

# NUCLEAR MAGNETIC RELAXATIONS AND MOLECULAR REORIENTATION FREQUENCIES OF $\alpha$ -HYDROQUINONE AND $\gamma$ -HYDROQUINONE

V. D. AGRAWAL AND R. C. GUPTA

DEPARTMENT OF PHYSICS, LUCKNOW UNIVERSITY, LUCKNOW.

(Received August 30, 1966; Resubmitted November 8, 1966)

**ABSTRACT.** The spin-lattice nuclear magnetic relaxations have been measured for stable ( $\alpha$ ) and meta-stable ( $\gamma$ ) Hydroquinones or Quinols. The studies were carried out as a function of temperature from 94°K to 360°K, at the radio frequency of 25 Mc/sec. The N.M.R. relaxations show the molecular rotation with the rise of temperature in both the cases. The activation energies and molecular reorientation frequencies have also been calculated.

## INTRODUCTION

The present work is an attempt to extend the work of Gupta (1963) on motion of  $\alpha$ -Hydroquinone and  $\gamma$ -Hydroquinone molecules. His results of  $\alpha$ -Hydroquinone for line-widths vs. temperature show first transition at about 341°K and second transition at about 388°K, with the specific heat anomaly which occurs at 325°K. In the case of  $\gamma$ -Hydroquinone first transition is found at about 365°K and second transition at about 375°K, with the heat anomalies occurring at temperatures 230°K and 336°K. These transitions are interpreted by him as being a reorientation of molecule about the molecular axis. The interchange of energy between nuclei and lattice may also be studied by means of spin-lattice relaxation time. The present N.M.R. relaxation measurements have been made on  $\alpha$ -Hydroquinone and  $\gamma$ -Hydroquinone in an attempt to obtain more detailed informations concerning the nature of molecular motions.

## EXPERIMENTAL ARRANGEMENT

The magnetic relaxations of solid  $\alpha$ -Hydroquinone and  $\gamma$ -Hydroquinone have been measured at 25 Mc/sec using a proton resonance spectrometer in a field of about 5998 gauss. The records of  $T_1$  have been recorded by one of us in University College of North Wales, Bangor, U. K. The records of  $T_1$  at room temperature have been shown in fig. (1) and fig. (2).

## THEORY

Bloembergen *et al* (1948) derived an expression for  $T_1$  in terms of a correlation time  $\tau_c$ , which sets a time scale to the random motion.  $\tau_c$  can be roughly defined

as the time taken by a molecule to turn through a radian or to move through a distance comparable with its dimensions.

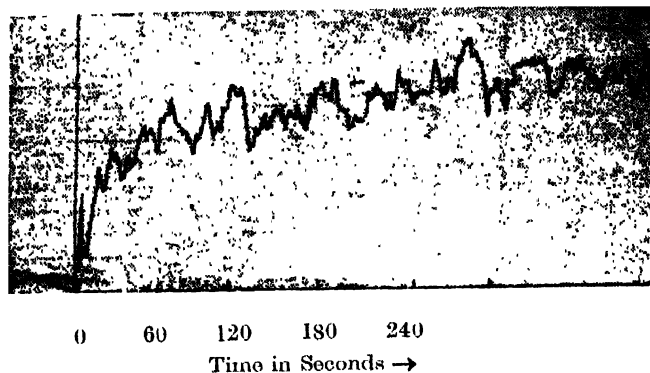


Fig. (1) Signal decay curve of  $T_1$  for  $\alpha$ -Hydroquinone at room temperature.

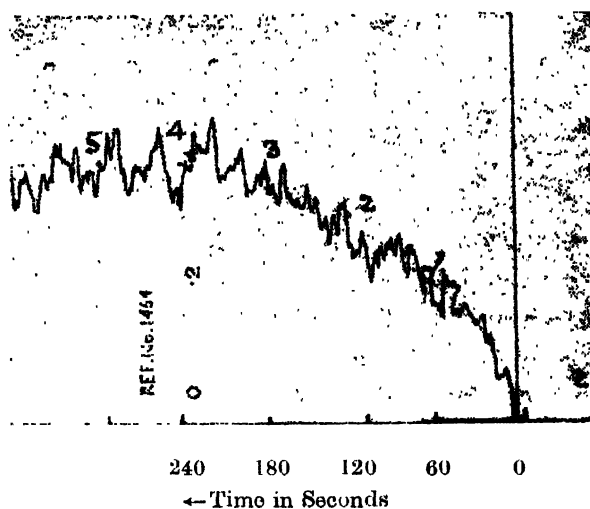


Fig. (2) Signal decay curve of  $T_1$  for  $\gamma$ -Hydroquinone at room temperature.

The expression has been slightly modified by Kubo and Tomita (1954) and obtained :

$$\frac{I}{T_1} = C_1 \left[ \frac{\tau_c}{I + \omega_0^2 \tau_c^2} \frac{4\tau_c}{I + 4\omega_0^2 \tau_c^2} \right]$$

where  $\omega_0 = 2\pi\nu_0$  and  $C_1$  is a constant.

Thus  $T_1$  decreases as the value of  $\tau_c$  increases, it reaches minimum when reorientation frequency and radio frequency become roughly equal, beyond which  $T_1$  rises with temperature, such behaviour has in fact been found for three isotopic species of benzene by Andrew and Eades (1953b). With the help of above equation,

the values of  $T_1$  at various temperatures can be converted in terms of  $\tau_c$ . The plot of  $\log \tau_c$  vs  $1/T$  yields a straight line and its slope will give the activation energy  $E_R$ . This procedure is the only approach when the plot of  $T_1$  against  $1/T$  gives no minimum value of  $T_1$  due to the intervention of solid-solid phase transition as in the case of Cyclohexane (Andrew and Eades, 1953a).

#### METHOD FOR MEASUREMENT OF $T_1$

In the present work for the measurements of relaxation times Linder's (1957) decay technique has been adopted. Measurement by this method is possible when  $T_1$  is long compared to the constant of the recording apparatus. The principle of the method is that when spin system is saturated by the application of the radio-frequency amplitude  $H_1$ , such that  $\gamma^2 H_1^2 T_1 T_2$  is much greater than unity, the observed intensity falls until the signal vanishes completely. The radio-frequency field is lowered to the unsaturated value of nuclear system and regrowth of signal is recorded. The growth is exponential and governed by the formula :

$$S(t) = S_0 \left( 1 - \exp \left( - \frac{t}{T_1} \right) \right)$$

where  $S(t)$  and  $S_0$  are the intensities of signals in saturated and unsaturated states. The slope of the curve  $s_0 - s(t)$  against time ( $t$ ) gives relaxation time  $T_1$ .

#### ACTIVATION ENERGY AND ROTATIONAL FREQUENCY

Gutowsky and Pake (1950) and Kubo and Tomita (1954) modified the theory of Bloembergen *et al* and modified expression is given as :

$$2\pi\nu_c = \alpha\gamma\delta H \left[ \tan \left\{ \frac{\pi(\delta H^2 - B^2)}{2(C^2 - B^2)} \right\} \right]^{-1}$$

where  $\nu_c$  is the correlation frequency for motion narrowing the line,  $C$  is the linewidth at temperature below the transition region,  $\delta H$  is the linewidth in the Transition region,  $B$  is the line width at higher temperature,  $\gamma$  is the gyromagnetic ratio and  $\alpha$  is  $(\ln 2)^{-1}$  and its value is  $(8 \times 0.6931)^{-1}$ .  $(C^2 - B^2)$  can be replaced by  $(C^2)$  if  $B^2$  is too small as compared to  $C^2$ . The correlation frequency  $\nu_c$  is assumed to obey Arrhenius equation :

$$\nu_c = \nu_0 \exp \left[ \frac{-E_R}{RT} \right]$$

where  $E_R$  is the activation energy and  $R$  is the gas constant/mole.

In the case of  $\alpha$ -Hydroquinone the value of  $C$  is 09.53 gauss and value of  $B$  is 0.31 gauss. In  $\gamma$ -Hydroquinone the value of  $C$  and  $B$  are 8.40 gauss and 0.40 gauss respectively. These values have been calculated with experimental linewidth vs temperature curve obtained by Gupta (1963).

The molecular reorientation frequencies for  $\alpha$  Hydroquinone have been shown in Table II and for  $\gamma$ -Hydroquinone in Table III. The plot of  $\log \nu_c$  vs  $1/T$  yields a straight line and its slope will give activation energy  $E_R$  for molecular rotation.

## RESULTS

The spin-lattice relaxation times measured by signal decay method for  $\alpha$ -Hydroquinone and  $\gamma$ -Hydroquinone are quoted in Table I.

TABLE I

Spin-lattice relaxation times of stable and *m*-stable Hydroquinone

Temperature °K	Stable Hydroquinone	<i>m</i> -stable Hydroquinone
94°	5.0 minutes	1.20 minutes
293°	3.0 ,,	0.90 ,,
353°	—	0.83 ,,
360°	1.4 ,,	—

TABLE II

Molecular reorientation frequencies for stable ( $\alpha$ ) Hydroquinone

Temperature °K	$\delta$ H (gauss)	$\nu_c$
366	7.81	3.41 Kc/sec.
374	6.56	5.48 Kc/sec.
388	1.52	30.48 Kc/sec.
400	0.43	—

TABLE III

Molecular reorientation frequencies for *m*-stable ( $\gamma$ ) Hydroquinone

Temperature °K	$\delta$ H (gauss)	$\nu_c$
350	8.06	0.8043 Kc/sec.
367	7.50	1.9272 Kc/sec.
370	5.00	6.2199 Kc/sec.
374	1.40	23.8720 Kc/sec.
380	1.00	36.6630 Kc/sec.

Thus with above results it is evident that  $T_1$  is greater for stable Hydroquinone in comparison to meta-stable Hydroquinone. Also for both  $\alpha$ -Hydroquinone and  $\gamma$ -Hydroquinone the values of  $T_1$  are reduced with rise of temperature. Most likely this is due to rotation of molecule about the molecular axis. The activation energies for both have been calculated. For  $\alpha$ -Hydroquinone it is found to be 5.26 K.cal/mole and for  $\gamma$ -Hydroquinone it is about 13.02 K.cal/mole which is a reasonable value to cross the potential barrier hindering rotation (Muzushima 1954). Furthermore, as obtained by Gupta (1963) the second moments and line-widths in both  $\alpha$ - and  $\gamma$ -Hydroquinone show a remarkable reduction in its values with the rise of temperature, giving added support to the theory of molecular rotation.

#### A C K N O W L E D G M E N T

Authors are highly indebted to Professor P. N. Sharma, D.Sc., Head of the Physics Department for his interest and encouragement throughout the work.

#### R E F E R E N C E S

- Andrew, E. R. and Eades, R. G., 1953a, *Proc. Roy. Soc. A*, **216**, 398.  
----- 1953b, *Proc. Roy. Soc. A*, **218**, 537.  
Bloembergen, N., Purcell, E. M. and Pound, R. V., 1948, *Phys. Rev.*, **73**, 679.  
Gupta, R. C., 1963, *Ph.D. thesis*, University College of North Wales, Bangor, U.K.  
Gutowsky, H. S. and Pake, G. E., 1950, *J. Chem. Phys.*, **18**, 162.  
Kubo, R. and Tomita, K., 1954, *J. Physical Soc. Japan*, **9**, 888.  
Linder, S., 1957, *J. Chem. Phys.*, **26**, 900.  
Mujushima, S., 1954, *Structure of molecules and internat rotation*. Academic Press, Inc. New York, 7.