Study of NMR spin lattice relaxation of several aldehydes

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The NMR spin lattice relaxation of various aldehydes has been investigated. The experimental values of NMR spin lattice relaxation time \( T_1 \) of benzaldehyde, anisaldehyde, o-chlorobenzaldehyde and p-hydroxybenzaldehyde have been correlated with the calculated value of NMR spin lattice relaxation time \( T_c \) obtained using various equations for dielectric relaxation time \( \tau \). It has been concluded that Writz equation and Murty equation are better substitute for the correlation time in calculating NMR spin lattice relaxation time than Debye equation as used by BPP (Bloembergen, Purcell and Pound).

Keywords: NMR spin lattice relaxation, Aldehydes

IPC Code: G01R33/20

1 Introduction

The NMR spin lattice relaxation investigation of organic polar molecules provides valuable information about the dipole-dipole interaction, spin rotational interaction between the nuclear magnetic moments and the magnetic fields produced at the positions of the nuclei by the rotation of the molecule. There have been extensive studies on the effect of molecular or group rotation on the broad line NMR spectra of organic samples. The molecular dynamics in liquid system have been studied by several researchers\(^1\)-\(^3\) using the spin lattice relaxation mechanism. Rugheimer and Hubbard\(^4\) measured the longitudinal nuclear magnetic relaxation time of several organic liquids to test the contribution of intra and inter molecular dipole interactions.

The nuclear spin lattice relaxation time \( T_1 \) is related to the interaction of the nuclear magnets with the rapidly fluctuating magnetic field produced by other nuclei in the same molecule and other molecule. Fluctuations of magnetic field arise because of rotational motion of the same molecule and translational motion of the other molecules. Both rotational and translational motion arise due to perturbation by collisions from time to time. Many collisions take place during the time a molecule takes turn around or moves through a distance, characteristic of one molecular spacing. BPP\(^5\) (Bloembergen, Purcell and Pound) have derived an expression for correlation time \( \tau_c \) by an extension of Debye\(^6\) theory of dielectric dispersion (\( \tau_c \) is a time factor characteristic of random motion and is a measure of time taken for the fluctuating field to lose memory of previous value). To evaluate \( \tau_c \) they used the value of dielectric relaxation time, \( \tau = (4 \pi \eta a^3/kT) \). However, it has been observed that many of the aldehydes have not yet been investigated for spin lattice relaxation studies. The purpose of the present work is to investigate spin lattice relaxation time of various aldehydes. An attempt has been made by various researchers\(^7\)-\(^9\) to correlate the spin lattice correlation time \( \tau_c \) with Debye equation as used by BPP. But it has been observed that the calculated values were ranging from 1/2 to 1/10 times of the experimental values. In order to narrow down the gap between the calculated and experimental values of spin lattice relaxation time \( T_1 \) of some aldehydes, the authors have modified BPP equation using various equations for dielectric relaxation instead of Debye equation.

2 Theory

The spin lattice relaxation of a single nuclear spin in a liquid is induced by the fluctuating local magnetic field of neighbouring spins. If the spin, which induces relaxation is attached to the molecule as relaxing spin, the fluctuating field is produced by molecular reorientational motion. The contribution of this mechanism to overall \( T_1 \) is denoted by \( (T_1)_{rot} \). If the spin, which induces relaxation and the relaxing spins
are attached to different molecules the contribution of this mechanism to overall $T_1$ is denoted by $(T_1)^{\text{trans}}$. Calculating the probability of transition induced, BPP obtained the expression:

$$(T_1)^{-1} = (T_1)^{-1}_{\text{rot}} + (T_1)^{-1}_{\text{trans}}$$  \hspace{1cm} (1)$$

where

$$(T_1)^{-1}_{\text{rot}} = \frac{3\gamma^4 h^2}{10\rho_0^6 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2}$$  \hspace{1cm} (2)$$

where $\gamma$ is the gyromagnetic ratio, $h = (h/2\pi)$, $\tau_c$ is the correlation time and $r_0$ is the sum of interproton distances within the molecule and $\omega_0$ is the resonance angular frequency.

Kubo and Tomita\textsuperscript{10} modified the above equation and obtained:

$$(T_1)^{-1}_{\text{rot}} = \frac{3\gamma^4 h^2}{2\rho_0^6} \tau_c$$  \hspace{1cm} (3)$$

The correlation time $\tau_c$ required in Eq. (3) is closely related to dielectric relaxation time $\tau_D$ of Debye's theory of dielectric dispersion in polar liquids as:

$$\tau_c = \tau_D/3$$  \hspace{1cm} (4)$$

The authors have calculated correlation time using Debye's equation\textsuperscript{6}, Perrin's modification\textsuperscript{11} of Debye's equation, Writz equation\textsuperscript{12} and Murty's equation\textsuperscript{13}. The different values of $\tau_c$ give different values of $(T_1)^{\text{rot}}$.

If it is assumed that BPP model is adequate to account for the translational contribution to the spin lattice relaxation time, $T_1$, then expression for $(T_1)^{\text{trans}}$ is given by:

$$(T_1)^{-1}_{\text{trans}} = \frac{9\pi^2 \gamma^2 h^2 \eta N}{10kT}$$  \hspace{1cm} (5)$$

where $N$ is the number of molecules per unit volume and $\eta$ is the viscosity of the compound.

3 Experimental Details

All the substances used are of the pure quality LR grade and have been obtained from M/s British Drug House, England. They have been used after distillation. The solvents, deuterated chloroform or benzene have been obtained from M/s British Drug House, England and are reported to be of purest quality. They have been distilled before use.

All the NMR experiments were performed on Bruker Avance DRX 300 MHz FT NMR spectrometer, equipped with 5 mm multi-nuclear inverse probe head with Z-shielded gradient (Fig. 1). For normal proton experiments, typical experimental conditions are as follows.

Flip angle 90°; spectral width 3919 Hz; data size 32 k; relaxation delay 5 s; number of transients 8. The FIDs were line broadened by 0.3 Hz prior to Fourier transformation. The sample concentrations were kept in the range of 32-50 m molar.

For $T_1$ experiments inversion recovery method (180°-t-90°) of Freeman and Hill\textsuperscript{14} was used in each system for evaluation of spin lattice relaxation time.

![Fig. 1 — Block diagram of high resolution pulse spectrometer](image-url)
The value of $t$ was chosen initially for 10 s, which was varied in graduated manner in order to obtain correct phase modulation of the series of NMR spectrum in each system so as to calculate accurately the $T_1$ values. The experiments were performed in automation mode using standard pulse programme from the Bruker pulse programme library.

4 Observations

Table 1 represents the chemical shift position and NMR spectrum of benzaldehyde, anisaldehyde, o-chlorobenzaldehyde and $p$-hydroxybenzaldehyde respectively. Contour plot of the inversion recovery sequence of benzaldehyde, anisaldehyde, o-chloro-

<table>
<thead>
<tr>
<th>Compound</th>
<th>Protons</th>
<th>Chemical shift (ppm)</th>
<th>NMR spin lattice relaxation time ($T_1$) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>H_a</td>
<td>7.55</td>
<td>6.19</td>
</tr>
<tr>
<td></td>
<td>H_b</td>
<td>7.65</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>H_c</td>
<td>10.04</td>
<td>5.72</td>
</tr>
<tr>
<td>Anisaldehyde</td>
<td>H_a</td>
<td>3.50</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>H_b</td>
<td>6.78</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>H_c</td>
<td>7.69</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>H_d</td>
<td>9.80</td>
<td>2.68</td>
</tr>
<tr>
<td>O-Chlorobenzaldehyde</td>
<td>H_a,H_b</td>
<td>6.97</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>H_c</td>
<td>7.78</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td>H_d</td>
<td>10.48</td>
<td>4.09</td>
</tr>
<tr>
<td>$p$-hydroxybenzaldehyde</td>
<td>H_a</td>
<td>6.85</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>H_b</td>
<td>7.66</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>H_c</td>
<td>9.80</td>
<td>3.86</td>
</tr>
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</table>

The chemical shift and NMR spin lattice relaxation time $T_1$ of various protons of aldehydes are given in Table 2. Table 3 shows the dielectric relaxation time of these aldehydes. NMR spin lattice relaxation time $T_1$ of these compounds have been shown in Table 4.

The proton NMR spectrum of benzaldehyde is shown in Table 1. The H_a proton of the -CHO in benzaldehyde is largely deshielded hence its NMR signal is obtained at for downfield shift at $\delta$ 10.04 ppm. The two H_b protons of the ring, which are orthocoupled to H_c protons show a doublet signal at $\delta$ 7.89 ppm. The two H_c protons show a triplet signal at $\delta$ 7.65 ppm. The H_d proton at para-position is shifted slightly towards upfield side giving a double doublet at $\delta$ 7.55 ppm.

Table 1 presents the proton NMR spectrum of anisaldehyde in which four signals are observed at four different chemical shift positions. The three protons H_a of CH$_3$ group are positioned at $\delta$ 3.50 ppm. The aldehyde proton H_d is shifted towards downfield side by anisotropic effect and by electron withdrawal by the carbonyl oxygen. This combination results the absorption at for downfield observed at $\delta$

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>$\tau$ Exp.</th>
<th>$\tau$Debye</th>
<th>$\tau$Perrin</th>
<th>$\tau$Writz</th>
<th>$\tau$Murty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>10.20*</td>
<td>60.00</td>
<td>21.60</td>
<td>10.20</td>
<td>9.00</td>
</tr>
<tr>
<td>2</td>
<td>Anisaldehyde</td>
<td>14.94@</td>
<td>66.74</td>
<td>240.3</td>
<td>11.97</td>
<td>15.73</td>
</tr>
<tr>
<td>3</td>
<td>o-Chlorobenzaldehyde</td>
<td>11.60*</td>
<td>62.52</td>
<td>22.50</td>
<td>10.98</td>
<td>12.53</td>
</tr>
<tr>
<td>4</td>
<td>$p$-Hydroxybenzaldehyde</td>
<td>6.87@</td>
<td>58.40</td>
<td>21.02</td>
<td>8.78</td>
<td>7.32</td>
</tr>
</tbody>
</table>

Ref. 15, @ Ref. 16.

Table 3 — NMR spin lattice relaxation time ($T_1$) in seconds at 298 K

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>$T_1$Exp.</th>
<th>$T_1$Debye</th>
<th>$T_1$Perrin</th>
<th>$T_1$Writz</th>
<th>$T_1$Murty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzaldehyde</td>
<td>5.86</td>
<td>0.61</td>
<td>1.59</td>
<td>4.99</td>
<td>4.29</td>
</tr>
<tr>
<td>2</td>
<td>Anisaldehyde</td>
<td>3.20</td>
<td>0.56</td>
<td>1.46</td>
<td>2.68</td>
<td>2.13</td>
</tr>
<tr>
<td>3</td>
<td>o-Chloro-benzaldehyde</td>
<td>3.54</td>
<td>0.59</td>
<td>1.54</td>
<td>2.84</td>
<td>3.55</td>
</tr>
<tr>
<td>4</td>
<td>$p$-Hydroxy-benzaldehyde</td>
<td>3.57</td>
<td>0.63</td>
<td>1.63</td>
<td>3.36</td>
<td>3.84</td>
</tr>
</tbody>
</table>
9.80 ppm. The two Hₖ and Hₗ protons are ortho-coupled to each other showing doublets at δ 6.78 ppm. and δ 7.69 ppm respectively.

Π-Hydroxybenzaldehyde gives several multiplets in its NMR spectrum Table 1. The doublet signal observed at δ 6.85 ppm corresponds to the two protons Hₗ. The other two ring protons Hₖ which are nearer to -OH group experience downfield shift and give a signal at δ 7.66 ppm. The Hₖ proton of CHO-group is represented by a singlet signal following a downfield shift at δ 9.80 ppm.

The PMR spectrum of o-chlorobenzaldehyde Table 1 gives three multiplet signals. The three benzoid protons Hₕ and Hₗ are observed at δ 6.96 ppm. While the proton Hₖ which is at ortho position to CHO-group shows a downfield shift due to deshielding effect and the signal is observed at δ 7.78 ppm. Due to the presence of an electronegative atom oxygen in CHO-group the proton Hₗ is represented by a signal at δ 10.48 ppm.

5 Results and Discussion

The proton of CHO-group in the NMR spectrum of benzaldehyde shows a spin lattice relaxation time $T₁$ of 5.72 s. The two Hₖ protons of ring show an increase in relaxation time with $T₁$ as 6.19 s. The two Hₗ protons adjacent to Hₖ and doubly orthocoupled to Hₕ and Hₗ show a decrease in relaxation time having $T₁$ as 5.46 s. The Hₖ proton, which is ortho-coupled Hₗ on both sides shows an increase in relaxation time $T₁$ with $T₁$ as 6.19 s. This increase in relaxation time of Hₖ is due to the chemical shift anisotropy observed at para position. The statistical average value of NMR spin lattice relaxation time $T₁$ of benzaldehyde is 5.86 s (Table 3). Table 2 shows the experimental and calculated values of dielectric relaxation time $τ$ of benzaldehyde.

In the NMR spectrum of anisaldehyde the Hₖ proton at the chemical shift position at δ 3.50 ppm shows a relaxation time $T₁$ of 3.12 s. The two Hₖ protons at para position whose chemical shift is δ 6.78 ppm give a relaxation time $T₁$ of 3.05 s. The proton attached to the carbonyl group shows greater relaxation time $T₁$ of 3.68 s, which may be due to the hindrance caused by carbonyl group to the rotation of H-atom. The Hₗ protons at ortho position to the aldehyde group shows a NMR spin lattice relaxation time $T₁$ as 3.25s. The overall relaxation time $T₁$ of anisaldehyde is 3.20s, which is quite small showing that the molecule as a whole comes to the equilibrium position very easily when disturbed by a radio frequency pulse. From Table 2 it is observed that the dielectric relaxation time of anisaldehyde is found to be 14.94 $× 10^{-12}$ s, which is a large value showing the possibility of molecular reorientation.

The possibility of reorientation of the CHO-group may be ruled out to account for the increase in the spin lattice relaxation time of Hₖ proton as it is rigidly bonded to the benzene ring. The reorientation of methoxy group may be taken into account for the increase in spin lattice and dielectric relaxation time of anisaldehyde. The methoxy group rotation in 3,4-di-methoxybenzoic acid was suggested by Kuwahura et al.17. It is observed that the rotation of methoxy group is hindered by the aldehyde group. Similar observation have been made by Santavy18 for 2, 3-di-methoxy benzoic acid which supported the rotation of methoxy group. The theoretical and experimental value of dielectric relaxation time $τ$ for Anisaldehyde is given is Table 2. Debye equation gives a quite large value for $τ$. When Perrin's modification is applied the value of dielectric relaxation time obtained is $24.03 × 10^{-12}$ s, which is nearer to the experimental value of $τ$ as $14.93 × 10^{-12}$ s. Murty and Writz equations give $15.73 × 10^{-12}$ and $11.97 × 10^{-12}$ s respectively for the dielectric time, which are in good approximation to the experimental value. From Table 3 it is clear that the Perrin equation yields $T₁$ as 1.46 s. While Writz and Murty equation give the values of $T₁$ as 2.68 and 2.13 seconds which are very near to the experimental value of $T₁$ as 3.2 s.

Table 1 represents the NMR spin lattice relaxation time $T₁$ of various protons present in o-chlorobenzaldehyde. Three Hₕ and Hₗ protons at δ 6.97 ppm show spin lattice relaxation time of 3.37 s, while the Hₖ proton represented by a chemical shift δ7.78 ppm yields $T₁$ as 3.51 s. The proton attached to the aldehyde group in the ring, which is positioned at δ 10.48 ppm gives $T₁$ as 4.09 s.

The dielectric relaxation time of o-chlorodenzaldehyde is given in Table 2. The experimental value of $τ$ is found to be $11.60 × 10^{-12}$ s, which is nearly 5-6 times the experimental value. The Perrin’s modification gives the dielectric relaxation time as
The experimental value of dielectric relaxation time agree with the experimental value. The Murty equation represents the value of dielectric relaxation time of 12.53 \times 10^{-12} \text{s}.

Table 3 represents the NMR spin lattice relaxation time $T_1$ of $o$-chlorobenzaldehyde at 298 K. The experimental value of $T_1$ for $o$-chorodenzaldehyde is found to be 3.54 s. The Debye value of $T_1$ is .59 s, while $T_1$ obtained using Perrin’s modification, Writz and co-workers-equation as well as Murty equation is found to be 1.54, 2.84 and 3.55 s, respectively, which are in better agreement with the experimental value.

At the room temperature the molecular group orientation is the major phenomenon for dielectric relaxation time. The decrease in relaxation time is caused by both molecular as well as intramolecular group rotation.

$p$-Hydroxybenzaldehyde has its importance in chemical and biological fields. The NMR investigation of crystal structure reveals that the hydroxy group present as para position is hindered by the aldehyde group. The theoretically calculated values of dielectric relaxation time and spin lattice relaxation time agree with the experimental value. The experimental value of dielectric relaxation time and spin lattice relaxation time of various protons of $p$-hydroxybenzaldehyde is found to be 6.87 \times 10^{-12} \text{s}, which is a very small value. This smaller value of $t$ implies that both the molecular and intermolecular group rotations take place.

Table 1 shows the NMR spin lattice relaxation time of various protons of $p$-hydroxybenzaldehyde at different chemical shift positions. Two $H_a$ protons of the ring at $\delta$ 6.85 ppm have spin lattice relaxation time $T_1$ as 3.58 s. Two $H_b$ protons nearer to the -OH group show a downfield shift at $\delta$ 7.66 ppm with a relaxation time $T_1$ as 3.33 s. the proton $H_c$ of the aldehyde group takes 3.86 s to come in the equilibrium position. This relaxation process is caused by the interaction of nuclear spin with the fluctuating local magnetic field. If we compare the $T_1$ for the proton of aldehyde group in anisaldehyde as 3.86 s, and $p$-hydroxybenzaldehyde as 3.86 s the increase in spin lattice relaxation time $T_1$ in $p$-hydrobenzaldehyde may be due to spin rotation mechanism.

Since the overall spin lattice relaxation time of $p$-hydroxybenzaldehyde is found to be 3.57 s which is greater than anisaldehyde and $o$-chlorobenzaldehyde. This may be due to the large chemical shift for the hydroxy group. Hence it can be concluded that the hydroxy group causes more hindrance to the rotation of the molecule, though the dielectric relaxation time of $p$-hydroxybenzaldehyde is small which is due to intramolecular group rotation taking place within the molecule. A similar type of result has been observed in $m$-nitrobenzaldehyde and $m$-hydroxypyridine by Dixit\textsuperscript{19}. The Debye equation used for evaluating $T_1$ gives a very small value 63 s. Perrine's equation when applied for calculation of $T_1$ gives 1.63 s. Writz and Murty equation are consistent with the experimental result as $T_1$ Murty is 3.84 s and $T_1$ Writz is 3.36 s. The correlation of calculated and experimental values of dielectric relaxation time and NMR spin lattice relaxation time in several ketones\textsuperscript{20} and methyl benzenes\textsuperscript{21} also indicate that Debye equation is not a better substitute for correlation time in calculating NMR spin lattice relaxation time as used by BPP.

Thus we observe that Writz and Murty equation are better substitute for the BPP theory than Debye phenomenon for spin lattice relaxation time in case of aldehydes.

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**References**