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NMR Spin-Lattice Relaxation Time and Activation Energy in Some Substituted Benzenes

AJAY KUMAR SINGH

Physics Department, Bareilly College, Bareilly- 243005 (INDIA)
Email : aksnmr@gmail.com

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Abstract

Present communication reports the experimental values of NMR spin-lattice relaxation time (T_1) of 2,4-Dinitrochlorobenzene, 2,4-Dinitrotoluene, 1,3-Dinitrobenzene, 4-Chloronitrobenzene and 3-Fluorobenzoic acid . The experimental values of T_1 have been correlated with the calculated values of T_1 obtained using various equations of the dielectric relaxation time (τ). It has been concluded that Murty Equation is a better representations of the dielectric relaxation phenomenon. The values of activation energy obtained using dielectric relaxation time have been correlated with calculated values of obtained using Arrhenius equation of NMR spin-lattice relaxation time (T_1) for these compounds.

Key words: NMR, Spin lattice relaxation time, Dielectric relaxation time, Activation Energy.

1. Introduction

The dielectric investigation of relaxation and nuclear magnetic resonance studies of organic polar complexes having different dipole bearing groups provides useful information about the structure of the molecules[1]. The dielectric relaxation time is very intimately connected with the molecular motion and intramolecular interaction in molecular species[2,3].

NMR spin-lattice relaxation time (T_1) has been used to investigate the rotational and transnational motions and their relations to molecular structure, size, shape and intramolecular forces causing internal friction. The value of chemical shift of the proton depends on the various substituent groups at different positions and is affected when positions of the substituent are interchanged or one polar group is replaced by another. Therefore, the measurements of chemical shift, spin-lattice relaxation time (T_1) and dielectric relaxation time (τ) are of paramount importance for study of molecular structure and intramolecular forces.

Bloembergen *et al.*[4] have derived an expression for the magnetic relaxation in terms of the correlation time (τ_c), which is closely related to Debye's theory[5] of the dielectric dispersion in polar liquids, according to which the dielectric relaxation time is given by

$$\tau = \frac{4\pi\eta_1 a_2^3}{kT} \quad (1)$$

Where η_1 is the viscosity of solvent and a_2 is the radius of solute molecule.

Many workers[6-8] have evaluated the spin-lattice relaxation time (T_1) from Bloembergen, Purcell and Pound (BPP)[4] theory and found that the calculated values of T_1 range from 1/2 to 1/10 times the experimental values. For narrowing the gap between the experimental and calculated values of T_1, we have used different models of dielectric relaxation.

Writz and Sperinol[9] modified the Debye equation to the form given by

$$\tau = \frac{4\pi\eta_1 a_2^3}{kT}\left[6\frac{a_1}{a_2} + \left(1+\frac{a_1}{a_2}\right)^{-3}\right]^{-1} \quad (2)$$

Where

$$a_i = \left[0.556\left(\frac{M_i}{\pi d_i N}\right)\right]^{1/3} \quad (3)$$

Here, Mi, d_i and a_i are molecular weight, density, and radius of molecule, respectively. Murty[10] has found a simple empirical equation for τ as

$$\tau = \frac{6\pi\eta_1\alpha}{(\varepsilon_1 + 2)kT} \quad (4)$$

Where α is the polarizability of the solute molecule and ε_1 is the dielectric constant of the solvent.

2. *Theory :*

The spin-lattice relaxation of a single nuclear spin in a liquid is induced by the fluctuating local magnetic field of neighboring spins. If the spin that induces the relaxation is attached to the same molecule as the relaxing spin, the fluctuating field is produced by the molecular reorientational motion. The contribution to this mechanism to the overall T_1 is denoted by $(T_1)_{rot}$. If the relaxation that occurs when the relaxing spin and the spin that induces relaxation are attached to different molecules, is denoted by $(T_1)_{trans}$.

BPP[4] have been calculated the probability of the induced transition and thus obtained the expression.

$$(T_1)^{-1} = (T_1)^{-1}_{rot} + (T_1)^{-1}_{trans} \quad (5)$$

Where

$$(T_1)^{-1}_{rot} = \frac{3\gamma^4\hbar^2}{10r_0^6}\left[\frac{\tau_c}{1+w_0^2\tau_c^2} + \frac{2\tau_c}{1+4w_0^2\tau_c^2}\right] \quad (6)$$

Here, γ is the gyromagnetic ratio, $\hbar = \frac{h}{2\pi}$, h is Planck's constant, r_0 is the sum of the interproton distances within the molecule, and ω_0 is the resonance angular frequency.

Kubo and Tomita[11] modified Eq. 6 and obtained

$$(T_1)^{-1}_{rot} = \frac{3\gamma^4\hbar^2}{2r_0^6}\tau_c \quad (7)$$

The correlation time (τ_c) required in Eq. 7 is closely related to the dielectric relaxation time (τ), of Debye's theory of dielectric dispersion in a polar liquid as

$$\tau_c = \tau/3 \quad (8)$$

We calculated the correlation time using Debye's equation[5], Writz and Sperinol equation[9] and Murty's equation[10].

In order to test the validity of these equations, different values of $(T_1)_{rot}$ have been obtained using different values of τ_c.

Assuming that BPP model is adequate to account for the translational contribution to the spin-lattice relaxation time (T_1), the expression for $(T_1)_{trans}$ is given by

$$(T_1)^{-1}_{trans} = \frac{9\pi^2\gamma^4\hbar^2\eta_2 N_0}{10KT} \quad (9)$$

Where N_o is the number of molecules per unit volume and η_2 is the viscosity of the compound.

Dielectric relaxation mechanism can be explained in terms of absolute rate theory[12] by treating dipole orientation as a rate process in which the polar molecules rotate from one equilibrium position to another. This process of rotation requires activation energy (ΔE_A) sufficient to overcome the potential barrier and separating the two mean equilibrium position and is given by

$$\tau = \frac{A}{T}\exp(\Delta E_A / RT) \quad (10)$$

Where $A = \frac{h}{k}$ is frequency -factor. The energy of activation (ΔE_A) is calculated from the slope of the plot of log $T\tau$ against (1/T).

The activation energy (ΔE_A) has also been evaluated using Arrhenius theory of rate process[13] and is given by

$$\tau_c = \tau_o \exp\left(\nabla E_A/RT\right) \quad (11)$$

Where τ_o is frequency factor and τ_c is correlation time.

The energy of activation (ΔE_A) can be obtained from the equation given by[14]

$$\Delta E_A = \frac{2.303R}{T_1}\cdot\frac{3\pi\gamma^4\hbar^2}{K}\left[\frac{\alpha\eta_1}{(\varepsilon_1+2)r_0^6} + \frac{\pi N_0\eta_2}{5}\right] \quad (12)$$

3. **Experimental Method**

All the compounds used were of pure quality LR grade obtained from M/s British Drug House Ltd., England. The purest quality of deuterated benzene obtained from M/s British Drug House, England, was distilled before use.

All the NMR experiments were performed on Bruker Avance DRX 400 MHz FT-NMR Spectrometer, equipped with 5mm multinuclear inverse probe head with Z-shielded gradient. For T1 experiments inversion recovery method (180^0-τ-90^0) of Becker *et*

al.[15] was used in each system for evaluation of spin-lattice relaxation time. The time was chosen initially for 10 second which 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 spin-lattice relaxation time T_1 values. The experiments were performed in automation mode using standard pulse programme from the Bruker software library.

4. **Results**

The experimental and calculated values of dielectric relaxation time (τ) and NMR spin-lattice relaxation time (T_1) of 2, 4-Dinitrochlorobenzene, 2, 4-Dinitrotoluene, 1, 3-Dinitrobenzene, 4-chloronitrobenzene and 3-Fluorobenzoic acid are given in Table 1 and 2 respectively at 293K. Table 3 shows the values of activation energy of these compounds.

5. **Discussion**

5.1 *Dielectric Relaxation Time :*

From Table 1 it is observed that the dielectric relaxation time of 2, 4-Dinitrotoluene is greater than that of 1, 3-Dinitrobenzene. This indicates that the addition of $-CH_3$ group in Dinitrobenzene sharply increases its relaxation time. It is interesting to note that 2, 4-Dinitrotoluene has greater relaxation time than those of 2, 4-Dinitrochlorobenzene, although the size of the former molecule is smaller than those of the latter. This indicates that methyl group in former molecule produces greater steric hindrance to the rotation of the molecule. 4-Chlornitrobenzene possesses the lowest relaxation time which can be explained by considering the fact that both the substituent groups are at Para-position to each other hence the dipole formed is weak.

The values of τ calculated using Debye equation are found to be much greater than the experimental values. The calculated values of τ using Writz and Sperinol equation are more nearer to observed values of τ. The values of τ calculated using Murty equation are found to be in quantitative agreement with the experimental values. It is therefore concluded that Murty equation is a better representation to the process of dipole orientation[16].

5.2 *NMR Spin-Lattice Relaxation Time :*

It is evident from Table 2 that the values of NMR spin-lattice relaxation time, calculated using BPP equation are smaller than the experimental values. The discrepancy in the theoretical and experimental values of the spin-lattice relaxation time (T_1) is due to Debye's value of τ used in the BPP equation which is valid only for the spherical molecules. The main source of the shortcoming of BPP formula lies in the evaluation of the rotational contribution to the spin-lattice of the relaxation time, which is much smaller than the experimental relaxation time. Moniz *et al.*[8] also agree with the view that the BPP treatment gives much smaller value of T_1. However, according to them the discrepancy in the results is due to time dependence of the rotational angular auto-correlation function of these molecules. They suggested that this time dependence is dominated by the dynamical coherence rather than by frictional forces, as used in the BPP theory.

When the equation of Writz and

Table 1. Dielectric Relaxation Time (τ)
(in 10^{-12} sec) at 293K.

Compound	$\tau_{Exp.}$	τ_{Debye}	τ_{Writz}	τ_{Murty}
2,4-dinitrochlorobenzene	15.42+	99.66	14.40	12.37
2,4-dinitrotoluene	19.92+	102.97	14.72	12.35
1,3-dinitrobenzene	10.79+	90.54	13.49	11.00
4-chloronitrobenzene	7.36+	90.35	13.66	10.54
3-Fluorobenzoic acid	11.10+	84.67	13.07	9.28

+ Ref. 16

Table 2. NMR Spin-Lattice Relaxation Time (T_1) (sec) at 293K

Compound	$T_{1Exp.}$	T_{1Debye}	T_{1Writz}	T_{1Murty}
2,4-dinitrochlorobenzene	1.68	0.56	3.73	4.41
2,4-dinitrotoluene	6.07	0.53	3.61	4.34
1,3-dinitrobenzene	10.35	0.60	3.99	4.96
4-chloronitrobenzene	5.64	0.14	4.73	5.63
3-Fluorobenzoic acid	3.39	0.64	4.16	5.86

Table 3. Values of Activation Energy for investigated Compounds

Compounds	ΔE_A (lit)(Kcal/mol)	ΔE_A (kcal/mol) Author's work
2,4-dinitrochlorobenzene	2.63[+]	2.92
2,4-dinitrotoluene	2.69[+]	2.97
1,3-dinitrobenzene	2.05[+]	3.10
4-chloronitrobenzene	1.94[+]	2.24
3-Fluorobenzoicacid	2.25[+]	1.63

+ Ref. 16

Sperinol is used, a better correlation is obtained. This is probably due to the introduction of a microfriction factor in the equation. However, the value of T_1 calculated using Murty's equation is in close agreement with the experimental values. This can be explained due to the polarizability of the molecules used to calculate the dielectric relaxation time (τ).

5.3 *Activation energy :*

From Table 3 it is clear that the values

of activation energy obtained using NMR spin-lattice relaxation time are found to be in good agreement with the values obtained using absolute rate theory. This shows that Murty equation for dielectric relaxation time is the appropriate substitute for correlation time (τ_c) in BPP equation for NMR spin-lattice relaxation time.

The value of the free energy of activation for 2, 4-Dinitrotoluene has been found to be greater than that of 1, 3-Dinitrobenzene, suggesting that the inner friction experienced by former molecule is greater than the later molecule. 4-Fluorobenzoic acid has higher value of free energy of activation than 4-Chloronitrobenzene. This suggests that the microscopic viscosity experienced by the former molecule may also be greater than that for later molecule.

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