quite a different phenomenon in the same molecule, namely, that of quantum mechanical tunneling at helium temperatures, deuterating the hydroxy proton has a nonnegligible effect both on the proton spin relaxation arising from tunneling rotation of the 4-methyl group (1) and on the tunneling frequency of the 4-methyl group (4). The conclusion of the present work that the hydroxy proton motion is significant is independent of the fitting procedure since R_{Δ} is just the difference between the two sets of experiments.

The quantities R_A and R_B can be associated with the *t*-butyl methyls. There are four groups involved since the other two contribute to the relaxation at much higher temperatures. That more than one BPP function is required is consistent with the structural analysis and the detailed calculations in Ref. (2). Again, it is the hydroxyl proton or deuteron responsible for the fact that different methyls see different environments. Clearly, the values of C for R_A and R_B should, in principle, be the same and that one is 25 % greater than the other (see Table 1) is just an indication that the four methyls are inequivalent. This further manifests itself in that the observed relaxation in sample D in the range $8.2 < 10^3 T^{-1} < 10 K^{-1}$ ($100 < T < 122$ K) is essentially temperature independent and the sum $R_D = R_A + R_B$ does not really reproduce this very well. This very fiat plateau is washed out to some extent in sample H. The addition of R_B with its maximum value at a higher temperature results in the observed asymmetry in the relaxation.

An interesting feature of the relaxation is the frequency dependence at low temperatures. The prediction of Eq. [2] that $\ln(R) \propto T^{-1}$ is observed at all four frequencies (the one reported here and three in Ref. (2)) below 95 K ($10^3 T^{-1} > 10.5 K^{-1}$), whereas the prediction of Eq. [2] that $R \propto \omega^{-2}$ is not observed. The previous study showed that at $10^3 T^{-1} = 11 K^{-1}$, $R \propto \omega^{-n}$ with $n = 2.1$ using 21, 31, and 59 MHz. Figure 3 shows the frequency dependence of R_H at $10^3 T^{-1} = 11 K^{-1}$ (90 K). The points all come from the original data and do not involve any of the fits. The error flags were obtained by drawing extreme lines which enclosed all the data points at low temperature. The uncertainties represent, therefore, much larger uncertainties than would result from a numerical fitting procedure. The three frequencies 21, 31, and 59 MHz give a value of $n = 2.21 \pm 0.26$. A good fit at one frequency would lead to a very poor fit at either of the other two frequencies if n were fixed at 2. The data at 16 MHz does not fall in this wide range resulting from the above uncertainty in n . This very liberal estimate of the uncertainty in n based on the higher frequencies leads to the very strong argument that the 16-MHz data is anomalous. One may suspect that this effect is connected with the shift of the R maximum to lower temperatures at lower frequencies but this is simply not consistent with the data. It is clear that measurements at lower frequencies are essential before detailed models of the effect are proposed.

Summary

Deuterating the hydroxy proton in MDBP has a pronounced effect on the spin-lattice relaxation rate in the vicinity of, and at temperatures above, the temperature at which the relaxation for the protonated sample goes through a broad asymmetric maximum. Deuteration does not change the broad nature of the maximum and, if anything, enhances it. It does seem, however, to remove some of the asymmetry. The fits of the data, suggest the four *t*-butyl methyl groups responsible for the relaxation should be divided into at least two inequivalent pairs. The different environments probably result from the position of the hydroxy proton or deuteron. Undoubtedly, an even better fit of the data would be obtained if it were assumed that all four methyls were inequivalent, a situation suggested by detailed computations (2). When an OD

group is replaced by an OH group there is an additional relaxation mechanism due to the motion of the hydroxy proton. This result is surprising in the light of steric potential calculations (2).

It would be interesting to study the proton relaxation of fully deuterated MDBP with a protonated hydroxy group and the deuteron relaxation of fully protonated MDBP with a deuterated hydroxy group. In both cases the signal would be down by a factor of 24 and in addition there would be a further reduction in signal to noise associated with the lower deuteron Larmor frequency.

It appears from the peculiar frequency dependence of the relaxation at low temperatures that the relaxation is even more complicated than suggested here. Further measurements at lower frequencies are essential.

Acknowledgements

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Figures

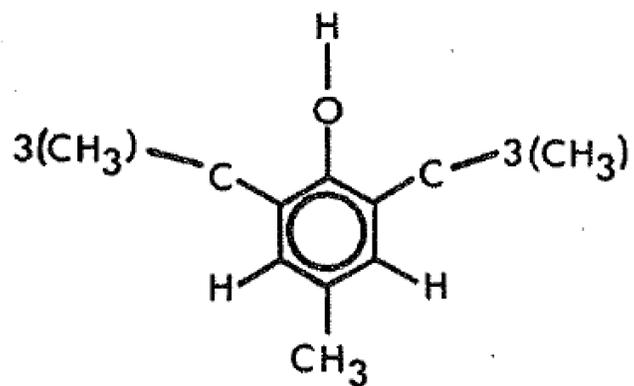


FIG. 1. A schematic diagram of MDBP. A more detailed discussion concerning the molecular and crystal structure may be found in Ref. (2) and references cited therein.

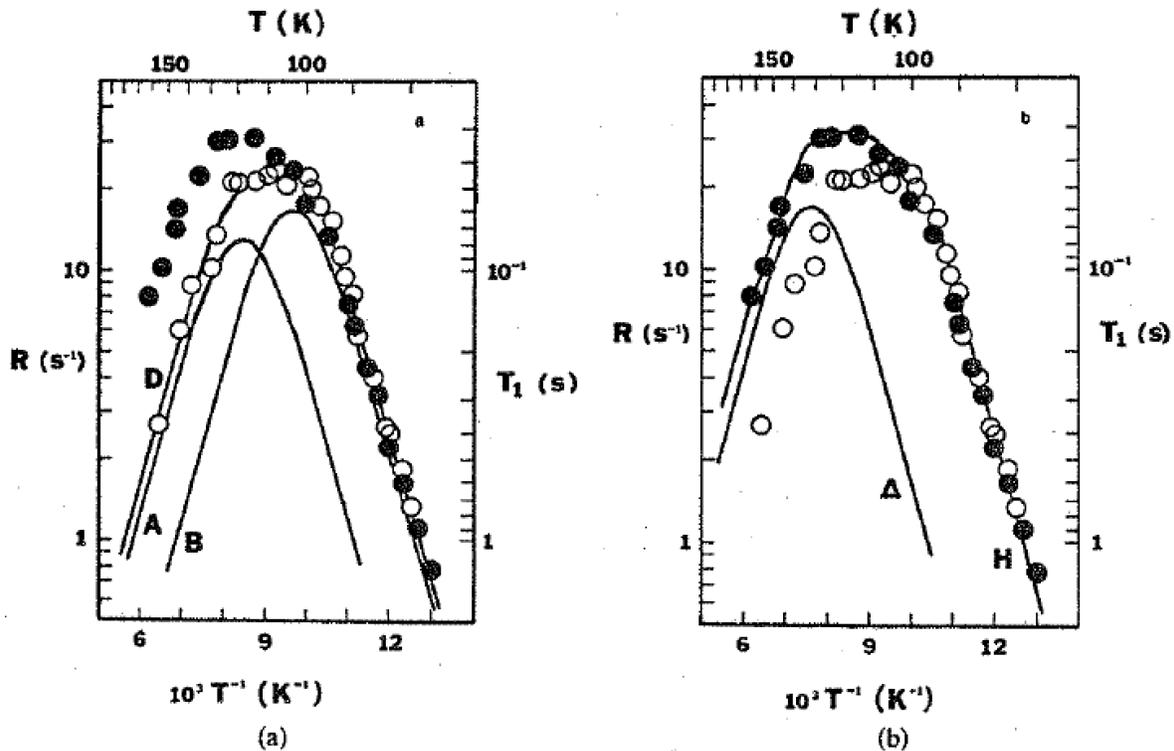


FIG. 2. The temperature dependence of the spin-lattice relaxation rate $R = T_1^{-1}$ in MDBP. The experimental results are indicated by closed circles for the fully protonated sample and by open circles for the sample with the deuterated hydroxy group. The solid lines labeled A and B in (a) and Δ in (b) are given by Eq. [1] with the parameters given in Table 1. The solid line labeled D in (a) is the sum of A and B in (a) and that labeled H in (b) is the sum of D in (a) and Δ in (b).

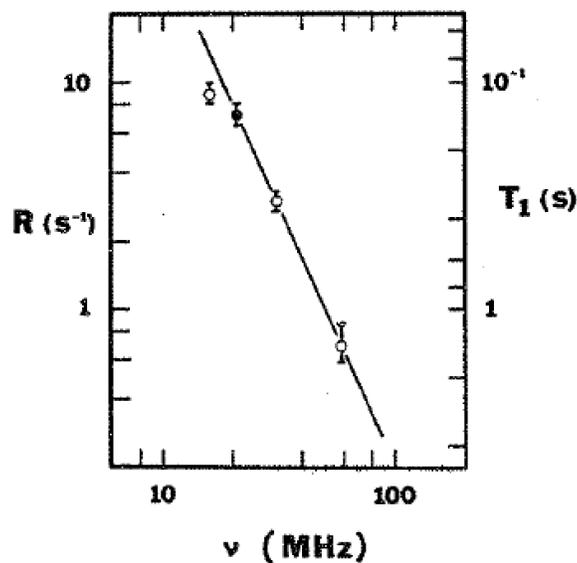


FIG. 3. The frequency dependence of the spin-lattice relaxation rate R in MDBP at $T = 91$ K ($10^3 T^{-1} = 11$ K⁻¹). The closed circle (21 MHz) is from the present work and the open circles (16, 31, and 59 MHz) are obtained from Ref. (2). The solid line is for $R \propto \omega^{-2.2}$.

Tables

TABLE 1
RELAXATION PARAMETERS^a

	R_A	R_B	R_Δ
$C \times 10^{-9} \text{ (sec}^{-2}\text{)}$	1.23	1.56	1.57
$\tau_0 \times 10^{14} \text{ (sec)}$	8.8	1.85	26.8
$R_{\max} \text{ (sec}^{-1}\text{)}$	13.3	16.9	17.0
$T_{\max}^{-1} \times 10^3 \text{ (K}^{-1}\text{)}$	8.5	9.7	7.6

^a $E_a = 10.6 \text{ kJ/mole} = 2.54 \text{ kcal/mole}$ in all cases.