

NMR spin-lattice relaxation time and activation energy of some substituted phenols

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The experimental values of NMR spin-lattice relaxation time (T_1) of *m*-aminophenol, *p*-aminophenol, *o*-nitrophenol, resorcinol and *p*-chlorophenol have been reported. The values of activation energy (ΔE_A) obtained using dielectric relaxation time, have been correlated with calculated values of ΔE_A obtained using Arrhenius equation of NMR spin-lattice relaxation time (T_1) for these compounds. A correlation between the experimental values of T_1 and its calculated values obtained using different equations of dielectric relaxation time (τ) has been established.

[**Keywords:** NMR spin-lattice relaxation time, Dielectric relaxation time, Energy of activation].

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1 Introduction

Structural studies of organic compounds using the dielectric relaxation mechanism and nuclear magnetic resonance have been a subject of interest. The study and correlation of dielectric relaxation time and NMR spin-lattice relaxation time present a critical analysis of the molecular and intramolecular motions and other parameters^{2,3}.

Bloembergen *et al.*⁴ have derived an expression for the magnetic relaxation in terms of correlation time (τ_c). To evaluate τ_c they used the value of dielectric relaxation time $\tau = \frac{4\pi\eta_1 a^3}{kT}$, in which the molecules

are treated as sphere of radius a moving in a medium of viscosity η_1 . The values of T_1 calculated from BPP theory were found ranging from $\frac{1}{2}$ to $\frac{1}{10}$ time of the experimentally observed values.

The possibility of narrowing the gap between the experimental and calculated values stimulated the present work reported in this paper. We also want to find out for these molecular systems whether the dipole orientation process is due to the molecular rotation only or by both the molecular and intramolecular rotations. The values of ΔE_A obtained using absolute rate theory were correlated with the calculated values obtained using Arrhenius equation of T_1 .

2 Theory

Dielectric relaxation mechanism can be explained in terms of absolute rate theory⁵ 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 an activation energy (ΔE_A) sufficient to overcome the energy barrier separating the two mean equilibrium positions and is given by:

$$\tau = \frac{A}{T} \exp\left(\frac{\Delta E_A}{RT}\right) \quad \dots (1)$$

where $A = \frac{h}{k}$ is frequency factor.

The activation of energy has also been evaluated using Arrhenius' theory of rate process. The energy of activation ΔE_A is given by:

$$\tau_c = \tau_0 \exp\left(\frac{\Delta E_A}{RT}\right) \quad \dots (2)$$

where τ_c is correlation time and τ_0 is frequency factor. On rearrangement, Eq. (2) yields:

$$\Delta E_A = 2.303RT \log_{10} \left(\frac{\tau_c}{\tau_0}\right) \quad \dots (3)$$

Kubo and Tomita⁶ established a relation between correlation time (τ_c) and NMR spin-lattice relaxation time (T_1) as:

$$(T_1)^{-1} = \left(\frac{3\gamma^4 \hbar^2}{2r_0^6} \tau_c \right) + \left(\frac{9\pi^2 \gamma^4 \hbar^2 \eta_2 N}{10kT} \right) \quad \dots (4)$$

where correlation time (τ_c) is related to dielectric relaxation time (τ) by the expression:

$$\tau_c = \frac{\tau}{3} \quad \dots (5)$$

Murty⁷ has derived an equation for dielectric relaxation time (τ) which is given by:

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

where the symbols have their usual meanings

Hence

$$\tau_c = \frac{2\pi\eta_1\alpha}{(\varepsilon+2)kT} \quad \dots (7)$$

The energy of activation ΔE_A can be obtained from the temperature variation of $\log T_1$ with absolute temperature T as given below:

$$\Delta E_A = 2.303 R \left[\frac{\partial \log T_1}{\partial \left(\frac{1}{T} \right)} \right] \quad \dots (8)$$

On substituting the values of T_1 , Eq. (8) yields:

$$\Delta E_A = \frac{2.303R}{T_1} \cdot \frac{3\pi\gamma^4 \hbar^2}{K} \left[\frac{\alpha\eta_1}{(\varepsilon+2)r_0^6} + \frac{\pi N\eta_2}{5} \right] \quad \dots (9)$$

where γ is the gyromagnetic ratio and r_0 is the sum of inter-proton distance within the molecules, α is the polarizability of compounds and ε is dielectric constant of solvent, N is the number of molecules per unit volume, η_1 and η_2 are the coefficient of viscosity of solvent and solute respectively.

The correlation time (τ_c) using Debye's equation, Perrin's modification of Debye's equation, Writz and Sperinol's equation and Murty's equation have been calculated. These equations are given in our earlier paper⁸. In order to test the validity of these equations,

different values of T_1 have been obtained using different values of τ_c and correlated with the experimental values.

3 Experimental Details

All the compounds used were of pure quality obtained from M/s British Drug House Ltd., England. The percentage purity of the investigated compounds ranged from 99.8 to 99.9%. The purest quality of deuterated benzene obtained from M/s BDH, England, was distilled before use.

NMR spectra were recorded in deuterated benzene at 300K temperature using Bruker Avance DRX 200 MHz FT-NMR spectrometer equipped with a 5 mm multi-nuclear inverse probe head with Z-shielded gradient. Chemical shifts are measured on δ -scale in ppm.

¹H NMR spectrum was recorded with a pulse of flip angle 90°, spectral width 4139.07 Hz, data size 32 k, relaxation delay 5 second, number of transients 8. The FID's were line broadened by 0.3 Hz prior to Fourier transformation. The sample concentration were kept in the range of 32 to 50 m molar.

For T_1 experiments inversion recovery method (180°- τ -90°) of Becker *et al.*⁹ was used in each system for evaluation of spin-lattice relaxation time. The time was chosen initially for 10 sec 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 T_1 value. The experiments were performed in automation mode using standard pulse programme from the Bruker software library.

4 Results

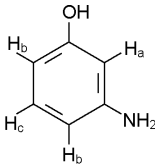
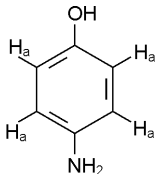
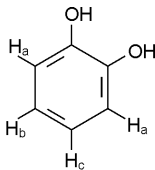
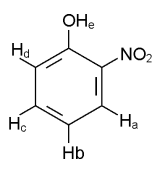
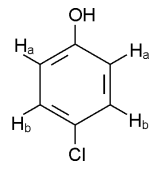
The chemical shift position and NMR spin-lattice relaxation time (T_1) of various protons of *m*-aminophenol, *p*-aminophenol, *p*-chlorophenol, *o*-nitrophenol and resorcinol are given in Table 1. Tables 2 and 3 show the experimental and calculated values of τ and T_1 of these compounds at 300K respectively. Table 4 shows the values of ΔE_A .

5 Discussion

5.1 Chemical shift

Table 1 shows that H_a proton of *m*-amiophenol gives a singlet at 7.031 ppm, H_c proton gives a triplet at 6.110 ppm and two H_b protons give a double doublet at 5.938 ppm.

Table 1— Chemical shift position (δ) and NMR spin-lattice relaxation time (T_1) of various protons of investigated compounds at 300 K

S.N	Compound	Proton	Chemical shift (δ) ppm	NMR spin-lattice relaxation time T_1 (s)
1		H _a	7.031	4.82
		H _b	6.110	4.86
2	<i>m</i> -aminophenol	H _c	5.938	5.61
3		H _a	6.554	5.48
		H _a	6.256	4.93
4		H _a	6.996	4.53
		H _b	4.189	4.39
5		H _a	7.736	4.80
		H _b	7.001	4.51
		H _c	6.880	4.64
		H _d	6.516	4.48
	<i>o</i> -Nitrophenol	H _e	10.611	4.56
5		H _a	6.567	3.20
		H _b	7.054	3.80

Since both $-\text{OH}$ and $-\text{NH}_2$ group show positive resonance effect and negative inductive effect, hence all the protons (H_a) are in the same environment. Four H_a protons of *p*-aminophenol give a singlet at 6.554 ppm. In *o*-nitrophenol H_e proton of $-\text{OH}$ group resonates at 10.611 ppm due to intra-molecular hydrogen-bonding with $-\text{NO}_2$ group.

Similar explanations can be given for chemical shift in the case of resorcinol and *p*-chlorophenol.

5.2 Dielectric relaxation time

Table 2 shows that dielectric relaxation times of *m*- and *p*-aminophenol are small as compared to resorcinol although they are all of nearly the same size. This shows that intra-molecular rotations in the former molecules contribute more to the process of dipolar orientation. The dielectric relaxation time of *m*-aminophenol is greater than *p*-aminophenol. This shows that amino group and hydroxyl group mutually

Table 2—Values of dielectric relaxation time (τ) (in 10^{-12} sec) at 300K for investigated compounds

Polar Compound	Molecular Weight	τ_{Exp}	τ_{Debye}	τ_{Perrin}	τ_{Writz}	τ_{Murty}
<i>m</i> -aminophenol	109.13 ⁺	7.05	80.10	28.83	14.17	9.35
<i>p</i> -aminophenol	109.13 ⁺	6.22	61.47	22.13	10.01	6.42
Resorcinol	110.11 [•]	17.76	69.06	24.86	11.66	16.23
<i>p</i> -chlorophenol	128.56 [*]	14.7	73.84	26.58	12.56	13.03
<i>o</i> -nitrophenol	139.1 [*]	13.7	77.52	27.91	13.39	13.54

⁺ Ref 12, [•] Ref 13, ^{*} Ref 14

Table 3—Values of NMR spin-lattice relaxation time (T_1) (in sec) at 300 K

Compounds	T_{1Exp}	T_{1Debye}	$T_{1Perrin}$	T_{1Writz}	T_{1Murty}
<i>m</i> -aminophenol	4.03	2.61	3.56	4.01	4.17
<i>p</i> -aminophenol	5.48	2.65	4.06	4.8	5.10
Resorcinol	4.70	1.54	1.86	4.19	4.23
<i>o</i> -Nitrophenol	4.60	1.53	1.87	4.05	4.10
<i>p</i> -chlorophenol	3.50	1.55	1.90	3.12	3.20

hinder their rotation around their bonds with the ring more effectively at the meta position.

The values of τ calculated using Debye equation are found to be much greater than the experimental values. When Perrin's modification is used, a better correlation has been obtained. The calculated values of τ using Writz and Sperinol equation are more nearer to the 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.

5.3 NMR spin-lattice relaxation time

Table 3 shows that the values of T_1 calculated using BPP theory are smaller than the experimental values. According to Moniz *et al.*¹⁰, the discrepancy in results is due to the time dependence of rotational angular auto-correlation functions of these molecules. They suggested that this time dependence is dominated by dynamical coherence rather than by frictional forces as used in BPP theory.

The experimental values of NMR spin-lattice relaxation time have been correlated with the calculated values of T_1 obtained using Debye equation, Perrin's modification to Debye equation, Writz and Sperical equation and Murty equation. It is concluded that Murty equation gives quantitative agreement between the experimental and calculated values. Similar results have been obtained by Anupam *et al.*¹¹ in case of same benzoic acids.

Table 4—Values of activation energy for investigated compounds

Compounds	ΔE_A (lit)(Kcal/mol)	ΔE_A (kcal/mol) Author's work
<i>m</i> -aminophenol	2.19 ⁺	2.46
<i>p</i> -aminophenol	2.12 ⁺	2.57
Resorcinol	2.82 [•]	2.41
<i>o</i> -nitrophenol	2.75 [*]	2.67
<i>p</i> -chlorophenol	2.78 [*]	3.68

⁺Ref 12, [•]Ref 13, ^{*} Ref 14.

5.4 Activation energy

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.

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